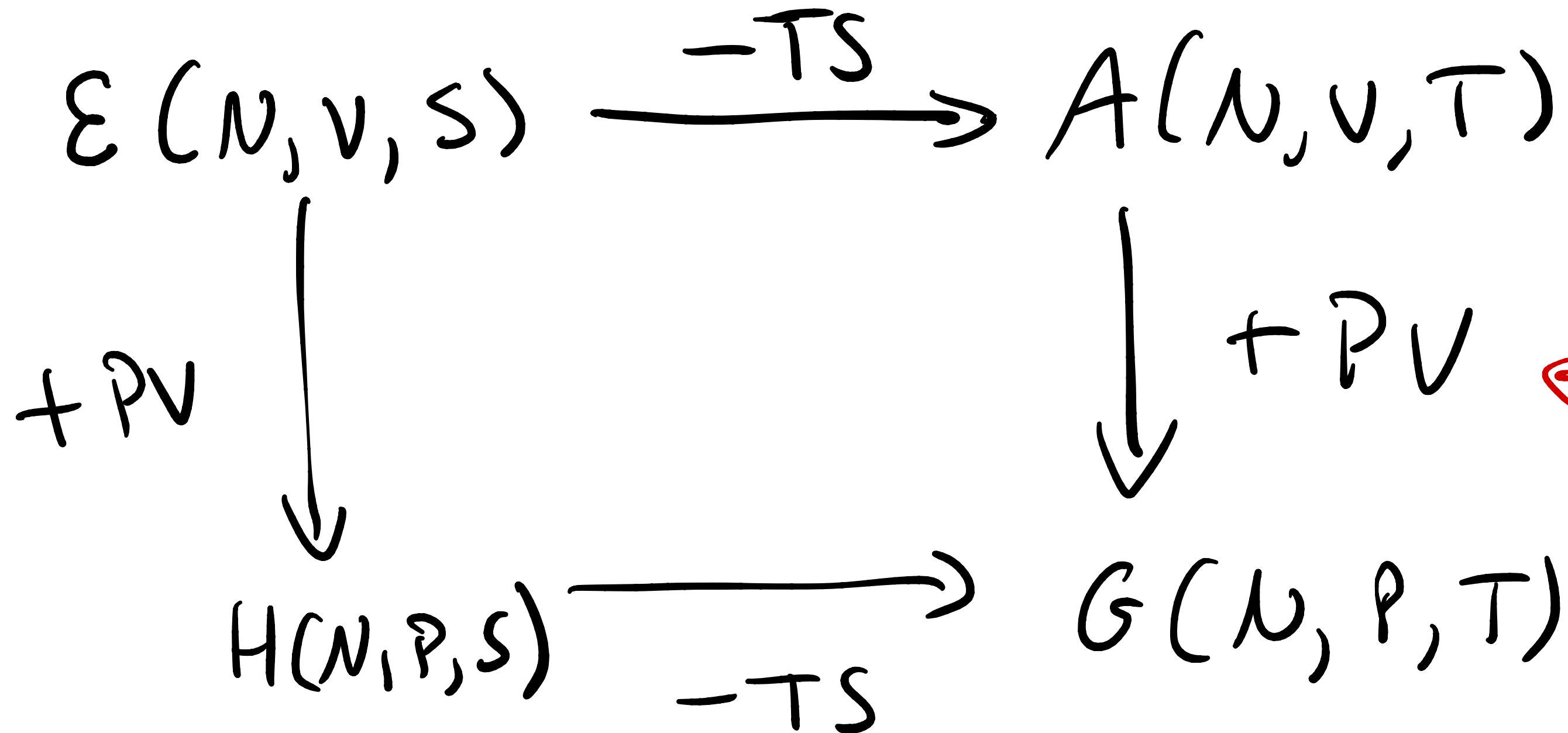


Lecture 10 - Mixtures & Phase Transitions



const S transformation $\Leftrightarrow d\zeta = 0$

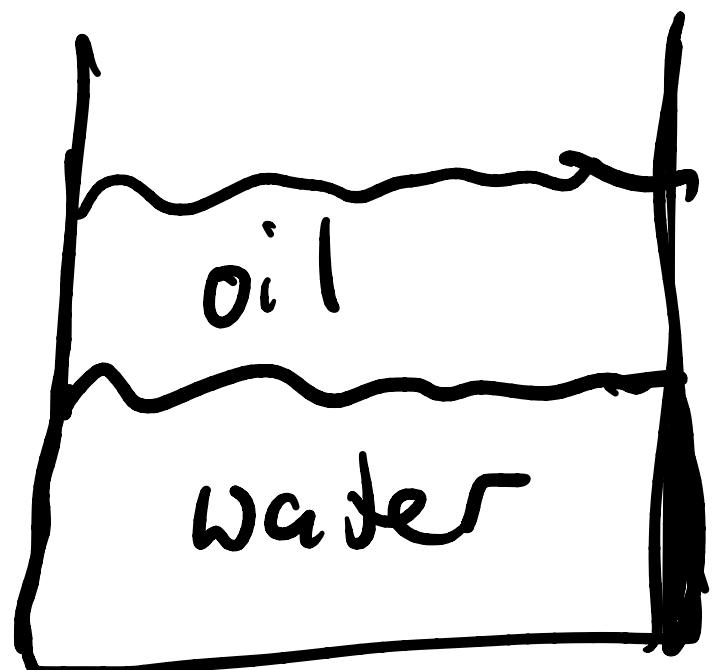
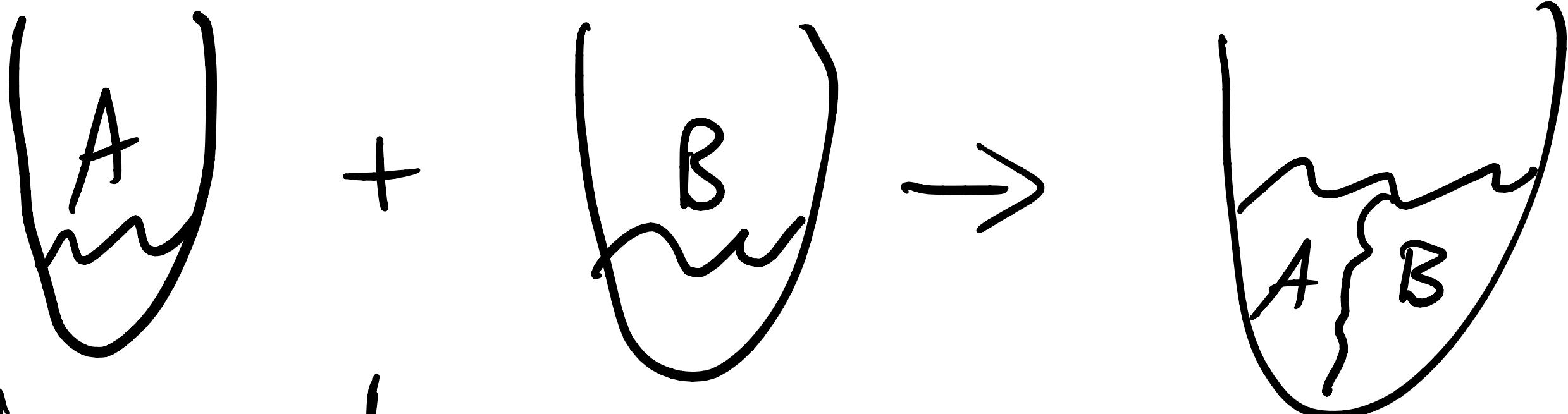
$$G = A + PV = A - \left(\frac{\partial A}{\partial V} \right)_{N,T} V$$

G \leftarrow Gibbs Free Energy

$$G = E - TS + PV$$

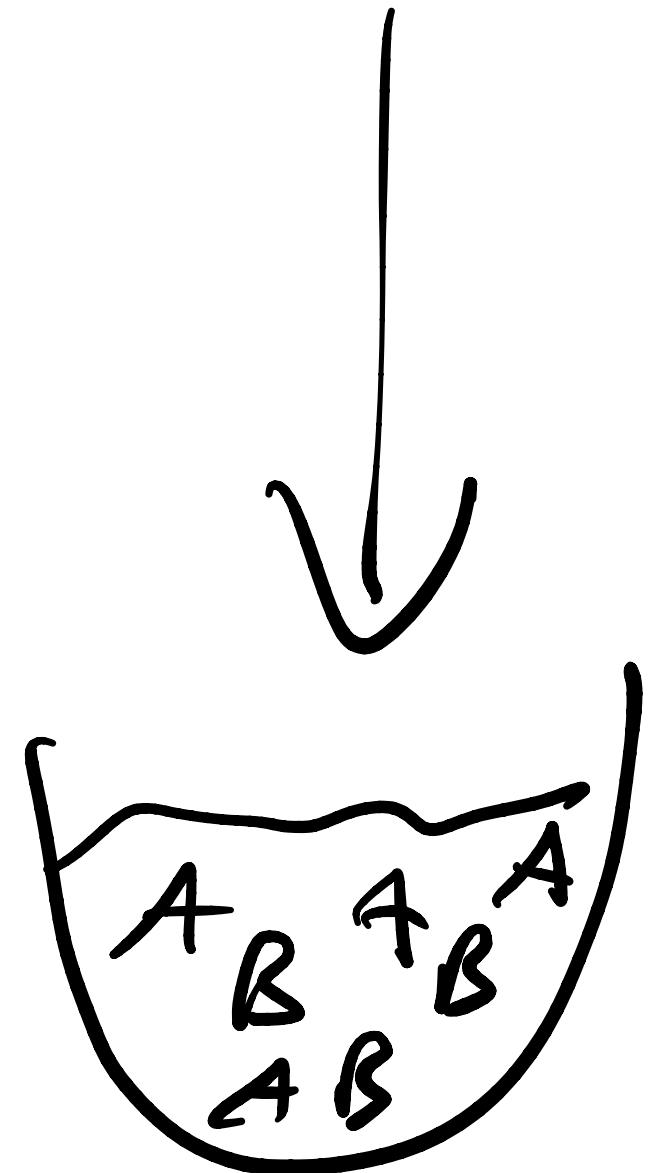
$$= H - TS$$

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



one possibility

What are the properties
of the mixture



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

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

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

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

mixtures are not "ideal" in reality

e)
ideal
gas {

$$\begin{aligned} \epsilon^{\text{ideal}} &= \epsilon_L + \epsilon_R \\ p^{\text{ideal}} &= P_L + P_R \end{aligned} \quad \text{within fixed volume}$$

$$S^{\text{ideal}} = S_L + S_R \quad \text{G probably not true}$$

— — — — — — —

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

— (energy) per mol

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

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

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

\uparrow (energy) per mol

averages
 $\bar{\epsilon}_A \neq \bar{\epsilon}_A^*$ 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

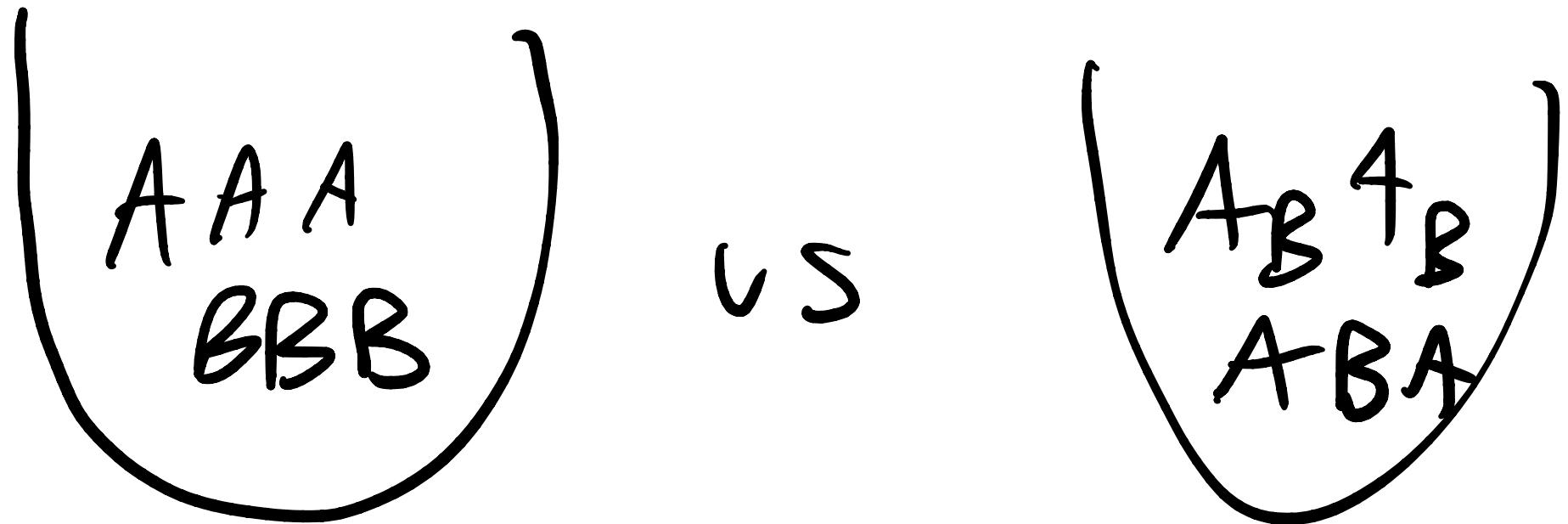
$$G = H - TS$$

IS G_{mix} lower than G_{separate}

$\Delta S_{\text{mixing}} \leftarrow$ always increases

favors mixing at $T > 0$

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

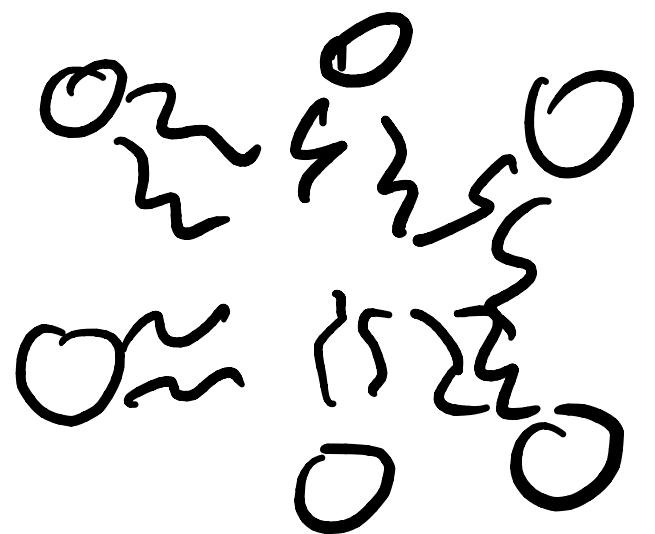
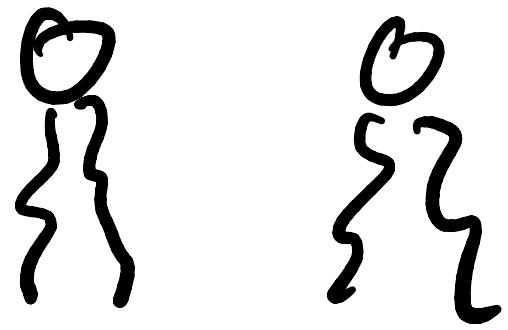


it can be that $A + B$ like to interact

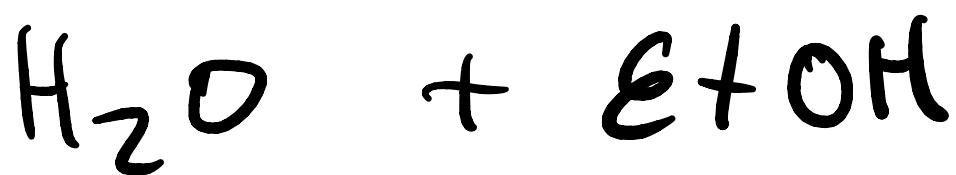
Consider $H_2O + oil$

H_2O has strong hydrogen bonds

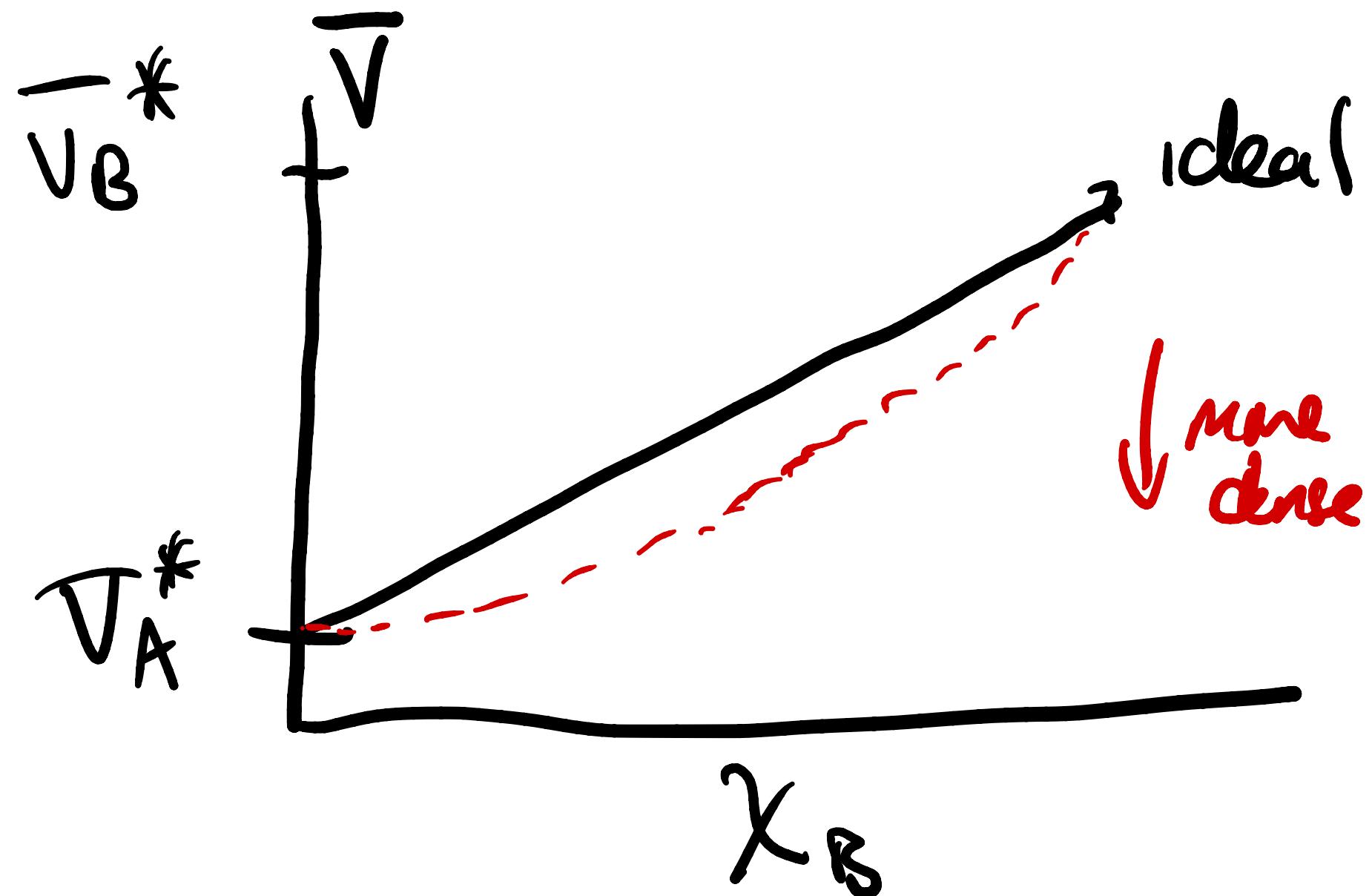
Another example



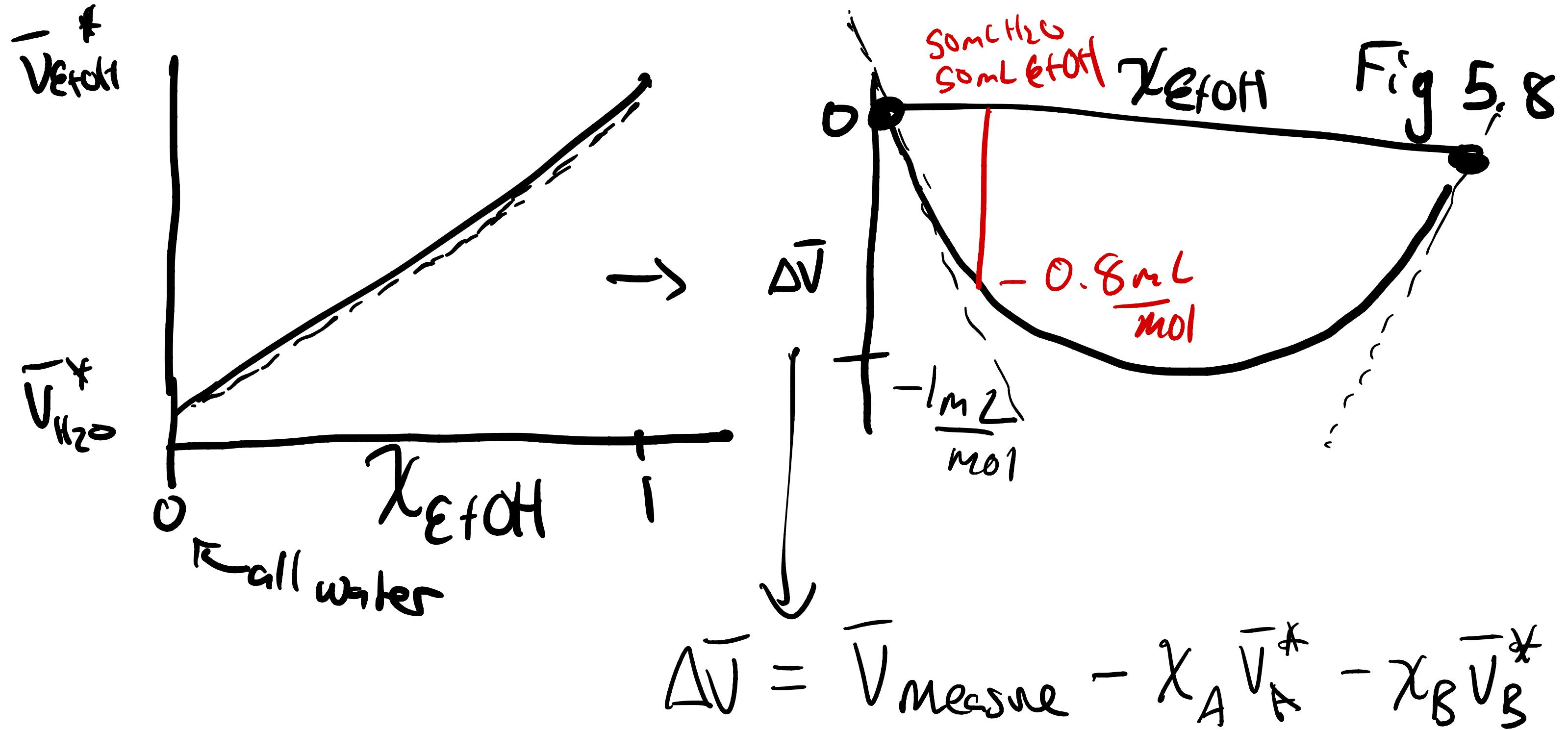
Volume Change on mixing



50 mL H_2O + 50 mL of EtOH \rightarrow 97 mL



$$\bar{V}_A = \frac{V}{n_A} = \frac{1}{\rho_A}$$
$$\bar{V}_B = \frac{V}{n_B} = \frac{1}{\rho_B}$$
$$\text{ideal: } \bar{V} = \chi_A \bar{V}_A^* + \chi_B \bar{V}_B^*$$



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

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

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

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

Molar density of water

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

50 mL of each

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

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

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

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

$$\textcircled{1} G(P, T, n_1, n_2)$$

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

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

P, T

$$\textcircled{2} \text{ const } P \& T \quad dG = \sum_i \mu_i dn_i$$

② from previous μ 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 $dG = SdT - VdP + \sum \mu_i dn_i$

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

$\text{at } dT/dP = 0, \quad \sum n_i d\mu_i = 0$

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

$$\chi_A d\mu_A + \chi_B d\mu_B = 0$$

