3.9: Irreversible Work and Internal Friction

Consider an irreversible adiabatic process of a closed system in which a work coordinate X changes at a finite rate along the path, starting and ending with equilibrium states. For a given initial state and a given change ΔX, the work is found to be less positive or more negative the more slowly is the rate of change of X. The work is least positive or most negative in the reversible limit—that is, the least work needs to be done on the system, or the most work can be done by the system on the surroundings. This *minimal work principle* has already been illustrated in the sections of this chapter describing expansion work, work in a gravitational field, and electrical work with a galvanic cell.

Let the work during an irreversible adiabatic process be w_{irr}, and the reversible adiabatic work for the same initial state and the same value of ΔX be w_{rev}. w_{irr} is algebraically greater than w_{rev}, and we can treat the difference $w_{\text{irr}} - w_{\text{rev}}$ as *excess work* w_{ex} that is positive for an irreversible process and zero for a reversible process.

Conceptually, we can attribute the excess work of an irreversible adiabatic process to *internal friction* that dissipates other forms of energy into thermal energy within the system. Internal friction occurs only during a process with work that is irreversible . Internal friction is not involved when, for example, a temperature gradient causes heat to flow spontaneously across the system boundary, or an irreversible chemical reaction takes place spontaneously in a homogeneous phase. Nor is internal friction necessarily involved when positive work increases the thermal energy: during an infinitely slow adiabatic compression of a gas, the temperature and thermal energy increase but internal friction is absent—the process is reversible.

During a process with irreversible work, energy dissipation can be either partial or complete. *Dissipative work*, such as the stirring work and electrical heating described in previous sections, is irreversible work with complete energy dissipation. The final equilibrium state of an adiabatic process with dissipative work can also be reached by a path in which positive heat replaces the dissipative work. This is a special case of the minimal work principle.

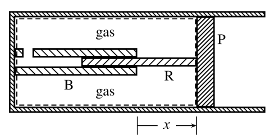

Figure 3.18 Cylinder and piston with internal sliding friction. The dashed rectangle indicates the system boundary. P—piston; R—internal rod attached to the piston; B—lubricated bushing fixed inside the cylinder. A fixed amount of an ideal gas fills the remaining space inside the cylinder.

As a model for work with partial energy dissipation, consider the gas-filled cylinder-and-piston device depicted in Fig. 3.18. This device has an obvious source of internal friction in the form of a rod sliding through a bushing. The contact between the rod and bushing is assumed to be lubricated to allow the piston to move at velocities infinitesimally close to zero. The *system* consists of the contents of the cylinder to the left of the piston, including the gas, the rod, and the bushing; the piston and cylinder wall are in the surroundings.

From Eq. 3.1.2, the energy transferred as work across the boundary of this system is

$$w = -\int_{x_1}^{x_2} F^{\text{sys}}\, \mathrm{d}x \tag{3.9.1}$$

where x is the piston position and F^{sys} is the component in the direction of increasing x of the force exerted by the system on the surroundings at the moving boundary.

For convenience, we let V be the volume of the gas rather than that of the entire system. The relation between changes of V and x is $\mathrm{d}V = A_{\text{s}}\,\mathrm{d}x$ where A_{s} is the cross-section area of the cylinder. With V replacing x as the work coordinate, Eq. 3.9.1 becomes

$$w = -\int_{V_1}^{V_2} (F^{\text{sys}}/A_{\text{s}})\,\text{d}V \tag{3.9.2}$$

Equation 3.9.2 shows that a plot of $F^{\text{sys}}/A_{\text{s}}$ as a function of V is an indicator diagram (Sec. 3.5.4), and that the work is equal to the negative of the area under the curve of this plot.

We can write the force F^{sys} as the sum of two contributions:

$$F^{\text{sys}} = pA_{\text{s}} + F_{\text{fric}}^{\text{int}} \tag{3.9.3}$$

(This equation assumes that the gas pressure is uniform, and that a term for the acceleration of the rod is negligible.) Here p is the gas pressure, and $F_{\text{fric}}^{\text{int}}$ is the force on the rod due to internal friction with sign opposite to that of the piston velocity $\text{d}x/\text{d}t$. Substitution of this expression for F^{sys} in Eq. 3.9.2 gives

$$w = -\int_{V_1}^{V_2} p\,\text{d}V - \int_{V_1}^{V_2} (F_{\text{fric}}^{\text{int}}/A_{\text{s}})\,\text{d}V \tag{3.9.4}$$

The first term on the right is the work of expanding or compressing the gas. The second term is the frictional work: $w_{\text{fric}} = -\int (F_{\text{fric}}^{\text{int}}/A_{\text{s}})\,\text{d}V$. The frictional work is positive or zero, and represents the energy dissipated within the system by internal sliding friction.

Consider the situation when the piston moves very slowly in one direction or the other. In the limit of infinite slowness $F_{\text{fric}}^{\text{int}}$ and w_{fric} vanish, and the process is reversible with expansion work given by $w = -\int p\,\text{d}V$.

The situation is different when the piston moves at an appreciable finite rate. The frictional work w_{fric} is then positive. As a result, the irreversible work of expansion is less negative than the reversible work for the same volume increase, and the irreversible work of compression is more positive than the reversible work for the same volume decrease. These effects of piston velocity on the work are consistent with the minimal work principle.

> The piston velocity, besides affecting the frictional force on the rod, has an effect on the force exerted by the gas on the piston as described in Sec. 3.4.1. At large finite velocities, this latter effect tends to further decrease F^{sys} during expansion and increase it during compression, and so is an additional contribution to internal friction. If turbulent flow is present within the system, that would also be a contribution.

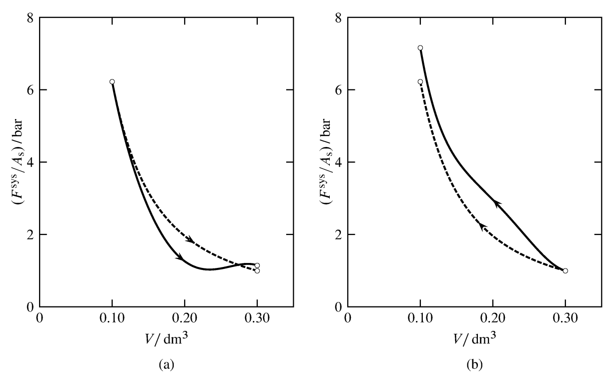

Figure 3.19 Indicator diagrams for the system of Fig. 3.18.
Solid curves: $F^{\text{sys}}/A_{\text{s}}$ for irreversible adiabatic volume changes at finite rates in the directions indicated by the arrows.
Dashed curves: $F^{\text{sys}}/A_{\text{s}} = p$ along a reversible adiabat.
Open circles: initial and final equilibrium states.
(a) Adiabatic expansion.
(b) Adiabatic compression.

Figure 3.19 shows indicator diagrams for adiabatic expansion and compression with internal friction. The solid curves are for irreversible processes at finite rates, and the dashed curves are for reversible processes with the same initial states as the irreversible processes. The areas under the curves confirm that the work for expansion is less negative along the irreversible path than along the reversible path, and that for compression the work is more positive along the irreversible path than along the reversible path.

Because of these differences in work, the final states of the irreversible processes have greater internal energies and higher temperatures and pressures than the final states of the reversible processes with the same volume change, as can be seen from the positions on the indicator diagrams of the points for the final equilibrium states. The overall change of state during the irreversible expansion or compression is the same for a path in which the reversible adiabatic volume change is followed by positive heat at constant volume. Since ΔU must be the same for both paths, the heat has the same value as the excess work $w_{\mathrm{ex}} = w_{\mathrm{irr}} - w_{\mathrm{rev}}$. The excess work and frictional work are not equal, because the thermal energy released by frictional work increases the gas pressure, making w_{ex} less than w_{fric} for expansion and greater than w_{fric} for compression. There seems to be no general method by which the energy dissipated by internal friction can be evaluated, and it would be even more difficult for an irreversible process with both work and heat.

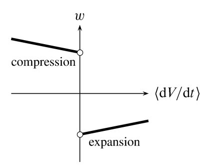

Figure 3.20 Adiabatic expansion work with internal friction for a fixed magnitude of ΔV, as a function of the average rate of volume change. The open circles indicate the reversible limits.

Figure 3.20 shows the effect of the rate of change of the volume on the adiabatic work for a fixed magnitude of the volume change. Note that the work of expansion and the work of compression have opposite signs, and that it is only in the reversible limit that they have the same *magnitude*. The figure resembles Fig. 3.17 for electrical work of a galvanic cell with the horizontal axis reversed, and is typical of irreversible work with partial energy dissipation.