2.6 Reversible vs. irreversible processes

The phrase "reversible" is essential for the understanding of thermodynamic processes. It implies that at any moment the flow direction of extensive parameters can be changed in both directions by an infinitesimal change of an intensive parameter.

To understand the meaning of this statement we discuss two experiments using the isotherm shown in Fig. 2.2:

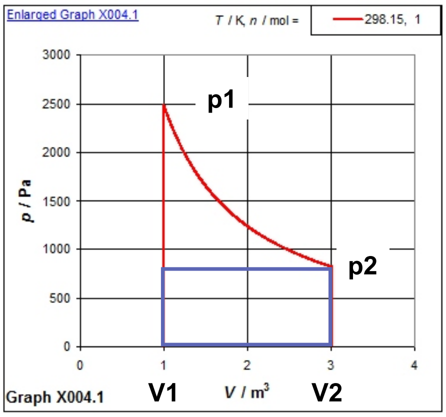

Figure 2.2: Reversible and irreversible gas expansion processes.

1. Starting at volume V_1 and pressure p_1 we have an expansion against a constant external pressure $p_{ex} = p_2$, for which the work can be calculated according to Eq. (2.14).
2. Expansion against a continuously changing pressure p_{ex} for which at any moment $p_{ex} = p$ holds. The work related to this experiment is defined by Eq. (2.16).

For the first experiment we have a spontaneous expansion from V_1 to V_2. It is impossible to invert this flow direction at each moment, e.g. directly at the beginning of the experiment, by an infinitesimal increase of the pressure p_2. So by definition this process is irreversible. In contrast, for the second experiment at each moment an external pressure is applied which equals the internal pressure. To increase infinitesimally the volume we infinitesimally decrease p_{ex}. To decrease infinitesimally the volume we infinitesimally increase p_{ex}. So by definition this process is reversible.

Several aspects of reversible processes become instantly clear from this short discussion:

- For reversible processes only infinitesimal changes are allowed, otherwise they cannot be inverted in flow direction by infinitesimal changes for all flow directions.
- Generally, reversible processes are slow, because only states fulfilling the thermodynamic equilibrium relations are allowed, and this can only be reached by infinitesimal changes.
- Reversible processes are never spontaneous.
- The definition of reversibility allows for an easy experimental check, thus being extremely practicable, in contrast to the "equivalent" statement that each state has to be in thermodynamic equilibrium.

The work performed within the first experiment is $w = p_{ex}(V_2 - V_1)$, corresponding to the area of the rectangle shown in Fig. 2.2. The work performed within the second experiment is given by Eq. (2.16), representing the area below the isotherm. Obviously the work performed in the reversible process is larger than the work performed in the irreversible process. Since we could have chosen any condition in Fig. 2.2 the connection between reversibility and maximum work holds quite obviously in general for a perfect gas. As we will see later, taking into account the second law of thermodynamics, it applies to all substances and all kinds of work.