

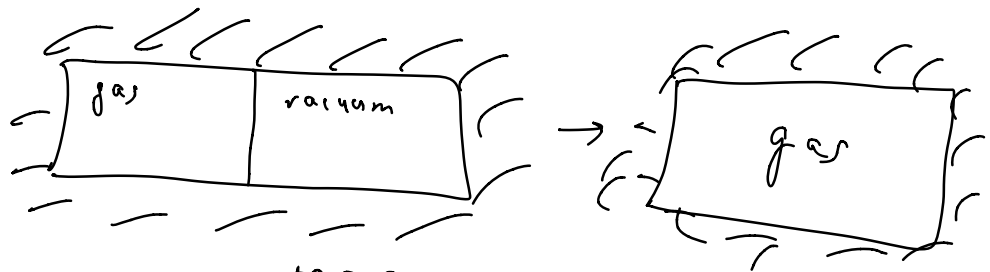
$$dS = \frac{dq_{rev}}{T}; \text{ state function: } \int_1^2 dS = \Delta S = S_2 - S_1$$

$\uparrow$   
 $S = \text{entropy}$

prescription for calculating  $\Delta S$

$\therefore$  "make up" your own process as long as it's Reversible

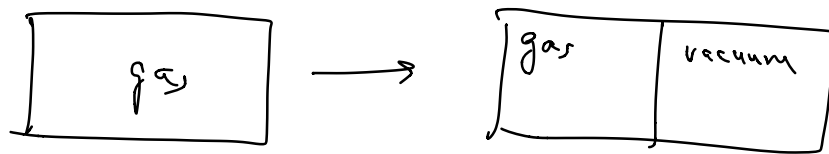
Free Expansion of I.G. (Isolated)



$$dq = 0$$

can't use  $dS = \frac{dq_{rev}}{T}$

make up another path



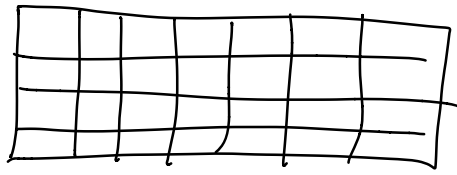
Isot: Reversible

$$\Delta S_{\text{expansion}} = -\Delta S_{\text{compression}} = nR \ln\left(\frac{V_{\text{uncompressed}}}{V_{\text{compressed}}}\right)$$

$$\Delta S > 0$$

IRREVERSIBLE  
Spontaneous

$$\boxed{\Delta S = nR \ln 2} \quad \Rightarrow \quad V_{\text{uncomp}} = 2 V_{\text{compressed}}$$



$N$  bins

$m$  particles

Indistinguishable

$$S! = 5 \times 4 \times 3 \times 2 \times 1$$

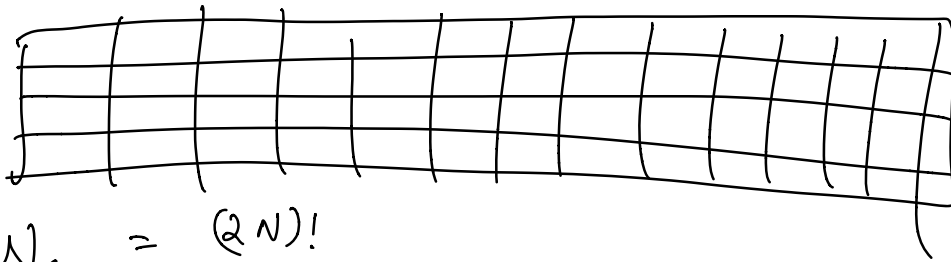
$$N \gg \gg m$$

how many unique ways

$$W_1 = \frac{N!}{m! (N-m)!}$$

Expansion

$2N$  bins  
 $m$  particles



$$W_2 = \frac{(2N)!}{m! (2N-m)!}$$

let  $N, m \rightarrow \infty$  (become very large)

$$\frac{m}{N} = \text{constant} = \text{density}$$

Consider  $\ln W_1$  and  $\ln W_2$

$$W_1 = \frac{N!}{m!(N-m)!}$$

$N, m \rightarrow \text{large}$   
 $\rightarrow \infty$   
 $N \gg m$

$$\ln W_1 = \ln(N!) - \ln(m!) - \ln((N-m)!)$$

$$\ln(N!) \cong N \ln N - N$$

$$\begin{aligned} \ln W_1 &= N \ln N - N - [m \ln m - m] - [(N-m) \ln(N-m) - (N-m)] \\ &= N \ln N - N - m \ln m + m - (N-m) \ln(N-m) + N - m \\ &= N \ln N - m \ln m - \underbrace{N \ln(N-m)}_{\cong N \ln N} + m \ln(N-m) \end{aligned}$$

$$\boxed{\ln W_1 \cong -m \ln(m) + m \ln(N-m)}$$

$$\ln W_2 = \ln \left[ \frac{(2N)!}{m!(2N-m)!} \right]$$

$W_2$

$$\begin{aligned} \ln W_2 &= \ln((2N)!) - \ln(m!) - \ln((2N-m)!) \\ &= (2N) \ln(2N) - \cancel{(2N)} - [m \ln m - \cancel{m}] \\ &\quad - [(2N-m) \ln(2N-m) - \cancel{(2N-m)}] \end{aligned}$$

$$= (2N) \ln(2N) - m \ln m - (2N-m) \ln(2N-m)$$

$$\cong \cancel{(2N) \ln(2N)} - m \ln m - \cancel{2N \ln(2N-m)} + m \ln(2N-m)$$

$$\ln W_2 \cong -m \ln m + m \ln 2 + m \ln N \quad \leftarrow$$

$$\ln W_1 \cong -m \ln m + m \ln(N-m)$$

Now:  $\ln W_2 - \ln W_1$

$$\ln W_2 - \ln W_1 = m \ln 2$$

$$pV = nRT$$

$$m = nN_A$$

$$n = \frac{m}{N_A}$$

$$pV = m$$

$$pV = nN_A RT$$

$$pV = \frac{m}{N_A} RT$$

$$pV = m \left( \frac{R}{N_A} \right) T$$

$$k_B \equiv \frac{R}{N_A}$$

↑ Boltzmann Constant

$$\ln W_2 - \ln W_1 = m \ln 2$$

$$= nN_A \ln 2$$

$$k_B = \frac{R}{N_A}$$

$$\ln W_2 - \ln W_1 = n \frac{R}{k_B} \ln 2$$

$$N_A = \frac{R}{k_B}$$

$$k_B [\ln W_2 - \ln W_1] = \underline{nR \ln 2}$$

$$\Delta S = S_{\text{final}} - S_{\text{initial}} = k_B \ln W_2 - k_B \ln W_1$$

$$S_{\text{initial}} = k_B \ln W_1$$

$$S_{\text{final}} = k_B \ln W_2$$

$$S = k_B \ln \Omega$$

||||'  
''''\|

$$S = k_B \ln \Omega$$

