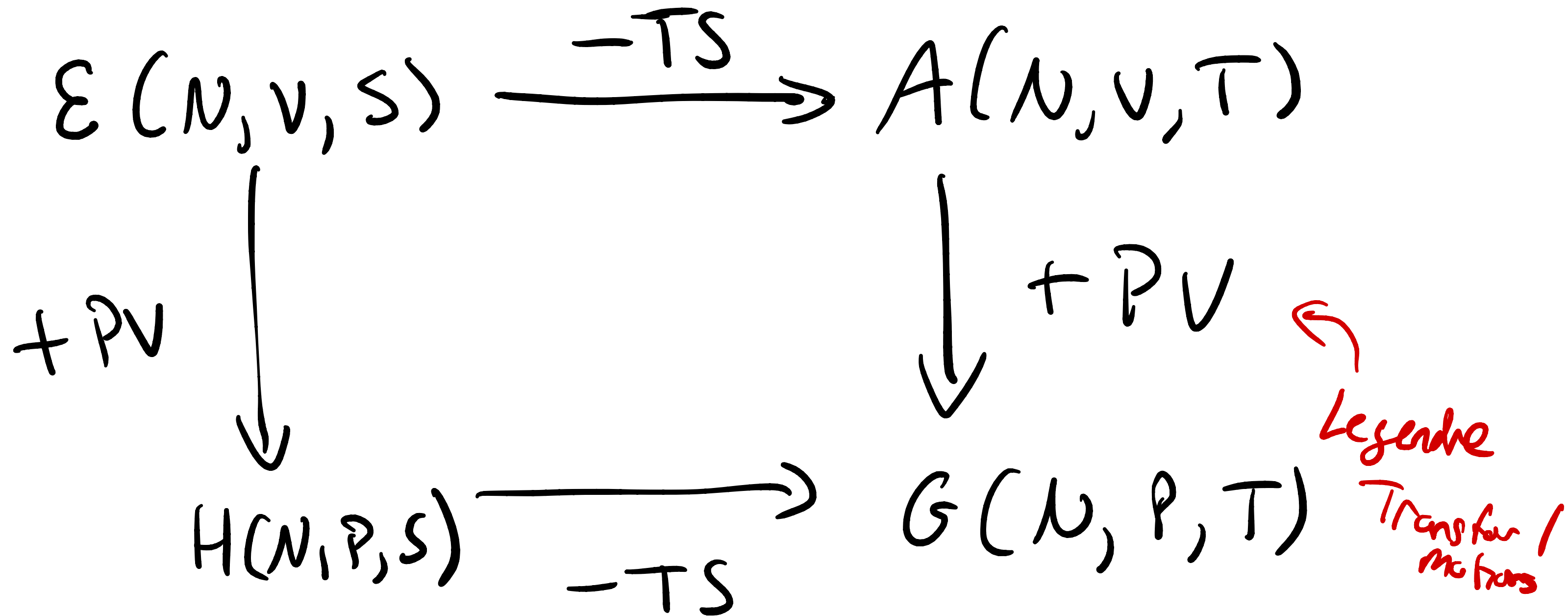


# Lecture 10 - Mixtures & Phase Transitions



const S transformation  $\leftrightarrow d\xi = 0$

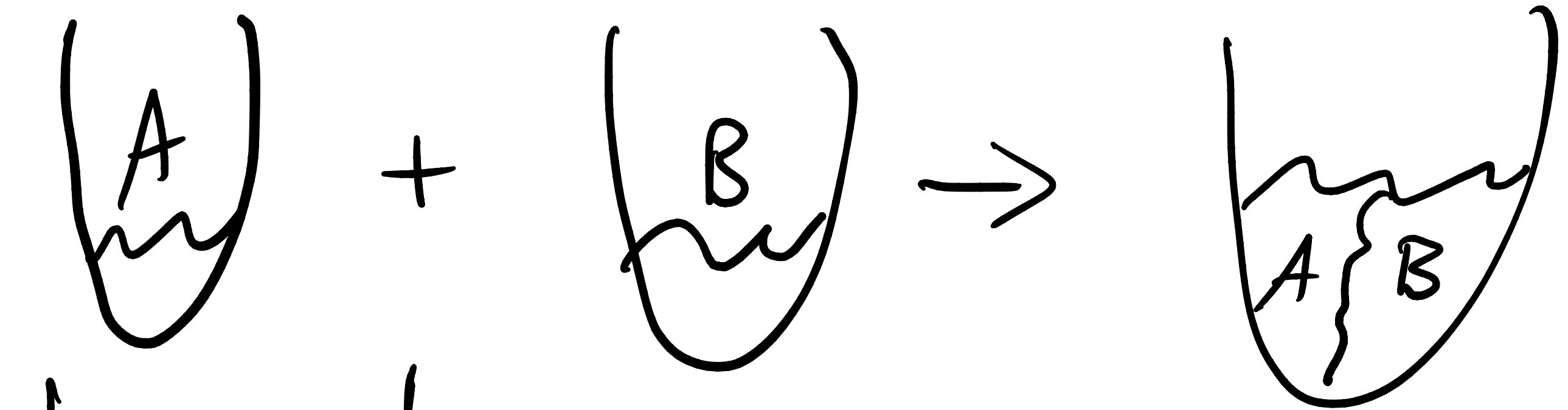
$$G = A + PV = A - \left( \frac{\partial A}{\partial V} \right)_{N, T} V$$

$G \leftarrow$  Gibbs Free Energy

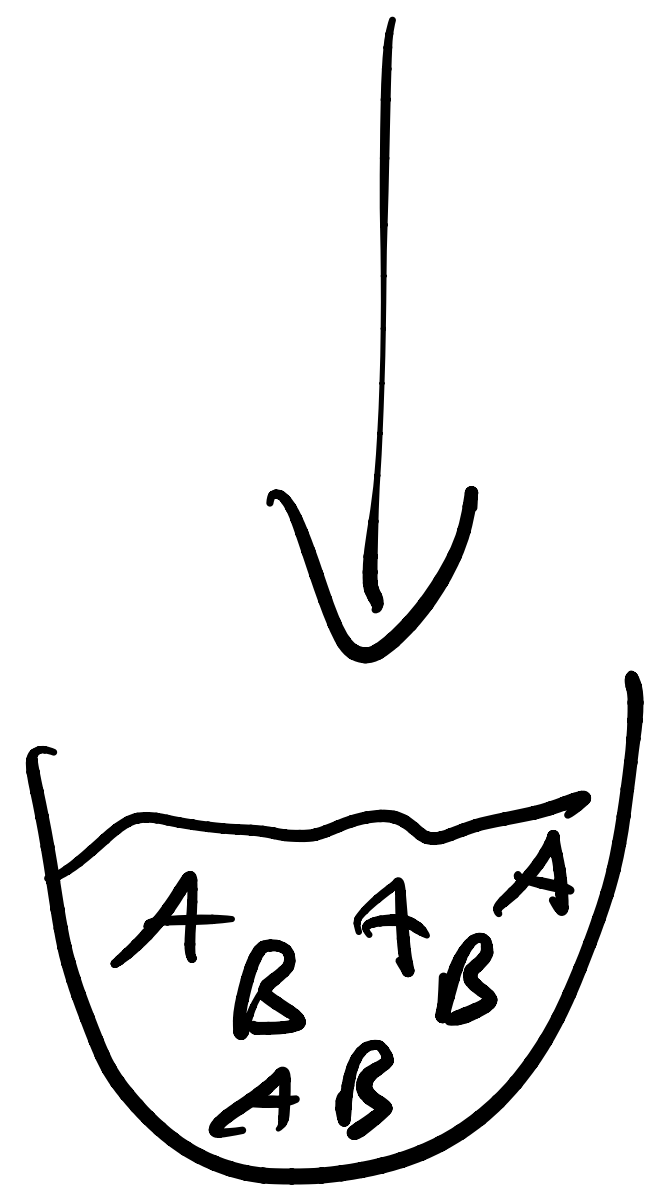
$$G = E - TS + PV$$

$$= H - TS$$

$G \downarrow$  for any spontaneous process  
at const  $P, T$



one possibility  
←



What are the properties of the mixture

$$G(P, T, N_A, N_B)$$

$$\frac{N_{\text{total}}}{N_A} = \frac{N_A + N_B}{N_A} = \sum_i N_i \quad (\text{extensive})$$

$$\frac{n_{\text{total}}}{n_{\text{total}}} = \frac{n_A + n_B}{n_{\text{total}}} = \sum_i n_i \quad (\text{extensive})$$

$$1 = \chi_A + \chi_B = \sum_i \chi_i \quad (\text{intensive})$$

Mixtures are not "ideal" in reality

eg ideal gas

$$\left\{ \begin{array}{l} E^{\text{ideal}} = E_L + E_R \\ P^{\text{ideal}} = P_L + P_R \\ S^{\text{ideal}} = S_L + S_R \end{array} \right. \begin{array}{l} \text{within fixed} \\ \text{volume} \\ \Leftarrow \text{probably not true} \end{array}$$

$$E_{\text{total}} = n_A \overline{E}_A + n_B \overline{E}_B$$

↑ (energy) per mol

if no mixture  $\bar{\epsilon}_A = \frac{\epsilon_A}{n_A}$

$$\epsilon = n_A \bar{\epsilon}_A$$

$$\epsilon_{\text{total}} = n_A \bar{\epsilon}_A + n_B \bar{\epsilon}_B$$

↑ (energy) per mol

averages  $\bar{\epsilon}_A \neq \epsilon_A^*$  ↪ molar energy in isolation

$$\epsilon_{\text{total}} = \epsilon_{A-A} + \epsilon_{A-B} + \epsilon_{B-B} + \epsilon_A^{\text{internal}} + \epsilon_B^{\text{internal}}$$

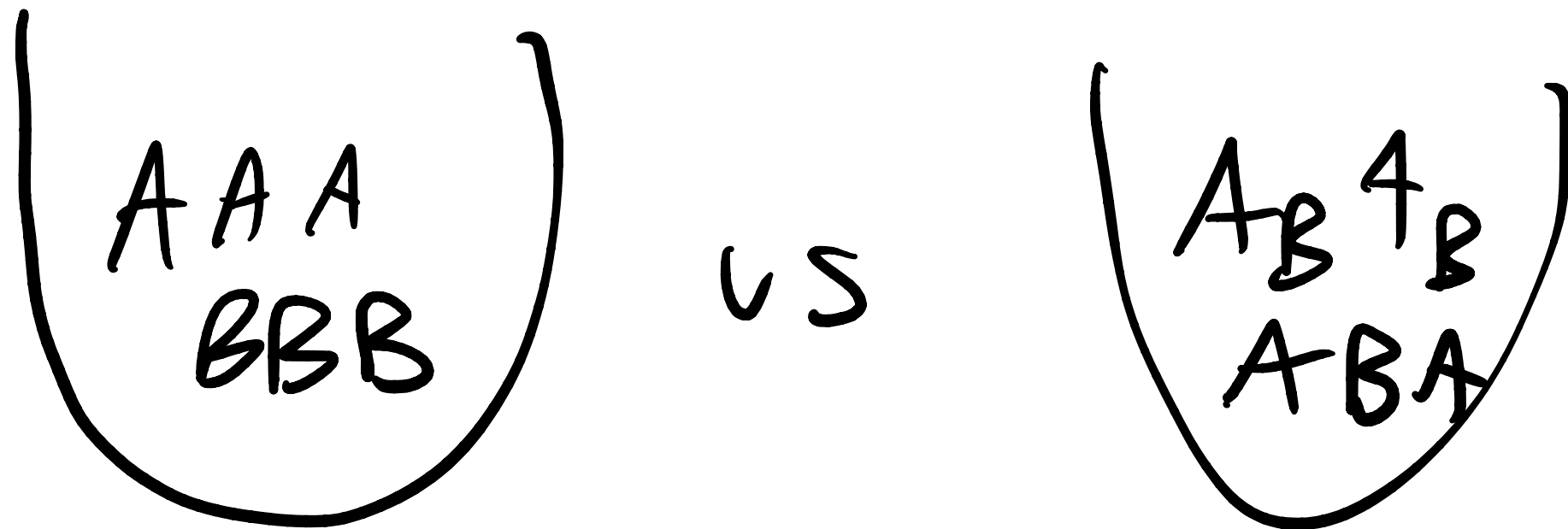
Why things mix or don't mix

$$G = H - TS$$

IS  $G_{\text{mix}}$  lower than  $G_{\text{separate}}$

$\Delta S_{\text{mixing}} \leftarrow$  always increases  
favors mixing at  $T > 0$

Don't mix if  $\Delta H_{\text{mix}} \uparrow$



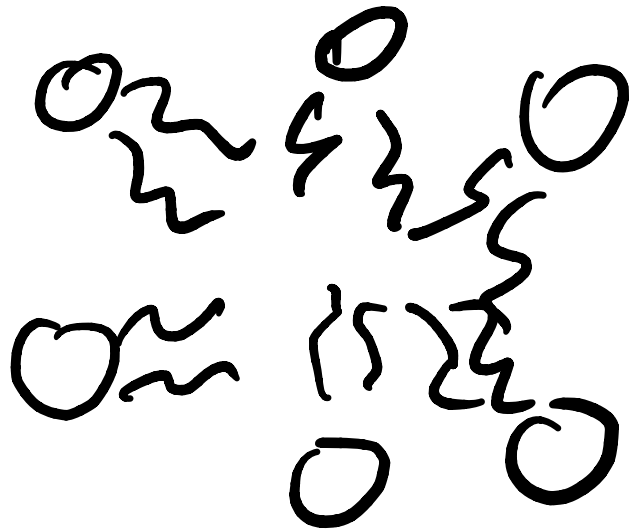
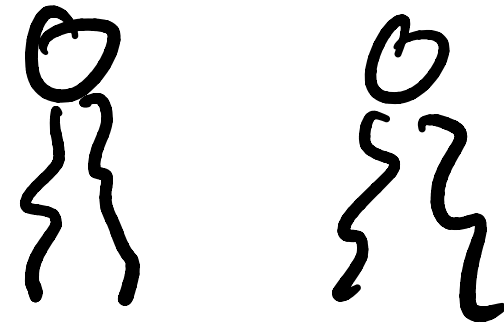
It can be that  $A + B$  like to interact

Consider  $H_2O + oil$

$H_2O$  has strong hydrogen bonds



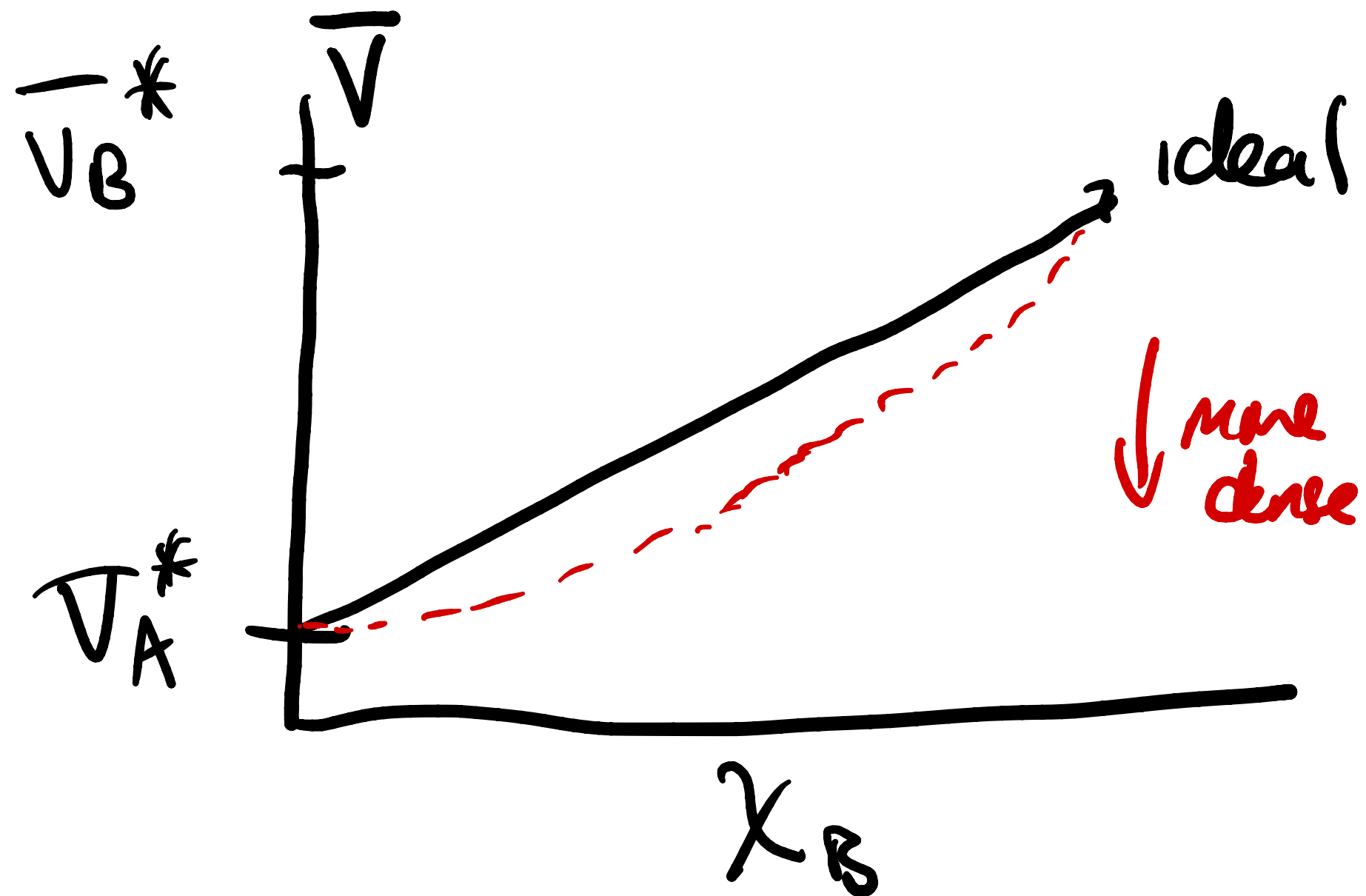
Another example



# Volume Change on mixing

H<sub>2</sub>O + EtOH

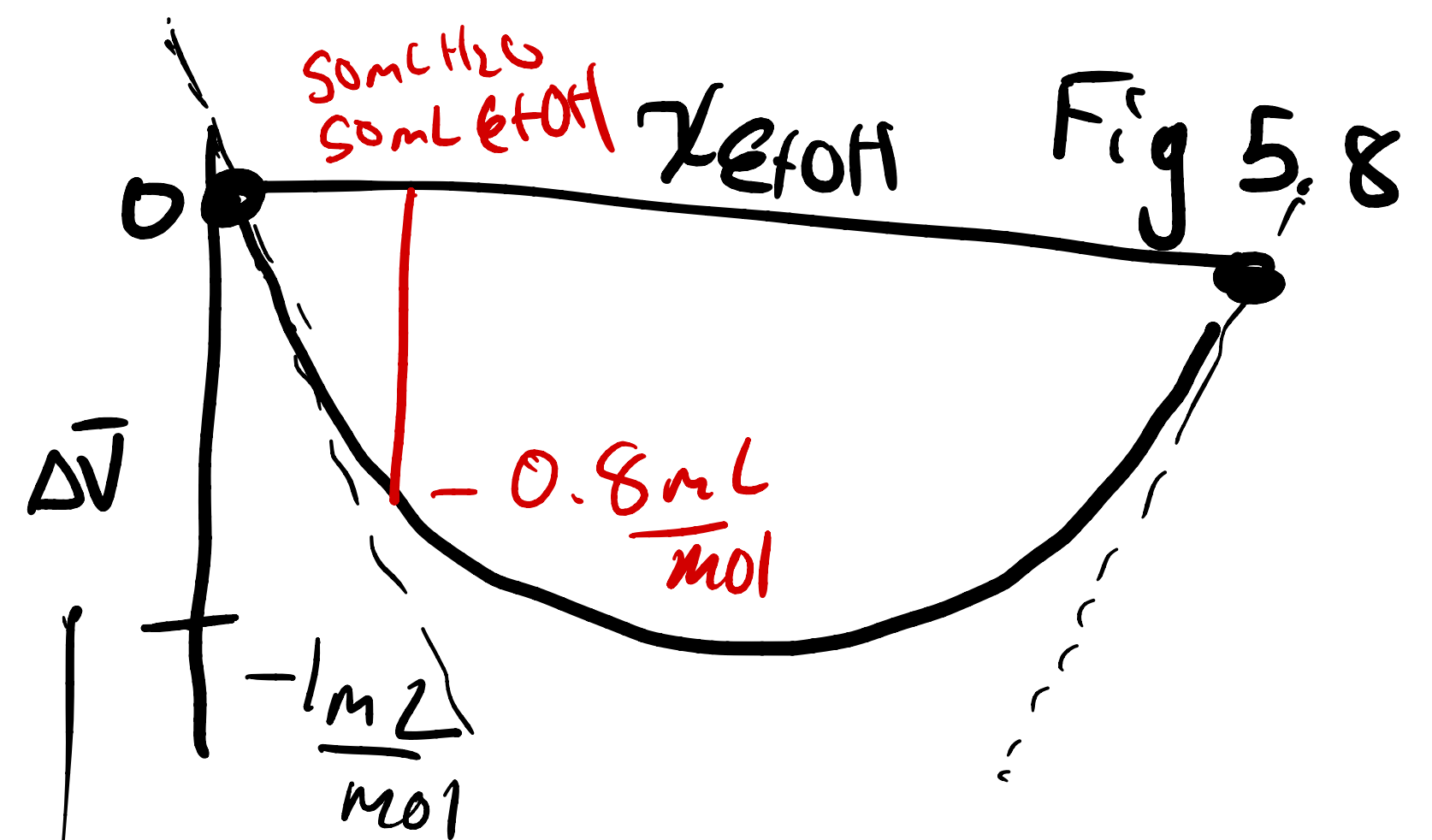
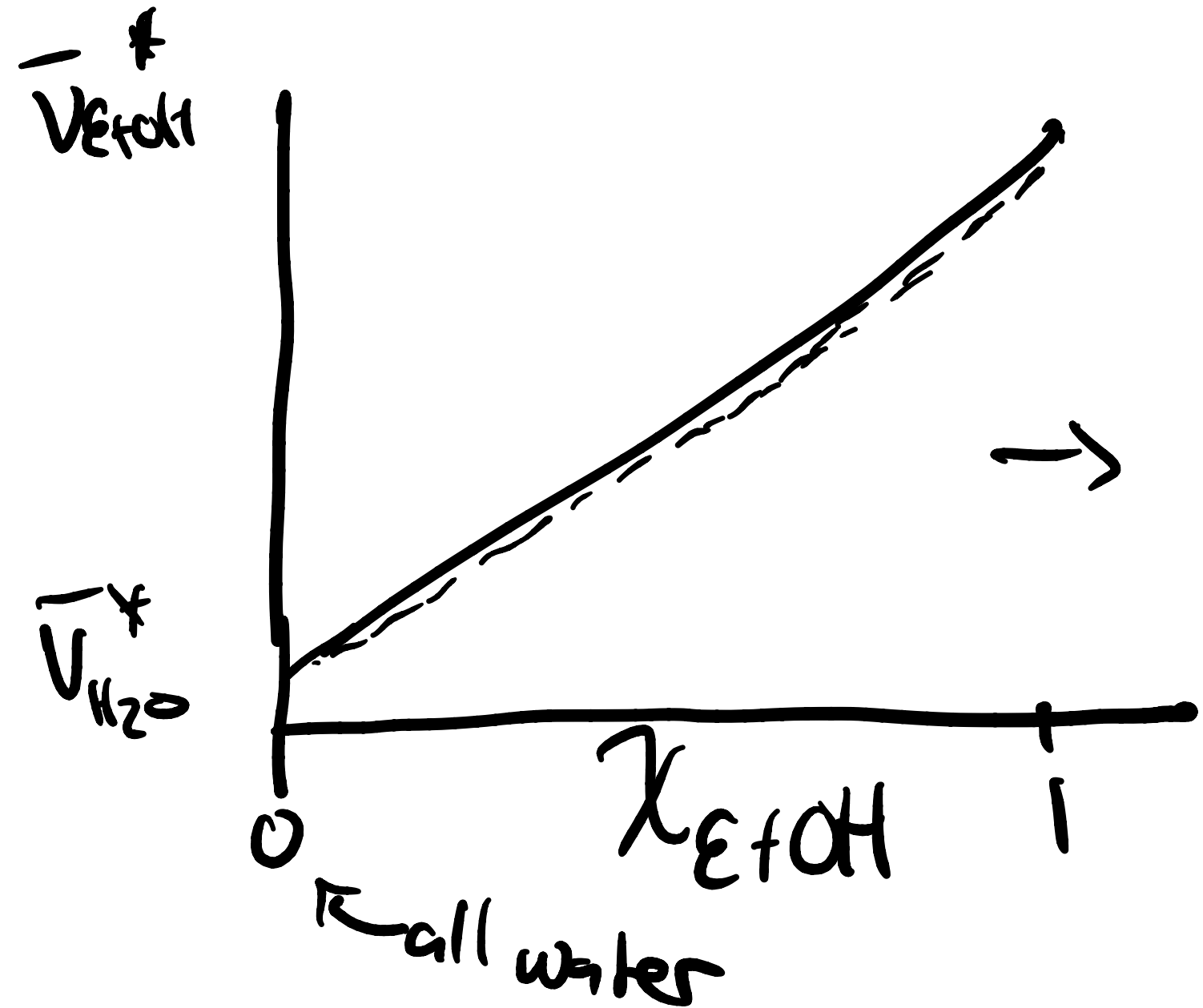
50 mL H<sub>2</sub>O + 50 mL of EtOH → 97 mL



$$\bar{V}_A = \frac{V}{n_A} = \frac{1}{\rho_A}$$

$$\bar{V}_B = \frac{V}{n_B} = \frac{1}{\rho_B}$$

ideal:  $\bar{V} = \chi_A \bar{V}_A^* + \chi_B \bar{V}_B^*$



$$\Delta \bar{V} = \bar{V}_{\text{measured}} - \chi_A \bar{V}_A^* - \chi_B \bar{V}_B^*$$

$$\bar{V}_{H_2O}^* = \frac{18 \text{ mL}}{\text{mol}}$$

$$\bar{V}_{EtOH}^* = \frac{57 \text{ mL}}{\text{mol}}$$

$$\rho_{H_2O}^{\text{@RT}} \sim 1 \text{ g/mL}$$

$$M_{H_2O} = 18 \text{ g/mol}$$

molar density of water

$$\frac{n}{V} = \frac{1 \text{ g/mL}}{(18 \text{ g/mol})} = \frac{1}{18} \frac{\text{mol}}{\text{mL}}$$

50 mL of each

$$n_{H_2O} = \frac{50}{18} = 2.8 \text{ mol}$$

$$n_{EtOH} = \frac{50}{57} = 0.88 \text{ mol}$$

$$\chi_{EtOH} = \frac{0.88}{2.8 + 0.88} \sim 0.24, \quad \Delta \bar{V} = -0.8 \frac{\text{mL}}{\text{mol}}$$

$$n_{\text{total}} = 2.8 + 0.88 = 3.68 \text{ mol} \rightarrow \Delta V = 3.68 \cdot (-0.8) = -2.9 \text{ mL}$$

$$① G(P, T, n_1, n_2)$$

$$dG = \left( \frac{\partial G}{\partial P} \right)_{T, n_1, n_2, \dots} dP + \left( \frac{\partial G}{\partial T} \right)_{P, n_1, n_2, \dots} dT + \left( \frac{\partial G}{\partial n_1} \right)_{P, T, n_i \neq n_1} dn_1 + \left( \frac{\partial G}{\partial n_2} \right)_{P, T, n_i \neq n_2} dn_2 + \dots$$

$$\left( \frac{\partial G}{\partial n_i} \right)_{P, T, n_i \neq n_j} = \mu_i(P, T, \dots)$$

$$\text{@ const } P \& T \quad dG = \sum_i \mu_i dn_i$$

② from previous  $\mu$  is  $G$  per mol

$$\mu_i = \bar{G}_i$$

$$G = \sum_i \mu_i n_i$$

$$dG = \sum_i (\mu_i dn_i + n_i d\mu_i)$$

before  $dG = SdT - VdP + \sum_i \mu_i dn_i$

Gibbs-Duhem relation  $SdT - VdP + \sum_i n_i d\mu_i = 0$

@  $dT, dP = 0, \quad \sum_i n_i d\mu_i = 0$

$$n_A d\mu_A + n_B d\mu_B = 0$$

$$x_A d\mu_A + x_B d\mu_B = 0$$

