STORAGE, FLOW, AND PRODUCTION OF HEAT

Thermodynamics is the science of heat and hotness, of how bodies and other physical systems respond to heat, and of how heat can be used to drive other processes. In this chapter, I will introduce the fundamental quantities and concepts of thermodynamics and create dynamical models of some interesting phenomena. I shall justify the generic laws of thermal physics which we are going to use throughout this book. Constitutive laws will be introduced on an informal basis when needed for getting answers to some special problems. They will be treated in great detail in the following chapters.

I will take a practical approach to thermal processes by creating dynamical models of the heating and cooling of simple materials, the storage of heat in such materials, the flow of heat through walls, production of heat, and the operation of heat pumps and heat engines. This development will be guided by the balance of quantities of heat, by the interpretation of temperature differences as the thermal driving force, and by Sadi Carnot's comparison of waterfalls and heat engines to motivate the relation between heat, hotness, and power. First however, let us take a look at what kinds of images and concepts can be formed about heat and hotness from our everyday knowledge of thermal processes.

4.1 THERMAL PHENOMENA, CONCEPTS, AND IMAGES

Thermal phenomena are part of our everyday experience. They allow us to conceive of the quantities which are necessary for a theory of thermal physics. Nature tells us where to begin and what to look for. On the basis of experience, we construct the concepts which we do not derive from anything else, i.e., those which are truly fundamental. I shall take these to be *hotness*, *heat*, and *energy*. We intuitively know the first two of these quantities, even though our knowledge is not precise in any scientific sense. We have become familiar with energy through our study of other parts of physics. By weaving the elements into a theory of thermal processes, and by comparing the predictions of the theory with new phenomena, we will find out whether our ideas are correct.

Assuming that you probably have had at least a moderate exposure to thermal physics, you might find this section the most demanding of all, even though there will not be a single equation to set up or to solve. It is imperative that you see very clearly how common sense reasoning and analogies can be used to understand the meaning of heat and hotness before we go on with the formal story.

4.1.1 Some Phenomena and Word Models

This subsection serves a simple purpose: To create word models of some basic thermal phenomena. These models which are created almost effortlessly on the basis of conventional language will demonstrate everyday conceptualizations of processes involving heat and hotness. The result is a language which could just as easily be used to speak about fluid and electric processes. There is a quantity of heat residing in bodies, making them warm, letting them expand or melting them. It is capable of flowing into or out of these bodies; it can be produced by fire, electrically, or by rubbing, and it can be used to drive engines. Temperature differences make all these things happen.

Two bodies of water in thermal contact. Water is poured into two identical compartments of a container separated by a thin metal wall. In one of the compartments there is hot water, in the other one the water is cold. The container is well insulated and covered by a styrofoam lid. The bodies of water are stirred continuously, so there is a uniform temperature for each body. It is found that the temperature of the hot water goes down whereas the temperature of the cold water rises. This continues until both temperatures are the same and pretty much equal to the average initial temperatures.

Temperatures equilibrate for bodies made of different materials and sizes as well. Data has been taken for a block of cold copper in hot water (Fig. 4.1). In general, the final temperature lies somewhere between the initial values for the bodies in thermal contact.

Figure 4.1: A hot body of water in thermal contact with a cold copper cylinder inside a well insulated container (left). The temperatures adjust until they have become equal (right).
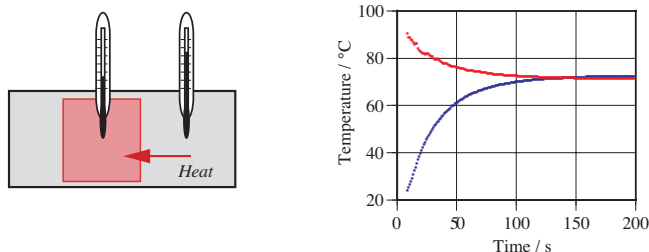
Interpretation. For a body of water to get colder, it has to lose heat, for it to get warmer, it must gain heat (Fig. 4.1, right). We say that heat flows from the hotter body of water to the colder one as long as there is a temperature difference. We interpret temperature differences as the *driving force for the flow of heat* and *temperature as the thermal level* because the behavior of the temperatures resembles that of water levels in communicating tanks, or of voltages of capacitors connected by a resistor (Fig. 1.1 or Fig. 1.3). The example in Fig. 4.1 demonstrates that thermal levels become equal, not quantities of heat residing in the bodies making them warm. Put differently, temperature does not measure quantities of heat, it tells us *how warm* a material is.

The water in the container would lose heat to the cool environment and the temperatures would drop further were it not for the insulation. Styrofoam insulation makes it difficult for heat to flow out of warm bodies.

Thermocouples, resistors, and air thermometers. Different devices and materials can be used to measure temperature. Basically, whenever we have a process or a material property dependent upon temperature or temperature differences, these can be exploited to build thermometers. Simple combinations of two metals—so-called ther-

mocouples, which are actually thermoelectric generators (see below in Fig. 4.11)—can be used to measure temperature differences. The resistance of electric resistors commonly depends upon temperature (Fig. 4.2, left), so we can build resistive thermometers. An important type of thermometer is made from a simple gas such as air whose pressure depends upon its temperature (Fig. 4.2, right).
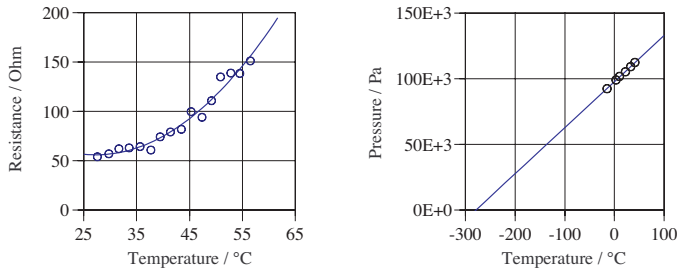

Figure 4.2: Resistance of a resistor as a function of temperature (left), and pressure of air at constant volume as a function of temperature (right; the relation is extrapolated backwards to zero pressure).

Interpretation. Using the gas thermometer, the pressure of a dilute gas such as air at standard conditions is measured at constant volume. It is found that—if the temperature is not too low—the pressure is a linear function of temperature. This relation is extrapolated backwards to a pressure of zero. The same temperature is found for zero pressure independent of the type of substance that is in a gaseous state; the result is a temperature of – 273°C, therefore it is assumed that this constitutes a special point. Since lower temperatures than the zero point of the air thermometer have never been found in any experiment, it is believed that it represents the lowest possible temperature that can be attained. The *Kelvin temperature scale* uses the zero point of the air thermometer as its starting point.

Compressing air. Air can be compressed quickly in a bicycle pump. If we do this repeatedly, the end of the pump becomes quite warm. We can perform the same process in a cylinder with a piston and put a small piece of tinder in the cylinder. Already after a single quick stroke the tinder is observed to ignite in a flash.

Interpretation. The fact that the tinder ignites tells us that the air has become very hot. This explains why a bicycle pump becomes hot after a few strokes. Heat flows from the hot air through the pump casing into the surroundings.

Why does the temperature of the air rise so dramatically as the result of a quick, strong stroke? After all, there is no fire to heat the air, heat cannot flow from the surroundings into the air (the air is hotter than the surroundings!). So we do not add heat from outside. There could be friction in the air, and indeed there is, but its effect is very small (this is explained by noting that the compressed air is almost ideally elastic, the volume would be restored if we just let the piston move out again). Since we do not add heat, and since heat is not produced, the quantity of heat of the air stays constant. The temperature of the air rises because its heat is compressed into a much smaller space; the heat of the air is lifted to a higher level (Fig. 4.3).
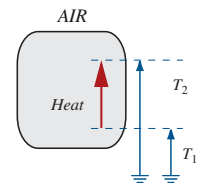

Figure 4.3: Process diagram of compression of air without heating or cooling. The temperature of the air rises. Figuratively speaking, the heat of the air is lifted to a higher level.

This example demonstrates very convincingly that temperature and heat cannot be the same quantity—remember, we already concluded this by observing that temperature, not heat, equilibrates. When air is compressed quickly, the quantity of heat stays constant while temperature rises dramatically.

Cooling and heating water in a can. Hot water is poured into a thin aluminum can.

The water is stirred continuously with the help of a magnetic stirrer, and its temperature is recorded (Fig. 4.4, top left). The temperature drops quickly at first, and more slowly later on. Finally, it reaches a constant value; interestingly this value is higher than the temperature of the environment.

If very cold water in a drinking can is left standing in a warm room, its temperature rises quickly at first, and then more slowly (Fig. 4.4, top right). In the case presented here, the drinking bottle is inside an insulating jacket, and the water is stirred during the observation. Note that the temperature of the water rises above that of the room.

Figure 4.4: Top left: Temperature of hot water left standing in a thin-walled aluminum can. The final temperature is above the temperature of the environment (here about 20°C). Top right: Temperature of cold water left standing in an insulated drinking bottle. The final temperature is above the temperature of the environment (the curve that starts at about 23°C). Bottom: Process diagram for heat flowing into or out of a storage element. A temperature difference drives the flow.
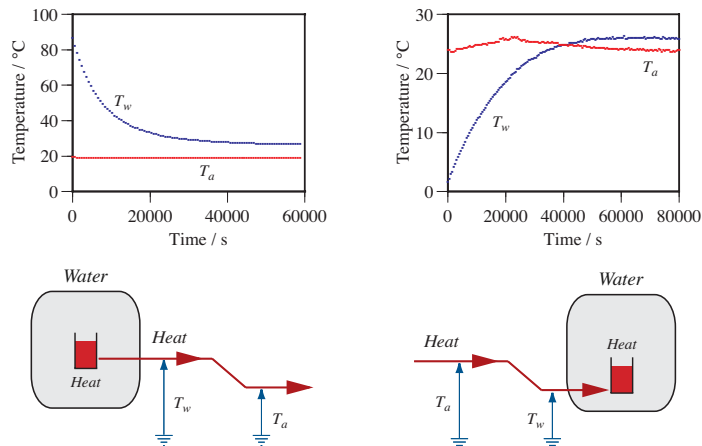
Interpretation. Hot water loses heat to the environment through the wall of its container (Fig. 4.4, bottom left). The difference of temperatures between the water and the environment serves as the *driving force* for the flow of heat. If the driving force is greater, the loss of heat is greater, letting the temperature go down faster. This explains the shape of the measured curve (see also Fig. 4.1). The magnetic stirrer used to stir the water produces some heat. That is why the temperature of the water settles above the temperature of the environment: In the end, the heat produced by the stirrer must leave the container, so there needs to be a temperature difference.

If the water is colder than the environment, heat will flow from the environment into the cold water (Fig. 4.4, bottom right). Again, if the temperature difference is high, the flow will be strong, the temperature of the water will change fast. Since heat is generated by the stirrer, the final temperature of the water will be above that of the environment (Fig. 4.4, top right).

Heat flows through a metal bar. A section of a copper bar is inserted into water in a glass. The rod is heated by a candle at the other end (Fig. 4.5, left). Over time, the temperature of the water rises. In a somewhat more sophisticated experiment, one end of a long, thin copper bar is stuck in ice water, and the other end is heated electrically. The bar is not insulated from the surrounding air. The temperature of the metal is measured at eight points along its length (Fig. 4.5, right). Temperatures first drop a little. Soon after the heater is turned on, the temperatures rise. The parts of the copper bar near the end that is heated become hot first. For the other points there is a more or less prolonged delay in response.

Interpretation. Heat is produced by the candle and transferred through the copper rod into the water. The flame is very hot, the copper rod is pretty hot at the heated end and cooler at the end stuck in the water; the water is cooler still. Heat flows from hot bodies to colder ones. Heat accumulates in the water and as a result, the temperature rises.

In the second case, some heat slowly flows out of the copper bar (which is at room temperature) into the ice water. If heat has to flow from points farther away, those parts get colder more slowly. When the electric heater is turned on, heat is produced (see Fig. 4.9) and it travels through the length of the bar toward the end stuck in the water. The parts of the bar closer to the heater receive the heat first, so their temperature rises most quickly. The rise of temperature is delayed in the sections of the bar farther away from the heated end. As time progresses, a fixed temperature gradient from hot to cold is established.
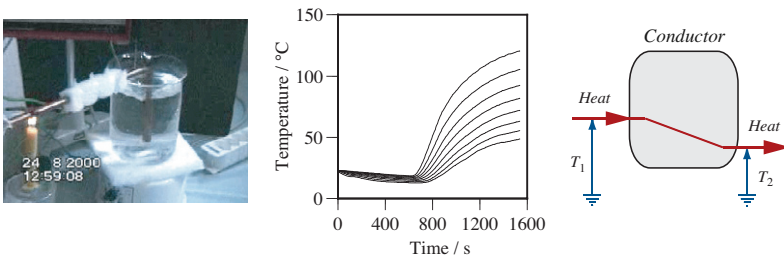

Figure 4.5: Left: A candle heats water indirectly. A copper rod transfers the heat produced by the candle to the water. Center: Temperatures of a long copper bar at different points as functions of time. First, the bar is at room temperature. One end is placed in cold water. Starting at $t = 700$ s, the other end is heated electrically. Right: Process diagram of heat flow.

The process of migration of heat through a material is called *conduction*. It is analogous to the conduction of electricity in metals. As the curves in Fig. 4.5 suggest, it is also similar to the flow of water through a chain of tanks, or the transport of charge through a chain of *RC* systems (Fig. 1.28).

Melting ice and freezing water. Ice placed in a warm environment melts. Alternatively, we can actively heat ice in a test tube placed in warm water and monitor the temperature of the mixture of ice and water forming from the ice, and of the water bath (Fig. 4.6). It is found that the temperature of a cold block of ice first rises to 0°C. Then the ice-water mixture in the test tube stays at a constant 0°C until all the ice has melted. Only then, upon further heating, does the temperature of the water in the test tube rise as expected. The temperature of the water bath decreases all the time.
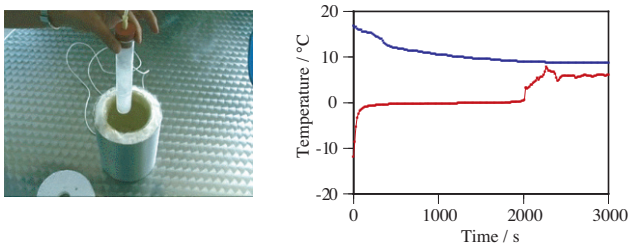

Figure 4.6: A test tube filled with cold ice is placed in water, everything is in a well-sealed glass container. Temperatures of the water bath (upper curve) and of the ice-water mixture in the test tube (lower curve) are recorded.

When water is placed in a cold environment (considerably colder than 0°C), the reverse happens. The temperature of the water drops to 0°C. Now ice starts to form and

the temperature of the freezing substance stays constant at 0°C. Finally, when there is only ice, the temperature continues to sink below the freezing point.

Interpretation. Obviously, heat is needed to melt ice. First, heat coming from the warm water raises the temperature of the cold ice to 0°C. Then the temperature of the substance in the test tube (Fig. 4.6) stays constant for quite a while. During this phase of constant temperature, ice transforms into water. Since the mixture is colder than the surrounding water, heat continues to flow into the melting mixture. In this case, heat does not raise the temperature of the material. Rather, it leads to the transformation of ice to water.

Again we have an example that demonstrates very clearly that heat and temperature are totally different concepts. While the temperature stays constant, the quantity of heat of the substance in the test tubes increases.

Vaporization of water. Water is placed in an open but otherwise well insulated can on top of a scale. The water is heated with an immersion heater. At a temperature of almost 100°C, it starts to boil. The power of the heater is kept constant. Temperature and mass of the water are recorded. We find that the temperature stays constant during vaporization, whereas the mass of the water decreases continually (see Fig. 4.7).

Interpretation. Again, we have a phase change that requires heat while the temperature of the substances undergoing the change (water and steam) stays constant. Heat is produced at a constant rate by the immersion heater. Since the mass of the water decreases linearly, we conclude that equal amounts of heat produce equal quantities of steam.

A Peltier cooler. Two bodies of water inside a well insulated tank are separated by a so-called Peltier device (Fig. 4.8, left; see also Fig. 4.11, left). This is a particular type of thermoelectric device. It can be hooked up to an electric power supply. If we set up a voltage across the device, we observe that one of the bodies of water becomes colder whereas the other one gets warmer (see the diagram in Fig. 4.8, right). Overall, the system gets warmer if the tank is sealed.
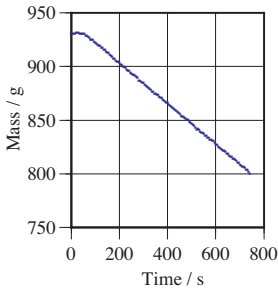

Figure 4.7: Water is vaporized in a can on top of a scale. The mass of the water is recorded as a function of time. (The temperature stays constant during vaporization.)

Figure 4.8: Two bodies of water inside an insulated tank are separated by a Peltier device (top left, see also Fig. 4.11). When operated, the Peltier device cools one body of water and heats the other. Bottom left: Process diagram of Peltier heat pump. Electric charge flowing from higher to lower electric potential releases energy which is used to drive the pump and to produce more heat.
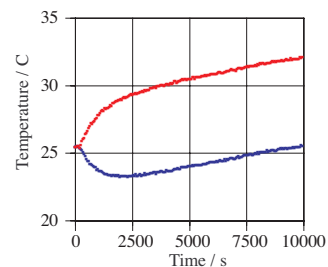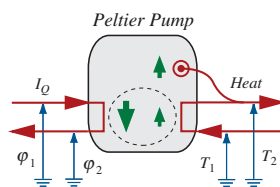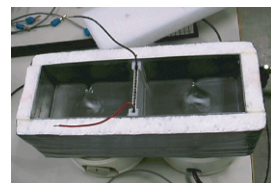
Interpretation. The body of water getting warmer is gaining heat, the other one is losing heat. It makes sense to assume that the heat added to the former is taken from the latter. Since heat goes from a cold to a hot body, it does not flow by itself as in conduction (Fig. 4.5). Heat is said to be *pumped* by the thermoelectric device. Like any other pump, this one also needs energy to do its job (Fig. 4.8, bottom left).

The Peltier device also produces heat; the material through which the electric charge flows has a certain resistance and heat is produced as it is in any electric resistor. As a consequence, the heat of the two bodies of water taken together increases, and the average temperature rises.

A thermoelectric device is a material that conducts electricity (electric charge) and heat. There are no moving parts, and no fluids transporting heat. Therefore, it appears that in a thermoelectric device electric charge can transport heat.

Immersion heaters. One of the simplest thermal devices is an electric heater to heat water. If it is immersed in water, and as long as it is operated, the water either gets warmer or boils away (Fig. 4.9, left).
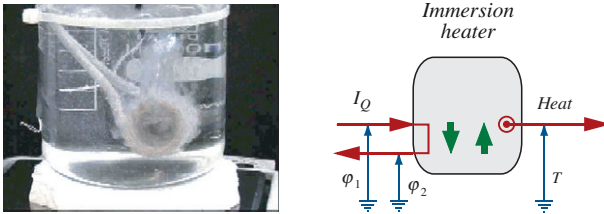

Figure 4.9: Left: An immersion heater heats water which starts to boil. It provides heat to the liquid. Right: Process diagram of an electric heater. Note the difference to the diagram of a Peltier device (Fig. 4.8): Heat does not flow in from a cold place.

Interpretation. We know from the foregoing discussions, that water needs heat if it is to get warmer or boil. Obviously, the heat must be supplied by the electric immersion heater. Since the heater can be operated almost indefinitely, it cannot supply the heat from its own store—there simply cannot be enough of it in the wire. We conclude that an electric heater produces heat, a process we have seen to be operating in many other cases as well. The process diagram of the heater (Fig. 4.9, right) explains how this is to be understood. Energy is released in the electric process and made available to a follow up process which is the production of heat. Heat is produced out of nothing, but not by itself—there has to be a process providing energy.

A Stirling engine. A Stirling engine is a classical heat engine. The engine is heated from outside (any type of heating will do: a fire, electrical heating, heating by concentrated solar radiation, etc.), and cold water is passed through it to cool the engine (the water leaving the engine is warmer than the water entering). When operated like this, the engine can drive mechanical processes (Fig. 4.10, left). The "working fluid" is air or some other simple gas. When the flow of cooling water is reduced, say, by a factor of two, the temperature difference of the fluid also changes by a factor of two, and the engine works somewhat less efficiently.
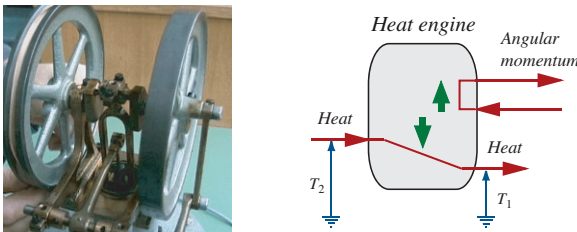

Figure 4.10: Left: The mechanical part of a Stirling engine. When the engine is heated and cooled, the wheels drive a mechanical process. Right: Process diagram: Heat falls from high to low temperature, thereby driving a rotational process.

Interpretation. The following interpretation is motivated by Sadi Carnot's explanation from his famous book *The Motive Power of Heat* (1824).[1] Heat (he also called it caloric) falls from the high temperature of the furnace to the low temperature of the cooler. Doing so it releases energy used for driving the mechanical process of the engine. All the heat supplied by the furnace has to leave through the cooler into the environment. This explains why the temperature of the cooling water rises more if its flow through the engine is smaller. And it explains why the engine is less efficient: The temperature drop from the furnace to the cooling water is smaller.

Note that the process diagram on the right in Fig. 4.10 is essentially the reverse of the one for the Peltier heat pump in Fig. 4.8. Stirling engines, by the way, make great heat pumps or refrigerators. They just have to be operated in reverse, i.e., they have to be driven mechanically.

Thermoelectric generator. A Peltier device can be run in reverse in which case it functions as a heat engine—in this case as an electric generator. Placed between a hot and a cold body of water, a voltage develops across the terminals of the device. If we attach a load to the device, it drives an electric process whose power can be measured from voltage and electric current (Fig. 4.11). Compared to mechanical heat engines operating between similar temperatures, the efficiency of the Peltier device is quite low.

Figure 4.11: Photographs of a Peltier device. The electric power of a thermoelectric generator (a Peltier device between two heat reservoirs at different temperatures) is proportional to the square of the temperature difference. Bottom right: Process diagram of the Peltier generator.
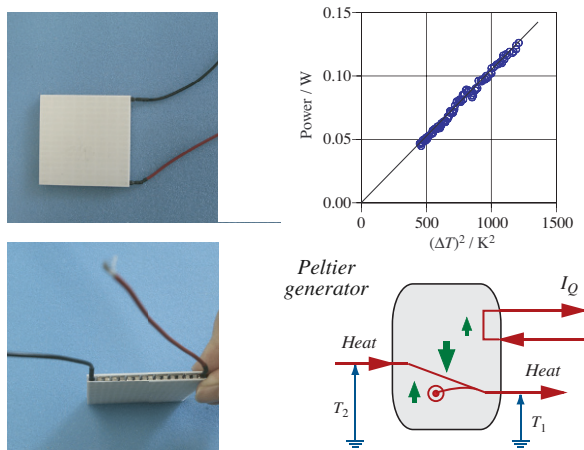
Interpretation. The process diagram explains the operation of the Peltier heat engine. Note that it is fundamentally similar to the one for the Sterling engine (Fig. 4.10). Heat falling from higher to lower levels releases energy which is used to drive the desired process, i.e., the flow of electric charge from lower to higher potentials. Here, however, it is quite clear that only a fraction of the energy released is used to drive electricity. Much of it is used to produce more heat; this is a consequence of the particular structure of the thermoelectric device.

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1.   S. Carnot (1824).

The measured power is proportional to the square of the temperature difference between the hot and the cold water (Fig. 4.11). This is analogous to what we know of the power of an electric load resistor which is proportional to the square of the voltage. Assume the energy released by heat to be proportional to the temperature difference. If the flow of heat is also proportional to the temperature difference, the resulting dependence of power on the temperature difference is what we observe in Fig. 4.11.

Reversing the operation of an electric water pump. In an electric pump, the electric process drives the hydraulic one (Fig. 4.12, left). At the same time, the device becomes warm: heat is generated. The system can be reversed. A system of turbine and generator reverses the electric and hydraulic processes (Fig. 4.12, right). When it is running, it becomes warm: heat is generated.
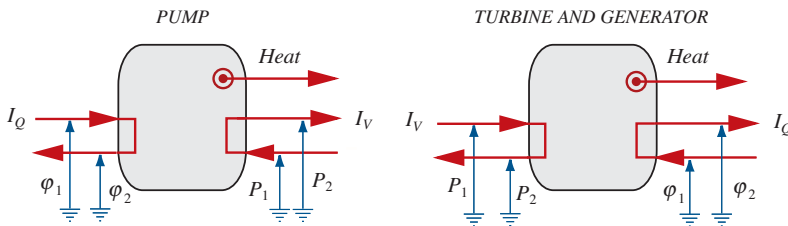

Figure 4.12: Process diagram of an electrically driven pump (left) and its reverse, a system of turbine and generator. Both systems produce heat. The production of heat cannot be reversed—this is what we mean by irreversibility.

Interpretation. Physical processes can be reversed, with one exception. This is the production of heat. If we had to reverse all the processes of a heat producing system, we would have to destroy heat. This does not happen. Instead, heat is again produced. We conclude that heat is a quantity that can be produced but not destroyed.

QUESTIONS

1. Why does the phenomenon shown in Fig. 4.1 show that temperatures rather than quantities of heat equilibrate when bodies are in thermal contact?

2. What does temperature measure?

3. In Fig. 4.1, the temperature reached by copper and water (diagram on the right) is above the average of the initial temperatures of the two bodies. Why is this so? How does this compare with similar phenomena in hydraulics or electricity?

4. What does the example of conduction of heat through a metal bar (Fig. 4.5) tell us about the role of temperature and the flow of heat?

5. Does heat always make a body warmer? Do we always need heat to make a substance warmer?

6. Why do the processes of melting (or of vaporization) and of compression of air demonstrate clearly that heat and temperature cannot be the same quantity?

7. To make water warmer, we need heat. Where can the heat come from? Does it matter for the water where the heat comes from?

8. What is the role of energy in the Peltier heat pump of Fig. 4.8? Why does the production of heat make the device less efficient?

9. Why does measuring the power of a Peltier generator (Fig. 4.11) suggest that the power of heat is proportional to the temperature difference through which heat flows?

10. What are some means of producing heat?

11. What kinds of processes can be reversed? Which ones cannot?

4.1.2 Hotness and Temperature

In this and the following subsections I am going to summarize the experience from the word models of thermal phenomena presented above and provide some additional background on the choice of primitive quantities—heat, hotness, and the power of thermal processes—to build the dynamical theory of heat for this book.

One of our most direct experiences with thermal phenomena is the observation that objects feel hot, warm, or cold. We have a sensation which allows us to place objects in a sequence which we label cold, cool, warm, hot, or very hot. From the *sensation of hotness* we abstract a primitive quantity which we call *hotness*. A primitive quantity is one which we do not derive in terms of other more fundamental quantities.

The concept of hotness goes back to E. Mach.[2] He considered it to be natural and fundamental, like so many other concepts upon which we build the foundations of science. Imagine it to be something like a line on which we organize bodies according to how hot they are, just like beads on a string. Mach wrote:[3]

> Among the sensations by which, through the conditions that excite them, we perceive the bodies around us, the sensations of hotness form a special sequence (cold, cool, tepid, warm, hot) or a special class of mutually related elements … . The essence of this physical behavior connected with the characteristic of sensations of hotness (the totality of these reactions) we call its hotness … . The sensations of hotness, like thermoscopic volumes, form a simple series, a simple continuous manifold … .

The sensation of hotness might serve as a first measure of the physical quantity, albeit not a very reliable one. Naturally, we would like to learn how to determine hotnesses reliably. There are measures of hotness which are more useful than our senses, such as the volumes of bodies which change with the hotness. We can build simple devices to tell how hot an object is. These devices are *thermometers*, with which we measure temperatures. Now, what does *temperature* have to do with the concept of hotness? There is a simple image which explains the relationship. Temperature is like a coordinate on the hotness manifold; it is a numerical indicator of hotness. This, by the way, lets us expect that there may be many possible *temperature scales*, just as there are many possible ways of introducing coordinates along a line. According to Mach:[4]

> The temperature is … nothing else than the characterization, the mark of the hotness by a number. This temperature number has simply the property of an inventory entry, through which this same hotness can be recognized again and if necessary sought out and reproduced … . This temperature number makes it possible to recognize at the same time the order in which the indicated hotnesses follow one another and to recognize between which other hotnesses a given hotness lies.

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2. E. Mach (1923) analyzed the development and the logical foundations of thermal physics. An interesting passage in his book compares the potentials associated with different phenomena (velocity for translational motion, electric and gravitational potentials, and temperature).

3. E. Mach (1923), p. 43. With the exception of the choice of a term the translation is from C. Truesdell (1979).

4. E. Mach (1923), p. 44. In recent years, efforts have been made to base the foundations of thermodynamics upon the hotness as a primitive concept (Truesdell, 1979, 1984; Pitteri, 1982).

There is an interesting and important feature of hotness: it has a lower limit. Experience tells us that this should be the case. Bodies cannot get colder than "really cold." We have never found bodies with a hotness below a certain level, which we call the *absolute zero of hotness*. Put differently, we can say that hotnesses are strictly positive. In fact, the point of absolute zero cannot be reached; it only can be approached. This has been done in experiments to an ever increasing degree. Nowadays, temperatures within a small fraction of one unit (1 Kelvin) from absolute zero can be reproduced.

4.1.3 Heat and Hotness

So far we have heat and hotness as the two primitive concepts for building a theory of thermodynamics. Still, many people do not consciously distinguish between the sensation of hotness, and amounts of heat. The term *heat* is often used in the sense of something being hot. Therefore it is important to stress again the difference between these concepts, and then say positively what we believe the properties of heat to be.

Heat and Hotness. Simple observations tell us that the two quantities cannot be the same. Take an amount of water. We assume that it contains a certain amount of heat. Divide the water into two equal volumes. What can you say about the heat contained in each part, and the sensation of hotness of the parts? Experience tells us that their hotnesses are equal and the same as that of the original body of water. However, the heat content has been divided equally among the parts. Therefore the sensation of hotness and amount of heat are clearly two different things. Hotness is called the *intensive* thermal quantity while heat is the *extensive* one.

Two phenomena demonstrate beyond any doubt that heating is not just another word for change of hotness (in which case there would not be any need for a new quantity!). The first is the melting of ice. When ice is heated, it melts, but its hotness does not change as long as there is a mixture of ice and water. The second one is the fast compression of air without heating or cooling (without adding or withdrawing any heat). The temperature of the air rises greatly whereas the heat of the gas is not changed.

Temperature differences as the thermal driving force. Consider the following example that serves to illuminate the role of hotness even further. Place two bodies at different temperatures in thermal contact and monitor their temperatures. We know what will happen. In the course of time the hotter body will cool down while the cooler one must heat up. Experience tells us that this continues as long as the temperatures are different. Finally, after some time, the hotnesses have become equal and the process stops (Fig. 4.1). Another interpretation of this phenomenon is to say that heat flows by itself from the hotter to the cooler body as long as there is a difference of temperatures.

We have seen analogous processes in other fields of physics (Table 4.1). Two containers filled with water and connected by a hose, or two charged bodies connected by a wire, behave similarly. In those cases we speak of the flow of a certain physical quantity as a consequence of a driving force. We have defined driving forces as the difference of potentials between the physical systems. If we take these phenomena as a guide, we can interpret a difference of temperatures as the *thermal driving force* and hotness as the *thermal potential*. In graphic language, hotness takes the role of the thermal level.

The driving force determines the type of process taking place. In this sense we say that a thermal process is one in which heat flows due to a difference of temperatures. Note

that not every mode of heat flow is a thermal phenomenon according to this definition. Witness the following example: you can carry around a bucket of hot water, which means that heat is being transported. But certainly this is not a thermal process. Hotness plays a central role in what we call a thermal phenomenon, and we may not forget the qualifier given in the definition above.

Table 4.1: Comparison of some processes

	Quantity	**Potential**
Water containers joined by a hose	Water	Water level
Charged spheres in contact	Electric charge	Electric potential
Bodies at different temperatures	Heat	Hotness

4.1.4 The Properties of Heat

There are two important points to consider at the beginning of any discussion concerning the nature of heat. First, we would like to know what is responsible for making a stone warm or for melting a block of ice. Second, we have to recognize the difference between a moving body, a charged sphere, and a hot stone, as well as how this difference can be expressed in a theory of physics.
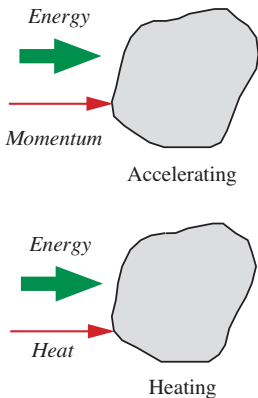
It is quite clear that *heat* makes a stone warm and melts an ice cube. We put more heat into a body such as a stone to make it warmer; taking heat out of the stone will make it cool down. If we put ice in a warm place, heat will enter the body and make it melt. *Heat* is the perfect quantity for describing what is happening in these situations.

What heat is not. The second question goes to the core of what heat is not. First try and answer this question: What do the moving, charged, and hot body have in common? Again the answer is quite clear this time for those who have studied physics. In all three situations the body has received energy (Fig. 4.13). In each case, the system contains more energy than if the body were not moving, if it were not charged, or if it were not hot. Seen from the viewpoint of energy, the situations are all the same, and we should rather ask about how a stone which is moving differs from a stone which is hot. We might learn more about how nature works from the answer to this question.

We could say that the difference lies simply in the fact that the moving body has received an amount of motion while in the case of the hot body we have added some heat (Fig. 4.13). We have learned that amounts of motion are measured in terms of momentum. Changing the motion of a body requires that we change its momentum. True, we also change the energy of the body at the same time, but knowing that the energy of a system can be different for many different reasons, we take momentum as the quantity which tells us why the body is moving rather than becoming hot.

Applying this argument to the hot body, we have to conclude that the stone is hot not because it contains energy but because it has more heat than if it were colder. A stone gets hot and an ice cube melts because of heat. Even though energy accompanies all processes, heating included, it cannot distinguish between them. The point is this: *heat is not energy*.

Energy

Momentum

Accelerating

Energy

Heat

Heating

Figure 4.13: Two processes compared. In the first we accelerate a stone. In terms of physics, we say that momentum is added to the body, which makes it move faster. We know that energy is added to the stone at the same time. In the second case, the stone is heated rather than accelerated. The difference between the situations is that now we add heat rather than momentum. Heat is responsible for making the stone warmer.

The laws of physics help us to assure ourselves of this point. You know that energy is a different measure of gravity or inertia (Chapter 3). Increasing the energy of a system means increasing its mass. It does not mean that the body has necessarily become faster, hotter, or both; it might just as well have become electrically charged. Energy, i.e., mass, cannot be used to distinguish between different processes. We absolutely need other quantities such as momentum or charge, if we wish to state what has happened to a body. Applied to thermal processes this means that if heat is the quantity responsible for warming a stone or melting ice, rather than making the bodies heavier, then heat cannot be energy.[5]

Heating and cooling: Transport of heat. Clearly, the hotness of objects can change. The sand at the beach is hot at noon, and cool at night. We can get hot water for coffee by heating it. Ice is produced by cooling water.

Therefore, there is more to thermal phenomena than just the hotness. We definitely need a means for changing this quantity. Again, on the basis of every-day experience, we can introduce the notion of *heating* (or cooling). We can heat bodies slowly or quickly; hence we often speak of the rate of heating. However, we have used the word *heating* already in the sense of a rate, namely the *rate of transfer of heat* to a body. *Cooling* stands for the rate of transfer of heat out of a body (Fig. 4.14). We clearly have to distinguish between heating and cooling on the one hand, and getting warmer or getting colder on the other.

Obviously, heat can be transported. Heat from the sun arrives at the Earth, where it is distributed in the atmosphere before it is radiated back into space. Heat flows out of the depths of the Earth to the surface. A metal bar which is heated at one end also gets hotter at the other end, which demonstrates that heat becomes distributed throughout the body. Large amounts of heat are transported from the Gulf of Mexico to Europe with the help of the Gulf Stream. Central heating systems transport heat from the burner to the radiators from where the heat flows into rooms. There are many aspects of life which are influenced by the flow, transport, or distribution of heat. We will therefore study this aspect of thermal physics in detail. Here, we will briefly introduce the three modes of *heat transfer*:

- *Conduction*. There is one class of phenomena in which heat flows through bodies. The bodies do not have to move for heat to get from one place to another. Experience tells us that heat flows only from places which are hotter to those which are cooler. A difference of hotness is needed for maintaining such a flow. Indeed, bodies in thermal contact stop exchanging heat when they are equally hot. This type of transport is called *conduction of heat*.

- *Convection*. Heat can be transported with bodies. There are many examples, such as the Gulf Stream, heated water flowing from a burner to a radiator, or hot air rising up in a chimney. In this case heat does not have to flow through the bodies. Heat which resides *in* bodies flows because the bodies themselves are
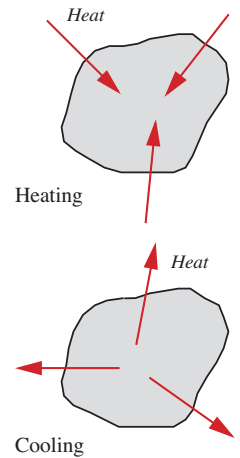
Figure 4.14: Heating and cooling. By *heating* we mean the flow of heat into a body. In the case of *cooling*, heat flows out of the body. We assume that heat is a quantity which can flow. Also, we believe that heat can be stored in bodies.

5. Obviously, then, you will have to look elsewhere for the quantity called *heat*. This is precisely what we will do in this section. Please be patient if I use the term *heat* for the quantity which makes your room warm, which is responsible for melting ice or metal, and which drives so many of the other processes going on around us. For the impatient among you, the property emerging from our knowledge of everyday phenomena is *entropy*. I hope to motivate the properties of this fundamental thermal quantity by tying it to the concept of heat before we start using the formal term *entropy*.

transported. The driving force of the process must be the one associated with the flow of matter, for example a pressure difference. If heat is transported in this manner we speak of *convective transport of heat*.

- *Radiation*. There must be a third type of transport which, for example, manages to get heat all the way through empty space from the sun to the Earth. You can feel this kind of heat flow when you sit near a fire, or behind a window with the sun shining on you. There is no need for the air to transport heat to you. Moreover, air conducts heat much too little for this to be of any effect. Therefore, heat must flow through another medium, namely a radiation field. This type of transport is called *radiation of heat*.

Storage of heat. If heating is the rate of transfer of heat, then some *quantity of heat* is transferred in a process. If we heat a body in a particular manner, we transfer more heat the longer we allow the heating to occur. The amount of heat communicated to a body can therefore be calculated simply from the heating. In this sense, heat is a quantity which can be derived from heating; it is not new or independent of what we already have introduced.

Still, there is something new about the notion of heat, something which is not trivial at all. Heating is taken as a term for describing a process or an action. The word *heat*, on the other hand, suggests the image of something tangible, something we can measure as it flows past us when heating occurs. There is an amount of something, like an amount of water, or more like an amount of electricity which can be stored in bodies. Where else should the heat be after it has been transferred to an object in the process of heating? Why would a little child ask whether a baked potato is heavier than a cold one, if it were not for the additional heat it contains when it is hot? For this discussion we shall accept the following:

> *Heat is a quantity we can imagine as being stored in bodies, and as being capable of flowing from body to body.*

Consequently, we can say that bodies contain a certain amount of heat, and this amount can change as a consequence of heating or cooling, i.e., as a consequence of the flow of heat. For a physicist, this suggests comparisons with other quantities which have been introduced in other theories, notably those of electricity and motion (Prologue). In this sense, *heat is the extensive or fluidlike thermal quantity* (Table 4.2).

Table 4.2: Fluidlike quantities

Process	Quantity
Electric	Electric charge
Gravitational	Gravitational mass
Translational motion	Momentum
Rotational motion	Angular momentum
Thermal	Heat

Remember what I said in the first three chapters about fluidlike quantities such as electrical charge or momentum. These quantities are abstract; they are not material in any sense of the word. Still, we can profit tremendously from forming simple graphical

images such as the ones used in this section. If we think of heat as an abstract "fluid," we will be led easily and directly to the formal mathematical laws that govern it. We just have to be careful not to take the naive picture too literally. Heat does not add weight to a body, it cannot be seen, nor can it be touched and, most interesting of all, heat can be produced. As we will find out shortly, this quantity is not conserved.[6]

The production of heat. We have not discussed an important question yet: Where does heat come from? Nature tells us that there must be sources of heat. In some cases heat simply flows out of bodies in the process of cooling. However, there are examples which are more interesting. Heat can come from the Sun, or out of the Earth. Heat is produced in a fire, by rubbing our hands, or by letting electricity flow through wires.

There appears to be a distinct difference between the first process, and the other ones listed above. In cooling, an object loses the heat it received in a process of heating. The body simply undergoes the reverse of the previous process. In the other cases, the body emitting the heat does not have to change its hotness. As far as we know, the degree of heat of the interior of the sun does not change much as it pours out vast amounts of heat (in fact, it gets even hotter). An electrical heater does not get cold as it heats water. And the heat produced by rubbing your hands has not been put into them previously. So, where does the heat come from in these cases?

We might believe that the amount of heat contained in bodies is always so large that the emission of some of it will not change their hotness. However, this is rather unlikely. Clearly there must be sources of heat in the true sense of the word. Heat which was not there before is pouring out of the body. Why does the electrical heater cool very noticeably when the electricity is turned off? Certainly, after switching off, it emits only a small amount of heat compared to what it emits while working. Why does the hotness change in the former case and not in the latter?

About two hundred years ago two sets of experiments were performed which were believed to demonstrate beyond any doubt that heat cannot be a conserved quantity. The first, the cannon-boring experiments of Count Rumford, have much in common with the electrical heating described above. Heat is produced by friction as long as the boring process is going on; so where does all this heat come from? The second experiment, by H. Davy, was thought to be even more important.[7] We can melt two blocks of ice by rubbing them against each other. Water which results from rubbing the ice certainly contains more heat than the ice it came from, because we need heat to melt ice. If we perform the experiment in an environment whose temperature is lower than

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6. We are in good company with these assumptions about heat. The Greeks used a similar picture, and in early modern times up to 1850, physicists used pretty much the same ideas. Back then, heat often was called caloric (remember Carnot's description of the operation of heat engines; Section I.3). There are several other terms which aptly describe what we mean by heat: thermal element (because of the similarity to Greek thinking), or thermal charge (in analogy to electricity; see McGraw-Hill Encyclopedia of Science and Technology). Heat, caloric, thermal element, and thermal charge, refer to the same thing, namely, the fluidlike thermal quantity which flows into bodies and is stored there if the bodies are heated, and which flows out of the bodies if they are cooled.

7. A critical reappraisal of the experiments shows that a proof of Davy's claim (Davy, 1839) was almost impossible (D. Roller, 1950). The question of where the heat comes from for melting the ice is less than trivial. However, if we could take care of all possible interferences, we would have no doubt as to whether or not we can melt ice by friction; it is certainly possible.

that of the melting ice, the heat added to the water cannot have come from outside. We have to conclude that after the process there is more heat in the world than before: the surroundings of the ice and water have not lost any heat, while the system contains more heat than before. Even though Rumford's reasoning is not tight, and Davy's experiment is difficult to perform in any quantitative manner,[8] we shall accept the evidence offered by nature: *heat can be created*.

Irreversibility. Heat can be created. Does this mean it can be destroyed as well? Since we have had to conclude that it is not a conserved quantity, the question is realistic. If we consider the evidence offered by nature, we come to the conclusion that *heat cannot be destroyed*; it can only be distributed to colder places. Heat which leaves a body goes into the surroundings to heat them. The reason why we often do not notice this effect on the surrounding bodies is simple: they usually are very much larger than the body which is losing heat.

Again, you can use your general knowledge of natural or man-made processes to come to far-reaching conclusions. You know that certain processes run one way but not necessarily in the reverse. Or if you make them run in the reverse, something else will change because of it. Real processes are said to be *irreversible*. If heat did not exist already, you would have to invent a physical quantity with its properties to account for irreversibility.

A simple example explains the meaning of irreversibility. A moving wooden block comes to rest on a horizontal surface. The reason is clear: friction hinders the motion and finally lets it "die." Friction also creates heat, so the production of heat is coupled to the block coming to rest.

What is irreversible out this? At first sight, *irreversible* should mean *cannot be reversed*. But the motion of the block can be reversed! We simply have to push the body across the surface, thereby accelerating it. Something, however, cannot be changed here: heat will also be created during the reversed motion; friction makes sure heat will be generated. You have never seen a block absorbing heat from the surroundings and destroying it, thereby starting to move by itself. This is what we mean when we say that a process is irreversible.

Another good example of irreversibility is the case discussed in Fig. 4.12. The operation of an electric water pump can be effectively reversed except for one crucial feature: the production of heat. The system that results from reversing the pump gets warm as well. Engines have to be cooled, not heated, pointing to the equivalence of irreversibility and the production of heat. Again, we can understand the behavior of some aspect of nature on the basis of the properties of heat. We now make the following definition:

> *An irreversible process is one during which heat has been created. A process without the creation of heat is called reversible.*

The term *irreversible* is somewhat unfortunate in the light of the examples given, considering that processes can be reversed with the exception of the production of heat. Another descriptive term has been coined for processes which produce heat: they are called *dissipative*.

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8. D. Roller (1950).

The balance of heat. All in all, we form a mental picture of heat as something like a "substance" or a "stuff." We picture bodies as *reservoirs for heat*, we may speak of the *heat content* of an object, which will be described by a function of the independent variables of the body. Also, this "substance" flows into and out of bodies. The process of the *flow of heat* into a body is called *heating*. (The opposite is called *cooling*, or *negative heating*.) By stating such ideas we add heat to the list made up of electric charge, gravitational mass (gravitational charge), momentum, and angular momentum (see Table 4.2). Heat is another *fluidlike* quantity which simply means that *heat can be pictured to be contained in bodies and to flow from one body to another*. No further assumptions are made. Specifically, heat is not conserved!

All of this tells us that we should deal with heat as we do with other fluidlike quantities and formulate a law of balance to deal with its dynamics. We know how to do this from fluids, electricity, and motion (Chapters 1-3), and this will be the first step in creating a formal theory in this chapter. In contrast to the laws of balance of charge or momentum, this law will include a production term. What this means, and how this is done, will become clear in Section 4.3 and beyond.

Quantifying heat, heating, and producing heat. It is instructive to list amounts of heat to get better acquainted with this quantity (Table 4.3). As always, a physical quantity has a *unit*. Since heat is a new and fundamental quantity which is not associated with anything else we know so far, it should have its own unit. Let us therefore introduce the unit of heat called the *Carnot* (Ct) which we are going to use for now.[9]

Table 4.3: Amounts of heat (rough values in Ct)

Process or state	S / Ct
Heat necessary to melt 1 cm^3 of ice	1
Heat added when heating 1 cm^3 of water from room temperature to boiling	1
Heat needed to vaporize one cm^3 of water	6
Heat content of 1 liter of gas at normal pressure and temperature	10
Heat content of 1 mole of argon gas at room temperature	10^2
Heat produced by a water heater in one minute	10^2
Heat generated when a fast travelling car brakes	10^3
Heat content of 1 liter of liquid or solid at room temperature	10^4
Heat generated in burning 1 kg of coal at room temperature	10^5
Heat escaping a standard home in one our in winter	10^5
Heat produced by 1 m^2 of a solar water heater on a sunny day	10^5

4.1.5 The Power of Heat

"Every one knows that heat can produce motion. That it possesses vast motive-power no one can doubt, in these days when the steam-engine is everywhere so well known.

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9. For historical reasons, the unit of heat is normally given in terms of other units. In Section 4.4 we will find that it should be expressed as 1 Ct = 1 Joule/Kelvin, where Joule and Kelvin are the SI units of *energy* and *temperature*, respectively.
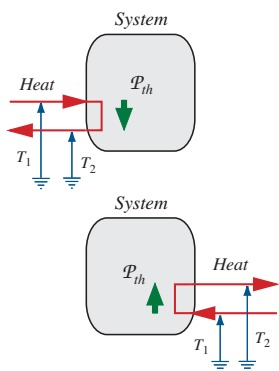
Figure 4.15: Process diagrams that explain the basic relationship of heat and energy. Top: Energy is released when heat "falls" from high to low temperature. Bottom: Energy is used when heat is pumped. The rate at which energy is released or used is called thermal power, $\mathcal{P}_{th}$.

To heat also are due the vast movements which take place on the earth. It causes the agitations of the atmosphere, the ascension of clouds, the fall of rain…."[10]

We have seen for ourselves that heat can produce or drive other phenomena. As before, we take this as an indication of the need for a new concept, namely *energy*, that stands in a particular relationship with the quantities we use to understand a phenomenon. It is fitting that we finally deal with the field where the form of the relationship stems from: Sadi Carnot's thermodynamics. His image of the fall of water as an analogy to the operation of heat in a heat engine (Section I.3) has served us well so far in fluids, electricity, gravity, and motion. Why shouldn't it serve us even better in its field of origin?

The process diagrams that accompany the interpretations of phenomena discussed in Section 4.1.1 (Fig. 4.8 through Fig. 4.11) tell the story. There is not much to be added.[11] When heat flows from a point of high to a point of low temperature, energy is released at a rate we assume to depend upon the flow of heat and the temperature difference (Fig. 4.15, top).[12] We shall call this rate *thermal power*; it is Sadi Carnot's *Puissance du Feu*, the *Power of Heat*. If heat is to be pumped from a lower to a higher temperature, we need energy at a rate that depends upon the rate at which heat is pumped and the temperature difference through which it is pumped (Fig. 4.15, bottom). See Section 4.4 for a quantitative discussion.

4.1.6 Heat, Thermal Processes, and the Properties of Bodies

So far, we have talked only about the generic properties of heat: it can be stored, it can flow, and it may be produced. These are the things that happen in thermal processes as far as heat is concerned. However, the interesting details of processes depend not upon heat so much as upon material bodies or systems being heated or cooled. Therefore, we will have to study in detail the special behavior of different types of physical bodies.

Different bodies contain different amounts of heat under given conditions, and different substances require different amounts of heat for melting. The form of heat flow and heat production, even the question of whether heat is produced in a particular process, will be found to depend upon the properties of the bodies suffering change. If you prefer, the answer to such questions depends upon the *models we construct of the bodies* undergoing processes.

4.1.7 Heat, Caloric, Entropy

The quantity I have been calling *heat* in the interpretations of thermal processes was called caloric by Sadi Carnot and his contemporaries. This easily visualized and intuitively understood quantity best fits what after 1850 was called *entropy* in physics, chemistry, and engineering. Therefore, the concept of entropy which, in standard presentations of thermodynamics is considered to be formal, derived, and non-intuitive,

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10. S. Carnot (1824), p. 3.

11. Actually, there is one thing that will be new to us, namely how to deal with the production of heat: How do we relate energy to the process of producing heat? See Section 4.4.

12. Read Carnot's words in the Introduction (Fig. I.3).

has simple and intuitive roots. It is analogous to volume and to charge in fluids and electricity, respectively.

What I have constructed is a generalized version of the fundamental quantity called entropy. In fact, the concept of heat used here is general enough for us to build modern continuum thermodynamics upon. The procedure is very simple. Let us accept that heat (entropy) has the properties of a non-conserved fluidlike (i.e., extensive) quantity. This will lead immediately to a law of balance of heat (entropy) as the most important expression of our assumptions about thermal processes.

From now on, the formal term *entropy* will be used for the quantity of heat. However, when speaking colloquially, I will always mean a quantity of entropy when referring to heat. In expressions such as "the body has been heated" or "in this process heat has been produced," *heat* will continue to stand for its formal equivalent, namely for entropy. Otherwise I will drop the word *heat*, i.e., I will *not* use it for the only acceptable meaning in traditional thermodynamics, namely amounts of energy exchanged in heating.

If you still believe that using the concept of entropy from the start is too difficult, consider what J. W. Gibbs once wrote:[13]

> One of the principal objects of practical research … is to find the point of view from which the subject appears in its greatest simplicity. … a method involving the notion of entropy … will doubtless seem to many far-fetched, and may repel beginners as obscure and difficult of comprehension. This inconvenience is perhaps more than counter-balanced by the advantages of a method which makes the second law of thermodynamics so prominent, and gives it so clear and elementary an expression … . If, then, it is more important for purposes of instruction and the like to familiarize the learner with the second law, than to defer its statement as long as possible, the use of the entropy-temperature diagram may serve a useful purpose in the popularizing of this science.

QUESTIONS

12. When air is compressed quickly, its temperature rises. Why shouldn't we say that the air has been heated? What could we say has happened to the air instead?

13. If a body receives 10 Ct entropy and does not lose any, does it mean that its entropy content changed by 10 Ct?

14. What is the meaning of the thermal power of a heat pump?

15. For a certain temperature difference and current of entropy, a thermoelectric device has an electric power of 1.0 W. A different thermoelectric device has an electric power of 1.2 W for the same thermal conditions. Is the thermal power different or the same in these cases?

16. A battery with an open circuit voltage of 4.5 V pumps an electric current of 1.0 A. The internal resistance of the battery is 1.0 Ω. What is the thermal power of the device? Where is the energy released/used that corresponds to this quantity?

17. When entropy flows through a copper bar, is there a measure we can call thermal power?

18. How much coal has to be burned to keep the home mentioned in Table 4.3 warm during a winter day?

13. J. W. Gibbs (1873).

4.2 A DYNAMICAL MODEL OF COOLING

Before we delve into a quantitative and more formal discussion of thermal processes, a dynamical model will be created for a concrete case—the cooling of hot water in a thin-walled aluminum can (Fig. 4.4, left). This should give us a better feeling for some of the questions we have to deal with in this chapter.

Hot water is poured into an aluminum can (a typical 0.5 L soda or beer can which was stripped of all its paint to reveal a polished aluminum surface). The can is placed on top of a magnetic mixer and a bar magnet is used to stir the water continuously to ensure uniform conditions. The idea is to have a single temperature of the body of water for us to deal with. The temperature is recorded as a function of time. Since the experimental result looks suspiciously like that of discharging a container or a capacitor, a model similar to those for an *RC* system (Section 1.5) might be what we need to understand the thermal phenomenon.

As before, we start constructing the dynamical model by considering appropriate laws of balance (Fig. 4.16, center). It appears that a single such expression will suffice. All we need to know is what happens to the entropy of the water. A reservoir (S_water) symbolizes the entropy of the water, and inflows and outflows represent thermal processes.

Figure 4.16: Diagram of a system dynamics model (center) and data and simulation result (right) for the cooling of hot water in an aluminum can. The hydraulic system (left) has a largely analogous structure compared to the thermal one.
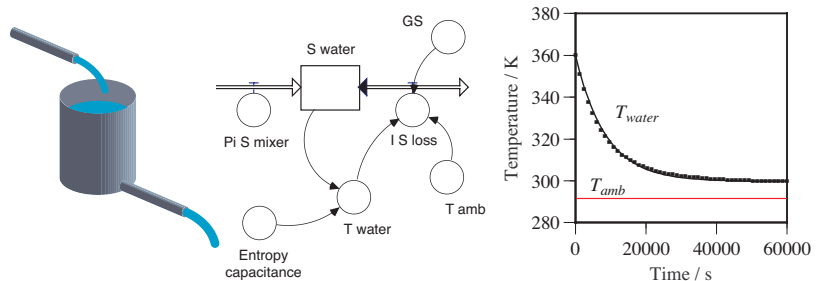
There are two processes to consider: The flow of entropy out of the system (I_S_loss) which is a consequence of the difference of temperatures between water (T_water) and environment (T_amb), and the rate of production of entropy as a result of mechanical stirring (Pi_S_mixer). The former leads to the (almost perfect) exponential decay of the temperature, the latter ensures that there is a constant final temperature above that of the environment (entropy produced must leave the system). Note that we can deal with the production rate of entropy as we do with an inflow; as far as the water is concerned, produced entropy is as good as entropy transported in from outside. All in all, this looks very much like a system composed of a water tank losing water through a pipe at the bottom and receiving water through a (fixed) inflow at the top (Fig. 4.15, left). This completes the expression of the law of *balance of entropy* for the system of hot water:

$$\frac{dS_{water}}{dt} = I_S + \Pi_S \tag{4.1}$$

S is the standard symbol for entropy. This makes I_S an *entropy current* analogous to currents of other fluidlike quantities such as charge or momentum, and Π_S is an *entro-*

py production rate that measures how many units of entropy are produced every second (Π is the symbol used for production and destruction rates in this book).

At this point we need to construct ideas for the processes identified in the first step of systems analysis. From what we know of the behavior of hydraulic or electric systems, the simplest model for the loss of entropy is to make it proportional to the difference of temperatures between water and environment:

$$I_S = G_S \left(T_{amb} - T_{water} \right) \tag{4.2}$$

with a flow factor G_S (which, for obvious reasons, can be called an *entropy conductance*) as the factor of proportionality. This is the basic form of a model of a resistive transport (Section 1.4.1).

We do not yet have any experience with entropy production, so let our experience with hydraulic models be our guide to how we might get the appropriate behavior of the temperature of the system for large times (see the graph in Fig. 4.15 on the right). If we have a constant inflow that is smaller than the outflow at $t = 0$, we should expect an exponentially decreasing curve that settles above the level of the environmental temperature. So let Π_S be some constant to be determined by simulation.

This leaves the problem of how to determine the temperature of the water. We know from experience that the more entropy that is stored in the water, the higher its temperature must be. Clearly, we shall have to study this point in more detail and derive temperature–entropy relations for the materials that are of interest to us. Part of this chapter will deal with this question. The simplest possible relation is linear, meaning

$$S = KT \tag{4.3}$$

Again for obvious reasons, we should call the factor of proportionality *K entropy capacitance*. Remember the description of pressure–volume and voltage–charge relations for containers and capacitors, respectively (Section 1.4.2).

There are three parameters in this model which have to be determined if we want to compare simulations to experimental data. When we attempt simulations, a problem turns up: there is not enough information to find all three parameters independently. Say we fix the entropy production rate, we can then find the entropy conductance in this model in terms of Π_S. All we have to do is consider the steady-state toward the end of the period of the experiment when the water temperature has become virtually constant. In the steady-state, the rate of change of entropy must be zero which makes I_S the negative of Π_S. Since we know the final temperature difference $T_{amb} - T_{water}$, we can determine G_S. Once we have this, simulation of the dynamical model lets us set an appropriate value of the entropy capacitance. The results of this procedure are very encouraging (see the graph in Fig. 4.15 on the right). We get a very close agreement between data and simulations. Even though we do not have actual values of the physical parameters of the system, the ideas implemented in the constitutive laws are at least a good start.

Apparently, everything depends upon knowing how to calculate an entropy production rate which means knowing how to quantify amounts of produced entropy. Naturally, we could have started at a different point, say, by fixing the capacitance and then determine the other parameters. Either way, we need to have a clearer understanding of how bodies respond to heat. We should learn how to quantify amounts of entropy,

how to determine temperature–entropy relations for simple materials, and how to find conductances for simple conductors. This is what we are going to do in more detail in the subsequent sections of this chapter.

4.3 ENTROPY AND TEMPERATURE

Hotness, or its quantitative measure called temperature, and entropy are the basic concepts we use to build thermal models. In this section, some of their formal aspects will be described, and examples of processes that can be visualized in temperature–entropy diagrams will be discussed. The examples are designed to give us an initial understanding of the use of the fundamental thermal concepts.

4.3.1 Temperature and Thermometry

Temperatures can be measured quite easily. Still, the concept of temperature is anything but trivial. In particular, we will not be able to find *the* temperature scale, i.e., the one and only scale which reads the "true" temperature. If there is anything like an *absolute temperature* independent of materials we cannot say yet. For now, we have to be satisfied with a couple of empirical scales. Some values of temperature can give us a feeling for the range of values (Table 4.4).

Table 4.4: Some temperatures (in °C)

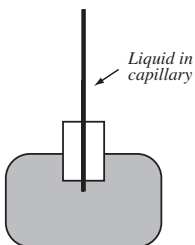|	
Boiling point of helium	– 269
Boiling point of nitrogen	– 196
Melting point of carbon dioxide	– 79
Melting point of mercury	– 39
Melting point of ice	0
Temperature of human body	37
Boiling point of water (1 bar)	100
Melting point of iron	1535
Surface temperature of sun	5800
Central temperature of sun	$13 \cdot 10^6$

Liquid in capillary

Figure 4.17: Thermometer based on the expansion of a liquid. The small changes of the volume of the liquid are made visible by the capillary.

The Celsius temperature scale. We are quite accustomed to measuring temperatures in everyday situations. For example, if you take your temperature you might use a thermometer based on the expansion of mercury in a thin capillary. Mercury expands when it is heated, and the expansion is measured and used to fix the temperature. When bodies are heated, the rise in temperature is accompanied by changes in one or more properties. Change in volume is just one of those possible changes. Others include changes in length, electrical resistance, color, and pressure of gases.

The change of volume of a liquid can be observed using a simple device (Fig. 4.17). Fill a small bottle with the liquid and close it with a cork through which a long and thin capillary has been fitted. Allow the liquid to fill the bottom of the capillary. If you hold the bottle in your hands for a while, the liquid in the capillary will climb (in most cases). How does this work? Heat flows from your warm hands to the colder liquid,

which expands. The change in volume is usually very slight, but it can be made visible by the capillary: since the capillary is very thin, even small changes in volume translate into large changes in the height of the column of liquid.

Historically, the first useful thermometers were based on this type of device. Today, we use mercury as the liquid (which we call a *thermometric substance*). On the basis of such thermometers, we may introduce a temperature scale, the *Celsius scale*. We measure the length of the column for two different temperatures, e.g., those encountered when water freezes and boils. The first point is assigned the temperature 0°C (zero degrees Celsius); the second corresponds to 100°C. The interval in the length of the column of mercury is divided into 100 equal parts, each part corresponding to a change in temperature of 1°C. The Celsius scale is not the one and only absolute coordinate system on the hotness manifold. Rather, we have arbitrarily set a certain change of temperature to be proportional to the change of length of the mercury column in the capillary.

We cannot be sure that other thermometric substances will deliver scales proportional to the one introduced on the basis of the expansion of mercury. We cannot even be sure that volume or length will always increase when the hotness increases! Water is a beautiful counterexample. Water exists in the range of temperatures spanning 0°C to 100°C. At low temperatures, near its freezing point, the volume of water first decreases, reaching a minimum at 4°C before finally increasing (Fig. 4.18). At temperatures above 4°C, water behaves as we might expect of a "normal" substance. The behavior of water at low temperatures is called an *anomaly*. This anomalous behavior prevents lakes from freezing totally, which saves the fish in them in winter.

Water, therefore, could not be used as a thermometric substance. While we would get meaningful results out of a water thermometer in the range of temperatures from 4°C up to 100°C, the same would not be true if we included the density extremum. (The question of why we should not use water as a thermometer in the range between 0°C and 4°C is more subtle.)

Thermal expansion. Bodies expand or shrink when their temperature is increased. Fig. 4.18 shows the result of measurements of the thermal expansion (or shrinking) of water. In Fig. 4.19 the change of the length of a bar is indicated. To describe the change mathematically, it is customary to introduce a *temperature coefficient of (linear) expansion* α_l. This coefficient is defined as the relative rate of change of length l of a body with (Celsius) temperature θ. This means that the relative change of length is obtained if we integrate the coefficient over temperature:

$$\frac{\Delta l}{l} = \int_{\theta_o}^{\theta} \alpha_l(\theta)d\theta \tag{4.4}$$

We can approximate the length of such a bar over a small range of temperatures by a linear relation. In other words, we may choose the constant value α_{l0} at θ_0 for α_l. In this special case, the relative change of length of a body is given by

$$\frac{l - l_0}{l_0} = \alpha_{l0}(\theta - \theta_0) \tag{4.5}$$

Here, l_0 is the length of the body at a reference temperature θ_0 (which might be 0°C). Values of the coefficient of expansion for some materials are listed in Table 4.5. Note that α_l has the unit 1/K (which is introduced below).
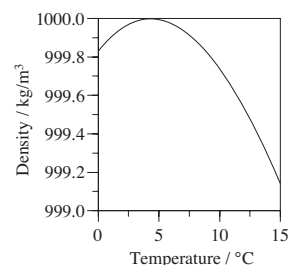

Figure 4.18: Variation with temperature of the density of water. The variation around 4°C is shown in some detail. The pressure is constant and equal to atmospheric pressure.
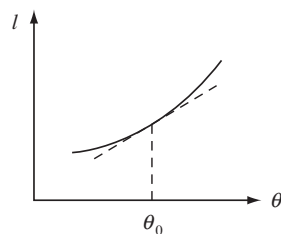

Figure 4.19: Change with temperature of the length of a long bar of a particular material. The relationship between length and temperature usually is a complicated one. Over a small range of temperatures, however, it may be approximated by a linear function.

In analogy to the formula for the change of length, the *change of volume* with temperature is often approximated by a linear expression:

$$V(\theta) = V_0\left(1 + \alpha_V\left(\theta - \theta_0\right)\right) \tag{4.6}$$

Here, α_V is the *temperature coefficient of volume expansion*; values for some materials are listed in Table 4.5. This coefficient has the unit 1/K.

Table 4.5: Linear coefficient of expansion

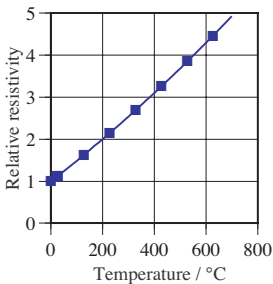| Substance	$\alpha_l / 10^{-6}\,\text{K}^{-1}$	Substance	$\alpha_V / 10^{-6}\,\text{K}^{-1}$
Copper	16.8	Alcohol	1100
Glass (pyrex)	3.2	Gasoline	1060
Glass (quartz)	0.45	Glycerine	500
Granite	3…8	Mercury	181
Ice (0°C)	0.502	Sulfuric acid	570
Iron	12.1	Water	207
Lead	29		
Sandstone	7…12		
Sodium	71		
Steel	10–16		
Teflon	60–100		
Titanium	9		

Figure 4.20: Relative electric resistivity of tungsten as a function of Celsius temperature. The reference point is 0°C.

Electric resistance. Another property which in many cases changes with the hotness is the *electric resistivity* of a material. Thus it can be used for thermometry as well. A widely used thermometer is based upon the electrical properties of platinum. This thermometer is applied for accurate measurements in the range from 253°C below freezing to roughly 1200°C. Very often, the empirical relationship between temperature and resistance is represented by a quadratic equation of the form

$$R(\theta) = R_0\left(1 + \alpha_R\left(\theta - \theta_0\right) + \beta_R\left(\theta - \theta_0\right)^2\right) \tag{4.7}$$

α_R and β_R are the linear and quadratic temperature coefficients of resistivity, respectively. There is nothing deep or fundamental about the form of this relationship; it is a representation of empirical data just like Equations (4.5) or (4.6). The example of tungsten is given in Fig. 4.20. However, these equations are important in a different sense: they are examples of constitutive relations. See Table 4.6 for some data.

The ideal gas temperature. The Celsius scale of temperature is only one of many we could construct. We will now introduce another scale that will be of great use in thermodynamics, namely the *Kelvin scale*, which is based on the *ideal gas temperature* and which is independent of the particular thermometric fluid. However, we will be able to demonstrate this feature only after we have discussed thermodynamics of gases in Chapters 5 and 10.

It is a common experience that the pressure of gases increases if they are heated while the volume is kept constant. For example, consider the build-up of steam pressure in

a pressure cooker: the volume does not change, and the pressure increases with increasing temperature. Somehow, the pressure of a gas must be related to its temperature. A simple setup called an *air thermometer* (Fig. 4.21) can be used to measure the temperature and pressure of a gas whose volume is kept constant. Fig. 4.22 shows the nature of the results one commonly obtains from measurements made with this apparatus (see also Fig. 4.2, right). If we draw the values of pressure as a function of (Celsius) temperature, we will find that the actual data closely follows a straight line. This behavior is interesting. (It is called the *Law of Gay-Lussac*.) Assume that air will behave in this manner at all temperatures. As a consequence, we can write the relationship between pressure and (Celsius) temperature θ in the following form:

$$P(\theta) = P_0\left(1 + \beta\theta\right) \tag{4.8}$$

where P_0 is the pressure of the gas at 0°C, and β is called the *temperature coefficient of pressure*. If we know this relationship, we can use the pressure as a measure of temperature in the interval covered by the experiment.

Figure 4.21: Glass bulb containing air serving as an air thermometer. The bulb is in a glycol bath whose temperature can be adjusted. The pressure of the air is measured via the capillary tube visible in the top left corner.

Table 4.6: Resistivity and temperature coefficients of resistivity (at 20°C)

Substances	Resistivity ρ / 10^{-8} $\Omega\cdot$m	Temperature coefficient α_R / 10^{-3} K^{-1}	Temperature coefficient β_R / 10^{-6} K^{-2}
Aluminum	2.8	3.9	0.6
Carbon	3500	− 0.5	
Copper	1.7	3.9	0.6
Iron	9.8	56	6.0
Platinum	10.5	3.0	0.6
Silver	1.6	3.8	0.7
Tungsten	5.6	4.1	0.96

Now there must be a temperature for which the pressure of the gas becomes zero. We find this point by extrapolating the straight line in Fig. 4.22 to lower temperatures. The pressure of a gas cannot vanish, and certainly, it cannot take on negative values. We have to conclude that this particular point must constitute a lower limit for the temperature of air.

This is quite surprising in itself. It is more interesting still when we observe that all *dilute* gases show this behavior (in fact this even includes substances dissolved in others, such as sugar in water), and moreover, all extrapolated curves intersect the line of zero pressure at the same point. Measurements put the value of the temperature coefficient of pressure at 1/273.15°C for *all dilute substances*. This means that for gases showing this type of behavior irrespective of their chemical composition, there is a hotness below which the ideal gas cannot exist and this temperature is the same for all such substances! From the value of β we find that this value must be 273.15°C below the freezing point of water.

Our experience with gases which behave in this simple manner (i.e., those whose P-θ curve is a straight line) is a strong indication that the temperature found by extrapolat-
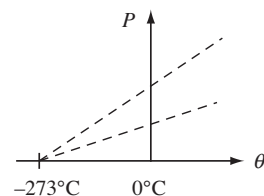
Figure 4.22: For simple dilute gases, the pressure is a linear function of temperature at constant volume. If we plot measurements for two different dilute gases, we obtain two straight lines for which $P = 0$ at the same temperature. This type of behavior is found in all gases which are sufficiently dilute and hot. The straight lines interpolating and extrapolating actual measurements represent the model of the ideal gas.

ing measurements constitutes a point of "absolute zero" for these kinds of fluids. This does not mean, however, that this temperature has any special meaning for other materials. Only further evidence can show if there are bodies which are capable of attaining hotnesses below the lowest one for dilute substances. Since we have never found such a case we believe that the value of – 273.15°C constitutes the *lowest possible value for hotnesses*.

Therefore, a natural scale of temperature would be one for which the temperature is taken to be zero at this lowest point, i.e., at – 273.15°C, and which is measured by the gas thermometer. This is done in the Kelvin scale which is defined on the following basis: zero Kelvin (0 K) corresponds to the point of absolute zero, and the interval of 1 Kelvin (1 K) corresponds to a change in temperature of 1°C. Therefore, we can convert Celsius temperatures θ into *Kelvin temperatures T* by:

$$T = \theta \, \text{K}/°\text{C} + 273.15 \, \text{K} \tag{4.9}$$

If we use the Kelvin scale, the relationship between the pressure and temperature of gases just demonstrated takes on a particularly simple form:

$$P = P_0 \beta T \tag{4.10}$$

We call the temperature measured by the gas thermometer the *ideal gas temperature* because it is based upon the ideal behavior of dilute gases (Chapter 5). The Law of Gay-Lussac is one property of such gases. As we shall see in Chapter 5, the temperature introduced here has an important additional feature: it can be taken as the basis of a scale which is independent of the thermometric substance. It is an *absolute scale*.

Thermal driving force. The last point takes us back to the fundamental property of temperature. Temperature is the measure of hotness, i.e., it tells us how warm a body is; it is the *intensive* thermal quantity. Temperature differences serve as the "driving force" of the flow of entropy (by itself, entropy flows from hotter to colder places; Fig. 4.23). Expressed still differently, *temperature is the thermal potential*, and the measure of hotness introduced in the relations of ideal gases such as Equ.(4.10) serves as the proper measure of this potential. The relation between entropy and energy will be based upon it (Section 4.4).
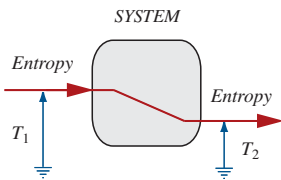

Figure 4.23: Symbolic representation of a temperature difference as the thermal driving force (of a flow of entropy).

4.3.2 Entropy

Entropy—what in lay terms would be called heat, or Carnot's caloric—is the fundamental thermal property that is *stored* in bodies (to make them warm, melt them, expand them…), *flows* from system to system, and *is produced* in irreversible processes. I am going to list some features of entropy and discuss the only relation that deals with entropy proper and nothing else, i.e., the *law of balance* of this quantity. Applications in the rest of this chapter and this book will show the power of this concept.

Some general properties. Thermal phenomena can be understood in terms of entropy and temperature. Entropy is the technical term for what we would call heat in everyday life. It is the *fluidlike* thermal quantity that obeys a law of balance. The most important properties of entropy are:

▶   it can be stored in bodies,

▶   it can flow into and out of bodies,

► it can be produced in irreversible processes (friction, burning, electric conduction, heat flow, diffusion, absorption of light…),

► it makes bodies warm, or is responsible for melting and evaporation, or it lets air expand…

► it can work (it can release energy and drive other processes),

► or it can be pumped if energy is available (heat pump).

The first three entries in this list will appear in the law of balance of entropy. All the others relate entropy either to concrete materials and processes, or to energy.

Balance of entropy. If entropy could be stored in systems and be transported, there would be a law of balance of the forms we have seen in Chapters 1–3: The rate of change of the stored quantity is equal to the sum of all terms that quantify transfer processes. In the case of entropy, this means

$$\frac{dS}{dt} = I_{S,net} \tag{4.11}$$

(Fig. 4.24). $I_{S,\,net}$ is the sum of all entropy currents with respect to a chosen system. From our study of fluid, electric, and mechanical processes, we know the meaning of dS/dt and of a current of S. If the rate of change of the entropy is known, the *change of entropy* of the system is calculated by its integral:

$$\Delta S_{(t_1 \rightarrow t_2)} = \int_{t_1}^{t_2} \dot{S}(t)dt \tag{4.12}$$

As before, integrals of currents over time denote quantities *transported* or *exchanged*. In this case, the *entropy exchanged* S_e:

$$S_{e,(t_1 \rightarrow t_2)} = \int_{t_1}^{t_2} I_S(t)dt \tag{4.13}$$

This definition holds separately for every current as well as for the net flux (the net current yields the net amount of entropy transferred during a period of time). If we introduce Equations (4.12) and (4.13) into the instantaneous (dynamical) form of the law of balance, we obtain the expression of balance of entropy valid for a period of time:

$$\Delta S_{(t_1 \rightarrow t_2)} = S_{e,net(t_1 \rightarrow t_2)} \tag{4.14}$$

Naturally, in Equ.(4.11), we have to include all types of transfer processes having to do with conduction, convection, and radiation. We will see later (Chapter 7) how to distinguish between these different modes in the law of balance. For now, we simply assume that expressing transports in terms of entropy currents I_S is all we need.

Entropy production and the law of balance. Entropy can be produced, and this must be apparent in the law of balance. Having a non-conserved quantity is new to us— charge, momentum and angular momentum are conserved and we assumed the same to be true for volume in the fluid processes we considered. In other words, there are no production terms in the laws of balance of those fluidlike quantities. So we have to learn how to handle production of a quantity such as entropy.
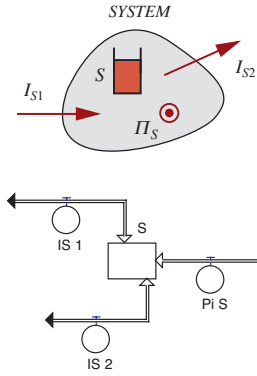
Production adds to a system just as inflow does. From the viewpoint of the balance for the system there is no difference, so a production rate is a process quantity just like a current or flux, and it is added to a law of balance like a flux. There are two important differences between production rates and currents, though. The first has to do with where the quantity accumulating in the system is coming from. In the case of a current, the quantity stems from a different system which means that it will be missing there where it comes from. When a quantity is produced, though, it will not be missing anywhere else; it literally comes from nowhere and simply appears on the scene. The second distinction between currents and production rates is mathematical. Production happens inside a system, and it is distributed over the inside, normally over a volume. A current, on the other hand, quantifies a transport across the systems' surface (a 2D-boundary). When we treat spatially non-uniform (continuous) systems in Parts III and IV, this distinction will become crucial. It means that a production rate has a (volume) density, whereas a surface density is associated with a current.

Figure 4.24: Balance of entropy. Top: Process diagram showing storage, flows, and production of entropy. Bottom: System dynamics diagram of the corresponding law of balance.

The process of entropy production can be quantified by a production rate Π_S and by the entropy produced in a process during a specified period of time for which I use the symbol S_{prod}. The two are related by

$$S_{prod(t_1 \rightarrow t_2)} = \int_{t_1}^{t_2} \Pi_S(t)dt \quad , \quad \Pi_S \geq 0 \tag{4.15}$$

The law of balance of entropy can now be expressed in dynamical form (Fig. 4.24):

$$\frac{dS}{dt} = I_{S,net} + \Pi_{S,net} \tag{4.16}$$

and in integrated form as it applies to a period of time:

$$\Delta S_{(t_1 \rightarrow t_2)} = S_{e,net(t_1 \rightarrow t_2)} + S_{prod,net(t_1 \rightarrow t_2)} \tag{4.17}$$

These are general forms of the law of balance of entropy (for the moment we disregard the question of how different transfer processes should be dealt with, Chapters 7-8).

Entropy producing processes. Where, when, and how is entropy produced? Everyday experience is a relatively good guide when it comes to identifying entropy sources. The major culprits are clear: mechanical friction, letting electricity flow through wires, and burning fuels. Several of the remaining important entropy producing phenomena can be identified by analogy with the flow of electricity and with friction. We know that heat is produced in resistive processes which we have been able to explain in terms of conductive transports of momentum and electricity (Chapters 1 and 3). If we take these processes as a guide, two more phenomena turn up as producing heat: the conductive transports of heat and of substances, i.e., diffusion of heat and substances. The former will play an important role in this and some of the following chapters in our treatment of heat transfer; the latter is central in physical and living systems and will be dealt with in Chapter 6. This leaves one highly irreversible processes to be listed: the absorption and emission of radiation which is fundamental to an understanding of the interaction of our planet with solar radiation (Chapters 7 and 15).

Since entropy production requires a driving process that makes energy available, the relation between energy and entropy lets us be precise about how to identify and quantify irreversibility. This issue will be taken up below in Section 4.4.

4.3.3 Thermal Processes and *TS* Diagrams

In this section I will describe a few simple thermal processes. By looking at some interesting cases we will learn to better understand the nature of heat (entropy). As examples, I shall choose two classes of thermal processes that have played a major role in the early development of thermodynamics.

Our first example is *heating or cooling of simple fluids, such as air, whose volume and temperature can be changed.* If we put air in a cylinder having a piston we have a device which lets us compress or expand the gas. At the same time, the air might be heated or cooled. (See Fig. 4.25.) We are interested in the exchange of entropy, and the change of the entropy content; i.e., we will try to *account for amounts of entropy*. Naturally we also want to know what happens to the *hotness* of the fluid. To make things as simple as possible, we shall conceive of *reversible* operations, i.e., processes which conserve entropy.

The second example is *the melting or vaporization of single substances.* Again we want to understand what happens to the entropy and temperature of the materials.

Adiabatic compression and expansion. Let me begin with a phenomenon which might appear rather surprising at first. Consider the special case of air in a cylinder having a piston. The setup is assumed to be perfectly insulated which makes the exchange of entropy impossible. We are allowed only to compress or expand the air. If this condition is satisfied, we say that the fluid may undergo only *adiabatic processes*. We know from experience with bicycle pumps that upon sudden compression, the temperature of the air rises abruptly (Section 4.1.1, Fig. 4.3). On the other hand, if the gas is allowed to expand under such circumstances it is found that the temperature drops steeply. In other words, in adiabatic compression or expansion of a fluid such as air, its hotness changes without heating or cooling.

To many observers this is surprising indeed. Would we not automatically believe that some heating must have occurred for the temperature of a body to increase? Heat has not been exchanged because of the perfect insulation, which in the case of a bicycle pump, may be simulated by performing the compression so suddenly that heat does not have any time to flow. We also assume that there are no sources of entropy as a result of friction. The theory of adiabatic reversible processes presented in Chapter 5 shows that the changes of hotness are a natural result of the change of volume of a fluid. Experiments beautifully verify this point.

In summary, the temperature of air changes upon compression or expansion without any heating having taken place and without any internal sources having supplied entropy. In other words, the entropy content of the gas must remain constant during adiabatic reversible changes. This is a simple case of accounting for amounts of entropy: nothing has gone in, nothing has come out, and nothing has been produced inside. There is a simple and useful tool which allows us to describe this phenomenon graphically, namely the *temperature-entropy diagram* (or *TS* diagram) of the process (Fig. 4.26). Since the entropy content of the body remains the same, the curve representing the process must be a vertical line in the diagram. The temperature rises upon compression, and it decreases as a result of expansion of air.

If for any reason the process considered is not reversible, i.e., if heat is generated in the fluid, the representation of an adiabatic change in the *TS* diagram will differ from the one in Fig. 4.26.

Heating at constant volume. Next, consider the heating of air if its volume is kept
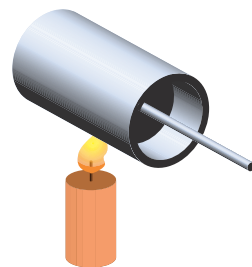

Figure 4.25: A simple device which allows us to put a fluid such as air through thermomechanical processes, i.e., processes which couple thermal and mechanical operations only. The volume may be changed with the help of the piston, and heating and cooling may be present.
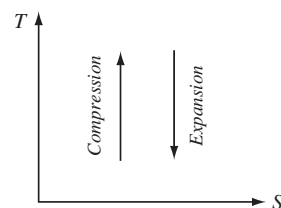

Figure 4.26: Adiabatic compression and expansion in the temperature-entropy diagram. This diagram is a valuable tool in thermodynamics as was observed by J.W. Gibbs (see Section 4.1.7).
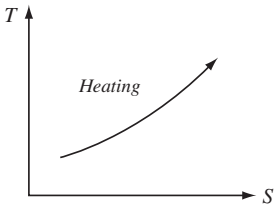
Figure 4.27: Heating at constant volume. If entropy is added, the temperature of the body must increase. How it increases depends on the properties of the body.
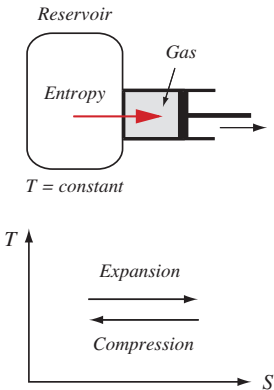

Figure 4.28: If a gas is to expand or contract at constant temperature, it has to be able to exchange entropy with the surroundings. The processes of isothermal expansion or compression are represented by horizontal lines in the *TS* diagram. On expansion, fluids usually absorb entropy. However, this does not always have to be the case: water in the range of temperatures between 0°C and 4°C behaves differently!

constant. We say that under these circumstances the fluid undergoes an *isochoric process*. It is very simple to keep the volume constant in the case of gases heated or cooled. Heat does what we usually believe it does. A body which is heated at constant volume gets hotter. Experience tells us that no matter what kind of body is heated at constant volume its temperature must increase if heat is absorbed, and it must decrease if heat is emitted.

Again, we can try to exhibit the process in the temperature-entropy diagram. Only here we have a real problem which cannot be solved without knowledge of the constitutive properties of the body: What is the concrete relationship between temperature and entropy content as entropy is added or removed? Since we do not have this information at this point, all we can do is give a qualitative impression of what the relationship might look like (Fig. 4.27). Below we will introduce a constitutive quantity which describes bodies heated in such a manner. This quantity is called the *entropy capacitance*. It measures how the temperature changes with the change of the entropy of the body.

Since we assume entropy to be conserved we know that the amount of entropy communicated to the body is equal to the change of its entropy content. Again, this is a particular case of accounting for entropy: the entropy content of a body can change by transfer only, since nothing is produced inside. The sum of what has been absorbed and emitted must be equal to the change of the contents.

Isothermal processes. Another interesting process is the heating of air at constant temperature. We speak of *isothermal processes* in this case. Since the temperature of air changes if it is heated at constant volume, we obviously have to let the volume change for an isothermal process to take place. On the other hand, we have seen that the temperature changes if the volume is changed without heating (adiabatic processes). Combining these experiences we can come up with the answer of how to perform an isothermal process. We may heat a body which would normally increase its temperature; if we let the fluid expand, its temperature should drop. We only have to combine and fine-tune the rates of heating and of expansion for the temperature to remain constant (Fig. 4.28). On the other hand, the hotness of air rises if it is compressed without heating. Therefore, we must cool it at just the right rate during compression for the temperature not to change. In summary, if a fluid such as air is to undergo an isothermal expansion it has to be heated at the same time; during an isothermal compression it has to be cooled. Therefore, if the volume of air increases isothermally its entropy content increases; entropy is literally sucked up by the gas. If the volume decreases the entropy content decreases; entropy is pressed out of the fluid like water out of a sponge.

There is an important exception to the details of adiabatic and isothermal processes just presented. Water in the range of temperatures between 0°C and 4°C behaves differently. Take the isothermal changes first. Water will be found to *emit* heat when *expanding* at a temperature in this range. Also, for part of an adiabatic compression the temperature decreases as the volume is decreased, only to go through a minimum whereupon it increases as is normally expected.[14] Even though there are very few cas-

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14. Kelvin was one of the first to discuss the significance of this behavior for thermodynamics (see Truesdell, 1980). A theory of classical thermodynamics allowing for the anomaly was first presented by Truesdell and Bharatha (1977).

es of anomalous behavior, the example of water demonstrates that we cannot simply leave it out of our considerations. Water is too important a fluid.

We would like to know how much entropy is required for a given change in volume of the fluid. Again this question is answered by a particular constitutive quantity, which is called *latent entropy*. It will be introduced in Chapter 5.

Melting and vaporization. Finally, let us take a brief look at *phase changes*. When a block of ice having a temperature below the freezing point is heated, we first observe a rise of temperature of the body (Fig. 4.6). The process is analogous to the heating of a fluid at constant volume (Fig. 4.27). The water which is produced from the ice by melting behaves similarly. We also know that water eventually turns into steam, which can be heated further at constant volume if we like. But what about the processes which turn ice into water, and water into steam?

If we monitor the temperature of ice, water, and steam as we add heat (see Fig. 4.6 and Fig. 4.29), we observe that the melting of ice and the vaporization of water take place at *constant temperatures*: they are *isothermal processes*. Again, this is a rather surprising result. Without thinking about it we often assume there to be a change of temperature during the heating of a mixture of ice and water, or of water and steam. However this is not true. As in the case of the isothermal heating of fluids, the entropy entering a body does not do what we think it normally does: it does not raise the temperature of the body.

The melting of ice has played an important role in the history of the theory of heat. The process served as a means for constructing ice calorimeters, and the melting of ice by rubbing two blocks of it against each other provided strong evidence that entropy can be created (Section 4.1.4).

As we have seen several times, the examples of adiabatic and isothermal changes clearly demonstrate that heat and hotness cannot be the same quantities. In one case, the hotness changes even though the entropy content does not; in the other, the amount of entropy in a body changes while the temperature remains constant.
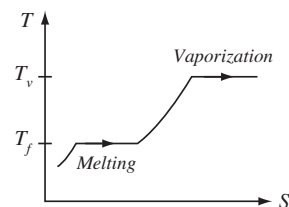

Figure 4.29: Relationship between temperature and entropy for melting or vaporization of ice and water. During the change of phase, the temperature of the body stays constant. The diagram gives only a qualitative representation of the relationships. (T_f: melting point, T_v: temperature of vaporization.)

QUESTIONS

19. What relations from electricity are analogous to Equ.(4.2) and Equ.(4.3)?

20. What observation suggests that an expression of the form given in Equ.(4.2) might be appropriate for a flow of entropy out of a hot body?

21. Why is water a bad thermoscopic material?

22. What observations suggest that hotness has a lowest possible value? Is an "absolute zero" point a general property of intensive quantities known from fluids, electricity, or motion?

23. Why does it make sense to assume that diffusion is an entropy producing process?

24. If there is a net *inflow* of entropy into a body, is it possible for its entropy to decrease?

25. If the sum of all currents of entropy with respect to a body is positive, is it possible for the body to get colder?

26. What is the *TS* diagram of adiabatic compression of a gas with internal friction?

27. Why is the representation of isothermal expansion of a gas a horizontal line to the right in the *TS* diagram?

28. What is the *TS* diagram of freezing of water? What does this mean for the entropy content of the system and entropy exchanged by the system with its environment?

EXAMPLE 4.1. Accounting for entropy.

Due to some irreversible process, entropy is produced in a body of water at a rate that increases linearly from 1.0 Ct/s to 1.5 Ct/s in 100 s. It is observed that the temperature of the water does not change (there are no phase changes!). (a) What is the rate of change of entropy of the body? (b) Are there any entropy currents with respect to the body of water? If so, how large are they? (c) How much entropy has been produced in these 100 s? (d) How much entropy has been exchanged with the environment? (e) What happens to the entropy of the body if it is thermally insulated?

SOLUTION: (a) Since water is a material whose temperature only changes if its entropy is changed, constant temperature means constant entropy. The rate of change of entropy is equal to zero. (Water has a very small compressibility which changes the result slightly.)

(b) If the rate of change of entropy is zero, the (net) entropy current is equal to the negative entropy production rate:

$$\dot{S} = I_{S\,net} + \Pi_S \quad, \quad \dot{S} = 0 \quad \Rightarrow \quad I_{S\,net}(t) = -\Pi_S(t) = -\left(1.0\frac{Ct}{s} + 0.0050\frac{Ct}{s^2}t\right)$$

(c) The entropy produced equals the integral over time of the production rate. Here, the integral of the entropy production rate over time is equal to 125 Ct.

(d) We can integrate the (net) entropy flux to obtain the entropy exchanged. Alternatively, we can apply the integrated form of the law of balance:

$$0 = S_{e\,net} + S_{prod} \quad \Rightarrow \quad S_{e\,net} = -S_{prod} = -125Ct$$

(e) Thermal insulation prevents the exchange of entropy of a body with its environment. If the body of water is thermally insulated, and if we have the entropy production rate as described here, the entropy of the body must change according to

$$\dot{S} = I_{S\,net} + \Pi_S \quad, \quad I_{S\,net} = 0 \quad \Rightarrow \quad \dot{S}(t) = \Pi_S(t) = 1.0\frac{Ct}{s} + 0.0050\frac{Ct}{s^2}t$$

In 100 s, the entropy of the body increases by 125 Ct.

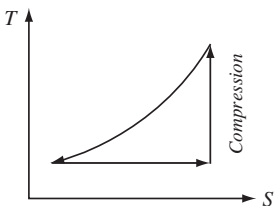**EXAMPLE 4.2.** Replace an adiabatic process by isochoric and isothermal steps.

Air in a bicycle pump is compressed adiabatically. How can the air be brought back to its original state if we first wait for the air to cool in the pump? Draw the steps performed in a *TS* diagram.

SOLUTION: If we compress air adiabatically, we raise its temperature without changing its entropy content (see figure). If we now wait for the air to cool without the piston being moved, the following will take place: Entropy flows out of the air at constant volume, thereby reducing its temperature. This step restores the initial temperature to that of the surroundings, but it reduces the entropy of the air. Therefore, as a last step, we have to increase the entropy content to its original value without changing the hotness of the system. This is achieved by isothermal heating which also brings the volume of the air back to its initial value.

Figure Ex.2

EXAMPLE 4.3. Irreversible adiabatic processes.

A certain amount of gas is put in a cylinder having a piston and which is perfectly insulated against the flow of heat. The gas is first compressed and then allowed to expand again to the

point where the temperature regains its initial value. The processes undergone by the gas are supposed to be irreversible, possibly because of viscous friction in the fluid. Is the volume at the end smaller than, equal to, or larger than that at the beginning? Write the equation of balance of entropy for adiabatic irreversible processes, and display the operations in the *TS* diagram.

SOLUTION: Because of the ideal insulation, the processes are adiabatic; i.e., there is no exchange of entropy. For this reason, the flux term in the equation of balance of entropy is equal to zero. The production term is not equal to zero, though, which leads to the following equation of balance of entropy:

$$\dot{S} = \Pi_S$$

Thus, the entropy of the body can only increase.

In a gas, the temperature increases as the result of adiabatic compression. Entropy is produced at the same time. Therefore, the amount of entropy in the system increases as the temperature rises, and the process is represented by a curve such as the one shown in the *TS* diagram. (Note that we do not have any information regarding the properties of the gas. For this reason we cannot actually calculate the details of the processes. The curves displayed in the *TS* diagram are to be taken only as a qualitative description of what is happening.)

The second step is an adiabatic expansion, which leads to a lower temperature. Again the process is irreversible, which causes entropy to be produced. When the initial temperature is reached, it stops. Compared to the beginning, there is more entropy in the gas at the same temperature. We have seen in Section 4.3.3 that for most substances (with the notable exception of water in the range between 0°C and 4°C) the volume increases if entropy is absorbed at constant temperature. The combined adiabatic irreversible steps are actually equivalent to isothermal heating. Therefore, the volume is expected to be larger at the end than at the beginning.
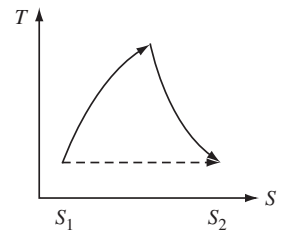

Figure Ex.3

4.4 ENERGY IN THERMAL PROCESSES

There are two main points to be discussed when energy is introduced to a new field. First, what is the relation of energy to the basic quantities used to model processes in the new field? Here, these quantities are entropy and temperature. Second, we have to answer the question of how the law of balance of energy changes if thermal processes are included. The former question is answered by appealing to analogies of thermal processes with other phenomena. The latter has an even simpler answer: Thermal processes, like any other phenomena, allow for the exchange of energy. Therefore we simply include a new type of energy exchange in the law of balance of energy by adding a term.

4.4.1 Balance of Energy Including Thermal Processes

Why can we be certain that thermal processes involve energy exchanges? The reasoning is simple. Thermal processes couple to other phenomena. Take the example of electric heating at one end of a copper bar (Fig. 4.5). If we do not want to suddenly change what we believe applies to energy in electric processes, we must conclude that energy is transferred from the electric wires together with the entropy produced in these wires. The balance of energy for the electric heater tells us this much. So if we consider the transfer of the entropy produced in the wires a thermal process, we can say that energy is transferred in thermal phenomena as well. The story can be continued by considering what happens to the entropy passed from the electric system to the heated end of the copper bar. Conduction in the bar tells us that entropy flows from a

hotter to a colder element. It should not matter if an element is heated electrically or by contact with a hot part. If energy is transferred with entropy in the first case, it will be transferred in the second example as well.

In summary, energy transfer accompanies entropy transfer in thermal processes. The change of the law of balance of energy including thermal phenomena is simple and minimal: We have to add an energy transfer term for the new type of phenomenon. We have used energy currents in fluid, electric, or mechanical phenomena to quantify energy transfer. Now we add a current of energy to quantify energy transfers as a consequence of heating or cooling:

$$\frac{dE}{dt} = I_{E,fluids} + I_{E,el} + \ldots + I_{E,th} \tag{4.18}$$

$I_{E,th}$ represents the new term which refers to *energy transfers in heating and cooling*; E is the energy stored in the system whose energy balance is being considered. Remember that heating and cooling refer to entropy flows from hotter or to colder bodies—relative to the body we are dealing with.[15]

As with all laws of balance, there is an integrated form which may be applied to processes lasting for a certain period of time $t_1 \rightarrow t_2$:

$$\Delta E_{(t_1 \rightarrow t_2)} = E_{fluid(t_1 \rightarrow t_2)} + E_{el(t_1 \rightarrow t_2)} + \ldots + E_{th(t_1 \rightarrow t_2)} \tag{4.19}$$

The remarks made about $I_{E,th}$ also apply to E_{th}. So far, the term E_x has been used to denote quantities of *energy transferred* in a process (Section 2.4.1). This usage will be continued with thermal processes. Therefore, E_{th} is the symbol for amounts of *energy transferred in heating or cooling* of bodies.[16]

4.4.2 Entropy, Temperature, and Energy

We might expect to be able to learn more about entropy if we manage to clarify its relation to energy in thermal processes. In his investigation of the motive power of heat, Carnot was the first to see this important point. We shall attack the problem head on by employing the full power of his comparison of heat and water (Section I.3 and

15. This statement is not as innocent as it may sound. What is a thermal process actually is open to debate. Should we include the transfer of entropy stored in a heated fluid together with that heated fluid, as in a central heating system? Or should this be regarded a fluid process? In fact, it is simpler to take the latter point of view and to exclude fluid transfer and even radiation from the list of proper thermal processes. This leaves conduction of entropy, and this is how $I_{E,th}$ in Equ.(4.18) will be interpreted: it is the energy current accompanying conductive entropy transfers. Conduction of entropy is the narrowest but simplest and clearest definition of heating and cooling.

16. After about 1850, the quantity E_{th}, which denotes amounts of energy transferred in heating or cooling, was given the name "heat." The symbol Q is commonly used for this quantity in thermal physics. Since I do not associate more meaning with an amount of energy transferred in heating or cooling than with any other quantity of energy transferred in whatever process we might study, I refrain from using specialized symbols. More importantly, however, it is less than helpful to use the conventional word *heat* for the last term in Equ.(4.19), i.e., for a quantity having to do with energy. As discussed in Section 4.1.4, energy plays an altogether different role than the one associated with it in traditional thermodynamics.

Section 4.1.5). We will assume that the role of energy in thermal processes is the same as that known from other fields of physics as discussed in Chapter 2. In summary, Carnot's investigation of the principle of operation of heat engines will deliver the following results:

1. A heat engine absorbs entropy from the furnace at higher temperature; if it could be operated reversibly, the same amount of entropy would be transferred to the cooler, i.e., to the environment at lower temperature.

2. By lowering entropy from a point of higher temperature to a point of lower temperature, energy is released at a certain rate (thermal power); this energy drives the mechanical process.

3. The energy released when entropy falls is supplied to the engine with entropy from the furnace. More generally, energy is transferred together with entropy in heating and in cooling.

In short, we simply add thermal phenomena to the list of processes known from other areas of physics. Accepting this, we will be able to directly state the formula for the motive power of heat, which will provide for the simplest possible entry into thermodynamics. (A derivation on the basis of some other assumptions can be found in Chapter 10.) The consequences of this idea will be developed for ideal engines and for entropy production in the present section.

Thermal power. On the basis of these observations regarding the operation of heat engines, Carnot was able to suggest a theory relating heat and energy. We already have presented the basic idea of how such engines work, by the usual *waterfall diagram* and associated process diagrams in Fig. 4.15. Therefore, in analogy to other fields of physics, we should expect the motive power of heat engines to be strictly proportional to the drop of the thermal potential. Compare the process depicted in Fig. 4.30 to the operation of a hydromechanical engine, i.e., a water turbine which is driven by water falling from an artificial lake at a high level, or any other type of engine. This immediately lets us write the thermal power in the form

$$\mathcal{P}_{th} = -(T_2 - T_1)I_S \qquad (4.20)$$

Entropy can be *pumped* like water, and as in the case of water the rate at which energy is used to pump a current of entropy is also given by Equ.(4.20).

Energy transfer in heating and cooling. A few simple but important facts are known about heat engines: First, they need a furnace and a cooling device; i.e., they operate between two environments at different temperatures; they absorb heat from the furnace, and they emit heat to the cooler. Second, the motive power of such engines depends on the temperatures of the furnace and the cooler; indeed, their power increases with an increasing difference between the upper and the lower temperatures.

Let us now turn to the first of these observations. Heating the engine first of all means that entropy is taken in from the furnace at the higher temperature. Since entropy cannot disappear, it has to be emitted if the engine is to operate steadily. This is accomplished with the help of the cooling device receiving the entropy rejected by the engine. We know from the properties of entropy that the current leaving the engine must be equal to that entering if all the operations are reversible, i.e., if entropy is not produced in the system. Since cooling takes place at a lower temperature, entropy flows from the hot furnace to the cooler and we say that heat engines are driven by the
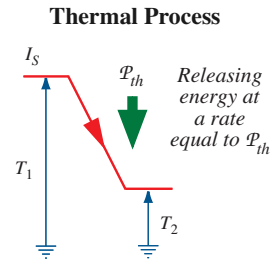
Thermal Process

Figure 4.30: Waterfall image of a thermal process: Entropy falls from a point of high temperature T_1 to a point of lower temperature T_2, thereby releasing energy at a well defined rate.

fall of heat (entropy). Temperature therefore plays the role of the *thermal potential*.

This we have seen already, but the discussion points to an additional aspect of energy in thermal phenomena. The entropy that is taken from the furnace carries with it some energy (Fig. 4.31), and the entropy emitted to the cooler also takes some energy along. If this were not the case, where would the energy released in the fall of entropy come from?

Figure 4.31: Left: Part of the process diagram of a heat engine. Energy is supplied and removed along with entropy coming from the furnace and leaving to the cooler. Note that nothing has been said about what the energy released is used for. Right: Symbolic representation of heating (or cooling) of a system at temperature T.
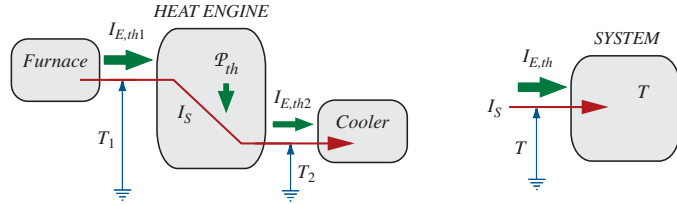
It makes sense to assume that the energy released is the difference of energy delivered and removed at high and low temperature, respectively. Therefore, we should calculate an energy current carried by an entropy current in heating or cooling of bodies by:

$$I_{E,th} = T I_S \qquad (4.21)$$

This is in complete analogy to what we have used in fluid, electric, and mechanical processes before (see Chapters 2 and 3). So there is an additional interpretation of entropy: it is the *carrier of energy in heating and cooling*.

If we wish to know how much energy has been transferred in a process of heating or cooling, and if we want the relation of this quantity to entropy and temperature, we simply integrate Equ.(4.21) over time:

$$W_{th} = \int_{t_1}^{t_2} T I_S dt \qquad (4.22)$$

Entropy production and dissipation. The qualitative discussion of entropy production and irreversibility in Section 4.1 should have made it clear that while entropy appears out of the blue, it does not do so on its own. There have to be processes that drive the production of entropy. Such processes are called irreversible or *dissipative*.

Generally, voluntary processes cause more than a single phenomenon. A water pump is built to pump water, and the energy released by the driving process is expected to go mostly toward the process the device was designed for. Invariably, however, part of the energy released drives the production of entropy—engines heat up and they have to be cooled. The part of the energy made available that is used for entropy production is said to be *dissipated*.

Equations (4.20) and (4.21), i.e., the relations for thermal power and energy currents in heating and cooling, allow us to calculate the energy needed to produce entropy at a given temperature. Consider a totally dissipative device such as an electric heater whose process diagram is shown in Fig. 4.32. Energy is supplied to the heater and is released in an electric process. Since the heater drives a single process—entropy production—all the energy released is dissipated; it drives the thermal process of produc-
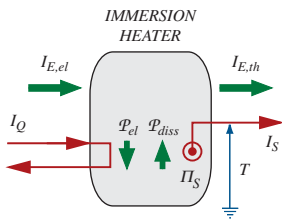

Figure 4.32: Process diagram of an immersion heater. The energy released in the electric process is completely dissipated (used to produce entropy).

ing entropy. As a consequence, the rate at which energy is dissipated is known; it is the thermal power of the process. The dissipated energy is then emitted by the heater together with the entropy that was produced. In summary, we can say that

$$\mathcal{P}_{diss} = T \, \Pi_S \qquad \qquad \textbf{(4.23)}$$

When entropy is produced at temperature T at a rate Π_S, we need energy at the rate given by Equ.(4.23); this is called the *dissipation rate* $\mathcal{P}_{diss}$.[17]

4.4.3 Heat Engines and Heat Pumps

Combining everything we have learned so far—balances of entropy and of energy, and the relation between entropy, temperature, and energy—will allow us to come up with some rather interesting and useful results regarding the operation of thermal engines in spite of the generality of the relations. More detailed models will require the study of particular constitutive laws of components making up real engines (see Chapters 9 and 15).

Ideal heat engines and heat pumps. When entropy flows through an engine from points of high to points of low temperature (from a burner to a cooler), energy is released (see Fig. 4.30). If all the energy that is released is used to drive the desired process (mechanical, electrical, etc.), the engine is said to be *ideal*. Ideal engines are non-dissipative. In this case, the process diagram of a heat engine takes the form shown in Fig. 4.33 (left). For heat pumps and refrigerators where entropy is pumped from lower to higher temperature, all we have to do is reverse the flows of fluidlike quantities and change the signs of potential differences (Fig. 4.33, right). If all the energy released by the driving process is used to pump entropy, the heat pump is said to be ideal.
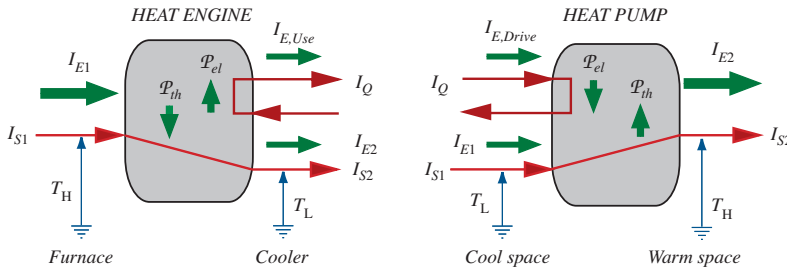
Figure 4.33: Process diagram of an ideal heat engine (left) and an ideal heat pump (right). Ideal means that there is no entropy production in the engines.

Here is a complete analysis of the ideal heat engine at the level of general relations discussed so far. There is one expression for the balance of entropy and three relating to the energy principle:

$$0 = I_{S1} + I_{S2} \qquad \qquad \textbf{(4.24)}$$

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17. To end up with proper signs, the dissipation rate has to be defined as the negative thermal power of the process of producing entropy. When entropy falls and releases energy (Equ.(4.20)), the power is positive, so in an involuntary thermal process where energy is used the power is negative. The dissipation rate, however, needs to be a positive quantity.

$$0 = I_{E1} + I_{E2} + I_{E,use}$$
$$0 = \mathcal{P}_{th} + \mathcal{P}_{el} \tag{4.25}$$
$$I_{E,use} = -\mathcal{P}_{el}$$

(Note that these relations hold for the steady-state.) We add to this the relations between entropy currents in heating and cooling and the associated energy currents:

$$I_{E1} = T_H I_{S1} \quad , \quad I_{E2} = T_L I_{S2} \tag{4.26}$$

Efficiencies. It is customary to introduce two measures of efficiency that can be derived from the foregoing. The first is the ratio of useful energy current to energy supplied by the burner (called the *thermal efficiency* or *first law efficiency*):

$$\eta_I = \left| I_{E,use} / I_{E1} \right| = \frac{T_H - T_L}{T_H} \tag{4.27}$$

The second is the ratio of useful power to thermal power (called the *second law efficiency*):[18]

$$\eta_{II} = \left| \mathcal{P}_{el} / \mathcal{P}_{th} \right| \tag{4.28}$$

For an ideal heat engine (Fig. 4.33, left), the second measure of efficiency is equal to 1. It seems to be the more natural and intuitive of the two measures. It tells us how well the engine performs, measured relative to what nature allows. We can only use the energy made available by the fall of entropy, i.e., $\mathcal{P}_{th}$.[19] If we can use all of it, we have designed a perfect engine. Moreover, Equ.(4.28) represents the same type of efficiency measure as those used in other devices such as pumps, turbines, motors, etc.

The so-called first law efficiency or thermal efficiency is commonly used to report the performance of heat engines; for example, the thermal efficiency of a large nuclear power plant is little more than 30%. For *ideal engines*, the efficiency is given by Equ.(4.27) which is called the *Carnot efficiency* η_C of heat engines. It is the highest possible value of thermal efficiency that can be achieved by any thermal engine running between a furnace at T_H and a cooler at T_L (H and L stand for high and low, respectively). This point will be discussed further below and again in Chapter 5.

It is important to realize that η_I is smaller than 1 no matter what we do unless we could build a cooler at the lowest possible temperature of 0 K. This is true even for non-dissipative engines, and, as we shall see shortly, even for the best of them, the Carnot engine. The reason for this is simple to understand if we consider the balance of entropy rather than just the balance of energy. Since the entropy supplied to an engine has to be emitted to the cooler, it will take a current of energy equal to $T_L I_S$ into the environ-

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18. In Section 4.4.5, a brief description of what are termed First Law and Second Law of thermodynamics will be given. This should explain where the names first law efficiency and second law efficiency come from.

19. In a fall of water in the Swiss Alps, we can only use the energy released which is proportional to the height difference. The level of the environment at the foot of the mountains defines the lowest possible point water can reach even though we can imagine the water to fall still further on its way in the river to Holland.

ment (Fig. 4.33, left). This is simply unavoidable.[20] It is not the fault of engineers who do not understand nature well enough.

There is actually a good reason for using the first law efficiency in Equ.(4.27) alongside the more intuitive measure in Equ.(4.28). The loss of energy to the environment actually starts when we produce the entropy that runs the heat engine by burning some fuel or splitting nuclei. The entropy produced must end up in the environment eventually. There is irreversibility here, just not in the engine but in the furnace. Carnot's formula accounts for this in the case of ideal engines, where "ideal" means that the core of the engine is non-dissipative.[21]

Coefficient of performance. Let us now briefly turn to *heat pumps*. For heat pumps, one introduces the *coefficient of performance* which is the ratio of the useful energy current—the energy current accompanying the entropy flow that heats the warm space (Fig. 4.33, right)—to the power of the driving process. If we perform a derivation analogous to what was done for engines, we get the *coefficient of performance* (*cop*)

$$cop = \left| I_{E2}/I_{E,drive} \right| = \frac{T_H}{T_H - T_L} \tag{4.29}$$

which is the inverse of the Carnot efficiency in Equ.(4.27). The result has been derived for ideal engines (real heat pumps do not even come close to this value). For refrigerators, the figure of merit is the ratio of the energy current removed from the cold space to the driving power, so the equations is different from Equ.(4.29).

Just as the first law efficiency η_I of a heat engine, Equ.(4.27), might give the wrong impression of the performance of a thermal engine, the coefficient of performance introduced in Equ.(4.29) tells only half the story. A better way of measuring the efficiency of heat pumps and refrigerators is to compare the thermal power for lifting entropy to the actual mechanical or electrical power of the engine:

$$\eta_{II} = \left| \mathcal{P}_{th}/\mathcal{P}_{el} \right| \tag{4.30}$$

This is a figure analogous to the second law efficiency of heat engines. Note that it is the inverse of what was defined in Equ.(4.28), just as the coefficient of performance is the inverse of the Carnot efficiency. Naturally, for ideal heat pumps and refrigerators, the efficiency η_{II} is equal to 1; otherwise it is lower than 1.

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20. This non-intuitive measure(η_I) has caused people to wonder why this should be so, or if it should be so at all. A cottage industry of inventors has developed that tries to design engines that use more than the fraction of energy supplied to the engine calculated by Equ.(4.27). Since traditional explanations of thermal phenomena are based almost exclusively on the energy concept, these inventors ask why it should be forbidden to make use of a higher proportion of the energy supplied to an engine. Simply shaking one's finger at them and appealing to the "Second Law of Thermodynamics" that "forbids" their dream to come true does not seem to help. This is one of the problems we created for ourselves when we started conceptualizing heat as a form of energy. There is simply no simple way out of this seeming paradox in traditional representations of thermal phenomena.

21. Note that the term *engine* is used for the central element of an entire thermal engine shown in Fig. 4.31, not for the complete system including the furnace and the cooler. Here, the engine is the part of the system that is designed to lower the entropy from high to low temperature and make use of the energy released in the fall of entropy.
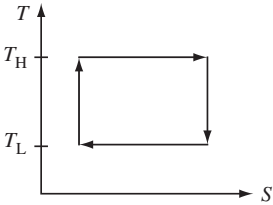
Carnot engines. The results derived in this section apply only to reversible devices and to what we might call *Carnot engines*. (There are reversible engines that are not Carnot engines, see Chapter 5.) An engine's task is to transport heat, i.e. entropy, from the furnace to the cooler. How can this be achieved? Consider, as Carnot did, an engine that absorbs entropy at *constant temperature* from a furnace. Then the absorbed entropy is lowered to the temperature of the cooler whereupon *all the entropy (heat)* is emitted, again at *constant temperature*. A heat engine operating in the manner described is called a *Carnot engine*. Actually, for us the *engine* is the working fluid employed, such as air or steam. The fluid operating in such an engine undergoes a cyclic process called a *Carnot cycle*, whose steps we can describe qualitatively in terms of the simple changes discussed in Section 4.3.3 (see Fig. 4.34). To be specific, let us assume the agent of the engine to be air. The first step in the cycle described above must be an isothermal expansion of the fluid. If air expands isothermally, it absorbs entropy at constant temperature. This is exactly what we want. Now the temperature of the air has to be lowered to the hotness of the cooler; this process has to take place without any heat being exchanged. Therefore this step must involve an adiabatic expansion. In other words, the air expands during the first two steps of the Carnot cycle.

Figure 4.34: Carnot cycle in the *TS* diagram. It consists of four steps, two of them isothermal, the other two adiabatic. If the steps are performed ideally, i.e., if no entropy is produced in the agent, the cycle has the simple form of a rectangle. In the case of a Carnot heat pump, the cycle is traversed in the opposite direction (counterclockwise).

Now the fluid has to emit the entropy it absorbed in the first step. Since the emission is to take place at constant temperature, this step must be an isothermal compression. In the end, we only have to return the agent to the starting point for it to be able to begin another cycle of operation. The final process is an adiabatic compression, which raises the temperature to the desired level, namely to the temperature of the furnace, without adding or removing entropy.

It might be instructive to quickly discuss the idea of a non-Carnot heat engine. Such a device absorbs and emits entropy at variable temperatures; most engines are designed in such a way that absorption and emission of entropy do not take place at constant temperature. If we call T_H the highest temperature during uptake of entropy, and T_L the lowest temperature during emission, the efficiency of an ideal heat engine is less than the Carnot figure, i.e., less than the famous factor $(T_H - T_L)/T_H$.

Dissipative heat engines. Real heat engines and heat pumps are dissipative. Entropy production can have several reasons, the main being heat transfer (we are going to discuss this in Section 4.6.3). We can neglect the actual sources of irreversibility for the moment and simply include a general source of entropy in an engine of the type depicted in Fig. 4.33; see Fig. 4.35. Adding entropy production to the model has important consequences. Some of the energy released in the fall of entropy from T_H to T_L will now be used for the process of producing entropy. The entropy resulting from dissipation must be emitted to the cooler and to the environment in addition to the entropy absorbed by the engine from the furnace. If we assume the temperature of the cooling process T_L to remain the same, the energy current to the environment will be larger than in the reversible case. This means that the energy available for the desired process is less than in a non-dissipative engine.

The real second law or first law efficiencies can be derived in analogy to Equ.(4.24) and Equ.(4.25). The equations that change are

$$0 = I_{S1} + I_{S2} + \Pi_S$$
$$0 = \mathcal{P}_{th} + \mathcal{P}_{el} + \mathcal{P}_{diss}$$

It turns out that both efficiencies are reduced from their maximum values by amounts proportional to the ratio of entropy production to entropy absorbed from the furnace.
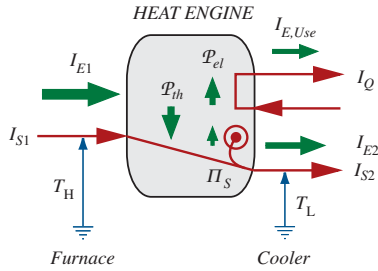
Figure 4.35: Process diagram of a dissipative heat engine. The difference between this and an ideal engine starts with an entropy production term. Adding this term changes all the quantities on the right side of the diagram. In particular, it reduces $\mathcal{P}_{el}$.

Available power and loss of power. The power of a fall of heat through a given temperature difference has been introduced in Equ.(4.20). It is often calculated with the temperature of the environment T_0 replacing the temperature of the cooler T_L. The power thus calculated is the maximum which can possibly be derived from a current of entropy emitted from a reservoir at temperature T in a given environment. For this reason it is called the *available power* $\mathcal{P}_{av}$ (or the *exergetic* power) of entropy:

$$\mathcal{P}_{av} = (T - T_0)I_S \tag{4.31}$$

Similarly, the loss of power due to irreversibility, i.e., as a consequence of entropy production, is expressed relative to the temperature of the environment T_0. The results introduced above show that there is a simple relation for the *loss of power* $\mathcal{L}$, i.e., the quantity by which the power of an engine is reduced relative to its maximum possible value for reversible operations:

$$\mathcal{L} = T_0 \Pi_S \tag{4.32}$$

Equ.(4.32) is simple to put into words, and simple to understand. If entropy is produced at a rate Π_S in an engine in an environment having temperature T_0, the entropy current from the device to the environment must be increased by Π_S. There is therefore an additional energy current to the environment, i.e., a loss, that is equal to $T_0\Pi_S$. This is what we call *lost power*.

Now we can understand why the Carnot efficiency, Equ.(4.27), is smaller than 1 (remember this is for an *ideal* engine). The power of the ideal engine is

$$\mathcal{P}_{el} = (T_H - T_L)I_S = (T_H - T_L)\Pi_{S,furnace} = I_{E1} - \mathcal{L}$$

i.e., it is smaller than the energy current supplied to the engine by the loss of power due to entropy production in the furnace.

4.4.4 Thermal Potential

When temperature and temperature scales were discussed in Section 4.3.1, the question was raised of whether any of them could represent a "true" thermodynamic temperature. If we take the conceptualization of the intensive thermal quantity seriously, the simplest meaning of "true" would be what we called *thermal potential*. The ideas of how entropy, temperature, and energy are related, and the results concerning en-

gines can be used to make the concept of thermal potential more precise. Take the formula for the Carnot efficiency in Equ.(4.27). This quantity depends only upon temperatures. If we assume this measure of efficiency to have concrete meaning, if we want it to take a unique value for a concrete case of an engine, then the quantity in the formula—temperature—obtains meaning independent of special materials and processes. This leads to the concepts of *absolute temperature*, absolute in the sense of independent of a thermometric substance. It appears we can use the quantity T in our relations as a measure of the thermal potential.

There is commonly a second meaning to the word "absolute" in the term *absolute temperature*. We often mean that there is an absolute zero point of hotness. Entropy production and the Carnot efficiency both indicate that this must be so. Take Carnot's formula first. If T were not fixed on an absolute scale, results for the efficiency would depend upon the particular scale chosen.

The relation between the energy dissipated and the entropy produced could not be applied unambiguously either. Imagine there were negative temperatures, so Equ.(4.23) would predict negative entropy production rates which contradicts what we have been assuming. Fluidlike quantities that can be created and/or destroyed must have an absolute potential.[22]

For an entropy production rate to have an unambiguous meaning, the temperature must always be positive. Note that the relation between power, entropy production rate and (absolute) temperature, Equ.(4.23), tells us that the energy needed to produce one unit of entropy is the same as that needed to pump one unit of entropy from 0 K to the same temperature at which entropy that is produced appears in the world.

4.4.5 First and Second Laws of Thermodynamics

The presentation of thermodynamics in this chapter makes use of old forms of thought, namely, what we find in Sadi Carnot's work. However, it is not historical since it does not use the concepts and terms developed in traditional thermodynamics after 1850. Anyone who has learned some thermal physics before will wonder where I have been hiding the First and Second Laws of thermodynamics.

The First Law appears in a strongly generalized form as the law of balance of energy in Equ.(4.18) or Equ.(4.19). The traditional form of the First Law is the law of balance of energy for systems that exchange energy in thermal and mechanical processes. Since dynamical representations are rarely used, the presentation is in the form of an integrated balance: the change of energy of a system equals the energy exchanged in heating and cooling plus the energy exchanged mechanically. The first term (the energy of the system) is called *internal energy*, the energy exchanged in heating and cooling is called *heat*, and the third (energy exchanged mechanically) is called *work*. Thus, the traditional form reads: Change of internal energy equals heat plus work.[23]

The case of the Second Law of Thermodynamics is more intricate. In the literature, we

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22. Take volume and pressure. Volume can be produced or destroyed by compression or expansion of a fluid, and pressure obviously has an absolute zero point.

23. Some authors add a twist to this by using different signs for energy exchanged thermally and mechanically. We might say "heat added to a system" and "work done by the system." So the former term receives a positive sign in the First Law, the latter gets a minus sign.

find countless different forms of "the" Second Law in the introductory course. Needless to say, it is highly unlikely that all the forms express the same concepts and details, so we are left wondering what "the" Second Law actually is. The best that can be said is that the forms are variations of our law of balance of entropy (Section 4.3.2) or a relation between entropy, temperature and energy similar to Equ.(4.22), or combinations thereof.

For our purposes, it suffices to know that the First Law has something to do with energy balances, and the Second Law is somehow related to entropy. This explains the terms first law efficiency (Equ.(4.27)) and second law efficiency (Equ.(4.28)) of thermal engines.

29. How does the law of balance of energy change if thermal processes are included?

30. The Stirling engine in Fig. 4.10 is cooled by letting water from a faucet flow through the cooler of the engine. What happens to the operation of the engine if the flow of water is increased?

31. Why does the result of measurements for the power of a thermoelectric device (Fig. 4.11) suggest that thermal processes (in particular, the relation between thermal processes and energy) can be described in analogy to electric processes?

32. What are the units of entropy, entropy currents, entropy production rates?

33. How big does an entropy current flowing from a point at 500 K to one at 300 K have to be for the thermal power to measure 1.0 MW?

34. A typical nuclear power plant is a thermal engine running between an upper and a lower temperature of about 600 K and 300 K, respectively. What is the ideal thermal efficiency? The real thermal efficiency is more like 30%. What is the real second law efficiency in this case?

35. In what way are the relations for thermal power and for a thermal energy current related?

36. Why is it possible to conceptualize the production of entropy as a pumping of entropy from absolute zero temperature?

37. An immersion heater is operated at an electric power of 400 W. It has a temperature of 400 K. What is the entropy production rate in this heater? What are the entropy current and the energy current emitted by the heater in steady state?

38. To keep the interior of a home at 27°C in winter, the heating power of the heater is 6 kW. What is the entropy current leaving the home?

39. How are the thermal power and the useful power of an ideal heat engine related?

40. Why is the thermal efficiency of an ideal heat engine smaller than 1?

41. What is the *cop* of an ideal heat pump operated between 270 K and 300 K?

42. Real engines have efficiencies that are smaller than those of ideal ones. Why does this tell us that the entropy production rate must be non-negative?

43. Why should hotness have an absolute zero point?

EXAMPLE 4.4. The current of entropy through an ideal Carnot engine.

Consider a Carnot engine working between a furnace at 300°C and a cooler at 40°C. This ideal engine is known to have a mechanical power equivalent to 5.0 MW. (a) How large must the current of entropy through this engine be? (b) If the current of entropy is unchanged, how large must the temperature difference be for a power of 4.0 MW?

SOLUTION: (a) This is a direct application of the relation for the motive power of a heat engine. First we have to conclude that the thermal power of the engine is equal to its mechanical counterpart, namely 5.0 MW. The thermal levels, i.e. the temperatures, are given. Therefore:

$$|I_S| = \left|\frac{\mathcal{P}_{th}}{\Delta T}\right| = \frac{5.0}{573-313}\frac{\text{MW}}{\text{K}} = 19.2 \cdot 10^3 \frac{\text{Ct}}{\text{s}} = 19.2 \cdot 10^3 \frac{\text{W}}{\text{K}}$$

W/K (= Ct/s) is the SI unit of a current of entropy.

(b) The motive power depends linearly upon the difference of temperatures between the furnace and the cooler. For a power which is only 4/5 of the original one, it suffices to have a temperature difference equal to 80% of the original one, i.e. 208 K.

EXAMPLE 4.5. The current of entropy absorbed by a river cooling a thermal power plant.

It is known from the operation of a thermal power plant that the water of a river used for cooling carries away an energy current of 600 MW. (a) How large is the current of entropy entering the environment if the temperature of the water is taken to be equal to 27°C? (b) Express the entropy absorbed by a reservoir at constant temperature in terms of the energy exchanged in heating or cooling and the temperature, and (c) for the power plant given here calculate the entropy absorbed by the river in one day.

SOLUTION: (a) Assume the temperature of the water to remain constant. The amount of water used for cooling is so large that its temperature does not change very noticeably. In this case, the temperature remains constant and the current of entropy is given by

$$I_{S,in} = \frac{I_{E,th,in}}{T} = \frac{600 \cdot 10^6}{(273+27)}\frac{\text{W}}{\text{K}} = 2.0 \cdot 10^6 \frac{\text{W}}{\text{K}}$$

The law relating currents of entropy and of energy describes an instantaneous situation. It is valid for any temperature, and for non-constant values as well. The currents will therefore generally change in time.

(b) Since the temperature of the water is constant during absorption of entropy, the amount exchanged can be computed easily according to Equ.(4.22):

$$W_{th} = T \int_{t_i}^{t_f} I_s dt = T S_e \quad \Rightarrow \quad S_e = \frac{W_{th}}{T}$$

Since entropy flows into the body of water at constant temperature, i.e., at a constant level, the energy exchanged is simply equal to the product of entropy exchanged and the temperature at which the exchange is taking place.

(c) The amount of energy exchanged in one day is equal to 600 MW · 86400 s = $5.2 \cdot 10^{13}$ J, and the numerical value for the entropy exchanged is $5.2 \cdot 10^{13}$ J / 300 K = $1.7 \cdot 10^{11}$ Ct (Ct = J/K).

EXAMPLE 4.6. Energy dissipated in an immersion heater.

An immersion heater is placed in water and hooked up to a voltage of 110 V. The electric current is measured to be 1.5 A. How large is the rate of production of entropy in the heater and water combined if the temperature is 20°C? How much entropy is created in 10 s if the temperature changes linearly to 22°C during this period? The electrical quantities remain constant.

SOLUTION: The energy current given off by the heater is equal to

$$|I_{E,el}| = U|I_Q| = 165\,\text{W}$$

which is equal to the rate of dissipation of energy. Therefore:

$$\Pi_S = \frac{\mathcal{P}_{diss}}{T} = \frac{165}{273 + 20} \frac{W}{K} = 0.563 \frac{W}{K}$$

The amount of entropy produced in this process is

$$S_{prod} = \int_{0s}^{10s} \Pi_S \, dt$$

$$= \int_{0s}^{10s} \frac{\mathcal{P}_{diss}}{T} \, dt = |I_{E,el}| \int_{0s}^{10s} \left[T_1 + (T_2 - T_1) \frac{t}{10s} \right]^{-1} dt$$

which is equal to

$$S_{prod} = 165 W \cdot 10s \cdot \ln\left(\frac{T_2}{T_1}\right)(T_2 - T_1)^{-1} = 5.61 \, J/K$$

Since the temperature is almost constant, the result is very nearly equal to $\Pi_S \Delta t$, with a constant rate of generation of entropy.

EXAMPLE 4.7. A thermal power plant.

The thermal energy current due to burning of coal in a thermal power plant is 1.5 GW, while the mechanical energy current leaving the turbines is 0.6 GW. The steam driving the engine is emitted at a temperature of 50°C. If the turbines operate as an *ideal engine*, what are (a) the current of entropy flowing through the engine, (b) the temperature of the furnace, and (c) the Carnot efficiency?

SOLUTION: (a) The thermal energy current emitted with the steam is equal to the difference between the energy current entering the engine and the one driving the generator. In other words, it is 0.9 GW. At a temperature of (273 + 50) K, the current of entropy associated with this thermal energy flux is

$$I_S = \frac{I_{E,th,out}}{T_L} = -2.79 \frac{MW}{K}$$

(b) The temperature of the furnace can be calculated in terms of the currents of entropy and energy absorbed by the engine:

$$T_H = \frac{I_{E,th,in}}{I_S} = 538 \, K$$

(c) According to Equ.(4.27), the Carnot efficiency is equal to

$$\eta_1 = \frac{538K - 323K}{538K} = 0.40$$

The same result could also have been obtained with the help of the energy currents:

$$\eta_1 = \frac{I_{E,mech}}{I_{E,th,in}} = \frac{0.60}{1.50} = 0.40$$

Note that in these equations the magnitudes of the fluxes have been used. The second law efficiency is naturally equal to 1.0.

EXAMPLE 4.8. Heating water with a heat pump.

Assume that a heat pump has been installed that requires an energy current of 165 W for operation. The pump takes entropy out of the ground in winter for heating water. (The temperature of the ground is 2°C.) (a) How large is the entropy current at the beginning, with 20°C water? (b) How large is the current when the temperature of the water has reached 100°C? (c) How large are the energy currents entering the water in these two cases?

SOLUTION: (a) The current of entropy is calculated to be

$$I_{S,in} = \frac{I_{E,mech}}{T_H - T_L} = \frac{165\,\text{W}}{18\,\text{K}} = 9.17\,\frac{\text{W}}{\text{K}}$$

if the water has a temperature of 20°C.

(b) If the water has reached a temperature of 100°C, the current of entropy diminishes to 165 W/ 98 K = 1.68 W/K. With the same amount of energy, less entropy can be pumped through a larger temperature difference. (This result should be compared to the entropy current out of an immersion heater having a power of 165 W, which according to Example 4.6 is equal to 0.56 W/K at 20°C.)

(c) The energy current leaving the heat pump at 20°C (and entering the water) will be

$$I_{E,th,out} = -\left(I_{E,mech} + I_{E,th,in}\right) = -\left(I_{E,mech} + T_L I_{S,in}\right)$$
$$= -\left(165\,\text{W} + 275\,\text{K} \cdot 9.17\,\text{W/K}\right) = -2690\,\text{W}$$

In the second case, it decreases to 627 W. Obviously, heating with an ideal heat pump must be more efficient than heating with an immersion heater.

EXAMPLE 4.9. The production of entropy in a non-ideal Carnot engine.

(a) For an engine with $\eta_I < \eta_C$, calculate the rate at which entropy is produced in the engine. Compute the numerical value for an engine operating between reservoirs at 600 K and 300 K, respectively, and which has an observed efficiency of 0.30. The thermal energy current entering the engine is 1.0 GW. (b) Show that there is a loss of available energy, and express the rate of loss in terms of the rate of production of entropy. How large is the loss for the engine described in (a) for one day?

SOLUTION: (a) In an engine which is operating in a steady state, the rate at which entropy is produced must be the difference between the rate at which entropy is emitted and the rate at which it is absorbed. Expressed more formally, according the law of balance of entropy Equ.(4.16) in the steady state ($dS/dt = 0$):

$$\Pi_S = -\left(I_{S,in} + I_{S,out}\right)$$

This equation can be transformed using the relations between currents of entropy and energy in heating. If we also use the expression for the efficiency of an ideal Carnot engine, Equ.(4.27), this changes to:

$$\Pi_S = -\left(\frac{I_{E,th,in}}{T_H} + \frac{I_{E,th,out}}{T_L}\right) = -\left(-(1-\eta_I)\frac{1}{T_L} + \frac{1}{T_H}\right) I_{E,th,in}$$
$$= \left((1-\eta_I) - \frac{T_L}{T_H}\right) \frac{I_{E,th,in}}{T_L}$$

or

$$\Pi_S = \left(\eta_C - \eta_1\right)\frac{I_{E,th,in}}{T_L}$$

If we introduce numerical values we obtain

$$\Pi_S = \left(0.50 - 0.30\right)\frac{1.0\,\mathrm{GW}}{300\,\mathrm{K}} = 0.67\,\frac{\mathrm{MW}}{\mathrm{K}}$$

The value of 0.5 is the Carnot efficiency of the engine operating between 600 K and 300 K. The rate at which entropy is absorbed is

$$I_{S,in} = \frac{1.0\,\mathrm{GW}}{600\,\mathrm{K}} = 1.7\,\frac{\mathrm{MW}}{\mathrm{K}}$$

which is 2.5 times larger than the rate of production.

(b) The loss of available power is the difference between the power available hypothetically and the actual mechanical power of the engine. According to the definition of the available power in Equ.(4.31), and the Carnot efficiency Equ.(4.27), we have:

$$\left|\mathcal{P}_{av}\right| - \left|I_{E,mech}\right| = \left(1 - \frac{T_L}{T_H}\right)\left|I_{E,th,in}\right| - \eta_1\left|I_{E,th,in}\right| = \left(\eta_C - \eta_1\right)\left|I_{E,th,in}\right|$$

This can be expressed using the result obtained above:

$$\left|\mathcal{P}_{av}\right| - \left|I_{E,mech}\right| = T_L \Pi_S$$

This result is important. It demonstrates that the loss of power due to dissipation is directly proportional to the production of entropy. At second glance, this is not so surprising. After all, the non-conservation of entropy leads to the loss in the first place. In one day, the loss is equal to $300\,\mathrm{K} \cdot 0.67\,\mathrm{MW/K} \cdot 86400\,\mathrm{s} = 1.74 \cdot 10^{13}\,\mathrm{J}$, which is equivalent to $4.8 \cdot 10^6$ kWh of energy. See Section 4.4.3 for an analysis of the loss of power and production of entropy.

EXAMPLE 4.10. Efficiency of a dissipative heat pump.

(a) Determine the coefficient of performance (*cop*) of a dissipative heat pump operating between the environment at temperature T_0 and a body to be heated at T. Show that it is smaller than that of an ideal pump. (b) Derive the relationship between the *cop* and the second law efficiency.

SOLUTION: (a) We start from the definition of the *cop* for heat pumps. It is the ratio of the heating power at temperature T and the mechanical power necessary for driving the pump. Taking into consideration the signs of the fluxes with respect to the pump we have:

$$cop = \frac{-I_{E,th}(T)}{I_{E,mech}} = \frac{-I_{E,th}(T)}{-\left(\mathcal{P}_{av} - \mathcal{L}\right)} = \frac{-T I_S(T)}{-\left(T - T_0\right)I_S(T) + T_0 \Pi_S}$$

$$= \frac{T}{\left(T - T_0\right) - T_0 \Pi_S / I_S(T)} < \frac{T}{T - T_0}$$

The last expression is the *cop* of an ideal heat pump; it is clearly larger than the actual value.

(b) According to the definition of the second law efficiency, the actual *cop* must be equal to the product of the ideal *cop* and the second law efficiency:

$$cop = \frac{-I_{E,th}(T)}{I_{E,mech}} = \frac{\mathcal{P}_{av}}{I_{E,mech}} \frac{-I_{E,th}(T)}{\mathcal{P}_{av}} = \eta_{II} cop(ideal)$$

We could calculate the second law efficiency from the result for the *cop* given in (a). This must agree with the direct definition, which leads to:

$$\eta_{II} = \frac{\mathcal{P}_{av}}{I_{E,mech}} = \frac{\mathcal{P}_{av}}{\mathcal{P}_{av} - T_0 \Pi_S} = \frac{(T - T_0)I_S(T)}{(T - T_0)I_S(T) - T_0 \Pi_S} < 1$$

Note that the second law efficiency of a heat pump is the inverse of what we defined for a heat engine in Equ.(4.28).

4.5 ENTROPY-TEMPERATURE CHARACTERISTIC OF SIMPLE FLUIDS

So far, the discussion of thermal processes has centered upon generic relations such as the laws of balance of entropy and energy, and the properties of hotness. Results for engines were derived that depend only upon this type of relation, not upon details of materials used in actual devices. In this and the following sections, we will finally turn to some constitutive relations in their simplest forms. Still, the results will allow us to work on some interesting and real cases of thermal dynamical processes.

In this section we will discuss a common problem—the heating of solids and liquids—in a greatly simplified manner. We shall construct a model of a body of uniform temperature which is undergoing processes of heating. Indeed, heating and cooling are assumed to be the only phenomena which can be associated with such systems. Their volume will be assumed to remain constant. Therefore, in the simplest case, there will be only one independent variable—one function of time—which determines the properties of such a body. We can take this function to be the temperature $T(t)$. Other choices are possible, namely quantities which are related to and change with temperature. Obviously, these must be the entropy content and the energy of the system. A first question must be asked, namely, how temperature and entropy content of a body are related. We will answer it by introducing the *entropy capacitance*. Using the generic laws of balance of entropy and energy, we hope to find the solution of the problem posed, namely the functions $T(t)$, $S(t)$, and $E(t)$, and expressed in terms of these the flux and the rate of production of entropy.
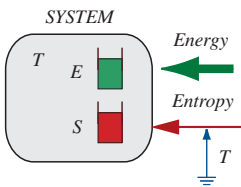
Figure 4.36: Process diagram of heating of a body: Entropy and Energy are added. If there are no other processes involved, the quantities added to the body are stored.

4.5.1 The Model of Uniform Heating

The model that will be constructed is one of uniform reversible heating or cooling. What this means is simple to express: When heated, a body receives entropy (and energy), but entropy may not be produced in the body as a consequence of this heating (Fig. 4.36). If this applies, and if it applies to cooling as well, entropy added to a body will be emitted in the reverse process. In between, it is stored in the system.

Is such a model realistic? In the Introduction, Section I.5, I discussed this question in some detail, so I can keep things short here. Commonly, entropy is produced when it spreads inside a body—we will understand this and be able to calculate entropy pro-

duction rates for this process later in this chapter (Section 4.6). This means that we have to make assumptions as to the properties of the materials being heated. We need a material that lets heat (entropy) pass easily without producing any. A similar situation is called superconductivity in electricity. Charge flows without needing a driving force—an electric potential difference—and without producing entropy. Even though it is not correct, we apply this behavior to models of electric circuits where wires are treated as if they were superconductors. This is exactly what we are going to do for reversible heating and cooling. We assume that entropy can spread inside a body being heated without needing a temperature difference for the transport of entropy. Therefore, we have a condition of uniform reversible heating: A thermal superconductor having a single temperature throughout which stores the entropy it receives without producing any.

In real life, stirred liquids that are heated or cooled come close to this model. As examples will show, the model can be applied successfully to the dynamics of such materials. If the heater is placed somewhere in a liquid, stirring it will lead to an even distribution of the entropy. If the body cools through its surface, stirring ensures that the outer layers do not get colder than the inner ones. Naturally, solids do not heat or cool in this manner. However, if the solid has a relatively high conductivity for entropy, and if we are not interested in very short term behavior, we can still apply our model of uniform heating (for an example, see the heating of copper Fig. 4.1).

Balance of entropy and of energy. The model discussed here is represented symbolically by the process diagram in Fig. 4.36. If heating and cooling are reversible, the law of balance of entropy for the body takes the form

$$\dot{S} = I_S \tag{4.33}$$

(see Equ.(4.11)). Since heating and cooling are the only processes allowed, the balance of energy is

$$\dot{E} = I_{E,th} \tag{4.34}$$

The relation between entropy and energy fluxes in heating (Equ.(4.21)) let us combine these laws of balance. This leads to a relation between how the entropy and the energy of the simple materials discussed here change:

$$\dot{E} = T \dot{S} \tag{4.35}$$

This is an example of what is generally called a *Gibbs Fundamental Form*. We will encounter GFFs again and again in different applications throughout this book. Note that this is a relation between quantities describing a system—it does not contain any terms referring to processes such as fluxes or production rates.[24] If we want to recover processes from our model, we need to combine the laws of balance with the Gibbs fundamental form.

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24. There are some aspects of the model presented here that need to be investigated in more detail, such as the use of time derivatives in the GFF, or the tacit assumption that the simple materials being heated go through reversible changes (this is part of the assumptions that led to Equ.(4.35)). These points will be discussed more fully in Chapter 5.

4.5.2 Adding Entropy to a Liquid

Consider electrical heating of water or ethylene glycol in an (almost) perfectly insulated container. This is achieved by thick insulation, but we also have to assume that inner layers of the container do not take up noticeable amounts of entropy. The electric heater produces entropy that is emitted to the liquid together with energy (Fig. 4.36). As a consequence, the temperature of the material changes.

The results of Section 4.4 allow us to determine the entropy produced and communicated to the liquid. To do so we need the electric power of the heater and the temperature of the water as functions of time. As in Example 4.6, the entropy production rate is calculated from the instantaneous values of dissipation rate and temperature, and the entropy production rate is integrated over time to obtain the (change of) entropy of the liquid. If we assume a certain value of entropy at a reference temperature, changes of entropy can be converted to entropy content. (In mechanical engineering, it is customary to set the entropy of materials equal to zero at 0°C.)

If we did the same experiment for 1 and 2 kg of a liquid, we would notice that the temperature rises more slowly in the second case (twice as slowly, to be precise). To make the results independent of the amount of the material and to get a temperature–entropy relation that is indicative of the material and not its amount, the measurements of the entropy of the body are referred to unit mass. This is called the *specific entropy s* of the material:

$$s = S/m \qquad \textbf{(4.36)}$$

In this way, the temperature of the material is made a function of its specific entropy. The relation between specific entropy and temperature can be represented graphically as a *Ts*–diagram (Fig. 4.37), in a table, or by an analytical approximation.
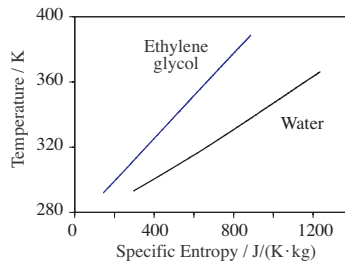
Figure 4.37: Experimental *Ts*-diagram of water and of ethylene glycol. The relation for glycol is almost linear, whereas the one for water resembles an exponential function. The entropy of the materials is arbitrarily set to zero at *T* = 273 K.

Experimental results for water and for ethylene glycol show two interesting features (Fig. 4.37). We need less entropy to make 1 kg of glycol warmer by 1 K than we need for water; and the shape of the temperature-specific-entropy or *Ts characteristic* of the materials is different. While it is close to being a linear function in the case of glycol, it is more of an exponential function for water.

4.5.3 Warming Factor and Entropy Capacitance

The meaning of the *Ts* characteristic for simple materials is analogous to that of a pressure-volume or voltage-charge characteristic of a tank or a capacitor, respectively (see

Section 1.4.2). Therefore, it can be described analogously to how this was done in hydraulics and electricity. The most significant feature of a material in the *Ts*-diagram is the slope of the $T(s)$ curve. It tells us how fast the temperature rises as a function of an increase in entropy. This slope is called the *warming factor* α_S (Fig. 4.38):

$$\dot{T} = \alpha_S \dot{s}$$
$$\alpha_S = \frac{dT}{ds} \tag{4.37}$$

Figure 4.38: The slope of the *Ts*-relation tells us how easy it is to warm a body by heating.

The warming factor tells us how easy it is to warm a material; the larger the easier. Compare this to the definition of elastance of containers and fluids, or of capacitors. If $T(s)$ is a straight line in the *Ts*-diagram, the temperature can be calculated easily with the help of the warming factor:

$$T = T_{ref} + \alpha_S \left(s - s_{ref} \right) \tag{4.38}$$

Glycol is an example of a material having a constant warming factor which leads to the linear temperature–entropy characteristic demonstrated experimentally in the data of Fig. 4.37.

Entropy capacitance. The inverse of the warming factor is commonly used to represent the relation between temperature and entropy of a material. The inverse of the heating factor is called the *specific entropy capacitance κ*:

$$\dot{s} = \kappa \dot{T}$$
$$\kappa = \frac{ds}{dT} \tag{4.39}$$

Figure 4.39: Temperature as a function of entropy capacitance. The diagram can be used to calculate the change of entropy of the body. The form of the diagram resembles that of a tank filled with entropy.

The *entropy capacitance*, $K = m\kappa$, has the usual meaning of a capacitance, as in hydraulics or electricity. In general, the entropy capacitance depends upon the temperature of the material. The change of entropy of a body can be calculated graphically from the temperature – capacitance diagram (Fig. 4.39).

4.5.4 The Energy of Simple Materials

It is common to introduce the *specific temperature coefficient of energy* (*specific heat*[25]) *c* which is calculated from the specific entropy capacitance by multiplying the latter by the temperature of the material ($c = T\kappa$). It allows us to directly determine the change of the energy of the simple materials discussed here (see the derivation below):

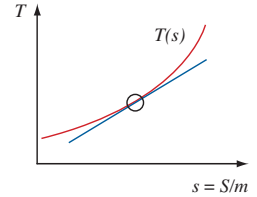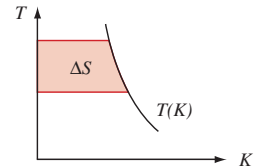$$\dot{e} = c\dot{T} \tag{4.40}$$

where

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25. The name specific heat (or specific heat capacity) is derived from the traditional usage in thermodynamics where a quantity of heat is measured in terms of energy. This usage is a remnant of the caloric theory in the thermodynamics formulated after 1850. Note that in the caloric theory, as in our conceptualization of thermal processes, the derivative of heat (caloric, entropy) with respect to temperature is a capacitance. The factor $c = Tds/dt$, however, is not.
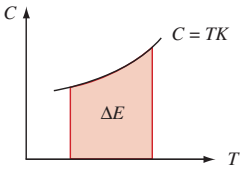
Figure 4.40: Temperature coefficient of energy (heat capacity) as a function of temperature, and energy change of a body.

$$c = T\kappa \tag{4.41}$$

Here, $e = E/m$, the energy per mass, is called the *specific energy* of the material. The specific heat of materials generally depends upon the temperature of the material. The change of energy of a body can be determined graphically from the specific heat – temperature diagram (Fig. 4.40).

Equ.(4.40) is derived simply from the balances of entropy and energy with the help of the relation between energy currents and entropy fluxes in heating, and Equ.(4.39):

$$\dot{E} = m\dot{e} = I_{E,th} = T\,I_S = T\,\dot{S} = Tm\kappa\dot{T}$$

It is quite common to report the values of specific heats of materials in tables and graphs. They are determined in the manner described above, by getting the temperature–entropy characteristic from which the entropy capacitance and the specific heat can be derived. Results for water (between 0°C and 100°C) and for some metals (down to 0 K) are shown in Fig. 4.41.

Figure 4.41: Left: Specific heat of water. Right: Molar specific heat $\bar{c} = T\bar{k}$, for several solids. At high temperatures, $\bar{c}$ reaches roughly $3R$ for most solids, where $R = 8.31$ J/(mole·K) is the universal gas constant. T_D is the Debye temperature which differs for different solids. (For copper and silicon the values are 343 K and 640 K, respectively.)
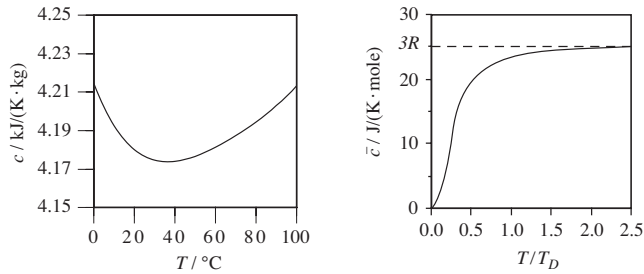
At high temperatures, which often mean room temperature or higher, c is a constant for solids. However, if we go to lower temperatures it becomes evident that c changes drastically. Specifically, at 0 K, entropy capacitances (and with them the values of c) become zero. This finding is equivalent to saying that it is impossible to reach 0 K in any experiment. Either statement is often called the *third law of thermodynamics*. In Fig. 4.41, values of c for some metals are shown. Table 4.7 lists values of κ and c for some liquids and solids for 20°C.

4.5.5 Materials With Constant Temperature Coefficient of Energy

Some materials (water, solids at high temperature) have almost constant specific heats. For these materials, entropy and energy can be calculated easily:

$$s = s_{ref} + c\,\ln\!\left(T/T_{ref}\right) \tag{4.42}$$

$$e = e_{ref} + c\!\left(T - T_{ref}\right) \tag{4.43}$$

The derivation of Equ.(4.42) follows from Equ.(4.39)$_1$ together with the definition of the temperature coefficient of energy $c = T\kappa$:

$$\dot{s} = \kappa \dot{T} = \frac{c}{T} \dot{T} \quad \Rightarrow \quad s(T) - s(T_{ref}) = \int_{t_0}^{t} \frac{c}{T} \dot{T} \, dt = c \int_{T_{ref}}^{T} \frac{1}{T} \, dT = c \ln(T/T_{ref})$$

Equ.(4.43) is derived even more easily. All we have to do is integrate Equ.(4.40) for a constant value of the temperature coefficient c.

Now we can understand the form of the temperature – entropy characteristic of water which can be seen in Fig. 4.37. According to Equ.(4.42), the temperature T is an exponential function of the specific entropy s of water.

Table 4.7: Entropy capacitance and temperature coefficient of energy at 20°C

Substances	Specific entropy capacitance κ / J · K^{-2}kg^{-1}	Molar entropy capacitance $\overline{\kappa}$ / J · K^{-2}mole^{-1}	Specific temperature coefficient of energy c / J · K^{-1}kg^{-1}
Aluminum	3.06	0.0826	896
Concrete	2.87		840
Copper	1.31	0.0837	383
Glass (pyrex)	2.87		840
Granite	2.56		750
Ice (0°C)	7.69	0.123	2100
Iron	1.54	0.0864	452
Lead	0.44	0.0911	129
Lithium	1.16	0.0080	339
Sand (dry)	2.87		840
Silicon	2.40	0.0672	703
Sodium	4.16	0.0958	1220
Steel (average)	1.57		460
Wood (average)	8.53		2500
Mercury	0.47	0.0954	139
Petroleum	7.30		2140
Water	14.26	0.257	4180

4.5.6 Dynamical Models, Entropy, and Temperature

The temperature of a body is a central quantity in any dynamical model of a thermal system. It can be calculated from the entropy of the body in two steps, first by computing the specific entropy, and then by applying the temperature – entropy characteristic of the material. Alternatively, we can apply concrete relations of the type found in Equ.(4.38) or Equ.(4.42). The part of a dynamical model that calculates the temperature may look like the one shown in Fig. 4.42.
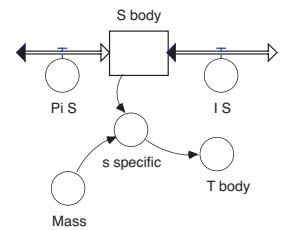

Figure 4.42: Diagram of a dynamical model for calculating the temperature of a body.

44. Why do we have to exclude compression or expansion from the model of heating or cooling of simple materials considered in this section?

45. Why is the warming factor of glycol constant? Does this mean that the entropy capacitance of glycol is constant as well?

46. The warming factor of glycol is about 0.13 K^2kg/J. What is its entropy capacitance?

47. What is the warming factor of a mixture of ice and water undergoing phase change?

48. Between 20°C and 30°C, the specific entropy capacitance of water is about 14 J/(K^2kg). How much entropy has to be added to 10 kg of water to change its temperature from 20°C to 30°C? How much energy is added to the water at the same time?

49. Why does Fig. 4.40 tell us that for water $\Delta E = mc\Delta T$?

50. Consider the temperature – entropy characteristic of water in Fig. 4.37. Does the warming factor increase or decrease with temperature? What does this mean for the entropy capacitance of water?

51. How does the entropy capacitance of water depend upon temperature? How can this be derived from Equ.(4.42)?

EXAMPLE 4.11. Measuring the entropy capacitance of water.

Assume that two liters of water inside an insulated bottle are being heated by an immersion heater. The voltage and electrical current are kept constant at 220 V and 1.36 A, respectively. The temperature of the water is monitored. It is found that the temperature is quite nearly a linear function of time, with dT/dt = 0.0356 K/s. Determine $K(T)$ and $C(T)$, and calculate the entropy capacitance and the temperature coefficient of energy per mass for a temperature of 20°C.

SOLUTION: dT/dt is constant, with a value of 0.0356 K/s. The energy current is constant as well:

$$\left| I_{E,th} \right| = \left| U I_Q \right| = 299 \mathrm{W}$$

Consequently, the temperature coefficient of energy is a constant (or nearly so) for water:

$$\left(TK \right) \dot{T} = \left| I_{E,th} \right|$$

The experimental results make $C = TK = 8400$ J/K for this body of water. The entropy capacitance of two liters of water is therefore equal to

$$K = \frac{8400 \, \mathrm{J/K}}{T}$$

while the temperature coefficient of energy is constant and equal to $C = TK = 8400$ J/K. The entropy capacitance per unit mass at 20°C is $\kappa = 8400/(2 \cdot 293)$ J/($K^2 \cdot$ kg) = 14.3 J/($K^2 \cdot$ kg). The temperature coefficient of energy per unit mass is $c = 8400/2$ J/(K$\cdot$kg) = 4200 J/(K$\cdot$kg). Note that accurate measurements of the value of $c = T\kappa$ show that it is almost constant over the range of temperatures given (see Fig. 4.41, left).

EXAMPLE 4.12. The entropy of solids.

According to a constitutive law named after P. Debye, the molar entropy capacitance of a solid

obeys the following relationship at very low temperatures:

$$\overline{\kappa}(T) = \frac{12\pi^4 R}{5 T_D^3} T^2$$

Here, $\overline{\kappa}$ is the molar entropy capacitance (entropy capacitance per unit amount of substance n; see Chapter 6), and T_D is the Debye temperature. The temperature of the solid must be much smaller than this critical value for the formula to hold; i.e., $T \ll T_D$ (Fig. 4.41, right). (a) If the entropy of a solid is equal to zero at 0 K, how large is the entropy content of one mole of such a body at a temperature T? (b) What is the temperature coefficient of energy of this body?

SOLUTION: (a) According to Equ.(4.39) we obtain for the entropy content

$$S(T) = \int_0^T K \, dT = n \frac{12\pi^4 R}{5 T_D^3} \int_0^T T^2 \, dT = n \frac{12\pi^4 R}{15} \frac{T^3}{T_D^3}$$

Note that this quantity actually corresponds to the change of entropy content due to heating from absolute zero. In writing this we have set the entropy content equal to zero at 0 K.

(b) The temperature coefficient of energy is defined as the product of temperature and entropy capacitance. Therefore we have

$$C(T) = T \, K(T) = n \frac{12\pi^4 R}{5} \frac{T^3}{T_D^3}$$

EXAMPLE 4.13. The temperature coefficient of energy (specific heat) of glycol.

According to the data in Fig. 4.37, the temperature of glycol is nearly a linear function of the specific entropy given by

$$T = \alpha_S \left(s - s_{ref} \right) + T_{ref} \quad , \quad \alpha_S = 0.131 \text{K}^2 \text{kg}/\text{J} \quad , \quad T_{ref} = 273 \text{K} \quad , \quad s_{ref} = 0 \text{J}/(\text{K} \cdot \text{kg})$$

Determine the specific entropy capacitance and the specific temperature coefficient of energy (specific heat) as functions of temperature for the range for which data has been taken.

SOLUTION: The specific entropy capacitance is the inverse of the warming factor α_S. Since α_S is constant, κ must be constant as well:

$$\kappa = 7.63 \text{J}/\left(\text{K}^2 \cdot \text{kg} \right)$$

The temperature coefficient of energy is equal to the entropy capacitance multiplied by the (Kelvin) temperature. Thus:

$$c = 7.63 \text{J}/\left(\text{K}^2 \cdot \text{kg} \right) T$$

Therefore, the specific heat c (specific temperature coefficient of energy) varies between 2240 J/(K·kg) at 20°C and 2850 J/(K·kg) at 100°C.

EXAMPLE 4.14. The time required to heat water using a heat pump.

Calculate the times needed to heat the same amount of water (a) using an ideal heat pump, and (b) using an immersion heater, if the electric power of both devices is the same.

SOLUTION: According to Equ.(4.34) and Equ.(4.40), the thermal energy current entering water

during heating is proportional to the time rate of change of the temperature:

$$I_{E,th} = C\dot{T}$$

with C constant.

(a) Consider the energy current to be delivered by an ideal heat engine. According to Equ.(4.29), it is given by

$$I_{E,th} = \frac{T_H}{T_H - T_L} I_{E,el}$$

If we combine this with the constitutive law stated above, we get the differential equation

$$C\dot{T} = \frac{T_H}{T_H - T_L} I_{E,el}$$

The entropy delivered by the heat pump is taken out of the ground at constant lower temperature, while the upper temperature varies from the initial temperature $T_i \geq T_L$ of the water to the final temperature T_f. Under these conditions, the solution of the differential equation delivers the time for heating using the heat pump:

$$t_p = \frac{C}{I_{E,el}} \left[T_f - T_i - T_L \ln\left(\frac{T_f}{T_i}\right) \right]$$

(b) In the case of the immersion heater, the thermal energy current heating the water is equal to the electrical energy current of the immersion heater. Therefore the time required for heating is

$$t_{ih} = \frac{C}{I_{E,el}} \left(T_f - T_i \right)$$

This value is definitely larger than the one obtained for the heat pump.

EXAMPLE 4.15. The availability of a body of water.

Take a body of water of mass m at temperature T_i. How large is its availability in an environment at temperature T_0?

SOLUTION: The availability of a body is defined as the amount of energy which may be released by letting its entropy fall to the level of the environment. With the expression for the available power (Equ.(4.31)),

$$\mathcal{P}_{av} = \left(T(t) - T_0 \right) I_S$$

and the balance of entropy and the definition of the entropy capacitance, we obtain

$$\mathcal{P}_{av} = -\left(T(t) - T_0 \right) \frac{C}{T(t)} \dot{T}$$

The availability E_{av} is computed as follows:

$$E_{av} = \int_{t_i}^{t_f} \mathcal{P}_{av} dt = -\int_{t_i}^{t_f} \left(T(t) - T_0 \right) \frac{C}{T(t)} \dot{T} dt = -\int_{T_i}^{T_a} \left(T(t) - T_0 \right) \frac{C}{T(t)} dT$$

Water
m, T_i

I_{E1}

$T(t)$ Entropy
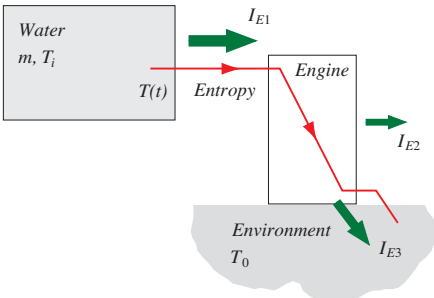
Engine

I_{E2}

Environment
T_0

I_{E3}

Figure Ex.15

which leads to

$$E_{av} = mc\left[T_i - T_0 - T_0 \ln\left(\frac{T_i}{T_0}\right)\right]$$

This is how much energy can be released by an ideal heat engine from a body of water at temperature T_i in an environment at temperature T_0. The term proportional to $T_i - T_0$ is equal to the change of the energy of the body while the second term represents the energy emitted to the environment together with the entropy which has been withdrawn from the body. You can calculate the result directly by considering these integrated quantities. (See Example 4.16 for how to do this.)

EXAMPLE 4.16. Heat transfer (between two equal amounts of water) using a heat engine.

Consider two bodies having identical and constant temperature coefficients of energy C. Their initial temperatures are assumed to be T_1 and $T_2 < T_1$. Entropy is transferred from the hotter to the cooler reservoir using an ideal heat engine. What is the value of the final temperature attained by the bodies, and how much energy is given off by the heat engine in the mechanical process?

SOLUTION: In this case no entropy is produced, which means that the change of the entropy content of the two bodies is zero. Put differently:

$$\Delta S = \Delta S_1 + \Delta S_2 = 0$$

or

$$\Delta S = \int_{T_1}^{T_f} K\,dT + \int_{T_2}^{T_f} K\,dT = \int_{T_1}^{T_f} \frac{C}{T}\,dT + \int_{T_2}^{T_f} \frac{C}{T}\,dT$$

$$= C\left[\ln\left(\frac{T_f}{T_1}\right) + \ln\left(\frac{T_f}{T_2}\right)\right] = C\ln\left(\frac{T_f^2}{T_1 T_2}\right)$$

$$\Delta S = 0$$

which leads to

$$T_f = \sqrt{T_1 T_2} \le \frac{1}{2}(T_1 + T_2)$$

The geometric mean is always smaller than or equal to the arithmetic mean. The energy released in the fall of entropy must be equal to the difference of the energy contents of the reservoirs at the beginning and at the end:

$$E_{mech} = \Delta E_1 + \Delta E_2 = C\left(T_f - T_1\right) + C\left(T_f - T_2\right)$$

$$= C\left[2\sqrt{T_1 T_2} - (T_1 + T_2)\right]$$

Since this quantity is negative, the bodies lose energy in the mechanical process.

EXAMPLE 4.17. Equilibrating temperatures in bodies in thermal contact.

Two bodies of water having equal mass and initial temperatures T_{1i} and T_{2i}, respectively, are brought in thermal contact. Otherwise, they are perfectly insulated from the environment. What is the final temperature reached, and how much entropy is produced in this process?

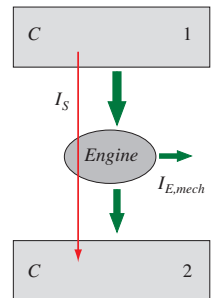*SOLUTION:* Water is a substance having constant temperature coefficients of energy (specific
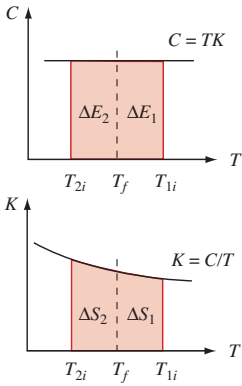
Figure Ex.16

Figure Ex.17

heats). For two equal amounts, the *CT* diagram (Fig. 4.40, Fig. Ex.17) is the same horizontal line. Using the balance of energy on the entire process from beginning (*i*) to end (*f*), we see that

$$\Delta E = \Delta E_1 + \Delta E_2 = 0$$
$$C\left(T_f - T_{1i}\right) + C\left(T_f - T_{2i}\right) = 0$$
$$T_f = \frac{1}{2}\left(T_{1i} + T_{2i}\right)$$

which we can read off the *CT* diagram shown here. The associated *KT* diagram (Fig. 4.39, Fig. Ex.17) shows, that the change of entropy of the two bodies together is greater than zero: entropy has been produced:

$$\Delta S = \Delta S_1 + \Delta S_2 = C\left[\ln\left(\frac{T_f}{T_{1i}}\right) + \ln\left(\frac{T_f}{T_{2i}}\right)\right] = C\ln\left(\frac{T_f^2}{T_{1i}T_{2i}}\right)$$
$$= C\ln\left(\frac{\left(T_{1i} + T_{2i}\right)^2}{4T_{1i}T_{2i}}\right) > 0$$

4.6   ENTROPY TRANSFER IN HEATING AND COOLING

Now that we know how to calculate the temperature of simple materials if their entropy is known, we can turn our attention to the second main job of creating dynamical models of thermal systems: how to find expressions for entropy currents heating or cooling a body. In this section, overall heat transfer (entropy transfer) through layers separating a body from its environment, or two bodies in thermal contact, will be studied. A simple example of the former situation is a well stirred body of water inside a container in an environment (Fig. 4.4); the latter case is exemplified by two bodies of water separated by a thin wall, or a body such as a copper cylinder submerged in water of a different temperature (Fig. 4.1).

There are two main findings of this study. First, we will see that a simple expression for overall entropy transfer through layers can model realistic situation very well—we do not have to consider details to obtain some useful results. Second, and most importantly for our understanding of the dynamics of heat, we will recognize that heat transfer is dissipative, i.e., that entropy is produced when it flows through materials.

4.6.1   Thermal Driving Force and Overall Entropy Transfer

Figure 4.43: Entropy and energy transfer through layers from higher to lower temperature.

When entropy flows we normally speak of heat transfer. Entropy flows as the result of (1) spontaneous flow through matter due to a temperature difference, (2) convective transport with fluids, or (3) radiation. If one or all of these processes lead to a flow through a series of layers from a hot body to a colder body, we speak of overall entropy flow. The entropy flux I_S is expressed in terms of an *overall entropy conductance G_S* and the temperature difference (Fig. 4.43):

$$I_S = -G_S\left(T - T_a\right) \tag{4.44}$$

Here, T_a is the temperature of the environment of the body whose temperature is equal to T. The equation is written with respect to the body gaining or losing entropy. When
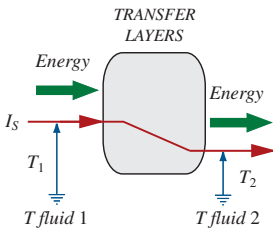
we have identical conditions, but twice the surface area of transfer layers for entropy to flow through, the current doubles. Therefore, the conductance is written in terms the product of an *overall entropy transfer coefficient h_S* and the surface A through which the flow takes place:

$$I_S = -A h_S (T - T_a) \tag{4.45}$$

The entropy flux through a surface is related to its associated energy current by the temperature T at the surface of the body (Fig. 4.43):

$$I_{E,th} = -G_E (T - T_a) \tag{4.46}$$

$G_E = T G_S$ is called the overall *energy conductance*. The product of the entropy transfer coefficient and temperature,

$$h = T h_S \tag{4.47}$$

is called the *overall heat transfer coefficient*.[26] Therefore, the energy current accompanying the entropy flow is

$$I_{E,th} = -A h (T - T_a) \tag{4.48}$$

Thermal interfaces and transfer layers. What are heat transfer layers made of? What types of layers are there, and how might they be arranged? Most importantly, how can they be identified? The answer given here is preliminary and essentially qualitative. To understand details of transfer layers we need to study heat transfer in considerably more details. This we will do in Chapter 7.

Consider the case of the flow of heat through a wall of a building in winter. It is warm inside and cold outside, and there are two fluids (air) separated by solids. Clearly, the basic condition for the existence of a thermal interface between two bodies whose dynamics we are interested in, is a temperature difference from one side to the other of the layers that make up the interface.

So the wall—which may be made up of several different layers—must be warmer on the inside than on the outside. The temperature drops in the materials in the direction to the cold environment: There are *temperature gradients* in the layers (Fig. 4.44), and entropy is transferred by *conduction*. These gradients depend not only upon the overall temperature difference but upon the type of material a layer is constructed of as well.

This is not the whole story, though. When you touch the surface of the wall or window on the inside of the building, you may notice that it is cooler than the air of the room; measurements will confirm this impression. Clearly, there is a temperature drop from the inside air to the inside surface of the wall (Fig. 4.44). Since the air in the room is more or less well mixed, the temperature should be about the same throughout. However, in a thin layer near the solid interface, there is a so-called *convective transfer layer* (Fig. 4.45) in which the temperature changes in the direction of the flow of entropy.
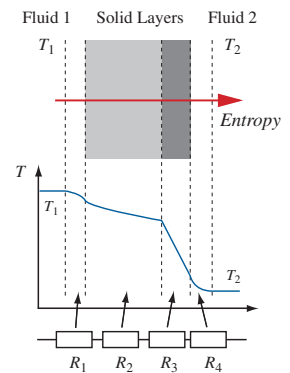

Figure 4.44: Entropy transfer through a series of layers. In each layer, the temperature drops (level diagram for temperature). Layers may be considered thermal resistors.
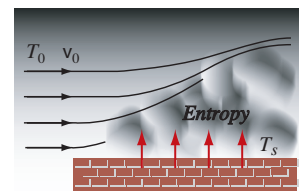

Figure 4.45: Entropy transfer from a solid body into a fluid (such as air or water) flowing past the solid surface.

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26. Remember that the word *heat* has been used for energy transferred in heating or cooling since about 1850. That is why the term *heat* is associated with transfer coefficients for energy flowing with entropy.

The nature of entropy transfer through a convective layer is very complex. There is conduction immediately where the fluid touches the solid. The entropy transferred to the fluid is then carried away—how this happens depends upon the details of fluid flow in the transfer layer (Fig. 4.44). Simultaneously, radiation may contribute to the loss of entropy from a warm surface or a body. In practice, we often include the effects of radiation in a combined expression for the transfer at the surface of the solid interface. So, we should actually speak of a *convective-radiative transfer layer*.

Naturally, we expect a similar convective layer on the outside surface of the wall. Again, there is a temperature drop in the direction of the transfer. In summary, we can say that the temperature drops in several steps through a composite interface. There are several layers in series through which heat flows. And if we take into consideration different walls and windows simultaneously, we say that these are arranged in parallel. This sounds very much like the situation we might encounter in an electric circuit with conductive elements (resistors) combined in series and in parallel. Indeed, a particular layer in a heat transfer interface may be considered a *thermal resistor* (Fig. 4.44).

4.6.2   An Example of a Dynamical Model

As we have already seen in Section 4.2, combining this simple expression of an entropy current through a series of layers with the relation of entropy and temperature of a body, and the entropy balance for that body, leads to useful dynamical models for the cooling or heating of uniform bodies (Fig. 4.46). Here, I am going to add the details of entropy flow and storage discussed in this and the previous section to the model created in Fig. 4.16, and I will apply it to the examples of cooling and heating of a single body of water already discussed in Fig. 4.4 and in Section 4.2.

Figure 4.46: Left: SD model diagram of the cooling (or heating) of a uniform body at temperature *T*. Right: Application to the heating of cold water in a drinking bottle. The water is stirred, the aluminum bottle is inside an insulating bag. The simulation result (solid line) is barely visible since it fits measured water temperatures (dots) almost perfectly.
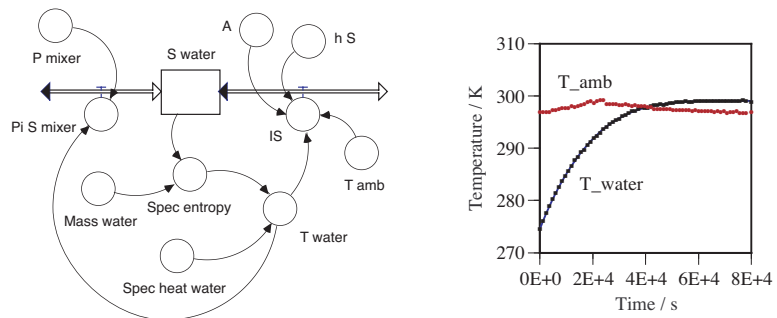
Take the concrete case of cold water in a drinking bottle sitting in a warm room. The water is stirred continuously. As always, we start with considering the balance of the relevant fluidlike quantity. Here it is the balance of entropy of the uniform body of water. Since there is a temperature difference between water and environment, entropy will flow; and since the water is stirred, there will be entropy produced inside the bottle. In summary, we have

$$\frac{dS_w}{dt} = I_S + \Pi_S \tag{4.49}$$

We need three constitutive laws to complete the model: (1) An expression for the re-

lation between entropy and temperature of the system (body of water), (2) a relation for the entropy current expressed in terms of the temperature difference between inside and outside, and (3) the expression that relates entropy production and dissipation rate:

$$
\begin{aligned}
T &= T_{ref} \exp(s/c) \\
I_S &= -A h_S (T - T_a) \\
\Pi_S &= \mathcal{P}_{diss}/T
\end{aligned}
\qquad \textbf{(4.50)}
$$

The first relation derives from Equ.(4.42) with T_{ref} = 273 K and s_{ref} = 0 Ct/kg. The second was just introduced. For a specific case of the third relation, let me assume a process at constant mechanical (stirring) power. T_a is taken from experimental data reported in Fig. 4.46. The law of balance and the constitutive relations have been implemented in the system dynamics model in the same figure (Fig. 4.46, left). Simulation of the model and comparison with measured water temperatures lead to $\mathcal{P}_{diss}$ = 0.28 W and h_S = 0.0145 W/(K^{2}m^2).

The exactly same model can be applied to the case of cooling of hot water in an uninsulated aluminum can (see also Section 4.2). In contrast to the slightly simplified model in Fig. 4.16, this one delivers even better results; there is virtually no difference between measured water temperatures and a simulation if we use $\mathcal{P}_{diss}$ = 1.7 W, h_S = 0.023 W/(K^{2}m^2).

The difference between the entropy transfer coefficients is a consequence of the insulation used in the case of the cold water in the drinking bottle. In Chapter 7, we will study how to use the results of overall transfer coefficients and theory regarding different types of heat transfer through different layers to obtain material properties such as entropy conductivities or convective transfer coefficients. At this point it suffices to say that we understand why the overall entropy transfer coefficient of the case of the drinking bottle is smaller than that of the uninsulated can: In the former case, there is an additional layer for entropy to cross, so the flow will be smaller for the same temperature difference.

According to Equ.(4.47), the heat transfer coefficient is related to the entropy transfer coefficient by the temperature of the water. If we use an average value, we obtain h = 7.6 W/(K·m^2) for the case of the polished aluminum can. This value must represent the heat transfer from the surface of the can to the outside since transfer from water to metal and through the thin metal are much more efficient than transfer through the surface air layer. (When there are a few efficient layers and one bad one, the latter dominates the value of the entropy or heat transfer coefficients.) When we look in tables we find values of 12 – 14 W/(K·m^2) for heat transfer coefficients from surfaces to (still) air. The one measured in our experiment is considerably smaller. The reason for this will become clear in Chapter 7: In most situations, radiation from a surface adds to entropy transfer due to the direct contact of surface and air, making the transfer coefficient larger. The polished aluminum surface, however, is like a mirror which is a poor emitter for thermal radiation (Chapter 7).

An analytic model. The simplest models of cooling of bodies making use of particular material properties lead to an exponentially decreasing temperature. This happens, for example, in the case of a hot fluid in a can having constant values of entropy capacitance and entropy transfer coefficient, or in a model using constant energy related values (temperature coefficient of energy and heat transfer coefficient). In the

latter case, the model equations are

$$\frac{dS}{dt} = I_S \quad , \quad S(t = 0) = S_0$$
$$\frac{dS}{dt} = K\frac{dT}{dt} = \frac{C}{T}\frac{dT}{dt}$$
$$I_S = -A\frac{h}{T}(T - T_a)$$

with constant C and h. The second and third equations are inserted into the law of balance of entropy to yield

$$\frac{C}{T}\frac{dT}{dt} = -A\frac{h}{T}(T - T_a)$$
$$\frac{dT}{dt} = -\frac{Ah}{C}(T - T_a) \quad , \quad T(t = 0) = T_0$$

The solution of this differential equation with its initial condition is

$$T(t) = T_a + (T_0 - T_a)\exp(-t/\tau)$$
$$\tau = C/(Ah)$$

(4.51)

τ is the time constant of this system, and Ah may be considered a thermal resistance. This behavior is analogous to what we know from simple RC systems in fluids, electricity, or mechanics.

4.6.3 Uniform Bodies in Thermal Contact

Imagine two bodies of different temperatures in thermal contact. Entropy flows from the hotter to the colder, and temperatures equilibrate (Fig. 4.1). However, this is not the entire story. When entropy flows from a hotter to a colder body, more entropy is produced; this means that the entropy current increases in the direction of flow.

In common language, we would say that heat is produced when heat flows. The phenomenon is not as obvious as the production of heat in a fire or as a consequence of mechanical friction, but the conclusion is unavoidable. We can list many reasons that should convince us of the irreversibility of entropy transfer through a series of layers between bodies at different temperatures. For one, conduction of entropy is analogous to conduction of charge or momentum which are entropy producing processes. A thermal conductor is a *thermal resistor* just as an electric conductor has resistive properties. Secondly, real heat engines are not nearly as efficient as the formula for ideal ones would indicate. Their irreversibility is mostly due to heat transfer through the heat exchangers between furnace and working fluid, and fluid and cooler (mechanical and other operations in classical heat engines can be designed relatively close to ideal conditions).

Lost power in thermal conduction. The most convincing argument may be this. In the conduction of entropy through a thermally resistive material, energy is released as a consequence of the fall of entropy. There is thermal power accompanying the phenomenon (Fig. 4.47)—this is equal to the power of an ideal Carnot engine driven by the fall of entropy from T_1 to T_2. Energy released can drive another process. In a sim-

ple conductor that cannot undergo any other process (chemical, electrical, mechanical, etc.), the energy made available is completely dissipated—it is used to produce entropy. In the language of Section 4.4.3, we can speak of lost power:

$$\mathcal{L} = (T_1 - T_2)I_{S1}$$

On the other hand, the lost power is proportional to the entropy production rate and the temperature at which the entropy is emitted (here, this is T_2, see Fig. 4.47 and Equ.(4.32)):

$$\mathcal{L} = T_2 \Pi_S$$

Combining these expressions for lost power leads to

$$\Pi_S = \frac{1}{T_2}(T_1 - T_2)I_{S1} \tag{4.52}$$

Figure 4.47: Entropy transfer due to a drop in temperature is dissipative: Entropy is produced as it flows.

Alternatively, this relation can be derived by combining the expressions for the balance of entropy and energy, and relations between energy and entropy currents. Note that the energy current passing through a series of transfer layers is constant in steady-state.

Entropy is always produced if entropy flows from a hotter to a colder place without driving another process. This effect has to be taken into account in dynamical models involving more than one body, i.e., as soon as we have two or more bodies in thermal contact whose thermal processes we want to understand.

Dynamical models of thermal capacitors and resistors. There appears to be an insurmountable obstacle to constructing simple dynamical models of entropy transfer between bodies at different temperatures. At least it seems that we cannot simply apply what we have already done, namely create models of spatially uniform dynamical systems. When entropy flows through bodies—specifically through solids—temperature changes from point to point, and so do the entropy currents. We will solve this problem later by producing continuum models (Chapter 13).

However, there is a simpler solution which combines ideas already used. Imagine two bodies of water which can be stirred to ensure homogeneous conditions. These bodies are separated by a solid wall through which entropy can flow. This system suggests a simple model: there are two spatially uniform bodies that store entropy and since they are supposed to be homogenous, let entropy pass easily. We have discussed this idea already: We may speak of thermal superconductors that store entropy—they are ideal *thermal capacitors*. These capacitors are joined by a thermal resistive element that conducts entropy as a consequence of a temperature difference but does not store entropy: The wall is a *thermal resistor*. A process diagram of this system is easily drawn; it explains in graphical terms what is meant by the model of uniform dynamical systems in thermal contact (Fig. 4.48). As the temperatures of the bodies of water equilibrate, this simple aggregate dynamical model produces the same amount of entropy as that calculated from the changes of state alone (see Example 4.17). Only, here we are able to follow the temperatures of the thermal capacitors in the course of time.

A possible representation of entropy production due to entropy transfer in a system dynamics model is shown in Fig. 4.49. The storage element in the middle is a symbol for the entropy of the transfer layer between the bodies. Since the transfer layer is a resis-
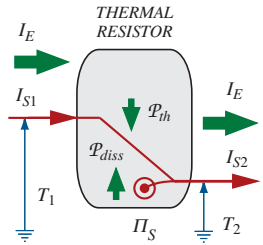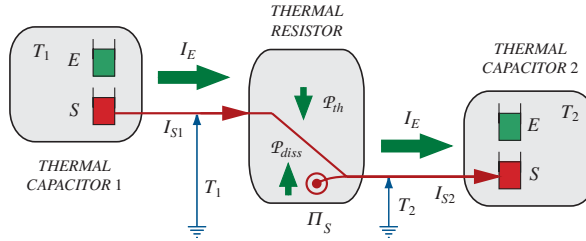
tor, it does not store entropy. Therefore, the flow out of this element equals the sum of the flow into and the entropy production rate in the element:

$$I_{S2} = I_{S1} + \Pi_S \tag{4.53}$$

Figure 4.48: Model of two spatially uniform bodies in thermal contact. Processes in these bodies are assumed to be reversible. Irreversibility originates in the interface between the bodies.

This is equivalent to the junction rule known from electric or hydraulic circuits. If the model in Fig. 4.49 is applied to the equilibration of temperatures of two bodies of water that are perfectly insulated from the environment, we obtain very good results. If we were to neglect entropy production due to heat transfer, the computed final temperature would be noticeably too low.

Figure 4.49: SD model diagram of heat transfer between two bodies. The transfer is dissipative. The central storage element serves as a node for the relation between entropy currents and entropy production rate.
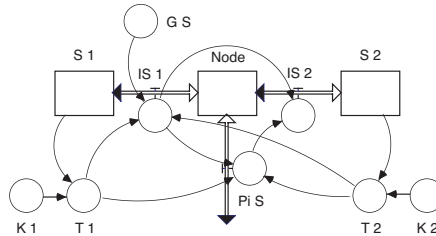
4.6.4 Thermal Conductances for Composite Interfaces

The entropy conductance G_S is the factor describing entropy transfer through layers (Equ.(4.44)). An interface between two bodies in thermal contact may be thought of as a combination of conductors in series and in parallel (Fig. 4.50). If the conductances are independent of temperature, there are simple rules for combining them. In the case of two parallel layers between the same temperature difference, the combined conductance is

$$G_S = G_{S1} + G_{S2} \tag{4.54}$$

Figure 4.50: Parallel (top) and series (bottom) transfer layers.

This is what we already know from electricity. The case of series connections is a little different because of the production of entropy in the elements (Fig. 4.50, bottom). With the relations used in this section and with a little algebra, we arrive at:

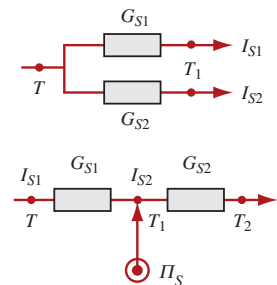$$\frac{1}{G_S} = \frac{1}{G_{S1}} + \frac{T}{T_1}\frac{1}{G_{S2}} \tag{4.55}$$

The factor T/T_1 is different from the corresponding relation that applies to electric circuits; the difference is to be found in the fact that electric charge is conserved whereas entropy is not.

We could also write combinations of thermal (energy) conductances. Again, if they are independent of temperature, a relation analogous to Equ.(4.54) holds for parallel layers. The relation for layers stacked in series is simpler than Equ.(4.55); in fact, it takes the same form as in electricity, since the energy is conserved in its transit through transfer layers:

$$\frac{1}{G_E} = \frac{1}{G_{E1}} + \frac{1}{G_{E2}} \qquad (4.56)$$

It is not possible for entropy conductances and energy conductances to be both independent of temperature. In real life, neither quantity will be constant. Still, either one of the assumptions—constant G_S or constant G_E—will suffice for many applications. Finding the one that delivers better results is a matter of trying them out.

QUESTIONS

52. What observations suggest that entropy currents through a heat transfer layer might be proportional to the temperature difference across the layer?

53. Why is heat transfer an entropy producing process?

54. Entropy flows through a layer from 600 K on the hot side to 300 K on the cold side. By what fraction does the entropy current increase?

55. Why does Equ.(4.53) apply to an entropy junction (node)?

56. For a given entropy current through a temperature difference, does the rate of entropy production only depend upon the temperature difference or does it matter at what level the temperatures actually are?

57. Why is the relation for combining conductances for transfer layers in series different from the form known to apply to electric circuits?

EXAMPLE 4.18. Response of a temperature probe to changing environments.

A temperature sensor is in air at room temperature. It is suddenly put into hot water. After the temperature reading has stabilized, it is taken out of the water, dried, and left lying in air at room temperature (data of process is shown in the diagrams of Fig. Ex.18.1; an enlargements of the initial rise is seen in the diagram on the right).
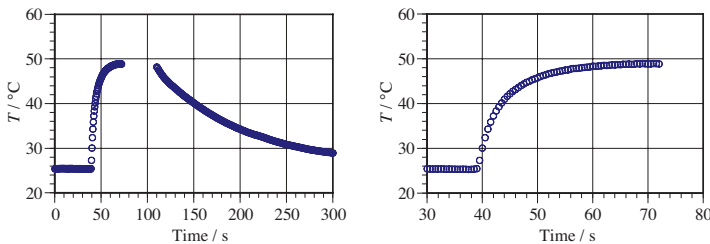

Figure Ex.18.1

(a) Determine the time constant by hand (without transforming the graph) for the temperature sensor in water. How could you do this most easily? What is the time constant? (b) Create a graph from the temperature data for the equilibration in air (after 120 s) in which the temperature might most likely be a linear function. Use this diagram to determine the time constant of the thermometer in air. What is the value of this time constant? (c) Assume the heat transfer coefficient from the thermometer (steel) to air to be about 14 W/(K·m²). How large is the heat transfer coefficient from water to the thermometer? (d) The thermometer is taken from the kitchen at 20°C and placed into an oven at 180°C for 1.5 minutes. Then it is placed in the kitchen again. Sketch the expected behavior of the temperature reading as a function of time (use numerical values where necessary and possible).

SOLUTION: (a) The time constant corresponds to the time it takes for the temperature to rise to 63% of the initial temperature difference. This difference is 49°C − 25.5°C = 23.5 K. 63% of this is 15 K. Therefore, after one time constant, a temperature of 25.5°C + 15°C = 40.5°C should be reached. We can simply count the points in the diagram in Fig. Ex.18.1 (right). After about 10 data points, the temperature is a little above 40°C. Therefore, the estimate of the time constant for the thermometer in water is 5.0 s.

Figure Ex.18.2
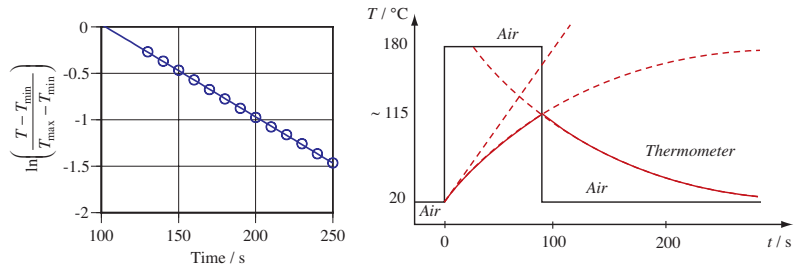
(b) We prepare a graph for the decreasing temperature with a logarithmic scale for the temperature. This can be done by using the (relative) difference of the temperature of the thermometer and the surrounding air:

$$y = \ln\left(\frac{T - T_{min}}{T_{max} - T_{min}}\right)$$

We expect $T(t)$ to be an exponentially decaying function:

$$T = T_{min} + \left(T_{max} - T_{min}\right)\exp\left(-(t - 100)/\tau\right) \quad \Rightarrow \quad \ln\left(\frac{T - T_{min}}{T_{max} - T_{min}}\right) = -\frac{t - 100}{\tau}$$

The slope of the logarithmic relation in Fig. Ex.18.2 is 0.010 s⁻¹, so $\tau = 100$ s.

(c) If we take as the dynamical model of the thermometer a uniform body having a certain entropy resistance from its surface to the environment, and having a certain entropy capacitance, the time constant of the system must then be

$$\tau = R_S K$$

Since K is the same for both phases of the process, the entropy resistance from water to thermometer must be 100/5.0 = 20 times smaller than that for air to thermometer. Therefore, the conductance must be 20 times larger. This applies to the energy conductance as well, or to the energy transfer coefficient. Therefore, $h = 20 \cdot 14$ W/(K·m²) = 280 W/(K·m²) for the transition from thermometer to air.

(d) For the dynamics of the thermometer, the behavior in air is required. The thermometer reacts to a sudden temperature change with a time constant of 100 s. Therefore we should have a response like the one constructed in the diagram on the right of Fig. Ex.18.2.

EXAMPLE 4.19. Heating a home and estimating entropy production in heat transfer.

Consider a home having a thermal conductance of 300 W/K to be heated in winter. In steady state, temperatures are 20°C and 0°C on the inside and the outside, respectively. (a) Estimate the entropy conductance of the home and the entropy current leaving the home. (b) If the radiators supplying the entropy are to have a surface temperature not exceeding 60°C, what must their surface area be? (The heat transfer coefficient from their surfaces to the air in the rooms is 14 W/(K·m²). (c) What is the relative error made in calculating entropy currents (from the radiators to the rooms, from the rooms to the outside environment) if entropy production due to transfer is neglected?

SOLUTION: (a) Entropy conductance and thermal (energy) conductance are directly related by temperature. If we take the temperature of the inside of the home, we have

$$G_S = \frac{1}{T_i} G_E = \frac{1}{293} 300 \frac{W}{K^2} \approx 1 \frac{W}{K^2}$$

This leads to an entropy current of

$$I_S = G_S(T_i - T_a) = 1 \cdot 20 \frac{W}{K} = 20 \frac{W}{K}$$

leaving the inside of the home. The associated energy current is roughly equal to 300 K · 20 W/K = 6000 W.

(b) According to Equ.(4.45), the entropy current from the radiators into the rooms is related to the temperature difference between radiators and rooms, the entropy transfer coefficient, and the surface area through which the current enters the space inside the home. If we assume the entropy current leaving the home to be equal to the one coming from the radiators, we have:

$$I_S = A h_S(T_r - T_i) \quad \Rightarrow \quad A = \frac{I_S}{h_S(T_r - T_i)} = \frac{I_S}{h/T_r(T_r - T_i)} = \frac{20 \cdot (273 + 60)}{14 \cdot (60 - 20)} \, m^2 = 12 \, m^2$$

(c) First, take the case of radiators and rooms. The entropy current entering the room is greater than the one leaving the radiators by the entropy production rate. The relative value of the error is

$$\frac{\Pi_S}{I_S} = \frac{T_r - T_i}{T_i} \approx \frac{40}{300} \approx 0.13$$

(see Equ.(4.52); this means that we have overestimated the surface area of the radiators in (b) by about 10%). The corresponding relative error for entropy transfer from the home to the environment is 0.07.

EXAMPLE 4.20. Conductors in series.

Very cold water is filled into an insulated aluminum bottle which is then sealed. The bottle is allowed to stand in a warm room for about one day. The water is constantly stirred by a magnetic stirrer. In the diagram (Fig. Ex.19) one sees the temperatures of both the water and the environment.

Use the experimental results to estimate the missing parameters of a model of the processes undergone by the water (power of the stirrer and overall entropy transfer coefficient). Use this to estimate the entropy transfer coefficient of the insulation.

Information: Height of the container: 15 cm, inner radius: 3.5 cm, thickness of the aluminum: very thin, thickness of the insulation: 6 mm. The lid and the bottom are perfectly insulated. The

inner heat transfer coefficient from the water to the container is very high. The outer one from the insulation to the air is 12 W/(K·m²). Treat the insulation as a flat layer.

Figure Ex.19
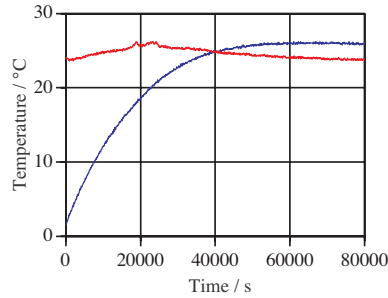
SOLUTION: The law of balance of entropy of the body of water includes the transfer of entropy from the environment and the entropy production rate:

$$\dot{S} = I_S + \Pi_S$$

The rate of change of entropy can be related to the rate of change of the temperature of the body of water:

$$\dot{S} = K\dot{T}$$

The entropy capacitance can be calculated from the specific entropy capacitance and the mass of the body of water which is equal to $0.15 \cdot \pi \cdot 0.035^2 \cdot 1000$ kg = 0.58 kg. Therefore, we find K = $14 \cdot 0.58$ J/K² = 8.1 J/K².

Entropy current and entropy production rate are expressed by

$$I_S = G_{S,total}(T_a - T) \quad , \quad \Pi_S = \mathcal{P}_{mech}/T$$

If we take two pieces of data from the experiment, the missing parameters can be determined. A first one can be obtained from conditions at $t = 0$ s:

$$K\dot{T} = G_{S,total}(T_a - T) + \mathcal{P}_{mech}/T$$
$$8.1 \cdot 1.38 \cdot 10^{-3} = G_{S,total}(24 - 2) + \mathcal{P}_{mech}/275$$

The rate of change of temperature at $t = 0$ s can be estimated graphically, and so can the relevant temperatures. For large times around 80,000 s we have

$$0 = G_{S,total}(T_a - T) + \mathcal{P}_{mech}/T$$
$$0 = G_{S,total}(26 - 23.8) + \mathcal{P}_{mech}/299$$

For steady-state, the rate of change of entropy equals zero. Temperatures have again to be taken from the experimental results. Now there are two linear equations for G and $\mathcal{P}$ which turn out to be equal to $4.6 \cdot 10^{-4}$ W/K² and 0.30 W, respectively. The entropy transfer coefficient turns out to be equal to $4.6 \cdot 10^{-4}$ W/K² / $(2\pi \cdot 0.035 \cdot 0.15)$ m² = 0.014 W/(K²·m²) (compare these results to the ones obtained from the dynamical model in Section 4.6.2).

The entropy transfer coefficient for the insulation alone is obtained as follows. Since the temperatures involved are not very different, we can simply add the inverse values of the conductances to obtain the inverse of the total conductance (Equ.(4.55)). Since the surface is (nearly) the same everywhere, this also holds for entropy transfer coefficients. Therefore, 1/0.014 = 1/G_S + 1/(14/295), or G_S = 0.020 W/(K²·m²).

EXAMPLE 4.21. Laws of balance of entropy in a model of equilibration.

Consider the experiment shown in Fig. 4.1. A copper block is submerged in water which is inside a jar made of glass. The jar is insulated from the environment, but the insulation is not perfect. Formulate all relevant laws of balance of entropy for a dynamical model of this system. Treat glass, water, and copper as three uniform bodies.

SOLUTION: There are three entropy storage elements (copper: c, water: w, glass: g) and two entropy transfer interfaces (between c and w, and w and g, respectively). The entropy transfer layers between glass and environment need not be included in the model. Combining these assumptions leads to a model diagram of the form shown in Fig. Ex.21.
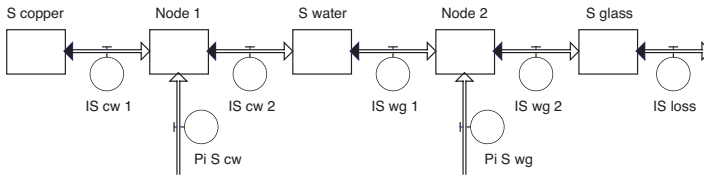
Figure Ex.21

The laws of balance of entropy for the storage elements are:

$$\frac{dS_c}{dt} = -I_{S,cw1}$$

$$\frac{dS_w}{dt} = I_{S,cw2} - I_{S,wg1}$$

$$\frac{dS_g}{dt} = I_{S,wg2} - I_{S,loss}$$

For the transfer layers they take the form of junction rules (Equ.(4.53)):

$$I_{S,cw2} = I_{S,cw1} + \Pi_{S,cw}$$

$$I_{S,wg2} = I_{S,wg1} + \Pi_{S,wg}$$

Note that laws of balance do not include constitutive information concerning flows etc.

4.7 THERMAL ENGINES AND HEAT TRANSFER

Thermal engines in general, and heat engines in particular, do not work reversibly. There are many reasons for concrete irreversibilities, i.e., for entropy production. If we disregard the origin of the entropy that drives the engine, the most important entropy producing processes are friction and heat transfer, and among these heat transfer dominates in a typical heat engine.

In this section, a simple model of a Carnot engine with heat transfers through sizeable temperature differences will be created. This prepares the ground for an interesting idea we will take up again in detail in Chapter 9, namely that processes should be designed in such a way that they minimize entropy production. Since entropy production in an engine means loss, this idea is certainly not farfetched. Then, thermoelectric devices will be modeled. We have advanced to a point in the theory of dynamical thermal processes where we can discuss in a rather simple manner a phenomenon that is commonly considered difficult to understand and model.

4.7.1 A Carnot Engine Between Heat Exchangers

The central part of a heat engine—the working fluid—operates by lowering entropy from a high to a low temperature. As we will see, the entropy transfer to and from this part of the engine is the source of the greatest irreversibility. Let us consider a Carnot engine, i.e., a device that receives entropy at *constant* high temperature T_{1E} (Fig. 4.51) and gives it up at *constant* low temperature T_{2E} (the index E denotes the actual engine). The lowering of the temperature of the working fluid—and therefore the lowering of the entropy from T_{1E} to T_{2E}—is the result of expansion of the gas in the engine. If we assume, as is fairly reasonable, that the mechanical operations in the engine are reversible, the core of the thermal system operates reversibly.

Figure 4.51: Process diagram of a reversible engine sandwiched between two heat exchangers. The heat exchangers make it possible for entropy to be transferred at finite rates, but they cause entropy production and loss of power.
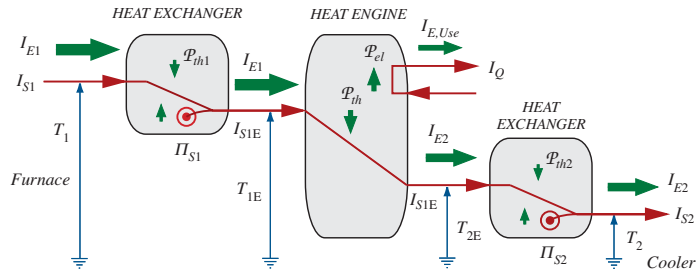
Now we have to take a close look at how entropy enters and leaves the reversible engine. Clearly, entropy comes from the furnace and goes to the cooler (Fig. 4.51). If we want heat transfer to happen in finite time, there need to be temperature differences across the heat exchangers that facilitate the flow of entropy to and from the engine. A zero temperature difference—which would be ideal for the engine so it could utilize the entire temperature range from T_1 to T_2 (Fig. 4.51)—leads to entropy currents that are zero. Completely perfect engines would simply not run.

If there are temperature differences that allow the engine to run at realistic speeds, there will necessarily be entropy production and, in the end, loss of power. This loss can be quantified by adding the entropy production rates in the heat exchangers and multiplying this sum by the lowest temperature of the system:

$$\mathcal{L} = T_2 \left(\Pi_{S1} + \Pi_{S2} \right) \tag{4.57}$$

Heat exchangers. The process diagram in Fig. 4.51 demonstrates, in a strongly simplified manner, how we can understand the function of actual heat exchangers. According to this model, they are nothing but a heat transfer interface between two bodies at different temperatures. Entropy flows through them, which causes more entropy to be produced. The transfer rate (current) depends upon the temperature difference across the exchanger and the heat transfer properties quantified by the entropy conductance of the device. The theory of heat exchangers according to this model is contained in the equations presented in Section 4.6. If we combine this theory with what we know about reversible engines, the model in Fig. 4.51 can be quantified.

An optimal endoreversible engine. As mentioned above, the main contribution of entropy production stems from heat transfer which takes place during heating and cooling of the working fluid. To effect this heating and cooling, heat exchangers are

added between the furnace and the fluid, and between the fluid and the cooler. In the simplest model of this kind, the fluid is assumed to operate reversibly. All irreversibilities take place in the heat exchangers (Fig. 4.51). Such a model engine is called *endoreversible*.

With T_1, T_2, and I_{S1} held fixed, the model can be optimized (see Chapter 9) by determining the condition of minimal entropy production rate (which coincides with maximum useful energy current). This leads to the so-called Curzon-Ahlborn efficiency:[27]

$$\eta_{I,CA} = 1 - \sqrt{T_2/T_1} \tag{4.58}$$

This is a much more realistic estimate of the actual efficiency than the Carnot efficiency derived in Equ.(4.27). It will be derived in Chapter 9, together with several other interesting applications of the concept of minimization of entropy production. To see how well it works, take the example of a large nuclear power plant. Data shows a thermal (first law) efficiency of 30% with upper and lower temperatures for the system of 300°C and 30°C. The Curzon-Ahlborn estimate yields a value of 28%. Compare this to a value of 47% obtained from Carnot's formula.

4.7.2 Thermoelectric Generators and Coolers

Thermoelectricity provides a beautiful example of thermal engines coupled with entropy transfer. The theory of thermoelectric effects is commonly considered an advanced topic, but you will see that we already know enough to produce a dynamical model of thermoelectric devices. It will provide an understanding of the overall function of a complete device without regard to material details of the processes (a brief description of the structure of thermocouples is given in Section 4.7.3). A more detailed study of thermoelectricity will be undertaken in Chapter 13.

Observations. Two observations regarding thermoelectricity let us understand the basic aspects of the phenomenon. First, if we place a thermoelectric device—a Peltier device as in Fig. 4.11—between two bodies at different temperatures, it operates as an electric generator that can drive an engine. Temperature differences produce a voltage (an open circuit voltage, if we do not connect a load). Observation shows that the open circuit voltage—the thermoelectric voltage U_{TE}—grows in proportion to the temperature difference across the device:

$$U_{TE} = \varepsilon(T_2 - T_1) \tag{4.59}$$

The coupling factor ε in this relation is called the *Seebeck coefficient*. U_{TE} can be viewed as the "electromotive force" as in a battery. In this case, chemical reactions are responsible for this voltage. Here, the temperature difference causes a conductive flow of entropy through the device from hot to cold which somehow must lead to an electric

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27. The type of heat engine called *endoreversible* was first proposed and analyzed by Curzon and Ahlborn (1975). They calculated the power of the engine and determined the condition for its maximum. The efficiency at maximum power, Equ.(4.58), has since been called the Curzon-Ahlborn efficiency. A simpler derivation was given by DeVos (1985). The problem was later investigated from the point of view of the minimization of the production of entropy (Salamon et al., 1980; Andresen et al., 1984).
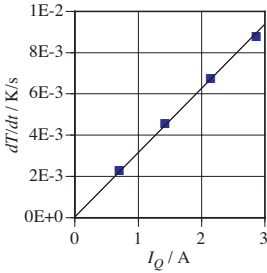
effect. This suggests that the thermoelectric effect is the result of a coupling of transports of entropy and of charge: As entropy flows through the device, charge is swept along leading to an electric field and a voltage. When the circuit is open, the flow of charge will stop and a certain voltage will have been established; this is U_{TE}. Remember that the voltage measured at the terminals will be different from the open circuit voltage if charge flows through the generator (see Equ.(4.63) further below).

The second observation confirms this basic idea. We can operate the Peltier device as a heat pump by driving it electrically. This means that we force an electric current through the element that leads to a flow of entropy in the direction opposite to its spontaneous flow. In other words, entropy is pumped. Consider the special case of starting the pumping of entropy when the temperature difference across the device is zero—so there is no conductive entropy current from hot to cold. Experiments show that the entropy current coupled to the charge current ($I_{S,TE}$) grows proportionally to the flow of charge (Fig. 4.52):

$$I_{S,TE} = \alpha I_Q \tag{4.60}$$

The coupling factor α is called the *Peltier coefficient*. It turns out that Seebeck and Peltier coefficients must be equal:

$$\alpha = \varepsilon \tag{4.61}$$

If they were not equal, the energy principle for the thermoelectric processes taking place would be violated. The validity of this statement will be demonstrated further below when we take a look at the power of thermoelectric devices.

Seebeck and Peltier coefficients can be positive or negative. The sign depends upon the sign of the charge being swept along with entropy through the conductor.

Dynamical model of a Peltier device. The observations discussed above concern the "pure" effects: thermoelectric voltage at zero electric current, and entropy pumped at zero temperature difference. In general, the special conditions will not hold and we have to deal with the conductive effects of the flows of entropy and charge as well. To understand this better, let us construct the simple dynamical model I have been mentioning. The starting point is the simple observation that under general conditions, a Peltier device looks like a panel having a hot and a cold side. At the same time, it has a side that is at high electric potential and one that is at lower potential. This suggests the following model. The device consists of two entropy storage elements (for the cold side and the hot side, respectively; entropy stored in bodies makes them warm), and two electric capacitors (for the high potential and the low potential, respectively; the charge of a capacitor leads to its electric potential).

A graphical representation of these ideas is presented in Fig. 4.53. Between the electric capacitors we have an electric generator responsible for U_{TE} and resistor for the conductive transport of charge—just like in a battery. Between the thermal capacitors there is a thermal resistor for the conductive flow of entropy from hot to cold. The coupled flows of entropy and charge that are responsible for the thermoelectric effect are like a bypass to this thermal resistor. There is a non-dissipative transport of entropy that is directly coupled to the electric current.

This model lets us construct the general equations for entropy transport through and voltage across the thermoelectric device. If there is no conductive transport of entropy, i.e., if the temperature difference across the Peltier device is equal to zero, there is only

Figure 4.52: Rate of change of temperature of the cold body of water shown in Fig. 4.8, as a function of the electric current through the Peltier device for $\Delta T = 0$ K. The rate of change of temperature is proportional to the entropy current withdrawn from the body of water.

a single entropy current, namely, the one given in Equ.(4.60). In general, however, the current of entropy is the sum of thermoelectric and conductive currents:

$$I_S = \alpha I_Q - G_S(T_2 - T_1) \tag{4.62}$$

G_S is the entropy conductance of the device. The thermoelectric voltage in Equ.(4.59), on the other hand, is the only electric potential difference between the electric capacitors if there is no flow of charge in the electric circuit. This is the case for open circuit conditions. Otherwise, the potential difference is the sum of thermoelectric and resistive parts:

$$U = \varepsilon(T_2 - T_1) + R_i I_Q \tag{4.63}$$

(This equation is analogous to what we have in the case of a battery having an internal resistance R_i. Note that a voltage is a negative electric potential difference.) The last two equations are the integral forms of the usual partial differential equation representation of thermoelectric processes (see Chapter 16).
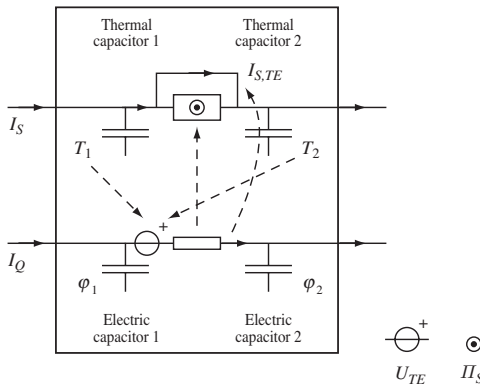
Figure 4.53: A dynamical model of a thermoelectric device. There are two storage elements for entropy (defining the temperatures of the cold and the hot end, respectively), and two capacitors (they define the high and low electric potentials). The elements comprise an electric generator ("electromotive force"), a coupled flow of charge and entropy, and conductive entropy and charge currents.

Naturally, we have to add relations for the irreversible effects of conductive transports of entropy and of charge as well as laws of balance of entropy and charge for the capacitors in the model of Fig. 4.53. The former lead to

$$\Pi_S = \frac{1}{T_2}\left(G_S(T_2 - T_1)^2 + R_i I_Q^2\right) \tag{4.64}$$

whereas the latter are best visualized in a complete system dynamics model diagram of a thermoelectric device. Fig. 4.54 provides an overview of the approach to thermoelectricity discussed here. Note the analogy between the structure of reservoirs and flows in the SD diagram and the capacitors and flows symbolized in Fig. 4.53.

Application of the dynamical model. The model presented in Fig. 4.54 is for a Peltier device such as the one pumping entropy from one body of water to another (see Fig. 4.8). To make use of the model it has to be completed by the dynamics of the bodies of water, entropy transfer to and from the device, entropy transfer to and from the environment, and data concerning the electric power supply used for driving the Pelt-

ier heat pump. Entropy transfer from water to the device is modeled according to what we have discussed above in Section 4.6.3 (see Fig. 4.49). There is also an entropy transfer "bypass" from the hotter to the colder fluid between the Peltier device and a lid on the double chambers of the container in Fig. 4.8. The parameters determining the thermal behavior of the tank in its environment can be obtained by an experiment that investigates the passive phenomena (thermoelectric device turned off) if we simply fill hot and cold water into the chambers and close the tank with a lid.

Figure 4.54: Diagram of a system dynamics model of a thermoelectric device. The structure of the model is depicted in Fig. 4.53. Note the representations of the four storage elements, two for entropy (hot and cold sides of the device) and two for electric charge (high and low electric potentials). There is a node taking the entropy production (Fig. 4.49) resulting from the conduction of entropy and charge. PC: Peltier coefficient, SC: Seebeck coefficient. R_S: entropy flow resistance; R_i: electric internal resistance. U_PE: terminal voltage of the device; U_TE: thermoelectric emf (Equ.(4.59)). IS_TE: nondissipative entropy current coupled to electric current (Equ.(4.60)). R_ext: Resistance of external electric circuit. U_B: voltage of external power supply (in pumping mode).
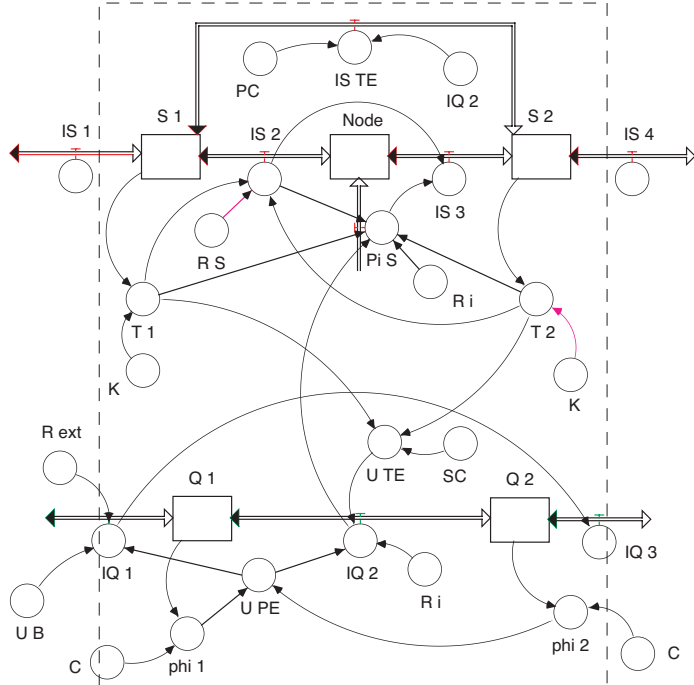
It does not make much sense to present data and simulation[28] together since agreement between the two is so close that the difference cannot be seen very well in a graph such as the one showing cooling of a body of water in Fig. 4.8.

Energy in thermoelectric processes. So far we have been able to analyze a thermoelectric device without recourse to energy considerations. We can hope to gain additional insight by appealing to the energy principle. Indeed, we will be able to derive the statement of the equality of the thermoelectric coupling coefficients (Seebeck and Peltier coefficients, see Equ.(4.61); this is called a reciprocity relation).

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28. There is an important numerical problem to consider when one attempts to perform a simulation of the model in Fig. 4.54. Realistic estimates of entropy and charge capacitances yield values that are many orders of magnitude apart (the electric capacitances are exceedingly small). This leads to stiff differential equations that can be solved successfully (and accurately) with dedicated numerical methods but not with standard explicit codes.

To be specific, consider a Peltier device in generator mode (Fig. 4.55). It is operated between temperatures T_1 and T_2. Entropy production due to transfer to and from the device is assumed to be external to the system being analyzed, and the production of entropy due to electric conduction has been drawn separately to clarify the role of U_{TE} as the direct result of the thermoelectric effect. Entropy flows through the device as a consequence of the driving temperature difference. Now we must distinguish between two components of this entropy flux: the conductive current $I_{S,c}$ and the thermoelectric current $I_{S,TE}$; the latter is coupled to the current of electric charge according to Equ.(4.60). The conductive current is purely dissipative, the energy released due to its fall from T_1 to T_2 is used to produce entropy. This is different for $I_{S,TE}$, its fall is non-dissipative, the energy released is used to drive the electric current through the potential difference U_{TE}.

Figure 4.55: Process diagram of a thermoelectric generator. The electric (internal) resistor has been drawn separately to make the role of U_{TE} clear (note that $I_{E,el} < \mathcal{P}_{el,TE}$). $\mathcal{P}_{th(c)}$ is the power of the conductive current of entropy, $\mathcal{P}_{th,TE}$ is associated with the entropy current that is coupled to the flux of charge.

Equality of Peltier and Seebeck coefficients. This concludes the conceptualization of the role of energy in a thermoelectric process. We can now turn to a simple proof that the thermoelectric coupling coefficients α and ε should be equal. The thermal and electric thermoelectric powers are expressed by

$$\mathcal{P}_{th,TE} = (T_1 - T_2)I_{S,TE}$$
$$\mathcal{P}_{el,TE} = U_{TE}I_Q$$

Since these expressions are equal, and since Equ.(4.59) and Equ.(4.60) hold for U_{TE} and $I_{S,TE}$, respectively, we have

$$(T_1 - T_2)I_{S,TE} = U_{TE}I_Q$$
$$(T_1 - T_2)\alpha I_Q = \varepsilon(T_1 - T_2)I_Q$$

which proves the assertion that the Peltier and Seebeck coefficients must be equal.[29]

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29. This is an example of what is called Onsager's reciprocity relations for "phenomenological" coefficients in coupled transports (such as thermo-diffusion and thermoelectricity). It is commonly assumed that the Onsager relations have to be proved by microscopic argument; see Jou et al. (1996), Woods (1975, Chapter 7). Thomson's (Lord Kelvin's) original argument (1882) bears some similarity to the one given above. The reason why the derivation is so simple here is the straightforward identification of the roles of $\mathcal{P}_{th,TE}$ and $\mathcal{P}_{el,TE}$. which parallels the distinction between entropy producing and non-dissipative processes in thermoelectric systems.

Second law efficiencies of thermoelectric devices. In Section 4.4.3, the Second Law efficiency was introduced as a natural measure of how well a device performs. For a simple engine such as in Fig. 4.35, it is equal to the power of the useful process divided by the power of the fall of entropy that drives the engine. This idea can be transferred to the case of thermoelectric generators (Fig. 4.55) and coolers (Fig. 4.56).

For a generator, the definition is straight forward. The second law efficiency equals the useful electric power (thermoelectric power minus power of electric resistive process) divided by the power of the fall of the entropy current I_{S1} from T_1 to T_2:

$$\eta_{\mathrm{II}} = \frac{\mathcal{P}_{el,TE} - R_i I_Q^2}{(T_1 - T_2)I_{S1}} = \frac{\varepsilon^2 R_L / (R_L + R_i)}{(R_L + R_i)G_S + \varepsilon^2} \tag{4.65}$$

This is the result for an ohmic load connected to the output of the thermoelectric generator. R_L is the electric resistance of the load (resistor), and R_i, G_S, and ε are the three parameters of the device (internal electric resistance, entropy conductance, and Seebeck coefficient, respectively). This result allows us to discuss how we might improve the efficiency under certain circumstances. For a given generator, we would want to find the load that optimizes the second law efficiency. Or given a certain type of application (load) we want to design the generator characteristics in order to improve the system performance.

The case of a thermoelectric cooler is similar. The Second Law efficiency can be defined as the ratio of the (useful) power of pumping the entropy current I_{S1} from T_1 to T_2 and the driving electric power $U_{ext}I_Q$ (see Fig. 4.56):

$$\eta_{\mathrm{II}} = \frac{(T_2 - T_1)I_{S1}}{U_{ext}I_Q} \tag{4.66}$$

After inserting the constitutive relations, we obtain an expression for η_{II} for given I_Q:

$$\eta_{\mathrm{II}} = \frac{\varepsilon I_Q - G_S(T_2 - T_1)}{\varepsilon(T_2 - T_1)I_Q + R_i I_Q^2}(T_2 - T_1) \tag{4.67}$$
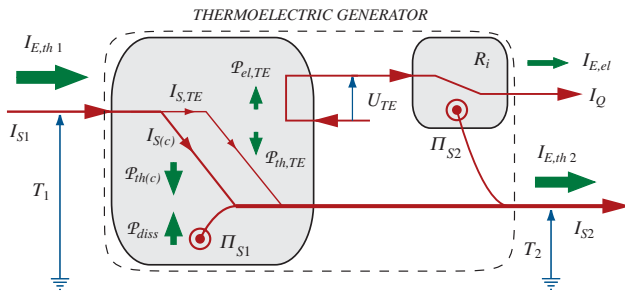
Figure 4.56: Process diagram of a Peltier heat pump. The electric (internal) resistor has been drawn separately to make the role of U_{TE} clear (note that $U_{ext} > U_{TE}$). $\mathcal{P}_{th(c)}$ is the power of the conductive current of entropy, $\mathcal{P}_{th,TE}$ is associated with the entropy current that is coupled to the flux of charge.

It is important to note that these equations denote the Second Law efficiencies calculated for the thermoelectric generator and cooler not taking into account entropy transfer to and from the devices (such as in Fig. 4.51). If we include the latter, the results will be considerably lower.

4.7.3 Structure of Thermocouples and Peltier Coolers

The foregoing discussion of the function of thermoelectric devices suggests that basically any single conductor should exhibit the features listed in Section 4.7.2. A wire made of copper going from a hot to a cold body transports entropy and charge, and the transports are (partly) coupled. However, it is clear that we cannot build an operating device in this manner. To let electricity flow, we need a closed circuit, so there needs to be a second conductor leading back from cold to hot (Fig. 4.57, left). If the second conductor is made of the same material it reverses the effect of the first; the same temperature difference will produce the reversed voltage making the device—called a *thermocouple*—electrically ineffective.
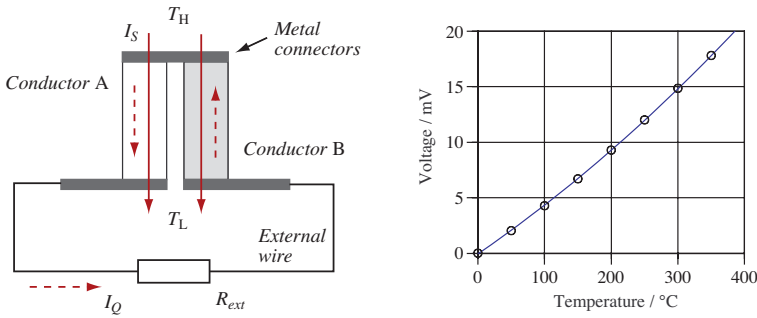

Figure 4.57: Left: A thermocouple is made of conductors of two different materials. Between two bodies at different temperatures T_H and T_L, it functions as a generator or a thermometer. (Entropy source and sink have to be insulated electrically from the thermocouple.) Right: Open-circuit voltage versus temperature difference for a T-type thermocouple made of copper and constantan (note that the relation is not perfectly linear).

Clearly, we must use a different material having a different Seebeck coefficient do have an effect. In Fig. 4.57, if $\varepsilon_A > \varepsilon_B$, electric charge can be conducted counter-clockwise. (Values of Seebeck coefficients for some metals and semiconductors are given in Table 4.8.)

Table 4.8: Seebeck coefficients at 0°C (relative to Platinum)[a]

| Metals	Seebeck coefficient ε / μV/K	Semiconductors	Seebeck coefficient ε / μV/K
Aluminum	3.5	Ge	300
Bismuth	− 72	Se	900
Constantan	− 35	Si	440
Copper	6.5	Te	500
Gold	6.5	PbTe	− 180
Nichrome	25	Bi_2Te_3 (n-type)	− 230
Nickel	− 15	Sb_2Te_3 (p-type)	185
Platinum	0		
Silver	6.5		
Tungsten	7.5		

a. The absolute Seebeck coefficient of Platinum is roughly 5 μV/K.

The discussion shows that the effective Seebeck coefficient of a thermocouple is the difference between the coefficients of the two materials employed. This is called the *differential Seebeck coefficient* (this is the coefficient ε in Equ.(4.59)). If we used just one conductor, say gold, and copper wires on a voltmeter, we could not even measure anything since copper and gold have effectively the same thermoelectric properties (see Table 4.8).

The effect becomes more pronounced if materials having positive and negative Seebeck coefficients can be used. This is the case for copper and constantan, to give just one example. The differential Seebeck coefficient of this combination is slightly more than 40 µV/K. A thermocouple made in this manner can be used as a thermometer.

Combining two strongly differing materials becomes essential if one wants to build thermoelectric coolers—otherwise the effect is just too small. Modern Peltier coolers are built with semiconductors where one leg of a thermocouple is a p-type and the other is an n-type conductor. If several or even many couples can be combined in series electrically and in parallel thermally, one obtains effective solutions for thermoelectric coolers (Fig. 4.58).

Figure 4.58: A combination of thermocouples made of n-type and p-type semiconductors can serve as an effective Peltier heat pump. Solid arrows: flow of entropy; dashed arrows: flow of electric charge. Note that the conductive flow of entropy which would be from the hotter to the colder body is not shown.
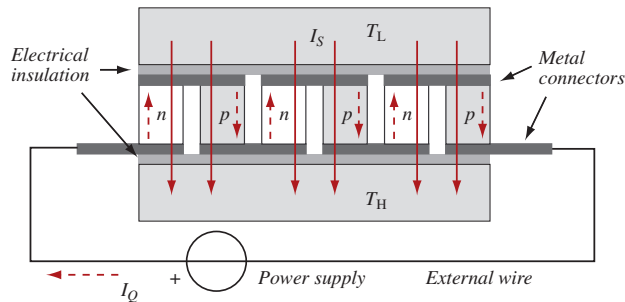
Take a closer look at a single thermocouple in Fig. 4.58. As charge flows through both legs of the couple to form a circuit, it flows up in one and down in the other. Since the first is an n-type material with negative Seebeck coefficient, entropy is pumped opposite to the flux of charge—here, this is downward from the colder to the hotter body. In the p-leg, entropy is carried in the same direction as charge flows. So both in the n-type and p-type semiconductors, entropy is pumped in the same direction.

QUESTIONS

58. If we have a furnace at T_1 and a cooler at T_2, why can a heat engine not make use of the maximum temperature difference $T_1 - T_2$?

59. What does it mean to have an endoreversible engine? What is reversible in this case? How realistic is this model?

60. What does it mean to model the working fluid of a heat pump as a Carnot engine?

61. What is the main assumption concerning thermoelectric devices leading to the proof of equality of Seebeck and Peltier coefficients?

62. Why would a Peltier cooler with low entropy conductance be better than one with high conductance?

EXAMPLE 4.22. Cooling water in a refrigerator.

Five liters of water having a temperature of 25°C are placed in a refrigerator. They should be cooled at a constant rate to 8°C in 2 hours. Construct the following model. The working fluid of the refrigerator takes the entropy of the water from the cold space which is at 4°C. The fluid itself is then at a temperature of – 10°C. It emits entropy to the kitchen which has a temperature of 25°C. Assume the heat exchangers at the cold and the hot ends to have essentially equal dimensions. The thermal engine is supposed to operate endoreversibly. (a) Draw a process diagram of the system. (b) What is the entropy current emitted by the water at the beginning and toward the end of the process? (c) What is the entropy current entering the cold space and the working fluid? (d) What must the upper temperature of the working fluid be during rejection of the entropy taken up? (e) What must be the power driving the refrigerator? What is the *cop*? How does it compare to the *cop* of a completely reversible process?

SOLUTION: (a) The idea for the process diagram can be taken from Fig. 4.51. Here, entropy is pumped by the refrigerator. As always, entropy flows downward in the heat exchangers.
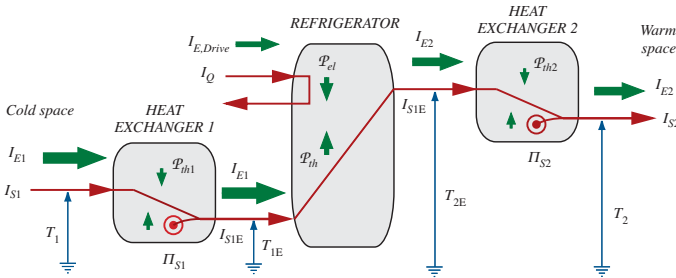
(b) The dynamics of the water is modeled according to Section 4.5 which yields

$$dS_w/dt = I_{S,w} \quad , \quad dS_w/dt = m\kappa \, dT_w/dt$$

$$I_{S,w} = m\kappa \, dT_w/dt = m\frac{c}{T}dT_w/dt = 5.0\frac{4200}{(25+273)}\frac{8-25}{7200}\frac{W}{K} = -0.166\frac{W}{K}$$

at $t = 0$ s. Toward the end, the temperature of water emitting entropy has changed to 8°C which gives a value of – 0.177 W/K for the entropy current.

(c) This current of entropy flows into the cold space and then through the heat exchanger at the cold end. Because of entropy production, the current entering the cold space will initially be

$$|I_{S1}| = |I_{S,w}| + \Pi_S = |I_{S,w}| + |I_{S,w}|\frac{T_w - T_1}{T_1} = 0.166\frac{W}{K} + 0.166\frac{25-4}{4+273}\frac{W}{K} = 0.179\frac{W}{K}$$

This value remains constant throughout the process (the energy current leaving the water is constant and it arrives at a constant 4°C). The current entering the working fluid at – 10°C is calculated in the same manner; the value obtained is 0.188 W/K.

(d) The entropy current rejected by the refrigerator is equal to the value calculated in (c). This current has to go through a heat exchanger equal to the one built at the cold end. The temperature difference needed for transfer is slightly higher than at the cold end:

$$T_{2E} - T_2 = (T_1 - T_{1E})\frac{|I_{S1E}|}{|I_{S1}|} = (4-(-10))\cdot\frac{0.188}{0.179} = 14.7\text{K}$$

So the temperature at the high end needs to be $T_{2E} = 25°C + 14.7°C = 39.7°C$.

(e) The entropy current I_{S1E} must be pumped from T_{1E} to T_{2E}. The power of this process is

$$\mathcal{P}_{th} = \left(T_{2E} - T_{1E}\right)I_{S1E} = \left(39.7 - (-10)\right) \cdot 0.188 \, \text{W} = 9.34 \, \text{W}$$

The definition of the *cop* of a refrigerator differs slightly from that of a heat pump given in Equ.(4.29). Here it is

$$cop = \frac{I_{E1}}{\mathcal{P}_{drive}} = \frac{T_{1E}I_{S1E}}{\mathcal{P}_{th}} = \frac{263 \cdot 0.188}{9.34} = 5.3$$

The *cop* of a completely reversible refrigeration process between T_L and T_H is

$$cop = \frac{T_L}{T_H - T_L}$$

If entropy leaves the water to be cooled at 25°C and enters the kitchen at 25°C, the *cop* should theoretically be infinitely high. Toward the end with the water at 8°C the cop becomes 16.5.

EXAMPLE 4.23. Cooling water with a thermoelectric cooler.

DATA

Device data from manufacturer:

$R_i = 0.98 \, \Omega$
$\varepsilon = 0.050 \, \text{V/K}$
Size: 6.0 cm by 6.0 cm

Experimental results at
$t = 1000 \, \text{s}$:

$m_w = 0.54 \, \text{kg}$
$G_{S,leak} = 2.0 \cdot 10^{-3} \, \text{W/K}^2$
$U_{ext} = 1.41 \, \text{V}$
$I_Q = 1.04 \, \text{A}$
$T_{w1} = 296.7 \, \text{K}$
$T_{w2} = 300.7 \, \text{K}$
$dT_{w1}/dt = -1.10 \cdot 10^{-3} \, \text{K/s}$
$dT_{w2}/dt = 1.9 \cdot 10^{-3} \, \text{K/s}$

In the experiment reported in Fig. 4.8, water in a sealed chamber is cooled with the help of a Peltier device (the water is stirred). The entropy is rejected to a second body of water in the same container. Manufacturer data and experimental data is given in the box on the side. (a) Sketch a qualitative temperature position diagram going from the first to the second body of water. (b) Determine the thermoelectric voltage of the device and use this to find the temperature difference from one side to the other of the cooler. (c) Determine the entropy current leaving the first body of water at $t = 1000$ s. Note that there is a leak around the Peltier device going from the warmer body of water to the colder one; the leak can be quantified by an entropy conductance of $2.0 \cdot 10^{-3} \, \text{W/K}^2$. (d) What is the entropy current through the Peltier device coupled to the electric current? Use this to find the conductive entropy current through the cooler and the entropy conductance of the device. (e) Estimate the entropy and energy transfer coefficient from water to the Peltier device. (f) Calculate the energy current emitted by the cooling water and determine the *cop* of the process.

SOLUTION: (a) The temperature of the water is uniform. The temperature must drop from the cooling water to the surface of the Peltier device for entropy to flow out of the liquid. In the device, the temperature rises to a value above that of the body of water that accepts the entropy. So the temperature drops from the warm surface of the thermoelectric cooler to the second body of water.

Figure Ex.23
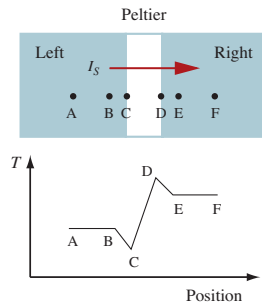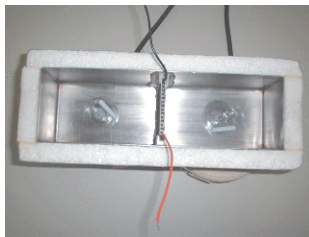
(b) In the experiment, both the total voltage across the Peltier device, U_{ext}, and the electric current I_Q were measured. Since the internal resistance R_i is specified by the manufacturer, we can calculate the voltage of the thermoelectric generator U_{TE} from simple circuit theory:

$$U_{TE} = U_{ext} - R_i I_Q = 1.41\,\text{V} - 0.98 \cdot 1.04\,\text{V} = 0.39\,\text{V}$$

Once the thermoelectric voltage is known, the associated temperature difference across the device (from C to D in Fig. Ex.23.1) can be calculated:

$$U_{TE} = \varepsilon(T_2 - T_1) \quad \Rightarrow \quad T_2 - T_1 = U_{TE}/\varepsilon = 0.39/0.050\,\text{K} = 7.8\,\text{K}$$

(c) To obtain the entropy current pumped from the body of water being cooled, we start with the law of balance and the constitutive capacitive and resistive relations:

$$dS_w/dt = I_{S,w} + I_{S,leak}$$
$$dS_w/dt = m\kappa\, dT_w/dt$$
$$I_{S,leak} = G_{S,leak}(T_{w2} - T_{w1})$$

The mass of the body of water, its temperature and rate of change of temperature at $t = 1000$ s have been obtained from the experiment. Together with the conductance of the entropy leak between the bodies of water we have:

$$I_{S,w} = m\kappa\, dT_w/dt - I_{S,leak} = m\frac{c}{T}dT_w/dt - G_{S,leak}(T_{w2} - T_{w1})$$
$$= 0.54\frac{4200}{296.7}(-1.1 \cdot 10^{-3})\frac{\text{W}}{\text{K}} - 2.0 \cdot 10^{-3}(300.7 - 296.7) = -16.4 \cdot 10^{-3}\frac{\text{W}}{\text{K}}$$

(d) The Peltier cooler pumps an entropy current equal to

$$I_{S,TE} = \varepsilon I_Q = 0.050 \cdot 1.04\,\text{W/K} = 5.2 \cdot 10^{-2}\,\text{W/K}$$

from C to D in Fig. Ex.23. Since the current leaving the water at point B is only 16.4 mW/K, there must be a conductive flow of entropy through the cooler (from D to C) as a result of the temperature difference $T_D - T_C$. If we assume the entropy production due to transfer from the water to the cooler to be negligibly small, we have

$$|I_{S,w}| = |I_{S,TE}| - |I_{S(c)}| \quad \Rightarrow$$
$$|I_{S(c)}| = |I_{S,TE}| - |I_{S,w}| = 5.2 \cdot 10^{-2}\,\text{W/K} - 16.4 \cdot 10^{-3}\,\text{W/K} = 3.56 \cdot 10^{-2}\,\text{W/K}$$

This allows us to find the conductance of the cooler:

$$I_{S(c)} = G_S(T_2 - T_1) \quad \Rightarrow \quad G_S = \frac{I_{S(c)}}{(T_2 - T_1)} = \frac{3.56 \cdot 10^{-2}}{7.8}\frac{\text{W}}{\text{K}^2} = 4.56 \cdot 10^{-3}\frac{\text{W}}{\text{K}^2}$$

(e) The temperature drops from the first body of water to the cooler, and from the cooler to the water at higher temperature. From B to C and from D to E we have two convective transfer layers. It is reasonable to assume that the temperature differences across the layers are the same at the cool and the warm ends. Since we have 7.8 K from C to D, and 4.0 K from B to E, there is a temperature drop of 1.9 K for each of the convective layers:

$$I_{S,w} = G_{S,wP}(T_1 - T_{w1}) = A h_{S,wP}(T_1 - T_{w1}) \quad \Rightarrow$$
$$h_{S,wP} = \frac{I_{S,w}}{A(T_1 - T_{w1})} \approx \frac{16.4 \cdot 10^{-3}}{0.060^2 1.9}\frac{\text{W}}{\text{K}^2\text{m}^2} = 2.4\frac{\text{W}}{\text{K}^2\text{m}^2}$$

The entropy transfer coefficient can easily be converted to the equivalent energy transfer coefficient:

$$h_{wP} \approx T_{w1} h_{S,wP} = 297 \cdot 2.4 \frac{\mathrm{W}}{\mathrm{K} \cdot \mathrm{m}^2} = 710 \frac{\mathrm{W}}{\mathrm{K} \cdot \mathrm{m}^2}$$

(f) The energy current from the body of water to the Peltier device is obtained from the entropy current and the associated temperature:

$$I_{E,w} = T_{w1} I_{S,w} = 296.7 \cdot \left(-16.4 \cdot 10^{-3} \right) \mathrm{W} = -4.87\,\mathrm{W}$$

The *cop* is defined as the magnitude of this current divided by the power of the electric process driving the pump:

$$cop = \frac{\left| I_{E,w} \right|}{U_{ext} I_Q} = \frac{4.87}{1.41 \cdot 1.04} = 3.3$$

This compares to a *cop* of 74 for a completely reversible process of pumping entropy from the cool to the warm water.

4.8 ENTROPY PRODUCTION, SYSTEMS, AND WALLS

Now that we have seen how a theory of the dynamics of heat can be constructed and applied in simple settings, let me return to some general considerations concerning thermal systems and how to analyze them.

In any physical analysis, there is always an important element to be considered. The analyst has to be clear about which system or body is being studied. Only then can the application of a law such as the law of balance of entropy work out successfully. In many situations, it is quite clear which system has been chosen for investigation, and we do not have to be particularly explicit about our choice. However, nowhere is it more important to be precise and explicit about which part of the world we are going to study than in thermodynamics. The very nature of heat — its tendency to increase through production — calls for careful analysis. We cannot be vague about where the production of entropy occurs in a given situation. Careless treatment of this problem has caused many confusing statements about thermal processes.

The first point to be kept in mind is that analysis of a situation applies only to the system chosen and to nothing else. Specifically, this means that the production of entropy takes place *inside the system*. No matter what might happen in the surroundings of the system, dissipation is related to that particular system only. If a body undergoes reversible changes while entropy is being created outside of it, we have to conclude that as far as our equations are concerned, entropy has not been produced. Our analysis cannot make a statement about anything but the body being studied. Conversely, if a process is irreversible, dissipation must have occurred in the body or we would not know about it.

This raises a second point. Consider a body at a uniform temperature in an environment of uniform, but different, hotness. Body and environment touch at the surface of the body. The surface is shared by both the system and its surroundings so you might ask, what is the temperature of the surface? Is it the temperature of the body, or of the environment? The problem becomes more acute if we consider the balance of entropy for a current across this surface. The geometrical surface certainly does nothing to dis-

turb the flux of energy accompanying the current of entropy. In other words, the current of energy must be continuous across the surface (Fig. 4.59). Therefore the current of entropy must be discontinuous; it increases in the direction of flow from the hotter to the cooler body. But then, where has entropy been produced? Where is the seat of dissipation? Unless we are prepared to treat the boundary between body and environment as a physical system in its own right, there is no system which can account for the production. Dissipation must take place in a proper physical system. Therefore, we are led to introduce surfaces or *ideal walls* across which temperature, entropy flux, and flux of energy are continuous. Such walls do not add to the processes occurring inside a system, particularly to the production of entropy.
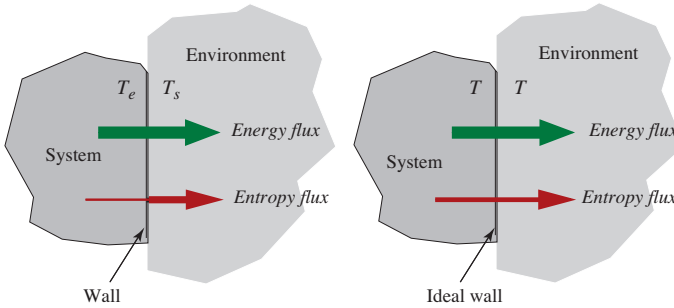

Figure 4.59: If we allow for the system and its environment to be separated by a wall across which the temperature is discontinuous, a current of entropy crossing this boundary will have to be discontinuous as well. Since this brings up the problem of where entropy has been produced, we conceive of ideal walls which do not add to dissipation. Temperature, entropy flux, and flux of energy are all assumed to be continuous across such a wall.

The puzzle presented by two systems at different temperatures can be solved in a number of ways. The ideal system wall may be placed in such a way that the dissipation takes place inside the system. Alternatively, we may exclude the drop of temperature from the system, thereby putting the burden on the analysis of the environment as a physical system. Finally, we may introduce a third system, a finite three-dimensional wall separating the first system and its surroundings. This third body is made responsible for the production of entropy due to the flow of heat from the hotter to the cooler body. The finite wall cannot have a uniform temperature. It exists for communicating between the system and its environment in a physically acceptable way. It is a body with all the physical attributes of the systems we are studying in this book. Like every proper system it, too, is assumed to be surrounded by an ideal wall.

In essence, then, we consider physical systems having ideal walls. Transfer of entropy and energy across such a wall into or out of the body is governed by the basic relationship between entropy flux, temperature, and associated energy current, Equ.(4.21):

> *At the surface of a system, the current of entropy and the flux of energy associated with it are related by the temperature at the surface according to Equ.(4.21). Possible production of entropy may take place inside the system, but not at its ideal wall.*

The assumptions stated here are fundamental for thermodynamic analysis. They facilitate the understanding of where and how dissipation may occur. In particular, they do away with statements about thermal energy being added to bodies reversibly or irreversibly. There is no such thing as an irreversible exchange of entropy and energy. The exchange takes place across an ideal wall and is always governed by Equ.(4.21), and

by nothing else. If any entropy has been produced, it will have taken place inside the system being analyzed.

By the way, if ideal walls did not exist, it would be hard to imagine how temperatures could be measured. A thermometer is a physical system. If its surface were not ideal it might show a different temperature from that of the immediate neighborhood. This point will be of great importance when we create a formal theory of the dynamics of heat in Chapters 10-12.

EXERCISES AND PROBLEMS

1. In what sense is hotness the intensity of heat? Why do we have to distinguish it from quantities of heat? What other quantities in physics may the intensity of heat be compared to?

2. Consider a moving body that splits into two halves which continue moving along together. Which mechanical quantity is divided among the bodies? Which other mechanical variable is not divided up, leaving each of the parts with its initial value? Compare electrical and thermal phenomena to this mechanical example. Which electrical or thermal quantities correspond to the mechanical variables?

3. List everyday phenomena which are responsible for our intuitive notion of heat content of bodies. Can you turn the qualitative idea into a physical quantity having a precise meaning?

4. Why shouldn't we think of energy as a mechanical, electrical or thermal quantity? Why would it be particularly wrong to identify stored energy as mechanical, electrical, thermal or other? What consequence does this have for identifying "heat" as stored energy?

5. What happens to all bodies under all circumstances if their energy is increased? Which physical quantity changes if this happens? What kind of conclusions *cannot* be drawn from the statement that the energy of a body has changed?

6. With the help of physical quantities, explain the *difference* between making a body rotate and making it warmer.

7. Compare different fluidlike physical quantities such as momentum, charge, amount of substance, and entropy. Which two properties do they all have in common? What are possible differences between the quantities listed?

8. Rephrase the following expressions in terms of entropy. In which cases would reference to energy be clearly wrong? Do any of the terms and expressions have nothing to do with entropy? (a) heat engine, heat pump; (b) heat exchanger; (c) heating and cooling; (d) heat flow, transfer of heat; (e) convective heat flow; (f) heat source; (g) storage of heat, heat reservoir; (h) phenomena in which heat causes motion; (i) solar heater; (j) production of heat; (k) heat transfer coefficient; (l) pumping heat from the cold enclosure; (m) heating power.

9. A copper bar having a constant cross section and length l_o is rigidly attached between walls. Assume it to be free of stress at a given temperature. If the temperature changes, the length of the bar changes, and momentum currents due to compression or tension are set up in the bar. Calculate the thermal stress resulting from a change of temperature of $\pm\, 30°$C. Young's modulus for copper is equal to $12.3 \cdot 10^{10}$ N/m^2.

10. Assume that a solid cube expands by expanding along each of its three axes equally. Show that the coefficient of volume expansion equals $3\alpha_l$ in this case, where α_l is the (linear) coefficient of expansion. What is the relative change of volume per degree Celsius of a cube of 1 kg copper?

11. It is found that the current through the tungsten filament of a light bulb is 0.010 A at a voltage of 1.0 V. At 150 V the current is equal to 0.50 A. What is the temperature of the filament at the higher reading, if the experiment is performed at room temperature (20°C)? The temperature coefficients are $\alpha = 4.11 \cdot 10^{-3}$ K^{-1} and $\beta = 9.62 \cdot 10^{-7}$ K^{-2} for the tungsten filament.

12. Measurements demonstrate that dilute gases show a linear relationship between volume and temperature, if the pressure is kept constant. (a) Express the law in a form equivalent to that of Equ.(4.8). Compare it with the linear approximation to the law of expansion of liquids and solid s and calculate the coefficient of expansion with respect to a temperature of 0°C. Is the coefficient independent of temperature? (b) It is found by measurement that $\alpha*(0°C) = 1/273.15$ K. Show that the ratio of the volumes at different temperatures (for equal pressure) is given by the ratio of the Kelvin temperatures.

13. Formulate the law(s) of balance of entropy in instantaneous (dynamical) and integrated forms for the following situations. (a) A uniform material is heated but not cooled. (b) Water in an open container is heated electrically and stirred at the same time. (c) A liquid in a well insulated container is stirred mechanically. (d) A viscous gas is compressed in a well insulated cylinder. (e) A hot stone cools in cold water inside a well insulated container. Take the stone and water first as separate systems, then as a single system. (f) Hot water cools in a thick walled container in a cool environment (take water and container as separate systems). (g) Water is heated in a tea kettle but it is not getting any hotter.

14. A body is heated and cooled at the same time. At one end, entropy flows into the body at a rate of 300 W/K. At the other end, entropy is removed at a rate of 200 W/K. What is the net heating, or the net entropy flux for the body? At what rate does the entropy content of the body change? Assume that entropy is conserved in this process.

15. A constant flux of entropy of 200 W/K leaves a system, while a current entering the system changes according to -20 W/(K·s)·t. (a) How much entropy is absorbed and emitted in the first 15 s? Refer the absorbed entropy to the current flowing into the system, and the emitted entropy to the current flowing out of the body. (b) How much entropy is exchanged in total? (c) What is the change of the entropy content of the body?

16. A body which is being heated undergoes an irreversible process. The net current of entropy changes from -100 W/K to zero in 20 seconds. During this time, the rate of creation of entropy is equal to 30 W/K. (a) What is the rate of change of the entropy in the body? (b) How large are the exchanged entropy and the change of entropy content in the first 20 s?

17. Give a graphical interpretation of the energy exchanged in thermal processes during the ideal Carnot cycle and represent the thermal work in the *TS* diagram.

18. (a) Consider a Carnot cycle, i.e. a cycle where entropy is absorbed and emitted at constant temperatures, for which the adiabatic expansion is dissipative. Draw the *TS* diagram and indicate the energy exchanged in the thermal processes. (b) Why is the cycle less efficient than its reversible counterpart? (c) Identify the lost available energy in the *TS* diagram.

19. An immersion heater has a temperature of 120°C as it emits an energy current equal to 0.80 kW. (a) How large is the current of entropy flowing across the surface of the heater? (b) If the temperature of the water receiving the heat is equal to 80°C, how much entropy flows into the water?

20. Consider water being heated by an immersion heater. (a) If you consider the body of water as a system, what is its equation of balance of entropy? (Assume the distribution of entropy through the system to take place reversibly; what does this mean for the conduction of entropy through the system?) (b) Answer the question for the case in which you take the system to be made up of water plus heating coil.

21. A metal bar conducts entropy from a container of boiling water to a mixture of ice and water. It is found that in the latter container, ice melts at a rate of 10.0 g per minute (see Table 4.3). Compute the rate at which entropy is produced in the conductor.

22. A small steel sphere falls in oil. The frictional force is calculated according to Stokes' law. What is the maximum rate of creation of entropy if the temperature of the medium is 20°C? Take the radius of the sphere to be 1 mm. The densities of steel and oil are 7700 kg/m^3 and 960 kg/m^3, respectively. The dynamic viscosity of oil is 0.99 Pa·s.

23. A large thermal power plant (such as a nuclear power plant) takes its entropy from a reactor at 600 K. The entropy is emitted again to the cooler at 300 K. The measured useful power

is 1.0 GW. (a) Sketch a process diagram (with carrier and energy currents) for the system (the system between reactor and cooler). (b) If the heat engine could operate ideally, what would be the entropy current through the engine? (c) The thermal efficiency of the power plant is only 30%. What must the real entropy current and energy current from the reactor to the heat engine be? (d) What is the entropy production rate in the heat engine (i.e., between the reactor and the cooler)? (e) What is the total entropy production rate (i.e., including the one in the reactor)?

24. A car engine is running at steady-state. Gasoline provides energy at a rate of 400 kW, the measured mechanical power of the engine is 100 kW. The entropy is provided at a temperature of 900 K and cooling takes place at 300 K. (a) Sketch a process diagram for the engine as a single system between "furnace" and "cooler." (b) What is the entropy current into the engine? (c) What is the thermal power? (d) What would the entropy current to the cooler be if the engine were operating ideally? What would the energy current to the cooler be? (e) What is the actual energy current to the cooler? (f) What is the entropy production rate in the engine?

25. A heat pump is used to heat water at 60°C. Heat is taken from the ground at 2°C. The observed coefficient of performance is 2.2 while the energy current associated with heating has a magnitude of 1.0 kW. (a) How large is the rate of production of entropy? (b) How large is the loss of available power? Show that it is equal to the product of the rate of generation of entropy and the temperature of the environment. (c) How large is the second law efficiency of the heat pump?

26. The temperature inside a freezer is kept at a constant – 23°C. The ambient temperature is 20°C. According to the technical information booklet, the freezer uses 1.2 kWh of electrical energy per day. We model the freezer as a coupled system (insulation, container, ideal heat pump, and heat exchangers). The heat pump pumps the heat reversibly from – 38°C to 42°C. (a) Calculate the entropy flow through the heat pump. (b) What is the energy current flowing into the freezer due to the temperature difference to the environment? (c) In our model, entropy is produced in three processes. Show where this happens in your sketch of the model. (d) What is the total rate of entropy production?

27. Determine the mechanical power of a thermomechanical engine undergoing a steady-state cyclic process. The engine works irreversibly. It is in contact with n heat reservoirs of constant temperatures, and with the environment at temperature T_o. Identify the loss as a result of dissipation, and compute the second law efficiency of the heat engine.

28. Not all types of solar heating are created equal (Fig. P.28). Consider the following means of keeping a supply of domestic water at 60°C. In a first setup (A), solar radiation is used directly to heat the water. In a second (B), solar radiation is used to heat a furnace to 700°C. The entropy from the furnace drives an ideal Carnot engine (*ICHE*) which rejects the entropy to the water at 60°C. The energy released by the engine is used to drive an ideal Carnot heat pump (*ICHP*) which pumps entropy from the environment at 0°C into the water at 60°C. Calculate the ratio of the rates of heating of the two processes. Take I_{E1} to be equal in both cases.

29. We are given a certain amount of hydrogen which we are to use for heating water. The water is to be kept at a constant temperature T which is higher than that of the environment (T_a), and lower than a possible flame temperature if we decide to burn the hydrogen. (a) Calculate the heating power for the water in terms of the energy released by the chemical reaction of hydrogen with oxygen for the following three modes of heating: (A) direct heating by burning the hydrogen; (B) heating with the help of an ideal heat engine driven by entropy from a furnace at temperature T_f which receives its entropy from burning of hydrogen, and an ideal heat pump driven by the heat engine (scheme B of Problem 28); (C) heating with the help of an ideal heat pump driven by an ideal fuel cell which uses the hydrogen. (b) Calculate the loss of power for scheme A, and show that it is equal to the product of the temperature of the water and the rate of production of entropy.

30. Measurements put the value of the entropy capacitance of 1 kg of ice at 8.1 J/K² at a temperature of 13°C below freezing, and at 7.7 J/K² at a temperature of 0°C. (a) Calculate the

Loss *Solar power*

Furnace T_H

I_{E1} ○ *ICHE*

I_{S1}

T_w

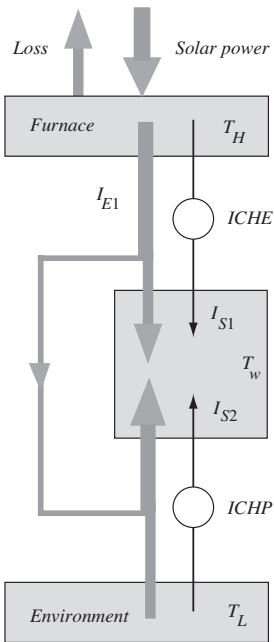I_{S2}

○ *ICHP*

Environment T_L

Figure P.28

current of entropy which is needed if a lump of ice having a mass of 1kg at a temperature of –13°C is to be heated so that its temperature rises by 1 K per minute. (b) Estimate the total entropy transmitted to the body if it is to be heated up to a temperature of 0°C.

31. How much entropy and energy are added to 1.0 kg of silicon if the body is heated from 160 K to 640 K? (See Fig. 4.41 for properties of silicon.)

32. A body made of a material having (known) variable entropy capacitance is heated (the current of entropy is assumed to be prescribed). (a) Represent the process by a system dynamics model diagram. (b) Write all the equations and derive the differential equation for the temperature of the body.

33. A rigid body has a constant entropy capacitance in a particular range of temperatures. How much energy does it emit if its temperature drops from T_i to T_f?

34. An ideal Carnot engine is driven with the heat from 2000 liters of water at 90°C. Entropy is rejected to the environment at a temperature of 20°C. How much energy does the engine release for mechanical purposes?

35. In an experiment, glycol was heated electrically in a perfectly insulated container. Electric power and temperature of glycol were recorded as functions of time. The mass of the glycol was measured. The experiment was used to determine the temperature – specific entropy diagram (see Fig. P.35.1). (a) Explain how the Ts diagram can be determined from the data of the experiment. (b) Determine the specific entropy capacitance of glycol at 300 K, 340 K and 380 K. What is your observation? (c) Use the results to determine the specific heat (specific temperature coefficient of energy). Is this quantity constant or does it increase or decrease with temperature? (d) Glycol is heated electrically at constant power in a perfectly insulated container. What would the temperature as a function of time be (qualitatively)? Why? (e) Glycol having a mass of 0.50 kg is heated at constant electric power of 20 W inside a sealed aluminum can. The temperature of the environment is 295 K. Explain why we get the measurements (temperature as a function of time) as shown in the graph (Fig. P.35.2). (f) Use the data to determine the entropy conductance of the aluminum can.

36. Hot water is filled into a thin-walled polished aluminum can. The water is stirred continuously. Data: Radius of can: 3.3 cm; height of can: 15.0 cm; mass of water: 490 g. The inside heat transfer coefficient is very high, the metal sheet is very thin. Lid and bottom are insulated. Power of the mixer: 2.0 W; temperature of the ambient is a constant 19°C. The temperature of the water has been measured as a function of time (see Table 4.9). (a) Explain the experimental data. (b) Sketch a diagram of a system dynamics model of the system and processes. (c) Write down all the equations of the model. (d) Determine the convective entropy and heat transfer coefficients at the outside surface of the polished can, and the power of the magnetic bar used for mixing.
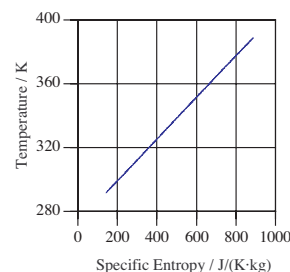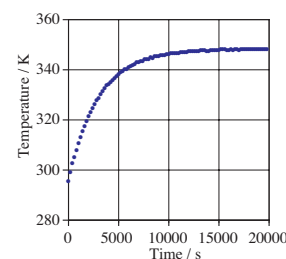

Figure P.35.1

Figure P.35.2

Table 4.9: Water temperature

$t\,/\,s$	$T\,/\,°C$	$t\,/\,s$	$T\,/\,°C$	$t\,/\,s$	$T\,/\,°C$
0	86.84	25000	30.74	50000	27.10
5000	58.44	30000	29.34	55000	27.05
10000	44.54	35000	28.45	60000	27.00
15000	37.30	40000	27.80	65000	26.95
20000	33.32	45000	27.40	70000	27.00

37. The inside and the outside of a house are at temperatures of 25°C and 35°C, respectively. If all doors and windows are closed, the home has an energy conductance of 300 W/K. There is no sunlight getting inside. (Imagine the house as an airtight and opaque box.) If we do not cool the house, the inside temperature will be 31.3°C after 10 hours. (a) Determine the entropy capacitance and the temperature coefficient of energy of the house. (b) What is the entropy current arriving inside at 25°C? (c) A heat pump is used to keep the
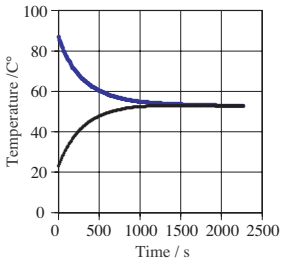
inside at 25°C. If the heat pump worked ideally, what would the power driving it be? (d) The coolant of the heat pump takes up entropy in the house at 10°C. It emits it at 45°C. What is the (minimal) real power for driving the pump?

38. Two amounts of water having equal mass of 0.951 kg each are inside two chambers separated by a thin metal wall. The dimensions of the chambers are 10 x 10 x 10 cm. The container chambers are well insulated from the environment. Hot water is filled into one of the chambers, cold water into the other. The water is thoroughly mixed the whole time. The temperatures are measured as functions of time (Fig. P.38). (a) What is the convective heat transfer coefficient from the water to the metal wall? Note that the thermal resistance of the metal wall is itself very small. (Use the data of the experiment and neglect heat loss to the environment and the effect of the mixer). (b) What is the change of energy of each of the bodies of water during the first 500 s? (c) Use the data to determine as carefully as possible the entropy conductance (or the energy conductance) for heat loss to the environment for the entire container. The power of the mixers in the two chambers adds up to 1.0 W, and the ambient temperature is equal to 22°C.

Figure P.38

39. Two different experiments are performed with a thick-walled PVC container. They are used to determine the specific heat (specific temperature coefficient of energy) and the thermal conductivity (energy conductivity) of PVC. When you have found these values, also determine the specific entropy capacitance and the entropy conductivity. Data for the container: Inside radius: 3.0 cm, outer radius: 4.65 cm, inside height: 0.105 m, density: 1400 kg/m^3.

Experiment 1: The container is completely insulated from the environment. It has an initial temperature of 23.4°C and is filled with hot water having a temperature of 89.5°C. Everything is now sealed, and the water temperature and the temperature at the middle of the container wall are measured (see graph Fig. P.39, left).

Experiment 2: Lid and bottom are perfectly insulated. Water and container have an initial temperature of 23.4°C, the same value as the (constant) temperature of the environment. The mixer dissipates energy at a rate of 2.0 W. Take values of 200 W/(K·m^2) and 13 W/(K·m^2) for the heat transfer coefficients on the inside and the outside of the PVC container. Fig. P.39, right, shows the water temperature as a function of time.

Figure P.39
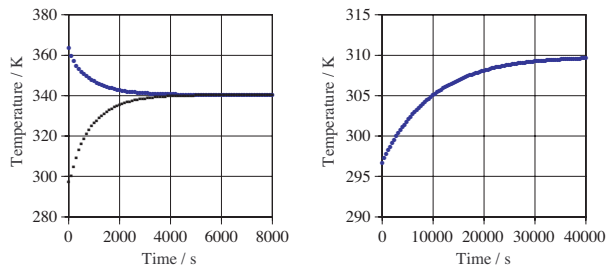
40. A container consists of three chambers made of thin metal sheets. Each chamber has a a size of 10 by 10 by 10 cm. The chambers are touching as shown in the figure. Each of them is filled with one liter of water. The initial temperatures are 80°C, 20°C, and 50°C, respectively. The assembly is perfectly insulated from the environment. Neglect dissipation due to stirring. (a) What does "thermally insulated" mean in a formal model? Explain using words and equations. (b) Is there entropy production in this system if we neglect stirring? (c) Sketch the diagram of a system dynamics model that can be used to simulate the behavior of the system. Use the energy representation. (d) The convective heat transfer coefficient from water to metal is 400 W/(K·m^2). Determine the (energy) conductance from the water in one chamber to the water in the adjacent chamber. (e) Determine the rates of change of the three temperatures right at the start. (f) Sketch the temperatures as functions of time. Use calculations to make the sketch as realistic as possible (show time constants).
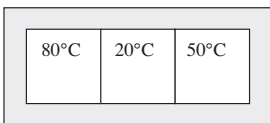

Figure P.40

41. A person is taking a shower and changes the position P of the lever of the shower mixer to adjust the temperature of the water (water is mixed from cold (T_C) and hot (T_H) water). The mixing temperature is given by

$$T = T_C + \left(T_H - T_C\right)P$$

where P is a number between 0 and 1. Zero means that only cold water is used, one means that only hot water comes out of the shower. In the figure, you see a diagram of a possible model of how the position P is adjusted by the person to a desired water temperature (T_D).
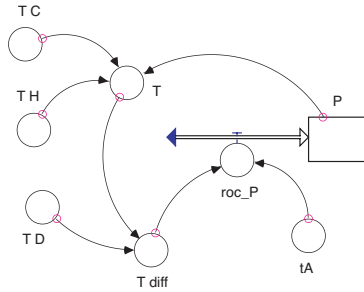

Figure P.41

(a) Derive the equation presented above for the mixing temperature of water. (b) The person changes the position P of the lever at a rate *roc_P* that depends linearly upon the difference of desired and actual temperatures. In the model, the process of adjustment introduces a kind of inertia t_A (larger inertia means slower adjustment). Formulate the equation for *roc_P* that corresponds to these ideas. (c) Formulate all the equations of the model. (d) Transform these equations into a single differential equation for the position P of the lever. (e) Assume 20°C and 60°C for cold and hot water, respectively, and 40°C for the desired temperature. Take a value of 50 K·s for the factor of inertia t_A. What is the time constant of this model? (f) Sketch the temperature of the water for the parameters according to problem (e) (show time constant and asymptote). Assume the initial condition to be $T(0) = 20$°C (Position $P(0) = 0$).

42. Two bodies of water of 0.50 kg each are separated by a Peltier device. The bodies are completely insulated from the environment. The Peltier device is driven electrically. It pumps entropy from the colder into the warmer water. The device works by creating a cold and a hot side. We consider a certain moment. Values of temperature, electric current and resistance are given in the table.

Table 4.10: Data for water and Peltier device

	Cold	Hot
Temperature of water	295.7 K	301.7 K
Temperature of Peltier device	294.5 K	303.4 K
Entropy current into/out of water	0.0122 W/K	0.0169 W/K
Electric current through device	1.02 A	
Electric resistance of device	0.98 Ω	

(a) Estimate the entropy production rate due to the electric process. (b) The entropy current leaving the cold water is 0.0122 W/K, the current into the warm water is 0.0169 W/K. What is the total entropy production rate in the system? What is the fraction due to electric dis-

sipation? (c) If the entire process were completely reversible, how much energy would be needed per second to pump the entropy current of 0.0122 W/K from the cold into the warm water? (d) The voltage that powers the Peltier device is 1.5 V. What is the efficiency of the device?

43. A Peltier device is used to separate two bodies of water in an otherwise perfectly insulated container (see Example 4.23). The Peltier device is operated as a heat pump. In the diagram, the temperatures of the two bodies of water are shown as functions of time. Data: Mass of a body of water: 0.50 kg; electric current through Peltier Device: 1.03 A; voltage across Peltier device: 1.37 V. In the following, consider $t = 1000$ s. (a) How large would the entropy current be if the Peltier device could pump entropy directly and without any dissipation from the body of water on the left to the one on the right? The water temperatures are to be found in the second diagram. The electric data are given above. (Hint: Determine the power of the Peltier device.) (b) What is the actual entropy current out of the water in the left chamber? Neglect the effect of the mixer and all losses of heat. Entropy flows only through the Peltier device. (Hint: Determine the rate of change of the temperature of water in the left chamber using the diagram.)

Figure P.43
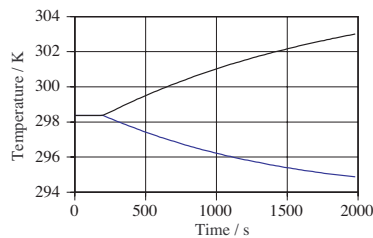
44. A Peltier device serves as a separating wall between two chambers in an insulated container. Hot water is poured into the left chamber, cold water into the right one (0.50 kg each). The water is stirred mechanically. A resistor is connected to the cables of the Peltier device. The lid of the container is closed. The temperatures of the two bodies of water and the voltage across the resistor are measured. The resistor has a resistance of 1.29 Ω. (a) Formulate the instantaneous form of the law of balance of entropy for one of the bodies of water. Explain. (b) Determine the rates of change of temperature of the bodies of water right at the beginning (at $t = 0$ s). (c) Estimate the entropy current through the Peltier device right at the beginning (at $t = 0$ s). (d) Determine the temperature difference between left and right and the electric power of the Peltier device for about 6 points (500 s, 750 s, …, 1750 s). Create a graph of the power as a function of the *square* of the temperature difference. (e) Explain why we should expect the result of problem d (i.e., interpret and explain what you obtained). (f) Compare the electric power to the ideal thermal power we should expect for the temperature difference between the right and the left sides (for $t = 0$ s).

Figure P.44