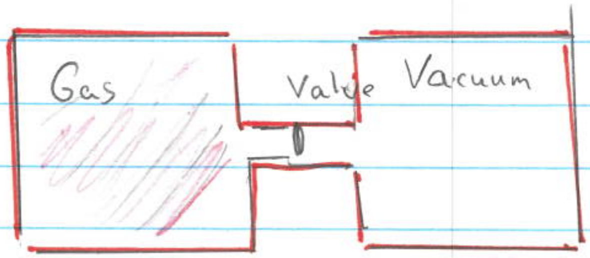
Joule Expansion

- Consider a gas in a thermally isolated Container with a valve



(see slide)

The gas rushes and fills the second half of the container, What is the change in entropy of the gas, the surroundings, and the total $\Delta S_{universe} \equiv \Delta S_{TOT}$

Statistical Approach

$$\Omega = C V^N E^{3N/2}$$

- Then the volume doubles, but no heat enters the system $E_f = E_i$, but $V_0 \rightarrow 2V_0$

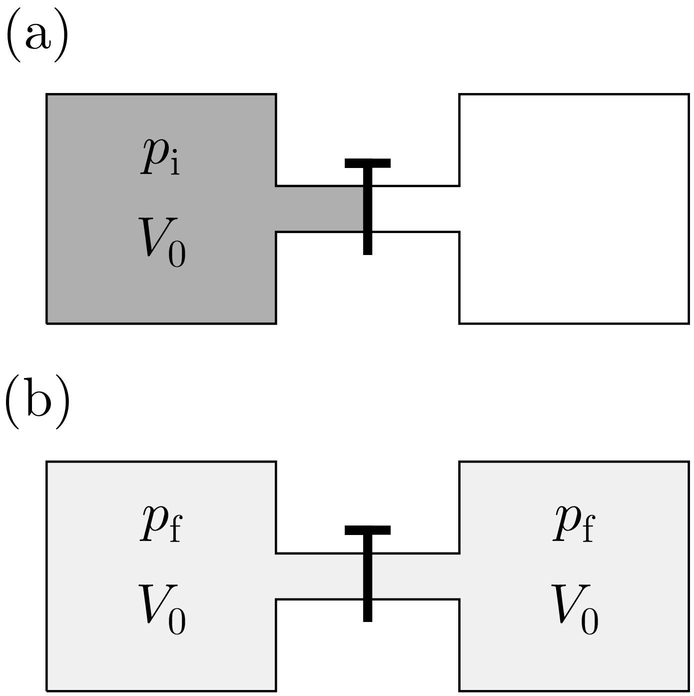
$$\Omega_{final} = C(2V_0)^N E^{3N/2} = 2^N \Omega_{initial}$$

$$S_f = k_B \ln \Omega_{final} = N k_B \ln 2 + \underbrace{k_B \ln \Omega_{init}}_{S_i}$$

So

$$S_f - S_i = N k_B \ln 2$$

Joule Expansion



The expansion
is a highly non-equilibrium process.

During the expansion no heat
enters the system. Thus the
energy initial equals the final energy

- We ~~could~~ could have used S instead

$$S_{\substack{\text{ideal}\\\text{gas}}} = Nk \ln V + \frac{3}{2} Nk \ln E + \text{const}$$

In the current case E is constant as no heat enters the system and no work was done

$$\Delta S = S_{\text{final}} - S_{\text{init}} = Nk \ln V_f - Nk \ln V_i$$

$$= Nk \ln \frac{V_f}{V_i}$$

$$\Delta S = Nk \ln 2$$

While the entropy change in the gas is $\Delta S_{\text{gas}} = Nk_B \ln 2$, the entropy change in the reservoir (or surroundings) is zero since no heat flows into the gas from the reservoir:

$$\Delta S_{\text{surroundings}} = 0\,.$$

Thus, the total entropy change of the universe (gas+surroundings) is

$$\Delta S_{\text{univ}} = \Delta S_{\text{gas}} + \Delta S_{\text{surroundings}} = Nk_B \ln 2 > 0\,.$$

Since this is positive, the Joule expansion is clearly an irreversible process. The gas will never go back to being on the left hand side of the container.

Joule Expansion from Thermo:

- Previously we found ΔS from $\Omega(E,V) = C(N)\,E^{3N/2}\,V^N$

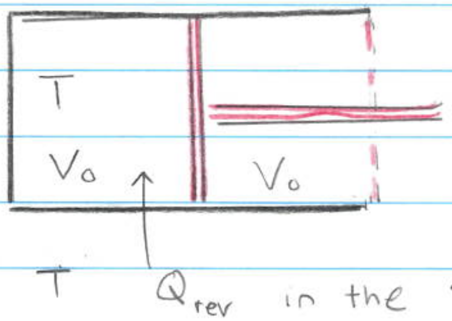
- Since No energy is transferred to the gas as it is expanding to fill the chamber, its temperature at the beginning and end are the same.

- Since the ΔS only depends on where you start and stop, let's replace the non-equilibrium actual expansion, with a fully equilibrated "dream" isothermal expansion (see slide) in contact with a reservoir

(see slide on next page)

$$dU = đQ + đW$$

$$0 = T\,dS - p\,dV$$



Q_{rev} in the "dream" equilibrated world heat flows reversibly into the system $dQ_{rev} = T\,dS$. The reservoir is also at temperature T

So

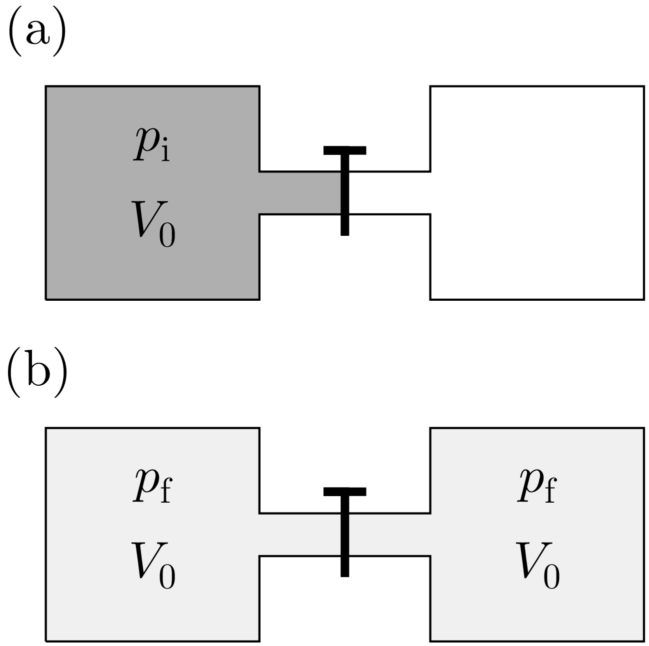
$$dS = \frac{p}{T}\,dV = \frac{dQ_{rev}}{T}$$

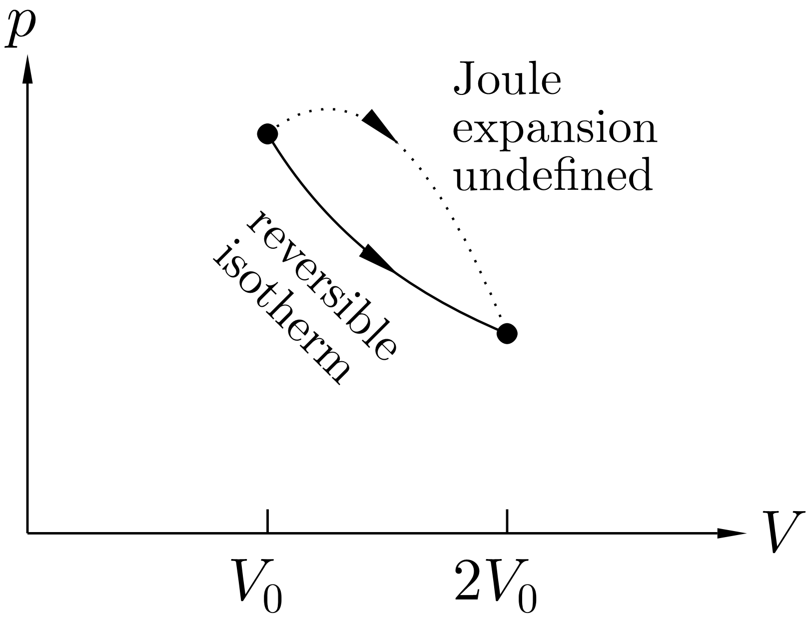
$$\Delta S_{sys} = \int_{V_0}^{2V_0} Nk\,\frac{dV}{V}$$

$$\Delta S_{sys} = Nk \ln \frac{2V_0}{V_0} = Nk \ln 2$$ same as before

We note that in the actual process no heat

Calculating the change in entropy: thermodynamic considerations





flows into the system $dQ/T_R = 0$ from the reservoir.

- Thus, we have illustrated the general result:

$$\Delta S_{AB} = \int_A^B \frac{dQ_{rev}}{T} \geq \int_A^B \frac{dQ}{T_R}$$

$$\uparrow$$

the change in entropy from A to B can ber computed by considering an equilibrated and reversible transfer of Heat from a sequence of baths at various temperatures. The change in entropy is greater than the actual $\frac{\text{heat}}{T_R}$ that enterred the system (which in this case is zero):

$$\boxed{\Delta S_{sys} = Nk \ln 2 > 0}$$

- Since the "system" (the gas in the container) is completely isolated from its surroundings, it is its own universe. We have

$$\boxed{\Delta S_{univ} > 0}$$

as we expect for an irreversible process.