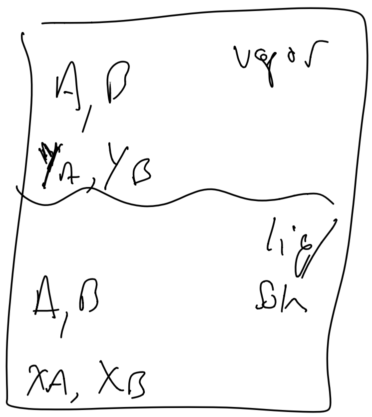
Phase Equilibria

2-component systems

Ideal (gas; solution)



T, P, x_A, x_B, y_A, y_B

Constraints $\begin{cases} x_A = 1 - x_B \\ y_A = 1 - y_B \end{cases}$

constraint

$$y_A P = y_A P^{TOT} = p_A = x_A \, p_A^*(T)$$

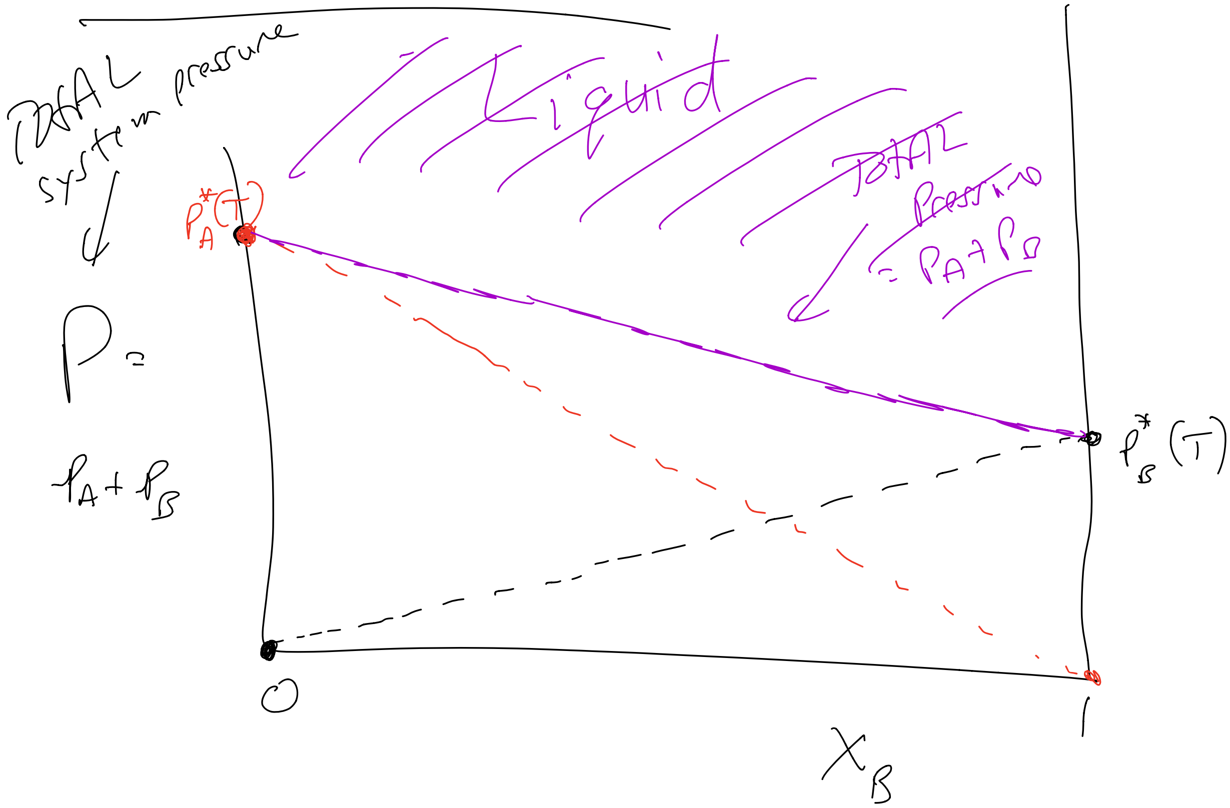
P → system pressure

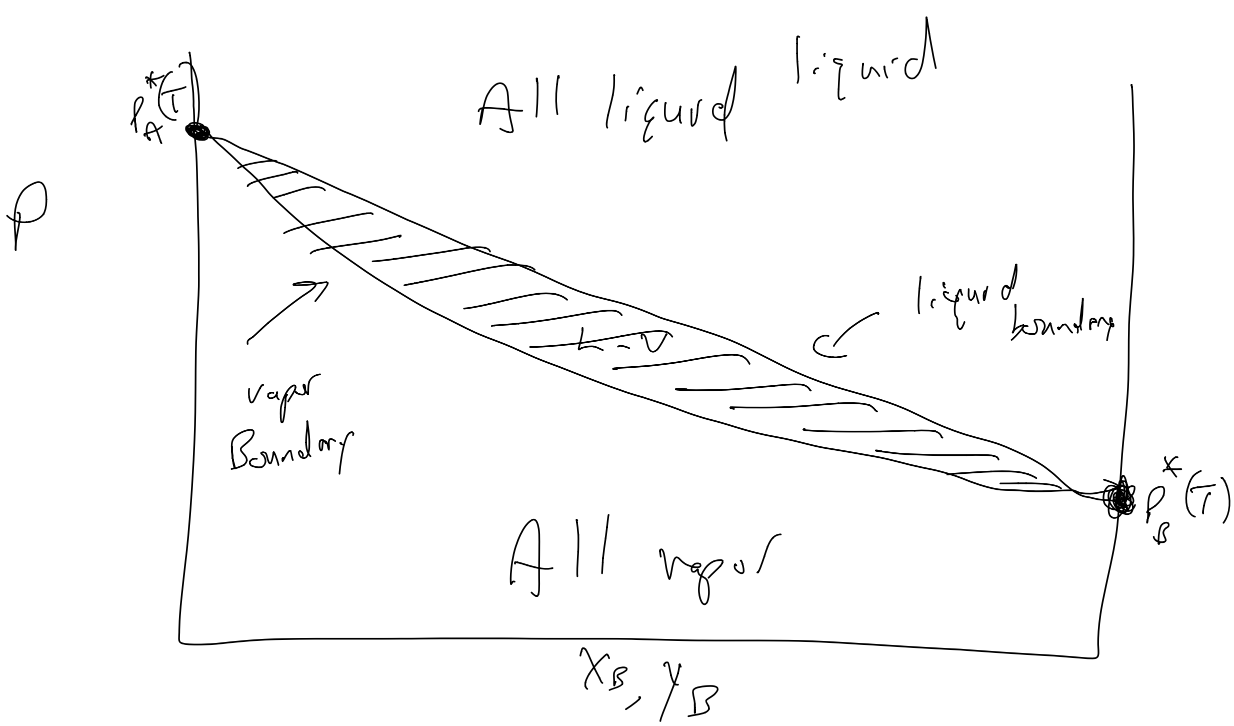
p_A → partial pressure of A in vapor

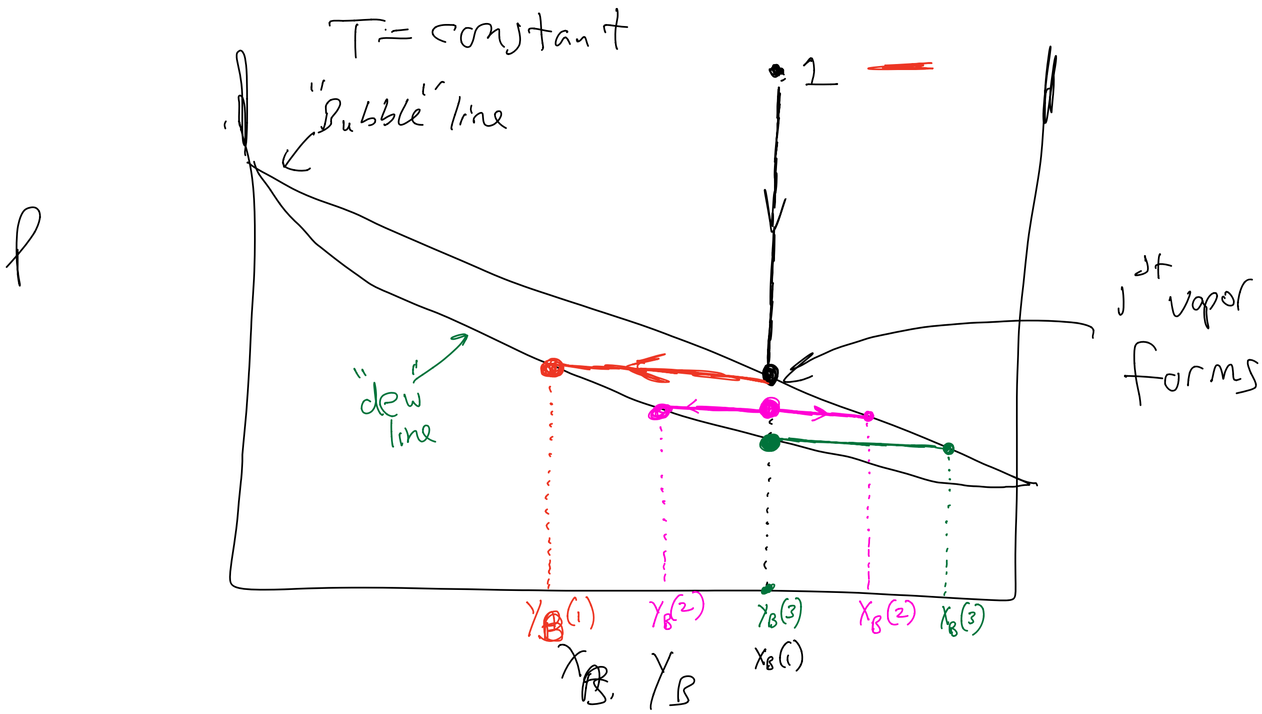
Raoult's "Law"

$$y_A = f(x_A)$$

T = constant

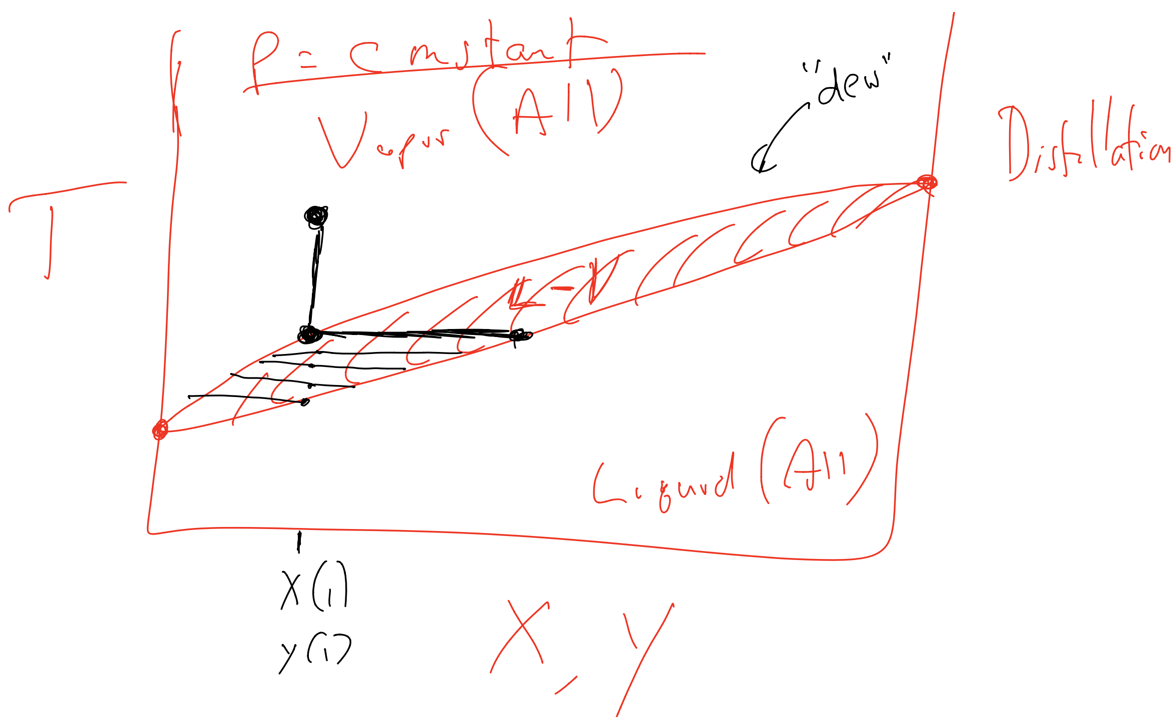

TOTAL system pressure
P = p_A + p_B
Liquid
TOTAL Pressure = p_A + p_B
p*_A(T)
p*_B(T)
0
1
x_B


liquid
All liquid
p*_A(T)
P
vapor Boundary
L-V
liquid boundary
p*_B(T)
All vapor
x_B, y_B



$X_B(3) > X_B(2) > X_B(1)$

$Y_B \uparrow$ $X_B \uparrow$!!!!! ✗



What happens if $x_A = y_A$

$(x_B = y_B)$??

Constraint

L – V

A, B

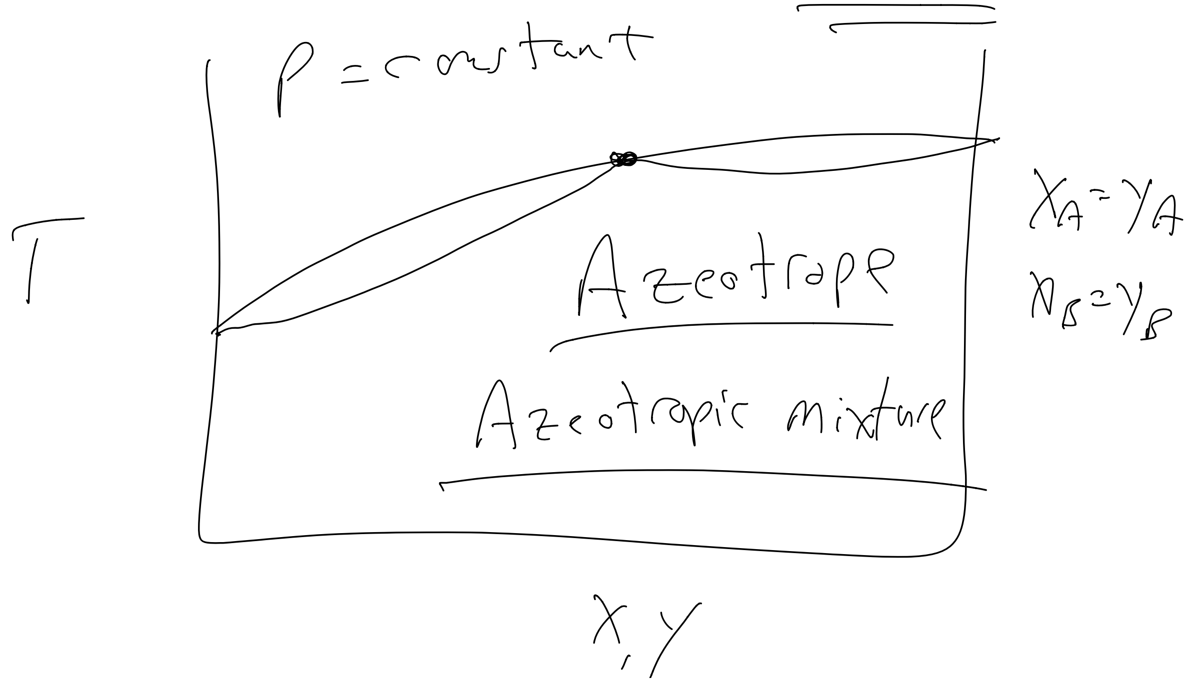
Ideal

$$D.O.F. = C + 2 - \pi$$

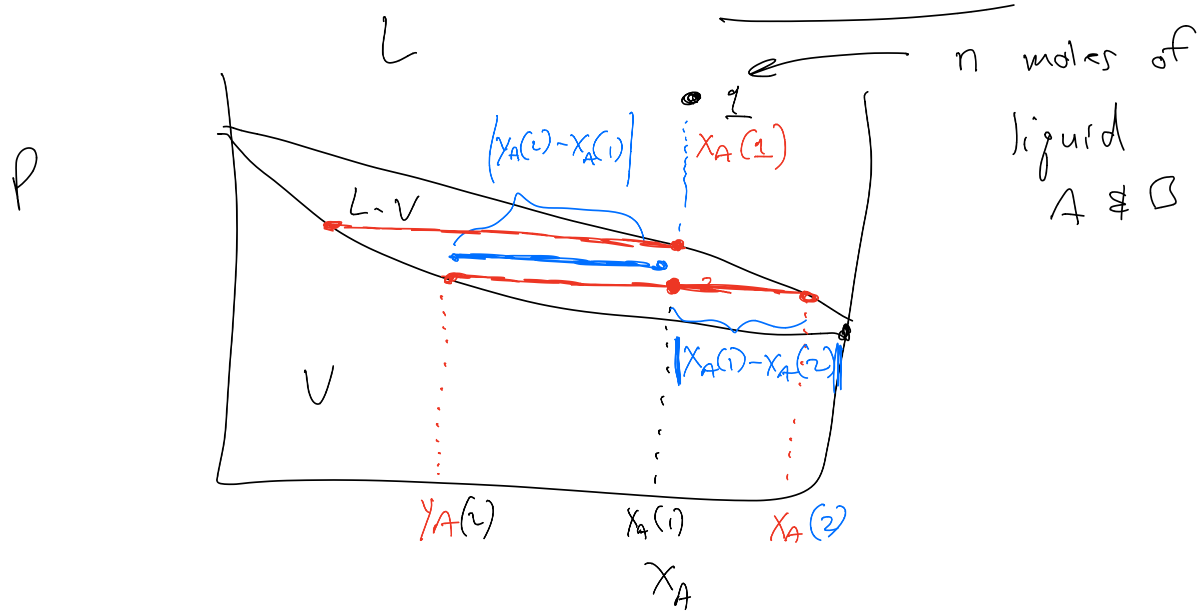
$$= 2 + 2 - 2$$

$$= 2$$

$$D.O.F = 1$$



Azeotrope ⟵ non-ideal



? what is $\frac{n^L}{n^V}$; $\frac{n^V}{n^L}$ at coexistence.

mole balances on A — initial A (moles) = final A (moles)

@ 1 $\quad n_A = x_A(1)\, n^{TOTAL}$

@ 2 $\quad n_A = x_A(2)\, n^L + y_A(2)\, n^V$

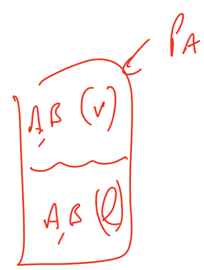
$$x_A(1)\, n^{TOTAL} = x_A(2)\, n^L + y_A(2)\, n^V$$

$$x_A(1)\left[n^L + n^V\right] = x_A(2)\, n^L + y_A(2)\, n^V$$

$$n^L \left[x_A(1) - x_A(2) \right] = n^V \left[y_A(2) - x_A(1) \right]$$

$$\frac{n^L}{n^V} = \frac{\left| y_A(2) - x_A(1) \right|}{\left| x_A(1) - x_A(2) \right|}$$

Chemical Potential of species A in ideal solution



Raoult's "Law"

$$\mu_A^l(T,P,\{x\}) = \mu_A^v(T,P,\{y\})$$

$$= \mu_A^v(T,P^\circ,\text{pure}) + RT\ln\left(\frac{p_A}{p^\circ}\right)$$

$$= \mu_A^v(T,P^\circ,\text{pure}) + RT\ln\left(\frac{x_A\, p_A^*(T)}{p^\circ}\right)$$

$$= \mu_A^v(T,P^\circ,\text{pure}) + RT\ln\left(\frac{p_A^*(T)}{p^\circ}\right) + RT\ln(x_A)$$

$$\mu_A^l(T,P,\{x\}) = \mu_A^v(T,P^*(T),\text{pure}) + RT\ln(x_A)$$

↑ ideal solution

Chemical potential of A in liquid

Non-Ideality

Departure from Ideality

μ_i

$$\mu_i^{real} - \mu_i^{ideal}$$

???

$$K = \frac{[A][B]}{[C]}$$