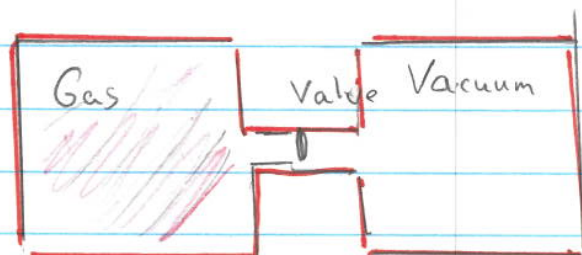


## Joule Expansion

- 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  $\Delta S_{\text{universe}} \equiv \Delta S_{\text{tot}}$

## Statistical Approach

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

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

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

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

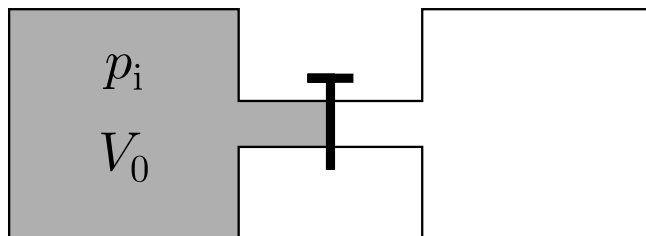
$S_o$   $S_i$

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

# Joule Expansion

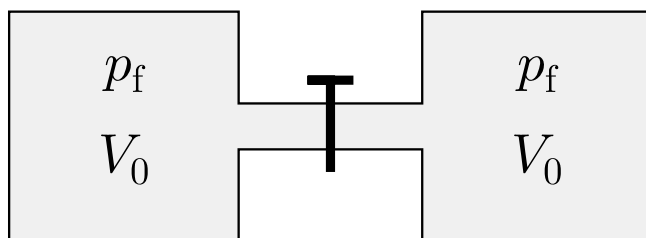
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(a)



The expansion is a highly non-equilibrium process.

(b)



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

- We could have not used  $\Omega$ :

$$S = Nk_B \ln V + \frac{3N}{2} \ln E + \text{const}$$

$$S_f - S_i = Nk_B \ln \frac{V_f}{V_i} = Nk_B \ln 2$$

- So

$$\Delta S_{\text{gas}} = Nk_B \ln 2$$

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

$$\Delta S_{\text{TOT}} = Nk_B \ln 2 > 0, \text{ this process}$$

is very clearly irreversible.

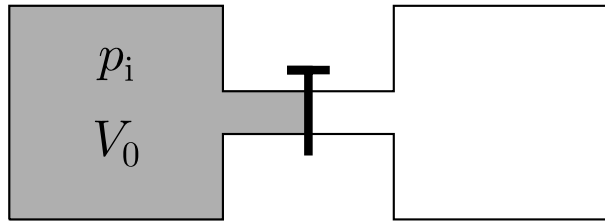
- Another approach is to use thermo-dynamics

- The system takes a non-equilibrium path to go from the initial point to the final point
- However the change in entropy depends only on the initial and final points. Since the initial and final energy are the same, the initial and final temperatures are the same,
- Thus we can consider a fully equilibrated

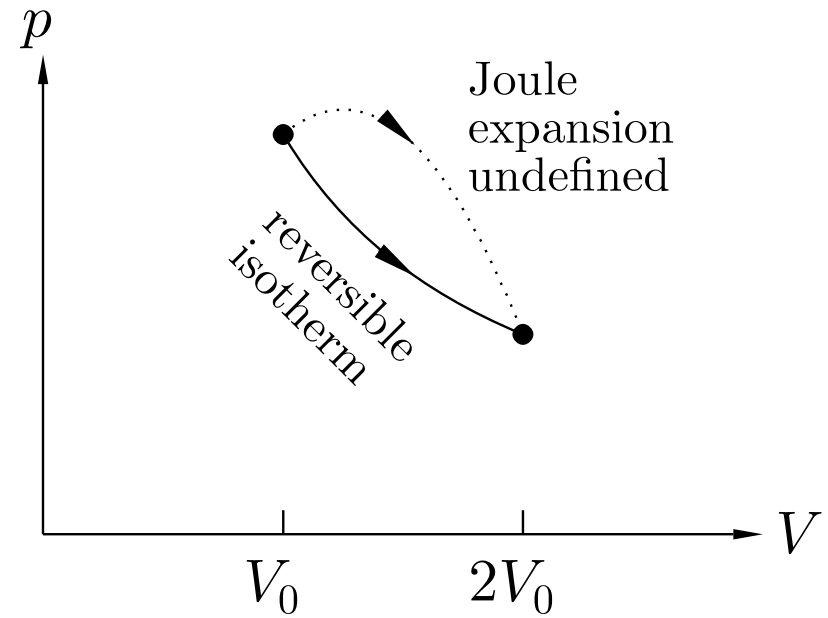
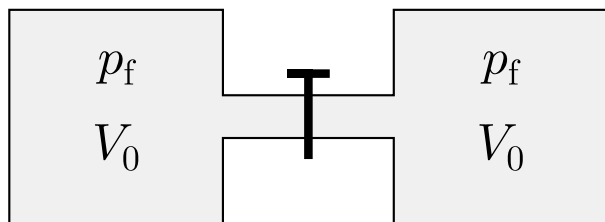
## Calculating the change in entropy: thermodynamic considerations

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(a)



(b)



- isothermal expansion to calculate the change in entropy of the expansion

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

no energy  
change in gas

this assures perfect equilibrium with a reversible exchange of heat from a reservoir at temperature  $T$ .

$$S_f - S_i = \int_i^f \frac{P}{T} dV = \int \frac{Nk_B}{V} dV$$

$$\Delta S_{\text{gas}} = Nk_B \ln \frac{V_f}{V_i} = Nk_B \ln 2$$

- This is only  $\Delta S$  for the gas. This agrees with the direct calculation given above. For the isothermal expansion occurring reversibly

$$\Delta S_{\text{surroundings}} = -\Delta S_{\text{gas}}$$

And

$$\Delta S_{\text{universe}} = \Delta S_{\text{gas}} + \Delta S_{\text{surroundings}} = 0$$

$$\Delta S_{\text{universe}} = \left( \frac{P_{\text{gas}}}{T_{\text{gas}}} - \frac{P_{\text{surrounding}}}{T_{\text{surround}}} \right) dV_{\text{gas}} \approx 0$$

the gas & surroundings always in equilibrium.