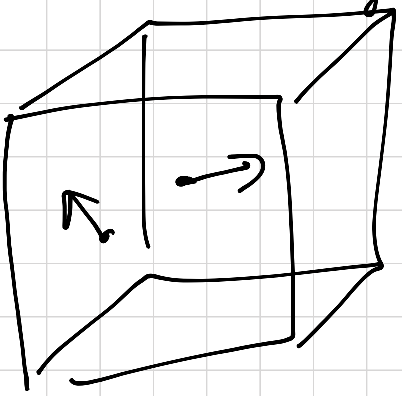
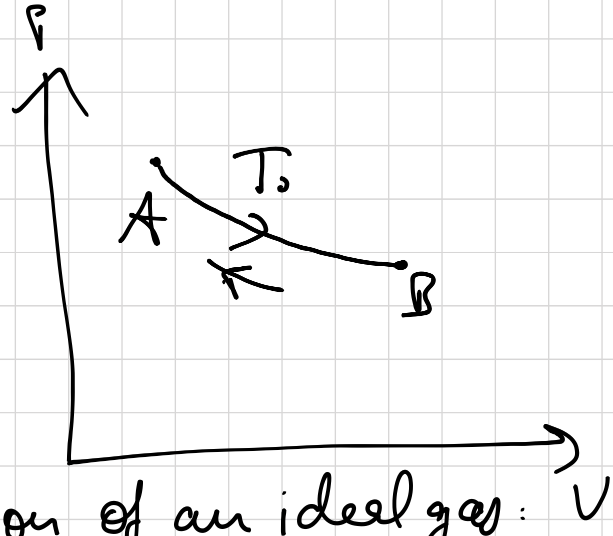
reversible change





isothermal expansion of an ideal gas:

$$W_{A\to B} = \int_A^B p\,dV = \int_{V_A}^{V_B} \frac{nRT_0}{V}\,dV =$$

$$nRT_0 \log\frac{V_B}{V_A} > 0 \quad \text{if} \quad V_B > V_A$$

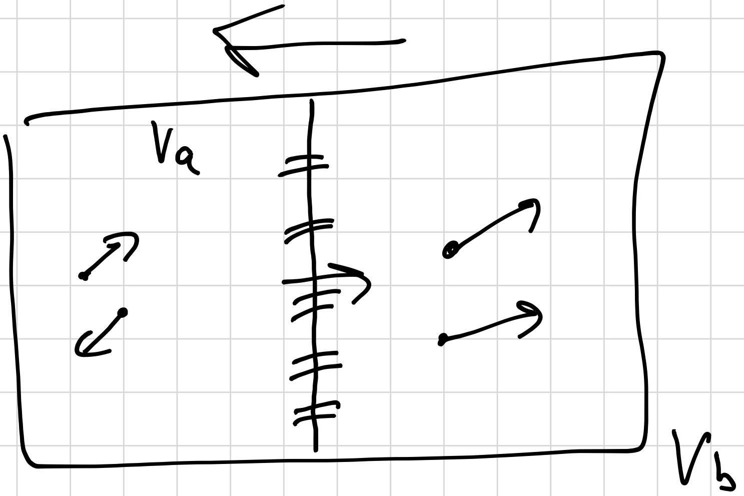
↑

Because T_0 is constant, $\Delta E(T_0) = 0$,

$\Delta E = Q - W$

$Q_{A\to B} = W_{A\to B}$ ↙

irreversible change - Joule (free) expansion



$Q = 0$ $\qquad$ $\Delta E = 0$ //

$W = 0$ $\qquad$ $\Delta T = 0$ //

Reversible and irreversible processes

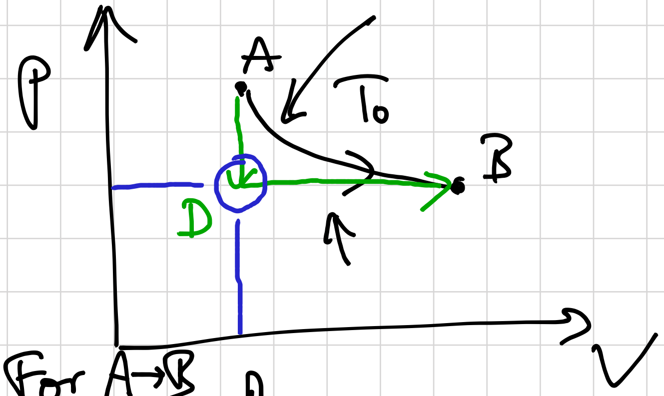
Entropy

$$\Delta S = \frac{Q}{T}$$ if T does not change in the process

More generally,

$$\Delta S = \int_A^B \frac{d'Q}{T}\Big)_R$$

Entropy is a state variable!



For A→B

$$\Delta S = \int_A^B \frac{dQ}{T_0} = \frac{Q_{A\to B}}{T_0} = \frac{nRT_0 \log \frac{V_B}{V_A}}{T_0}$$

$$= nR \log \frac{V_B}{V_A} > 0$$

For $A \to D$

$\Delta V = 0$

$Q = nC_v \Delta T$

$$\Delta S = \int_A^D \frac{dQ}{T} = \int_A^D \frac{nC_v\,dT}{T} = nC_v \int_A^D \frac{dT}{T}$$

$$= nC_v \log \frac{T_D}{T_A} \Leftarrow$$

For $D \to B$

$$\Delta S = \int_D^B \frac{dQ}{T} = \int_D^B \frac{nC_p\,dT}{T} = nC_p \log \frac{T_B}{T_D}$$

$$= n(C_v + R) \log \frac{T_B}{T_D} \leftarrow$$

For $A \to D \to B$:

$$\Delta S = nC_v \log \frac{T_D}{T_0} + n\underbrace{(C_v+R)}_{} \log \frac{T_0}{T_D}$$

$$= n\cancel{C_v} \log \boxed{\frac{T_D}{T_0}} + n\cancel{C_v} \log \boxed{\frac{T_0}{T_D}} +$$

$$nR \log \frac{T_0}{T_D}$$

$$= nR \log \frac{T_0}{T_D}$$

$pV = nRT$, $nRT_0 = p_A V_A = p_B V_B$

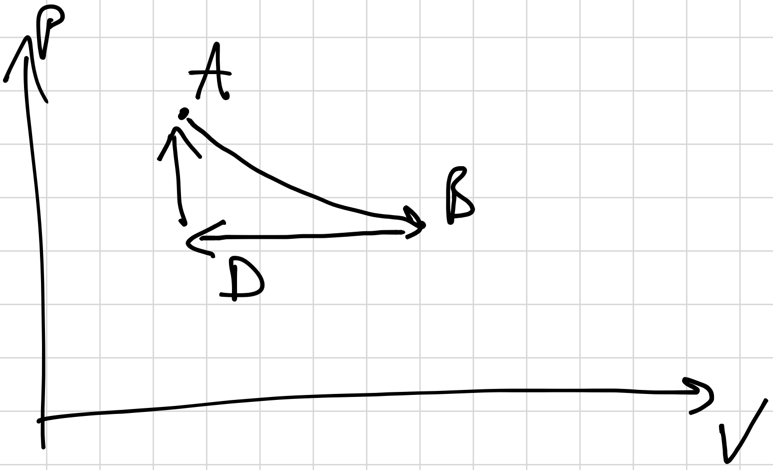
$nRT_D = p_B V_A$

$$= nR \log \frac{p_B V_B \cancel{nR}}{p_B V_A \cancel{nR}}$$

$$\Delta S_{A\to D\to B} = nR \log \frac{V_B}{V_A} > 0$$

$$\underline{\Delta S_{A\to B}} = \underline{\Delta S_{A\to D\to B}}$$ ✓

→ S (entropy) is a state variable



$$S_{A\to B} + \underbrace{S_{B\to D} + S_{D\to A}}_{-S_{A\to D\to B}} = 0$$

$$\oint \frac{dQ}{T} = 0$$

Comparing the isothermal and the free expansion,

$$\left.\begin{aligned} \Delta S_{reversible} &= nR \log \frac{V_B}{V_A} > 0 \\ \Delta S_{irreversible} &= 0 \end{aligned}\right\}$$

And in general,

$$\Delta S = \underbrace{\int_A^B \frac{dQ_{reversible}}{T}} > \underbrace{\int_A^B \frac{dQ_{irreversible}}{T}}$$

Example:

w/o friction

w/ friction

Second law of Thermodynamics

thermally isolated system:

$$\Delta S \geq 0$$

Third law of Thermodynamics

$$T \to 0 \qquad \underline{S \to 0} \leftarrow$$

$T \to 0$ $\underline{S \to S_0}$ ←

Entropy and the first laws of thermodyn.

for a reversible process, we can write

$dS = \frac{dQ}{T}$, $dQ = TdS$ $dW = pdV$

$dE = TdS - pdV$ ←

$dE = \underset{\sim}{\overset{\#}{dQ}} - \underset{\sim}{\overset{\#}{dW}}$ ←

Statistical interpretation of entropy

$dE = \underset{\uparrow}{T}dS - pdV$,

$= \left.\frac{\partial E}{\partial S}\right|_V$ $\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_V$ *

← # of microstates

$$\frac{d \ln \Omega(E)}{dE} = \frac{1}{k_B T} \quad *$$

$$k_B \frac{d \ln \Omega}{dE} = \left.\frac{\partial S}{\partial E}\right|_V$$

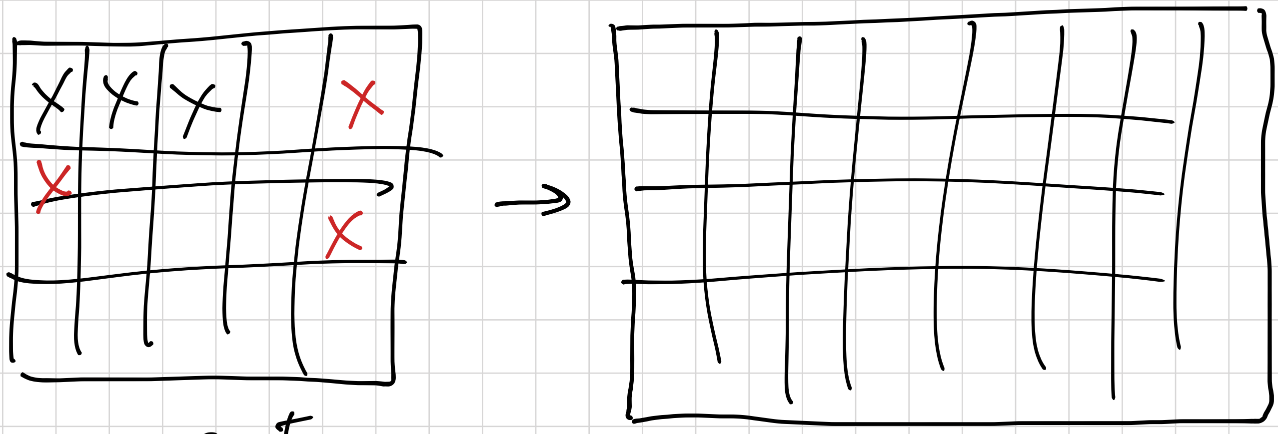
$S = k \ln \Omega$ ←

Since the 2^{nd} law of thermodynamics

$$\Delta S \geq 0,$$

more order (fewer microstates) → less order (more microstates)

Free expansion:



m spots

$S = k_B \ln \Omega$

$$\boxed{\Omega = \frac{m!}{(m-N)!\,N!} = \binom{m}{N}}$$

sterling's formula: $\ln x! = x \ln x - x$

$$S = k_B \ln \frac{m!}{(m-N)!\,N!}$$

$$= k_B \left[\ln m! - \ln (m-N)! - \ln N! \right]$$

$$\approx k_B \left[m \ln m - \cancel{m} - (m-N)\ln(m-N) + \cancel{m-N} - N \ln N + \cancel{N} \right]$$

$$= k_B \left[m \ln m - (m-N) \ln (m-N) - N \ln N \right]$$

$$= k_B \left[\underline{m \ln m} - \underline{m \ln (m-N)} + \underline{N \ln (m-N)} - \underline{N \ln N} \right]$$

$$= k_B \left[-m \ln \frac{m-N}{m} + N \ln \frac{m-N}{N} \right]$$

$$= k_B \left[-m \ln \Big(1 - \underbrace{\frac{N}{m}}_{\to 0}\Big) + N \ln \Big(\underbrace{\frac{m}{N}}_{\to \infty} - 1\Big) \right]$$

m spots, $m \to \infty$

$$\approx k_B \left[-m \left(-\frac{N}{m}\right) + N \ln \frac{m}{N} \right]$$

$$= k_B \left(N + N \ln \frac{m}{N} \right)$$

ΔS : $m \to \boxed{2m}$

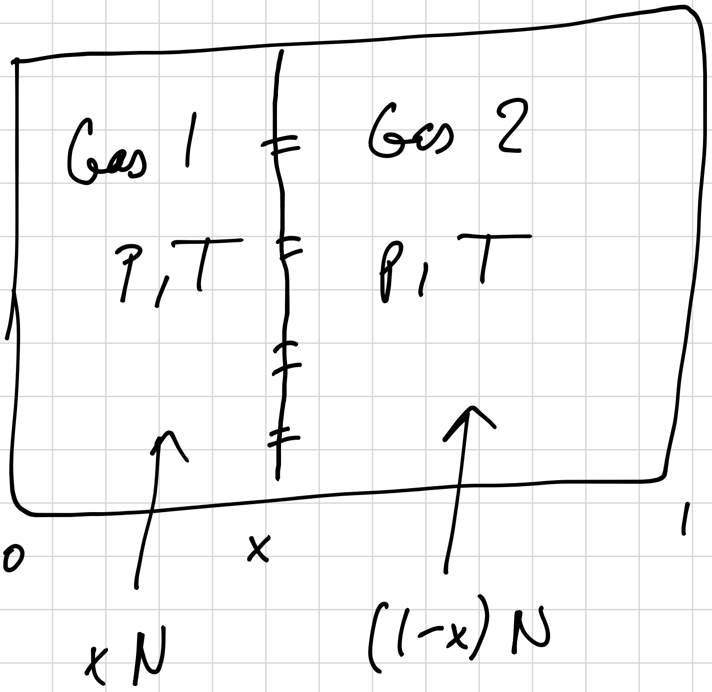
$$S(2m) - S(m) = k_B \left(\cancel{N} + N \ln \frac{\boxed{2}m}{N} \right) - k_B \left(\cancel{N} + N \ln \frac{m}{N} \right)$$

$$= k_B N \ln \left(\frac{2\cancel{m}}{\cancel{N}} \frac{\cancel{N}}{\cancel{m}} \right)$$

$$= k_B N \ln \boxed{2}$$

$$\Delta S = k_B N \underset{\ln}{\underset{\parallel}{\log}} \frac{V_b}{V_a} \Bigg|_{V_b = 2V_a} = k_B N \log 2$$

Entropy of mixing

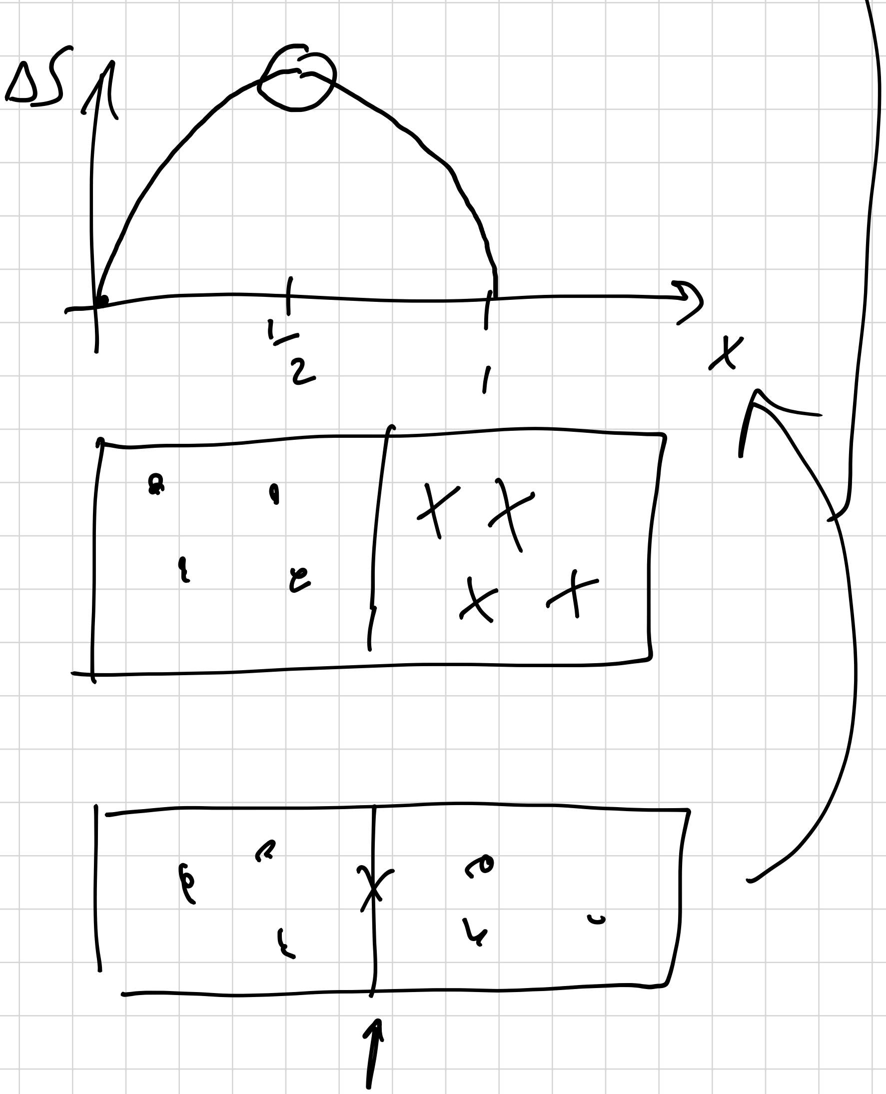


$$\underline{\Delta S} = \Delta S_1 + \Delta S_2 = k_B\, x N \log\left(\frac{1}{x}\right)$$

$$+ k_B (1-x) N \log\left(\frac{1}{1-x}\right)$$

$$= k_B N \left[\underset{\uparrow}{-} x \underset{\uparrow}{\log} x \underset{\uparrow}{-} (1-x) \log (1-\underset{\uparrow}{x}) \right]$$

$$\uparrow$$


ΔS
1/2
1
x