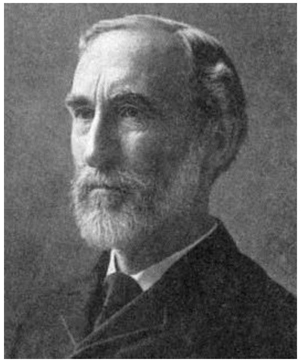
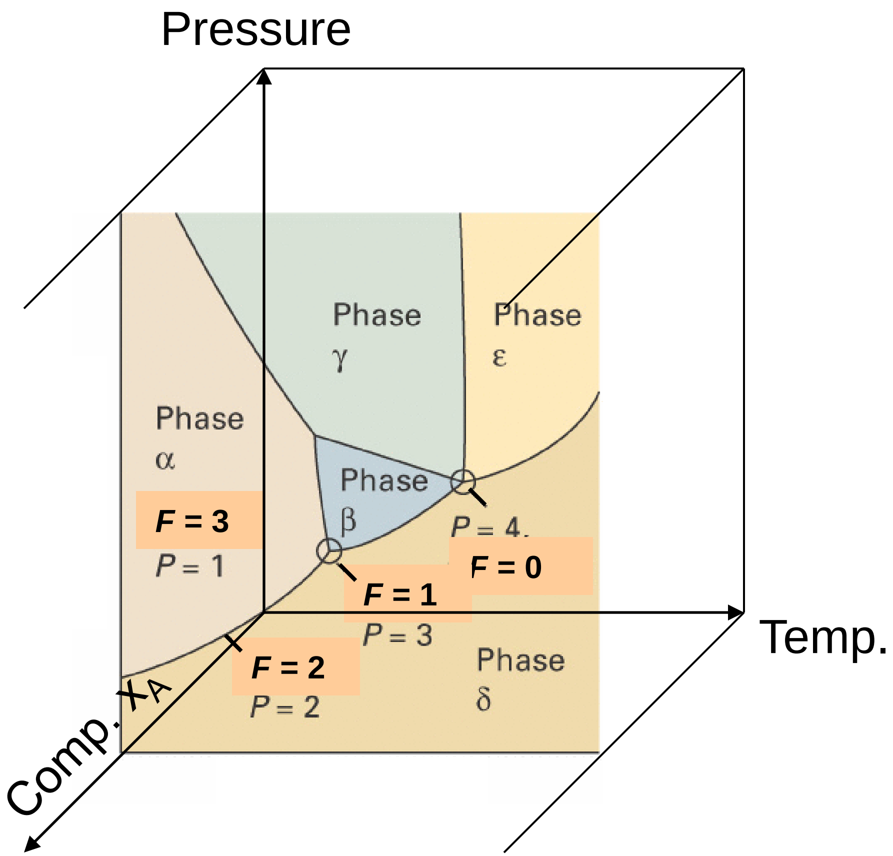
# Summary of Lecture 3

# Phase diagrams of binary systems

## C = 2





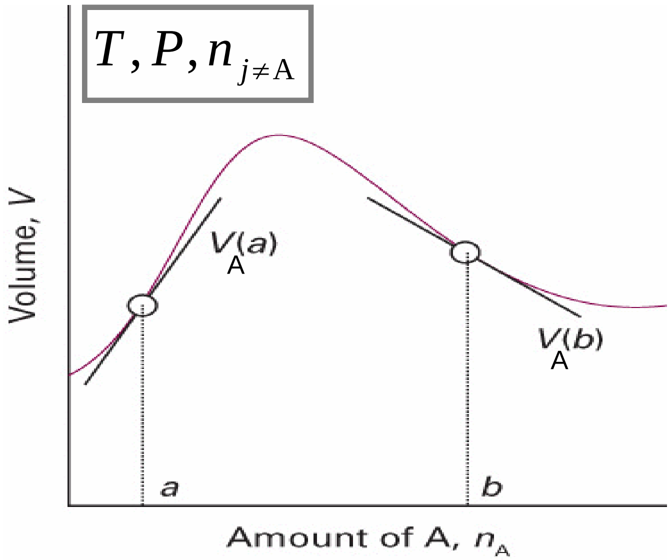

**Gibbs phase rule**

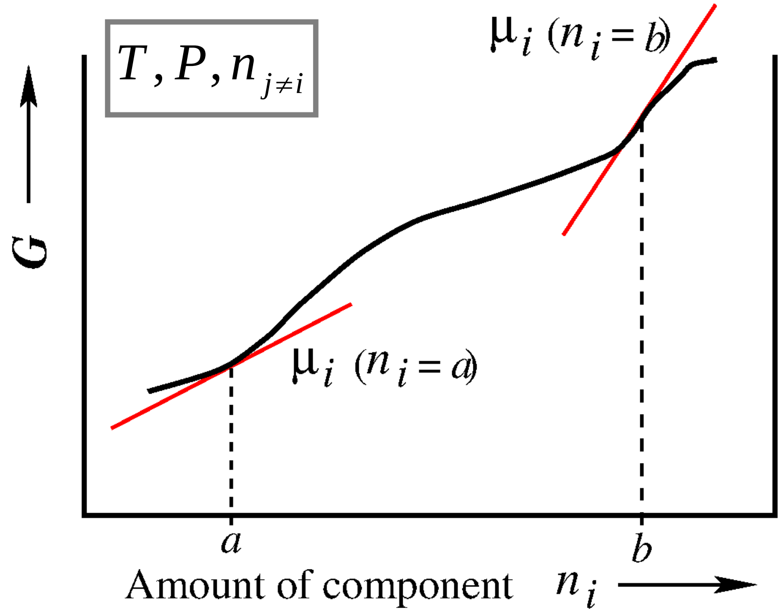
$$\boxed{F = C - P + 2}$$

# Partial molar quantities

$$V_i \equiv \left(\frac{\partial V}{\partial n_i}\right)_{P,T,n_{j\neq i}}$$

$$\mu_i \equiv G_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}}$$




$$V = n_A V_A + n_B V_B = n\left[x_A V_A + x_B V_B\right]$$

**Exercise 10**

$$G = n_A \mu_A + n_B \mu_B = n\left[x_A \mu_A + x_B \mu_B\right]$$

**Exercise 12**

# Mixing processes of perfect gases:binary mixture

## Perfect gas mixing @ *P,T*

$$\boxed{\overset{P,T}{H_2O\,(g)}} + \boxed{\overset{P,T}{\text{EthOH}\,(g)}} \rightarrow \boxed{\overset{P,T}{H_2O\,(g) + \text{EthOH}\,(g)}}$$

$$\boxed{\Delta_{\text{mix}} G^{\text{ideal}} = nRT\left(x_A \ln x_A + x_B \ln x_B\right)}$$

$$\begin{cases} \boxed{\Delta_{\text{mix}} S^{\text{ideal}} = -nR\left(x_A \ln x_A + x_B \ln x_B\right)} \\ \boxed{\Delta_{\text{mix}} H^{\text{ideal}} = 0} \end{cases}$$

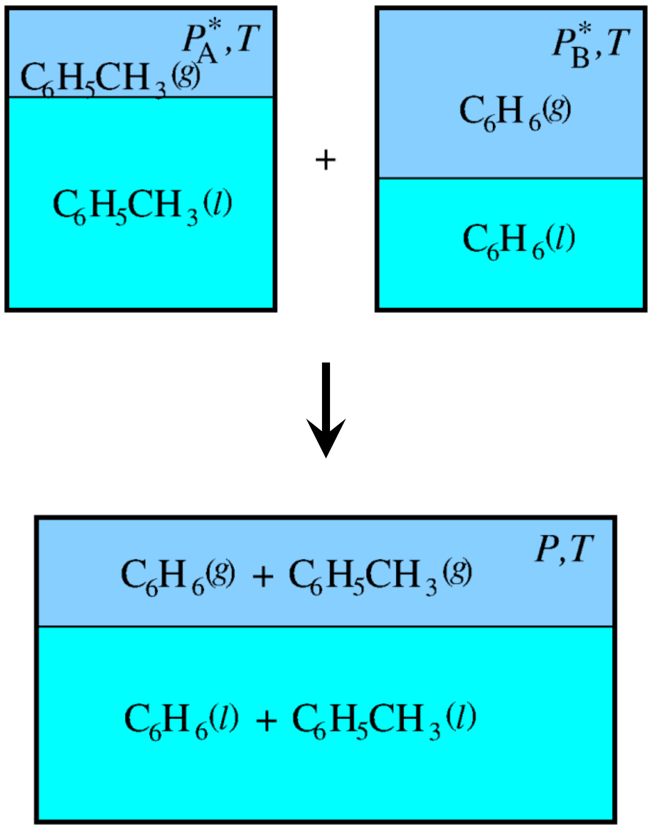
$$\boxed{\frac{P_i}{P} \equiv \frac{n_i}{n} = x_i}$$

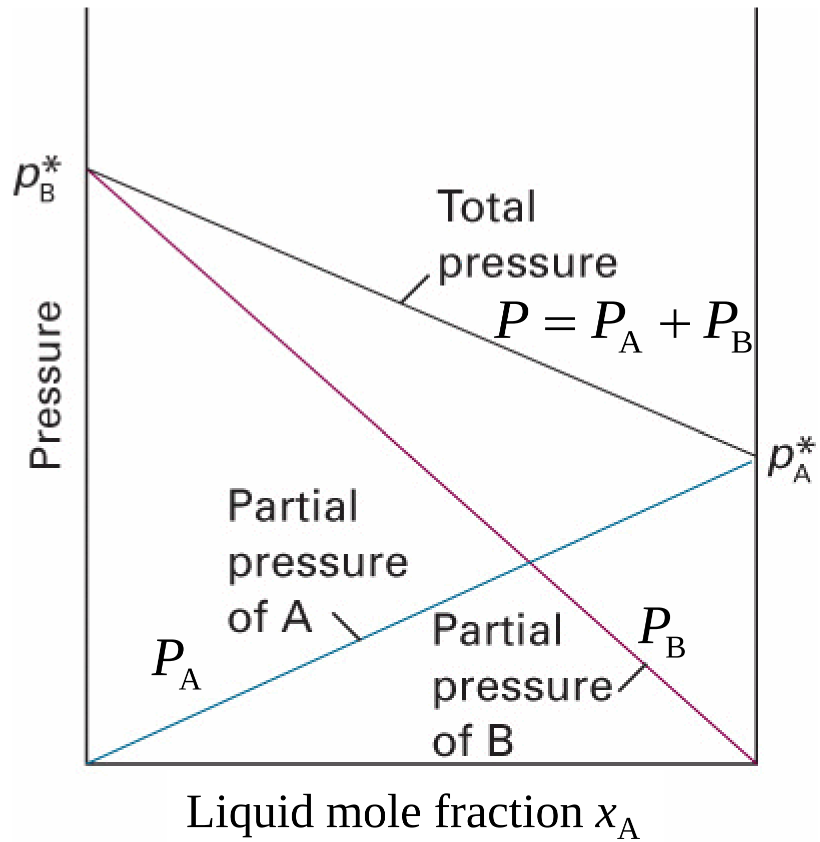
**Mole fraction**

# Mixing processes of $l,g$ equilibrium: binary mixture

## Ideal solution @ $T$

$$\Delta_{\text{mix}} G^{\text{ideal}} = nRT\left(x_A \ln x_A + x_B \ln x_B\right)$$




**Exercise 11**

Ideal solution (Raoult)

$$P_A = x_A^l P_A^*$$

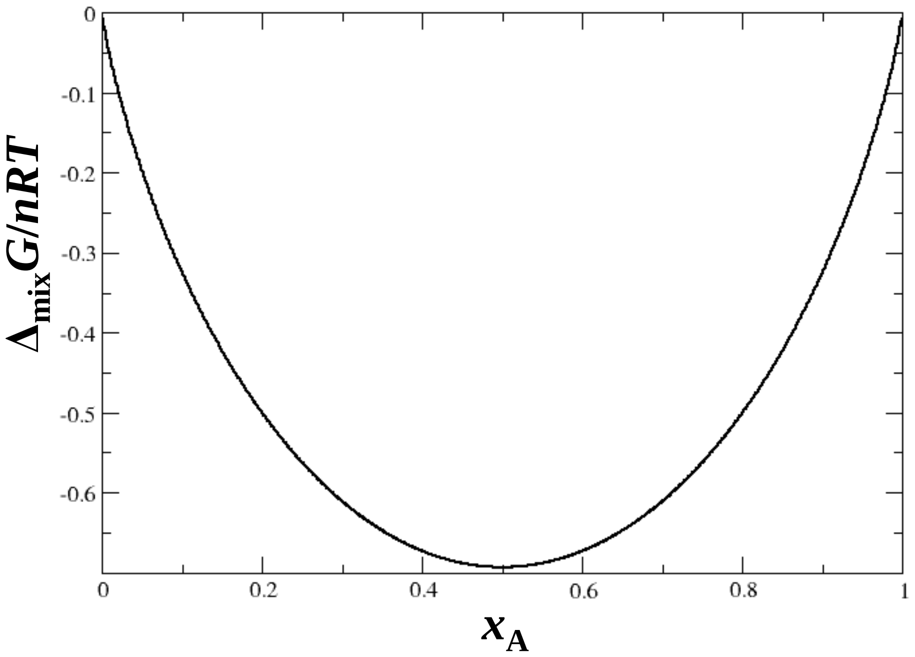
$$P_B = x_B^l P_B^*$$

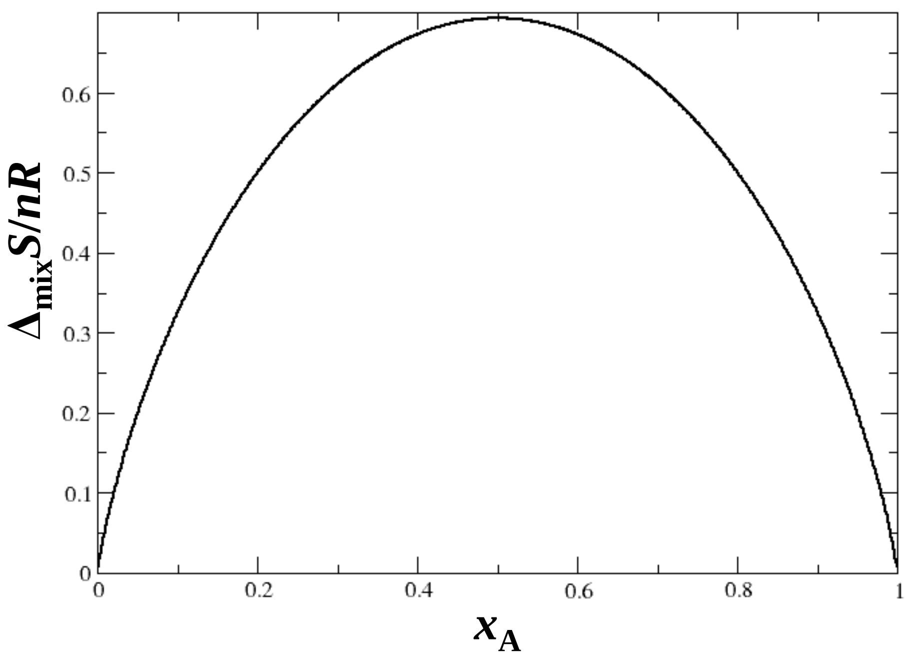
# Thermodynamics of ideal mixing

**(perfect gas mixtures and ideal solutions)**

$$\Delta_{\mathrm{mix}} G^{\mathrm{ideal}} = nRT\left[x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}\right]$$

$$\Delta_{\mathrm{mix}} S^{\mathrm{ideal}} = -nR\left[x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}\right]$$

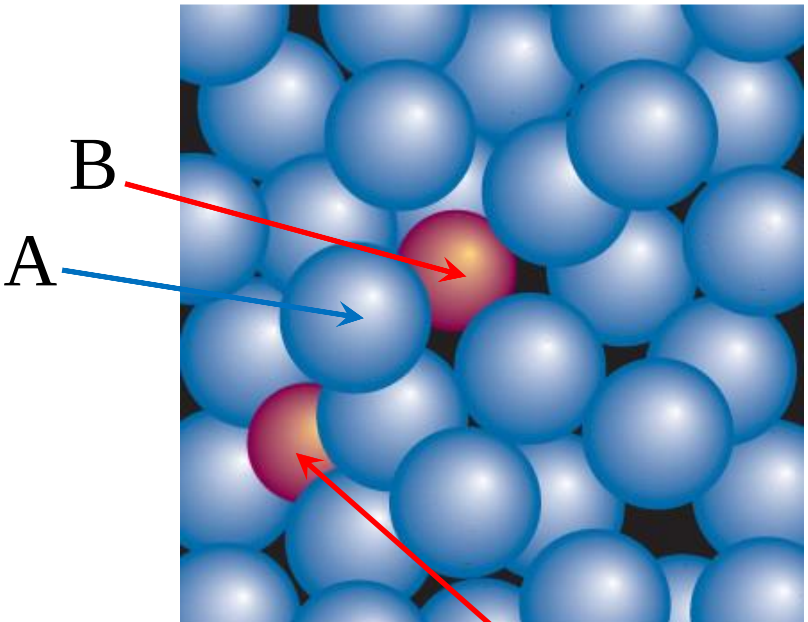


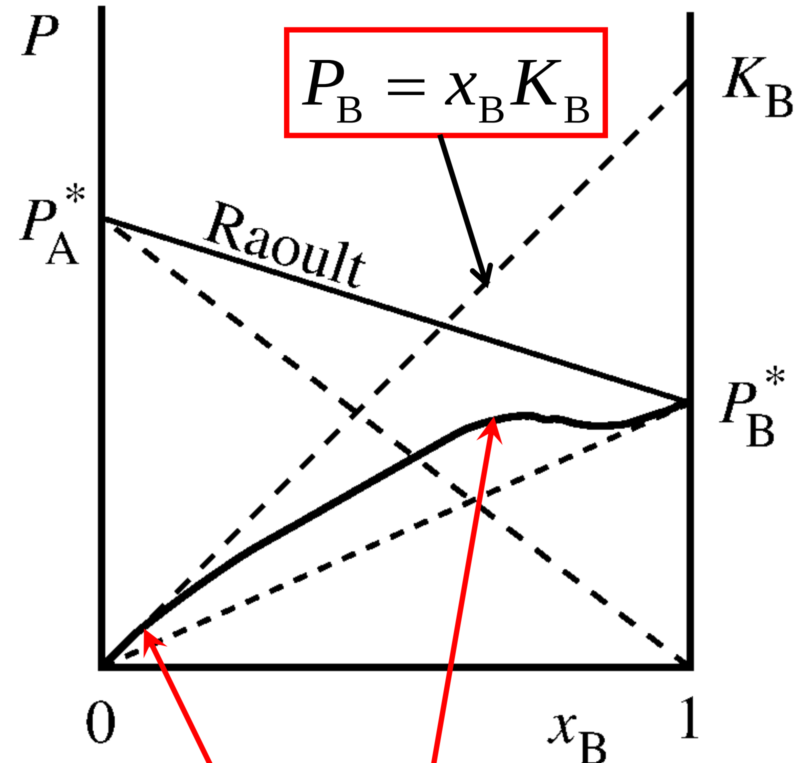

$$\Delta_{\mathrm{mix}} H^{\mathrm{ideal}} = 0$$

# Thermodynamics of non-ideal mixing liquids

**almost pure solvent A**




**Ideal-dilute solution**




**very low concentration of solute B**

**solute B expelled from solution**

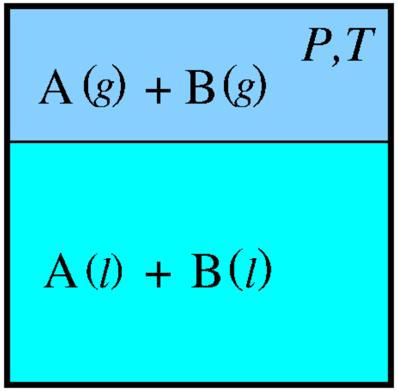
**Ideal-dilute solutions: Henry constant $K_B$**

**Exercise 13**

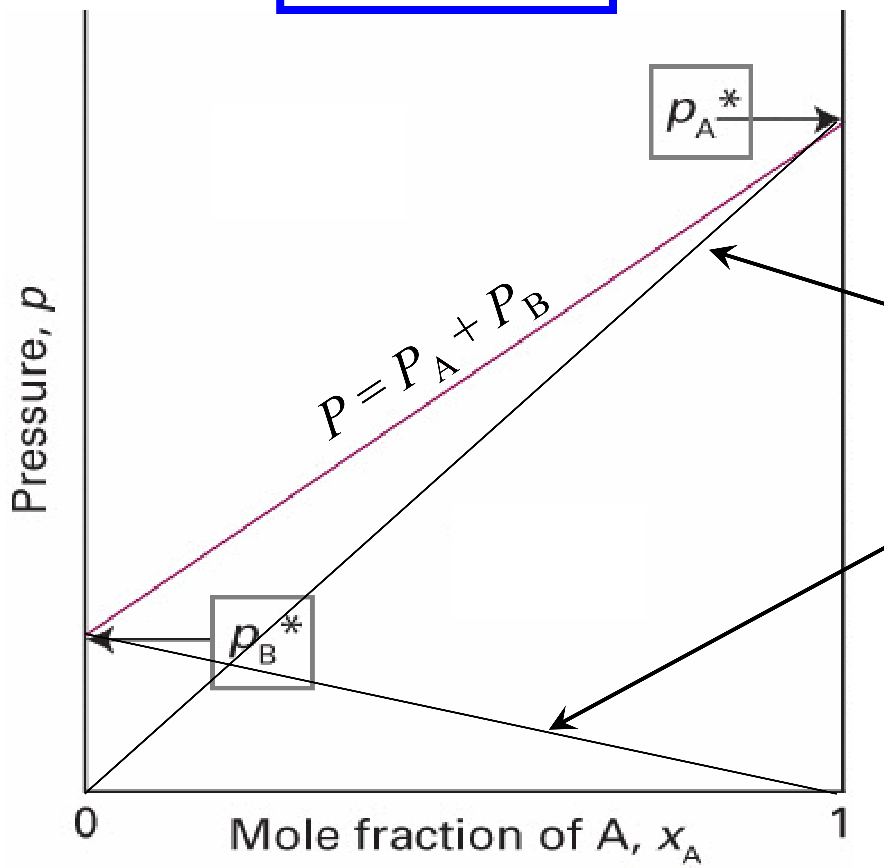
# Lecture 4

## Vapour-liquid diagrams of binary systems

# Vapour-liquid diagrams of binary systems




**Fixed *T***




Ideal solution

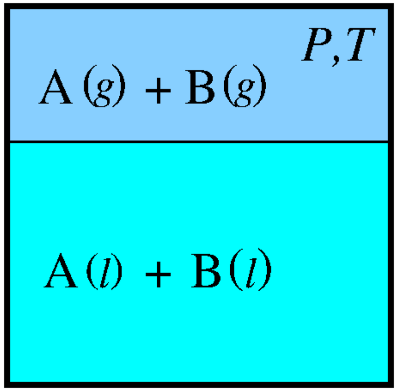
(Raoult)

$$P_A = x_A P_A^*$$

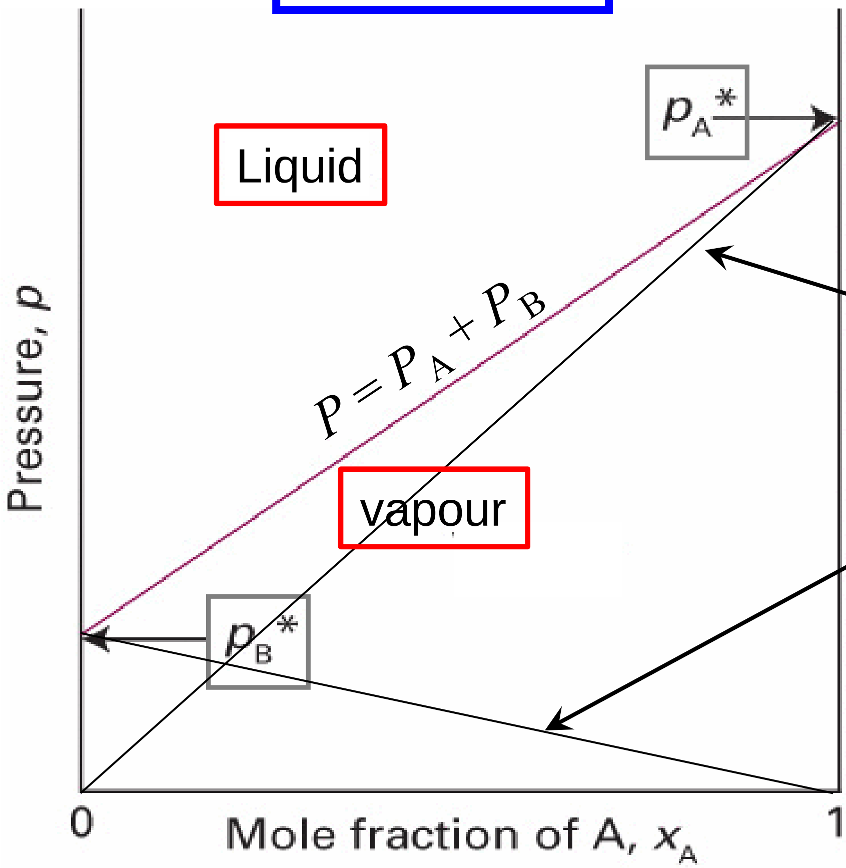
$$P_B = x_B P_B^*$$

$$P = P_A + P_B = x_A P_A^* + x_B P_B^*$$

# Vapour-liquid diagrams of binary systems




**Fixed *T***




Ideal solution

(Raoult)

$$P_A = x_A P_A^*$$

$$P_B = x_B P_B^*$$

$$P = P_A + P_B = x_A P_A^* + x_B P_B^*$$

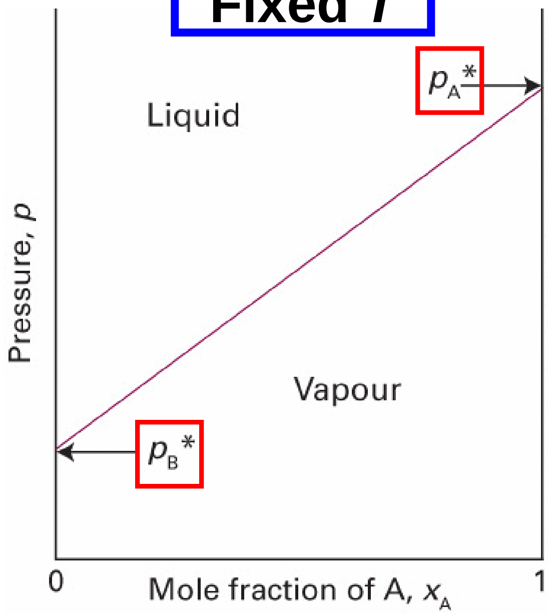
# Vapour-liquid diagrams of binary systems

C = 2

$$\frac{P_\mathrm{A}}{P_\mathrm{A}^*} = x_\mathrm{A} \equiv \frac{n_\mathrm{A}^l}{n^l}$$

Ideal solution

**Fixed *T***



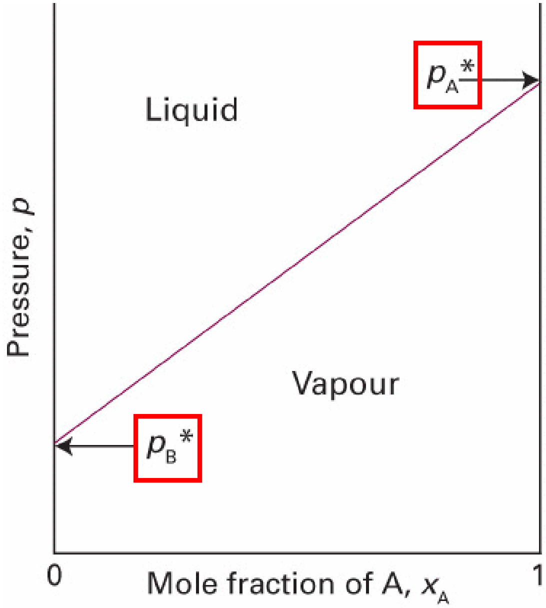

$$P = x_\mathrm{A} P_\mathrm{A}^* + x_\mathrm{B} P_\mathrm{B}^*$$

# Vapour-liquid diagrams of binary systems

C = 2

$$\frac{P_{\mathrm{A}}}{P_{\mathrm{A}}^{*}} = x_{\mathrm{A}} \equiv \frac{n_{\mathrm{A}}^{l}}{n^{l}}$$

Ideal solution




$$P = x_{\mathrm{A}} P_{\mathrm{A}}^{*} + x_{\mathrm{B}} P_{\mathrm{B}}^{*}$$

$$y_{\mathrm{A}} \equiv \frac{n_{\mathrm{A}}^{g}}{n^{g}} = \frac{P_{\mathrm{A}}}{P}$$

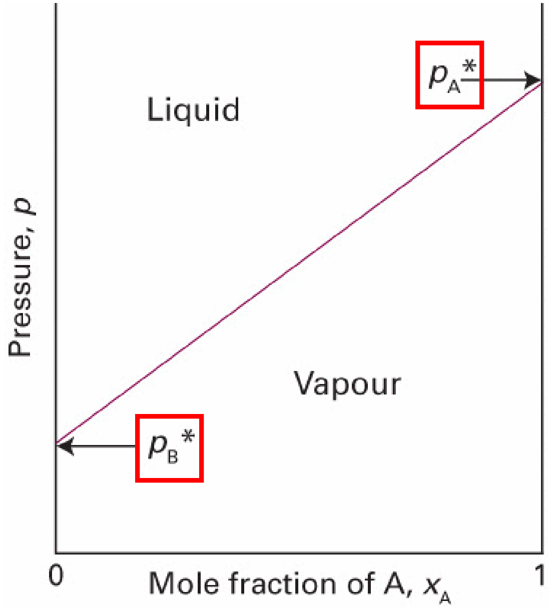
we use $y$ for the mole fractions in the gas phase

# Vapour-liquid diagrams of binary systems

C = 2

$$\frac{P_A}{P_A^*} = x_A \equiv \frac{n_A^l}{n^l}$$

Ideal solution




$$P = x_A P_A^* + x_B P_B^*$$

$$y_A \equiv \frac{n_A^g}{n^g} = \frac{P_A}{P}$$

$$(x_B = 1 - x_A)$$

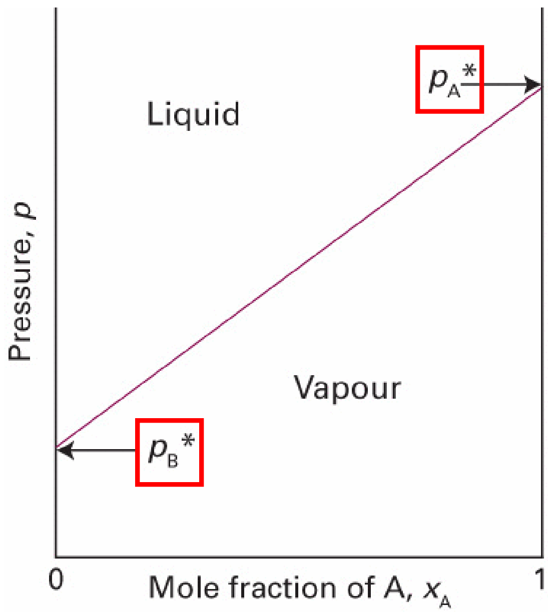
$$y_A = \frac{x_A P_A^*}{P_B^* + \left(P_A^* - P_B^*\right)x_A}$$

# Vapour-liquid diagrams of binary systems

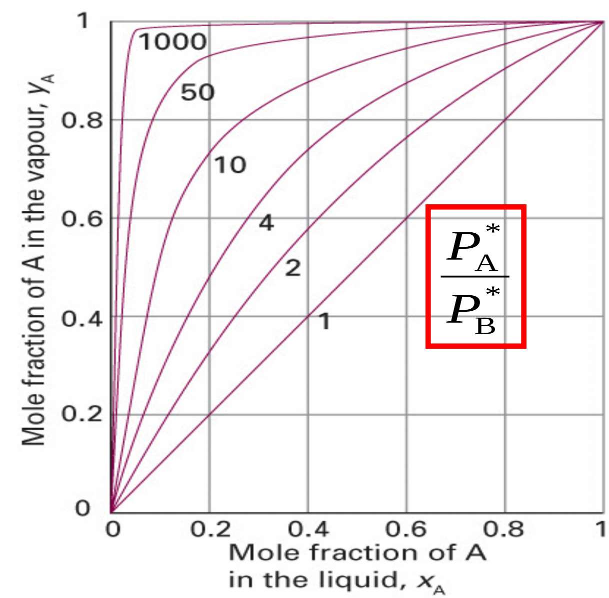
C = 2

$$\frac{P_A}{P_A^*} = x_A \equiv \frac{n_A^l}{n^l}$$

Ideal solution




$$P = x_A P_A^* + x_B P_B^*$$




$$y_A \equiv \frac{n_A^g}{n^g} = \frac{P_A}{P}$$

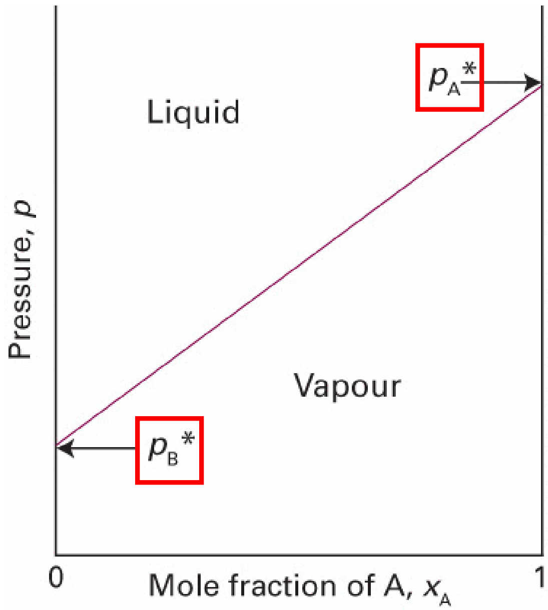
$$y_A = \frac{x_A P_A^*}{P_B^* + \left(P_A^* - P_B^*\right) x_A}$$

# Vapour-liquid diagrams of binary systems

$C = 2$

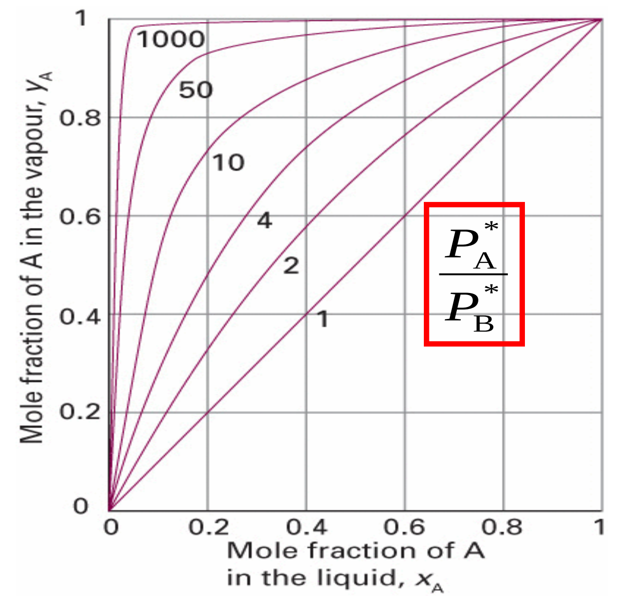
$$\frac{P_A}{P_A^*} = x_A \equiv \frac{n_A^l}{n^l}$$

Ideal solution




$$P = x_A P_A^* + x_B P_B^*$$

$$P = P(y_A)?$$




$$y_A \equiv \frac{n_A^g}{n^g} = \frac{P_A}{P}$$

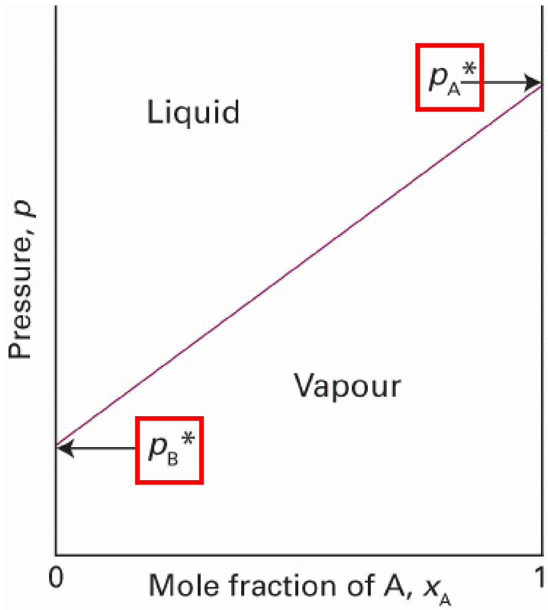
$$y_A = \frac{x_A P_A^*}{P_B^* + (P_A^* - P_B^*) x_A}$$

# Vapour-liquid diagrams of binary systems

**C = 2**

$$\frac{P_{\mathrm{A}}}{P_{\mathrm{A}}^{*}} = x_{\mathrm{A}} \equiv \frac{n_{\mathrm{A}}^{l}}{n^{l}}$$

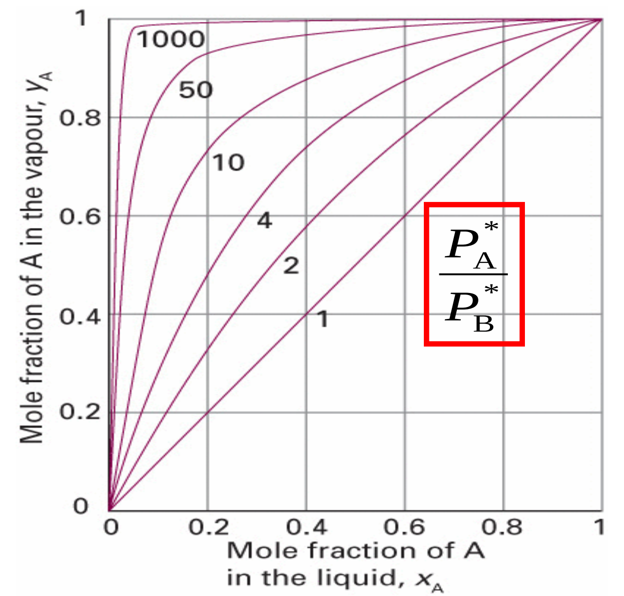
Ideal solution




$$P = x_{\mathrm{A}} P_{\mathrm{A}}^{*} + x_{\mathrm{B}} P_{\mathrm{B}}^{*}$$

$$\left(x_{\mathrm{B}} = 1 - x_{\mathrm{A}}\right)$$

$$P = \frac{P_{\mathrm{A}}^{*} P_{\mathrm{B}}^{*}}{P_{\mathrm{A}}^{*} + \left(P_{\mathrm{B}}^{*} - P_{\mathrm{A}}^{*}\right) y_{\mathrm{A}}}$$

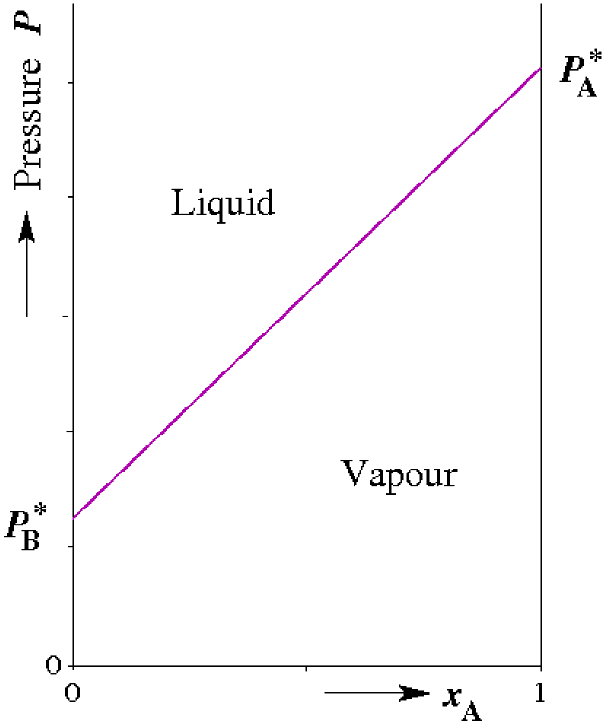



$$\frac{P_{\mathrm{A}}^{*}}{P_{\mathrm{B}}^{*}}$$

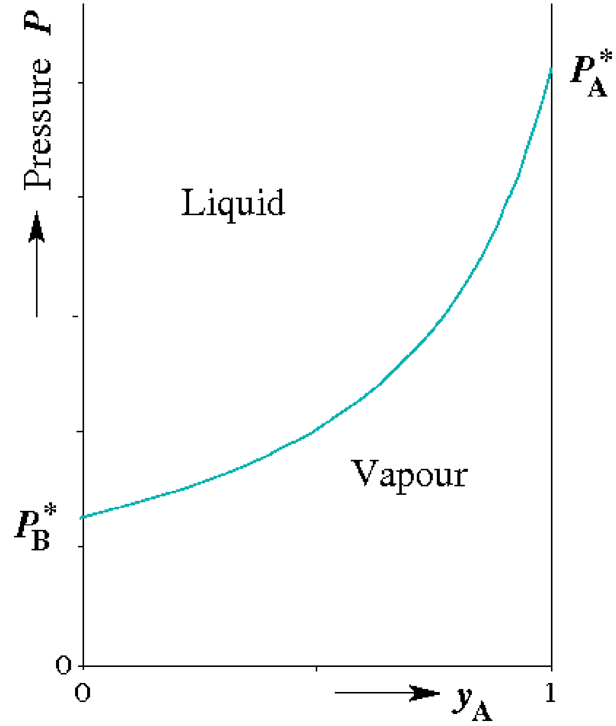
$$y_{\mathrm{A}} \equiv \frac{n_{\mathrm{A}}^{g}}{n^{g}} = \frac{P_{\mathrm{A}}}{P}$$

$$y_{\mathrm{A}} = \frac{x_{\mathrm{A}} P_{\mathrm{A}}^{*}}{P_{\mathrm{B}}^{*} + \left(P_{\mathrm{A}}^{*} - P_{\mathrm{B}}^{*}\right) x_{\mathrm{A}}}$$

# Vapour-liquid diagrams of binary systems




## Ideal solution




$$\boxed{P = x_A P_A^* + x_B P_B^*}$$

$$\boxed{P = \frac{P_A^* P_B^*}{P_A^* + \left(P_B^* - P_A^*\right) y_A}}$$

$$\boxed{\frac{P_A^*}{P_B^*} = 4.12}$$

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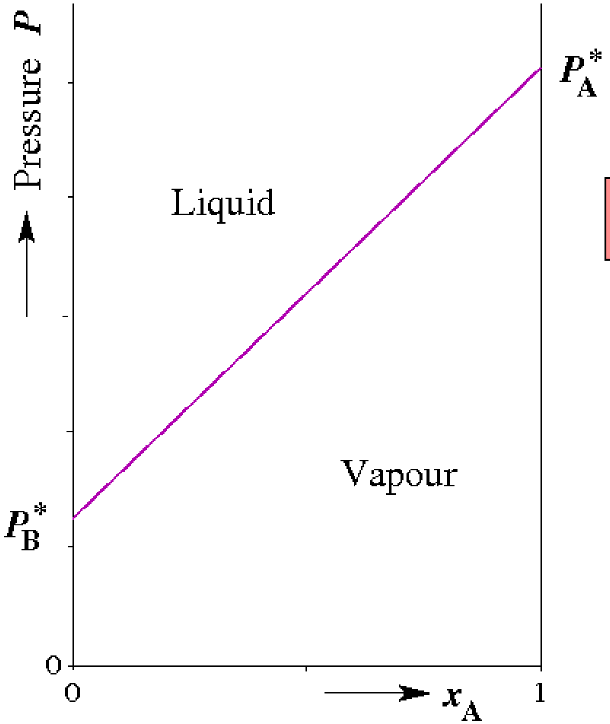
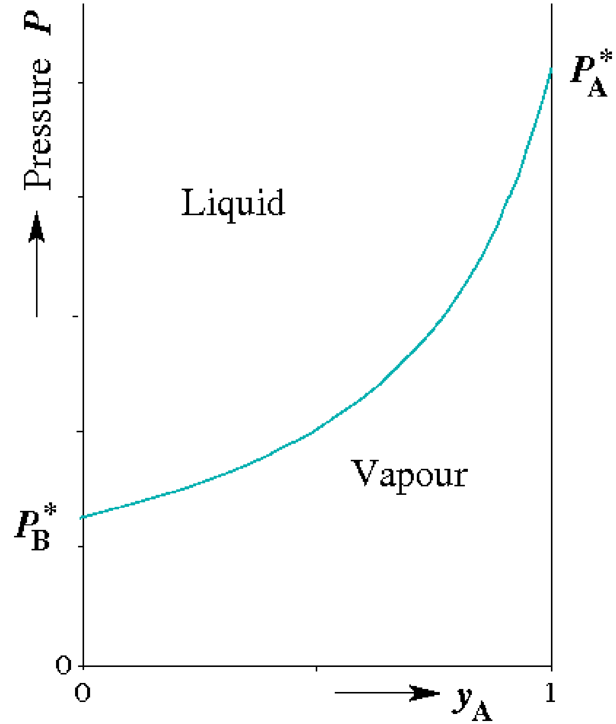
# Vapour-liquid diagrams of binary systems

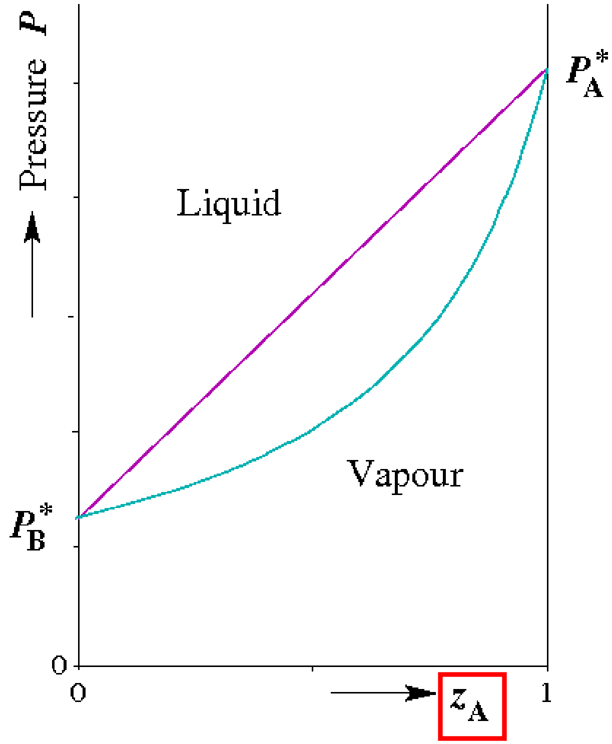



## Ideal solution




$$P = x_A P_A^* + x_B P_B^*$$

$$P = \frac{P_A^* P_B^*}{P_A^* + \left(P_B^* - P_A^*\right) y_A}$$




$$\frac{P_A^*}{P_B^*} = 4.12$$

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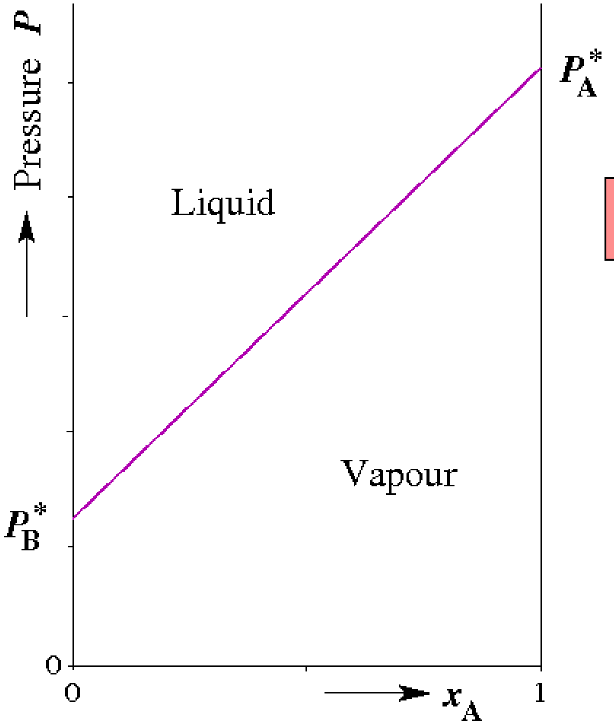
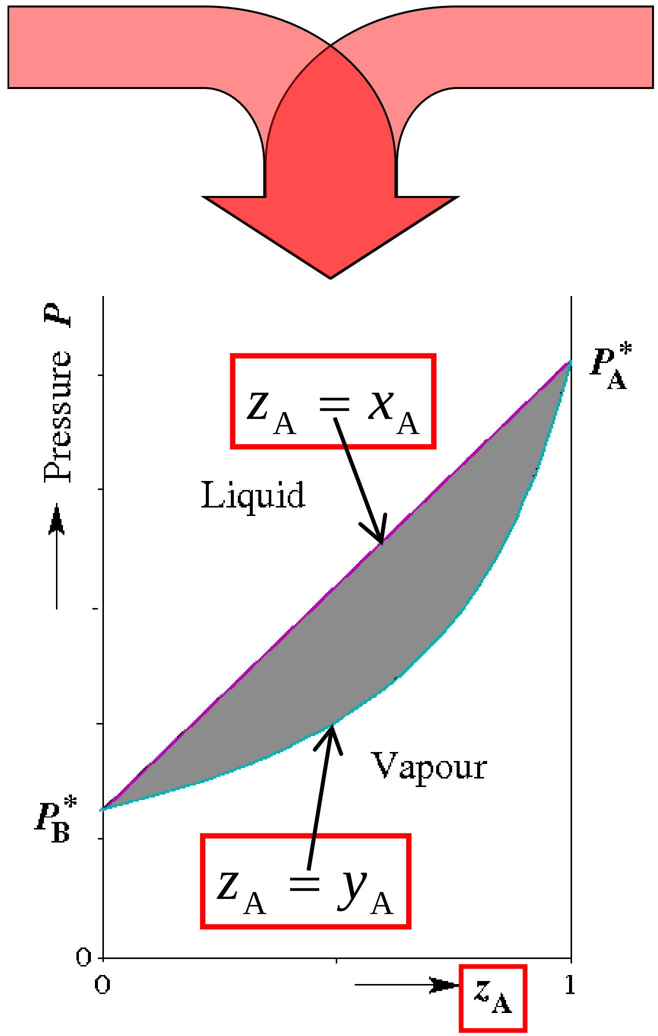
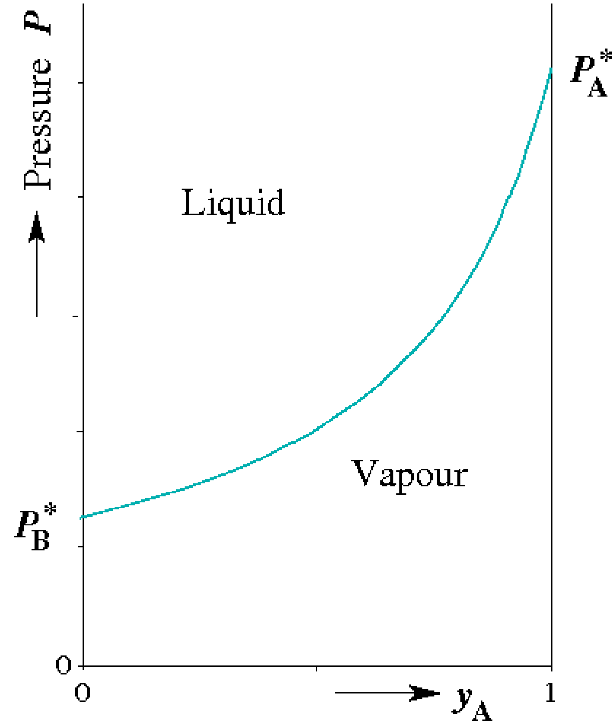
# Vapour-liquid diagrams of binary systems

## Ideal solution




$$P = x_A P_A^* + x_B P_B^*$$

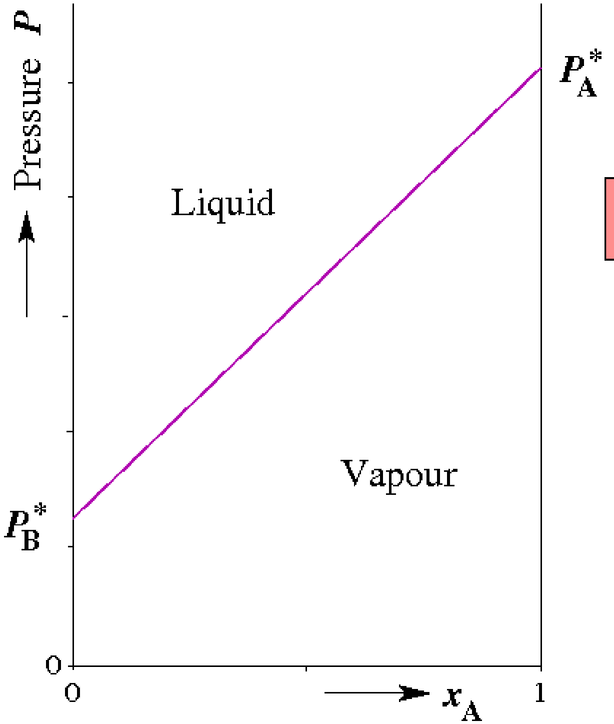
$$P = \frac{P_A^* P_B^*}{P_A^* + \left(P_B^* - P_A^*\right) y_A}$$

$$\frac{P_A^*}{P_B^*} = 4.12$$

$$\frac{P_A^*}{P_B^*} = 4.12$$

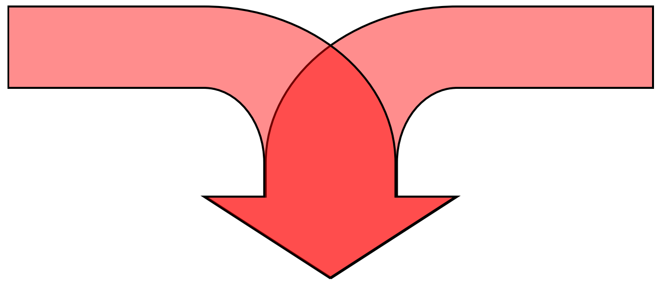
# Vapour-liquid diagrams of binary systems

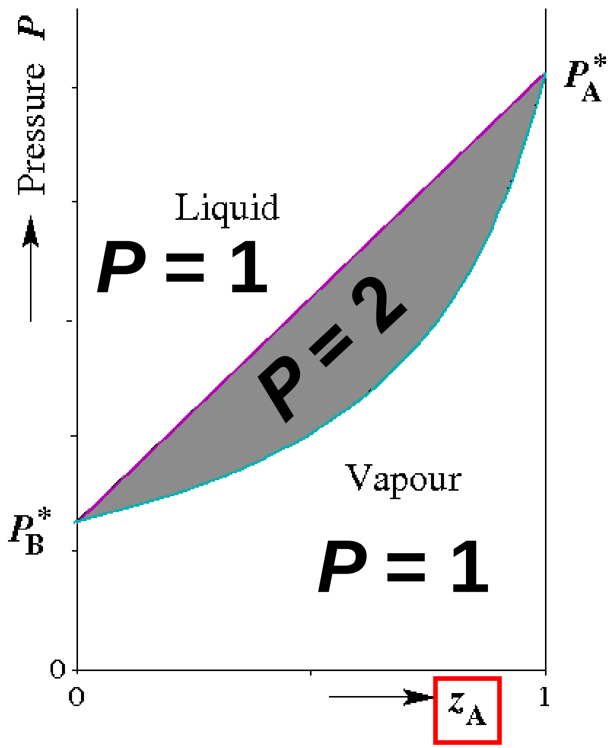
## Ideal solution

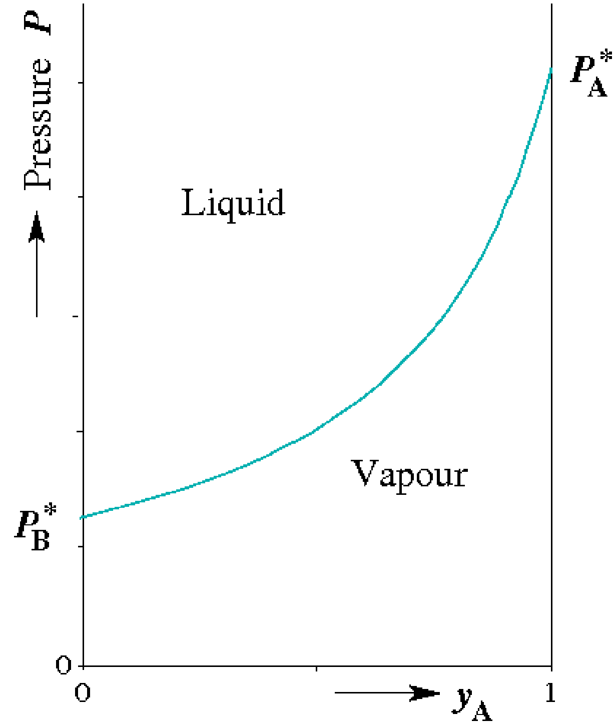



$$P = x_A P_A^* + x_B P_B^*$$

$$\frac{P_A^*}{P_B^*} = 4.12$$



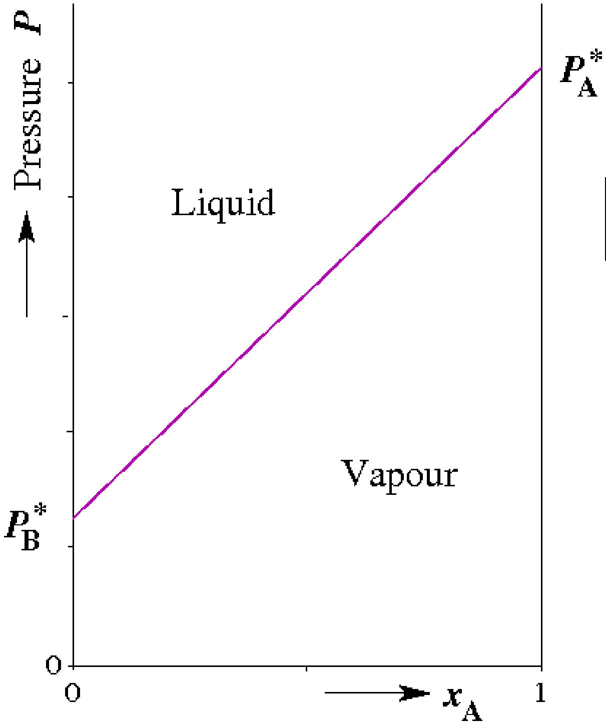



$$P = \frac{P_A^* P_B^*}{P_A^* + \left(P_B^* - P_A^*\right) y_A}$$

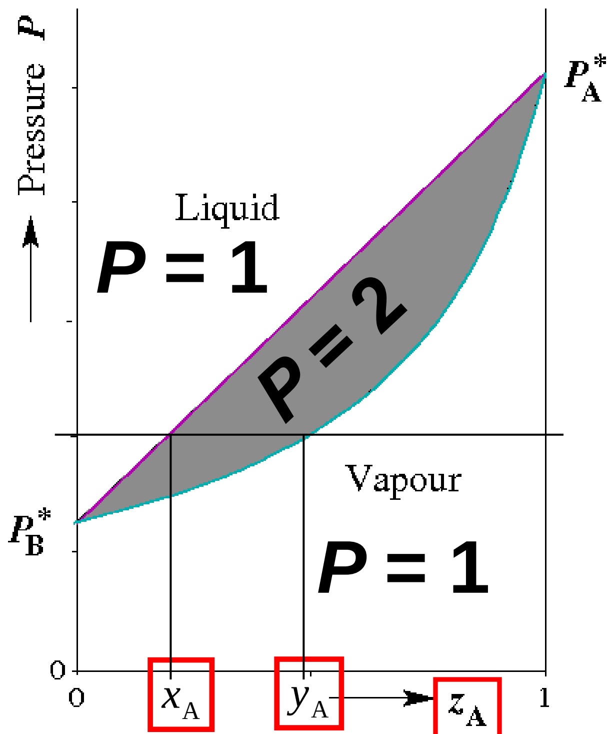
$$\frac{P_A^*}{P_B^*} = 4.12$$

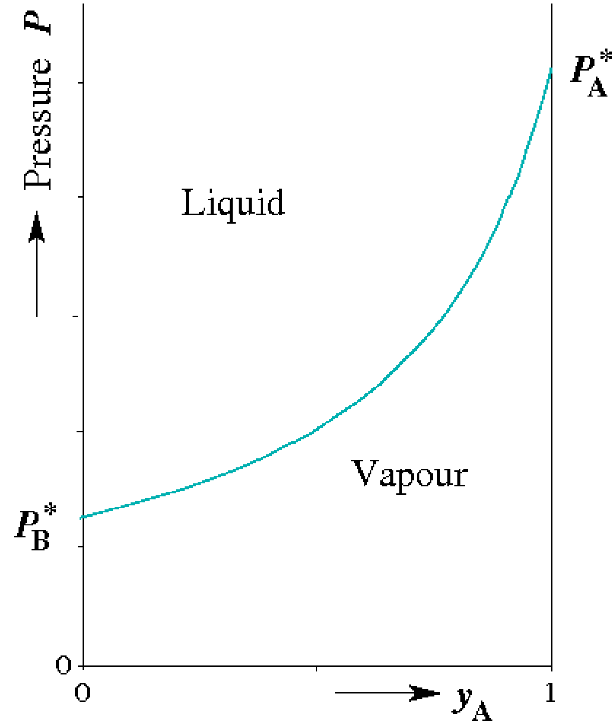
# Vapour-liquid diagrams of binary systems




Ideal solution

**Fixed *T***




$$\boxed{F = C - P + 2}$$

$$\boxed{F' = C - P + 1}$$

Ideal solution

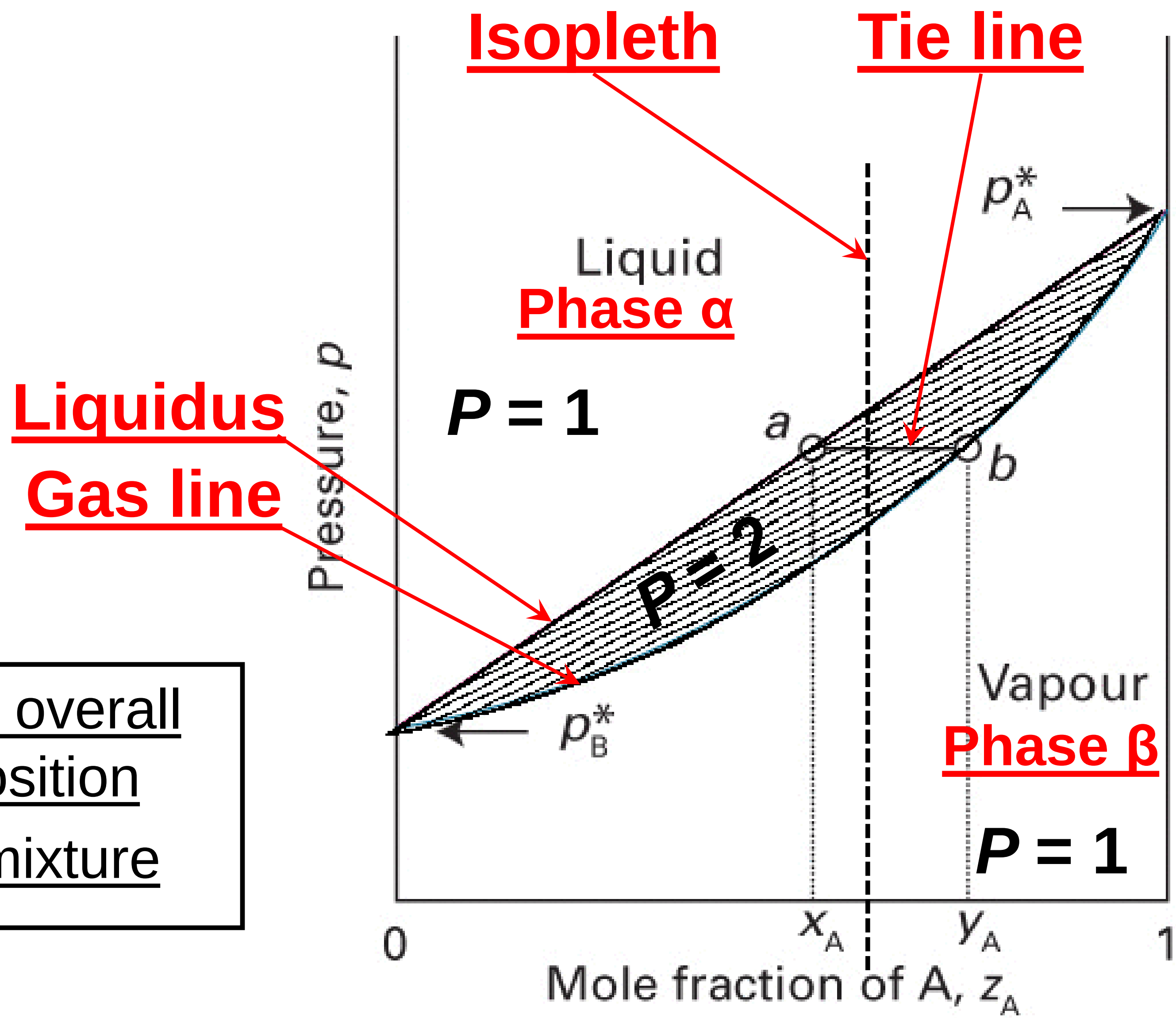
**Exercise 14**

$$P = \frac{P_A^* P_B^*}{P_A^* + \left(P_B^* - P_A^*\right) y_A}$$

$$\frac{P_A^*}{P_B^*} = 4.12$$

# Lever rule

$C = 2$

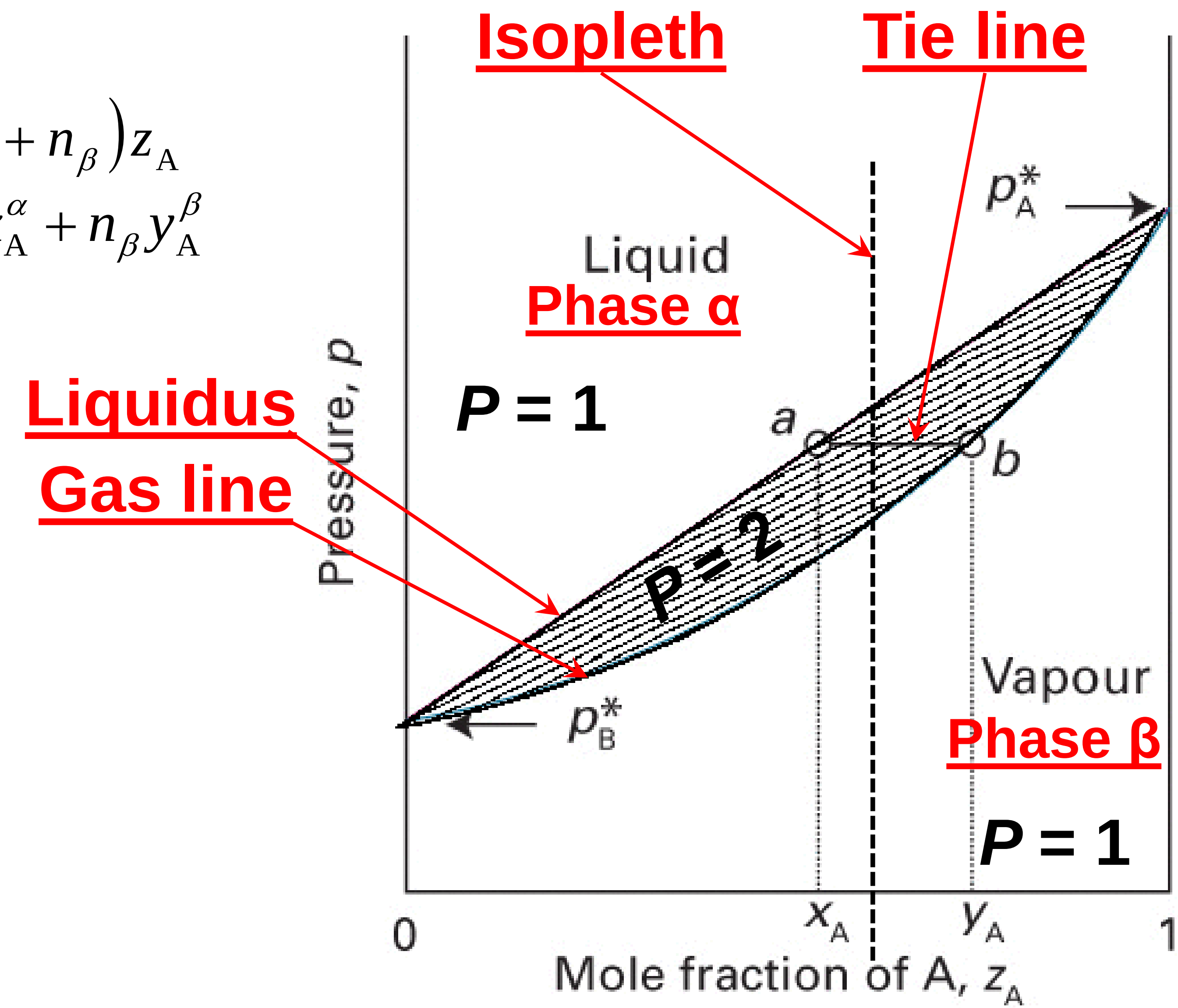



$z_A$ is the overall composition of the mixture

# Lever rule

C = 2

$$\begin{cases} nz_A = (n_\alpha + n_\beta) z_A \\ nz_A = n_\alpha x_A^\alpha + n_\beta y_A^\beta \end{cases}$$



# Lever rule

$C = 2$

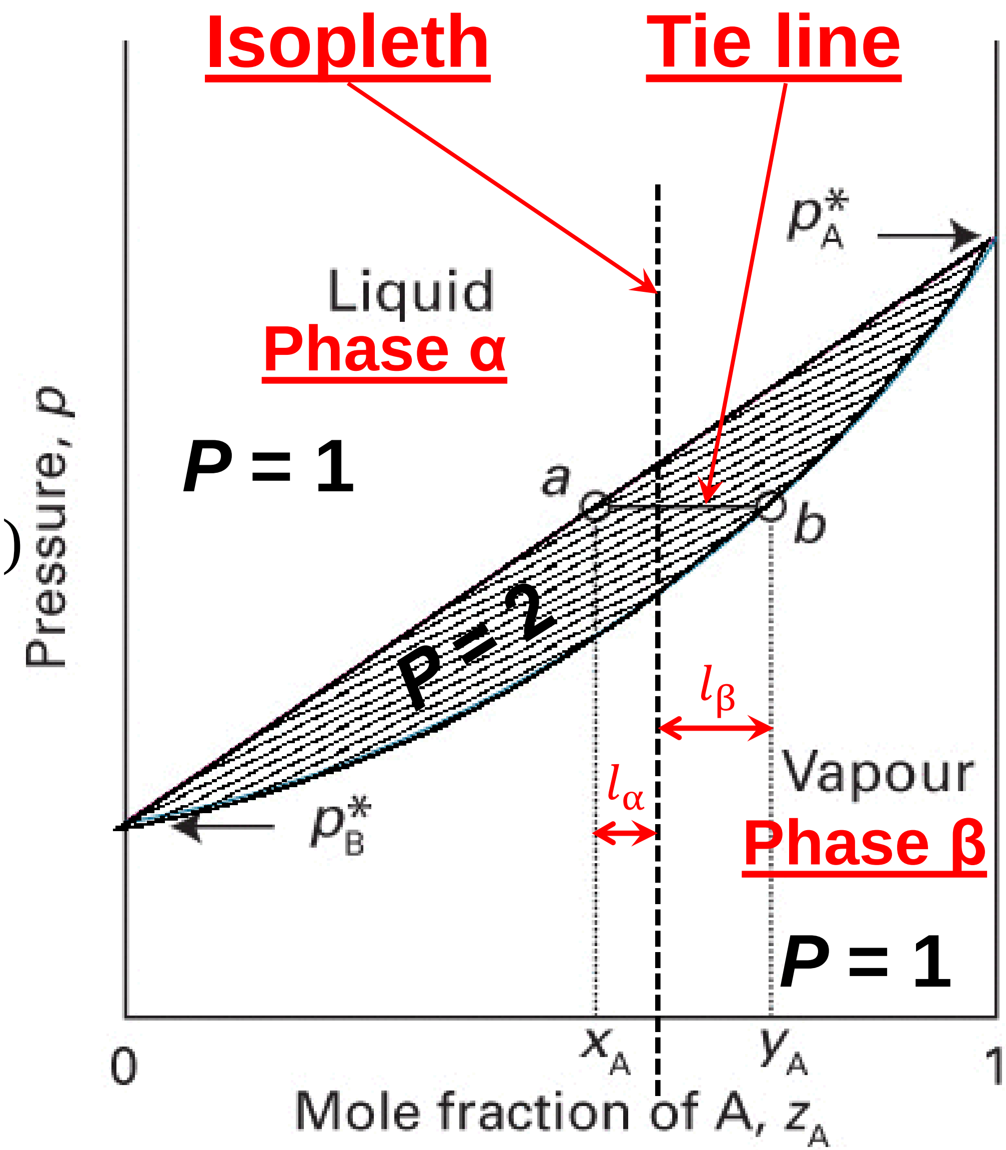
$$\begin{cases} nz_A = (n_\alpha + n_\beta) z_A \\ nz_A = n_\alpha x_A^\alpha + n_\beta y_A^\beta \end{cases}$$

$$n_\alpha (z_A - x_A^\alpha) = n_\beta (y_A^\beta - z_A)$$

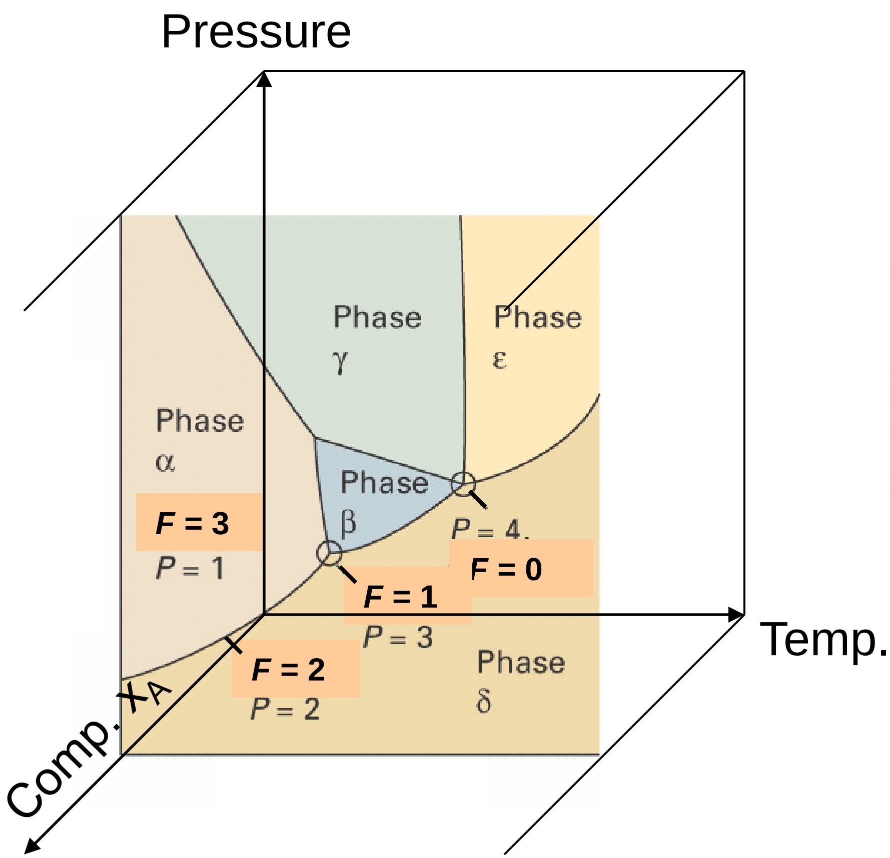
$$\boxed{n_\alpha l_\alpha = n_\beta l_\beta}$$

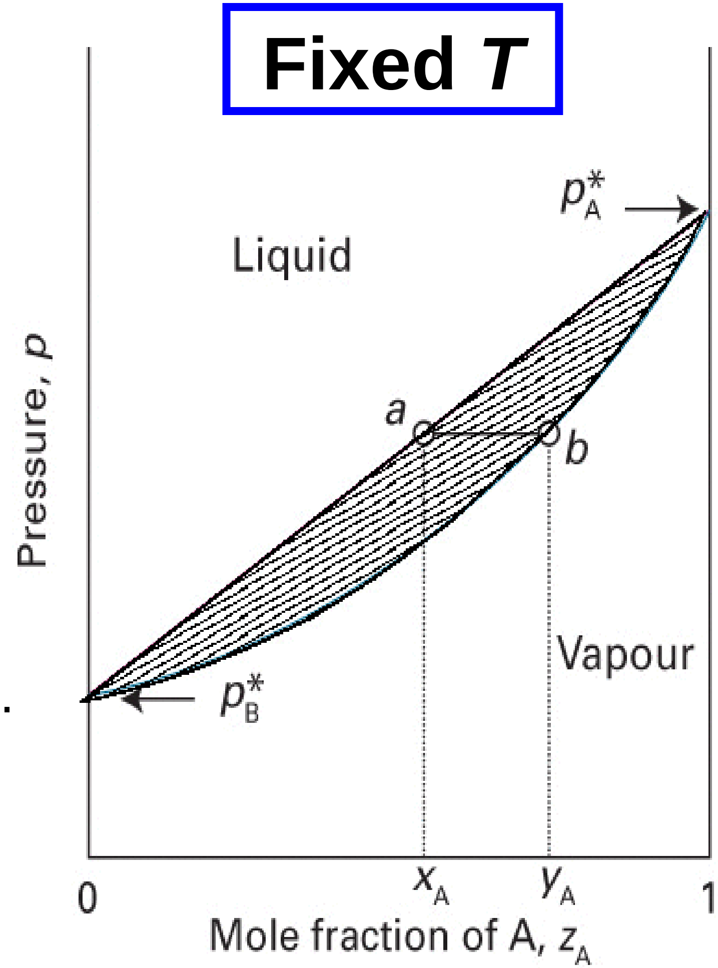
**Lever rule**

$$\boxed{\frac{n_\alpha}{n_\beta} = \frac{l_\beta}{l_\alpha}}$$

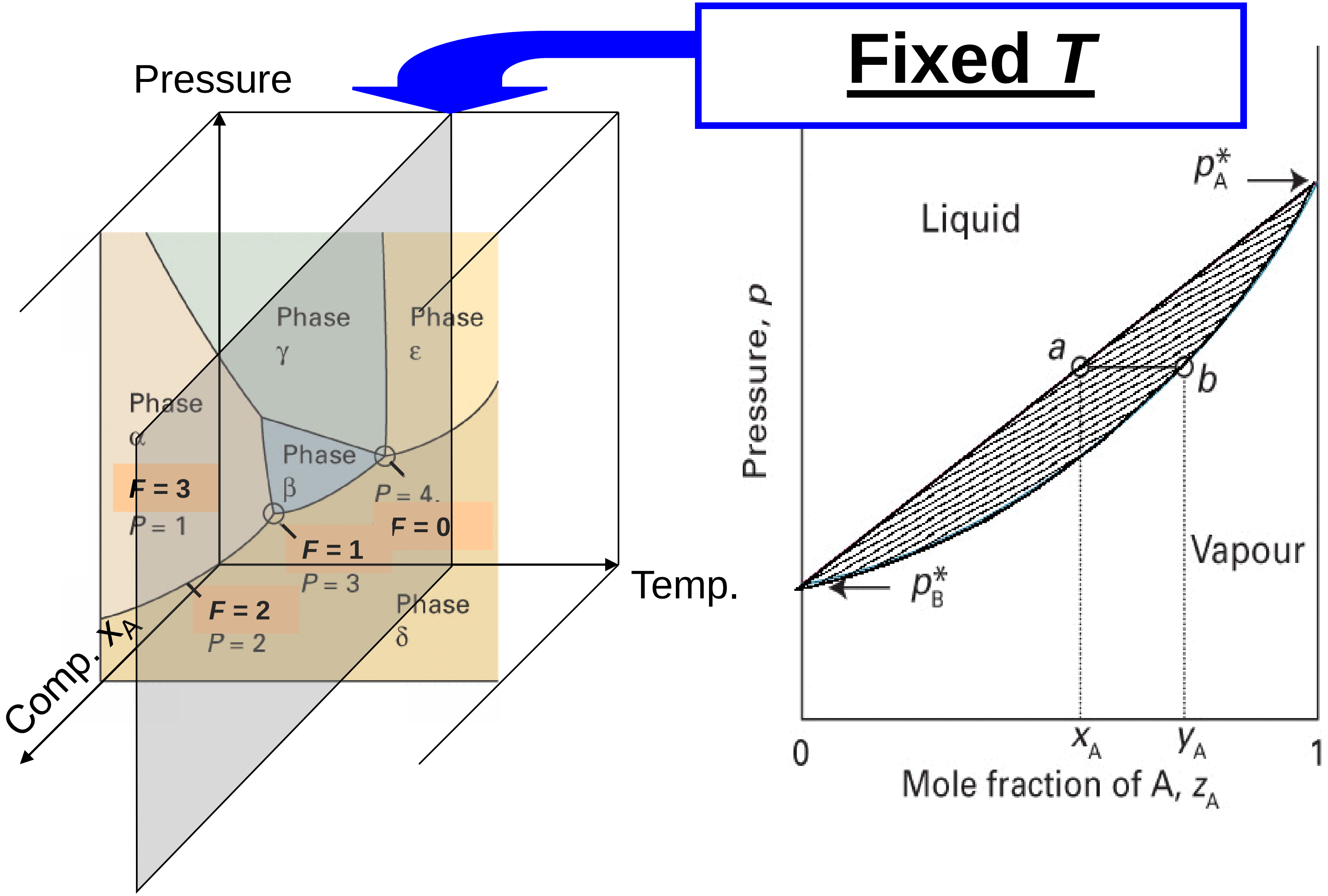


# Pressure-composition diagrams

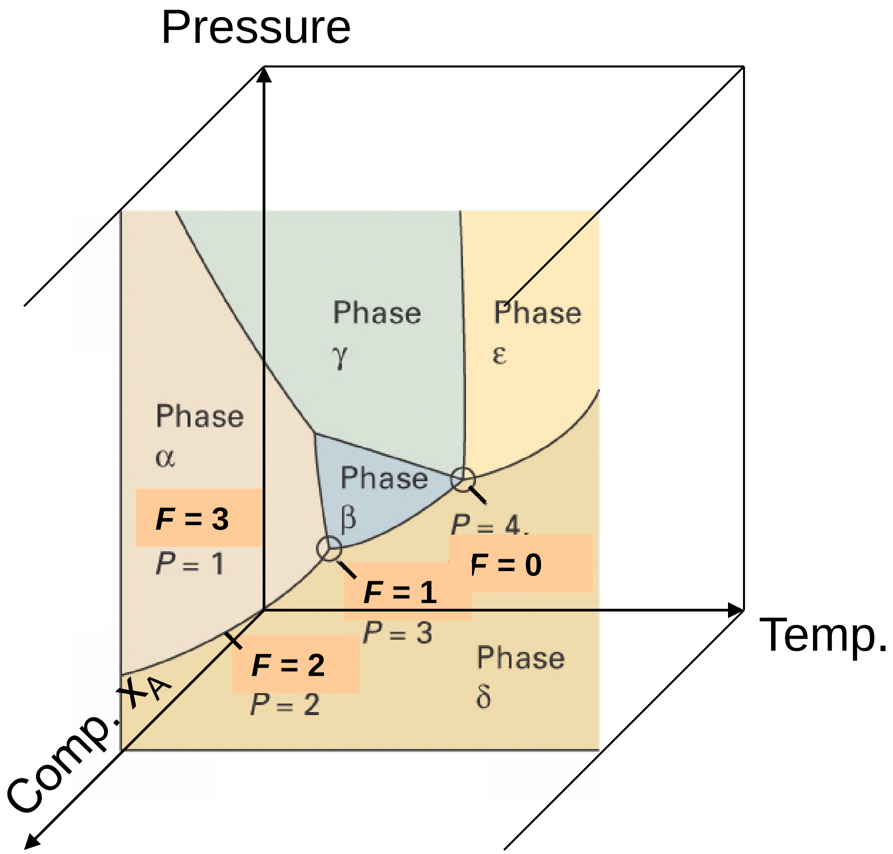


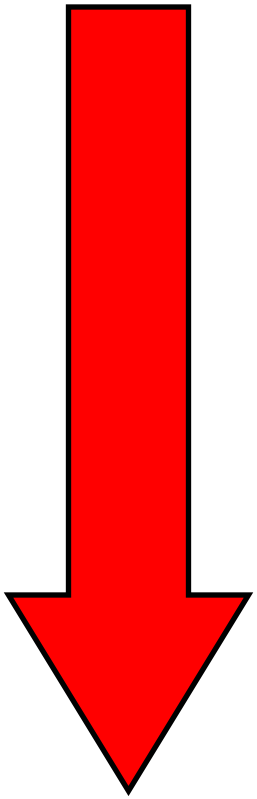



# Pressure-composition diagrams



# Pressure-composition diagrams

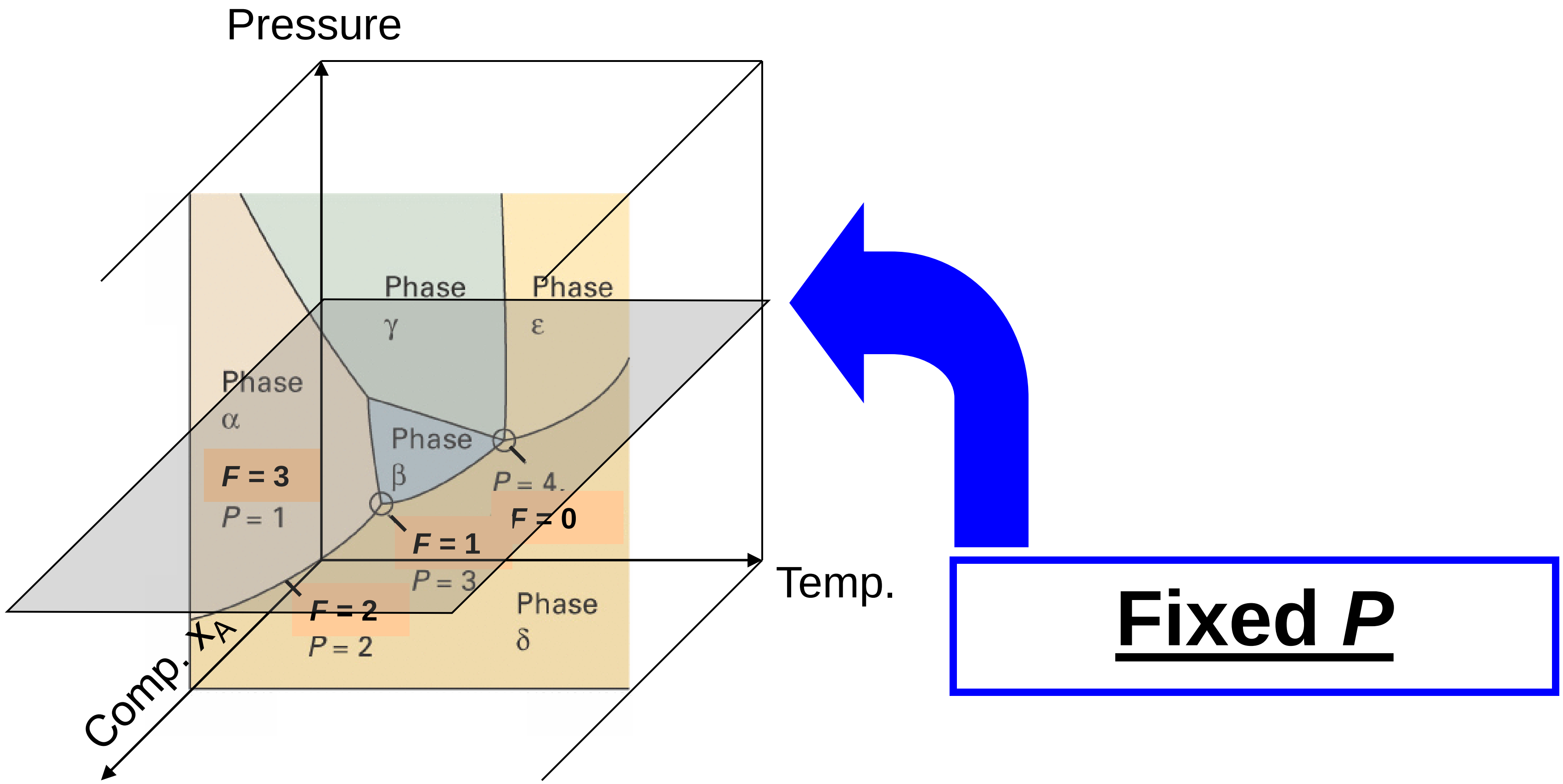


# Temperature-composition diagrams

**(important for distillation processes)**

# Temperature-composition diagrams




Temperature-composition diagrams

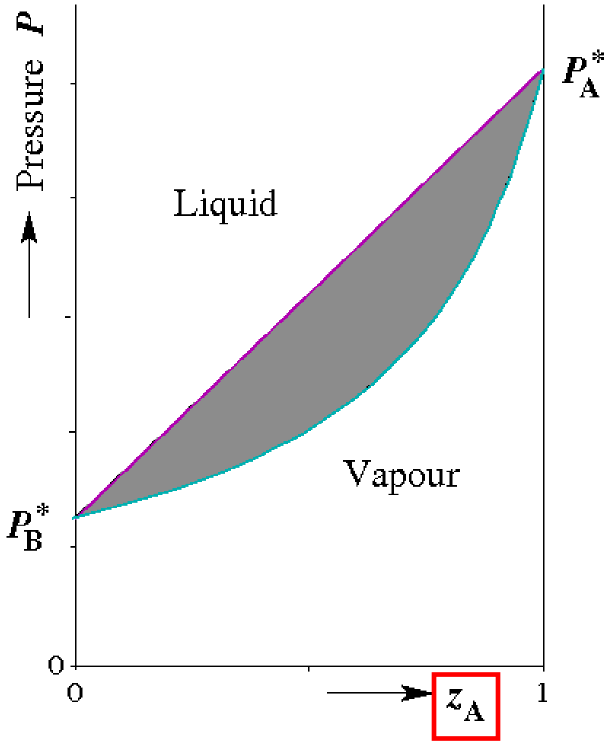
**(important for distillation processes)**

# Pressure-composition diagrams

## Ideal solution

$$P(x_A) = x_A P_A^* + (1 - x_A) P_B^*$$

$$P(y_A) = \frac{P_A^* P_B^*}{P_A^* + (P_B^* - P_A^*) y_A}$$




$$x_A(T) = \frac{P - P_B^*(T)}{P_A^*(T) - P_B^*(T)}$$

$$y_A(T) = \frac{P_A^*(T)\left[P - P_B^*(T)\right]}{P\left[P_A^*(T) - P_B^*(T)\right]}$$

**Fixed *T***

# Temperature-composition diagrams

$$\boxed{x_A(T) = \frac{P - P_B^*(T)}{P_A^*(T) - P_B^*(T)}}$$

$$\boxed{y_A(T) = \frac{P_A^*(T)\left[P - P_B^*(T)\right]}{P\left[P_A^*(T) - P_B^*(T)\right]}}$$

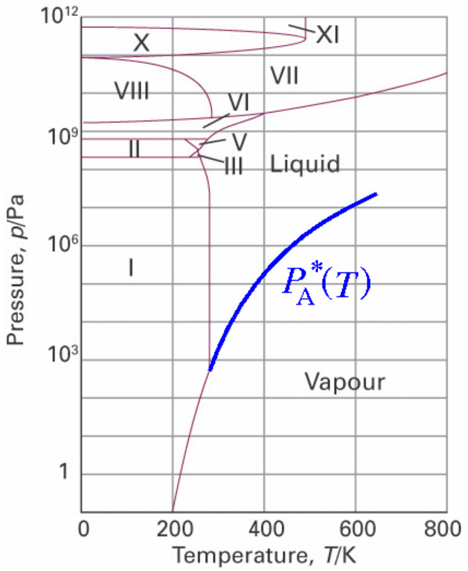
Ideal solution

# Temperature-composition diagrams

$$x_A(T) = \frac{P - P_B^*(T)}{P_A^*(T) - P_B^*(T)}$$

Ideal solution

$$y_A(T) = \frac{P_A^*(T)\left[P - P_B^*(T)\right]}{P\left[P_A^*(T) - P_B^*(T)\right]}$$




$$\frac{dP_A^*}{dT} = \frac{\Delta_{vap} H_A^*(T)}{T\Delta_{vap} V_A^*(T)}$$

(Clapeyron)

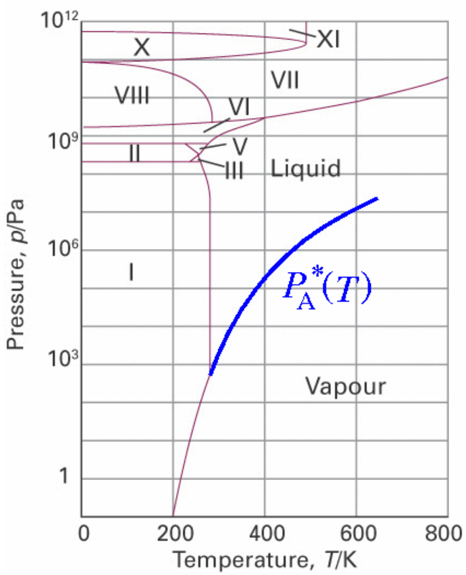
**($P,T$)-diagram**

**component A**

# Temperature-composition diagrams

$$x_A(T) = \frac{P - P_B^*(T)}{P_A^*(T) - P_B^*(T)}$$

$$y_A(T) = \frac{P_A^*(T)\left[P - P_B^*(T)\right]}{P\left[P_A^*(T) - P_B^*(T)\right]}$$



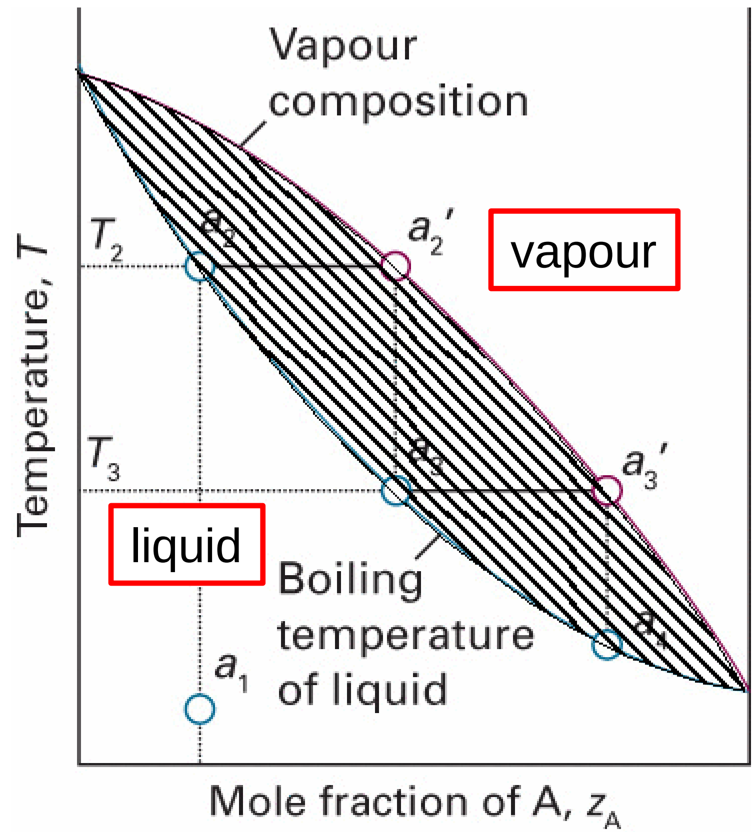

$$\frac{dP_A^*}{dT} = \frac{\Delta_{vap} H_A^*(T)}{T \Delta_{vap} V_A^*(T)}$$

(Clapeyron)

**(*P*,*T*)-diagram**

**component A**

## Ideal solution



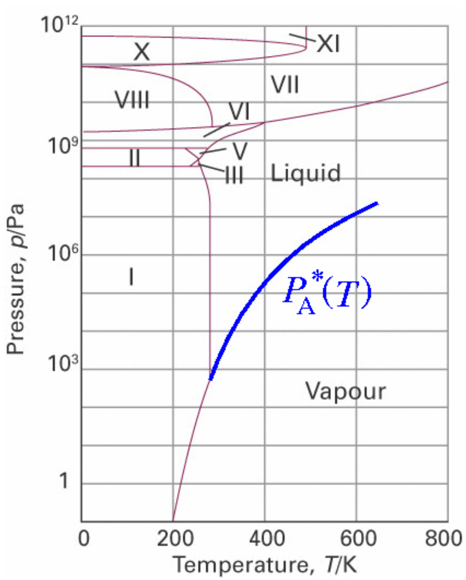

**important for distillation processes**

# Temperature-composition diagrams

$$x_A(T) = \frac{P - P_B^*(T)}{P_A^*(T) - P_B^*(T)}$$

$$y_A(T) = \frac{P_A^*(T)\left[P - P_B^*(T)\right]}{P\left[P_A^*(T) - P_B^*(T)\right]}$$

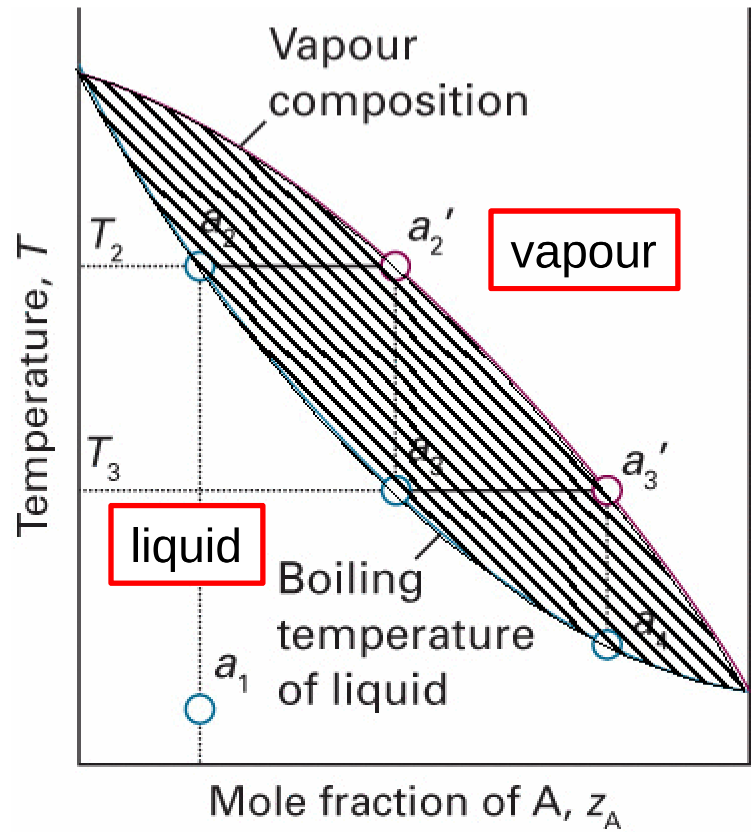
## Ideal solution




$$\frac{dP_A^*}{dT} = \frac{\Delta_{vap} H_A^*(T)}{T \Delta_{vap} V_A^*(T)}$$

(Clapeyron)

**(*P*,*T*)-diagram component A**




$$F = C - P + 2$$

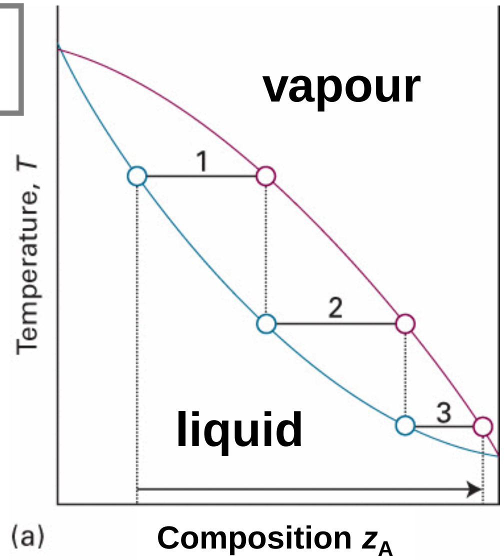
$$F' = C - P + 1$$

**Fixed *P***

# C = 2 Temperature-composition diagrams

$$\boxed{G^{\mathrm{E}} = 0}$$

ideal solution




Deviations from ideal solution behaviour

Excess Gibbs free energy

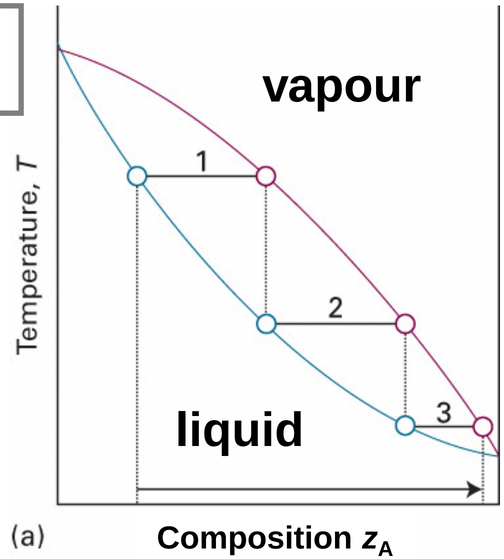
$$G^{\mathrm{E}} \equiv \Delta_{\mathrm{mix}} G - \Delta_{\mathrm{mix}} G^{\mathrm{ideal}}$$

$G^{\mathrm{E}}$ is the excess Gibbs free energy of the *liquid* mixture

# C = 2 Temperature-composition diagrams

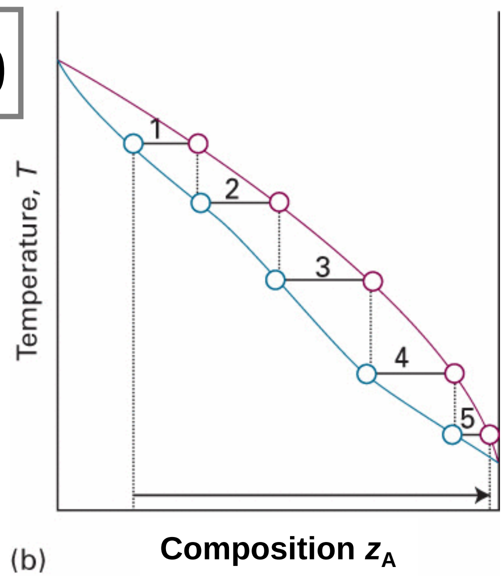
$$G^{\mathrm{E}} = 0$$

ideal solution




$$G^{\mathrm{E}} < 0$$

non-ideal solutions




Deviations from ideal solution behaviour

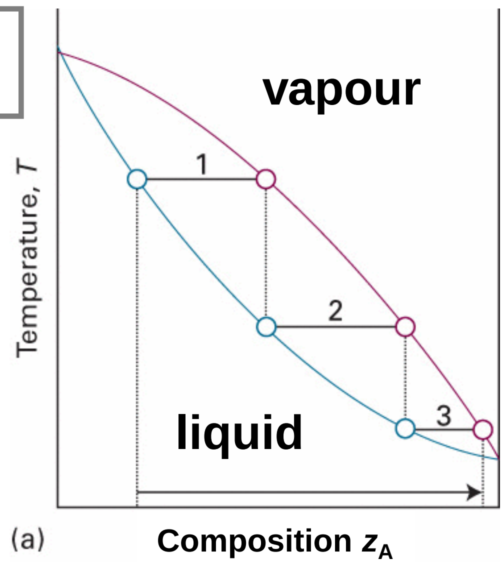
Excess Gibbs free energy

$$G^{\mathrm{E}} \equiv \Delta_{\mathrm{mix}} G - \Delta_{\mathrm{mix}} G^{\mathrm{ideal}}$$

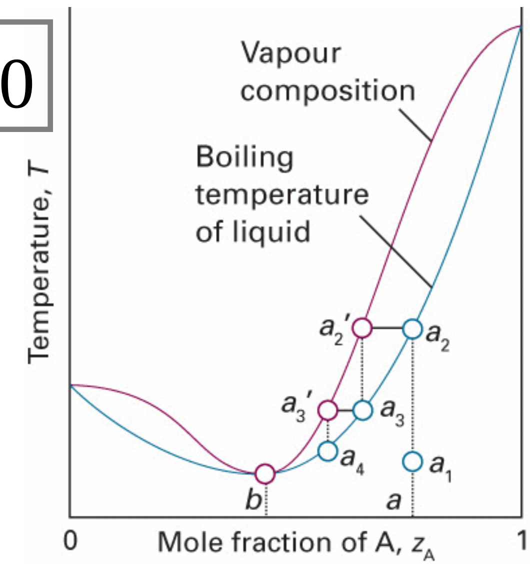
# C = 2 Temperature-composition diagrams

$G^E = 0$

ideal solution

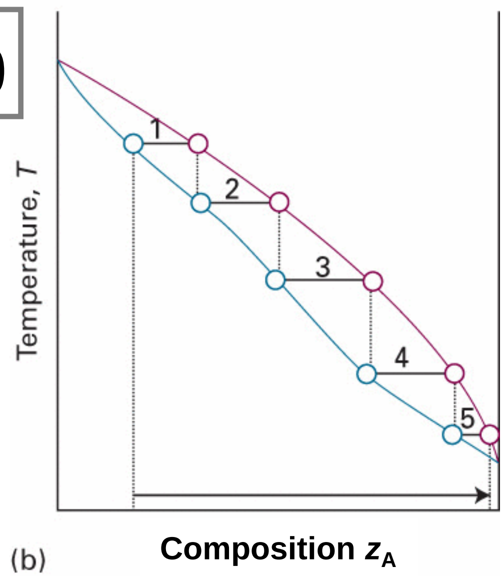



$G^E >> 0$

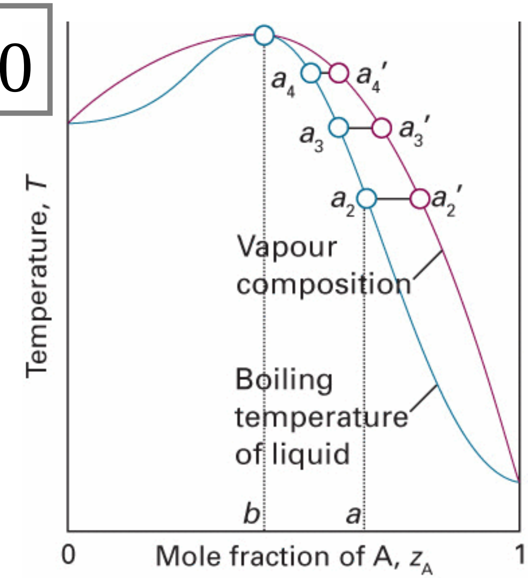



$G^E < 0$

non-ideal solutions



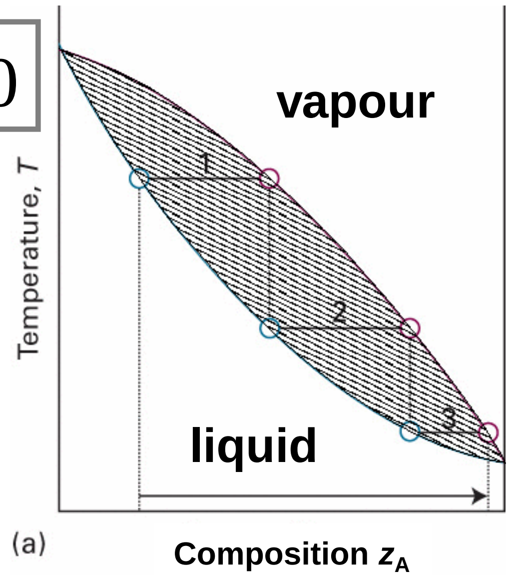

$G^E << 0$



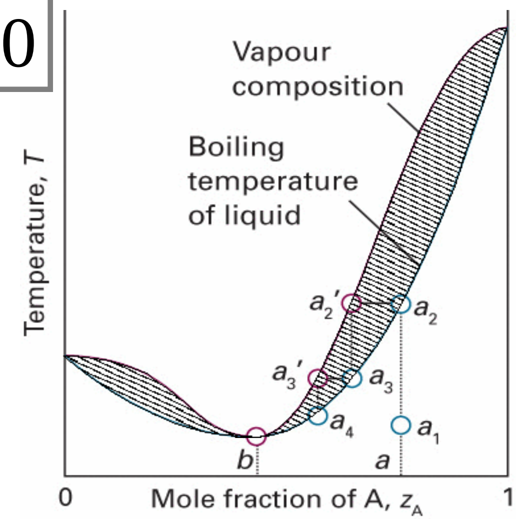
# C = 2 Temperature-composition diagrams

$G^{E} = 0$

ideal solution

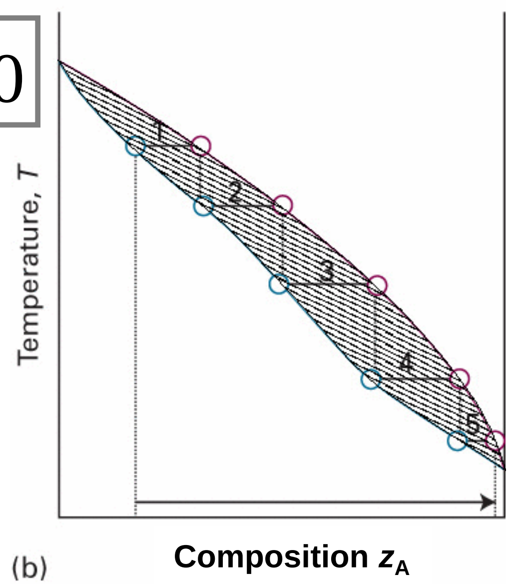



$G^{E} >> 0$

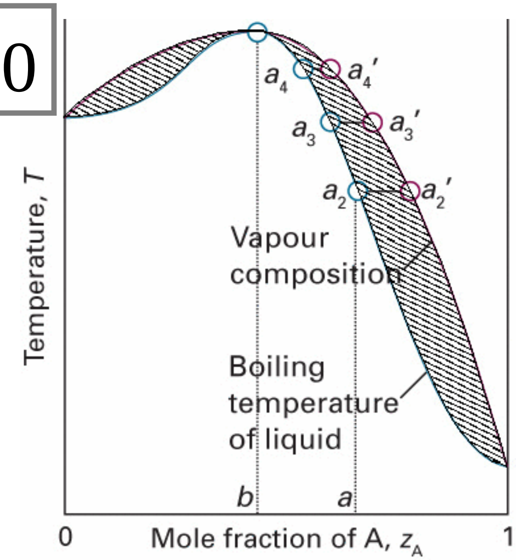



$G^{E} < 0$

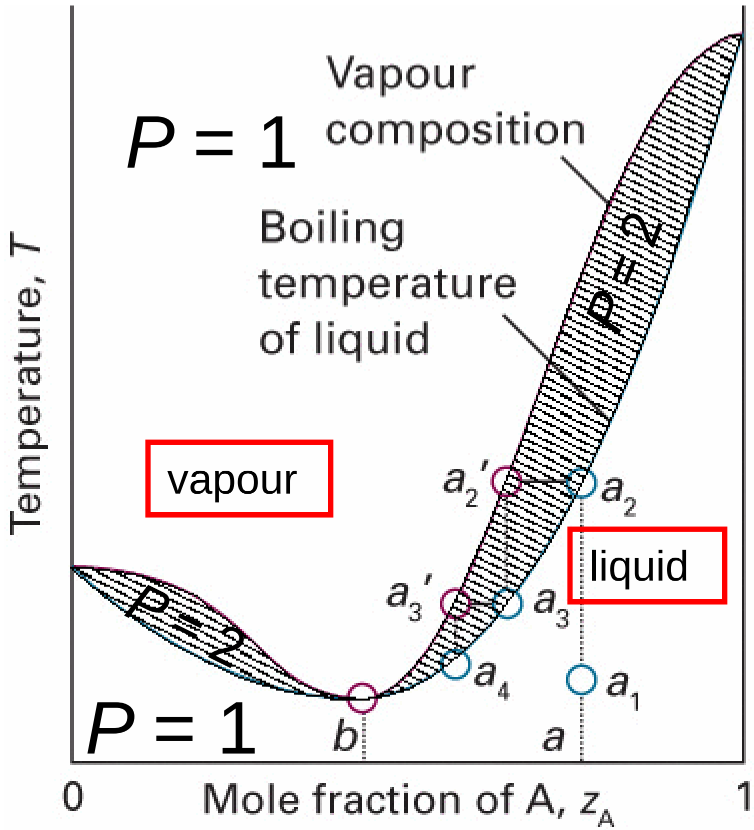
non-ideal solutions



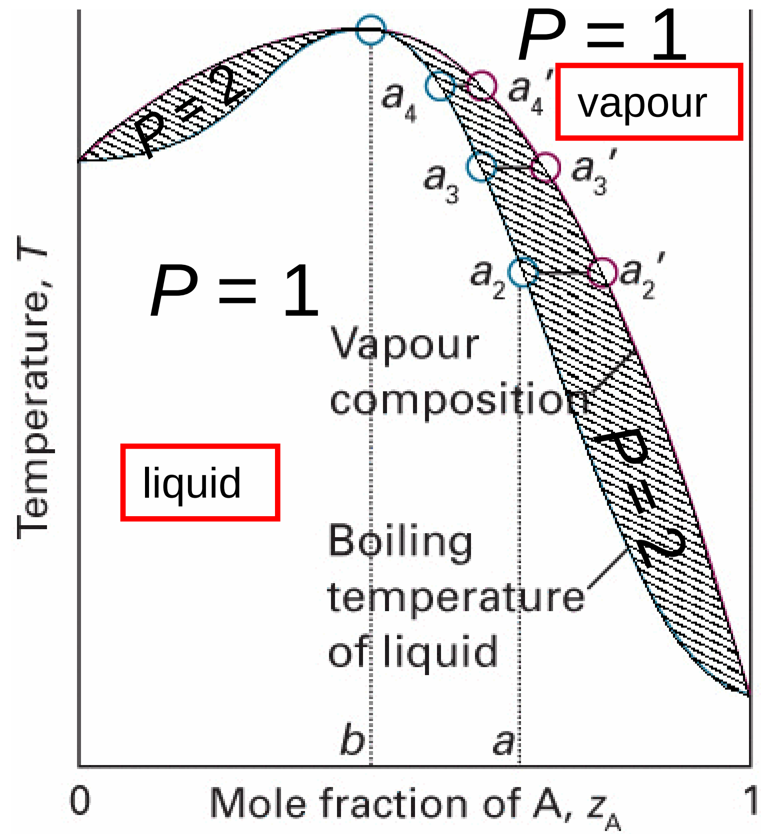

$G^{E} << 0$



# $C = 2$ Temperature-composition diagrams




Low boiling azeotrope



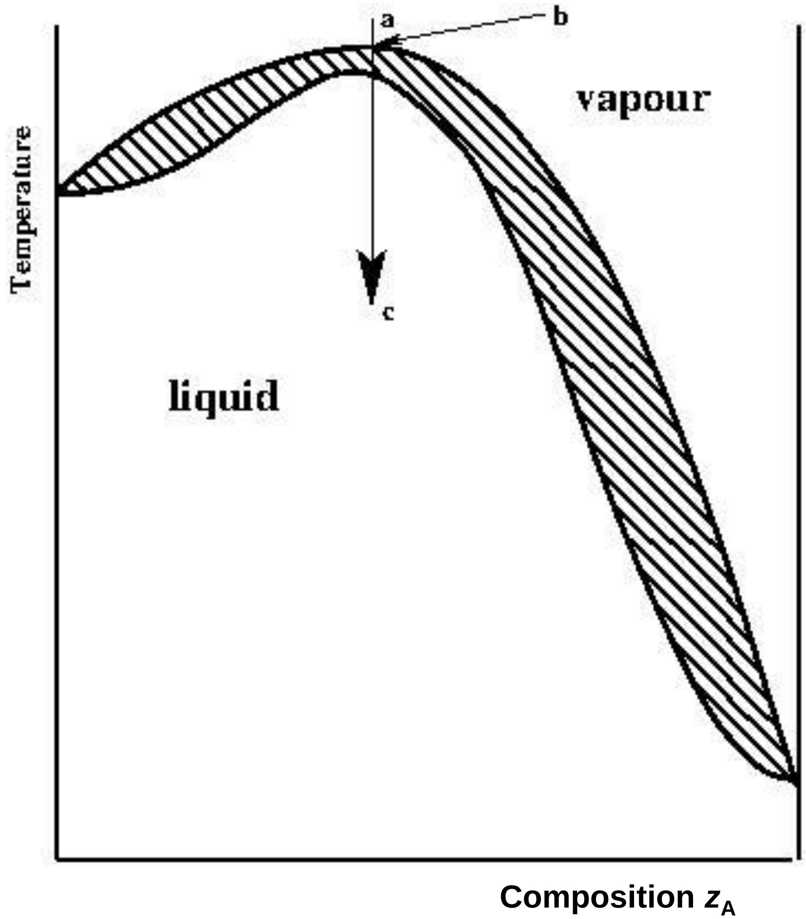

High boiling azeotrope

| | |
|---|---|
| $H_2O$/Eth: 4 wgt%$H_2O$ @ 78°C | $H_2O$/HCl: 80 wgt%$H_2O$ @ 108.6°C |

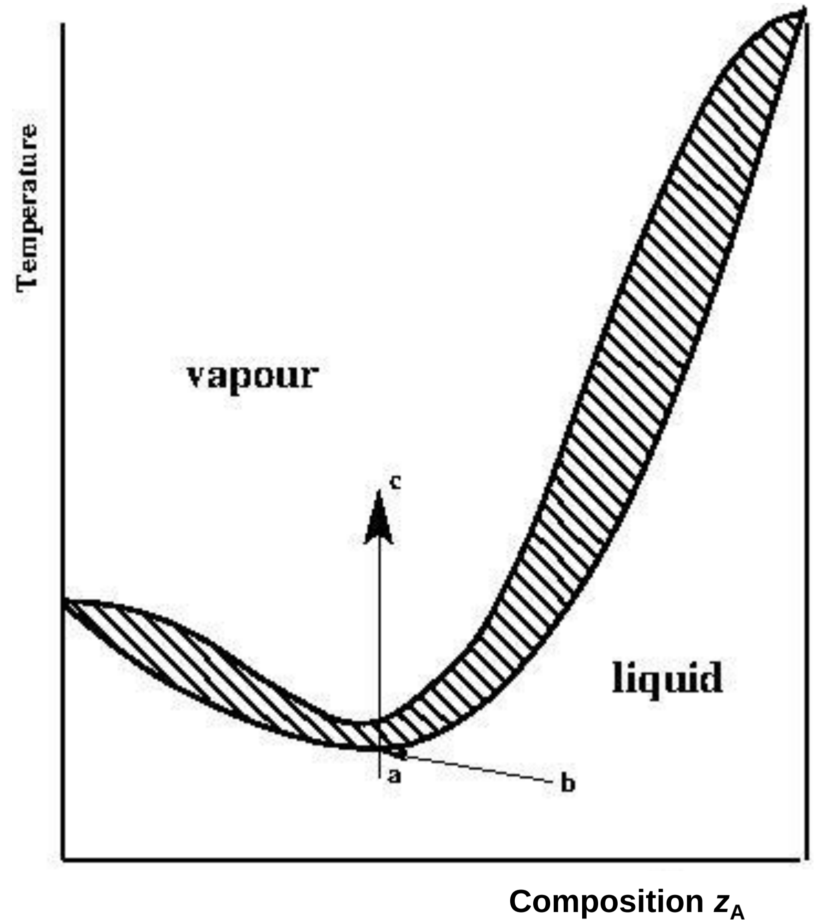
**Exercise 15**

# $C = 2$

# Impossible azeotropes

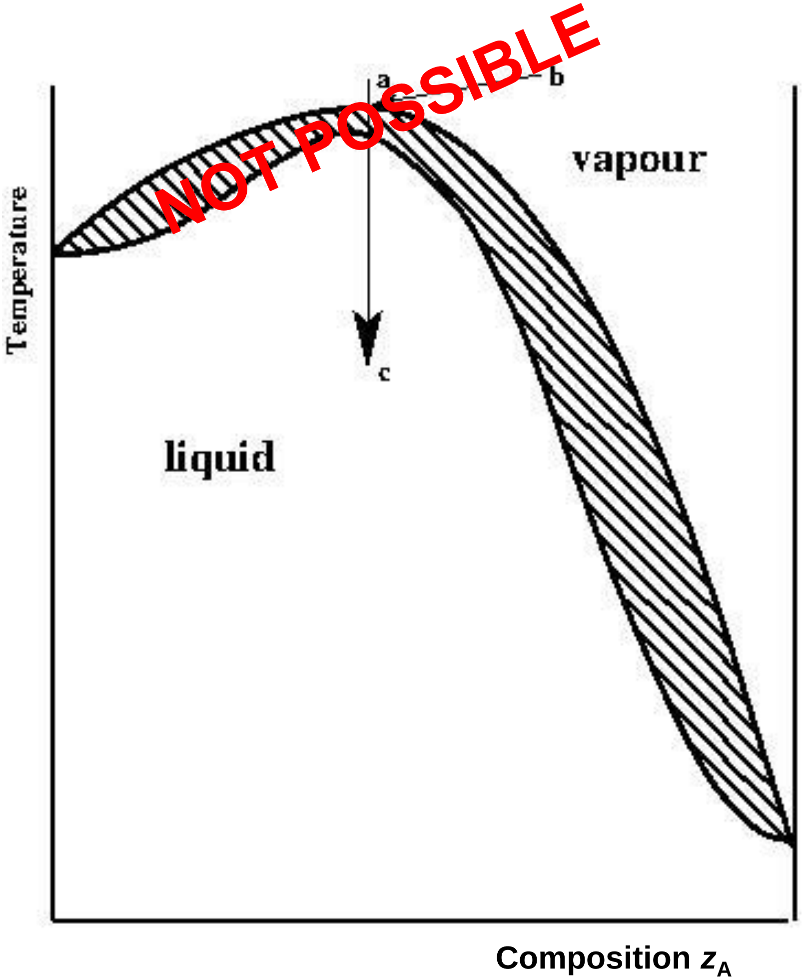



Would lead to g-g separation on cooling the vapour

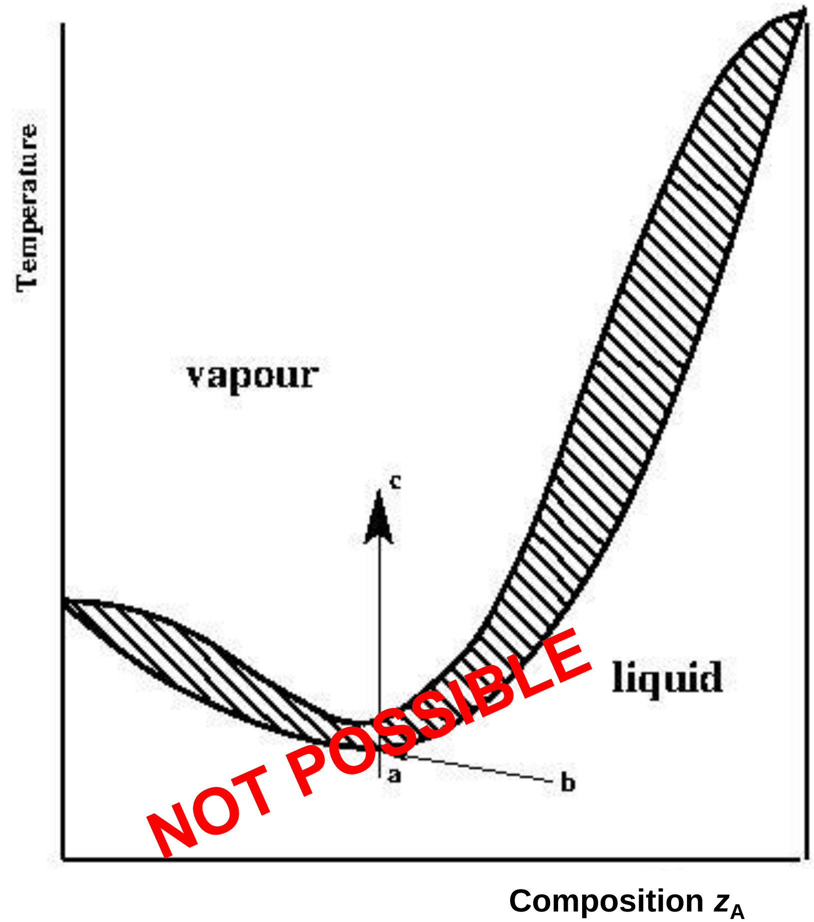



On heating the boiling liquid has no vapour line

# Impossible azeotropes




Would lead to g-g separation on cooling the vapour




On heating the boiling liquid has no vapour line

# Excess functions

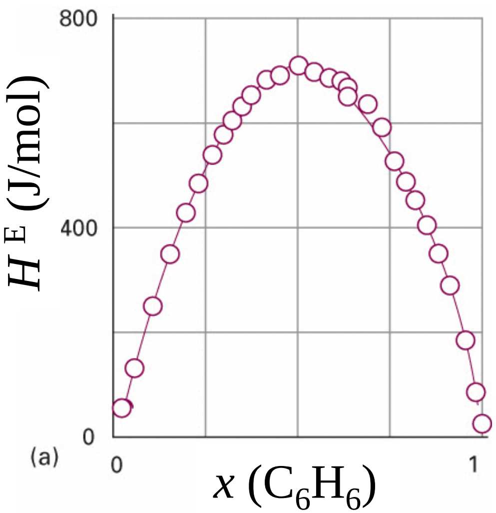
# Excess functions

## Non-ideal mixing

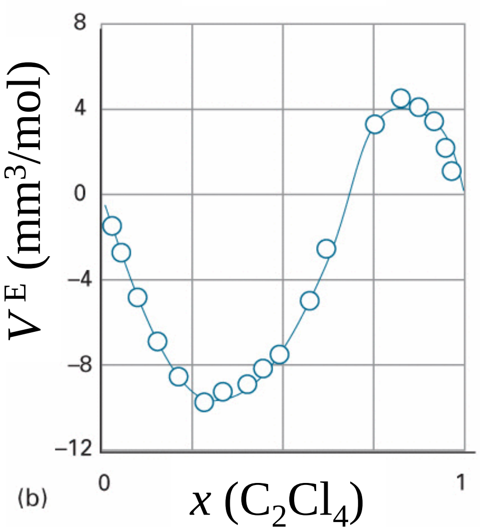
**(Excess functions)**

$$\begin{cases} S^{\mathrm{E}} \equiv \Delta_{\mathrm{mix}} S - \Delta_{\mathrm{mix}} S^{\mathrm{ideal}} \\ H^{\mathrm{E}} \equiv \Delta_{\mathrm{mix}} H - \Delta_{\mathrm{mix}} H^{\mathrm{ideal}} = \Delta_{\mathrm{mix}} H \end{cases}$$

Benzene/cyclohexane




$Cl_4$ethene/cyclopentene




$$\boxed{G^{\mathrm{E}} = H^{\mathrm{E}} - TS^{\mathrm{E}}}$$

| | | Ideal | Regular | Quasi regular |
|---|---|---|---|---|
| $S^{\mathrm{E}}$ | | =0 | =0 | ≠0 |
| $H^{\mathrm{E}}$ | | =0 | ≠0 | ≠0 |

$$\Delta_{\mathrm{mix}} H^{\mathrm{ideal}} = 0$$

$$\Delta_{\mathrm{mix}} S^{\mathrm{ideal}} = -nR\left[x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}\right]$$

# Excess functions

$$\boxed{\Delta_{\mathrm{mix}} H - T\Delta_{\mathrm{mix}} S = \Delta_{\mathrm{mix}} G}$$

Regular solution

$$\boxed{\Delta_{\mathrm{mix}} H} \quad -T \quad \boxed{\Delta_{\mathrm{mix}} S} \quad = \quad \boxed{\Delta_{\mathrm{mix}} G}$$

$(\Delta_{\mathrm{mix}} H^{\mathrm{ideal}} = 0)$

(Regular solution: $H^{E} \neq 0$)

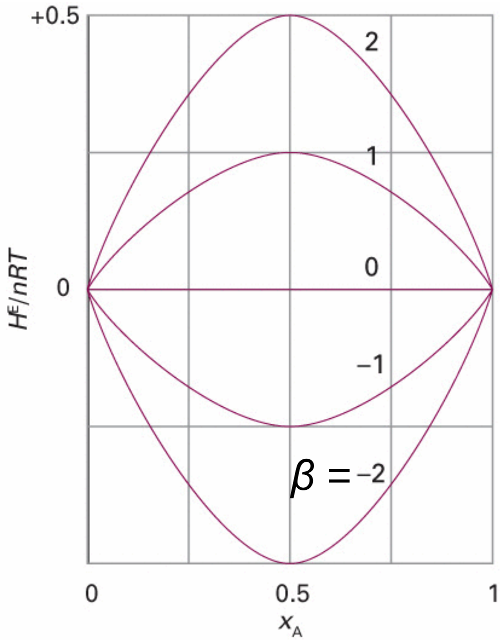
(Regular solution: $S^{E} = 0$)

$$\boxed{H^{\mathrm{E}} = \Delta_{\mathrm{mix}} H - \Delta_{\mathrm{mix}} H^{\mathrm{ideal}} = \Delta_{\mathrm{mix}} H}$$

# Excess functions

$$\boxed{\Delta_{\mathrm{mix}} H - T\Delta_{\mathrm{mix}} S = \Delta_{\mathrm{mix}} G}$$

Regular solution




$$-T \boxed{\Delta_{\mathrm{mix}} S} = \boxed{\Delta_{\mathrm{mix}} G}$$

$$\boxed{H^{\mathrm{E}} = n\beta RTx_{\mathrm{A}}x_{\mathrm{B}}}$$

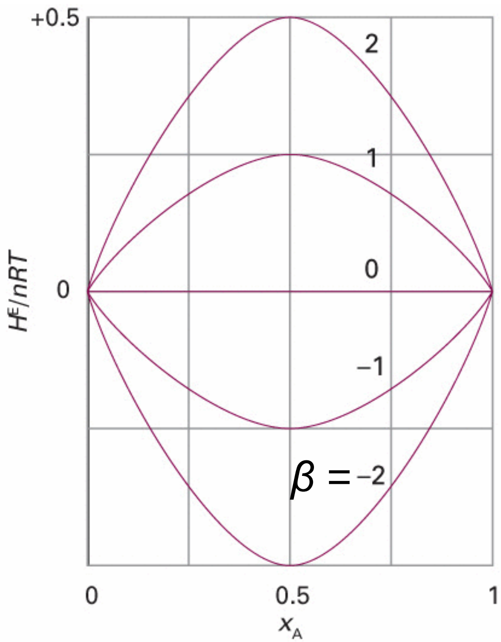
(Regular solution: $H^{\mathrm{E}} \neq 0$)

$$\boxed{H^{\mathrm{E}} = \Delta_{\mathrm{mix}} H}$$

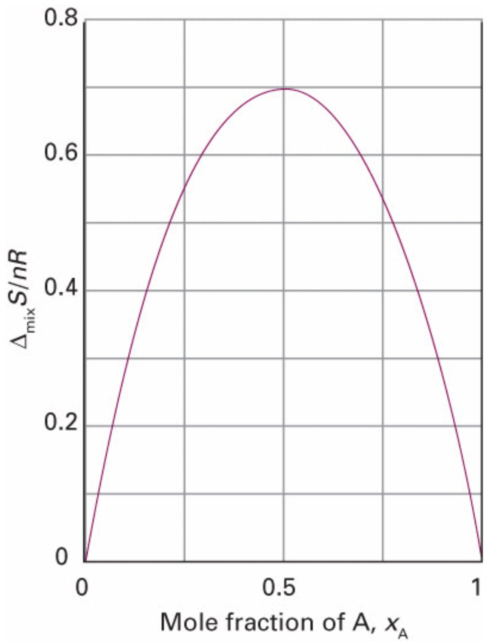
# Excess functions

$$\boxed{\Delta_{\mathrm{mix}} H - T\Delta_{\mathrm{mix}} S = \Delta_{\mathrm{mix}} G}$$

Regular solution




$-T$




$=$ $\boxed{\Delta_{\mathrm{mix}} G}$

$$\boxed{H^{\mathrm{E}} = n\beta RT x_{\mathrm{A}} x_{\mathrm{B}}}$$

$$\boxed{\Delta_{\mathrm{mix}} S^{\mathrm{ideal}} = -nR\left[x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}\right]}$$

(Regular solution: $H^{\mathrm{E}} \neq 0$)

(Regular solution: $S^{\mathrm{E}} = 0$)

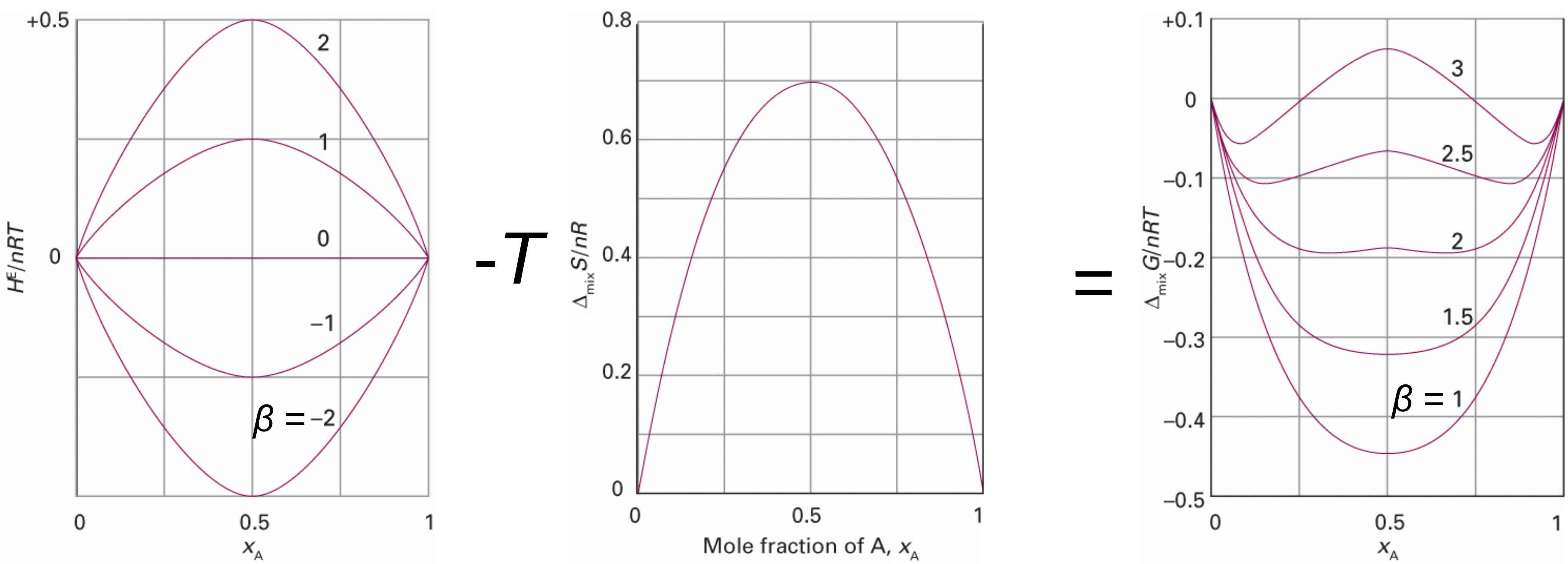
$$\boxed{H^{\mathrm{E}} = \Delta_{\mathrm{mix}} H}$$

$$\boxed{S^{\mathrm{E}} = \Delta_{\mathrm{mix}} S - \Delta_{\mathrm{mix}} S^{\mathrm{ideal}}}$$

# Excess functions

$$\Delta_{mix} H - T\Delta_{mix} S = \Delta_{mix} G$$

Regular solution

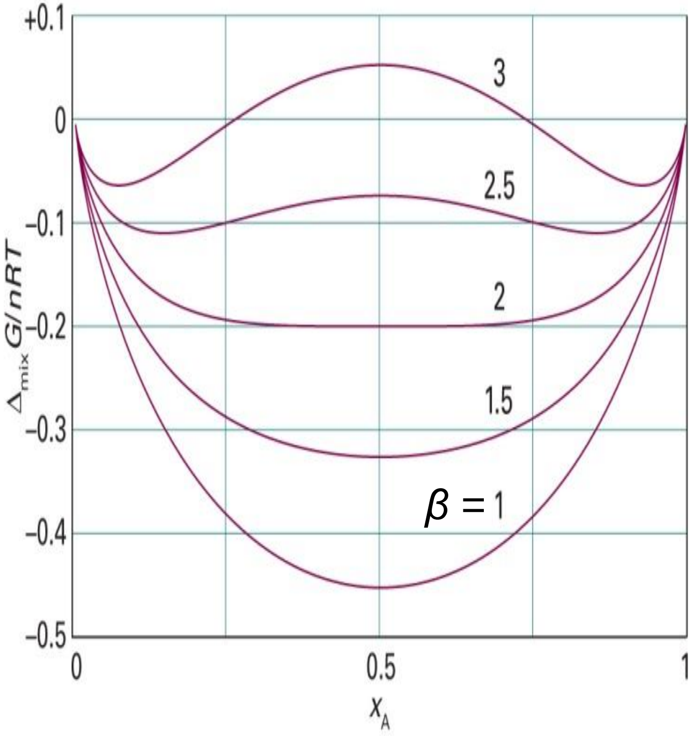



$$H^E = n\beta RTx_A x_B$$

$$\Delta_{mix} S^{ideal} = -nR[x_A \ln x_A + x_B \ln x_B]$$

(Regular solution: $H^E \neq 0$) (Regular solution: $S^E = 0$)

# Liquid-liquid separation for Regular solution

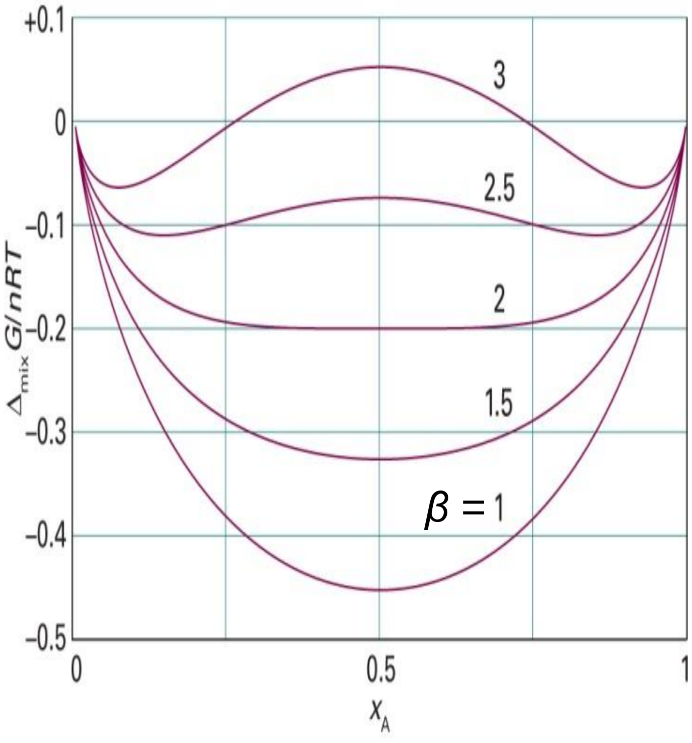


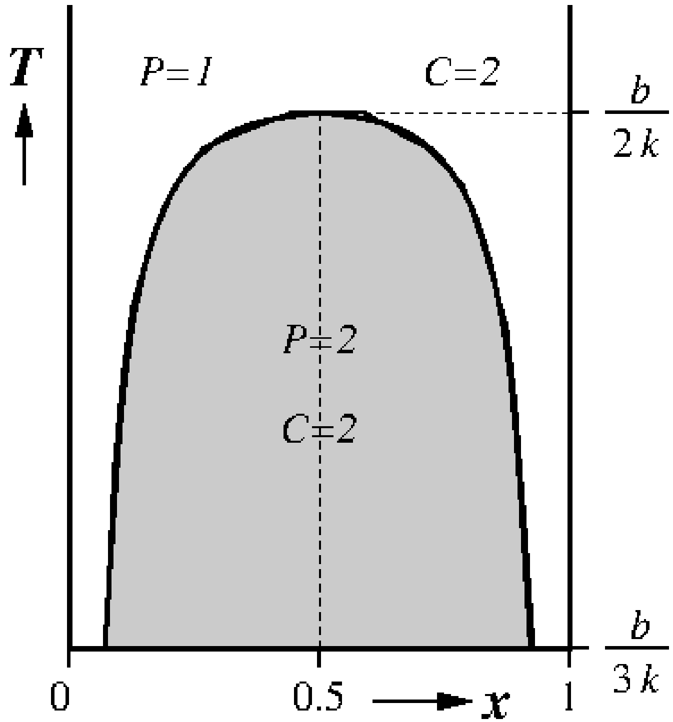

$$\boxed{H^E = n\beta RT x_A x_B}$$

Model regular solution

**often:** $\boxed{\beta = \dfrac{b}{kT}}$ **so** $\boxed{T = \dfrac{b}{\beta k}}$

# Liquid-liquid separation for Regular solution



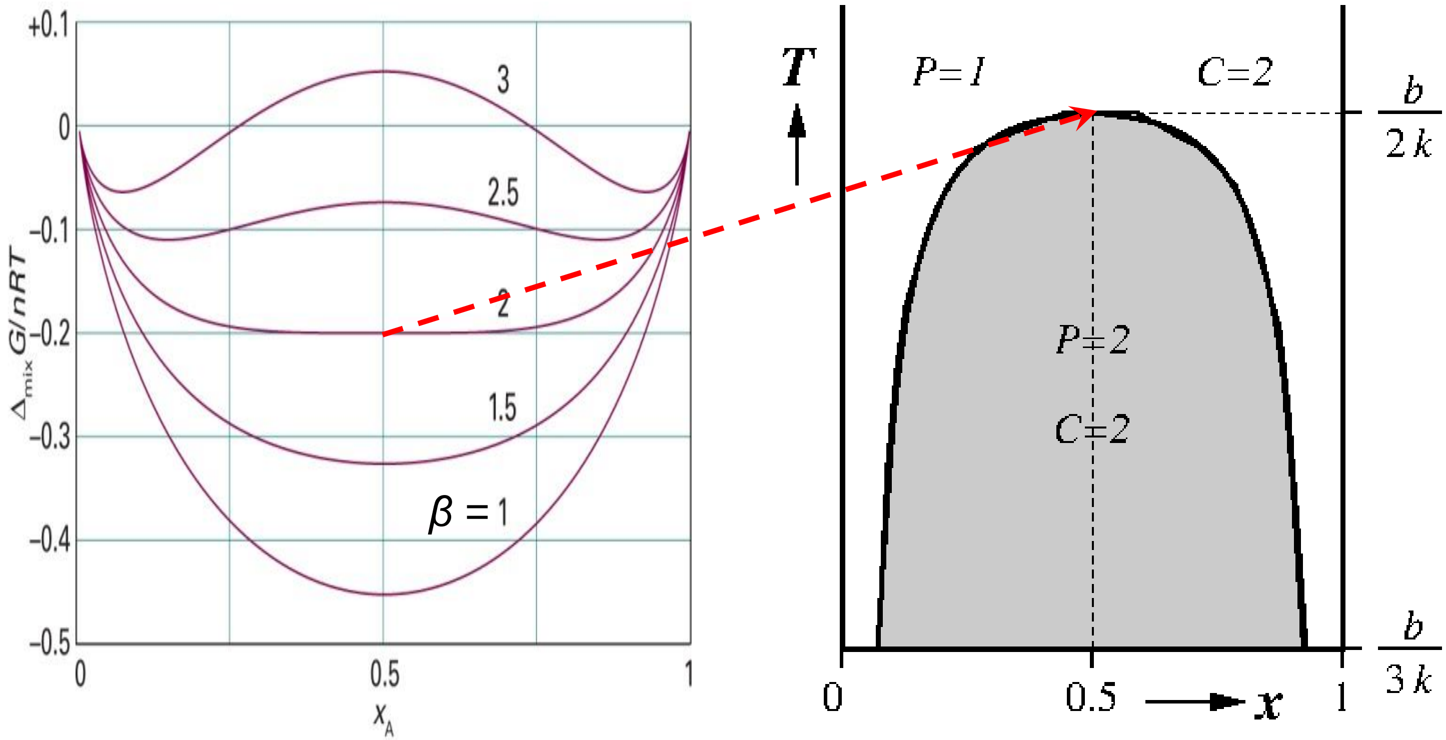




$$\boxed{H^{E} = n\beta RT x_{A} x_{B}}$$

<u>Model regular solution</u>

**often:** $\boxed{\beta = \dfrac{b}{kT}}$ **so** $\boxed{T = \dfrac{b}{\beta k}}$

# Liquid-liquid separation for Regular solution

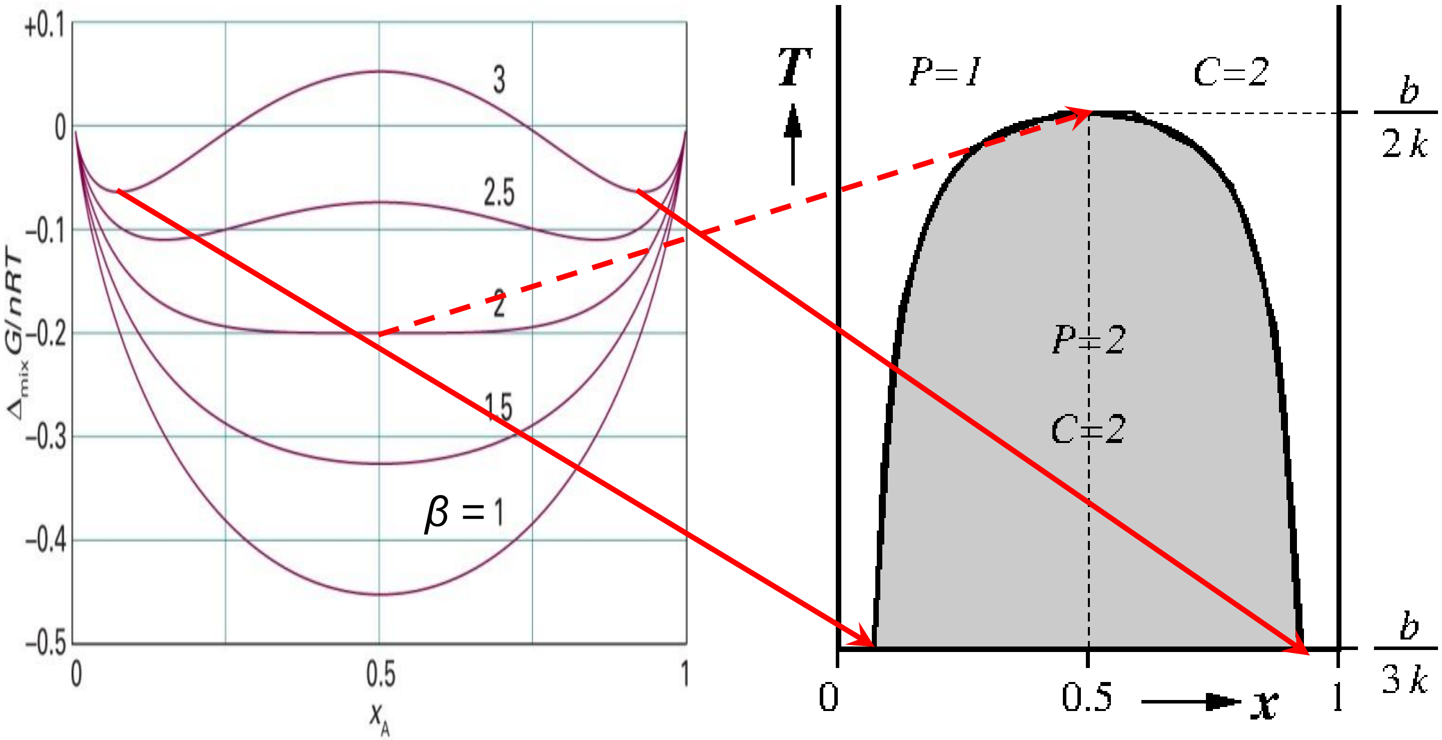



$$\boxed{H^{E} = n\beta RTx_{A}x_{B}}$$

Model regular solution

**often:** $\boxed{\beta = \frac{b}{kT}}$ **so** $\boxed{T = \frac{b}{\beta k}}$

# Liquid-liquid separation for Regular solution

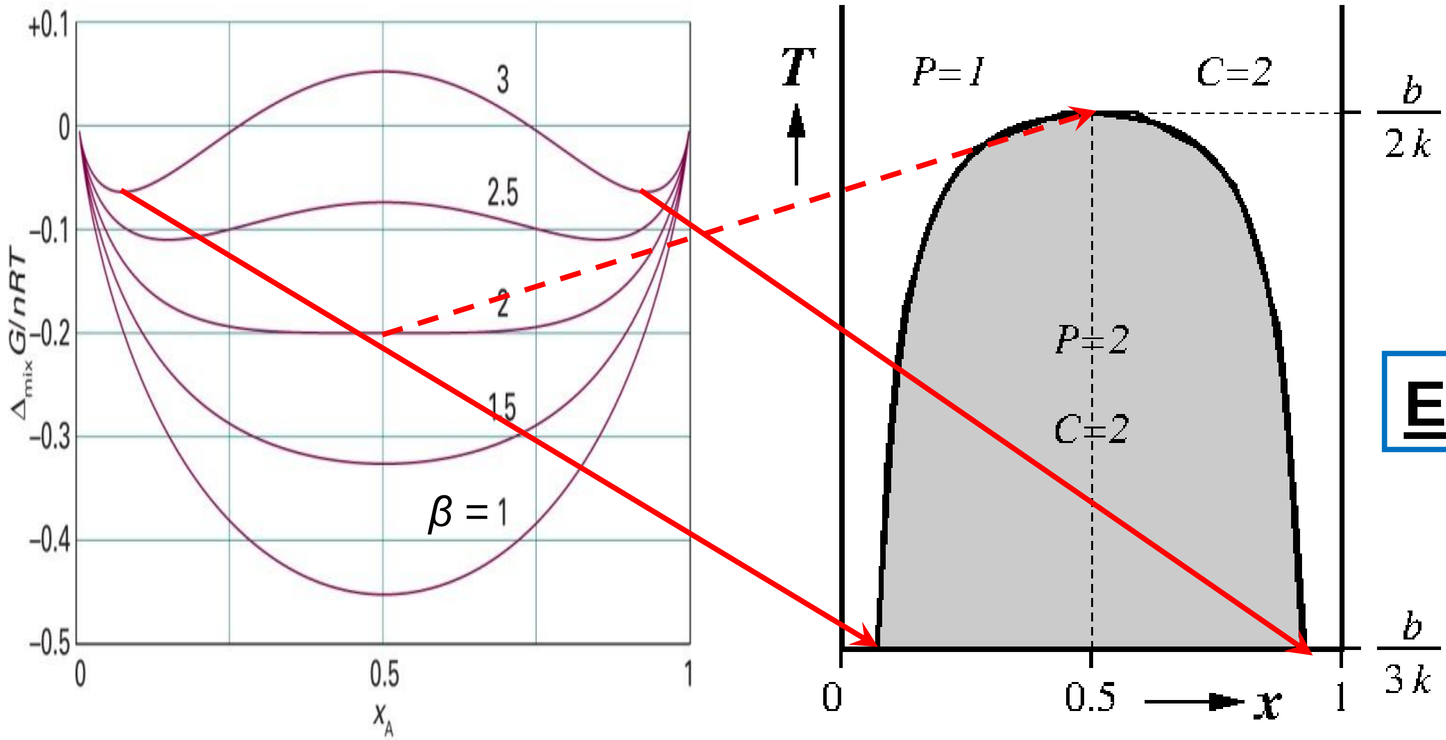



$$\boxed{H^{E} = n\beta RTx_{A}x_{B}}$$

Model regular solution

**often:** $\boxed{\beta = \frac{b}{kT}}$ **so** $\boxed{T = \frac{b}{\beta k}}$

# Liquid-liquid separation for Regular solution




**Exercise 17**

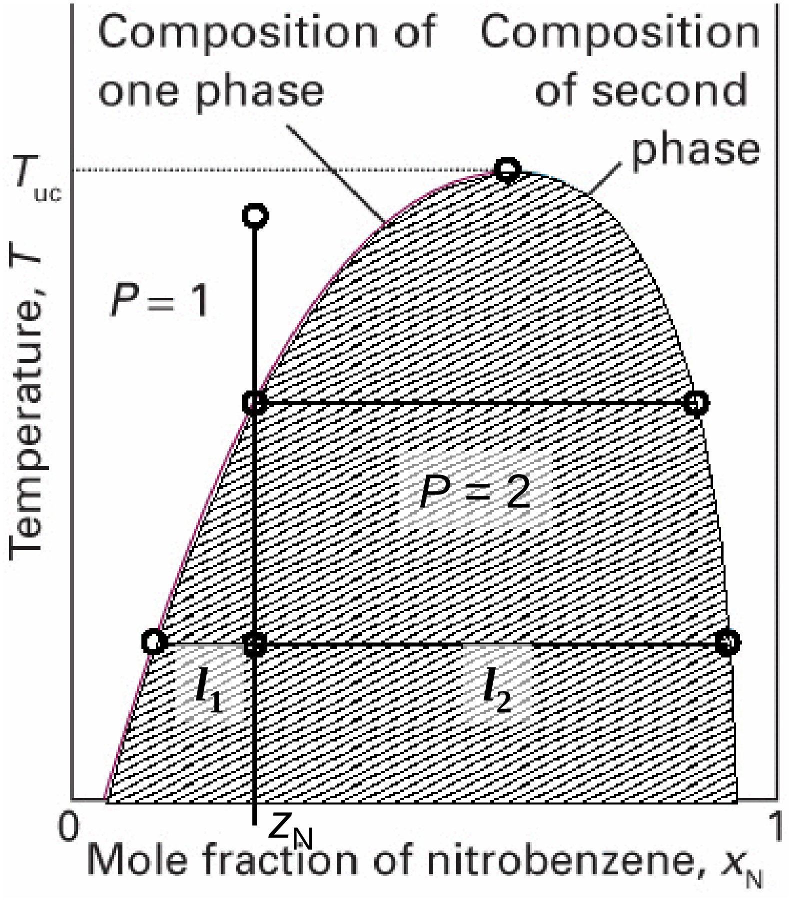
**Liquid-liquid separation**

$$\boxed{H^{\mathrm{E}} = n\beta RTx_{\mathrm{A}}x_{\mathrm{B}}}$$

Model regular solution

**often:** $\boxed{\beta = \dfrac{b}{kT}}$ **so** $\boxed{T = \dfrac{b}{\beta k}}$

# Liquid-liquid separation for quasi regular solution

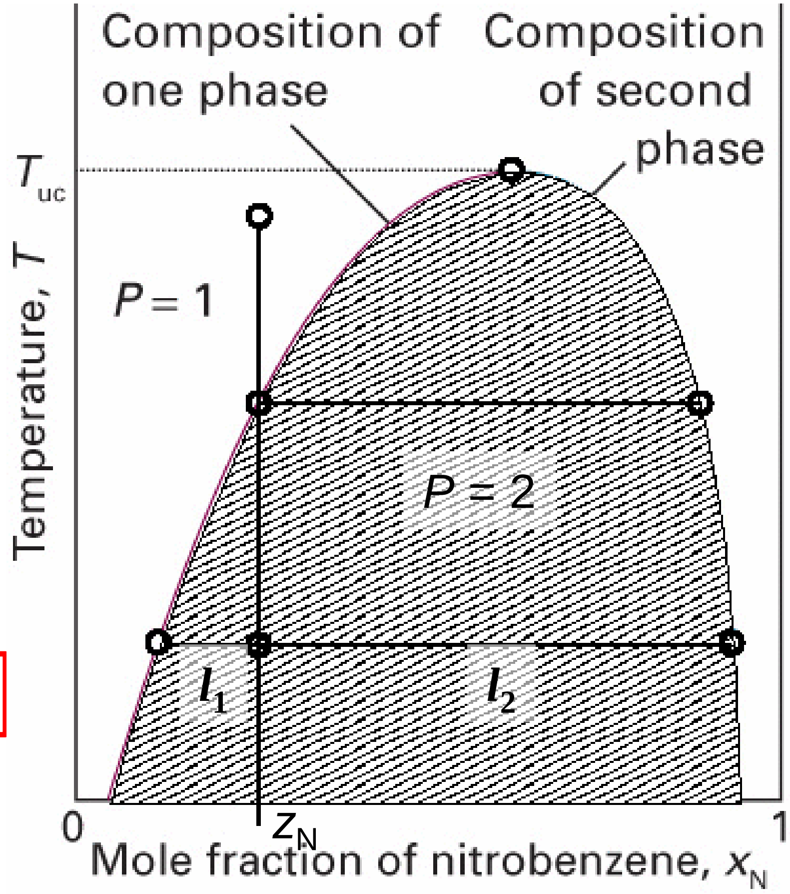



Nitrobenzene in hexane

$$\boxed{H^{E} \neq 0}$$

$$\boxed{S^{E} \neq 0}$$

# Liquid-liquid separation for quasi regular solution




Nitrobenzene in hexane

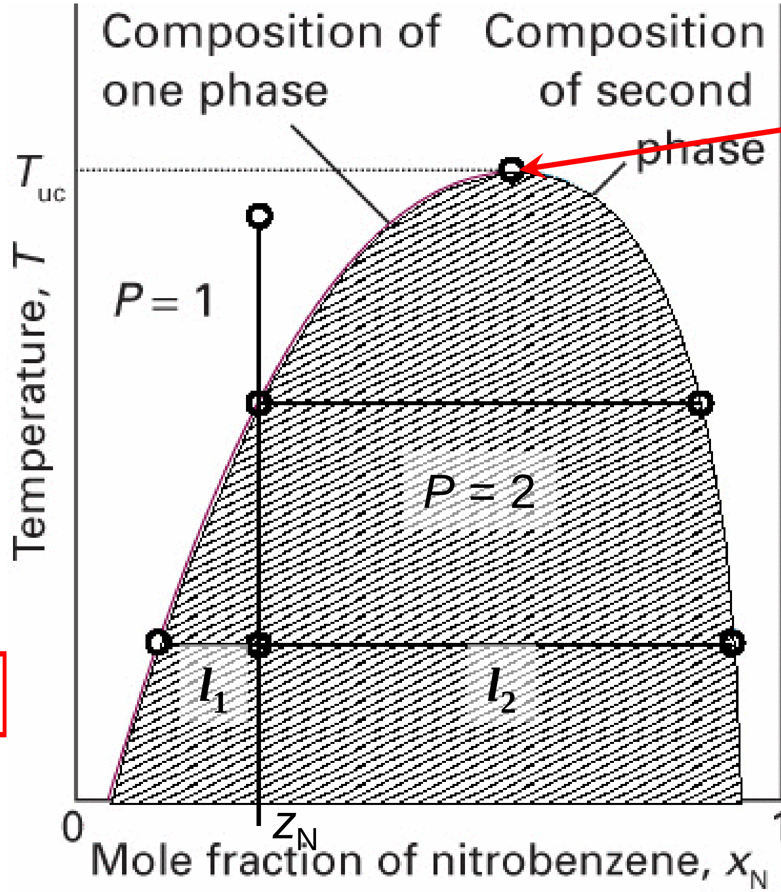
$$H^E \neq 0$$

$$S^E \neq 0$$

$$n_1 l_1 = n_2 l_2$$

**Lever rule**

# Liquid-liquid separation for quasi regular solution




**Upper Critical temperature**

$$H^E \neq 0$$

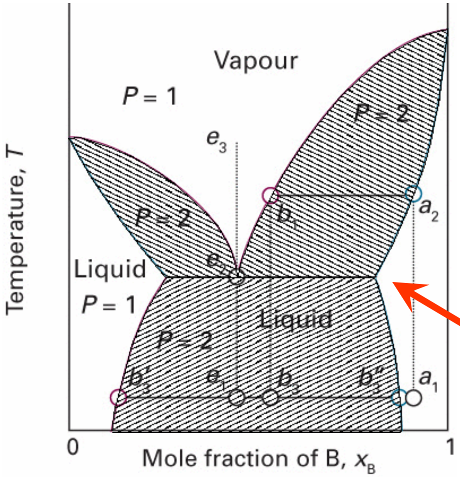
$$S^E \neq 0$$

$$n_1 l_1 = n_2 l_2$$

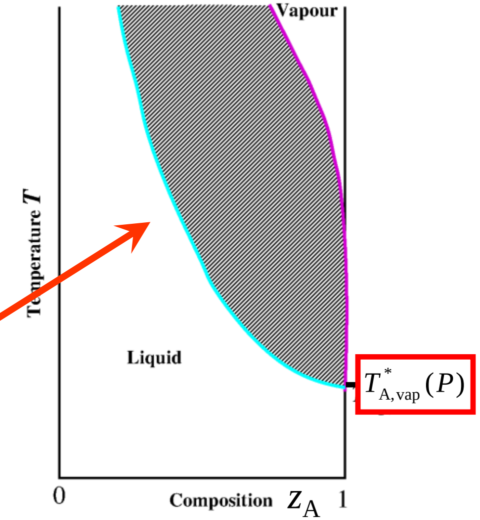
**Lever rule**

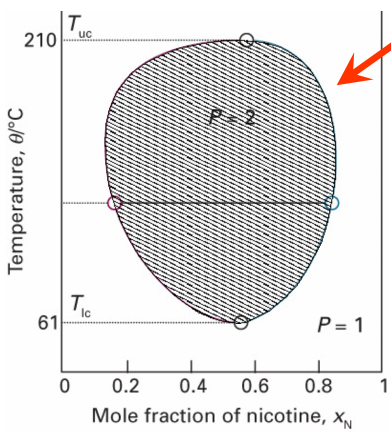
Nitrobenzene in hexane

# Sneak preview of Lecture 5




- colligative properties
- liquid-gas phase diagrams
- liquid-liquid phase diagrams
- solid-liquid phase diagrams
- ternary phase diagrams




$H_2O$ / nicotine

*P,T*