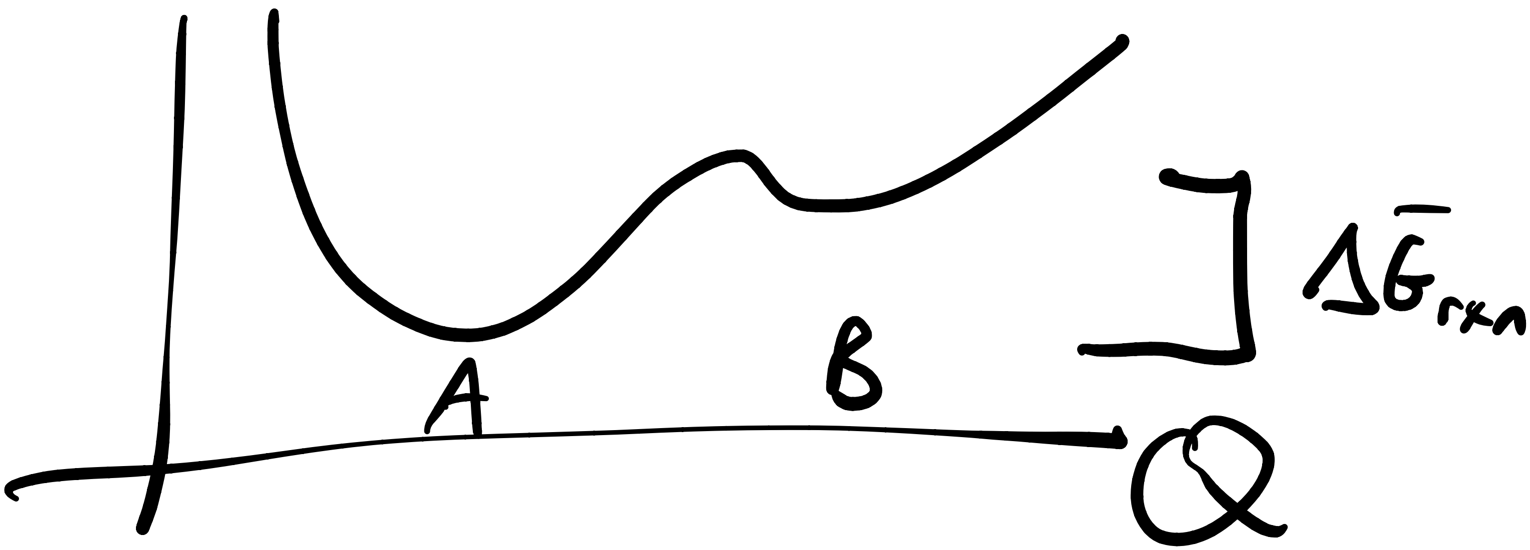
Recap

$$A \rightleftarrows B$$



$$K_{eq} = [B]_{eq} / [A]_{eq}$$

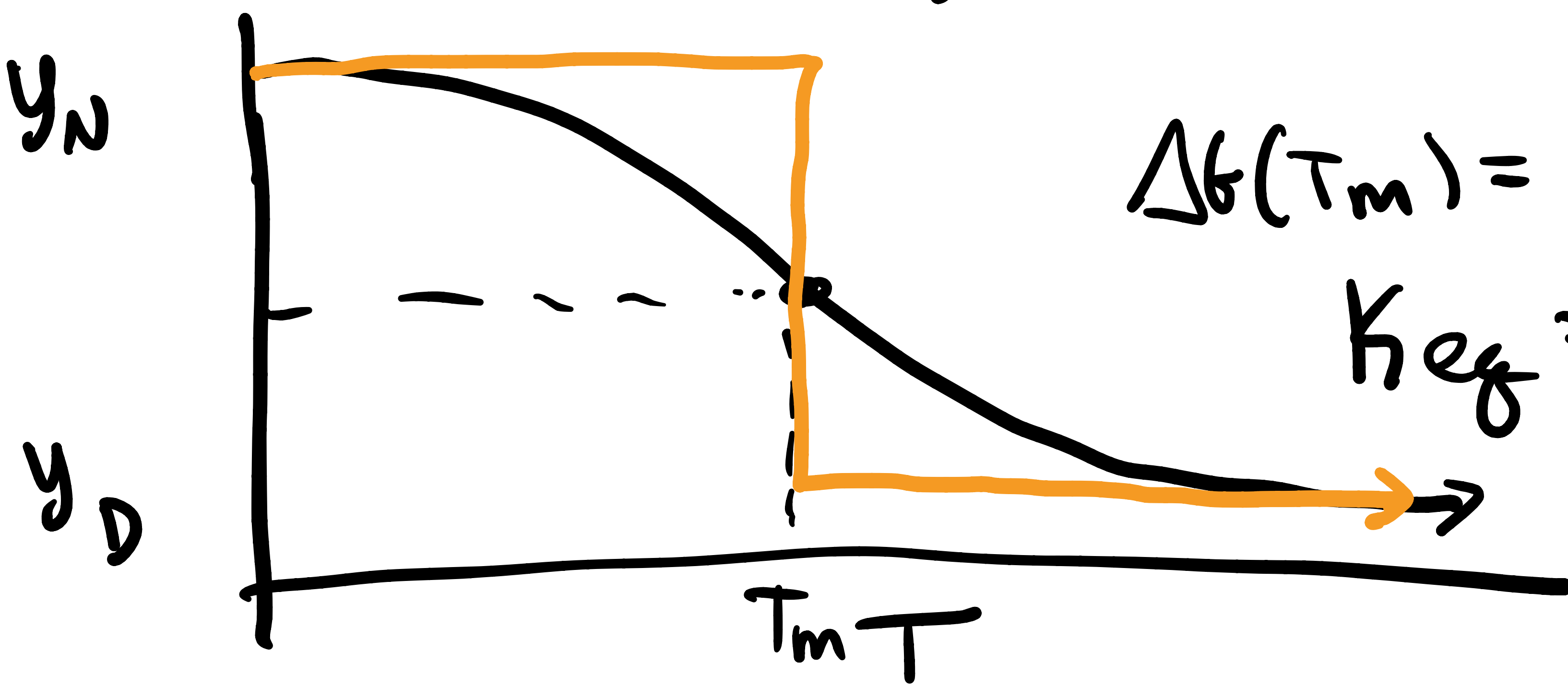
$$\Delta \bar{G}_{rxn} = -RT \ln K_{eq}$$

$$\Delta \bar{G} = \Delta \bar{H} - T \Delta \bar{S}$$

can only see one state

then you can't learn $\Delta \bar{H}, \Delta \bar{S}$

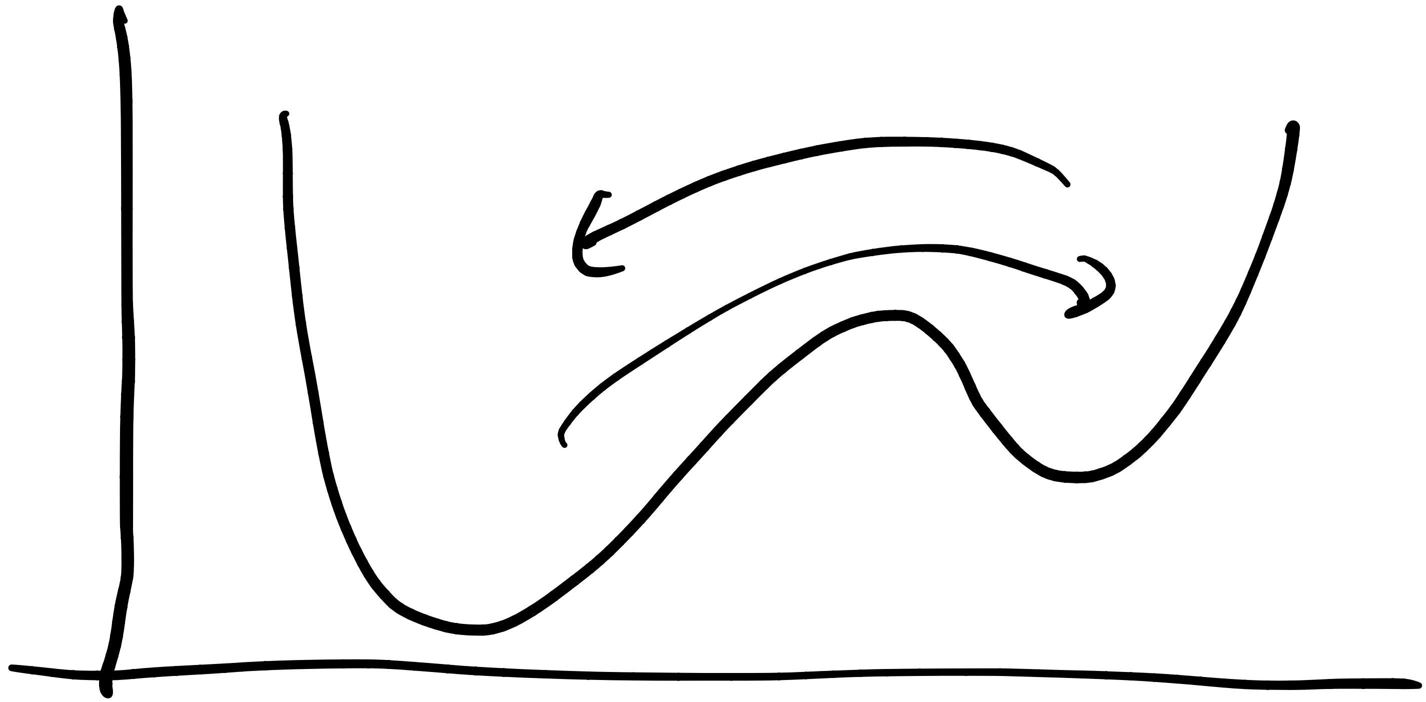
Measure y_{obs}, change T



(not phase transition)

$$\Delta G(T_m) = 0$$

$$K_{eq} = 1$$

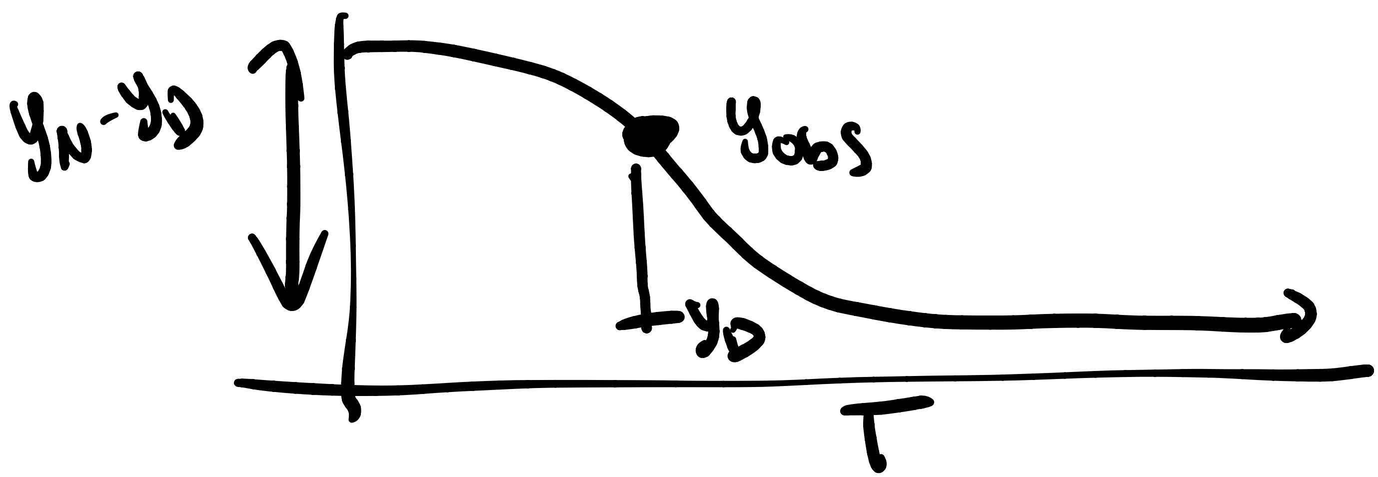


$$y_{obs} = f_N y_N + f_D y_D$$

$$= f_N y_N + (1 - f_N) y_D$$

$$= y_D + f_N (y_N - y_D)$$

$$f_N = \frac{y_{obs} - y_D}{y_N - y_D}$$ ← partial drop / ← total drop



$$y_{obs} = f_N y_N + (1 - f_N) y_D$$

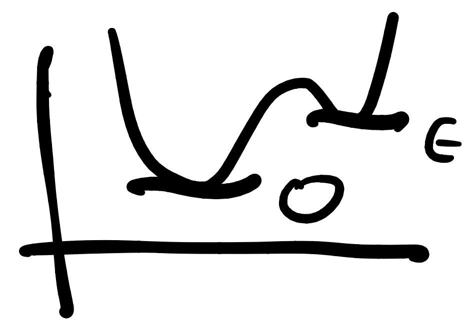
$$= \frac{K}{1+K} y_N + \frac{1}{1+K} y_D$$

check

$$= y_D - (y_D - y_N) \frac{K}{1+K}$$

$$K = e^{-\Delta G^\circ/RT}$$

$$\frac{y_D + y_N e^{-\Delta G/RT}}{1 + e^{-\Delta G/RT}}$$



$E = +\Delta G_{rxn}$

$$y_{obs} = \frac{y_D + y_N e^{-\Delta G/RT}}{1 + e^{-\Delta G/RT}}$$

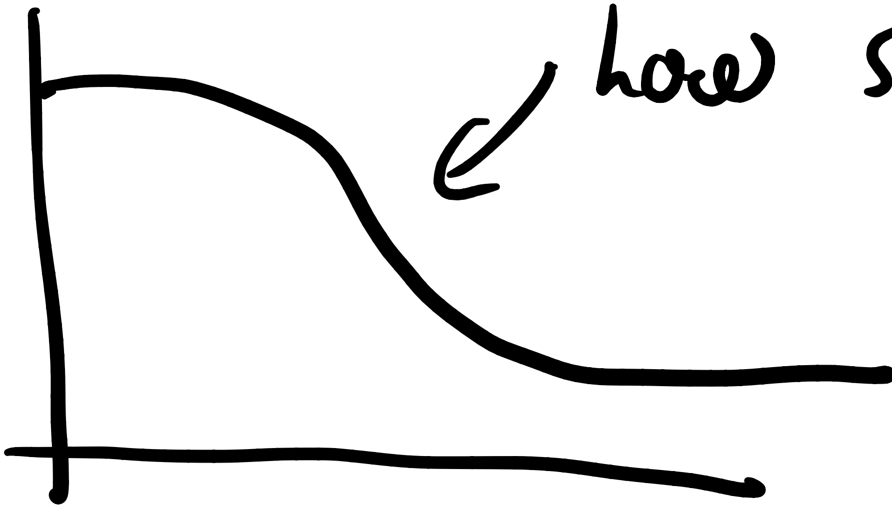
$$\Delta G = \Delta H - T\Delta S$$

assume constant

T_m has $\Delta G = 0$ & $f_N = f_D = 0.5$

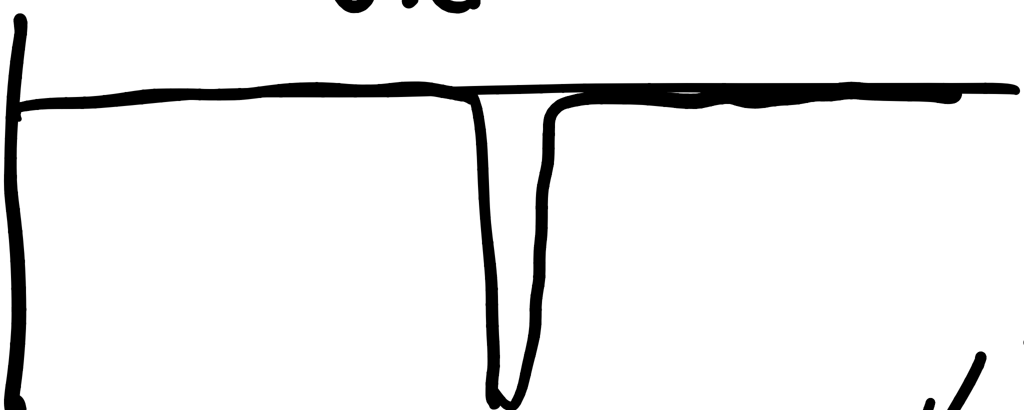
and $T_m = \Delta H / \Delta S$

if constant



how steep is the transition

Calculate dy/dt

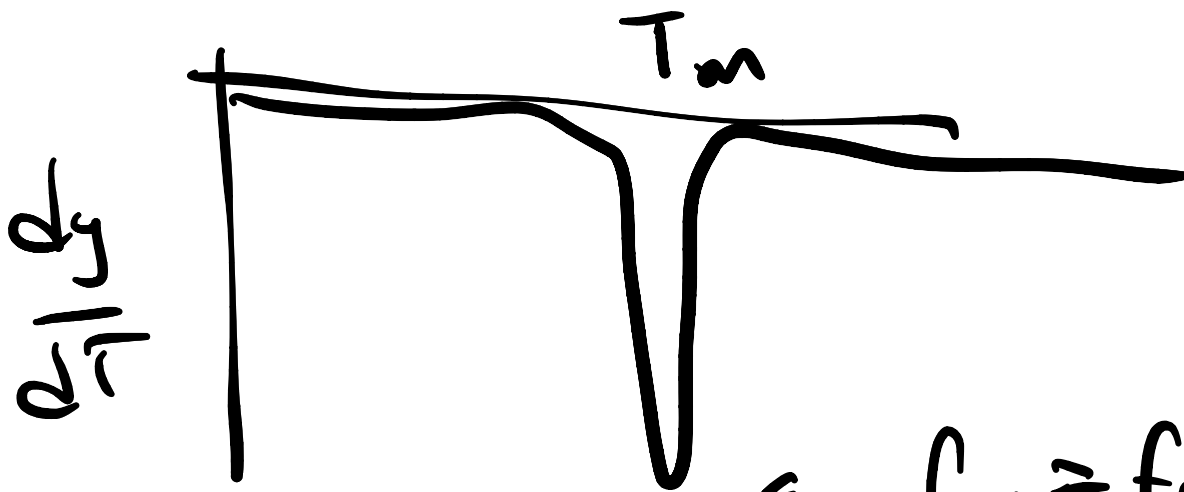


$f_N f_D$

$$dy/dT = (y_N - y_D)\frac{K}{(1+K)^2}\frac{\Delta \bar{H}^\circ}{RT}$$

$$\frac{dy}{dT} = (y_N - y_D)\, f_N f_D \frac{\Delta \bar{H}^\circ}{RT^2}$$

$\Delta H^\circ = T_m \Delta S^\circ$



$\leftarrow f_N = f_D = 1/2$

entropy/enthalpy difference controls skewness

$$K = e^{-\Delta \bar{G}^\circ / RT} = e^{\Delta H^\circ (T - T_m)/(R T T_m)}$$

Constant heat capacity model

$$d\bar{H} = \bar{C}_p \, dT \qquad / \quad dS = \frac{\bar{C}_p}{T} dT$$

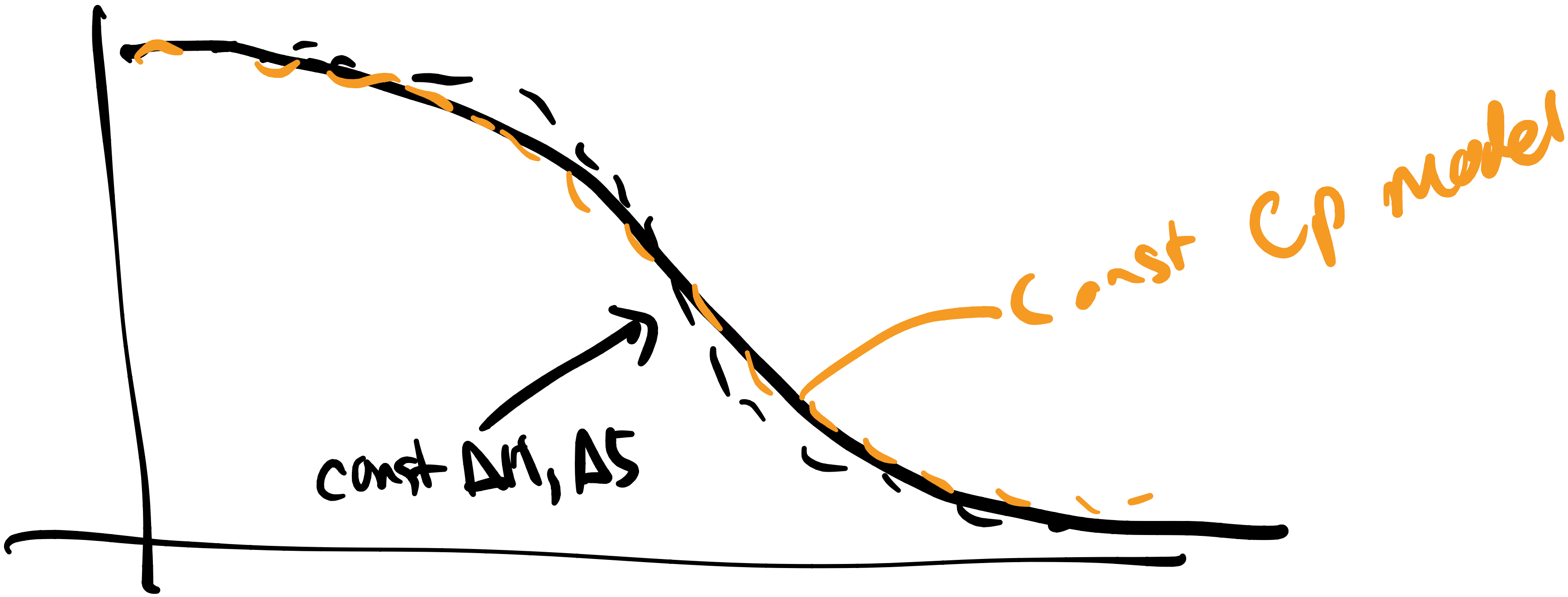
$$\bar{H}_N = \bar{H}_N^{ref} + \bar{C}_p (T - T_{ref})$$

$$\bar{H}_D = \bar{H}_D^{ref} + \bar{C}_p (T - T_{ref})$$

$$\Delta\bar{H} = \Delta\bar{H}_{ref} + \Delta\bar{C}_p (T - T_{ref})$$

could take ref state as T_m

$$\Delta\bar{S} = \Delta\bar{S}_{ref} + \Delta\bar{C}_p \ln (T/T_{ref})$$



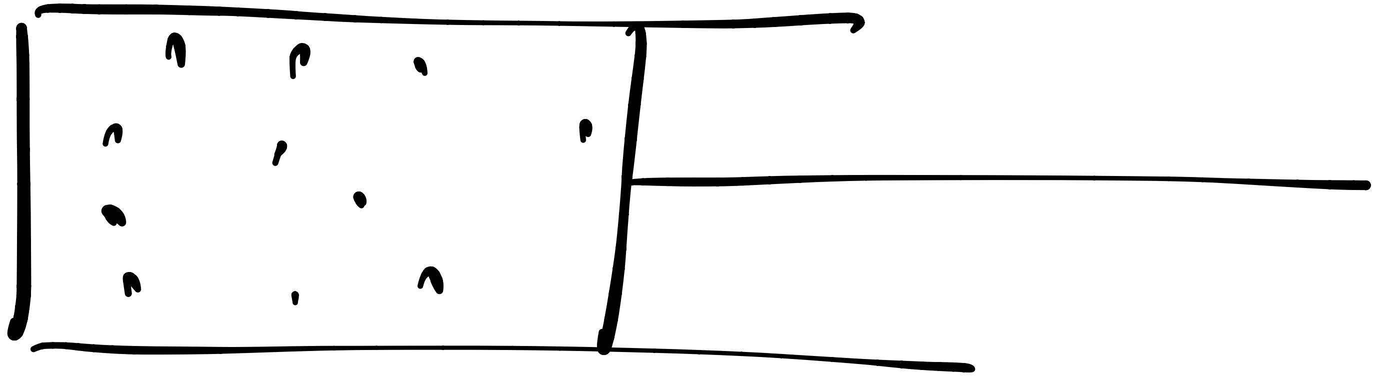
const Cp model
const ΔH, ΔS

Kinetics / Kinetic theory of gasses

molecular picture - molecules should follow Newtonian mechanics

Problem: can't solve $F = ma$ for more than 2 particle analytically for most potentials

What are the gas molecules doing on average?



ideal gas, molecules don't interact

One molecule in one dimension

$$KE = \frac{1}{2}mv^2 = p^2/2m$$

$$p = mv$$

Boltzmann equation says: $P(E) \propto e^{-E/k_BT}$

One particle in one dimension:

$$P(\varepsilon) \propto e^{-KE/k_BT} = e^{-\frac{1}{2}mv^2/k_BT}$$

$$P(v) \propto e^{-\frac{mv^2}{2k_BT}}$$

Normal dist with mean

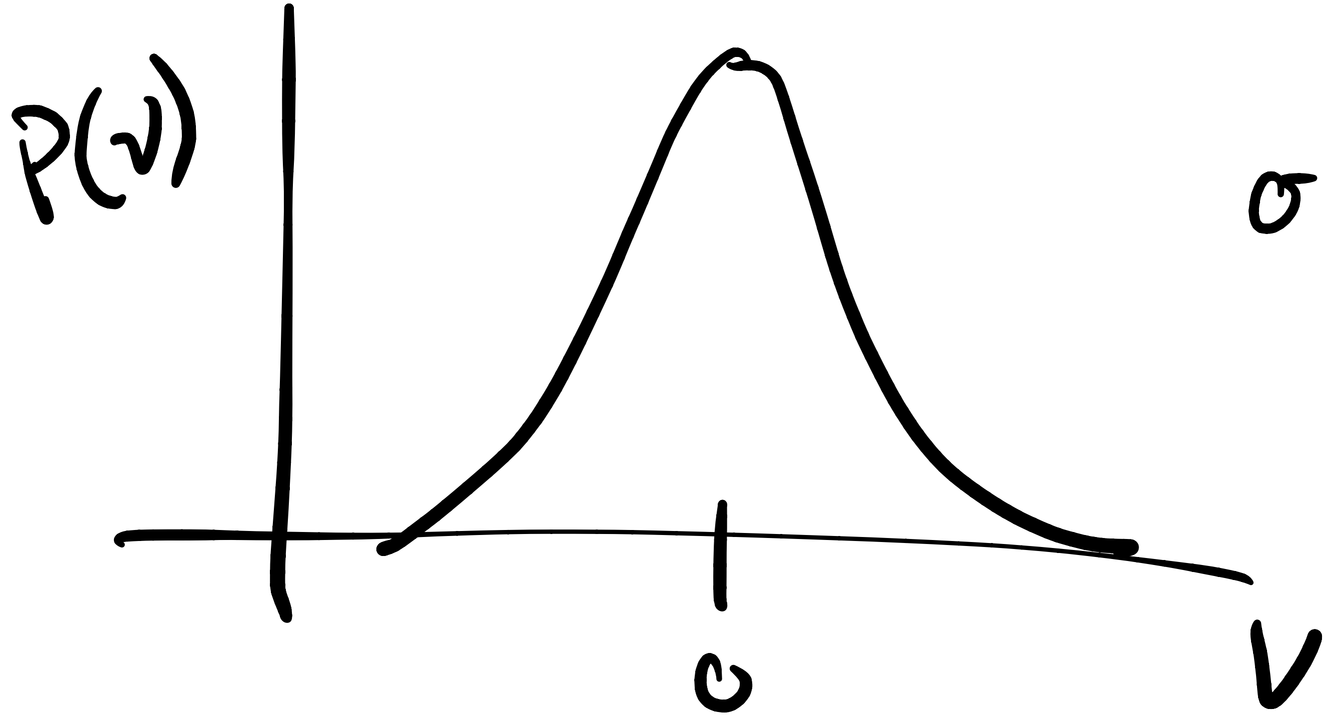
$\mu = 0$

$\sigma = k_BT/m$

$$N(\mu,\sigma) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

$$P(v) = \frac{1}{\sqrt{2\pi k_BT/m}} e^{-\frac{1\,mv^2}{2k_BT}}$$

$R = N_A k_B$

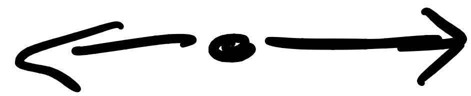


$$\sigma^2 = k_B T / m$$

$$\sigma^2 = \langle v^2 \rangle - \underbrace{\mu^2}_{=0} = \langle v^2 \rangle$$

$$\sigma = \sqrt{\langle v^2 \rangle} = v_{r.m.s.}$$

Average energy

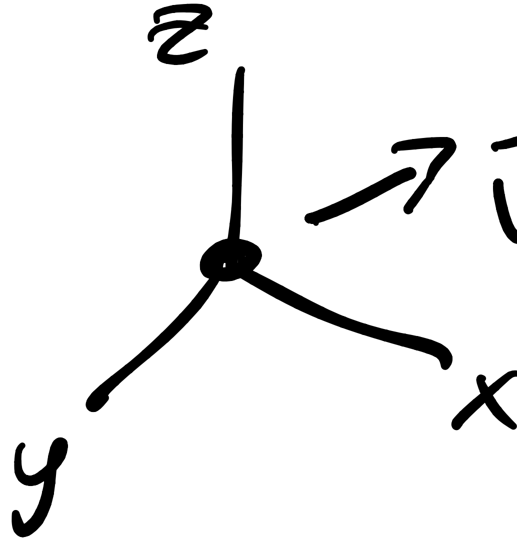


$$\langle \varepsilon \rangle = \left\langle \tfrac{1}{2} m v^2 \right\rangle = \frac{m}{2} \langle v^2 \rangle$$

$$= m/_2 \; k_B T/m$$

$$= k_B T/2$$

In 3d



$\vec{v} = (v_x, v_y, v_z)$

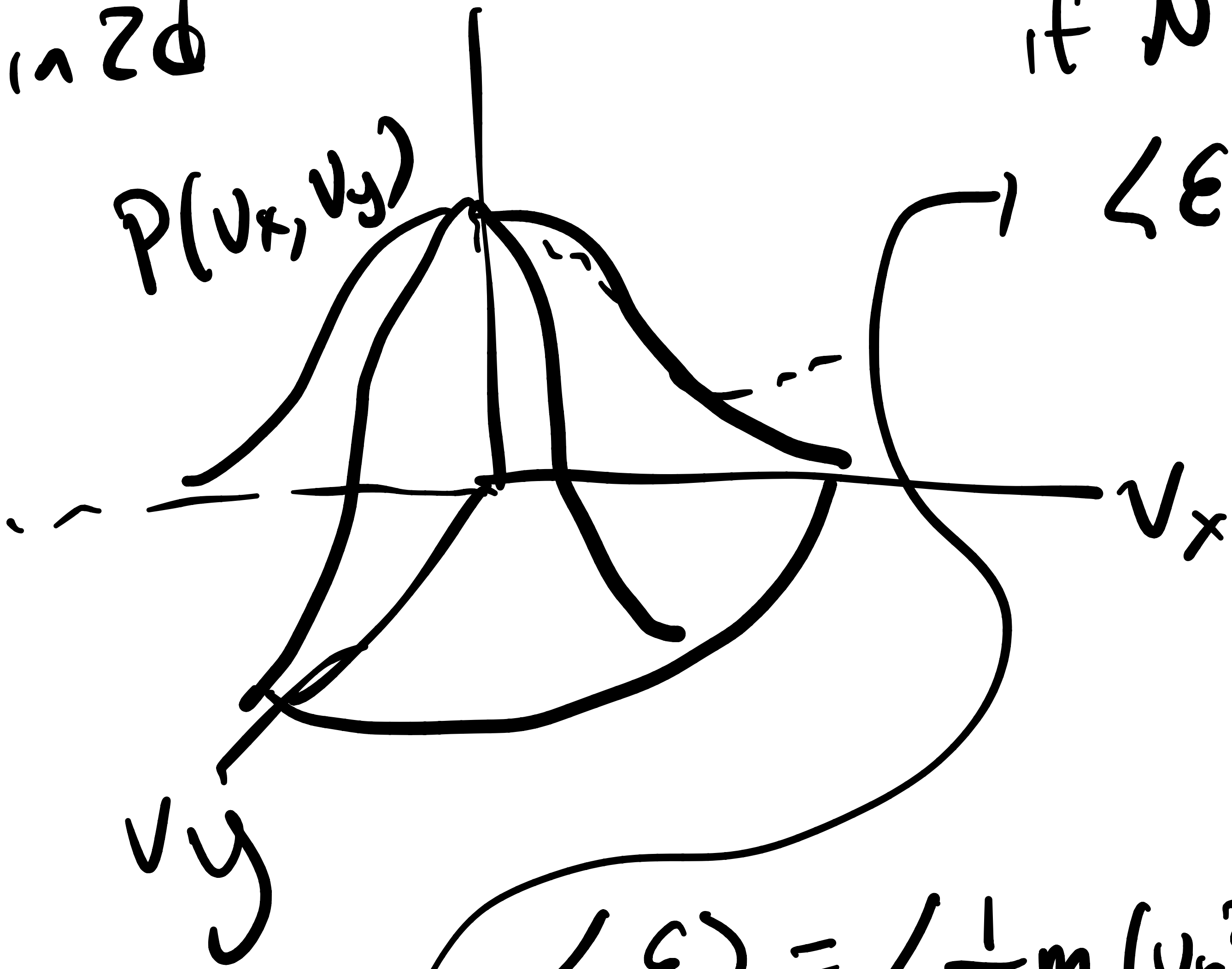
$$\mathcal{E} = \frac{1}{2} m |\vec{v}|^2 = \frac{1}{2} m \left(v_x^2 + v_y^2 + v_z^2 \right)$$

$$P(\mathcal{E}) \propto e^{-\frac{1}{k_B T}\mathcal{E}} = e^{-\frac{m}{2k_B T}\left(v_x^2 + v_y^2 + v_z^2 \right)}$$

$$= e^{-m/2k_B T\, v_x^2} e^{-\frac{m}{2k_B T} v_y^2} \cdots$$

$$= P(\mathcal{E}_x) P(\mathcal{E}_y) P(\mathcal{E}_z)$$

Eg in 2d

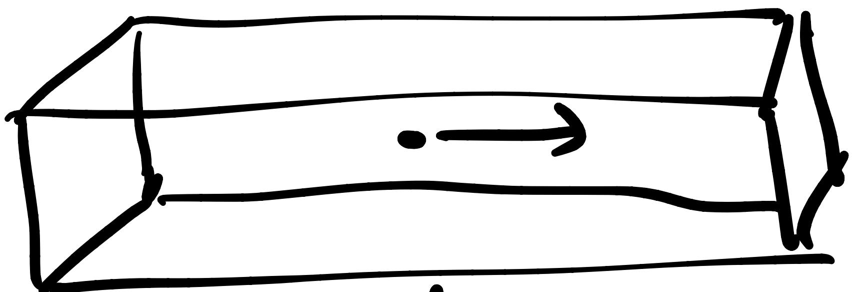


if N molecules

$$\langle \varepsilon \rangle = \frac{3}{2} N k_B T$$
$$= \frac{3}{2} n R T$$

$$\langle \varepsilon \rangle = \left\langle \frac{1}{2} m \left(v_x^2 + v_y^2 + v_z^2 \right) \right\rangle$$
$$= 3 \left\langle \frac{1}{2} m v^2 \right\rangle$$
$$= 3 \cdot k_B T / 2$$

What about pressure



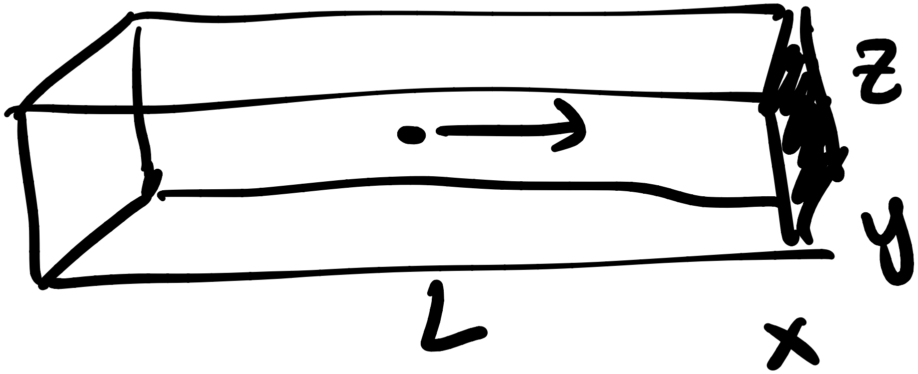
speed v_x

$|v_x|$ stays same, turns around at the wall

change in momentum is

$$mv_x - (-mv_x) = 2mv_x$$

$$F = \frac{\Delta p}{\Delta t} \qquad \Delta t = \frac{2L}{v}, \quad \left[F = \frac{m v_x^2}{L_x} \right.$$



speed v_x

$$P = \underbrace{\frac{N}{V} k_B T}$$

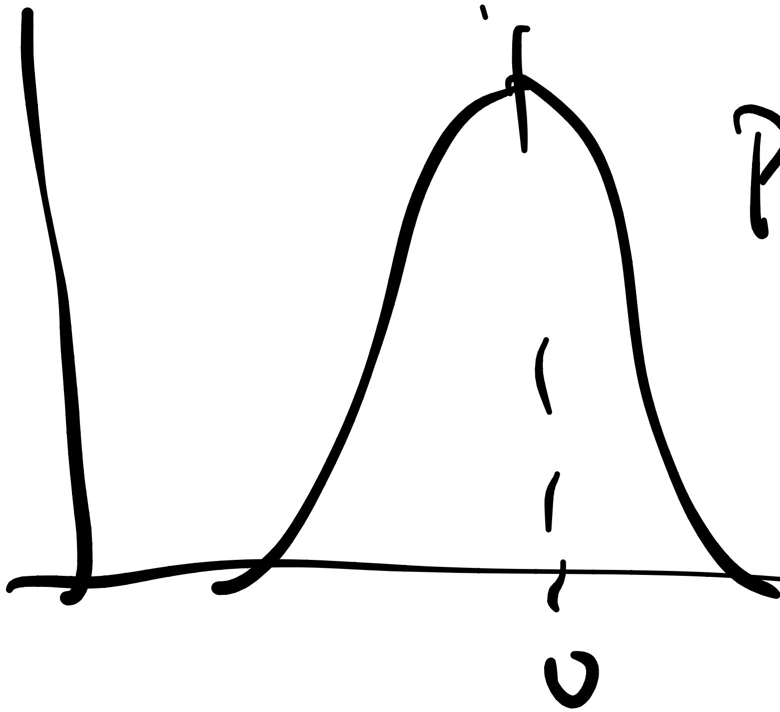
ideal gas law

$$F_x = m v_x^2 / L_x$$

$$P = F/A = F/L_y \cdot L_z$$

$$= m v_x^2 / L_x L_y L_z = \frac{m v_x^2}{V}$$

$$P_{total} = \sum_{i=1}^{N} P_i = \sum_{i=1}^{N} \frac{m v_i^{x2}}{V} = \frac{m}{V} \cdot N \cdot \overbrace{\frac{1}{N} \sum_{i=1}^{N} v_i^2}^{k_B T/m \;=}$$



$$P(v_x) \propto e^{-\frac{1}{2}mv^2}$$

speed

$$P(s) = P(|v|) \propto s^2 e^{-\frac{ms^2}{2k_BT}}$$

$$e^{-\frac{1}{2}mv_x^2} \; e^{-\frac{1}{2}mv_y^2} \; e^{-\frac{1}{2}mv_z^2}$$

→ polar coordinates, integrate angles