

Reminder

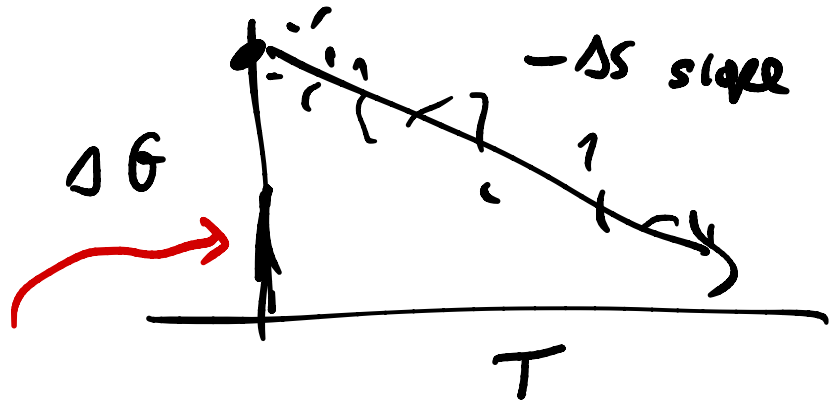
thermodynamic potential for a system
under certain conditions, this
quantity always goes down (or stays same)
minimized on way to equilibrium

$$\begin{array}{ccc}
 E(N, V, S) & \xrightarrow{-TS} & A(N, V, T) \\
 +PV \downarrow & & \downarrow +PV \\
 H(N, P, S) & \xrightarrow{-TS} & G(N, P, T)
 \end{array}$$

come from a Legendre transform

$$A(N, V, T) = E - S \left(\frac{\partial E}{\partial S} \right)_{N, V} \leftarrow T$$

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



$$dG^{(P,T)} = dP \left(\frac{\partial G}{\partial P} \right)_T + dT \left(\frac{\partial G}{\partial T} \right)_P$$

$$G(N, P, T) = E - TS + PV$$

$$dG = dE - Tds - SdT + PdV + v dP$$

$$= -SdT + v dP$$

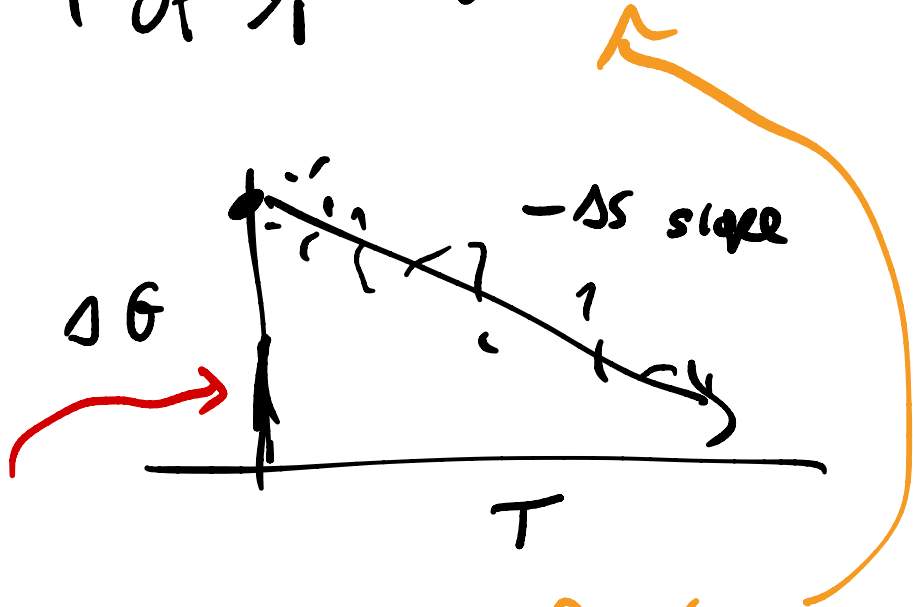
$$dE = Tds - PdV$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

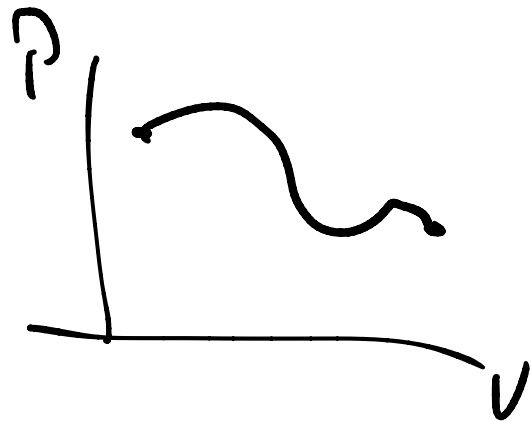
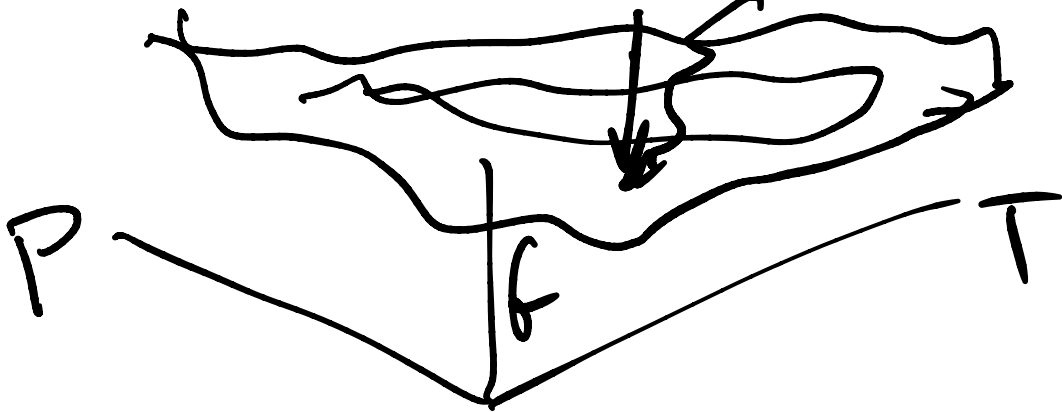
$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

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

actually
measure Entropy



Can be used
to measure Volume
Changes in rxn



$$G = E - TS + PV$$

$$G_f - G_i$$

$$= \underbrace{E_f - E_i}_{\Delta E} - \underbrace{(T_f S_f) + (T_i S_i)}_{-TS} + \underbrace{P_f V_f - P_i V_i}_{\Delta H}$$

$$dG^{(P,T)} = dP \left(\frac{\partial G}{\partial P} \right)_T + dT \left(\frac{\partial G}{\partial T} \right)_P$$

$$\frac{\partial^2 M}{\partial x \partial y} = \frac{\partial^2 M}{\partial y \partial x}$$

$$\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P} \right)_T = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T} \right)_P$$

\uparrow V \uparrow $-S$

Ex: Maxwell Relation

$$\left(\frac{\partial V}{\partial T} \right)_P = \left(-\frac{\partial S}{\partial P} \right)_T$$

easy to measure

hard

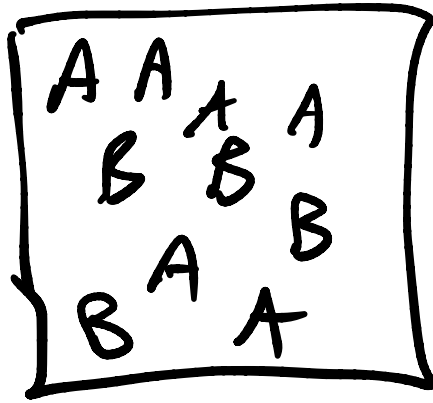
$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

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

$$\left(\frac{\partial S}{\partial \mathcal{E}}\right)_{V, N} = \frac{1}{T}$$

$$\begin{aligned} &= \frac{1}{T} \\ \partial S &\sim \frac{1}{T} \partial \mathcal{E} \end{aligned}$$

Mixtures



~~N, V, E~~

N_A, N_B, V, E

2 component system - 4 quantities

N_A, N_B, V, T or N_A, N_B, P, T

$$N = N_A + N_B$$

$$E_{\text{total}} = E_A + E_B + \overset{\sim 0}{E_{AB}} \quad \text{approximation}$$

mol fraction / number fraction

$$\chi_A = \frac{N_A}{N_A + N_B} = \frac{n_A}{n_A + n_B}$$

(number fraction, mol fraction)

$$\chi_A + \chi_B = 1$$

Extensive vs intensive

intensive \rightarrow extensive / amount

$$\bar{E} = \frac{E_{\text{tot}}}{N}$$

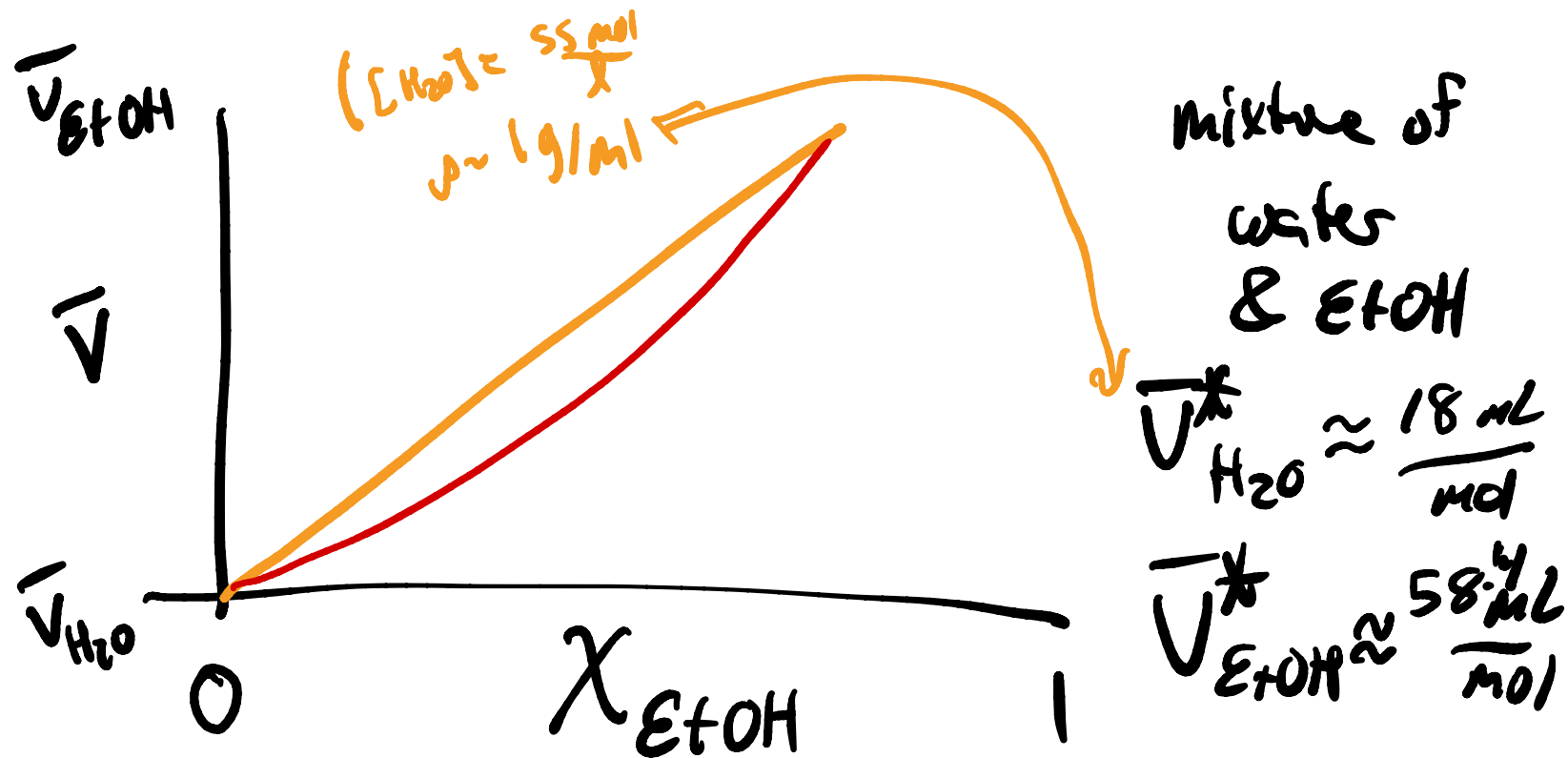
$$\bar{E}_A = \frac{E_A}{n_A}$$

\swarrow pure A system

$$\bar{E}_B = \frac{E_B}{n_B}$$

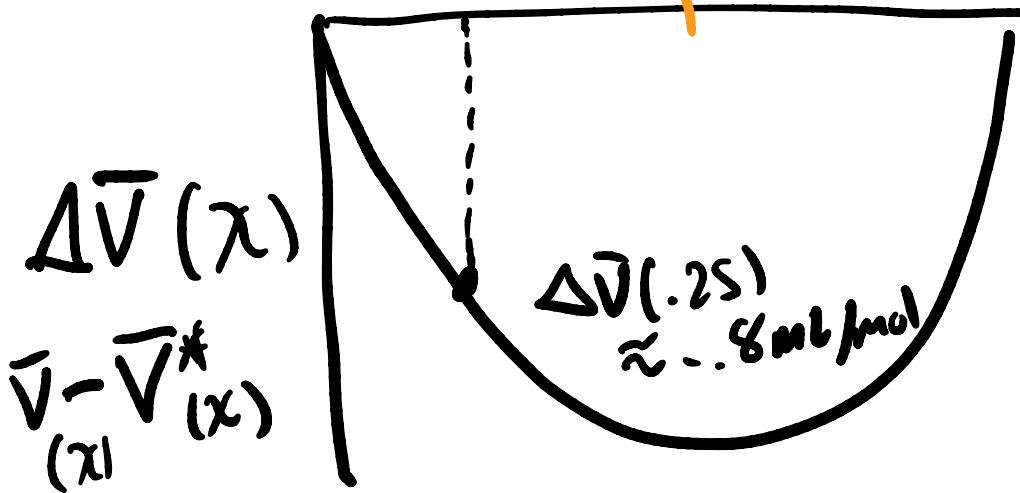
\swarrow pure B

$$E = \chi_A \bar{E}_A + \chi_B \bar{E}_B$$



$$\bar{V}_{\text{ideal}} = X_{\text{EtOH}} \bar{V}_{\text{EtOH}}^* + (1 - X_{\text{EtOH}}) \bar{V}_{\text{H}_2\text{O}}^*$$

50 mL + 50 mL \rightarrow 97 mL
non-ideal



x_{EtOH}

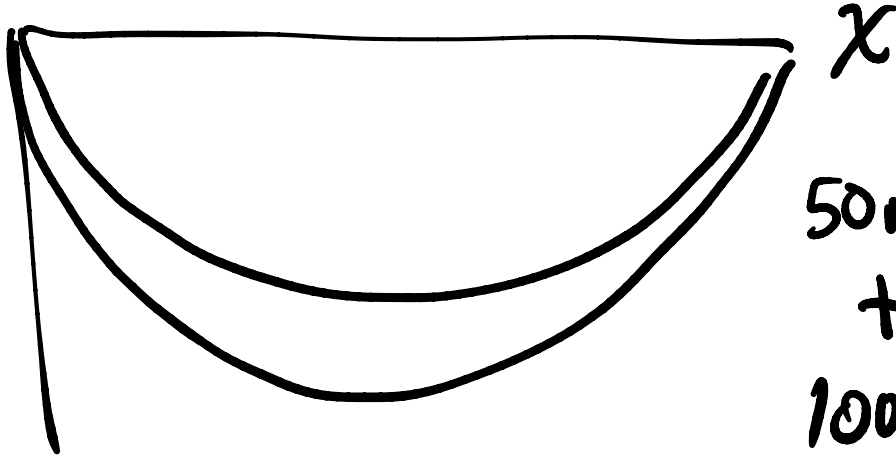
$$\Delta V_{total} = -0.8 \frac{\text{mL}}{\text{mol}} \cdot 3.68$$

$$= -2.9 \text{ mL}$$

$$n_{H_2O} = \left(\frac{50 \text{ mL}}{18 \text{ mL/mol}} \right) = 2.8 \text{ mol} \quad n_{EtOH} = \frac{50 \text{ mL}}{57.58 \text{ mL/mol}} \approx 0.88 \text{ mol}$$

$$x_{EtOH} = \frac{0.88}{2.8 + 0.88} = 0.24$$

ΔV



50 mL H₂O
+ x EtOH
100 mL H₂O
+ x EtOH

$$V(n_A, n_B) \Rightarrow dV = \left(\frac{\partial V}{\partial n_A} \right)_{n_B} dn_A + \left(\frac{\partial V}{\partial n_B} \right)_{n_A} dn_B$$

$\nwarrow \quad \nearrow$
 $\bar{V}_A \quad \bar{V}_B$