3.3: Heat Transfer

This section describes irreversible and reversible heat transfer. Keep in mind that when this e-book refers to *heat transfer* or *heat flow*, energy is being transferred across the boundary on account of a temperature gradient at the boundary. The transfer is always in the direction of decreasing temperature.

We may sometimes wish to treat the temperature as if it is discontinuous at the boundary, with different values on either side. The transfer of energy is then from the warmer side to the cooler side. The temperature is not actually discontinuous; instead there is a thin zone with a temperature gradient.

3.3.1 Heating and cooling

As an illustration of irreversible heat transfer, consider a system that is a solid metal sphere. This spherical body is immersed in a well-stirred water bath whose temperature we can control. The bath and the metal sphere are initially equilibrated at temperature $T_1 = 300.0\,\mathrm{K}$, and we wish to raise the temperature of the sphere by one kelvin to a final uniform temperature $T_2 = 301.0\,\mathrm{K}$.

One way to do this is to rapidly increase the external bath temperature to $301.0\,\mathrm{K}$ and keep it at that temperature. The temperature difference across the surface of the immersed sphere then causes a spontaneous flow of heat through the system boundary into the sphere. It takes time for all parts of the sphere to reach the higher temperature, so a temporary internal temperature gradient is established. Thermal energy flows spontaneously from the higher temperature at the boundary to the lower temperature in the interior. Eventually the temperature in the sphere becomes uniform and equal to the bath temperature of $301.0\,\mathrm{K}$.

Figure 3.3(a) graphically depicts temperatures within the sphere at different times during the heating process. Note the temperature gradient in the intermediate states. Because of the gradient, these states cannot be characterized by a single value of the temperature. If we were to suddenly isolate the system (the sphere) with a thermally-insulated jacket while it is in one of these states, the state would change as the temperature gradient rapidly disappears. Thus, the intermediate states of the spontaneous heating process are not equilibrium states, and the rapid heating process is not reversible.

To make the intermediate states more nearly uniform in temperature, with smaller temperature gradients, we can raise the temperature of the bath at a slower rate. The sequence of states approached in the limit of infinite slowness is indicated in Fig. 3.3(b). In each intermediate state of this limiting sequence, the temperature is perfectly uniform throughout the sphere and is equal to the external bath temperature. That is, each state has thermal equilibrium both internally and with respect to the surroundings. A single temperature now suffices to define the state at each instant. Each state is an *equilibrium* state because it would have no tendency to change if we isolated the system with thermal insulation. This limiting sequence of states is a *reversible* heating process.

The reverse of the reversible heating process is a reversible cooling process in which the temperature is again uniform in each state. The sequence of states of this reverse process is the limit of the spontaneous cooling process depicted in Fig. 3.3(c) as we decrease the bath temperature more and more slowly.

In any real heating process occurring at a finite rate, the sphere's temperature could not be perfectly uniform in intermediate states. If we raise the bath temperature very slowly, however, the temperature in all parts of the sphere will be very close to that of the bath. At any point in this very slow heating process, it would then take only a small decrease in the bath temperature to start a *cooling* process; that is, the practically-reversible heating process would be reversed.

The important thing to note about the temperature gradients shown in Fig. 3.3(c) for the spontaneous cooling process is that none resemble the gradients in Fig. 3.3(a) for the spontaneous heating process—the gradients are in opposite directions. It is physically impossible for the sequence of states of either process to occur in the reverse chronological order, for that would have thermal energy flowing in the wrong direction along the temperature gradient. These considerations show that a spontaneous heat transfer is irreversible. Only in the reversible limits do the heating and cooling processes have the same intermediate states; these states have no temperature gradients.

Although the spontaneous heating and cooling processes are irreversible, the energy transferred into the system during heating can be fully recovered as energy transferred back to the surroundings during cooling, provided there is no irreversible work. This recoverability of irreversible heat is in distinct contrast to the behavior of irreversible work.

3.3.2 Spontaneous phase transitions

Consider a different kind of system, one consisting of the liquid and solid phases of a pure substance. At a given pressure, this kind of system can be in transfer equilibrium at only one temperature: for example, water and ice at 1.01 bar and 273.15 K Suppose the system is initially at this pressure and temperature. Heat transfer into the system will then cause a phase transition from solid to liquid (Sec. 2.2.2). We can carry out the heat transfer by placing the system in thermal contact with an external water bath at a higher temperature than the equilibrium temperature, which will cause a temperature gradient in the system and the melting of an amount of solid proportional to the quantity of energy transferred.

The closer the external temperature is to the equilibrium temperature, the smaller are the temperature gradients and the closer are the states of the system to equilibrium states. In the limit as the temperature difference approaches zero, the system passes through a sequence of equilibrium states in which the temperature is uniform and constant, energy is transferred into the system by heat, and the substance is transformed from solid to liquid. This idealized process is an *equilibrium* phase transition, and it is a reversible process.
