4.5: Irreversible Processes

We know that during a reversible process of a closed system, each infinitesimal entropy change $\mathrm{d}S$ is equal to $đq/T_\mathrm{b}$ and the finite change ΔS is equal to the integral $\int(đq/T_\mathrm{b})$—but what can we say about $\mathrm{d}S$ and ΔS for an *irreversible* process?

The derivation of this section will show that for an infinitesimal irreversible change of a closed system, $\mathrm{d}S$ is greater than $đq/T_\mathrm{b}$, and for an entire process ΔS is greater than $\int(đq/T_\mathrm{b})$. That is, the *equalities* that apply to a reversible process are replaced, for an irreversible process, by *inequalities*.

The derivation begins with irreversible processes that are adiabatic, and is then extended to irreversible processes in general.

4.5.1 Irreversible adiabatic processes

Consider an arbitrary irreversible adiabatic process of a closed system starting with a particular initial state A. The final state B depends on the path of this process. We wish to investigate the sign of the entropy change $\Delta S_{\mathrm{A}\rightarrow\mathrm{B}}$. Our reasoning will depend on whether or not there is work during the process.

If there is work along any infinitesimal path element of the irreversible adiabatic process ($đw \neq 0$), we know from experience that this work would be different if the work coordinate or coordinates were changing at a different rate, because energy dissipation from internal friction would then be different. In the limit of infinite slowness, an adiabatic process with initial state A and the same change of work coordinates would become reversible, and the net work and final internal energy would differ from those of the irreversible process. Because the final state of the reversible adiabatic process is different from B, there is no reversible adiabatic path with work between states A and B.

> All states of a reversible process, including the initial and final states, must be equilibrium states. There is therefore a conceptual difficulty in considering reversible paths between two states if either of these states are nonequilibrium states. In such a case we will assume that the state has been replaced by a constrained equilibrium state of the same entropy as described in Sec. 4.4.3.

If, on the other hand, there is no work along any infinitesimal path element of the irreversible adiabatic process ($đw$=0), the process is taking place at constant internal energy U in an *isolated* system. A reversible limit cannot be reached without heat or work (Sec. 3.2.1). Thus any reversible adiabatic change from state A would require work, causing a change of U and preventing the system from reaching state B by any reversible adiabatic path.

So regardless of whether or not an irreversible adiabatic process A→B involves work, there is no *reversible* adiabatic path between A and B. The only reversible paths between these states must be *non*adiabatic. It follows that the entropy change $\Delta S_{\mathrm{A}\rightarrow\mathrm{B}}$, given by the value of $đq/T_\mathrm{b}$ integrated over a reversible path from A to B, cannot be zero.

Next we ask whether $\Delta S_{\mathrm{A}\rightarrow\mathrm{B}}$ could be negative. In each infinitesimal path element of the irreversible adiabatic process A→B, $đq$ is zero and the integral $\int_\mathrm{A}^\mathrm{B}(đq/T_\mathrm{b})$ along the path of this process is zero. Suppose the system completes a cycle by returning along a different, reversible path from state B back to state A. The Clausius inequality (Eq. 4.4.3) tells us that in this case the integral $\int_\mathrm{B}^\mathrm{A}(đq/T_\mathrm{b})$ along the reversible path cannot be positive. But this integral for the reversible path is equal to $-\Delta S_{\mathrm{A}\rightarrow\mathrm{B}}$, so $\Delta S_{\mathrm{A}\rightarrow\mathrm{B}}$ cannot be negative.

We conclude that because the entropy change of the irreversible adiabatic process A→B cannot be zero, and it cannot be negative, it must be *positive*.

In this derivation, the initial state A is arbitrary and the final state B is reached by an irreversible adiabatic process. If the two states are only infinitesimally different, then the change is infinitesimal. Thus for an infinitesimal change that is irreversible and adiabatic, $\mathrm{d}S$ must be *positive*.

4.5.2 Irreversible processes in general

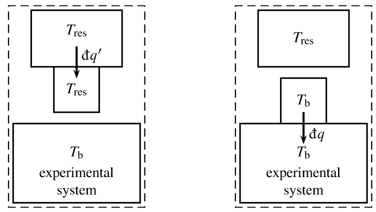

Figure 4.11 Supersystem including the experimental system, a Carnot engine (square box), and a heat reservoir. The dashed rectangle indicates the boundary of the supersystem.

To treat an irreversible process of a closed system that is nonadiabatic, we proceed as follows. As in Sec. 4.4.1, we use a Carnot engine for heat transfer across the boundary of the experimental system. We move the boundary of the supersystem of Fig. 4.8 so that the supersystem now includes the experimental system, the Carnot engine, and a heat reservoir of constant temperature T_{res}, as depicted in Fig. 4.11. During an irreversible change of the experimental system, the Carnot engine undergoes many infinitesimal cycles. During each cycle, the Carnot engine exchanges heat $đq'$ at temperature T_{res} with the heat reservoir and heat $đq$ at temperature T_b with the experimental system, as indicated in the figure. We use the sign convention that $đq'$ is positive if heat is transferred to the Carnot engine, and $đq$ is positive if heat is transferred to the experimental system, in the directions of the arrows in the figure.

The supersystem exchanges work, but not heat, with its surroundings. During one infinitesimal cycle of the Carnot engine, the net entropy change of the Carnot engine is zero, the entropy change of the experimental system is dS, the heat transferred between the Carnot engine and the experimental system is $đq$, and the heat transferred between the heat reservoir and the Carnot engine is given by $đq' = T_{res}\,đq/T_b$ (Eq. 4.4.1). The heat transfer between the heat reservoir and Carnot engine is reversible, so the entropy change of the heat reservoir is

$$dS_{res} = -\frac{đq'}{T_{res}} = -\frac{đq}{T_b} \tag{4.5.1}$$

The entropy change of the supersystem is the sum of the entropy changes of its parts:

$$dS_{ss} = dS + dS_{res} = dS - \frac{đq}{T_b} \tag{4.5.2}$$

The process within the supersystem is adiabatic and includes an irreversible change within the experimental system, so according to the conclusions of Sec. 4.5.1, dS_{ss} is positive. Equation 4.5.2 then shows that dS, the infinitesimal entropy change during the irreversible change of the experimental system, must be greater than $đq/T_b$:

$$dS > \frac{đq}{T_b} \tag{4.5.3}$$
(irreversible change, closed system)

This relation includes the case of an irreversible *adiabatic* change, because it shows that if $đq$ is zero, dS is greater than zero.

By integrating both sides of Eq. 4.5.3 between the initial and final states of the irreversible process, we obtain a relation for the finite entropy change corresponding to many infinitesimal cycles of the Carnot engine:

$$\Delta S > \int \frac{đq}{T_b} \tag{4.5.4}$$
(irreversible process, closed system)