

CHAPTER 3 Heat and Thermoelectricity

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. An interesting type of coupling of processes can be demonstrated nicely in thermoelectric phenomena.

3.1 SOME IMPORTANT OBSERVATIONS

Two bodies of water in thermal contact. Water is poured into two compartments of a container separated by a thin metal wall (Fig. 3.1). 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 falls whereas the temperature of the cold water rises. This goes on until both temperatures are the same.

Temperatures equilibrate for different bodies as well (a block of cold copper in hot water, Fig. 3.1). This shows that temperatures become equal, not quantities of heat.

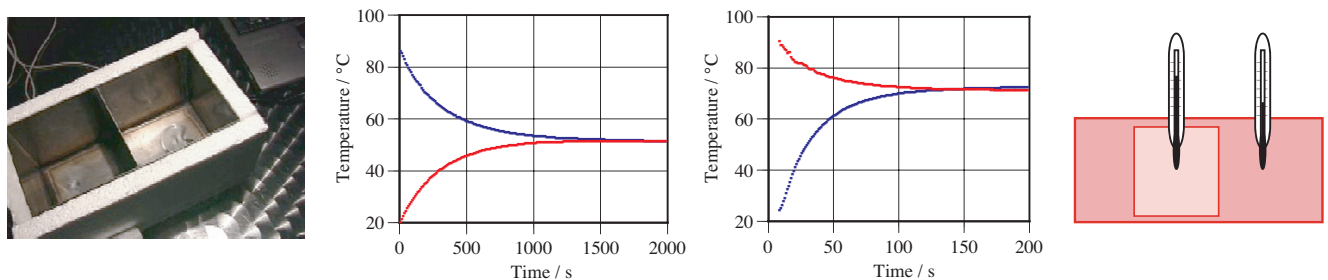


Figure 3.1: A hot and a cold body of water in thermal contact inside a well insulated container (left). The temperatures adjust until they have become equal (graph at center). The same happens if a cold block of copper is put into hot water in a well insulated tank (graph on the right).

Interpretation. For a body of water to cool down, it has to lose heat, for it to get warmer, it must gain heat. We say that heat flows from the hotter body of water to the colder one as long as there is a temperature difference. Since the behavior of the

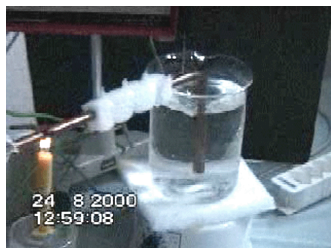


Figure 3.2: A candle indirectly heats water. A copper rod transfers the heat produced by the candle to the water.

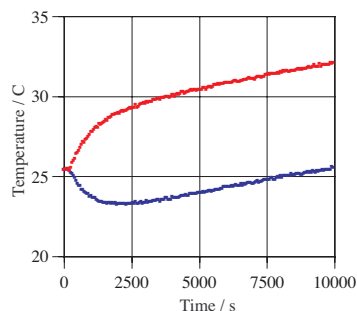
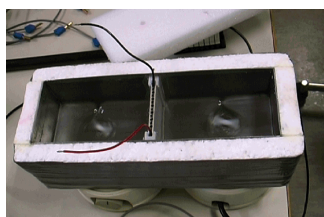


Figure 3.3: Two bodies of water inside an insulated tank are separated by a Peltier device. When operated, the Peltier device cools one body of water and heats the other.

temperatures resembles that of water levels in communicating tanks, or of voltages of capacitors connected by a resistor, we interpret *temperature as the thermal level* quantity.

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.

Heating water. Water can be made warmer by placing it over a fire, by heating it with an immersion heater, by vigorously stirring it, by exposing it to the Sun, or by bringing it in contact with a hotter body.

Interpretation. To make a body of water warmer, we need to add heat. Heat can be transferred from outside from another body, it can be produced by a fire or an immersion heater and then transferred, it can be produced inside by stirring the water, or by absorbing sunlight. The effects of producing heat or just transferring it from another body are the same.

Heat flows through a metal bar. A piece of a metal bar is inserted into water in a glass. The copper rod is heated by a candle at the other end (Fig. 3.2). Over time, the temperature of the water rises.

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, as a result the temperature rises.

Using a Peltier cooler. Two bodies of water inside a well insulated tank are separated by a so-called Peltier device (Fig. 3.3, top). 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 warmer whereas the other one gets colder (see the diagram in Fig. 3.3). Overall, both bodies of water heat up if the tank is sealed.

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 here the heat goes from a cold to a hot body, it does not flow by itself from a higher to a lower thermal level. Heat is said to be *pumped* by the thermoelectric device. Like any other pump, this one also needs energy to do its job.

The Peltier device produces heat as it pumps heat. Therefore, 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.

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 only very little. We can understand this as follows: 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 example demonstrates that temperature and heat cannot be the same quantity. Here, the quantity of heat stays constant while temperature changes.

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, and of the water bath (Fig. 3.4). It is found that the temperature of a cold block of ice first rises to 0°C . Then the ice-water mixture stays at a constant 0°C until all the ice has melted. Only then, upon further heating, does the temperature of the water rise as expected. The temperature of the water bath decreases all the time.

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 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, the heat coming from the warm water raises the temperature of the cold ice to 0°C . The the temperature of the substance in the test tube (Fig. 3.4) stays constant for quite a while before starting to rise. During the phase of constant temperature, ice transforms into 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 (Fig. 3.5).

Interpretation. Again, we have a phase change that requires heat while the temperature of the substances undergoing phase 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.

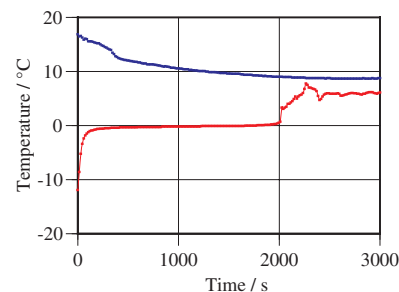


Figure 3.4: A test tube filled with cold ice is placed in water, everything is in a well-sealed container. Temperatures of the water bath (upper curve) and of the ice-water mixture in the test tube (lower curve) are recorded.

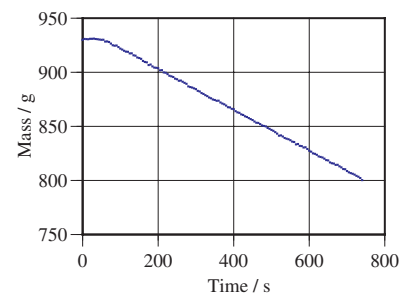


Figure 3.5: Water is vaporized in a can on top of a scale. The mass of the water is recorded as a function of time. (The temperature stays constant during vaporization.)

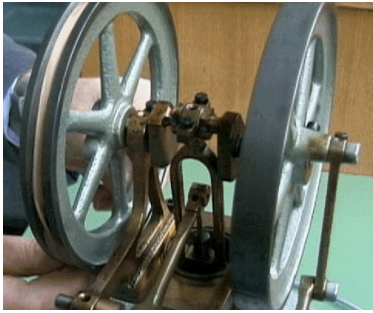


Figure 3.6: The mechanical part of a Stirling engine. When the engine is heated and cooled, the wheels drive a mechanical process.

A Stirling engine. A Stirling engine is a classical heat engine. The engine is heated from outside (any type work, a fire, electrical heating, heating by concentrated solar radiation), and cold water is passed through it to cool the engine (the water leaving the engine is warmer). When operated like this, the engine can drive mechanical processes (Fig. 3.6). 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 changes by a factor of two as well.

Interpretation. The following interpretation is by Sadi Carnot from his famous book *The Motive Power of Heat* (1824). “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. 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 and of meteors, the currents of water which channel the surface of the globe, and of which man has thus far employed but a small portion. Even earthquakes and volcanic eruptions are the result of heat.

“According to established principles at the present time, we can compare with sufficient accuracy the motive power of heat to that of a fall of water The motive power of a fall of water depends on its height and on the quantity of the liquid; the motive power of heat depends also on the quantity of caloric used, and on what may be termed, on what in fact we will call, the height of its fall, that is to say, the difference of temperature of the bodies between which the exchange of caloric is made. In the fall of water the motive power is exactly proportional to the difference of level between the higher and lower reservoirs. In the fall of caloric the motive power undoubtedly increases with the difference of temperature between the warm and the cold bodies.”

Heat (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. That explains why the cooling water gets warmer if its flow through the engine is smaller.

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.

Interpretation. The measured power is proportional to the square of the temperature difference between the hot and the cold water (Fig. 3.7). This is analogous to what we know of the power of an electric load resistor which is proportional to the square of the voltage. The energy released is proportional to temperature differences. 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. 3.7: Power depends upon the square of the temperature difference.

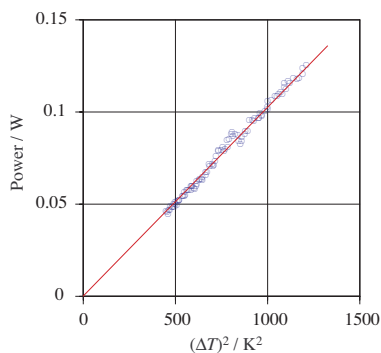


Figure 3.7: The electric power of a thermoelectric generator (a Peltier device between two heat reservoirs at different temperatures) depends upon the square of the temperature difference.

Thermocouples, resistors, and air thermometer. 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 thermocouples, which are actually thermoelectric generators—can be used to measure temperature differences (Fig. 3.7). The resistance of electric resistors commonly depends upon temperature (Fig. 3.8, 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. 3.8, right).

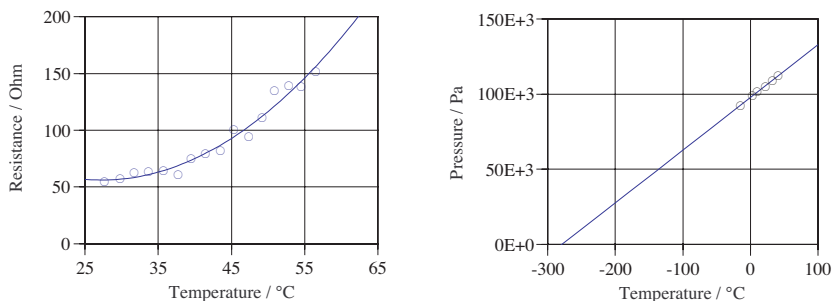


Figure 3.8: Resistance of a resistor as a function of temperature (left), and pressure of air at constant volume as a function of temperature (right; the relation is extrapolated backwards to zero pressure).

Interpretation. Using the gas thermometer, the pressure of a dilute gas is measured at constant volume. It is found that—if the temperature is not too low—the data points follow a linear relationship. This relation is extrapolated backwards to a pressure of zero. Since the same temperature is found for a zero value of pressure independent of the type of substance that is in a gaseous state, it is assumed that this value constitutes the lowest possible temperature that can be attained (it is -273°C). It turns out that a temperature scale that starts here with a value of zero serves as a measure of the thermal potential (thermal level). In contrast to electricity—but in analogy to hydraulics—the thermal potential is absolute: It has an absolute zero value.

Cooling and warming water in a can. Hot water is poured into a thin, shiny aluminum can. The water is stirred, and its temperature is recorded (Fig. 3.9). The temperature drops quickly at first, and more slowly later on. Finally, it reaches a constant value; interestingly this value is above 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. 3.10). In the case presented here, the drinking bottle is inside an insulating jacket, and the water is stirred during the observation.

Interpretation. Hot water loses heat through the wall of its container to the environment. The difference of temperatures between the water and the environment serves as the driving force for the flow of heat. The magnetic stirrer used to stir the water

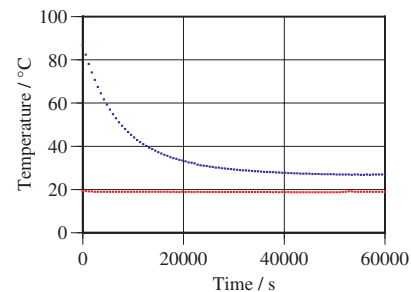


Figure 3.9: Temperature of hot water left standing in a thin-walled aluminum can. The final temperature is above the temperature of the environment (here about 20°C).

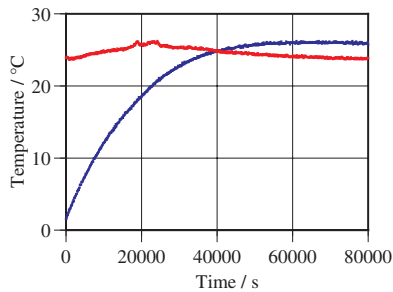


Figure 3.10: Temperature of cold water left standing in an insulated drinking bottle. The final temperature is above the temperature of the environment (the curve that starts at about 23°C).

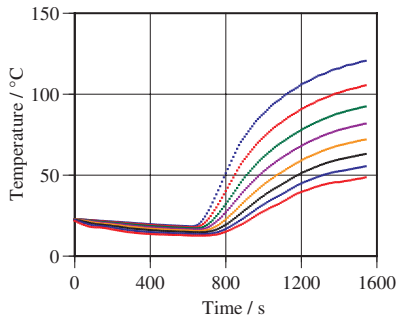
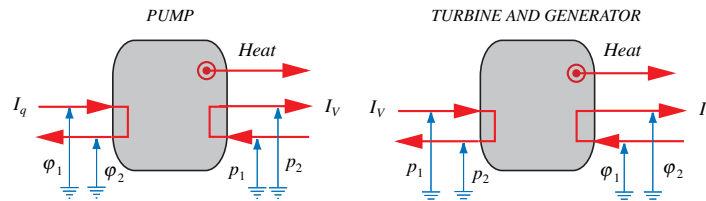


Figure 3.11: Temperatures of a long copper bar at different points as functions of time. First, the bar is at room temperature. One end is placed in cold water. After some time, the other end is heated electrically.

Figure 3.12: Process diagram of an electrically driven pump (left) and its reverse, a system of turbine and generator. Both systems produce heat.



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 we still need a temperature difference.

If the water is colder than the environment, heat will flow from the environment into the cold water. 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. 3.10).

Conduction through a long bar. A long, thin copper bar is stuck in ice water at one end, and heated electrically at the other end. The bar is not insulated from the surrounding air. The temperature of the bar is measured at eight points along its length (Fig. 3.11). Temperature values first drop a little. Soon after the heater is turned on, the temperature 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. First, some heat slowly flows out of the copper bar (which is at room temperature) into the ice water. Since the heat has to flow from points farther away through the part immersed in the cold water, those parts get colder more slowly.

When the electric heater is turned on, heat is produced 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 will be established.

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. 3.11 suggest, it is also similar to the flow of water through a chain of tanks (Fig. 1.10).

Reversing an electric pump. In an electric pump, the electric process drives the hydraulic one. At the same time, heat is generated. The system can be reversed, except for the production of heat. A system of turbine and generator reverses the electric and hydraulic processes (Fig. 1.13). However, heat is not destroyed, it is again produced.

Interpretation. Physical processes can be reversed, with one exception. This is the production of heat. If we had to reverse all 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.

Heat, caloric, entropy. The quantity we have been calling heat in our 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 a completely abstract quantity, has simple and intuitive roots. It is analogous to volume and to charge in fluids and electricity, respectively.

3.2 ENTROPY AND TEMPERATURE

Entropy. Thermal phenomena can be understood in terms of entropy and temperature. Entropy is the technical term for what in everyday life we would call heat. It is the substancelike thermal quantity that obeys a law of balance. The 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 (rubbing, burning, electric conduction, absorption of light...)
- it makes bodies warm, or is responsible for melting and evaporation, or it lets air expand...
- it can work, i.e., it can release energy and drive other processes (in heat engines),
- or it can be pumped if energy is available (heat pump).

Temperature. Temperature is the measure of hotness, i.e., it tells us how warm a body is. Hotness has a lowest possible value. Therefore we introduce a temperature scale which starts with a value of (absolute temperature scale or Kelvin scale).

Temperature 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. 3.14). Temperature is the thermal potential.

Balance of entropy. A quantity that cannot be produced (or destroyed) can only flow. Therefore, the quantity stored in a system can only be changed by inflow or outflow. It satisfies the type of law of balance encountered in electricity or fluids: The rate of change of the quantity stored equals the sum of all currents ($I_{S,net}$). Since entropy can be produced (but not destroyed), we must introduce a production rate Π_S that is included in the law of balance:

$$\dot{S} = I_{S,net} + \Pi_S \quad (3.1)$$

Entropy, temperature, and energy. The observation that heat can do work establishes the relation between entropy, temperature, and energy.

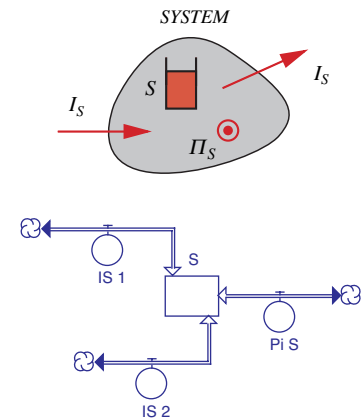


Figure 3.13: Energy transfer together with angular momentum depends upon the particular angular speed at which angular momentum is transferred.

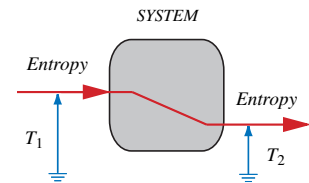


Figure 3.14: Energy transfer together with angular momentum depends upon the particular angular speed at which angular momentum is transferred.

3.3 MEASURING TEMPERATURE

Challenges of thermometry. (1) Temperature can be determined practically by any substance whose property or properties change if its hotness changes (thermoscopic property). Using such a thermoscopic property, a thermometer and an associated temperature scale can be introduced. Such a scale depends upon the material used in the thermometer. (2) The second challenge of thermometry is to find the value of the lowest possible temperature on the scale introduced in step one. (3) Thermodynamics rest upon a temperature scale which is independent of any material and can be used as an absolute scale. Such an absolute scale is needed to express the relations between entropy, temperature, and energy.

Empirical temperatures. A practical empirical temperature can be based upon the mercury thermometer: The change of volume of the liquid is used as the thermometric property. Using such a thermometer, we can introduce the Celsius scale: The temperature of the freezing point of water is set to 0°C , and 100°C is the temperature of vaporization of water at an air pressure of 1 bar.

Many other materials and material properties are used for thermometry. The electric resistance of electric conductors serves as a practical means for determining temperatures. Concrete measurements (Fig. 3.8) can be approximated by different functions, such as a quadratic one:

$$\rho_{el} = \rho_{el,ref} \left(1 + \alpha(T - T_{ref}) + \beta(T - T_{ref})^2 \right) \quad (3.2)$$

α and β are called the linear and quadratic temperature coefficients, respectively. T_{ref} is an arbitrary reference temperature.

Gas thermometer. An air thermometer yields another useful temperature scale. For a dilute gas, the gas pressure is a linear function of the temperature of a mercury thermometer (Fig. 3.8):

$$p = p_o(1 + \alpha\theta) \quad \text{where} \quad \alpha = 1/\theta_o \quad (3.3)$$

β is called the linear temperature coefficient of pressure. For all types of dilute gases the pressure vanishes at the same value of $\theta_o = -273^\circ\text{C}$. That means that all dilute gases have the same temperature coefficient of pressure, namely, $\beta = 1/273^\circ\text{C}$. Therefore we can introduce a new temperature T

$$T = \theta + \theta_o \quad \text{where} \quad \theta_o = 273^\circ\text{C} \quad (3.4)$$

which allows us to express the gas pressure in a simpler form:

$$P = \frac{P_o}{\theta_o} T \quad \text{where} \quad \frac{P_o}{\theta_o} = \frac{nR}{V}$$

T is called the (empirical) Kelvin temperature. A gas that satisfies the relation

$$pV = nRT \tag{3.5}$$

is called an *ideal gas*, and T is also called the *ideal gas temperature*.

Solution of the third challenge: The ideal gas temperature can be used as an *absolute temperature* scale (independent of any material) that is needed to express thermodynamic relations.

3.4 ENERGY IN THERMAL PROCESSES

Entropy releases energy when it flows from a higher to a lower thermal level (Fig. 3.15). Sadi Carnot compared heat (he called it caloric) to water which, when falling down, can drive an engine. Taking this idea we postulate that the thermal power (the rate at which energy is released when entropy falls from a higher to a lower temperature) is given by

$$P_{th} = -(T_2 - T_1)I_S \tag{3.6}$$

Entropy can be pumped like water, and as in the case of water the rate at which energy is needed to pump a current of entropy is also given by Eq.2.

A special case of pumping of entropy occurs when entropy is produced in an irreversible process (Fig. 3.16). If it is produced, the entropy appearing in a system has to be lifted from absolute zero to the temperature of the body. Therefore the relation between the rate at which energy is used to produce entropy (which is called dissipation rate), the entropy production rate and the temperature of the system is

$$P_{diss} = T \Pi_S \tag{3.7}$$

As in all other physical processes, the energy released does not appear out of the blue. It is usually brought to the system by a flow of entropy (Fig. 3.17). In conductive entropy transport we have

$$I_W = T I_S \tag{3.8}$$

3.5 ENTROPY-TEMPERATURE CHARACTERISTIC OF SIMPLE FLUIDS

In the simplest type of material (water, sandstone, iron...) the temperature simply depends upon how much entropy it contains. More precisely, the temperature of the material is a function of its specific entropy (entropy per mass) only. The relation between specific entropy and temperature must be measured, and it can be represented graphically (Fig. 3.18), in a table, or by an analytical approximation.

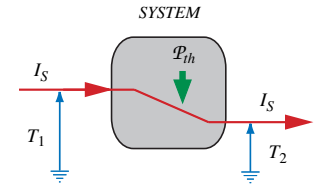


Figure 3.15: Energy transfer together with angular momentum depends upon the particular angular speed at which angular momentum is transferred.

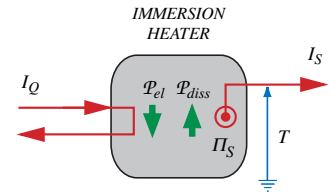


Figure 3.16: Process diagram of an immersion heater. The energy released in the electric process is completely dissipated (used to produce entropy).

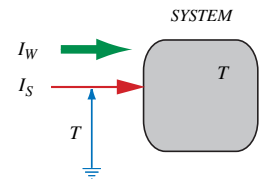


Figure 3.17: Process diagram of heating (inflow of entropy with an associated energy current).

Figure 3.18: Ts -diagram of water and of ethylene glycol. The relation for glycol is almost linear, whereas the one for water resembles an exponential function.

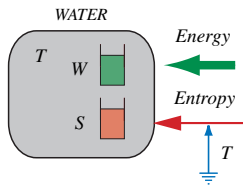


Figure 3.19: Heating means transferring entropy together with energy.

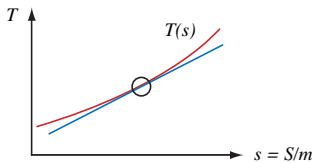


Figure 3.20: The slope of the Ts -relation tells us how easy it is to warm a body by heating.

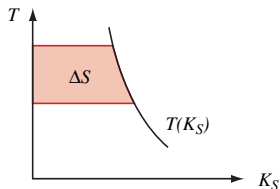
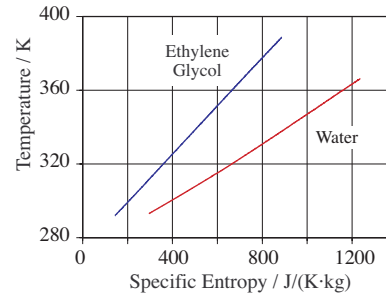


Figure 3.21: Temperature as a function of entropy capacitance. The diagram can be used to calculate the change of entropy of the body.



Measuring the entropy added to a body is simplest in the case of a liquid such as water since it can be stirred during heating which makes the temperature the same throughout the body. The entropy added can be calculated from the energy flowing from the heater (Fig. 3.19): $I_S = I_W / T$.

We introduce the specific entropy of a material as the ratio of the entropy it contains and the mass of the body:

$$s = S/m \quad (3.9)$$

Note that the choice of zero point of the entropy is arbitrary. Mechanical engineers often use 0°C for this purpose, chemists use 25°C .

The most significant feature in the Ts -diagram of a material 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* (Fig. 3.20):

$$\alpha_s = dT/ds \quad \text{or} \quad \dot{T} = \alpha_s \dot{s} \quad (3.10)$$

If $T(s)$ is a straight line in the Ts -diagram, the temperature can be calculated easily with the help of the warming factor:

$$T = T_{ref} + \alpha_s (s - s_{ref}) \quad (3.11)$$

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

$$k_S = ds/dT \quad \text{or} \quad \dot{s} = k_S \dot{T} \quad (3.12)$$

The *entropy capacitance*, $K = mk$, has the usual meaning of a capacitance, as in hydraulics or electricity. In general, the entropy capacitance depends upon the temperature. The change of entropy of a body can be calculated graphically from the temperature – entropy capacitance diagram (Fig. 3.21).

It is common as well to introduce the *specific heat* c which is calculated from the specific entropy capacitance by multiplying the latter by the temperature of the material ($c = Tk$). It allows us to determine directly the change of the energy of the simple materials discussed here:

$$\dot{w} = c\dot{T} \quad \text{where } c = Tk_s \quad (3.13)$$

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. 3.22). Note that the meaning of the specific heat is that of the (specific) temperature coefficient of energy (it is not a capacitance!). Some materials (water, solids at high temperature) have almost constant specific heats. For these materials, entropy and energy can be calculated easily:

$$s = s_{ref} + c \ln\left(T/T_{ref}\right) \quad \text{and} \quad w = w_{ref} + c\left(T - T_{ref}\right) \quad (3.14)$$

3.6 HEATING AND COOLING OF SIMPLE FLUIDS

When entropy flows we normally speak of heat transfer. Entropy flow is 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 entropy conductance G_S and the temperature difference

$$I_S = -G_S \Delta T \quad (3.15)$$

Usually, the conductance is written in terms the product of an (average) entropy transfer coefficient h_s and the surface A through which the flow takes place:

$$I_S = -h_s A \Delta T \quad (3.16)$$

The entropy flux through a surface is related to its associated energy current by the temperature T at the surface (Fig. 3.23):

$$I_W = -G_W \Delta T \quad \text{where} \quad G_W = T G_S \quad (3.17)$$

G_W is called the overall energy conductance. $h = Th_s$ is called the overall heat transfer coefficient.

Dynamical models. Combining this simple expression of an entropy or energy 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. 3.24). The simplest models of cooling of

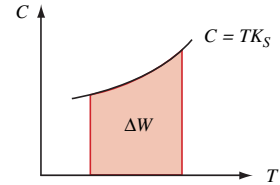


Figure 3.22: Energy capacitance (heat capacity) as a function of temperature, and energy change of a body.

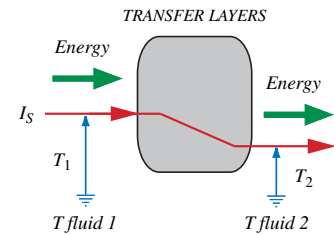


Figure 3.23: Entropy and energy transfer through layers from high to low temperature.

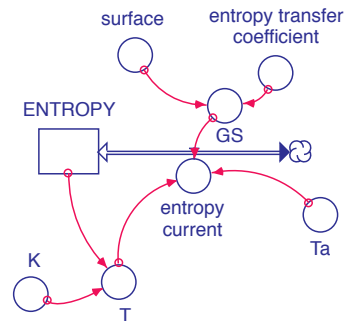


Figure 3.24: SD model diagram of the cooling (or heating) of a uniform body at temperature T .

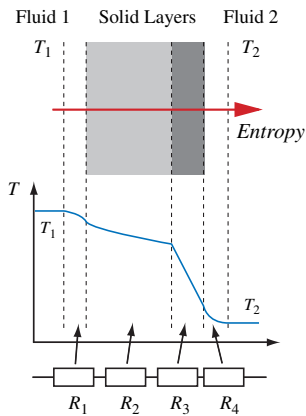


Figure 3.25: Entropy transfer through a series of layers. In each layer, the temperature drops.

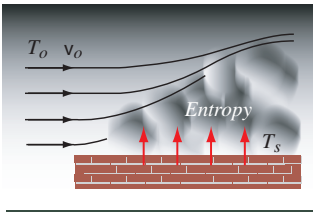


Figure 3.26: Entropy transfer from a solid body into a fluid (such as air or water) flowing by.

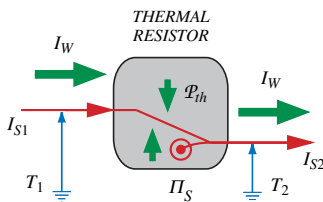


Figure 3.27: Entropy transfer due to a drop in temperature is dissipative: More entropy is produced.

bodies making use of constant material properties leads to an exponentially decreasing temperature.

Energy conductance. The energy conductance of a series of layers (Fig. 3.25) is equal to the inverse of the thermal resistance of this series:

$$G_W = \frac{1}{R_W} \quad (3.18)$$

which in turn is the sum of the resistances of all the layers:

$$R_W = R_{W,1} + R_{W,2} + R_{W,3} + \dots \quad (3.19)$$

The resistance of a layer depends upon its properties and the type of heat flow. The resistance of a flat conductive layer is

$$R_{W,cond} = \frac{1}{A} \frac{\Delta x}{\lambda} \quad (3.20)$$

λ is the thermal (energy) conductivity of the material ($\lambda_S = \lambda/T$ is the entropy conductivity), Δx is the thickness of the layer, and A is its cross section. Conductive resistances R_{cond} depend on the geometry of the body conducting heat. Therefore, the expression in Equ. 3.20 is different for container walls such as a thick cylindrical shell or a spherical shell.

The resistance of a convective interface between fluids and solids (Fig. 3.26) is

$$R_{W,conv} = \frac{1}{A h_{conv}} \quad (3.21)$$

Here, h_{conv} is the convective heat transfer coefficient which includes all the interesting and difficult details of this type of transfer which depends upon the characteristics of the flow (for example the speed) of the fluid past the solid surface.

3.7 FLUIDS IN THERMAL CONTACT

Heat transfer, i.e., conductive entropy transfer, is irreversible. Entropy is produced always if entropy flows from a hotter to a colder place. 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.

Since entropy production is a consequence of the transfer of heat, and the transfer takes places through transfer layers, we have to modify our model of a thermal resistive element (or elements). The process diagram of a thermal resistive element must include a source due to entropy production (Fig. 3.27 and Fig. 3.28).

The entropy production rate in a thermal resistive element is again calculated from the dissipation rate. The energy dissipated is the energy released by the fall of entropy from T_1 to T_2 (Fig. 3.27). The entropy production rate is

$$\Pi_S = \frac{T_1 - T_2}{T_2} I_{S1} \quad (3.22)$$

A possible representation of entropy production due to entropy transfer in a system dynamics model is the is shown in Fig. 3.29. The stock in the middle is as a symbol for the entropy of the transfer layer between the bodies. Since the transfer layer is a resistor, it does not store entropy. Therefore, the flow out of this element equals the sum of the flow in and the entropy production rate in the element:

$$I_{S2} = I_{S1} + \Pi_S \quad (3.23)$$

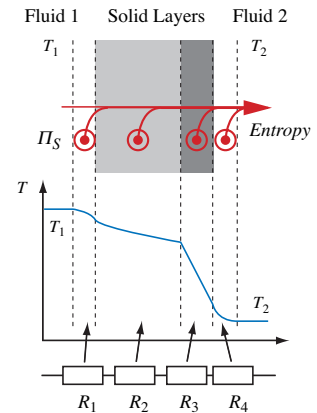
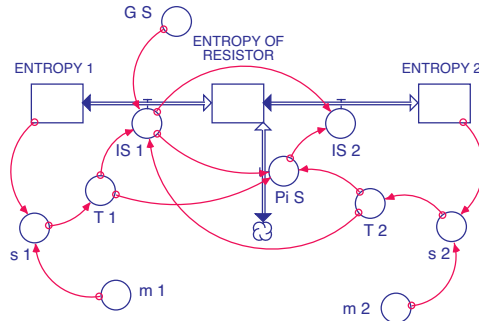


Figure 3.28: Entropy transfer through a series of layers. In each layer, the temperature drops. The transfer is dissipative (entropy is produced).

Figure 3.29: SD model diagram of heat transfer between two bodies. The transfer is dissipative.

3.8 MELTING AND VAPORIZATION

When a substance is melted or vaporized, entropy is needed for the phase change (Fig. 3.30). This means that entropy and energy are added to the substance, and the stored quantities of entropy and energy (of the system composed of both phases) increases. Some energy may be emitted (or absorbed) as the consequence of a volume change of the systems (this is important in vaporization, but much less so in melting). The laws of balance of entropy and energy for the systems are

$$\dot{S} = I_S \quad (3.24)$$

$$\dot{W} = I_{W,th} + I_{W,mech} \quad (3.25)$$

At the same time, a chemical process takes place (Fig. 3.31): One of the phases of the substance disappears, whereas the other is produced. The laws of balance of

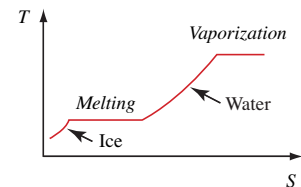


Figure 3.30: Ts -diagram of phase changes of water. Notice the horizontal section that represent the phases of melting and of vaporization.

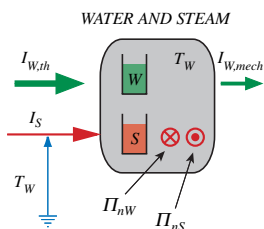


Figure 3.31: Process diagram of vaporization of water. Π_{nW} and Π_{nS} represent the rates at which the amount of substance of water and steam disappears or appears, respectively.

amount of substance are

$$\dot{n}_1 = \Pi_{n1} \quad , \quad \dot{n}_2 = \Pi_{n2} \quad , \quad \Pi_{n1} = -\Pi_{n2} \quad (3.26)$$

The constitutive law of a phase change expresses the relation between the rate at which entropy is needed and the rate at which one of the phases is produced. The two are proportional and simply depend on the substance and its conditions:

$$\dot{S} = \lambda_m \dot{n} \quad (3.27)$$

λ_m is called the *molar latent entropy of fusion* or of *vaporization* of the substance undergoing phase change. The *specific latent entropy* is calculated as follows: $\lambda = \lambda_m/M_o$, where M_o is the molar mass of the substance.

Since the temperature during phase change is constant, the energy flow accompanying the entropy flow in the heating during phase change is calculated by

$$I_{W,th} = q\dot{n} \quad , \quad q = T\lambda \quad (3.28)$$

Phase change temperatures and latent entropies depend upon the circumstances of the phase change. The most important factor is the pressure. This is particularly important in the case of vaporization. The temperature of vaporization is sensitive to the pressure of the fluid. There is a unique pressure-temperature relation for the phase change which is called the vapor pressure of the substance. The vapor pressure of water at 100°C is 1 bar. The Ts -diagram therefore depends upon the pressure of the fluid as well (see Chapter 8).

3.9 SPATIALLY CONTINUOUS MODELS OF CONDUCTION

In extended bodies, conditions change from point to point. So, for example, do the temperature, entropy, entropy current, and entropy production rate in conduction through a long bar. We can deal with this by dividing the bar into smaller elements in the direction of flow. Consider the law of balance of entropy for one of the elements (such as Element 3 in Fig. 3.32 which we label as element i) of the bar:

$$\frac{dS_i}{dt} = I_{S,i-1} - I_{S,i} + \Pi_{S,i} \quad (3.29)$$

We introduce densities and surface densities for the quantities in this equation:

$$\begin{aligned} S_i &= \rho_{S,i} A \Delta x \\ \Pi_{S,i} &= \pi_{S,i} A \Delta x \\ I_{S,i} &= j_{S,i} A \end{aligned}$$

Introducing these definitions into the equation of balance yields

$$\frac{\partial \rho_S}{\partial t} + \frac{\partial j_S}{\partial x} = \pi_S \quad (3.30)$$

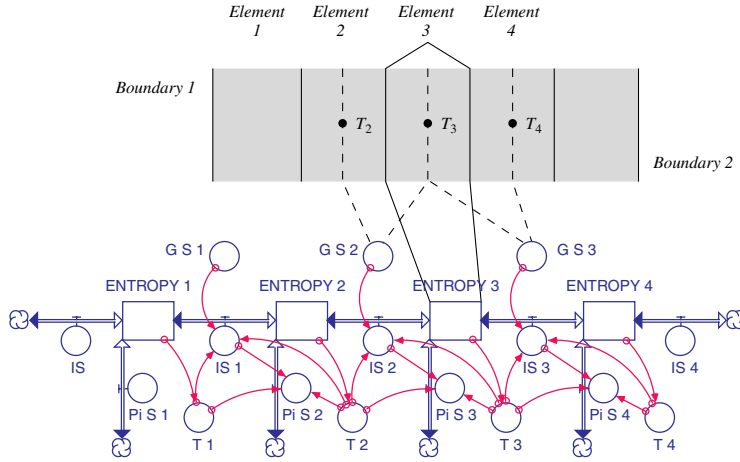


Figure 3.32: Flow (and production) of entropy in a long bar. The bar is divided into a finite number of elements (therefore the name *finite element method* for this type of model). Entropy flows from one element to another across the element surface, and entropy is produced in the volume occupied by the element.

The local form of the constitutive laws for the current density, the density of the production rate of entropy, and the rate of change of the density of entropy can be derived in the same manner:

$$\begin{aligned} j_S &= -\lambda_s \frac{dT}{dx} \\ \pi_S &= -\frac{1}{T} j_S \frac{dT}{dx} \\ \dot{\rho}_S &= k_s \dot{T} \end{aligned} \quad (3.31)$$

If we insert the second and third of these equations into Equ. 3.30, we are left with two first order partial differential equations for T and j_S . To these we have to add an initial condition, and two boundary conditions (at one or both ends of the rod).

3.10 THERMOELECTRIC GENERATORS AND COOLERS

Two observations regarding thermoelectric devices let us construct a dynamical model. One, temperature differences produce a conductive flow of entropy which produce a voltage (an open circuit voltage, if we do not connect a load). Second,

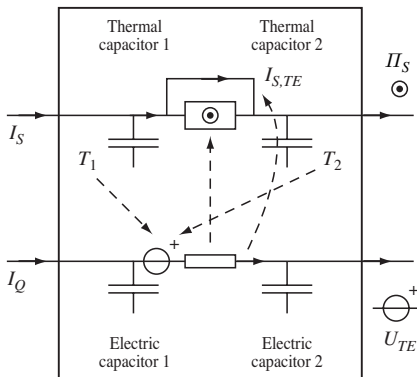


Figure 3.33: A dynamical model of a thermoelectric device. There are two storage elements for entropy (defining the temperatures of the cold and the hot end, respectively), and two capacitors (they define the high and low electric potentials). The elements comprise an electric generator (“electromotoric force”), a couple flow of charge and entropy, and conductive entropy and charge currents.

forcing and electric current through the element leads to pumping entropy in the direction opposite to its natural flow. Together, the observations tell us that entropy and charge transports are coupled. In a dynamical model (Fig. 3.33) we have two entropy storage elements (for the cold side and the hot side, respectively), and two electric capacitors (for the high potential and the low potential, respectively). Between these we have an electric generator and resistor, a thermal resistor, the conductive flows of charge and entropy, and the coupled flows of entropy and charge. Observation shows that the entropy current coupled to the charge current (the bypass in Fig. 3.33) grows proportionally to the flow of charge:

$$I_{S,TE} = \alpha I_Q \quad (3.32)$$

The coupling factor α is called the *Peltier coefficient*. On the other hand, we observe the thermoelectric voltage (open circuit voltage) to grow in proportion to the temperature difference across the device:

$$U_{TE} = \varepsilon (T_2 - T_1) \quad (3.33)$$

The coupling factor ε in this relation is called the *Seebeck coefficient*. Seebeck and Peltier coefficients are found to be equal:

$$\alpha = \varepsilon \quad (3.34)$$

(If they were not equal, the balance of energy would be violated for the thermoelectric processes taking place.) If there is no conductive flow of entropy, i.e., if the temperature difference across the Peltier device is equal to zero, the entropy flow given in Equ. 3.32 is the only one. Otherwise, the flow of entropy is the sum of thermoelectric and conductive currents:

$$I_S = \alpha I_Q - G_S (T_2 - T_1) \quad (3.35)$$

On the other hand, the thermoelectric voltage in Equ. 3.33 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:

$$U = \varepsilon (T_2 - T_1) + R I_Q \quad (3.36)$$

(Note that a voltage is a negative electric potential difference. This equation is analogous to what we have in the case of a real battery, having an internal resistance R_i .) The last two equations are the integral forms of the usual partial differential equation representation of thermoelectric processes.