

Reminder

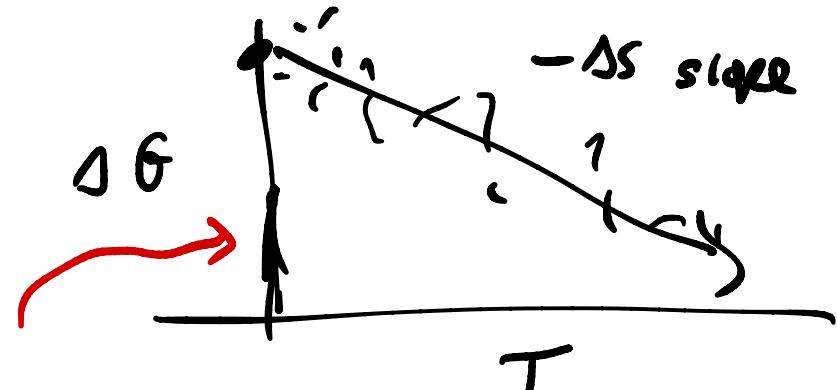
thermodynamic potential for a system
under certain conditions, this
quantity always goes down (or stays same)
minimized on way to equilibrium

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

Come from a legendre transform

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

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



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

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

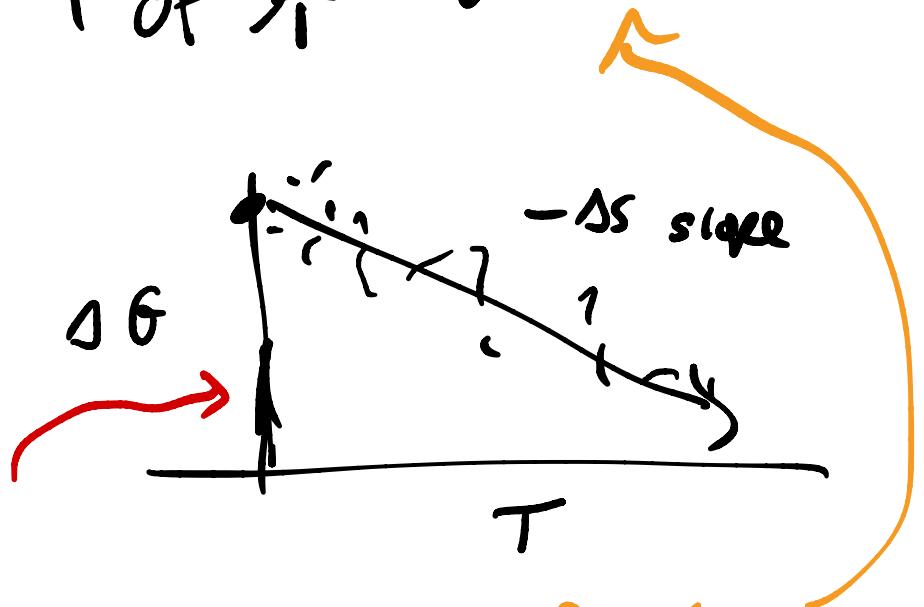
$$\begin{aligned} dG &= dE - TdS - SdT + PdV + VdP \\ &= -SdT + VdP \end{aligned}$$

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

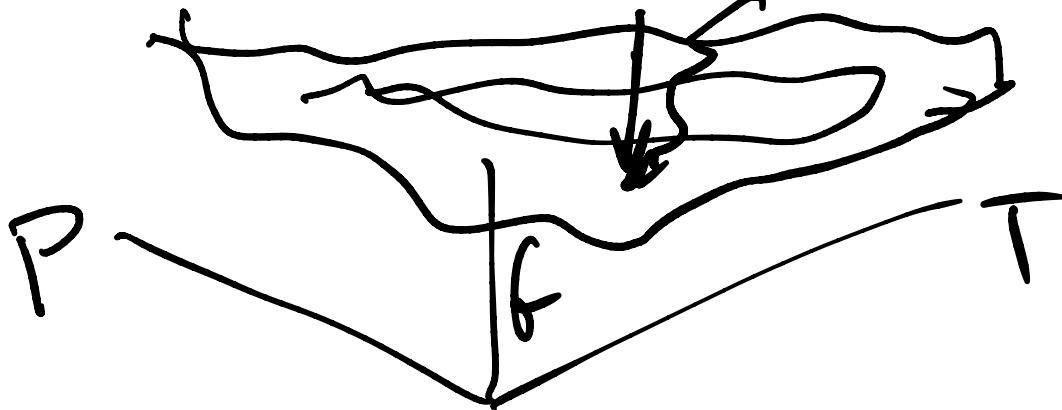
$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

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

actually
measure
Entropy



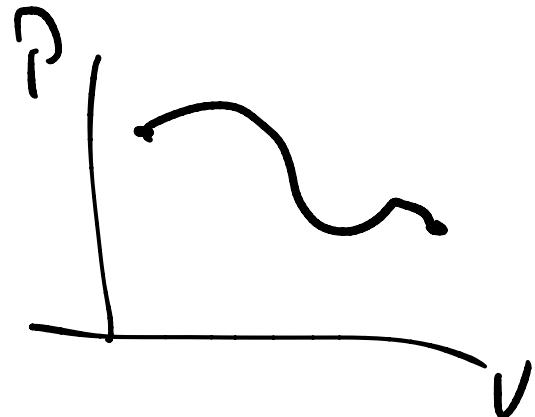
Can be used
to measure Volume
Changes in rxn



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

$$G_f - G_i$$

$$= \underbrace{\mathcal{E}_f - \mathcal{E}_i}_{\Delta \mathcal{E}} - \underbrace{(T_f S_f) + (T_i S_i)}_{\Delta(TS)} + \underbrace{P_f V_f - P_i V_i}_{\Delta PV}$$



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

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

Ex: Maxwell Relation

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

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

easy to measure hard

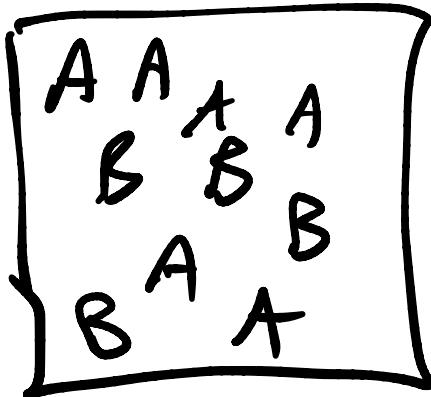
$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

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

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

$$\frac{\partial S}{\partial E} = \frac{1}{T}$$

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_S, 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

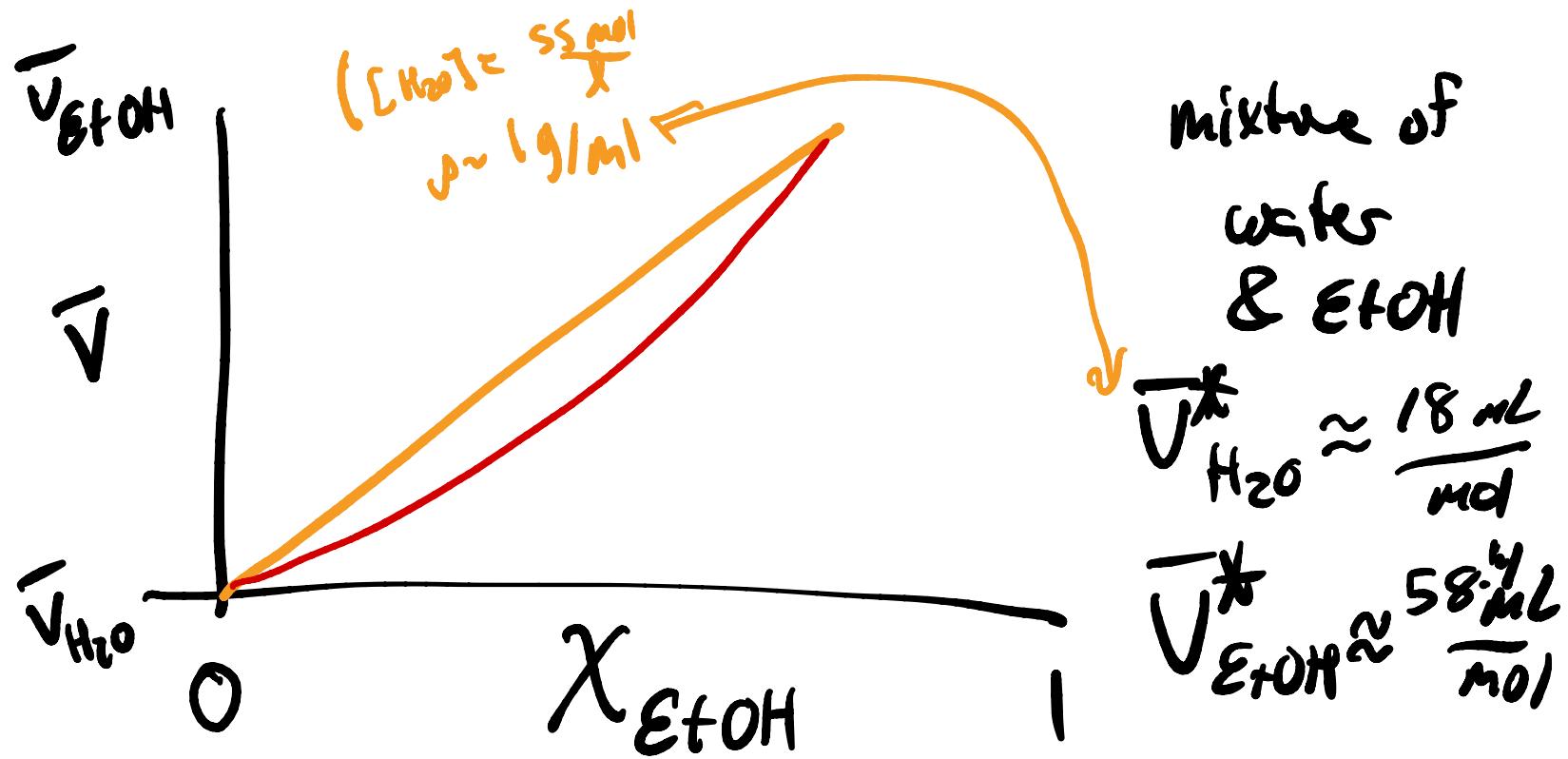
Intensive \rightarrow extensive / amount

$$\bar{\epsilon} = \frac{\epsilon_{\text{tot}}}{N}$$

$$\bar{\epsilon}_A = \frac{\epsilon_A^{\text{pure system}}}{n_A}$$

$$\bar{\epsilon}_B = \frac{\epsilon_B^{\text{pure B}}}{n_B}$$

$$\bar{\epsilon} = x_A \bar{\epsilon}_A + x_B \bar{\epsilon}_B$$

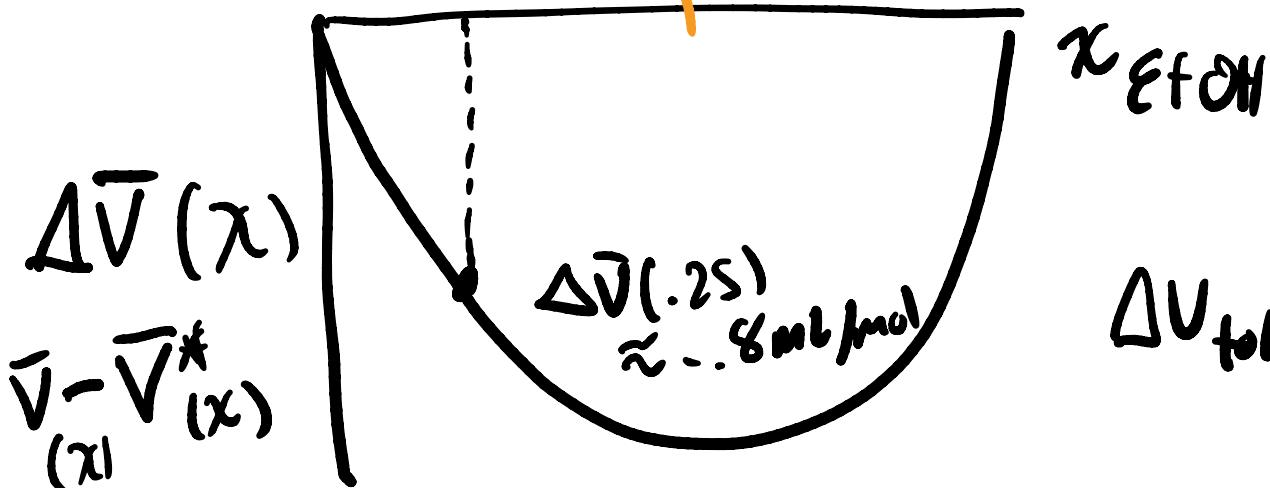


$$\bar{V}_{\text{ideal}} = x_{\text{EtOH}} \bar{V}_{\text{EtOH}}^* + (1 - x_{\text{EtOH}}) \bar{V}_{\text{H}_2\text{O}}^*$$

$$50 \text{ mL} + 50 \text{ mL} \rightarrow 97 \text{ mL}$$

0.5

non-ideal

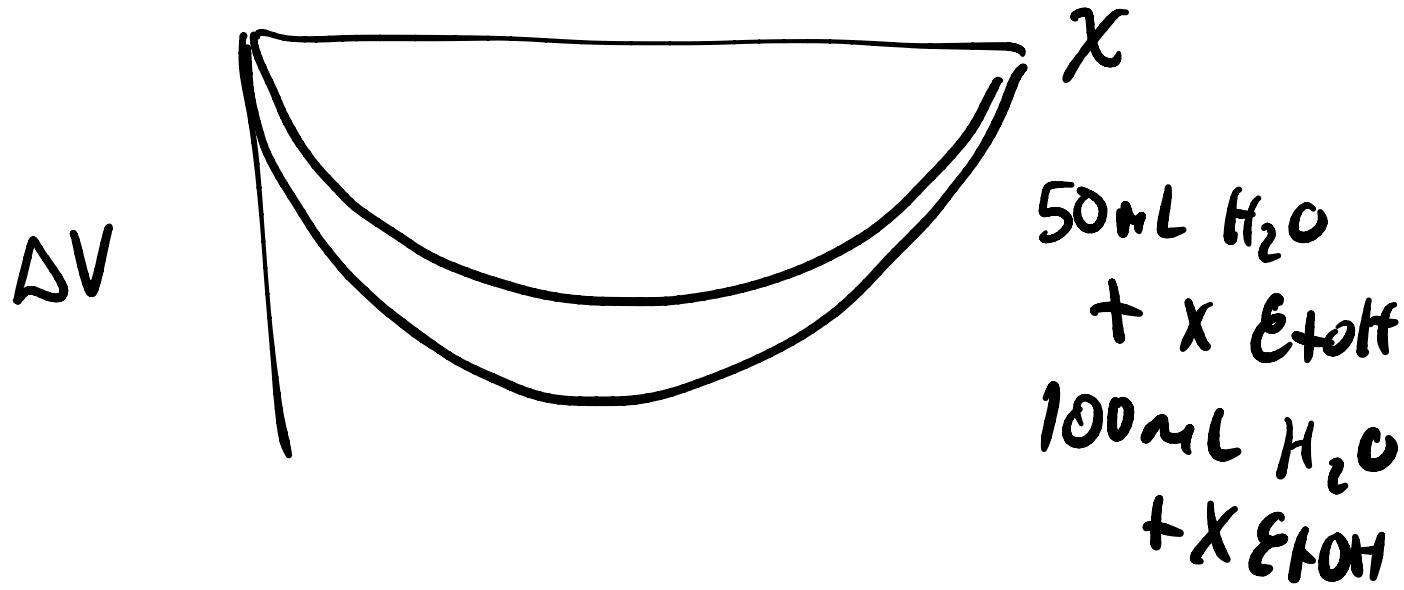


$$\begin{aligned}\Delta V_{\text{total}} &= -\frac{0.8 \text{ mL}}{\text{mol}} \cdot 3.68 \\ &= -2.9 \text{ mL}\end{aligned}$$

$$n_{\text{H}_2\text{O}} = \left(\frac{50 \text{ mL}}{18 \text{ mL/mol}} \right) = 2.8 \text{ mol}$$

$$n_{\text{EtOH}} = \frac{50 \text{ mL}}{57.58 \text{ mL/mol}} \approx 0.88 \text{ mol}$$

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



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

$\underbrace{V_A}_{n_A}$
 $\overbrace{V_B}^{n_B}$