Lecture 15

Tuesday, November 5, 2024 09:59

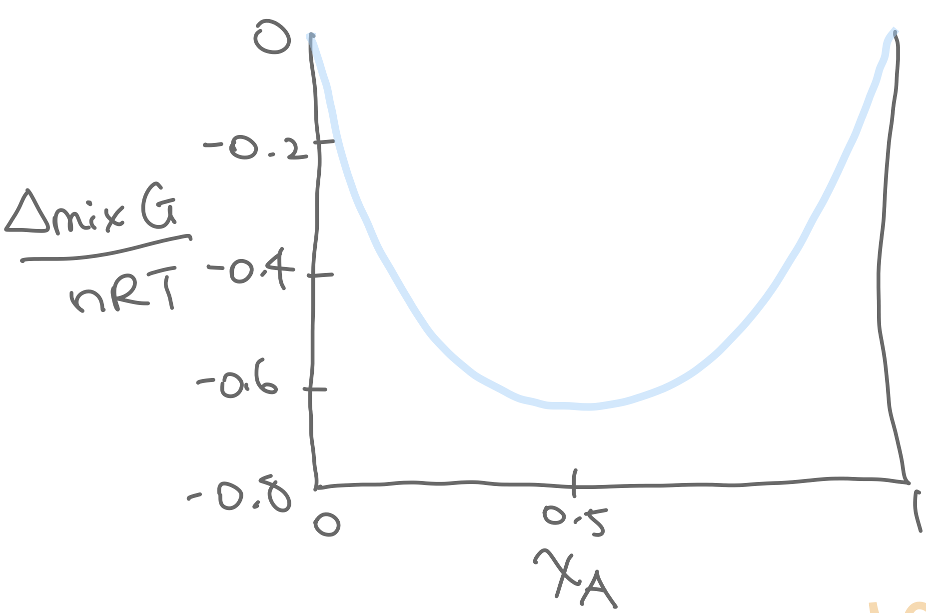
Last day of class (Nov. 28)

Puzzle Challenge !

- bonus marks !
  participation <u>and</u> performance

Last time : Gibbs energy of mixing

$$\Delta_{mix} G = nRT(x_A \ln x_A + x_B \ln x_B)$$

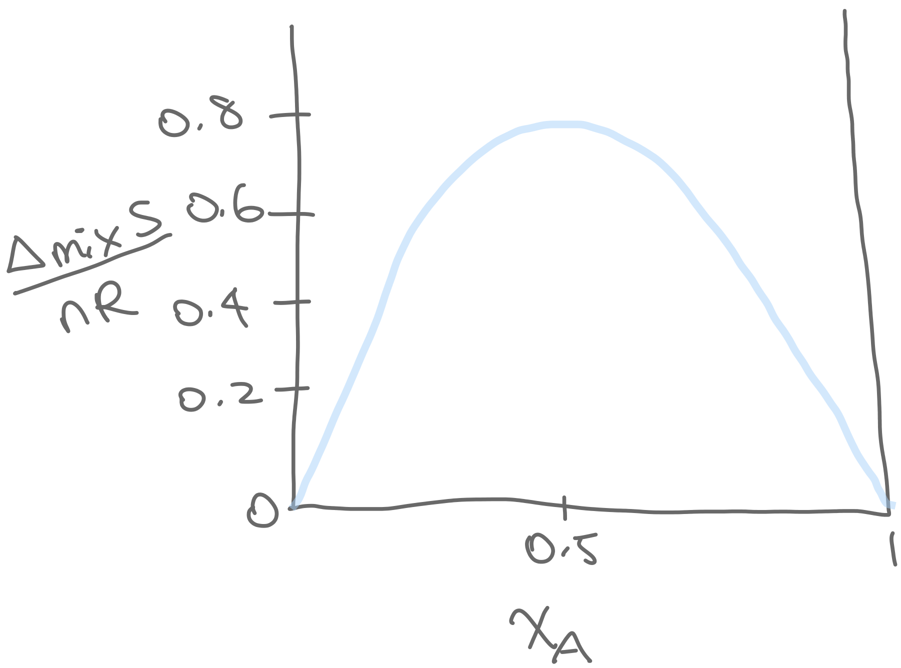


$dG = Vdp - SdT$

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

$\text{mix} \quad (\partial T \quad)_p$

$$\Delta_{mix} S = -nR(x_A \ln x_A + x_B \ln x_B)$$



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

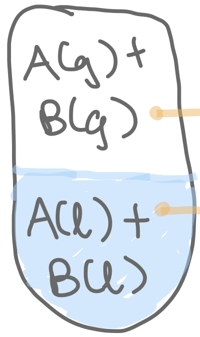
$\therefore \Delta_{mix} H = 0$ for perfect gases

Chemical Potentials of Liquids

Ideal Solutions

pure substance

$$\underbrace{\mu_A^*(l)}_{\text{liquid}} = \underbrace{\boxed{\mu_A^\ominus(g)} + RT \ln p_A^*}_{\text{vapour}}$$



$\mu_A(g, p)$

$\parallel$

$\mu_A(l)$

at equilibrium

$$\mu_A(l) = \underline{\mu_A^{\ominus}(g)} + RT \ln p_A$$

when present in a mixture

$$\mu_A^{\ominus}(g) = \boxed{\mu_A^*(l) - RT \ln p_A^*}$$

$$\mu_A(l) = \mu_A^*(l) - RT \ln p_A^* + RT \ln p_A$$

$$\mu_A(l) = \mu_A^*(l) + RT \ln \frac{p_A}{p_A^*}$$

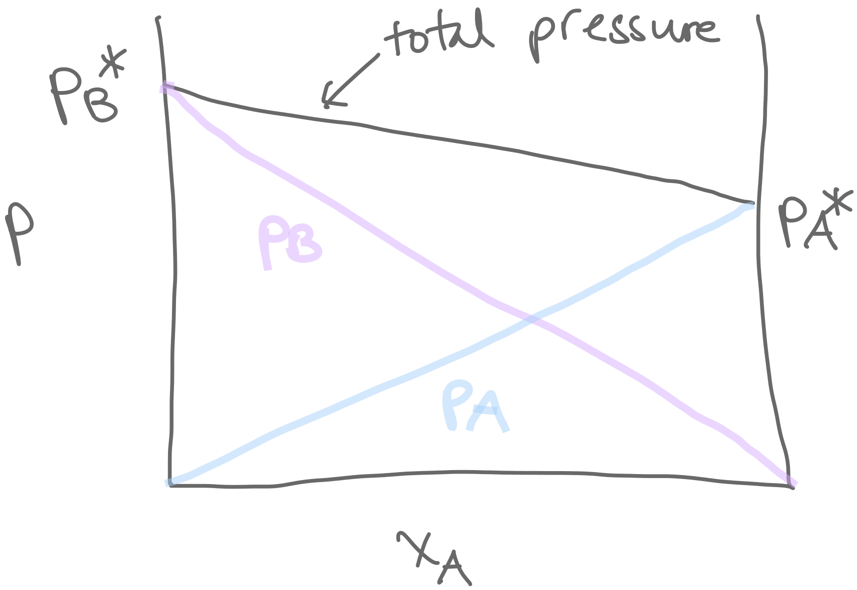
Raoult's Law :

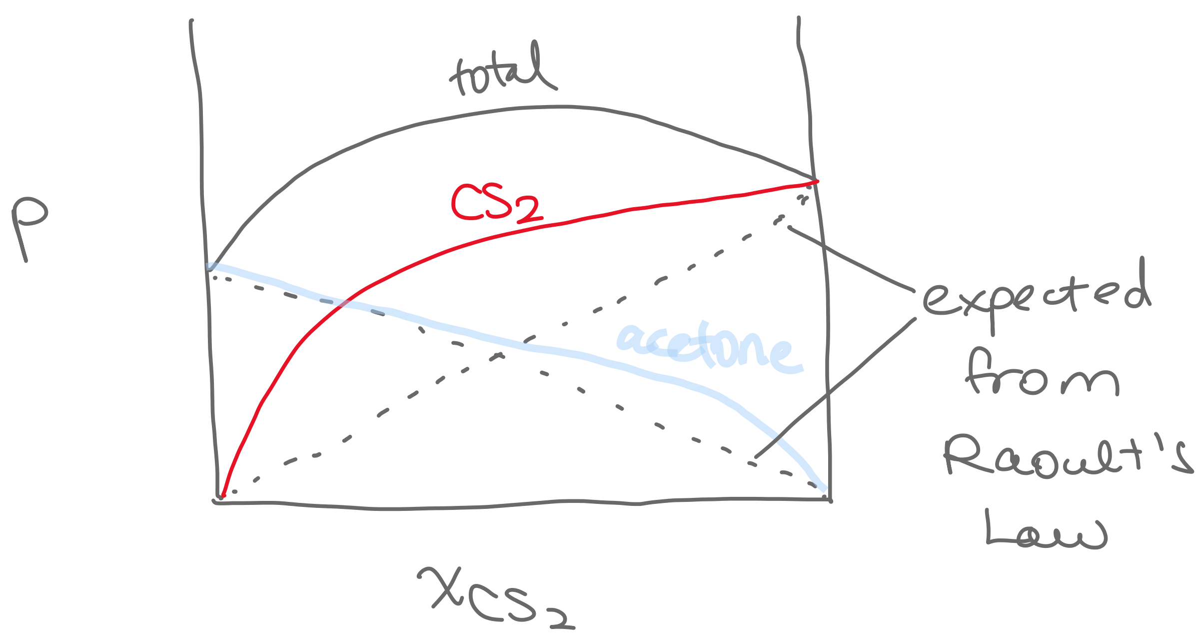
$$p_A = x_A p_A^*$$

empirically determined

$$\boxed{\mu_A(l) = \mu_A^*(l) + RT \ln x_A}$$

chemical potential of an ideal solution

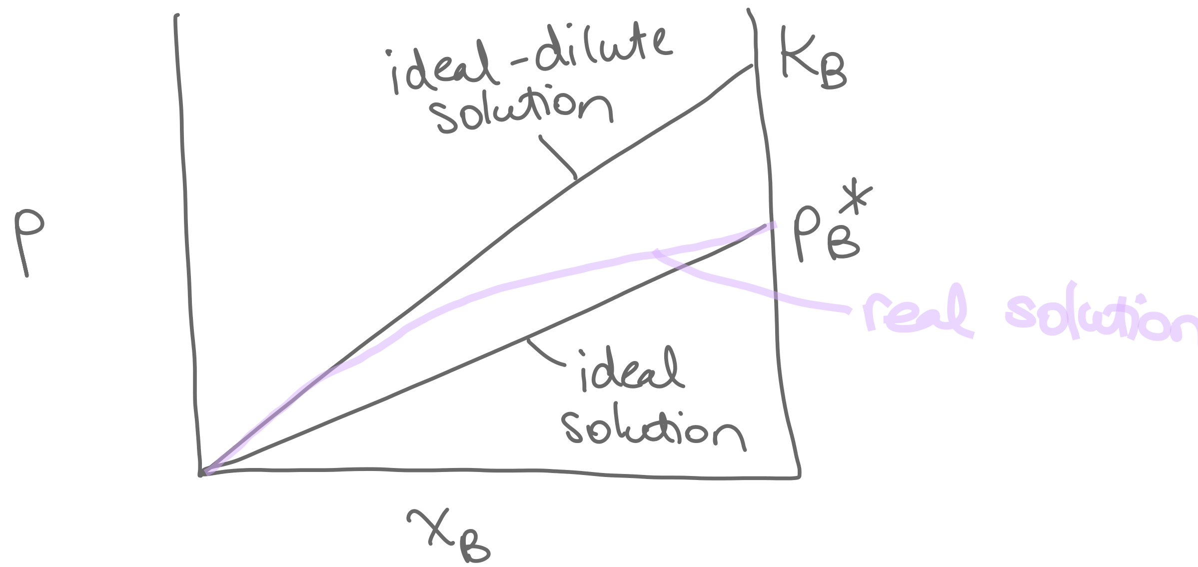


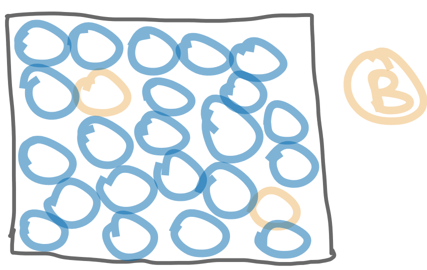


Ideal-Dilute Solutions

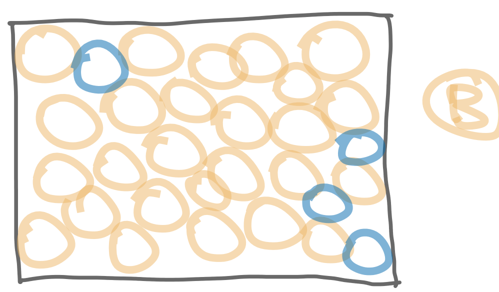
Henry's Law : $p_B = x_B K_B$

K_B : empirically measured constant





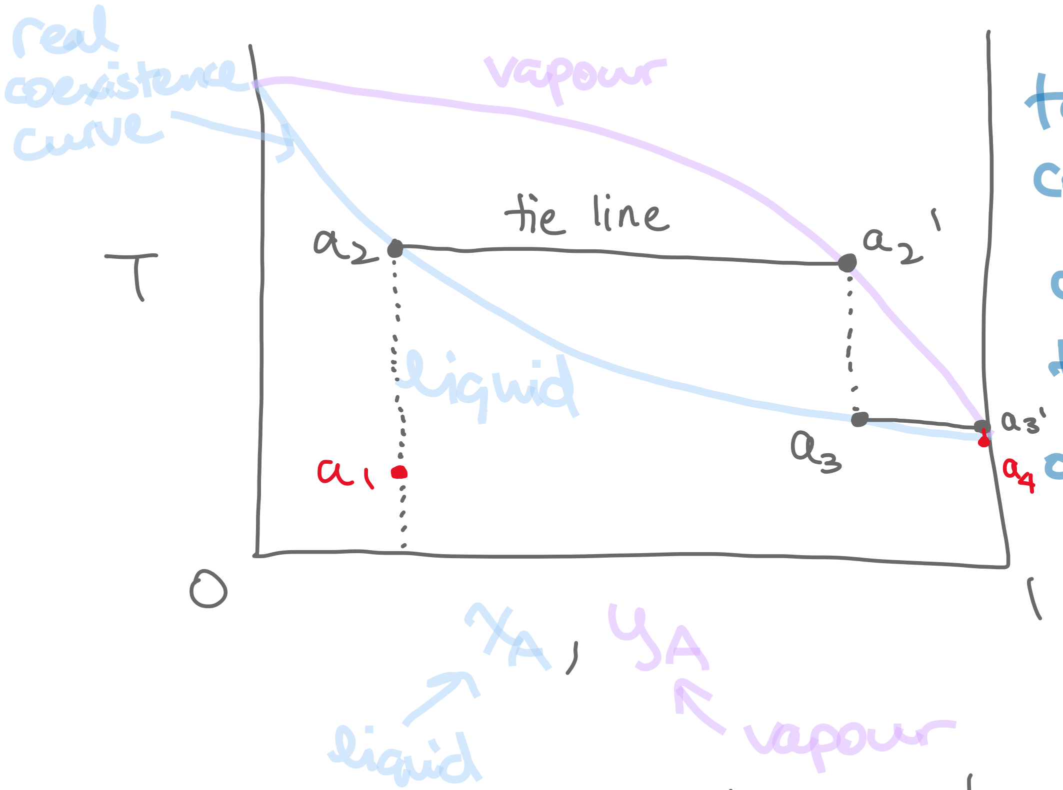
environment for B is drastically different from pure liquid



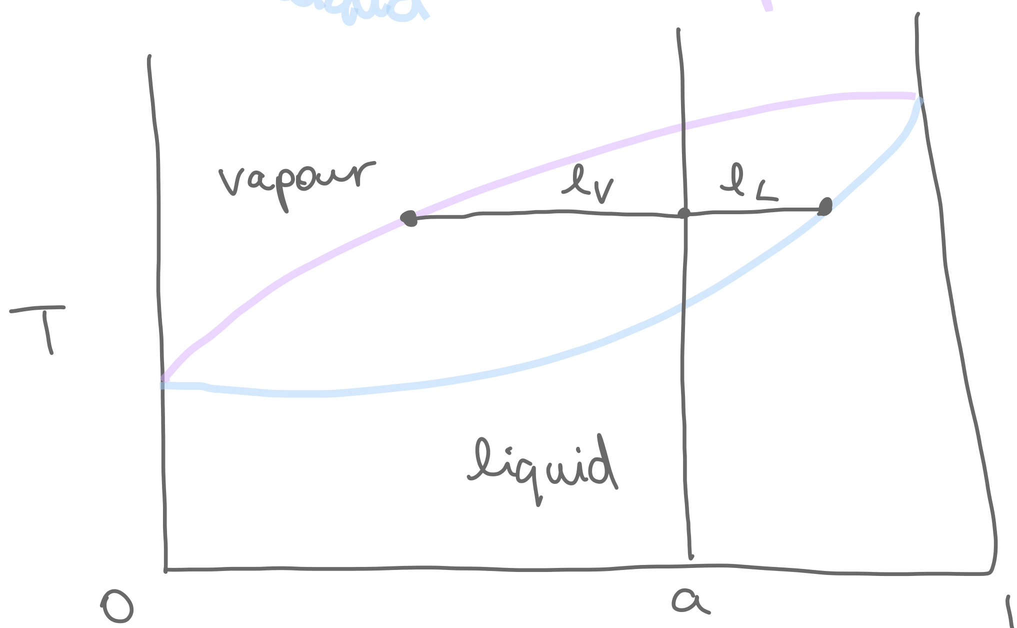
environment for B is similar to that in the pure liquid

(Skip Chapter 5B)

Topic 5C : Phase Diagrams of Binary Systems (Liquids)



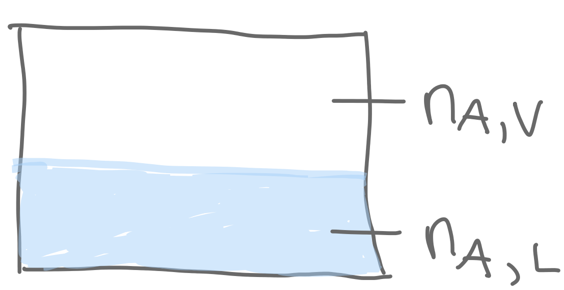
temperature-composition diagram; typically obtained at 1 atm



z_A ← overall mole fraction

Lever Rule

$$n_A = n_{A,V} + n_{A,L}$$



$$n_B = n_{B,V} + n_{B,L}$$

$$z_A = \frac{n_{A,V} + n_{A,L}}{n_A + n_B}$$

$$n_L = n_{A,L} + n_{B,L}$$

$$n_V = n_{A,V} + n_{B,V}$$

$$n = n_L + n_V$$

$$n_A = n_L x_A + n_V y_A$$

$$n_A = n z_A = n_L z_A + n_V z_A$$

$$n_L x_A + n_V y_A = n_L z_A + n_V z_A$$

$$n_V \underbrace{(y_A - z_A)}_{l_V} = n_L \underbrace{(z_A - x_A)}_{l_L}$$

$$\boxed{n_V l_V = n_L l_L}$$ lever rule

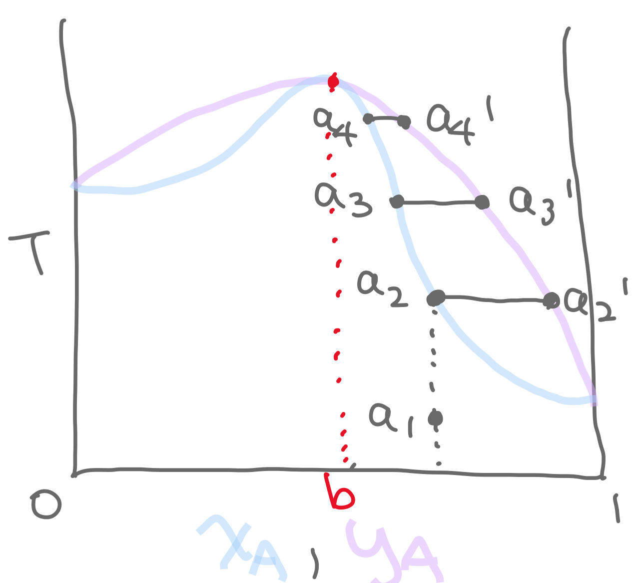
$$l_V = 2 l_L$$

$$n_V 2\cancel{l_L} = n_L \cancel{l_L}$$

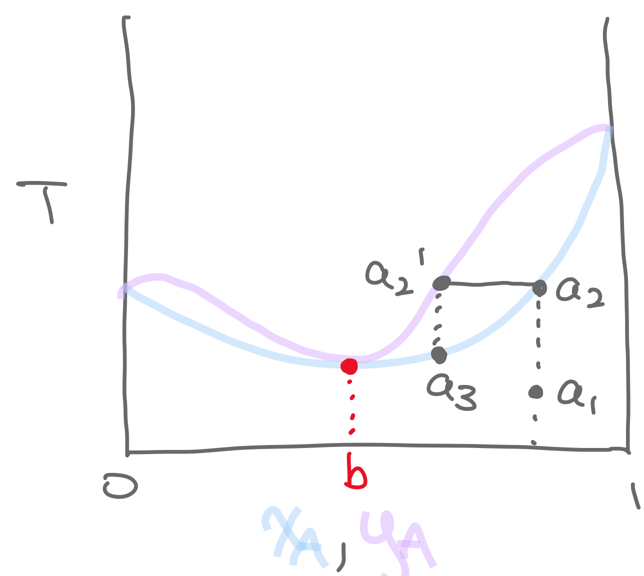
$$2n_V = n_L$$

∴ At point a on the above graph, the lever rule tells us that there are twice as many liquid molecules as there are vapour molecules.

Azeotropes



high-boiling



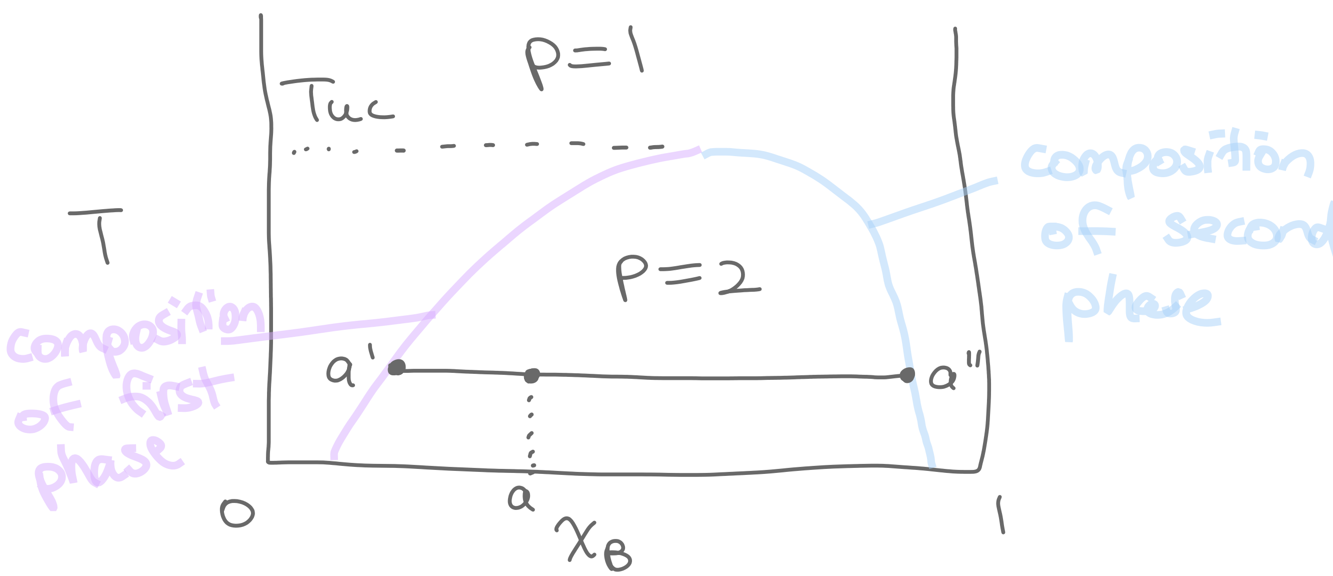
low-boiling

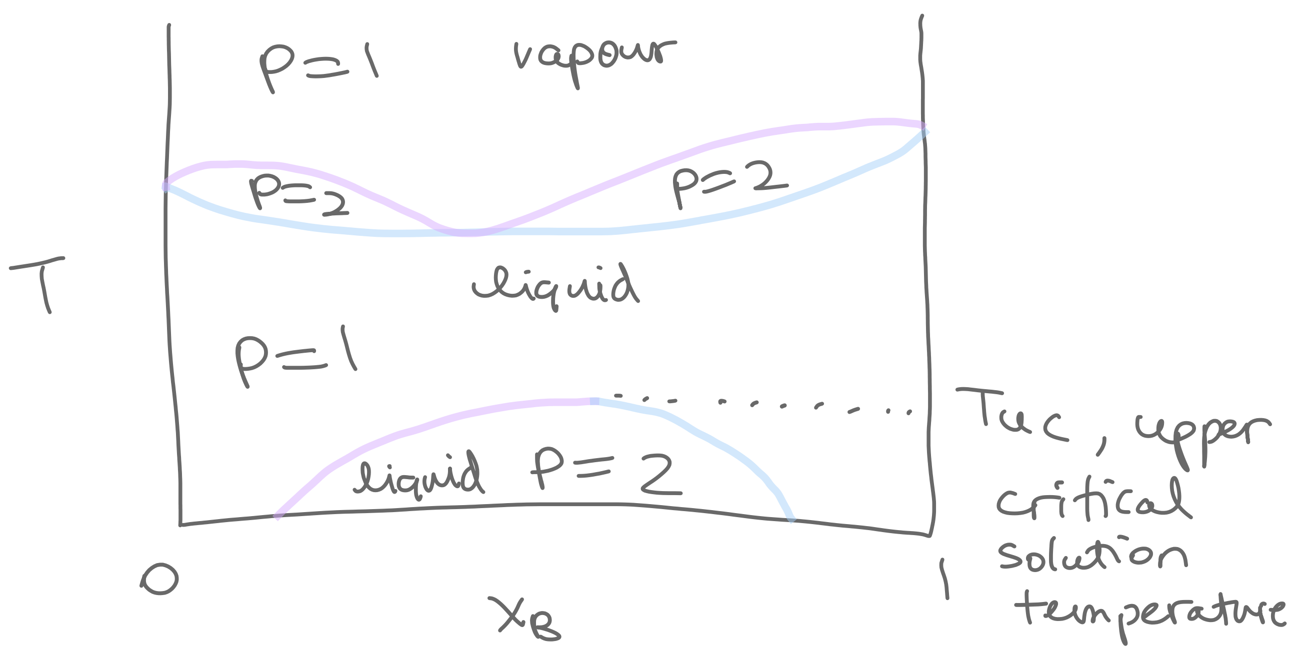
azeotrope
A-B interactions favoured

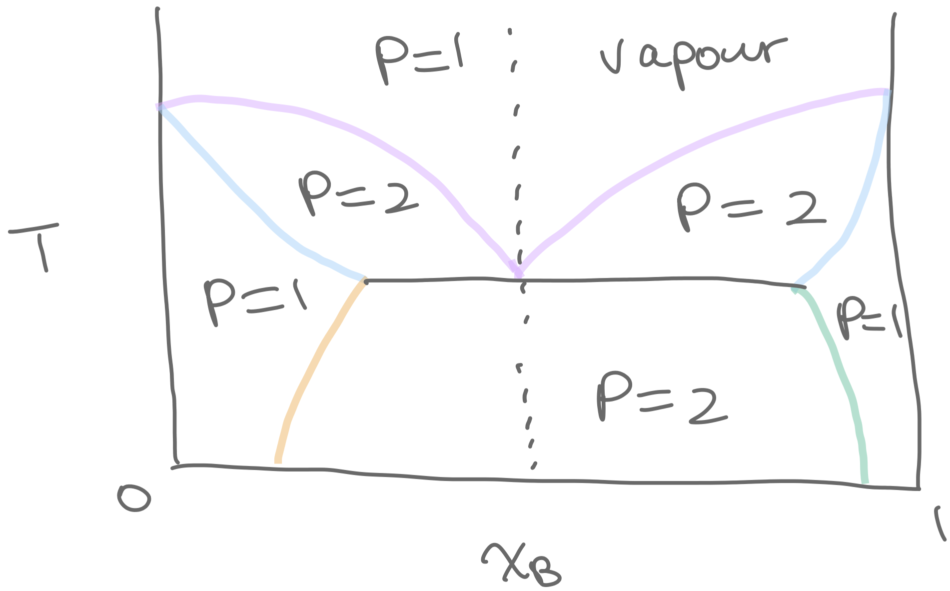
azeotrope
pure interactions favo

Pure Liquid : A-A B-B

Mixture : A-B






P=1
vapour
P=2
P=2
T
P=1
P=1
P=2
0
1
x_B