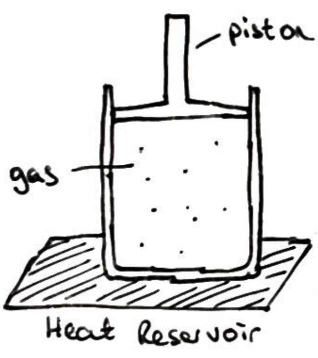
Spontaneous vs Reversible Changes

A reversible process is a thermodynamic path that remains constantly infinitesimally close to equilibrium (i.e it is quasistatic) and that can be traced back to obtain exactly the original state.

A spontaneous process happens without external intervention, it is always irreversible. The isobaric expansion we saw previously is an example of this. The heat flowed from the thermal reservoir to the gas by itself. The gas will not spontaneously cool and transfer heat back to the heat source.

The experiment is reversible if we consider the system to be only the gas vessel as then, if we replace the hot plate with a cold plate, the gas will undergo isobaric compression and return to its original state.

Consider an isothermal process:



Here, the system is maintained at constant temperature while the piston is pulled. As the volume of the gas increases, the temperature of the gas would fall unless kept constant by the heat reservoir. So how much heat is put into the system to maintain temperature?

Note: we know that compressing a gas increases its internal energy since work is done on the gas. Hence we can say expanding a gas will cause it to cool.

First we need to identify the change in internal energy of the gas.

$\Delta U = C_V \Delta T$ and $\Delta T = 0$ since its temperature is not allowed to change.

$\therefore \Delta U = 0$

Using the first law of thermodynamics:

$\Delta U = Q + W \quad \therefore \quad Q = -W$ since $\Delta U = 0$

$W = -\int P dV$, the work done on the gas where P is given by $PV = Nk_BT$ since the process is reversible

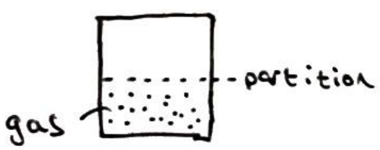
$$\therefore W = -\int \frac{Nk_BT}{V} dV$$

$$= -Nk_BT \ln\left(\frac{V_2}{V_1}\right)$$

so $Q = Nk_BT \ln\left(\frac{V_2}{V_1}\right)$ which is positive as we expect heat to flow into the system to maintain temp.

Joule Expansion

This is an example of free expansion where the initial and final states of the system are identical to the previous process:



The partition is removed and the gas is allowed to expand. No work is done on the gas and there is no heat exchange so $Q = W = 0$. Yet something happened and energy would need to be put in in the form of work to bring the system back to its initial state. Hence, this process is irreversible whereas the previous process was reversible.