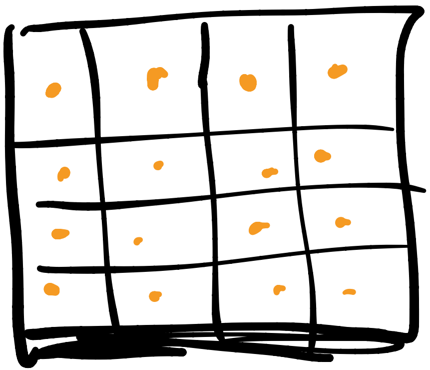
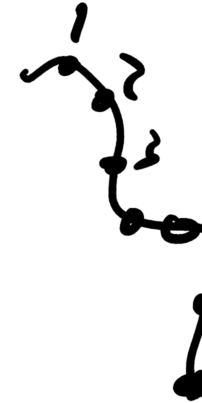


Ideal gas lattice:

m molecules

N_c spaces

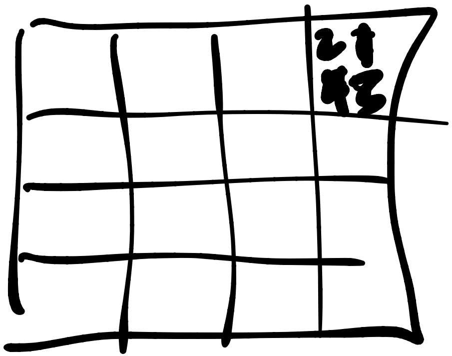


$$\# \text{ ways} = W = \overbrace{N_c \cdot N_c \cdots N_c}^{m \text{ times}}$$

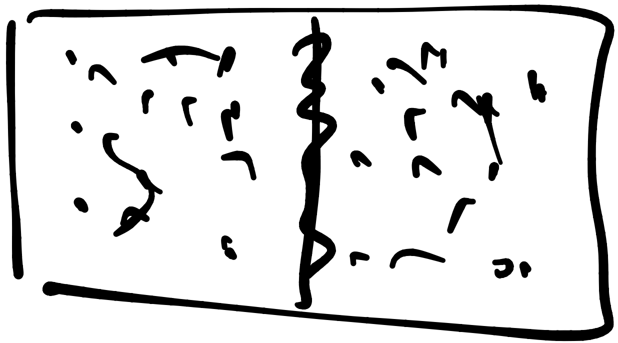
$$= N_c^{m} / m!$$

Excluded volume $W_{ex} = N_c \cdot (N_c - 1) \cdots (N_c - m) = \dfrac{N_c!}{m!\,(N_c-m)!}$

If indistinguishable: $m!$ $\qquad \binom{N_c}{m}$



$$\frac{N_c^4}{4!}$$ total configurations



Gibbs mixing paradox

$S = k_B \ln W$ $\qquad W = N_c^{m}/m!$

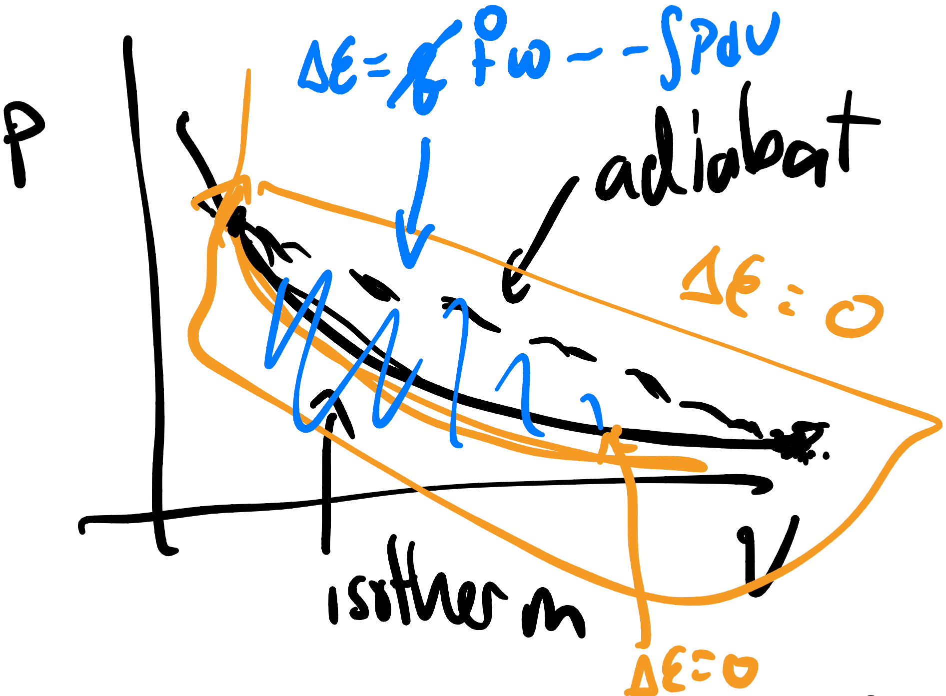
expansion from $N_i \to N_f$

$$S_f = k_B \ln (N_f^{m}/m!)$$

$$S_i = k_B \ln (N_i^{m}/m!)$$

$\ln(A/B) = \ln A - \ln B$

$$\Delta S = k_B m \ln(N_f/N_i) \Leftrightarrow nR \ln(V_f/V_i)$$



ideal gas

can this happen?

- 1st law ←
- 2nd law

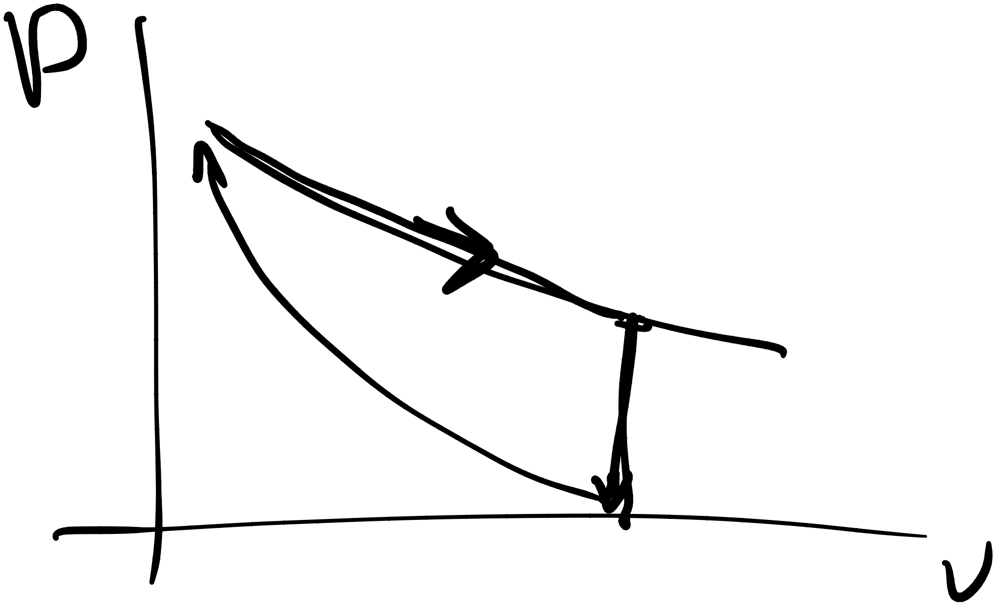
Can't happen:

cons energy - loop

$\Delta S \geq 0$

isotherm, Temp doesn't change

adiabat cools down

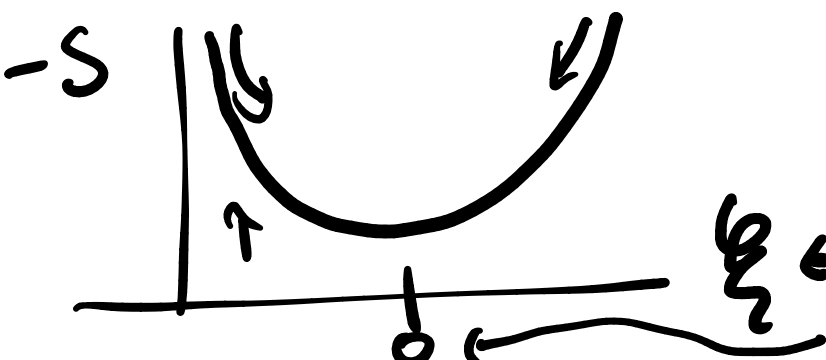

p
v

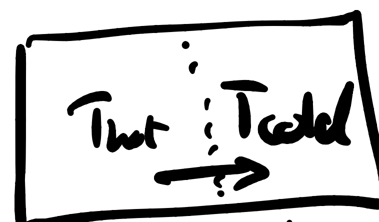
Thermodynamic Potentials

quantity which is minimized at equilibrium under certain conditions

closed system

$$dS \geq 0 \iff -dS \leq 0$$





$$2H_2 + O_2 \rightleftharpoons 2H_2O$$

1 mol	.5 mol	0
$-2x$	$-x$	x

$$dS \geq đq/T \qquad \text{((clausius inequality)}$$

$$dE = đq + đw \qquad đq \leq TdS$$

$$= đq - PdV$$

$$\leq \underbrace{TdS}_{\text{if } 0} - \underbrace{PdV}_{\text{if } 0}$$

when is $dE \leq 0$

then $dE \leq 0$ — Energy is a potential for constant S, V

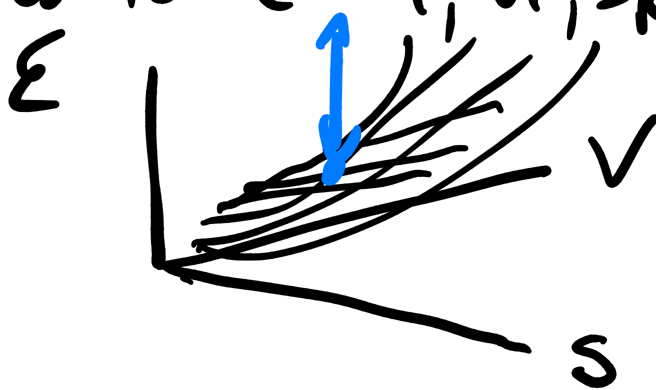
Ch 5, ideal gas

how does E depend on S & V

book typo

$$E(S,V) = \frac{3}{2} nRT_r\, e^{(S-S_r)/C_V} \left(V_r/V\right)^{2/3}$$

compared to ref T_r, V_r, S_R



$dE \le 0$ for this case

Consider

$$H = \mathcal{E} + pV$$

$$dH = d\mathcal{E} + p\,dV + V\,dp$$

$$d\mathcal{E} \le T\,dS - p\,dV$$

$$\le T\,dS + V\,dp$$

when is $dH \le 0$? $\leftarrow S, p$ constant

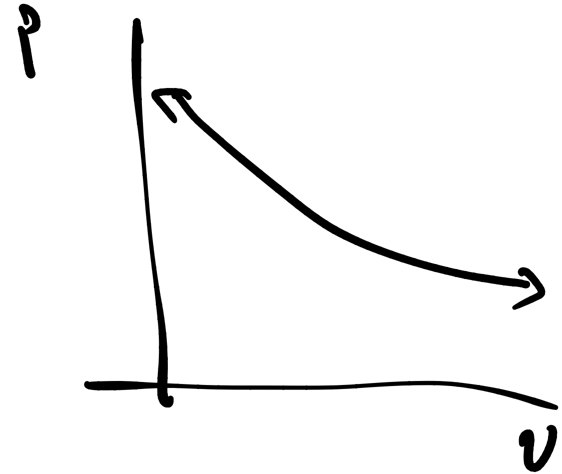
Consider $G = H - TS = \mathcal{E} + PV - TS$

$$dG = dH - TdS - SdT$$

$$\leq TdS + Vdp$$

$$\leq VdP - SdT$$

when is $dG \leq 0$, pressure & temp constant?



d go up

$$G = \mathcal{E} + pV - TS$$ ← go up

const const

~~so down~~

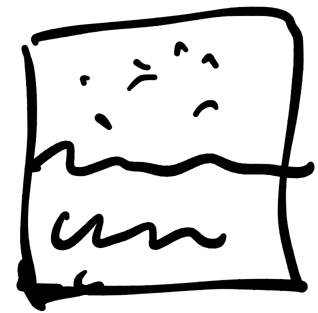
ideal gas

For completeness

$$A = \mathcal{E} - TS$$ Helmholtz FE

$$dA = d\mathcal{E} - TdS - SdT$$

$$\leq TdS - pdV$$



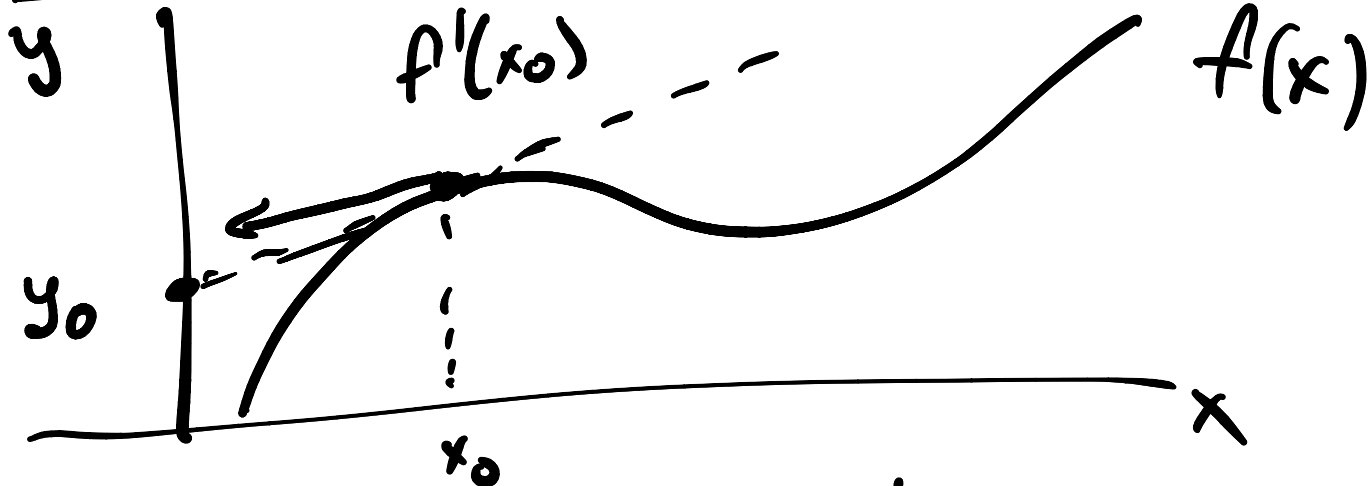
$$\leq -pdV - SdT$$

A is potential for const V&T

Unifying concept

$$
\begin{tikzcd}
E \arrow[r, "-TS"] \arrow[d, "E+pV"'] & A \arrow[d, "+PV"] \\
H \arrow[r, "-TS"'] & G
\end{tikzcd}
$$

Legendre Transformation



$$y = f'(x)\,x + y_0 \leftarrow b(x_0)$$

$$b(x_0) = y - f'(x_0)\,x$$

$\mathcal{E}(S)$

T

$\mathcal{E}(N,S,V)$

$$A \equiv \mathcal{E} - \left(\frac{\partial \mathcal{E}}{\partial S}\right) S$$

$$\mathcal{E} - TS$$

Need to show

$= -p$

$$\mathcal{E} - \left(\frac{\partial \mathcal{E}}{\partial S}\right)_V S = A(T,V)$$

$$G \equiv A - \left(\frac{\partial A}{\partial V}\right) V = A + pV$$