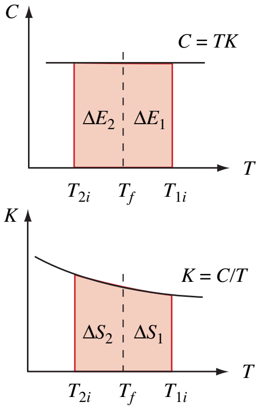


SOLUTION: Water is a substance having constant temperature coefficients of energy (specific heats). For two equal amounts, the *CT* diagram (Fig. 4.39) is the same horizontal line. Using the balance of energy on the entire process from beginning (*i*) to end (*f*), we see that

$$\Delta E = \Delta E_1 + \Delta E_2 = 0$$

$$C\left(T_f - T_{1i}\right) + C\left(T_f - T_{2i}\right) = 0$$

$$T_f = \frac{1}{2}\left(T_{1i} + T_{2i}\right)$$

which we can read off the *CT* diagram shown here. The associated *KT* diagram (Fig. 4.38) 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 very 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

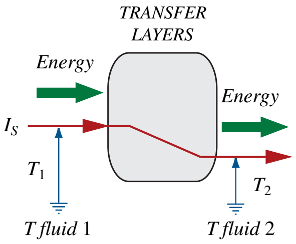


Figure 4.42: Entropy and energy transfer through layers from higher to lower temperature.

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. 4.42):

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

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:

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

The entropy flux through a surface is related to its associated energy current by the temperature T at the surface of the body (Fig. 4.42):

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

$G_E = TG_S$ 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

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

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. 4.43), 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. 4.43). 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. 4.44) in which the temperature changes in the direction of the flow of entropy.

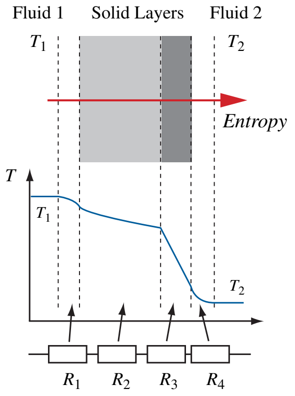


Figure 4.43: Entropy transfer through a series of layers. In each layer, the temperature drops. Layers may be considered thermal resistors.

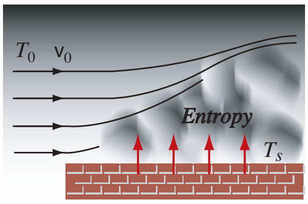


Figure 4.44: Entropy transfer from a solid body into a fluid (such as air or water) flowing past the solid surface.

---

[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* it is associated with transfer coefficients for energy.

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. 4.43). Simultaneously, radiation may contribute to the loss of entropy from a warm surface. 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. 4.43).

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. 4.45). 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.

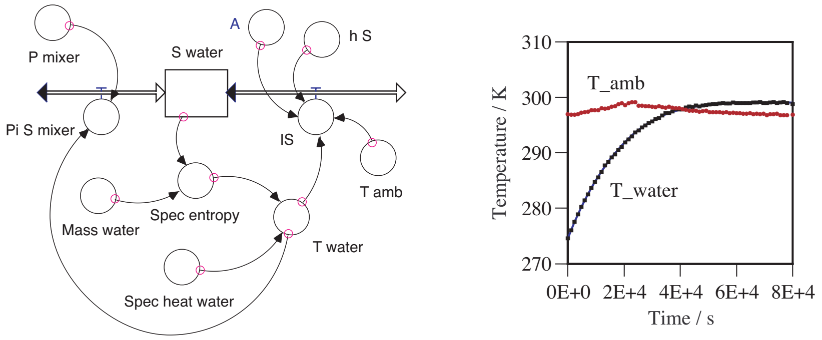


Figure 4.45: Left: SD model diagram of the cooling (or heating) of a uniform body at temperature *T*. Right: Application to the heating of cold water in a drinking bottle. The water is stirred, the aluminum bottle is inside an insulating bag. The simulation result is barely visible since it fits measured water temperatures 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

$$\frac{dS_w}{dt} = I_S + \Pi_S \qquad \textbf{(4.49)}$$

We need three constitutive laws to complete the model: (1) An expression for the relation 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. 4.45. The law of balance and the constitutive relations have been implemented in the system dynamics model in the same figure (Fig. 4.45, 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 is 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

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

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

$$
\begin{aligned}
&\frac{C}{T}\frac{dT}{dt} = -A\frac{h}{T}\left(T - T_a\right) \\
&\frac{dT}{dt} = -\frac{Ah}{C}\left(T - T_a\right) \quad , \quad T(t=0) = T_0
\end{aligned}
$$

The solution of this differential equation with its initial condition is

$$
\begin{aligned}
&T(t) = T_a + \left(T_0 - T_a\right)\exp\left(-t/\tau\right) \\
&\tau = C/(Ah)
\end{aligned}
\tag{4.51}
$$

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 a thermal power accompanying the phenomenon (Fig. 4.46)—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 simple 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. 4.46 and Equ.(4.32)):

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

Combining these expressions for lost power leads to

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

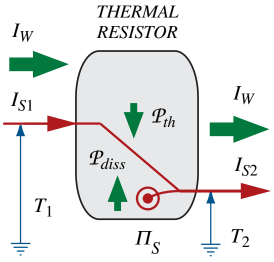


Figure 4.46: Entropy transfer due to a drop in temperature is dissipative: More entropy is produced.

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. 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 12).

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. 4.47). 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. 4.48. 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 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:

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

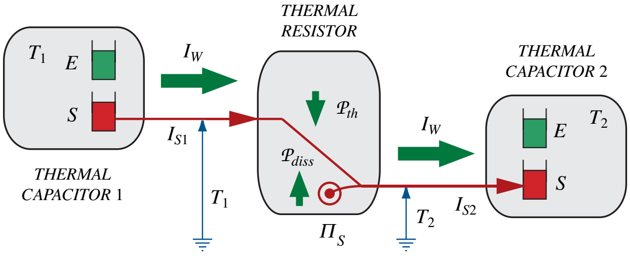


Figure 4.47: Model of two spatially uniform bodies in thermal contact. Processes in these bodies are assumed to be reversible. Irreversibility originates in the interface between the bodies.

This is equivalent to the junction rule known from electric or hydraulic circuits. If the model in Fig. 4.48 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.

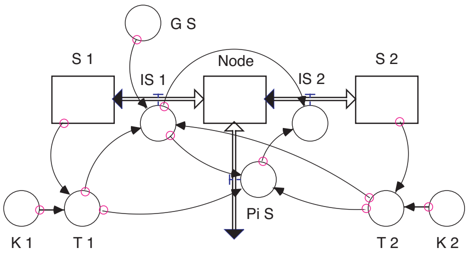


Figure 4.48: SD model diagram of heat transfer between two bodies. The transfer is dissipative. The central storage element serves as a node for the relation between entropy currents and entropy production rate.

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. 4.49). 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

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

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. 4.49, bottom). With the relations used in this section and with a little algebra, we arrive at:

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

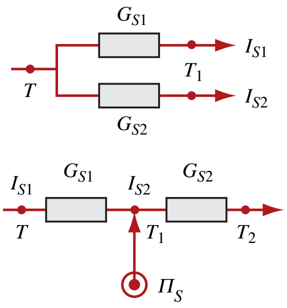


Figure 4.49: Parallel (top) and series (bottom) transfer layers.

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:

$$\frac{1}{G_E} = \frac{1}{G_{E1}} + \frac{1}{G_{E2}} \tag{4.56}$$

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; an enlargements of the initial rise is seen in the diagram on the right).

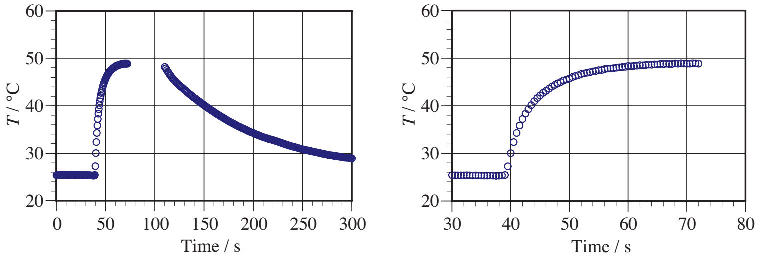
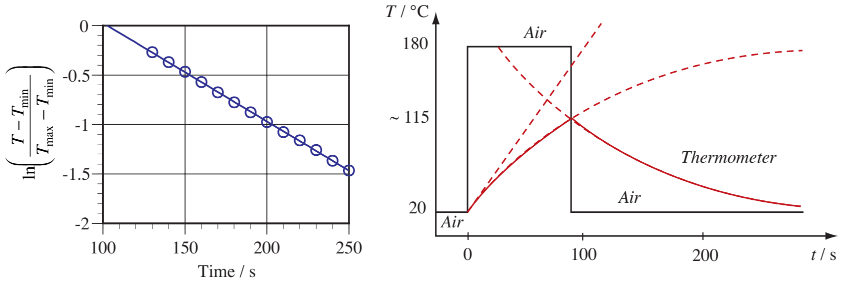


Figure Ex.18.1

(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·m^2). 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 64% of the initial temperature difference. This difference is 49°C – 25.5°C = 23.5 K. 64% 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 = 20·14 W/(K·m^2) = 280 W/(K·m^2) 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.