

## Muddiest Point – Reversible

*I am still confused about what reversible means, and the difference between reversible and irreversible.*

In general a process takes place *reversibly* when it proceeds via a series of steps that are so small (infinitely small) that the system is never displaced from *equilibrium* during the process. Creating a reversible path for a process also provides us with a well defined path for calculating the change in thermodynamic variables associated with a process. For the variables that are state functions ( $U$ ,  $H$ ,  $S$ ) it does not matter what path you take and a calculation for a fictional reversible path provides the change in these variables for any real path. For variables that are path depended, such as work, then the reversible path provides a well defined limiting case that serves as a useful point of reference.

While a reversible process represents a limit that we cannot quite reach in real life, we can get pretty close. For example, let's consider our standard model system, an ideal gas, and one of our standard model processes, an isothermal expansion. Now imagine we do the expansion by having a cylinder with a pile of sand on top and removing one grain of sand at a time.

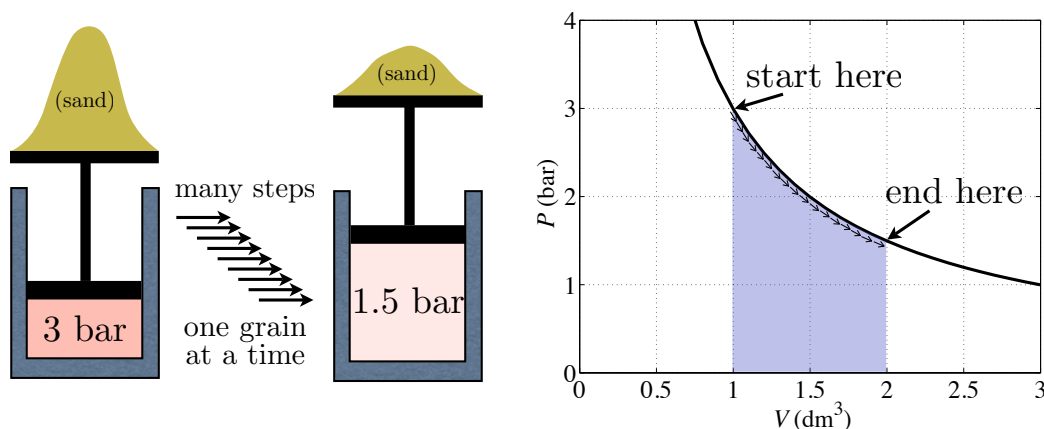


Figure 1: Consider a reversible isothermal expansion where you remove one grain of sand at a time. The plot on the right is for 0.12 moles of an ideal gas at 300 K.

Note that since we are taking such small steps (think of the infinitely small limit) that the external pressure from the sand pile is always equal to the internal pressure of the ideal gas. The system is in *equilibrium* throughout the process. Now if we consider the work associated with this reversible process, we know the external pressure throughout the process because it is in equilibrium with the internal pressure throughout the process, and the internal pressure at every step is  $P = \frac{nRT}{V}$ . So the work is,

$$w = - \int_{V_{\text{initial}}}^{V_{\text{final}}} P dV = - \int_{V_{\text{initial}}}^{V_{\text{final}}} \frac{nRT}{V} dV = -nRT \int_{V_{\text{initial}}}^{V_{\text{final}}} \frac{1}{V} dV = -nRT \ln \left( \frac{V_{\text{final}}}{V_{\text{initial}}} \right)$$

This is the area under the path taken for the process, and is shown graphically as the shaded area in figure 1.

Also note that since we took the path that kept us in equilibrium all the way, ie the reversible path, we followed the equation of state line for our isothermal ideal gas as we went from the initial  $P$  and  $V$  to the final  $P$  and  $V$ . Try to think of a path where the area under it, the work, is larger than the reversible path that we took. You will not find one. Any path that allows for the expansion at constant temperature will require steps that lower the pressure. If you lower the pressure for any one step more than the infinitely small steps that we took in the reversible path, the area under that path, ie the work, will be smaller (try drawing another path for yourself remembering that you must lower the pressure in each step). For example, consider doing the expansion in one step by simply removing the mass from the piston all at once,

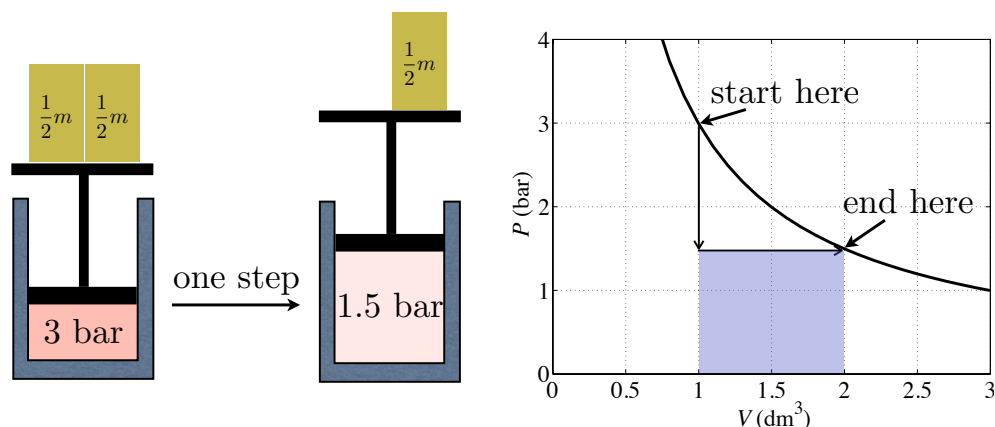


Figure 2: Consider an irreversible isothermal expansion where you lower the external pressure all at once by knocking off half the mass. The plot on the right is for 0.12 moles of an ideal gas at 300 K.

Notice that by removing the mass from the top of the piston all at once, the path that the expansion takes is at constant external pressure (one step). The work in this case is now,

$$w = - \int_{V_{\text{initial}}}^{V_{\text{final}}} P dV = -P \int_{V_{\text{initial}}}^{V_{\text{final}}} dV = -P\Delta V$$

Without plugging in any numbers you can compare the areas under the paths taken in figures 1 and 2 and see that the work in the reversible case is larger than in the irreversible case. *The reversible expansion is the path that does the greatest amount of work on the surrounding, and any other path will do less.*

**So why do we call it “reversible”?** Now consider returning our system to where we started. First, take the reversible path back (infinitely small steps that keep the system in equilibrium). In our example, this means put the sand back one grain at a time, and

taking such small steps we will remain at equilibrium all along the way. Since we were in equilibrium all the way for the reversible expansion, this means we will exactly retrace our steps in the reversible compression. Comparing the reversible compression, figure 3, with the reversible expansion, figure 1, you can see that we have exactly retraced our steps. As a result, the work is the same with the opposite sign - you can see that the area under the path is the same but the change in the volume has the opposite sign. *This is why we call it the reversible path, this is the only path that you can take in both directions, and that is because it is the path that keeps the system in equilibrium at every step along the way (ie the steps are infinitely small).*

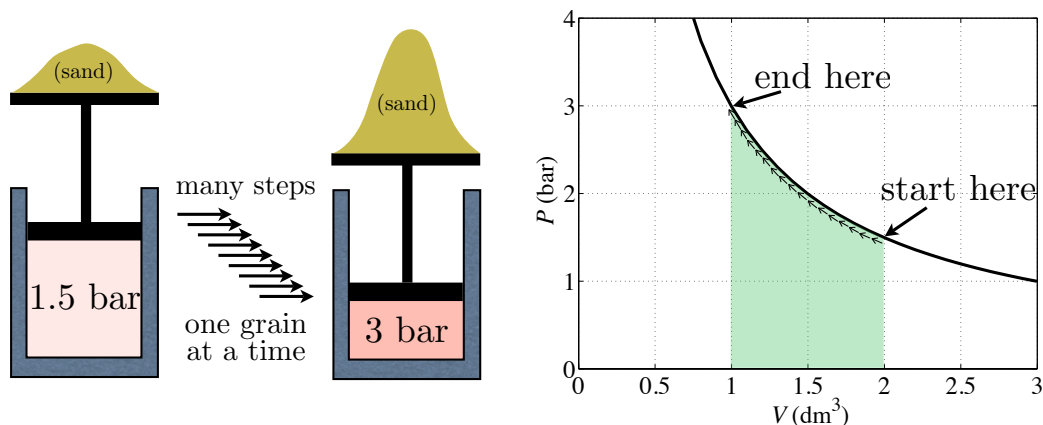


Figure 3: Consider a reversible isothermal compression where you add one grain of sand at a time. The plot on the right is for 0.12 moles of an ideal gas at 300 K.

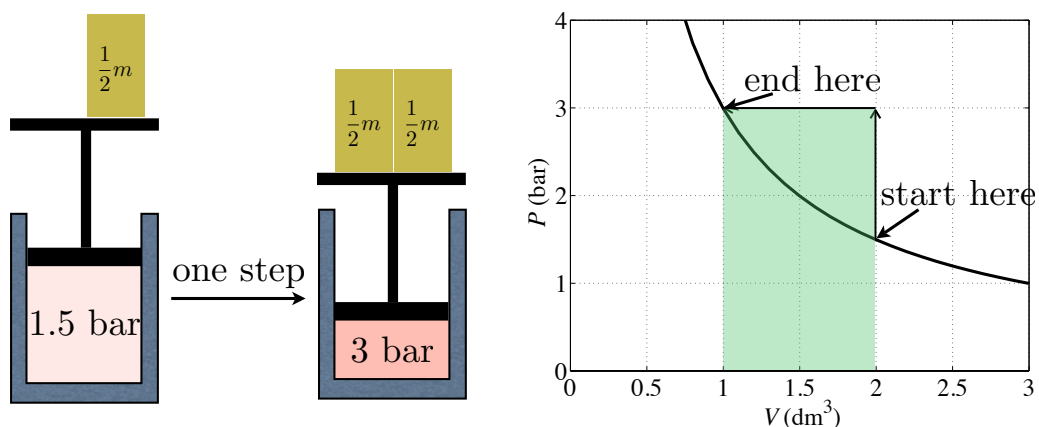


Figure 4: Consider an irreversible isothermal compression where you raise the external pressure all at once by putting the mass back. The plot on the right is for 0.12 moles of an ideal gas at 300 K.

Now contrast the reversible path with the example we have for an irreversible path. To return to where we started in figure 2 we simply put the mass back on top of the piston and compress in one step. Comparing figures 4 and 2 you can see that you do NOT take the same path back that you took in the expansion. Even though we did the same thing in reverse, we put the weight back on the piston, we do not follow the same path back because the pressure, mass on the piston, is different during the expansion compared to the compression. The fact that you cannot take the same path back (note that the gas does not compress at the same pressure that we did the irreversible expansion) is why we call this “irreversible”.

The work (area under the path) is much larger in the compression than the expansion (figure 2), and in fact it is much larger than the work required to do the compression reversibly as shown in figure 3. Note that there is no path that requires less work done on the system to compress the gas than the reversible path. The reversible path is the minimum work required. In the irreversible case more work had to be done on the system to compress it back to the starting point than it did on the surrounding during the expansion.

Associate the following with a reversible path:

- The path where the system remains at *equilibrium* throughout the process.
- The maximum amount of work done on the surroundings.
- The minimum amount of work required from the surroundings.