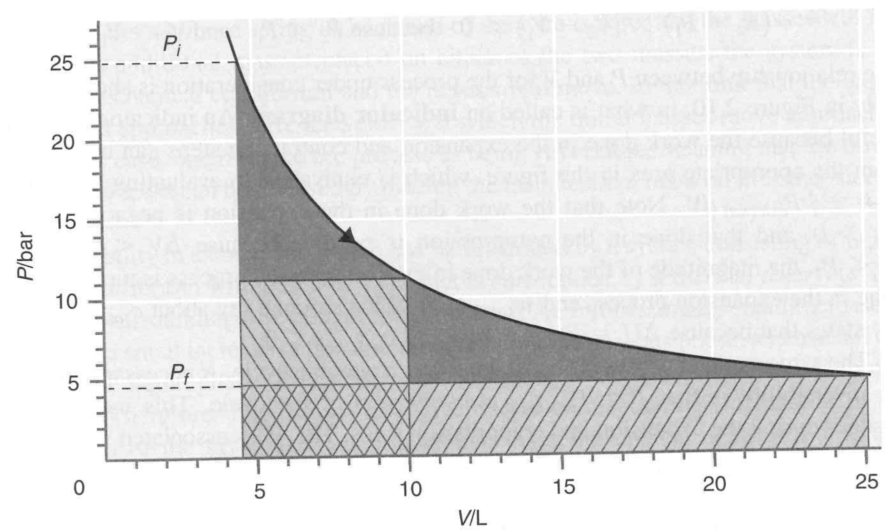
EXAMPLE PROBLEM 2.4

In this example, 2.00 mol of an ideal gas undergoes isothermal expansion along three different paths: (1) reversible expansion from $P_i = 25.0$ bar and $V_i = 4.50$ L to $P_f = 4.50$ bar, (2) a single-step irreversible expansion against a constant external pressure of 4.50 bar, and (3) a two-step irreversible expansion consisting initially of an expansion against a constant external pressure of 11.0 bar until $P = P_{external}$, followed by an expansion against a constant external pressure of 4.50 bar until $P = P_{external}$.

Calculate the work for each of these processes. For which of the irreversible processes is the magnitude of the work greater?

Solution

The three processes are depicted in the following indicator diagram by colored and hatched areas:



We first calculate the constant temperature at which the process is carried out, the final volume, and the intermediate volume in the two-step expansion:

$$T = \frac{P_iV_i}{nR} = \frac{25.0 \text{ bar} \times 4.50 \text{ L}}{8.314 \times 10^{-2} \text{ L bar mol}^{-1}\text{K}^{-1} \times 2.00 \text{ mol}} = 677 \text{ K}$$

$$V_f = \frac{nRT}{P_f} = \frac{8.314 \times 10^{-2}\text{L bar mol}^{-1}\text{K}^{-1} \times 2.00 \text{ mol} \times 677 \text{ K}}{4.50 \text{ bar}} = 25.0 \text{ L}$$

$$V_{\text{int}} = \frac{nRT}{P_{\text{int}}} = \frac{8.314 \times 10^{-2}\text{L bar mol}^{-1}\text{K}^{-1} \times 2.00 \text{ mol} \times 677 \text{ K}}{11.0 \text{ bar}} = 10.2 \text{ L}$$

The work of the reversible process is given by

$$w = -nRT_1 \ln\frac{V_f}{V_i}$$

$$= -2.00 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 677 \text{ K} \times \ln\frac{25.0 \text{ L}}{4.50 \text{ L}} = -19.3 \times 10^3 \text{ J}$$

We next calculate the work of the single-step and two-step irreversible processes:

$$w_{single} = -P_{external}\Delta V = -4.50 \text{ bar} \times \frac{10^5 \text{ Pa}}{\text{bar}} \times (25.0 \text{ L} - 4.50 \text{ L}) \times \frac{10^{-3}\text{m}^3}{\text{L}}$$

$$= -9.23 \times 10^3 \text{ J}$$

$$w_{two\text{-}step} = -P_{external}\Delta V = -11.0 \text{ bar} \times \frac{10^5 \text{ Pa}}{\text{bar}} \times (10.2 \text{ L} - 4.50 \text{ L})$$

$$\times \frac{10^{-3}\text{m}^3}{\text{L}} - 4.50 \text{ bar} \times \frac{10^5 \text{ Pa}}{\text{bar}} \times (25.0 \text{ L} - 10.2 \text{ L}) \times \frac{10^{-3}\text{m}^3}{\text{L}}$$

$$= -12.9 \times 10^3 \text{ J}$$

The magnitude of the work is greater for the two-step process than for the single-step process, but less than that for the reversible process.

Example Problem 2.4 shows that the magnitude of w for the irreversible expansion is less than that for the reversible expansion, but also suggests that the magnitude of w for a multistep expansion process increases with the number of steps. This is indeed the case, as shown in Figure 2.12. Imagine that the number of steps n increases indefinitely. As n increases, the pressure difference $P_{external} - P$ for each individual step decreases. In the limit that $n \rightarrow \infty$, the pressure difference $P_{external} - P \rightarrow 0$, and the total area of the rectangles in the indicator diagram approaches the area under the reversible curve. In this limit, the irreversible process becomes reversible and the value of the work equals that of the reversible process.

By contrast, the magnitude of the irreversible compression work exceeds that of the reversible process for finite values of n and becomes equal to that of the reversible process as $n \rightarrow \infty$. The difference between the expansion and compression processes results from the requirement that $P_{external} < P$ at the beginning of each expansion step, whereas $P_{external} > P$ at the beginning of each compression step.

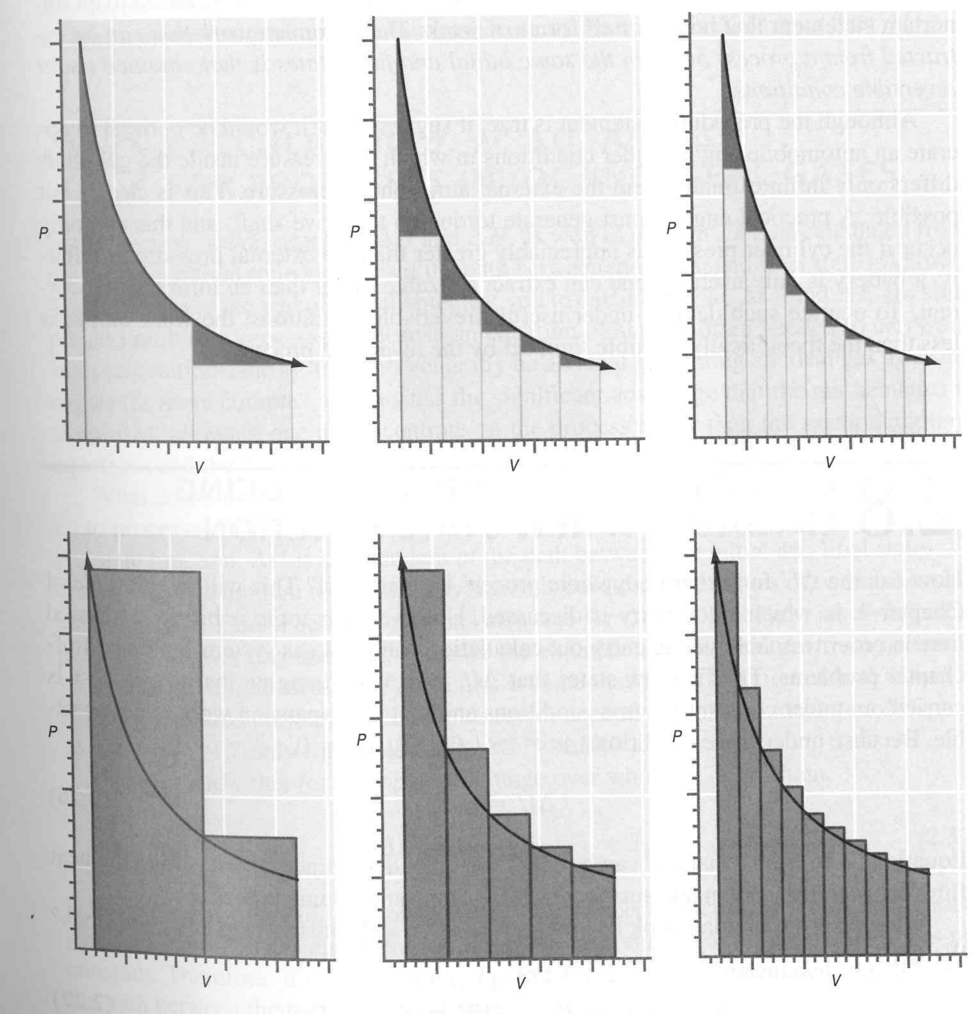


FIGURE 2.12
The work done in a reversible expansion (red and yellow areas) is compared with the work done in a multistep series of irreversible expansion processes at constant pressure (yellow area) in the top panel. The bottom panel shows analogous results for the compression, where the area under the black curve is the reversible compression work. Note that the total work done in the irreversible expansion and compression processes approaches that of the reversible process as the number of steps becomes large.