

7.18: Reversible vs. Irreversible Pressure-Volume Work

In Section 7.16 we consider heat transfer in reversible processes. Similar considerations apply to the exchange of work between a system and its surroundings. When we use a piston to compress a gas in a cylinder, we must apply sufficient inward force on the piston to overcome the outward force applied by the gas. In any real system, it is necessary also to overcome the force of friction in order to slide the piston into the cylinder. We ignore friction, imagining that we can make its effects arbitrarily small.

The gas can be compressed only if the applied pressure exceeds the gas pressure. If the applied pressure equals the gas pressure, the piston remains stationary. If the applied pressure is greater than the gas pressure by any ever-so-small amount, the gas will be compressed. Conversely, if the applied pressure is infinitesimally less than the gas pressure, the gas will expand. The work done under such conditions is reversible work; an arbitrarily small change in the relative pressures can reverse the direction in which the piston moves. We summarize these conditions by saying that reversible pressure-volume work can occur only if the system and its surroundings are at mechanical equilibrium.

Now, let us think about calculating the reversible work for isothermally compressing a gas by sliding a piston into a cylinder. In any real experiment, we must have $P_{\text{applied}} > P_{\text{gas}}$, and any real experiment is necessarily irreversible. In a reversible experiment, we have $P_{\text{applied}} = P_{\text{gas}} = P$, and the reversible work, w^{rev} , is

$$\begin{aligned} w^{\text{rev}} &= \int_{V_1}^{V_2} -P_{\text{applied}} dV \\ &= \int_{V_1}^{V_2} -P_{\text{gas}} dV \end{aligned}$$

For one mole of an ideal gas, we have $P = RT/V$. Since the temperature is constant, the reversible isothermal work becomes

$$w^{\text{rev}} = \int_{V_1}^{V_2} -\frac{RT}{V} dV = -RT \ln \frac{V_2}{V_1}$$

where V_1 and V_2 are the initial and final volumes of the gas, respectively. This has a straightforward graphical interpretation. For an ideal gas at constant temperature, $-P_{\text{gas}}$ is inversely proportional to V_{gas} . As sketched in Figure 7, the reversible work corresponds to the area between this curve and the abscissa and between the initial, V_1 , and the final, V_2 , gas volumes.

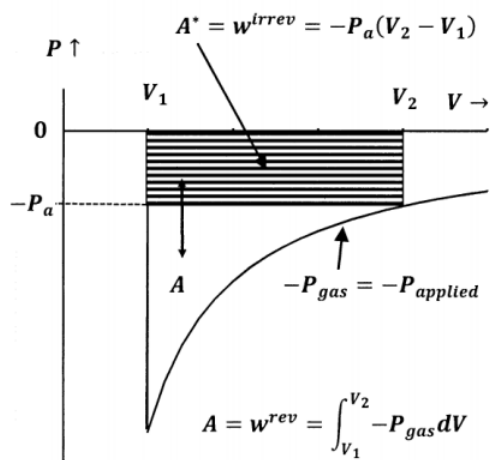


Figure 7. Reversible versus irreversible expansion of an ideal gas.

In contrast, an irreversible expansion corresponds to movement of the piston when $P_{\text{gas}} > P_{\text{applied}}$, or equivalently, $-P_{\text{gas}} < -P_{\text{applied}}$. Therefore, the work done on the gas is less in the reversible case than it is in the irreversible case. (Both work terms are less than zero. The absolute value of the reversible work is greater than the absolute value of the irreversible work.) From our definitions of reversible and irreversible pressure-volume work, we have $dw^{\text{rev}} < dw^{\text{irrev}}$ and $w^{\text{rev}} < w^{\text{irrev}}$, so long as the initial and final states are the same in the irreversible process as they are in the reversible constant-temperature process. The shaded area in Figure 7 represents the work done on the gas when the applied pressure is instantaneously decreased to the final pressure, P_a , attained by the gas in the reversible process.

For the reversible process, the pressure–volume curve accurately depicts the state of the gas as the volume increase takes place. The temperature of the gas is constant along this curve. While we can trace a similar line of pressure–volume points for the irreversible expansion, this line does not define a set of intermediate states that the system occupies during the irreversible expansion. The state of the gas is well defined only in the equilibrium state that precedes the irreversible pressure drop and in the equilibrium state that the system ultimately attains. It is convenient to describe these two processes as a reversible process and a spontaneous process that “take the system from the same initial state to the same final state.” However, this language obscures a significant point. In the initial state for the reversible process, we have

$$P_{gas} = RT/V_1 = P_{applied}$$

In the initial state for the spontaneous process, we have

$$P_{gas} = \frac{RT}{V_1}$$

and

$$P_{applied} = \frac{RT}{V_2}$$

What we mean, of course, is that the values of all of the state functions for the hypothetical initial state of the spontaneous process are the same as those for the equilibrium initial state of the reversible process.

So long as we can say that the process takes the system from the same initial state to the same final state, a similar argument can be made for reversible and irreversible work of any kind. Whatever the force, the isothermal reversible work done on the system is always less than the irreversible work for taking the system between the same two states. This is an important result. In [Chapter 9](#), we find that it is a logical consequence of the second law of thermodynamics.

Finally, let us consider a reversible process in which a system completes a pressure–volume cycle. The system traverses a closed path in the pressure–volume plane. Such a path is depicted in Figure 8. We let the smallest and largest volumes reached during the cycle be V_ℓ and V_h , respectively. The closed path is composed of a high-pressure segment and a low-pressure segment that meet at V_ℓ and V_h . On each of these segments, the pressure is a function of volume. We let pressures on the high- and low-pressure segments be $P_h(V)$ and $P_\ell(V)$, respectively. (In the interval (V_ℓ, V_h) , we have $P_h(V) > P_\ell(V) > 0$. At the limiting volumes, we have $P_h(V_h) = P_\ell(V_h)$ and $P_h(V_\ell) = P_\ell(V_\ell)$.) The system temperature varies continuously around the closed path. The work done on the system as it traverses the high-pressure segment from V_ℓ to V_h is represented in Figure 8 by area A_h .

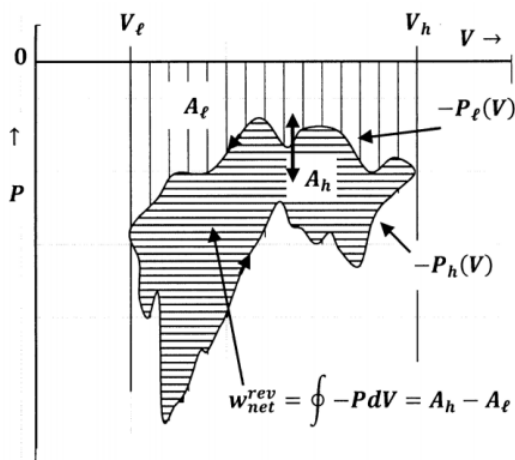


Figure 8. Reversible pressure-volume work in a cycle.

We have

$$w_h(V_\ell \rightarrow V_h) = \int_{V_\ell}^{V_h} +P_h(V) dV = A_h < 0$$

The work done on the system as it traverses the low-pressure segment from V_ℓ to V_h is represented by area A_ℓ . We have

$$w_{\ell}(V_{\ell} \rightarrow V_h) = \int_{V_{\ell}}^{V_h} -P_{\ell}(V) dV = A_{\ell} < 0$$

When the low-pressure segment is traversed in the opposite direction, we have $w_{\ell}(V_h \rightarrow V_{\ell}) = -A_{\ell} > 0$. When the system traverses the cycle in the counterclockwise direction, the net work done on the system is

$$\begin{aligned} w_{net} &= w_h(V_{\ell} \rightarrow V_h) + w_{\ell}(V_h \rightarrow V_{\ell}) \\ &= \int_{V_{\ell}}^{V_h} -P_h(V) dV + \int_{V_h}^{V_{\ell}} -P_{\ell}(V) dV \\ &= \oint -P(V) dV \\ &= A_h - A_{\ell} < 0 \end{aligned}$$

Thus the net work done on the system is represented on the graph by the area $A_h - A_{\ell}$, which is just the (negative) area in the pressure–volume plane that is bounded by the closed path.

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