2.2: Reversible and Irreversible Transitions

We now introduce another set of words for the path dependence of work, that being reversible for the efficient path and irreversible for the inefficient. The origins of the "reversible" terminology will be made clear later, but in the meantime, let's understand how to maximize the work out of a system. Figure 2.5 will help us understand the difference by studying how a piston expands. Expansion work, or negative work ***out of a system***, is generally considered "useful" because we design our machines to push things along. After all, you don't feel that your car is dragging you behind it, do you? We will show here that reversible expansion work is the most negative work out of a machine and is the most efficient. We start with a piston under external compression and then turn down the external pressure (P_{ext}) by a very small amount. The interior pressure (P) of the piston is allowed to equilibrate with the exterior pressure before the exterior pressure decreases again. Thus, $P_{ext} = P$. This is important because, as in the previous example, the exterior pressure in the work equation is "hiding" a factor of volume in it since $P = \frac{nRT}{V}$ if we assume perfect gas behavior. The volume factor is part of the integral (equation 2.4) as shown here:

$$\int \partial w_{rev} = \Delta w_{rev} = \int -P_{ext} \cdot \partial V \; P_{ext} = P \rightarrow int - P \cdot \partial V \; P = \frac{nRT}{V} \rightarrow int \frac{-nRT}{V} \cdot \partial V$$

Now we must set limits, and note that n, R and T are constant and can be removed from the integral:

$$\Delta w_{rev} = -nRT \cdot \int_{V_i}^{V_f} \frac{\partial V}{V} = -nRT \cdot \ln\left(\frac{V_f}{V_i}\right) \tag{2.2.1}$$

One interesting thing about this equation is that, for small changes in volume: $\ln\left(\frac{V_f}{V_i}\right) \approx \frac{V_f - V_i}{V_i} = \frac{\Delta V}{V}$. Consequently, work is proportional to the fractional change in volume times some constants that give it units of Joules; hopefully this will make remembering this equation easier.

Irreversible work is much easier to calculate because there is a sudden change in the exterior pressure that occurs before the system can respond. As a result, P_{ext} can be removed from the integral (equation 2.4) as:

$$\Delta w_{irrev} = -P_{ext} \cdot \int_{V_i}^{V_f} \partial V = -P_{ext} \cdot \Delta V \tag{2.2.2}$$

To demonstrate, Figure 2.5 represents the expansion work by the shaded area under the curve for both the reversible (blue, single hatch) and irreversible (red, cross hatch) paths. We can present work this way because integrals are areas under curves. We see that the reversible region encompasses the irreversible, and as such the area under the reversible expansion is greater than the irreversible. And due to the negative sign in the work equation: $\partial w = -P_{ext} \cdot \partial V$, the reversible process generates the most negative work possible.

On the next page are a series of examples of a piston that is compressed and then expands to help solidify your ability to perform calculations on isothermal reversible and irreversible work. Example problems 2.1 & 2.2 show that an irreversible compression / expansion cycle *consumes* a positive quantity of work. Note that we state *consumes* because the work is performed *on the system*, the energy from which comes quite literally from you. In contrast, example problems 2.3 & 2.4 show that the sum of the work due to reversible cycle is 0 J. This is in fact the origin of the word "reversible", as opposed to the irreversible situation in