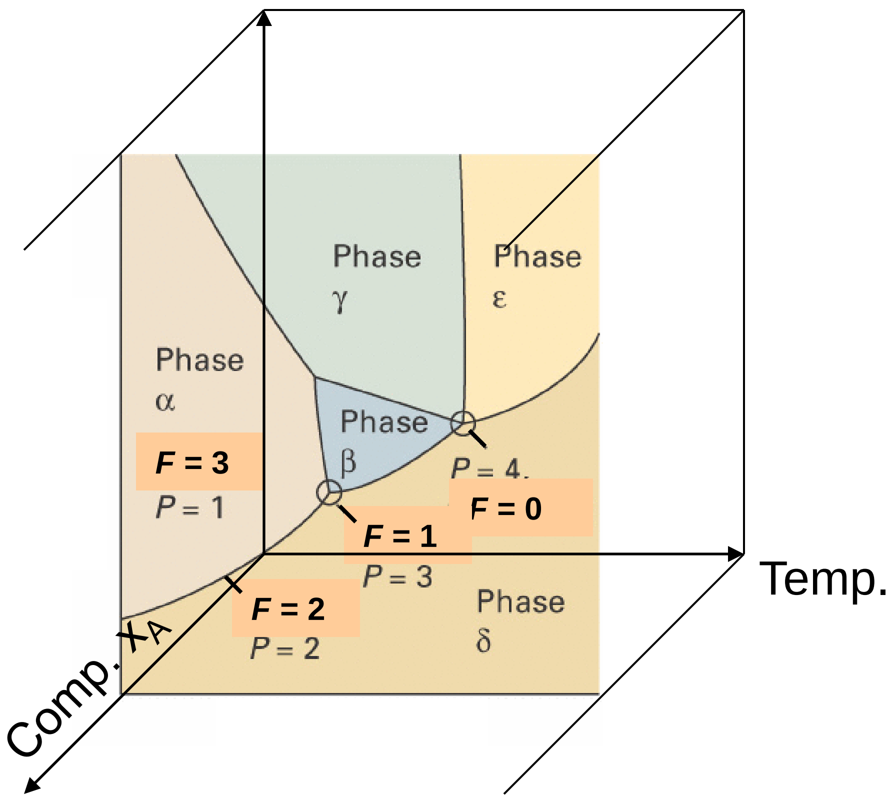
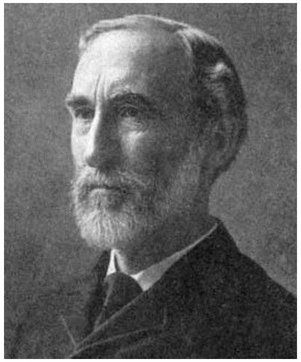
Phase diagrams of binary systems

C = 2





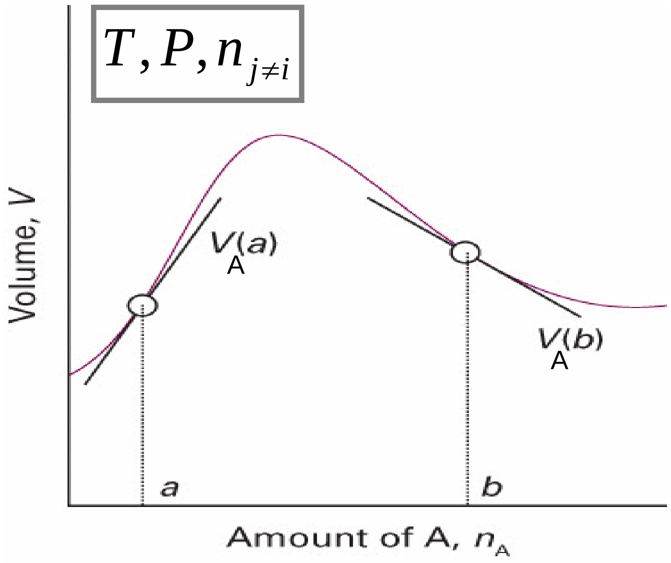
Gibbs phase rule

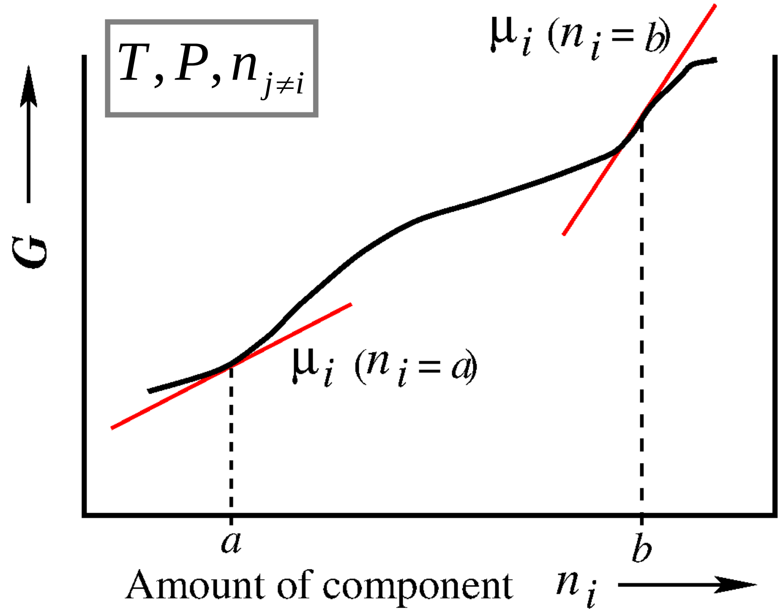
$$F = C - P + 2$$

Partial molar quantities

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

$$\mu_j \equiv G_j = \left(\frac{\partial G}{\partial n_j}\right)_{P,T,n_{i\neq j}}$$



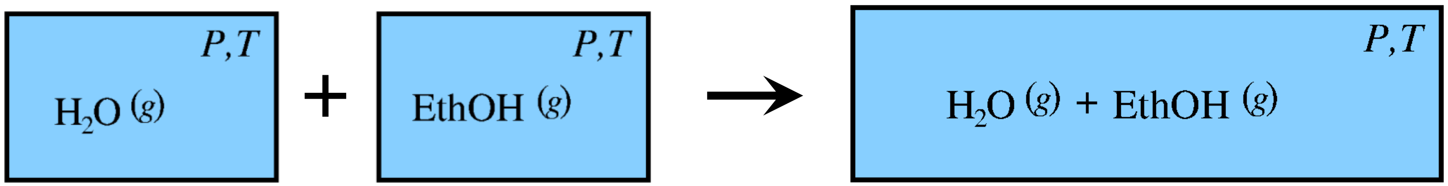


$$V = n_A V_A + n_B V_B = n[x_A V_A + x_B V_B]$$

$$G = n_A G_A + n_B G_B = n[x_A \mu_A + x_B \mu_B]$$

Mixing processes of perfect gases: binary mixture

Perfect gas mixing @ *P*,*T*



$$\Delta_{\text{mix}} G^{\text{ideal}} = nRT\left(x_{\text{A}} \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}}\right)$$

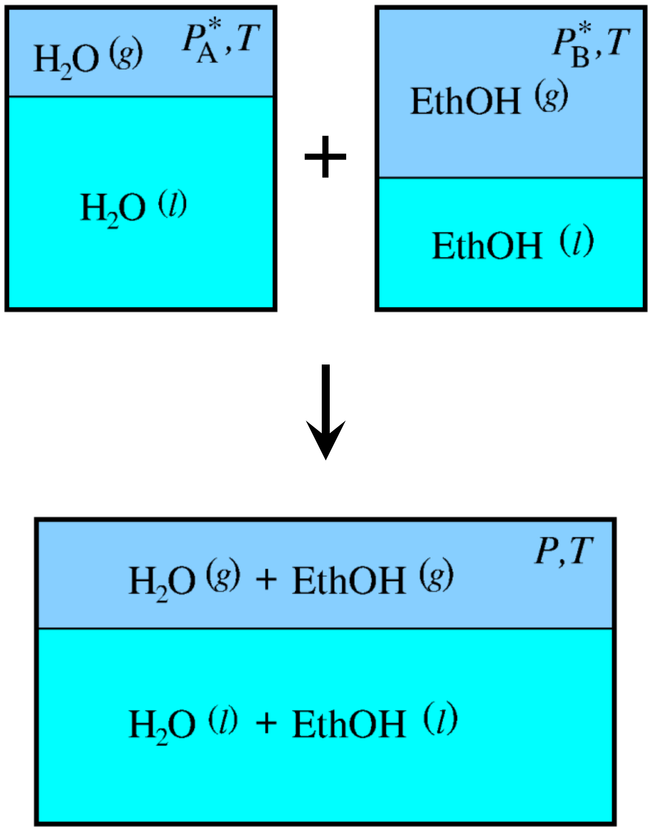
$$\begin{cases} \Delta_{\text{mix}} S^{\text{ideal}} = -nR\left(x_{\text{A}} \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}}\right) \\ \Delta_{\text{mix}} H^{\text{ideal}} = 0 \end{cases}$$

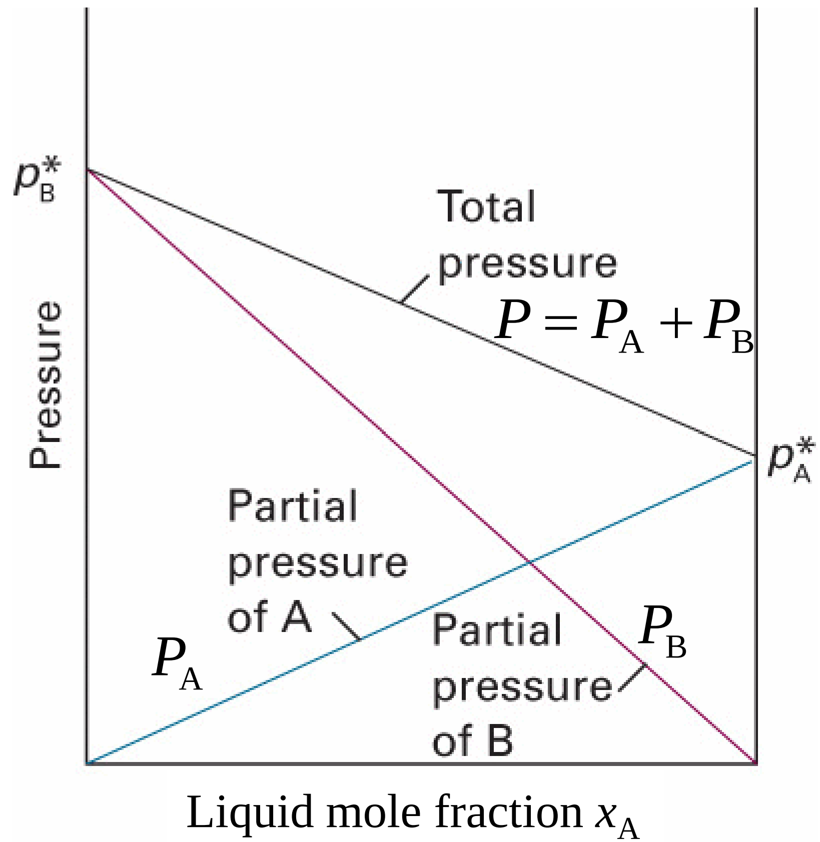
Mole fraction $$x_i = \frac{n_i}{n} \equiv \frac{P_i}{P}$$

Mixing processes of l,g equilibrium: binary mixture

Ideal solution @ T

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





Ideal solution (Raoult)

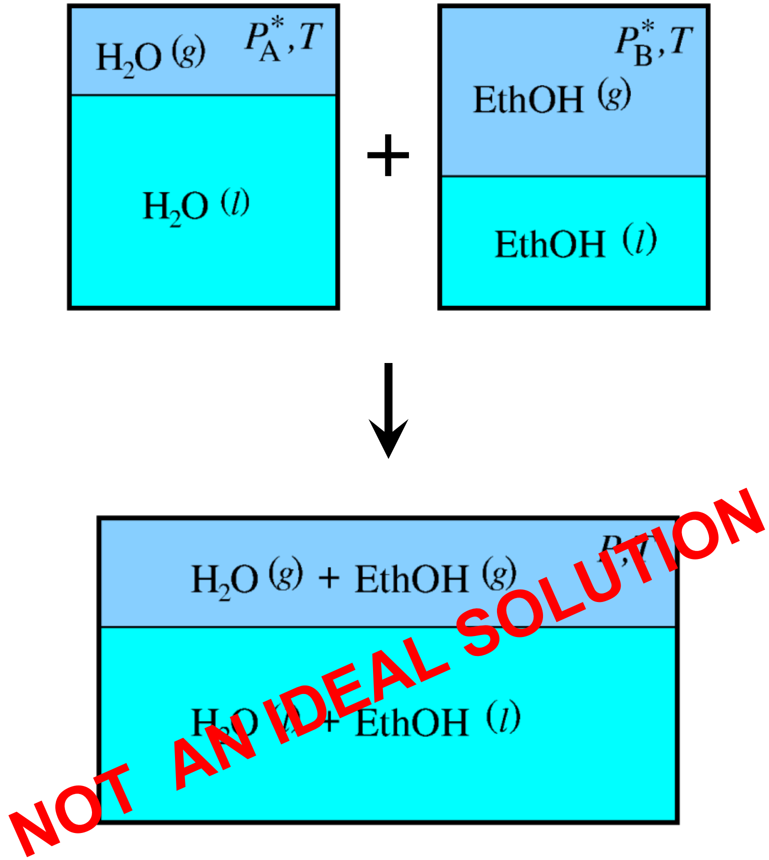
$$P_A = x_A P_A^*$$

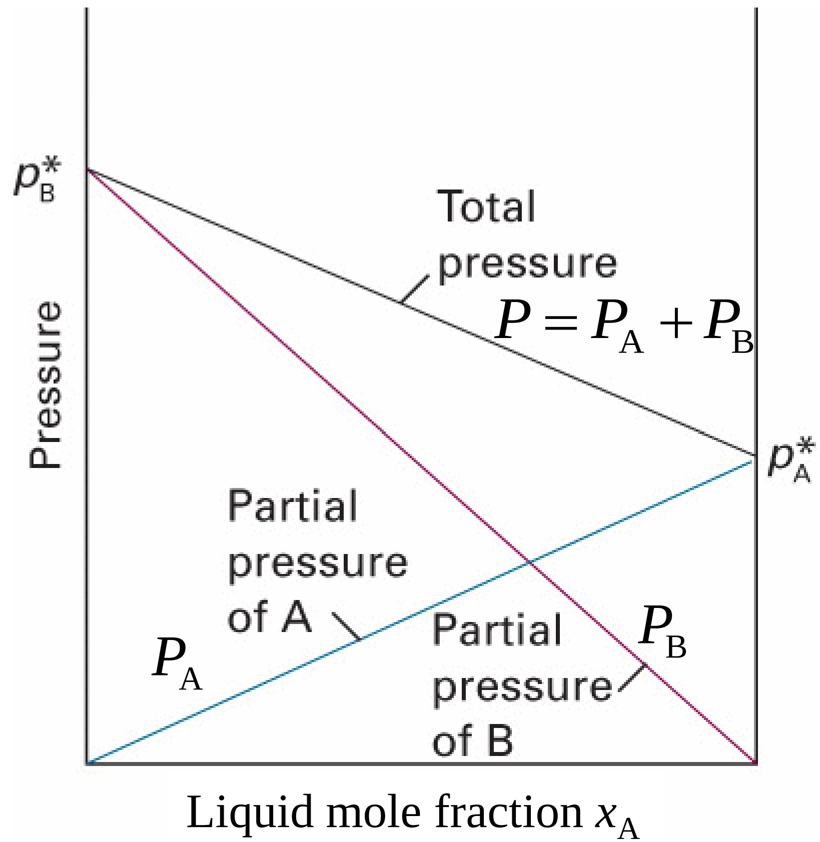
$$P_B = x_B P_B^*$$

Mixing processes of l,g equilibrium: binary mixture

Ideal solution @ T

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





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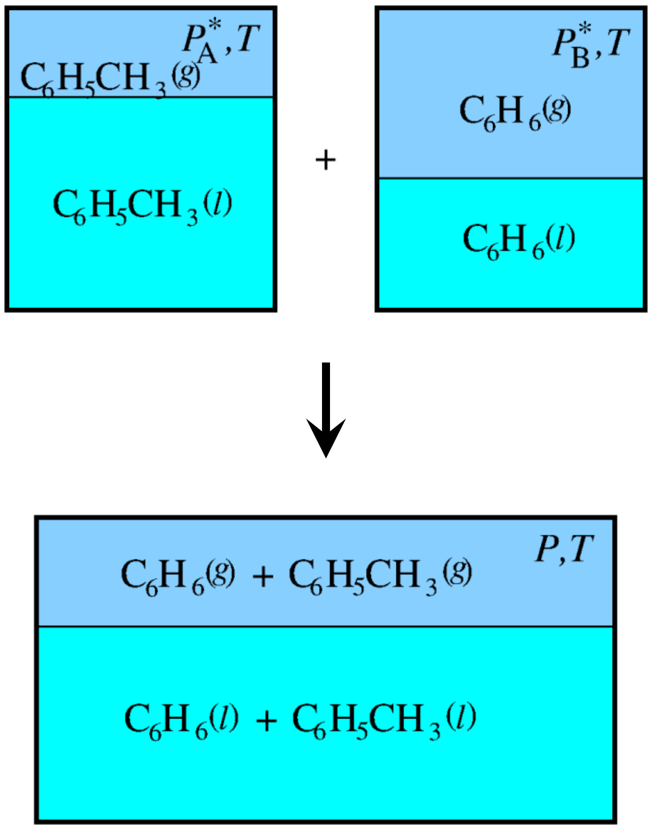
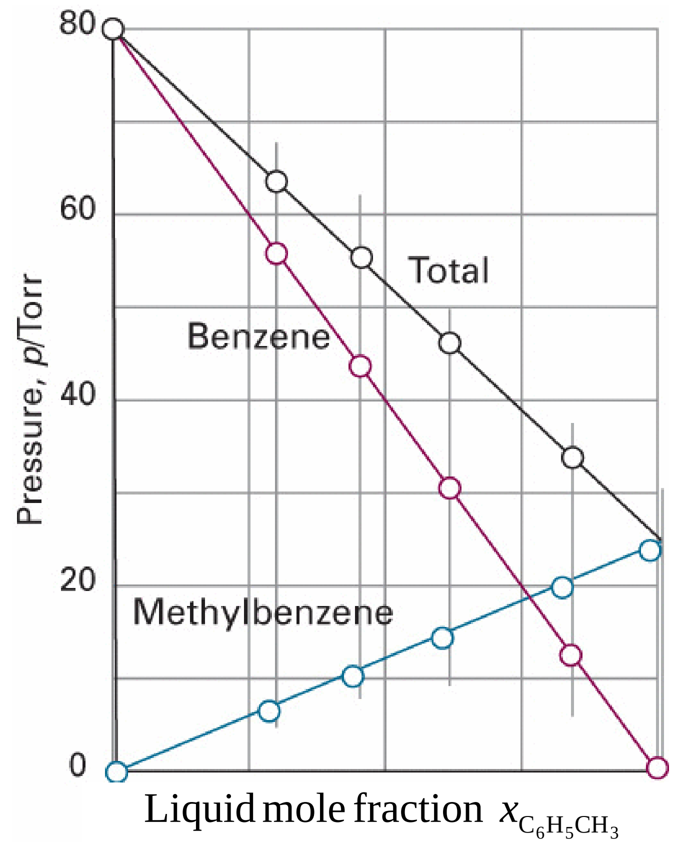
Mixing processes of l,g equilibrium: binary mixture

Ideal solution @ T

$$\Delta_{\text{mix}} G^{\text{ideal}} = nRT\left(x_\text{A} \ln x_\text{A} + x_\text{B} \ln x_\text{B}\right)$$





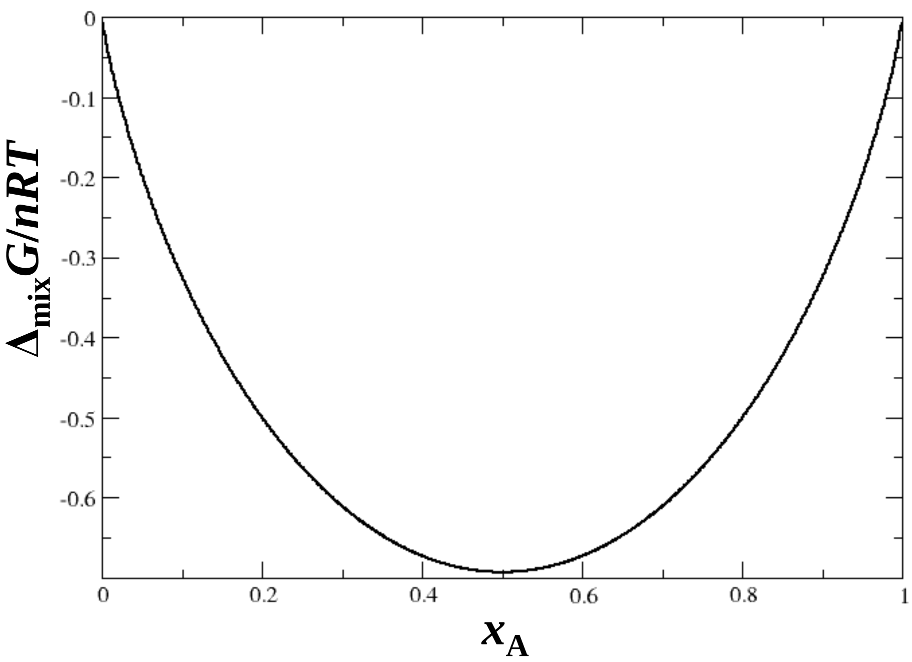
Ideal solution (Raoult) $P_\text{A} = x_\text{A} P_\text{A}^*$ $P_\text{B} = x_\text{B} P_\text{B}^*$

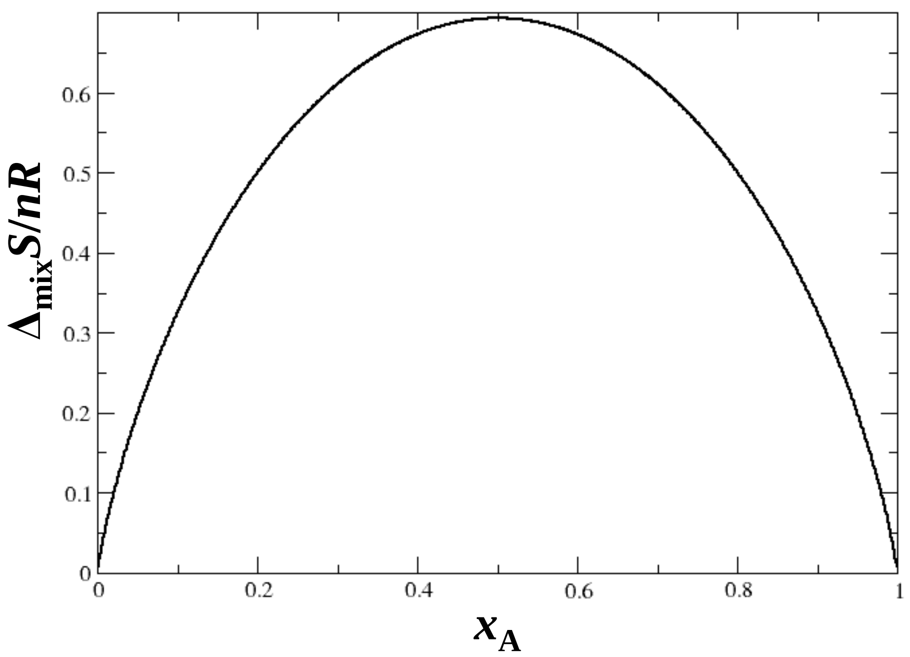
Thermodynamics of ideal mixing

(perfect gas mixtures and ideal solutions)

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

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

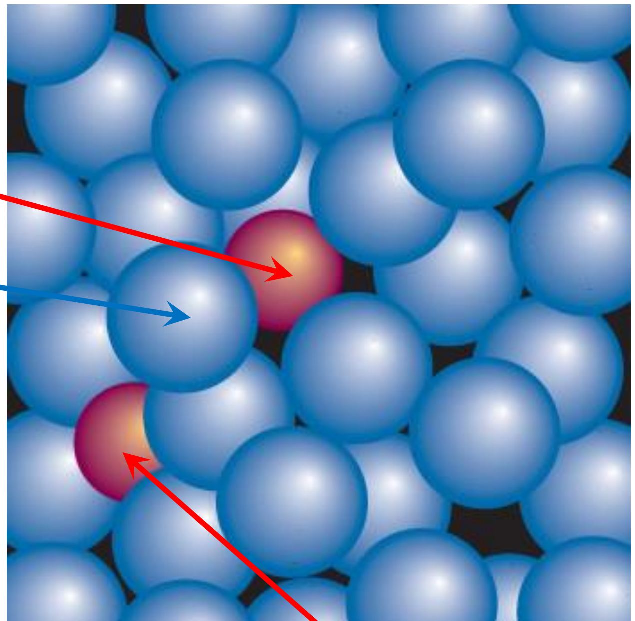




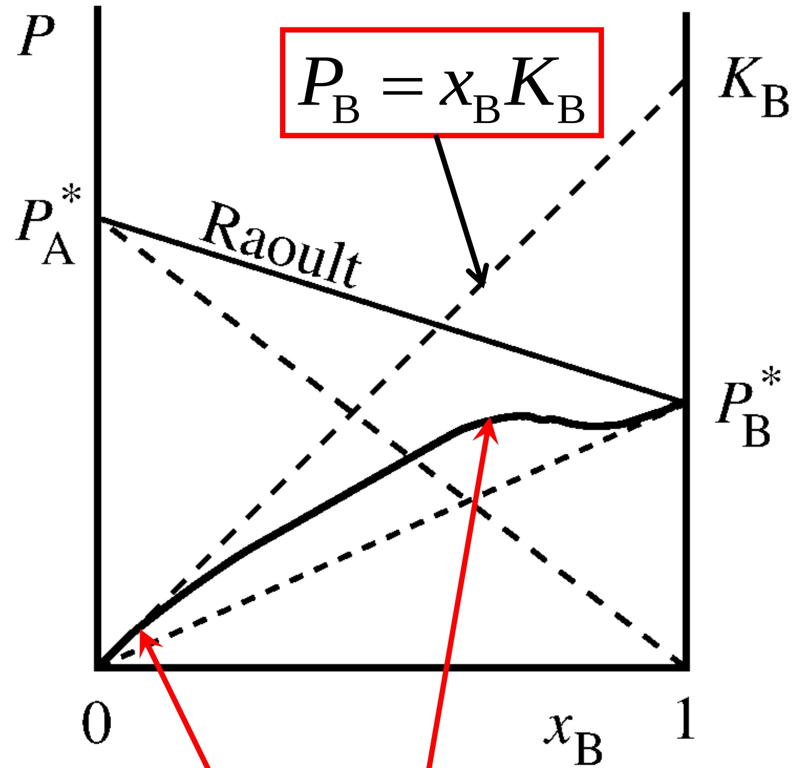
$$\Delta_{\text{mix}} H^{\text{ideal}} = 0$$

Thermodynamics of non-ideal mixing liquids

almost pure solvent A



Ideal-dilute solution



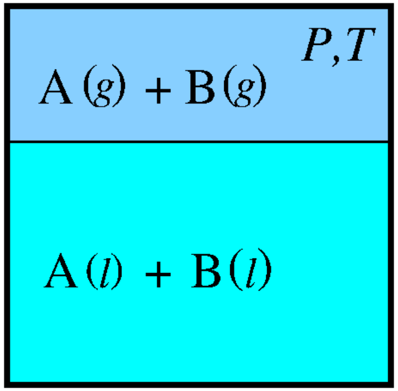
very low concentration of solute B

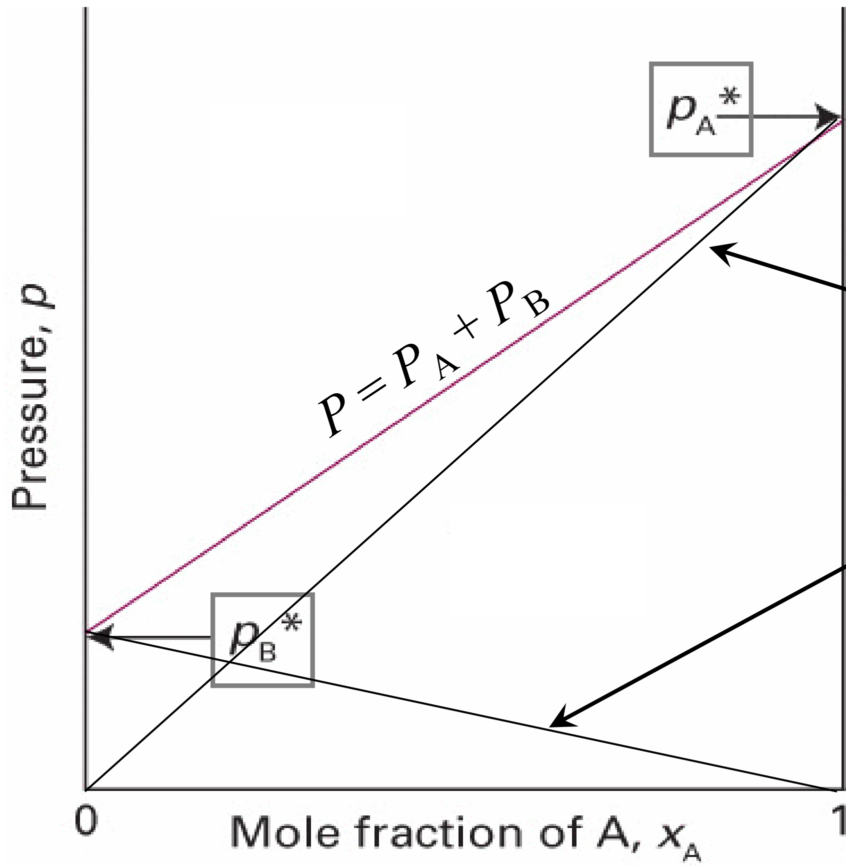
solute B expelled from solution

Ideal-dilute solutions: Henry constant K_B

Vapour-liquid diagrams of binary systems

Vapour-liquid diagrams of binary systems





$$P_A = x_A P_A^*$$

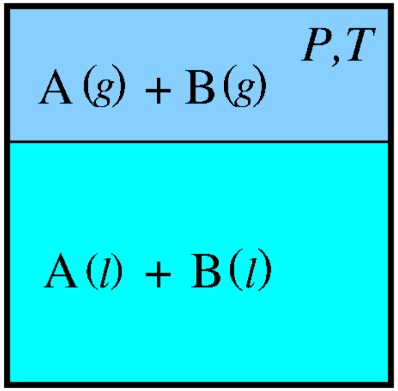
$$P_B = x_B P_B^*$$

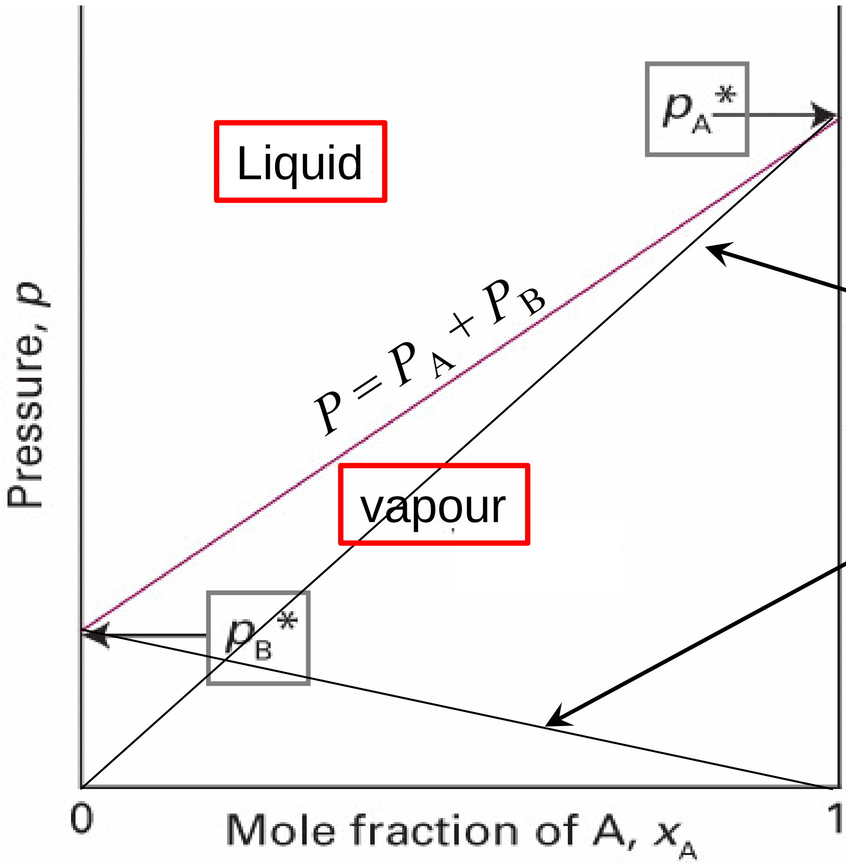
Ideal solution

(Raoult)

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

Vapour-liquid diagrams of binary systems





$$P_A = x_A P_A^*$$

$$P_B = x_B P_B^*$$

Ideal solution

(Raoult)

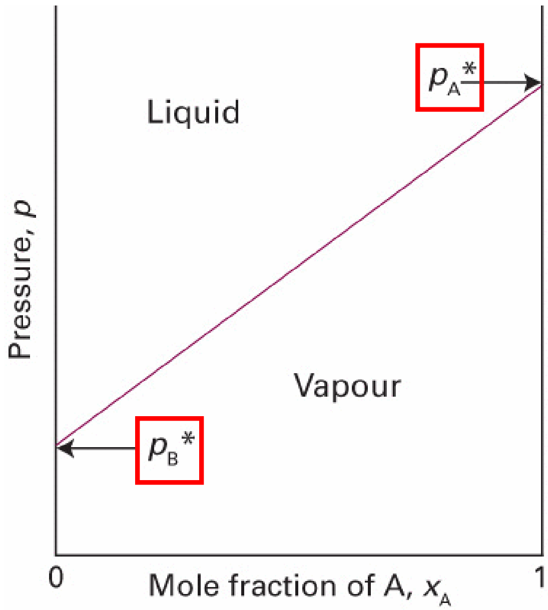
$$P = P_A + P_B = x_A P_A^* + x_B P_B^*$$

Vapour-liquid diagrams of binary systems

C = 2

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

Ideal solution



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

Vapour-liquid diagrams of binary systems

C = 2

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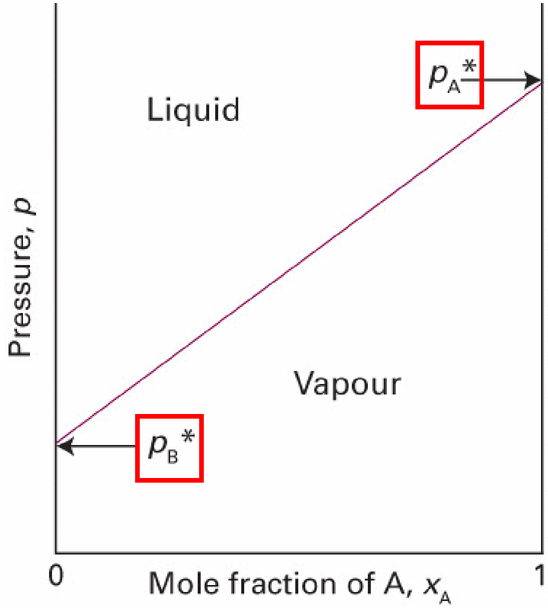
Ideal solution



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

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

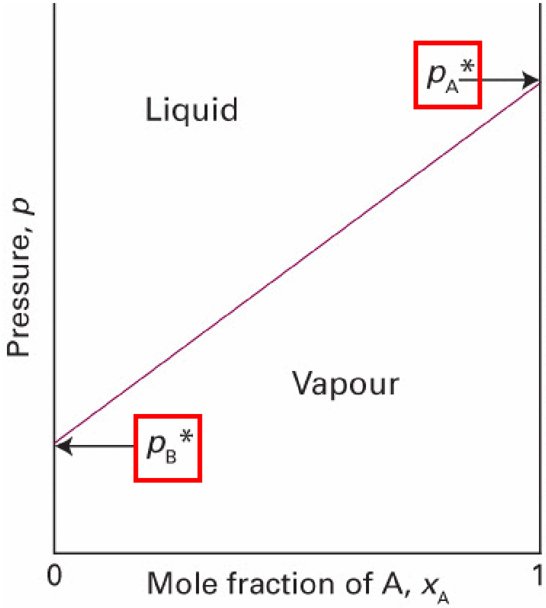
we use y for the mole fractions in the gas phase

Vapour-liquid diagrams of binary systems

C = 2

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

Ideal solution



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

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

$$(x_B = 1 - x_A)$$

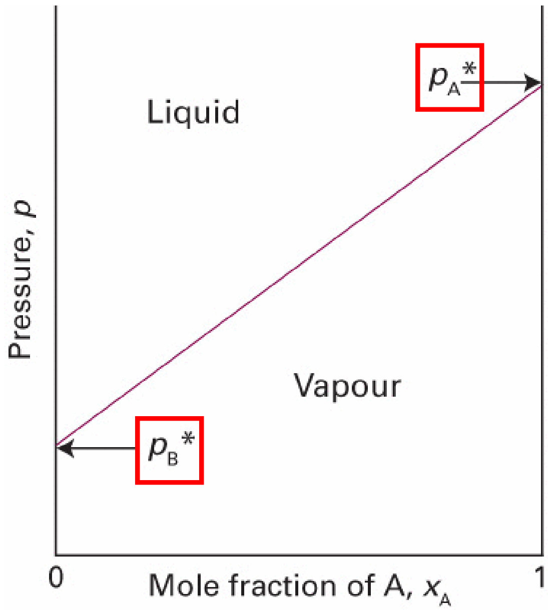
$$y_A = \frac{x_A P_A^*}{P_B^* + \left(P_A^* - P_B^*\right) x_A}$$

Vapour-liquid diagrams of binary systems

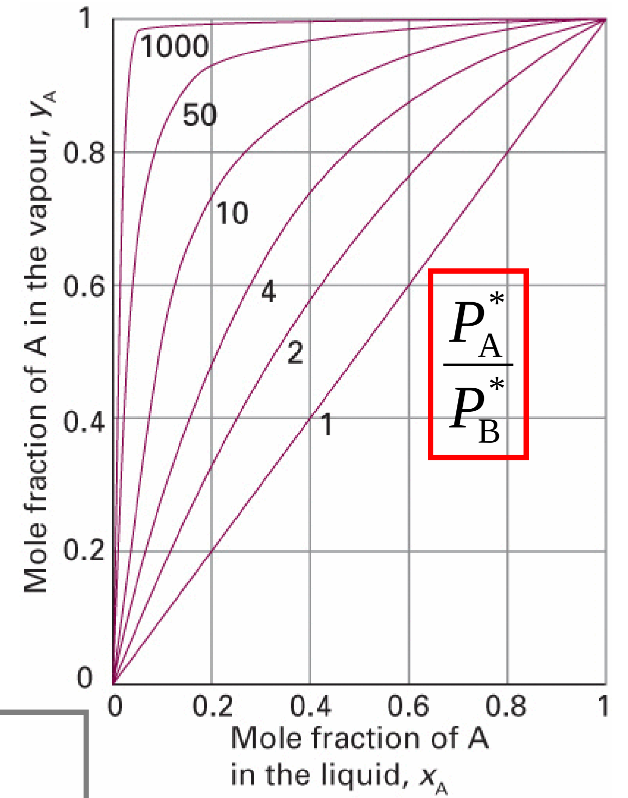
C = 2

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

Ideal solution



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



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

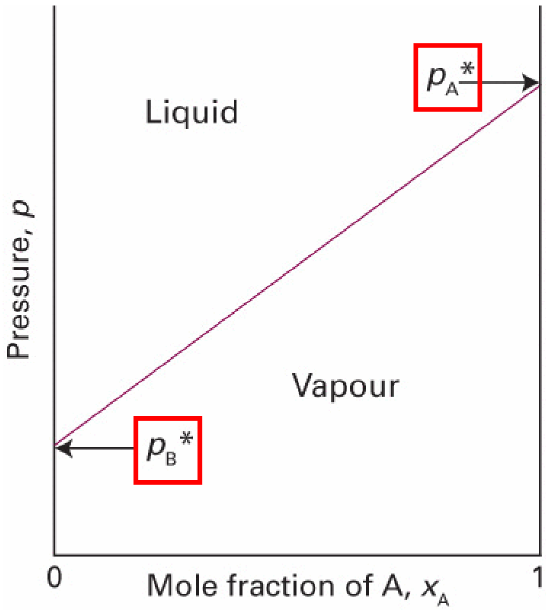
$$y_A = \frac{x_A P_A^*}{P_B^* + \left(P_A^* - P_B^*\right) x_A}$$

Vapour-liquid diagrams of binary systems

C = 2

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

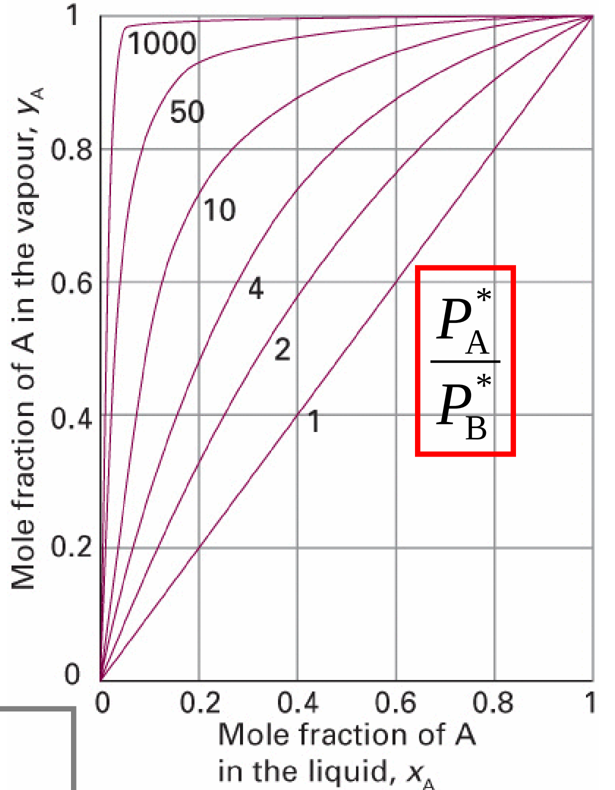
Ideal solution



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

$$(x_B = 1 - x_A)$$

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



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

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

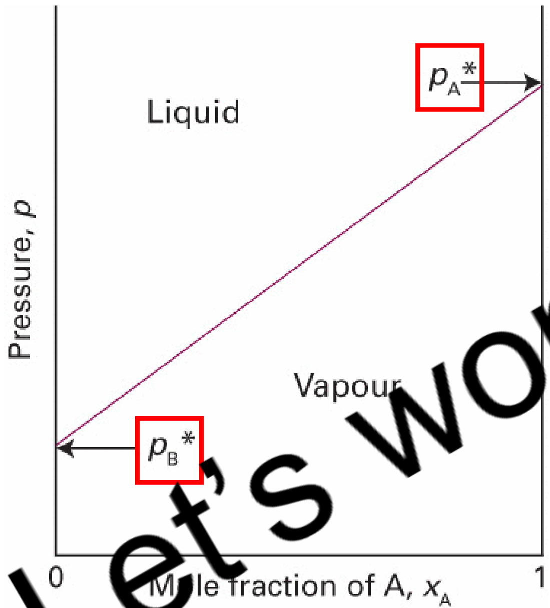
Vapour-liquid diagrams of binary systems

C = 2

Let's work this out in detail

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

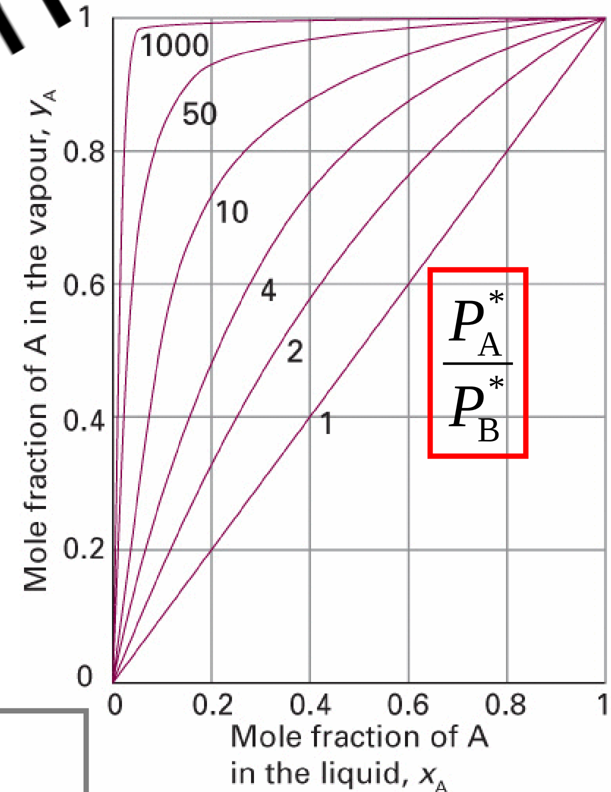
Ideal solution



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

$$\left(x_B = 1 - x_A\right)$$

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



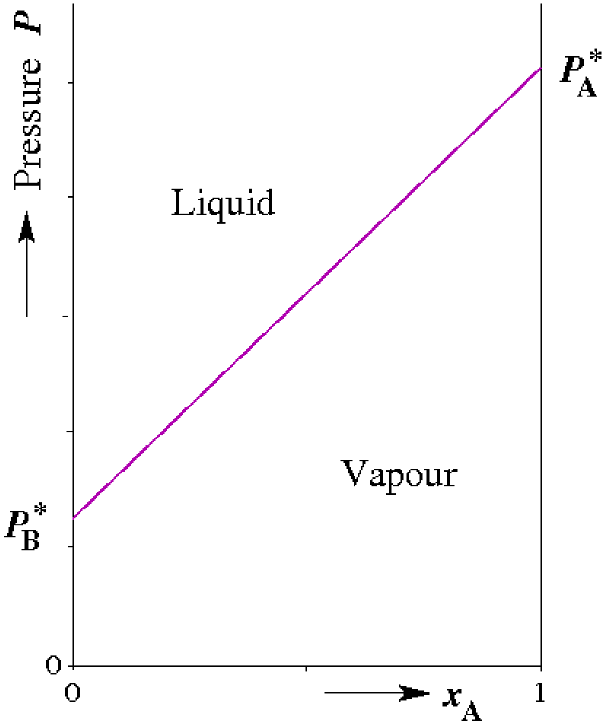
$$\frac{P_A^*}{P_B^*}$$

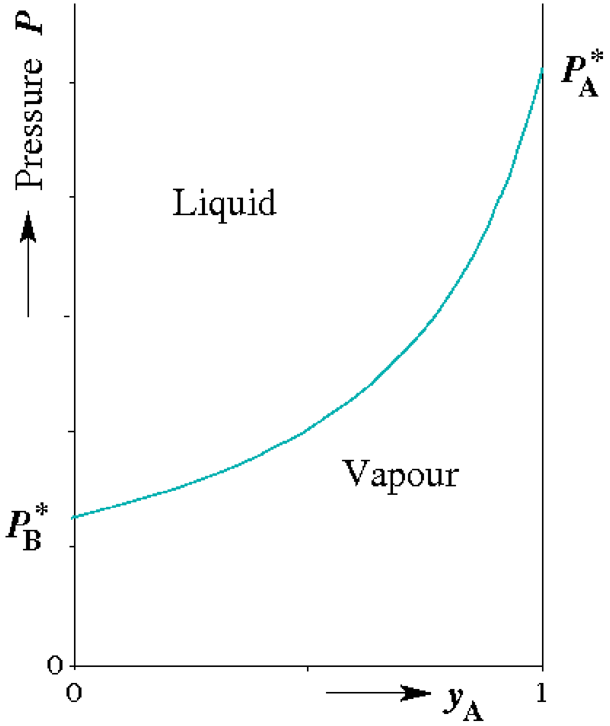
$$y_A \equiv \frac{n_A^g}{n^g} = \frac{P_A}{P}$$

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

Vapour-liquid diagrams of binary systems

Ideal solution





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

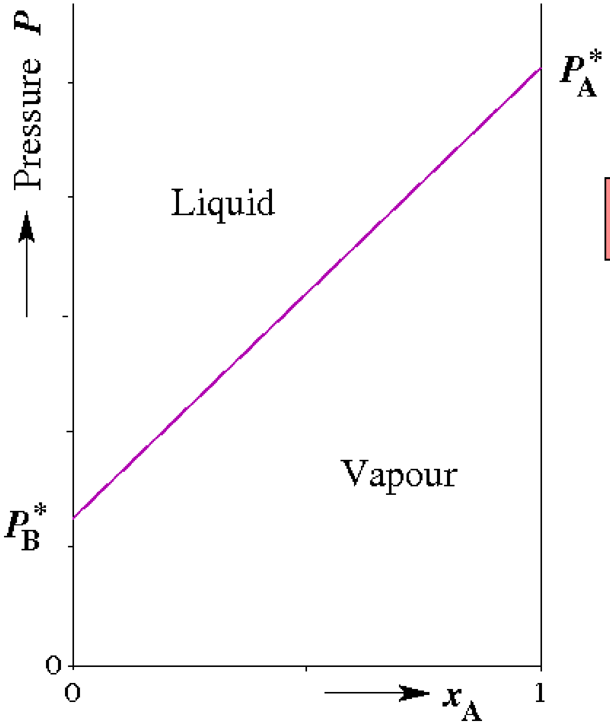
$$P = \frac{P_A^* P_B^*}{P_A^* + \left(P_B^* - P_A^*\right) y_A}$$

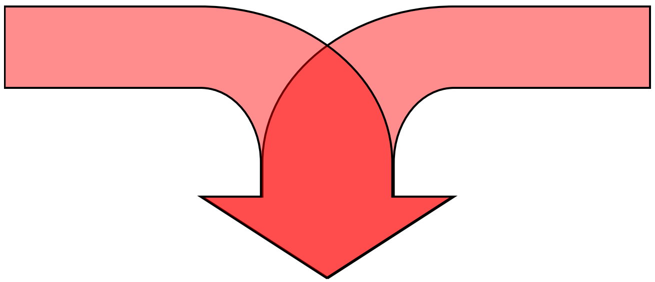
$$\frac{P_A^*}{P_B^*} = 4.12$$

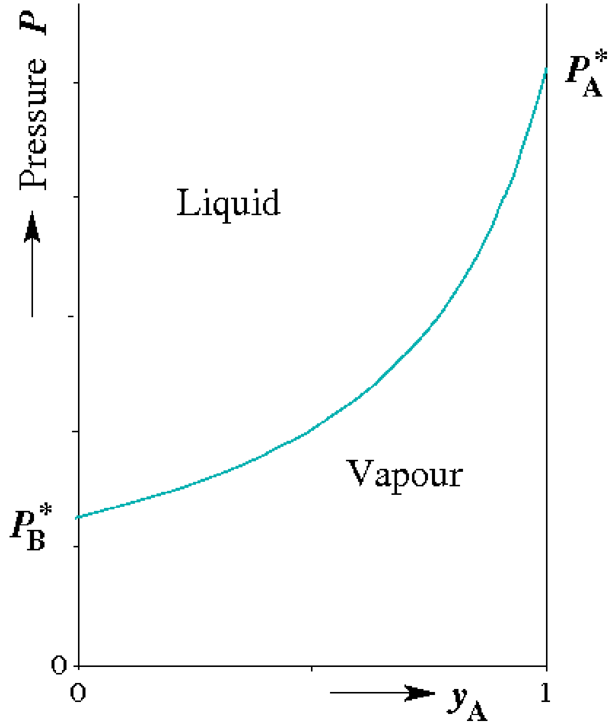
$$\frac{P_A^*}{P_B^*} = 4.12$$

Vapour-liquid diagrams of binary systems

Ideal solution

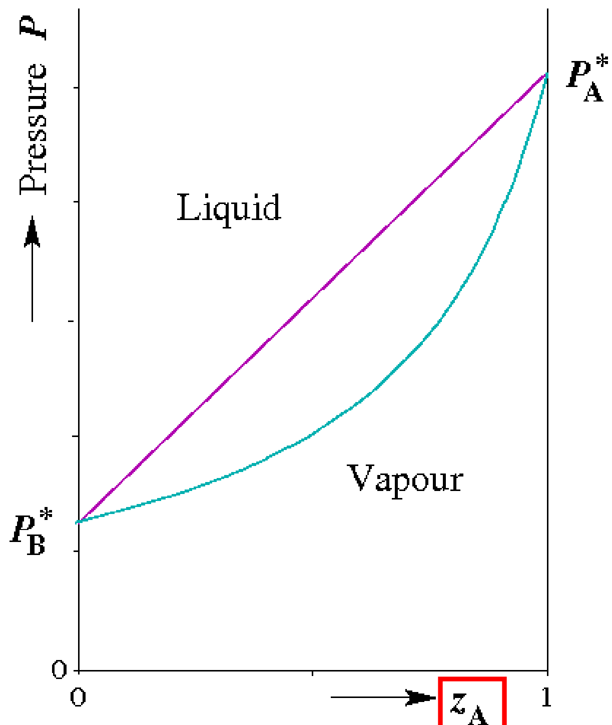






$$P = x_A P_A^* + x_B P_B^*$$

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



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

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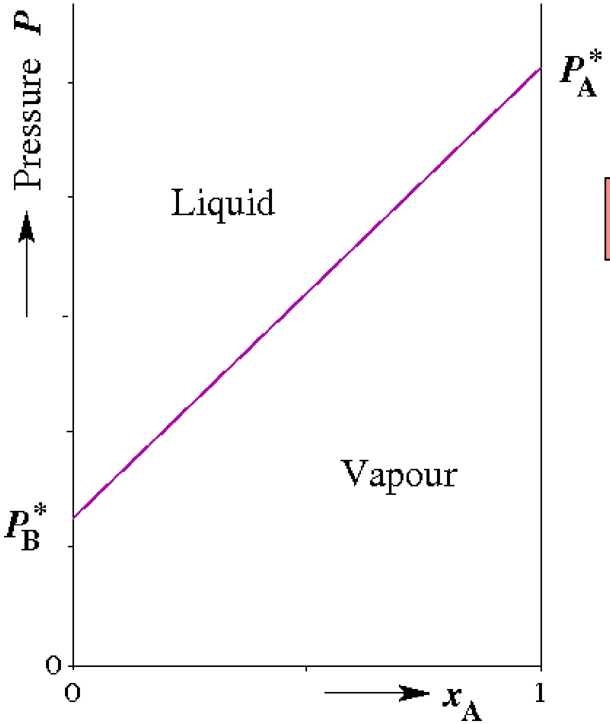
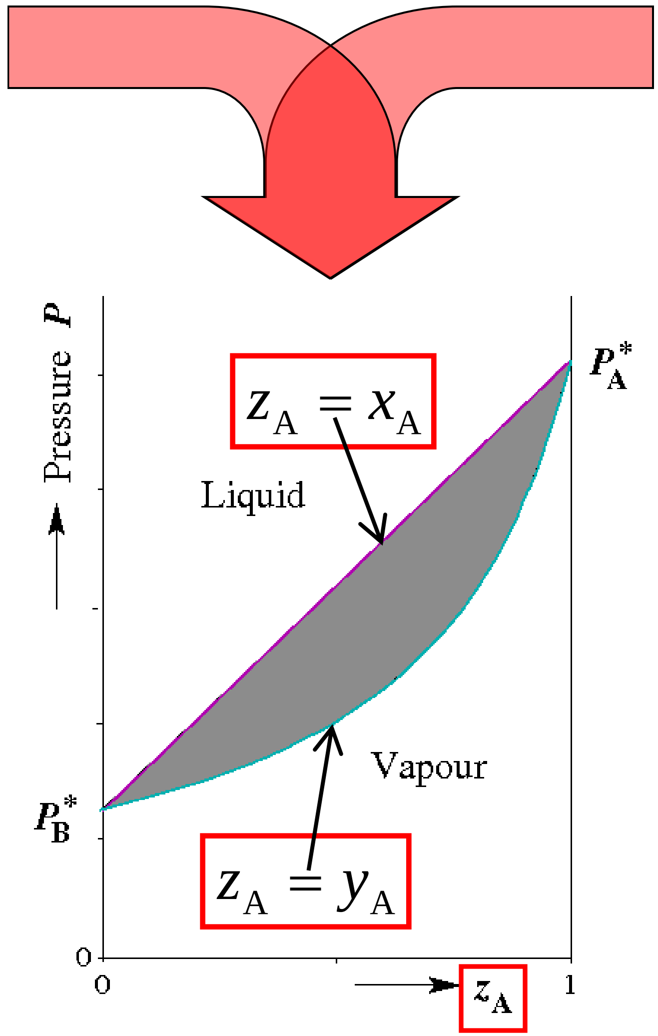
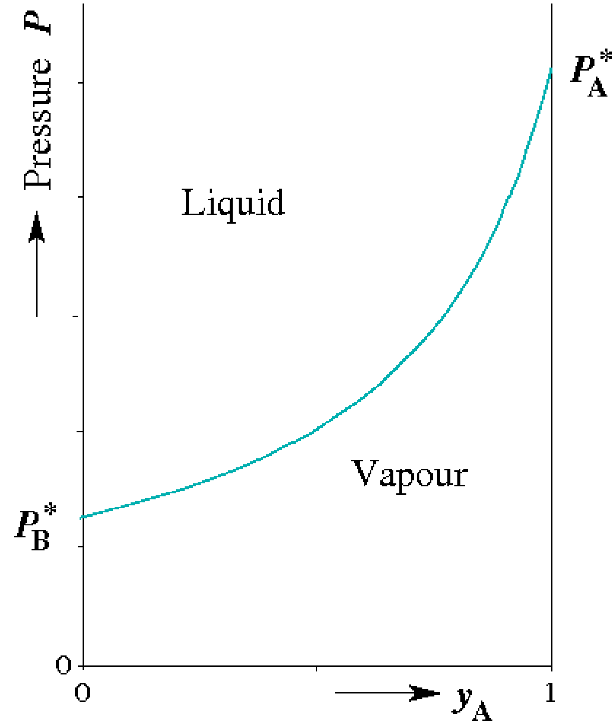
Vapour-liquid diagrams of binary systems

Ideal solution







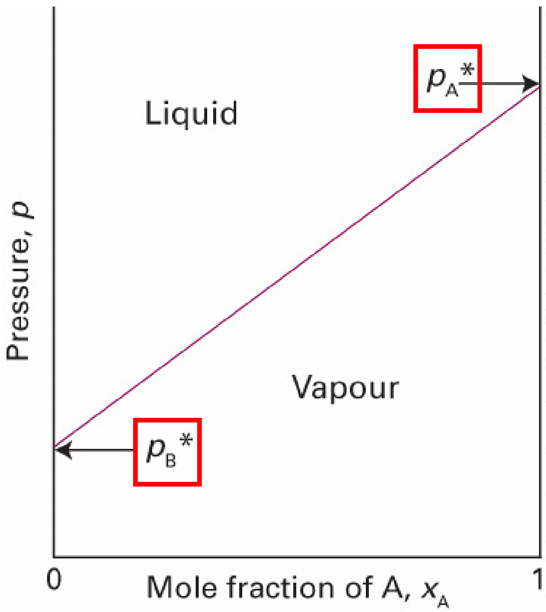
$$P = x_A P_A^* + x_B P_B^*$$

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

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

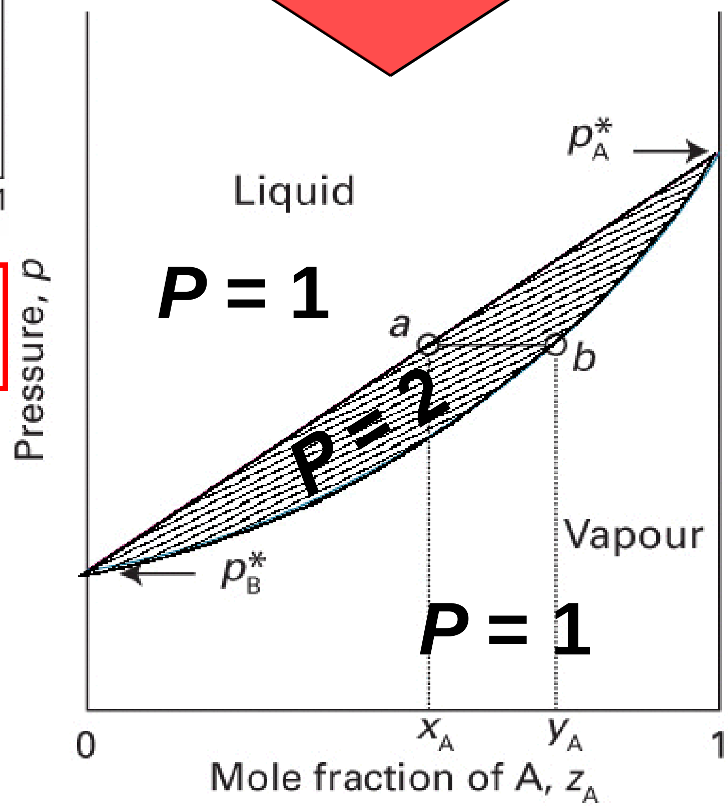
$$\frac{P_A^*}{P_B^*} = 4.12$$

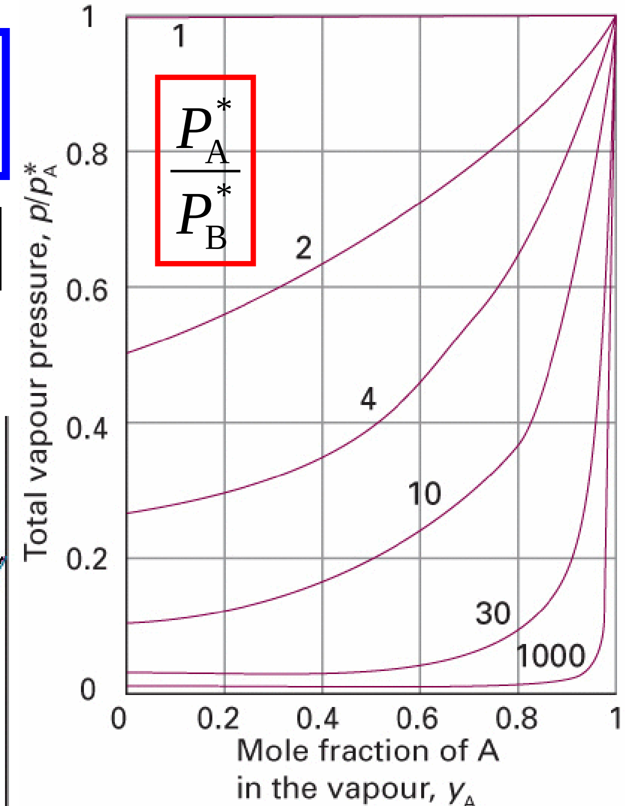
Vapour-liquid diagrams of binary systems



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

Fixed *T*

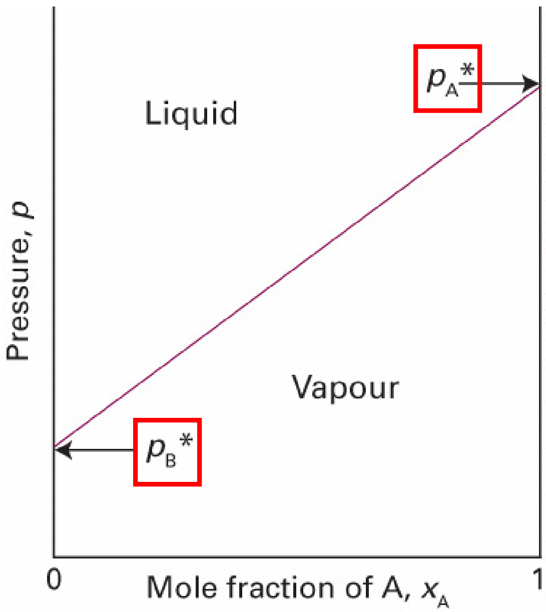




$$P = \frac{P_A^* P_B^*}{P_A^* + \left(P_B^* - P_A^*\right) y_A}$$

Ideal solution

Vapour-liquid diagrams of binary systems



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

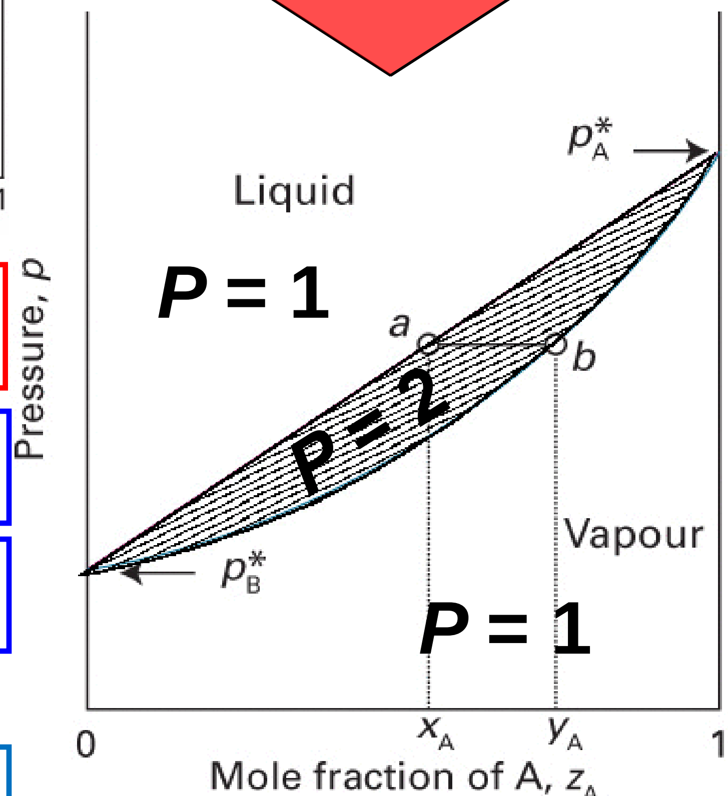
$$F = C - P + 2$$

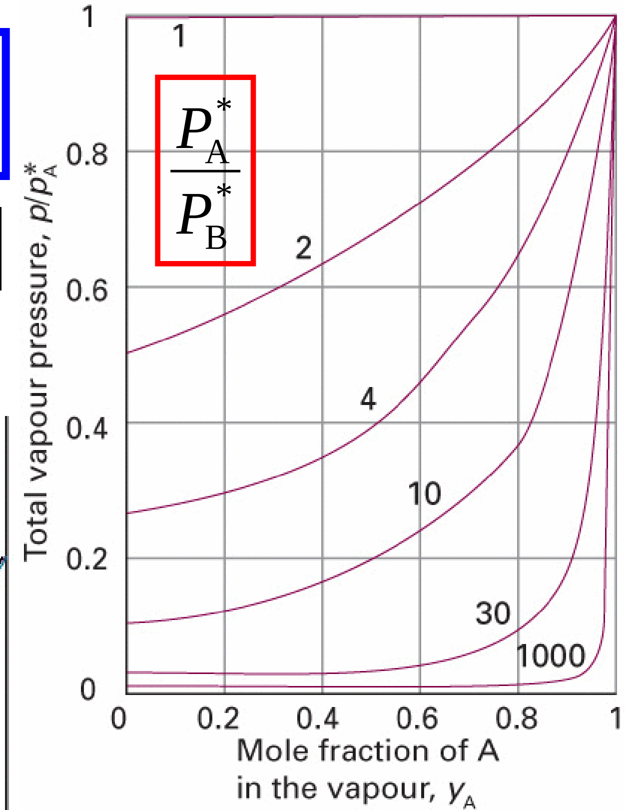
$$F' = C - P + 1$$

Ideal solution

Exercise 14-15

Fixed *T*

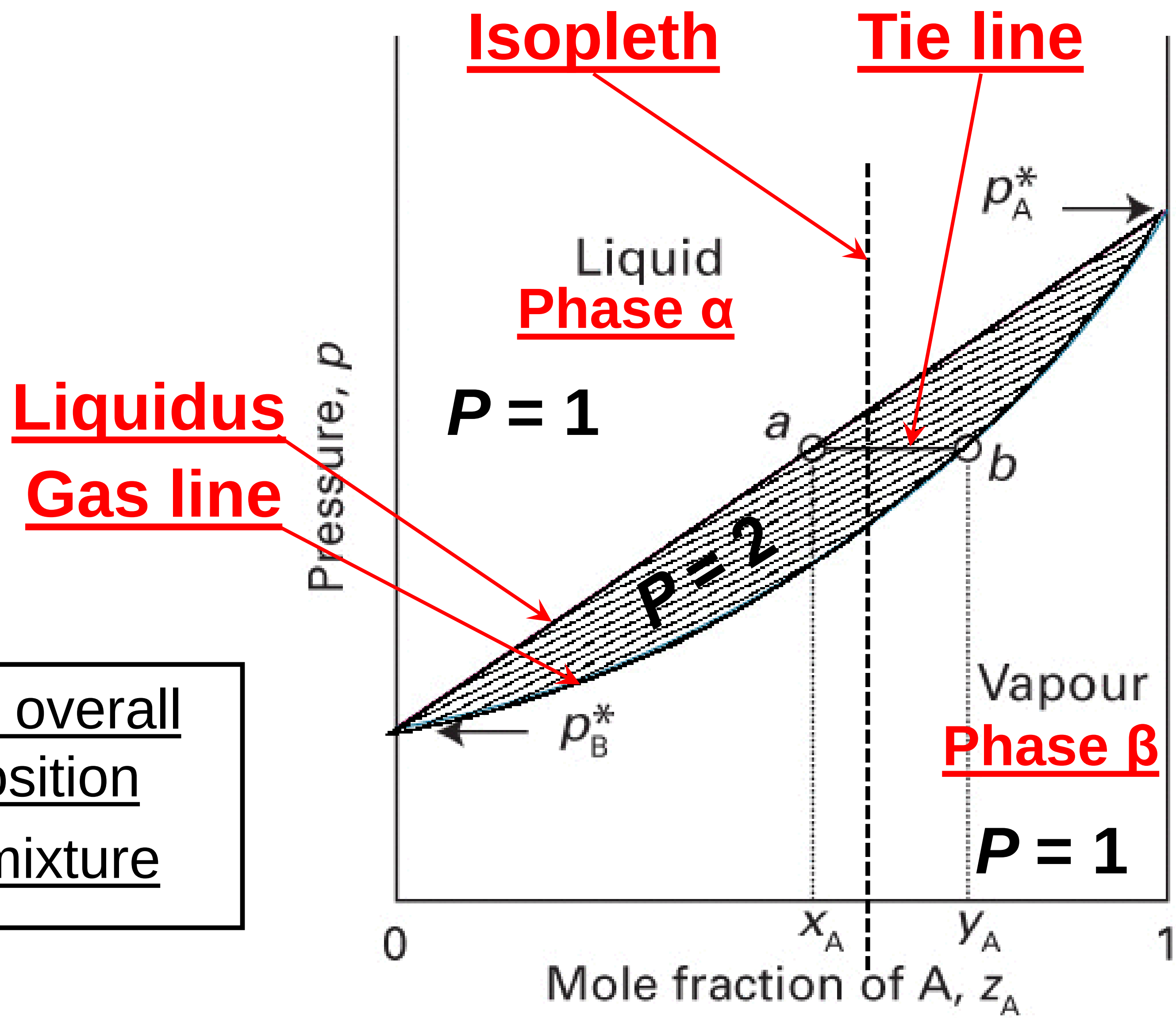




$$P = \frac{P_A^* P_B^*}{P_A^* + \left(P_B^* - P_A^*\right) y_A}$$

Lever rule

C = 2

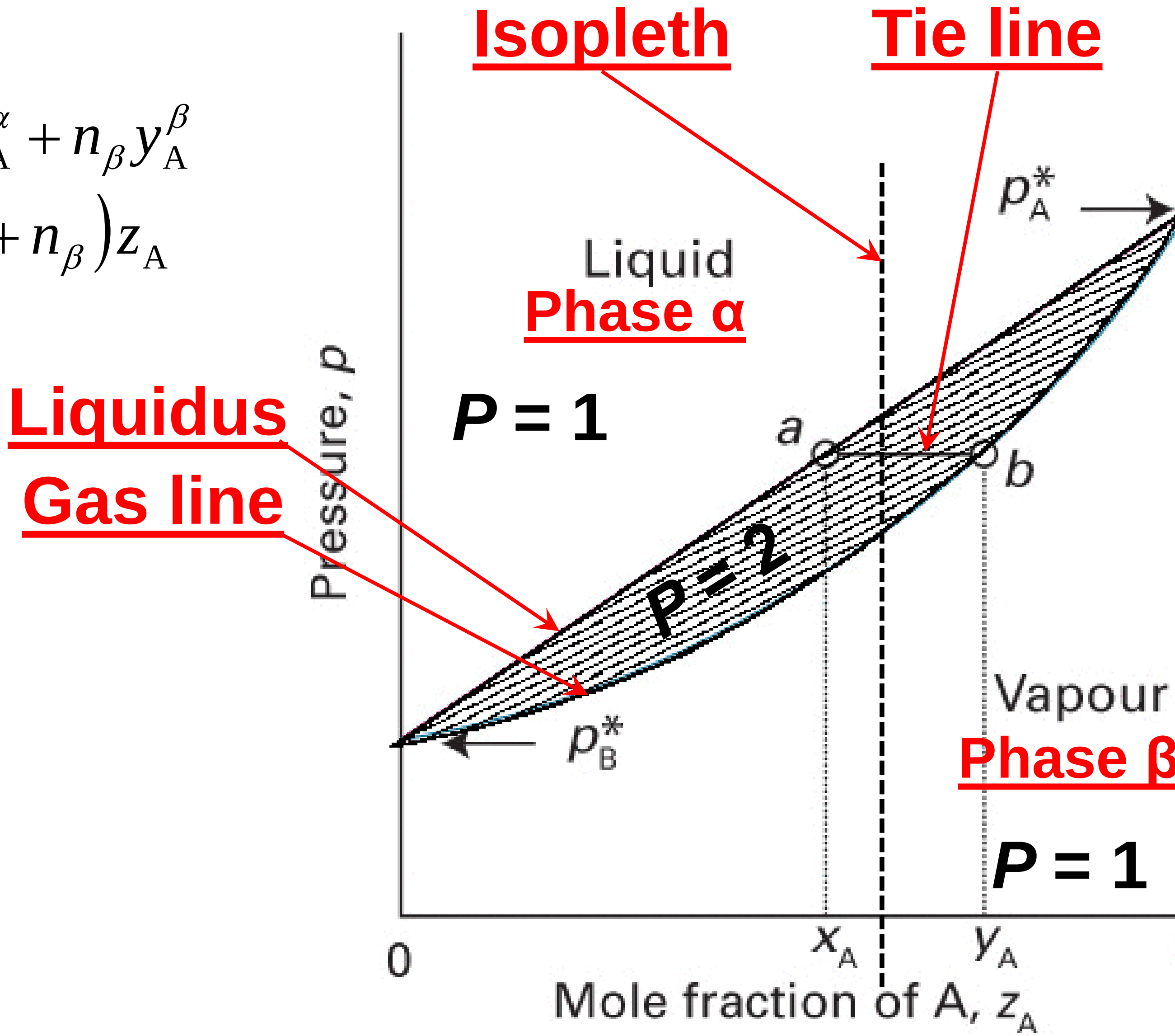


z_A is the overall composition of the mixture

Lever rule

C = 2

$$\begin{cases} nz_{\mathrm{A}} = n_\alpha x_{\mathrm{A}}^{\alpha} + n_\beta y_{\mathrm{A}}^{\beta} \\ nz_{\mathrm{A}} = \left(n_\alpha + n_\beta\right) z_{\mathrm{A}} \end{cases}$$



Lever rule

$C = 2$

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

$$\Downarrow$$

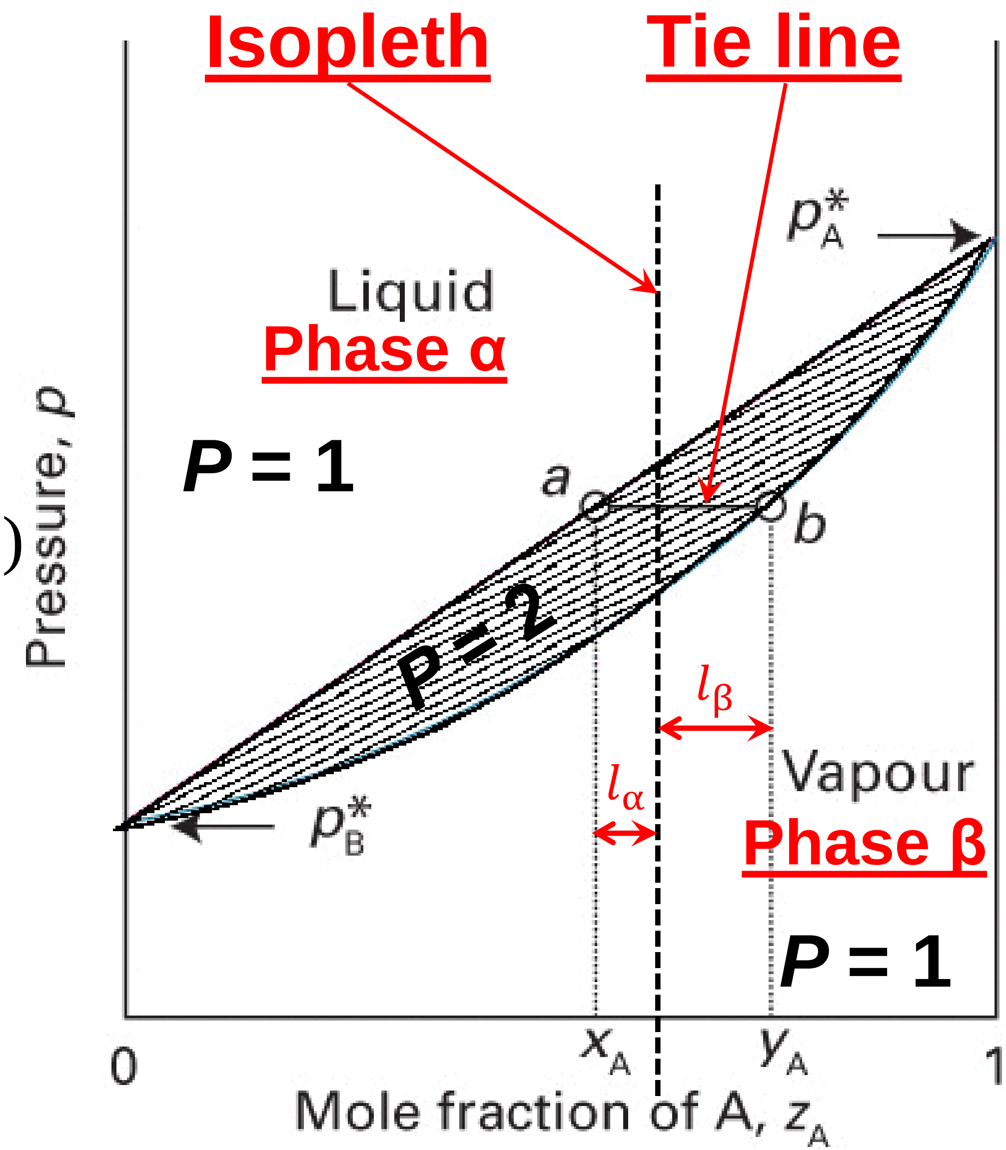
$$n_\alpha (z_A - x_A^\alpha) = n_\beta (y_A^\beta - z_A)$$

$$\Downarrow$$

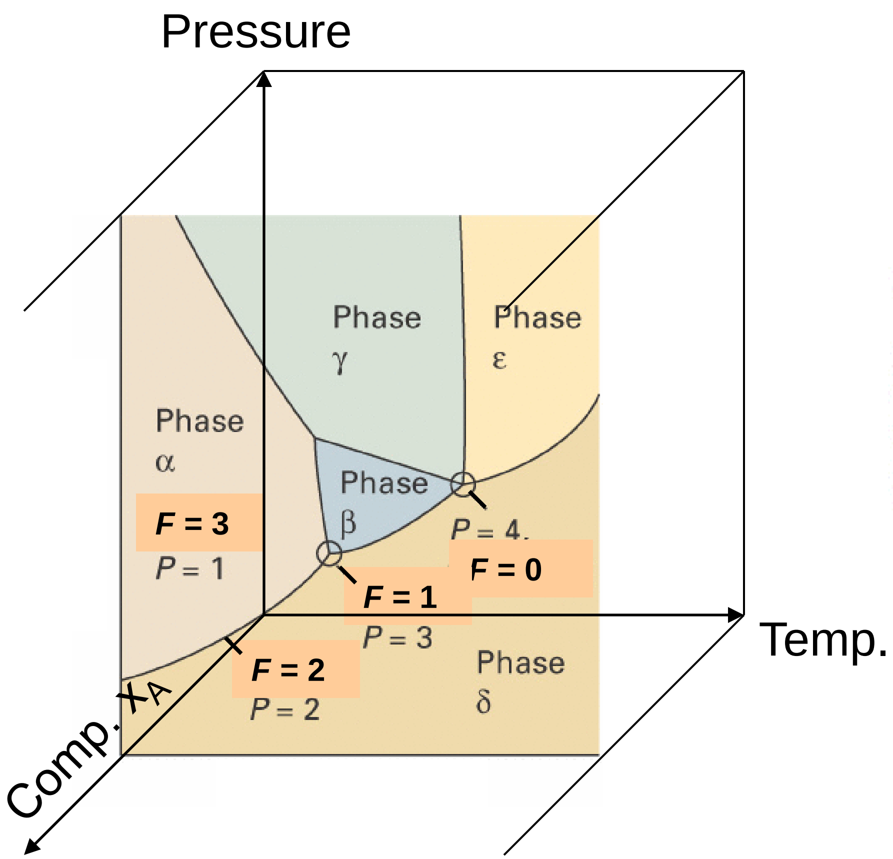
$$n_\alpha l_\alpha = n_\beta l_\beta$$

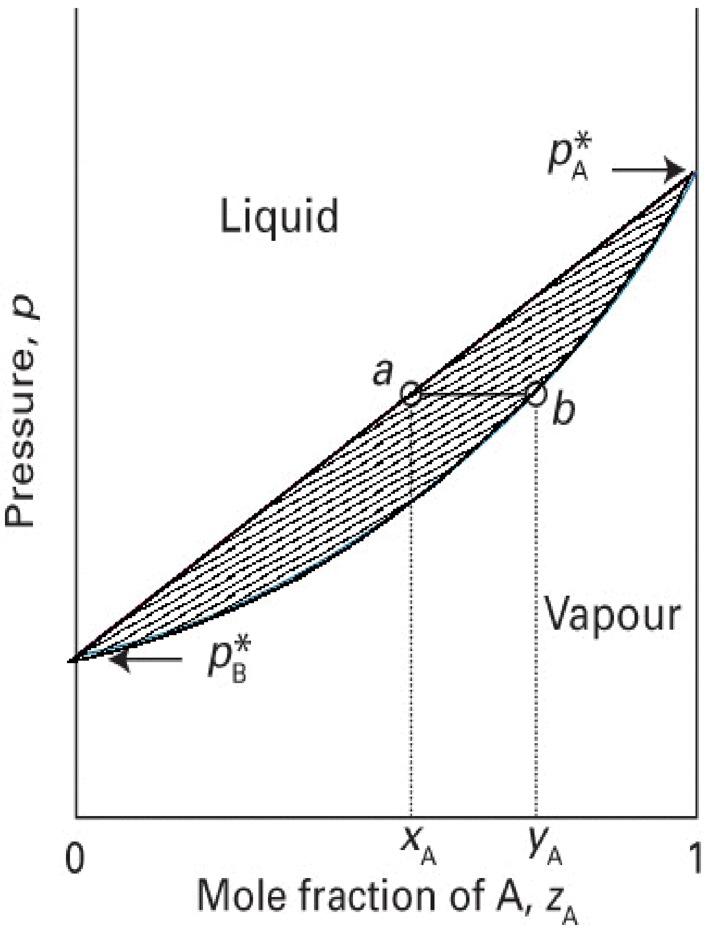
Lever rule

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

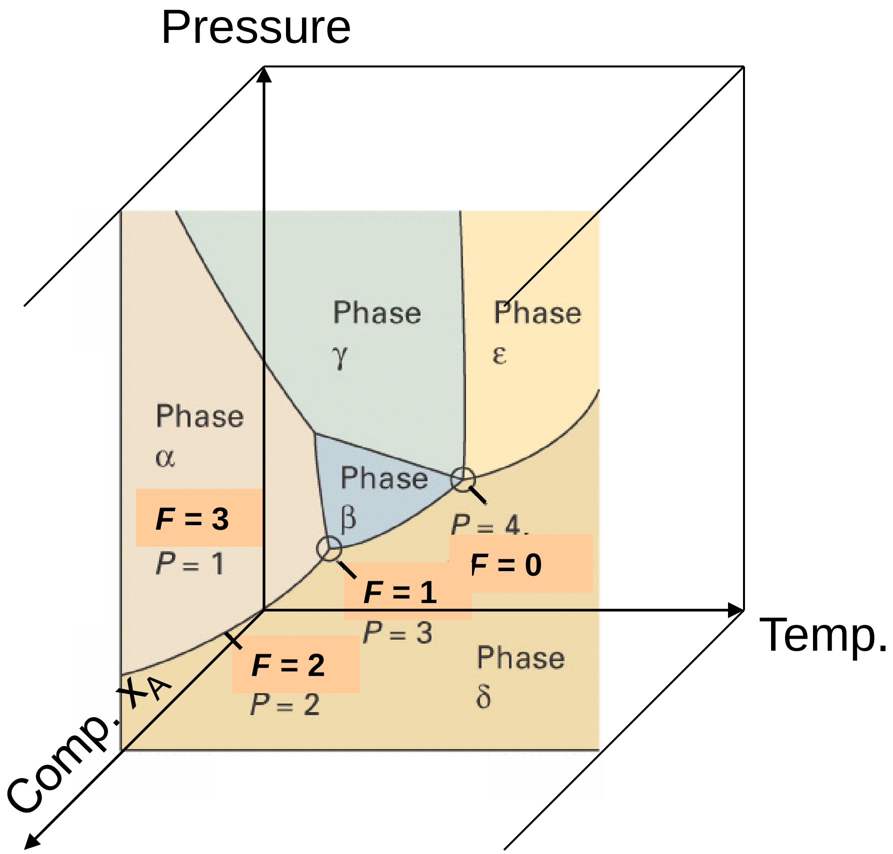


Pressure-composition diagrams





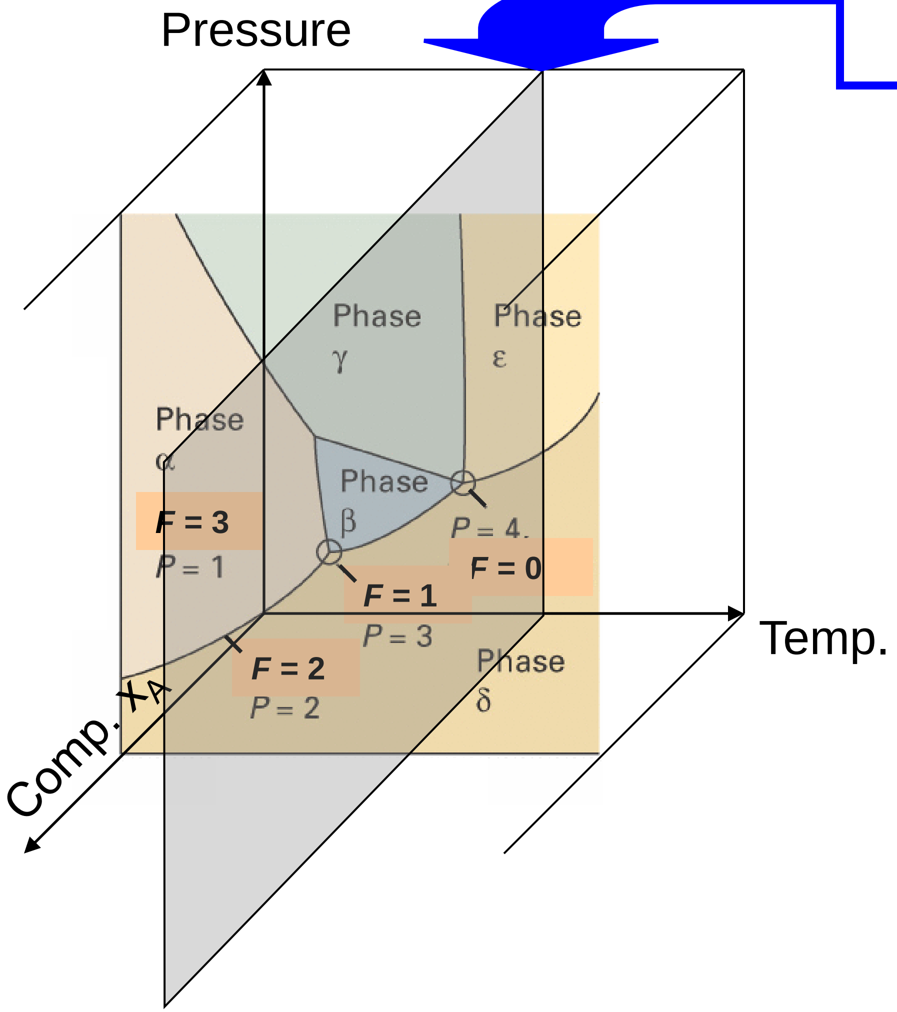
Pressure-composition diagrams

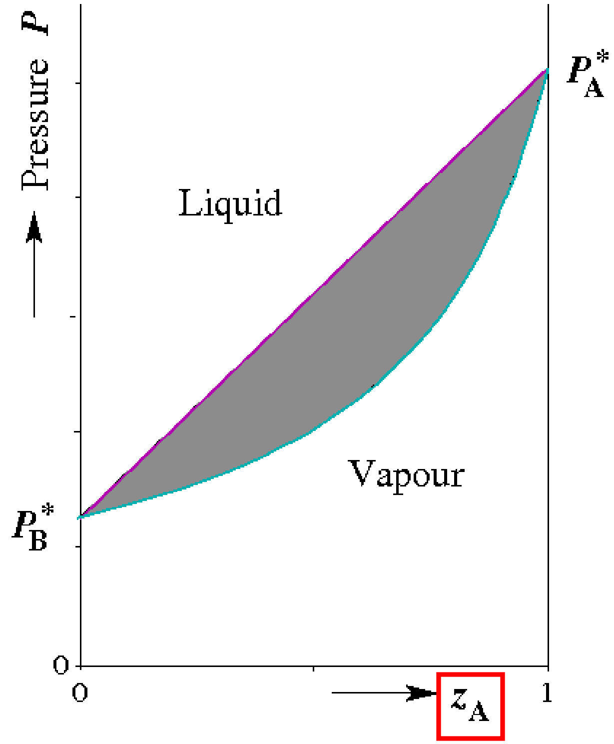


Temperature-composition diagrams

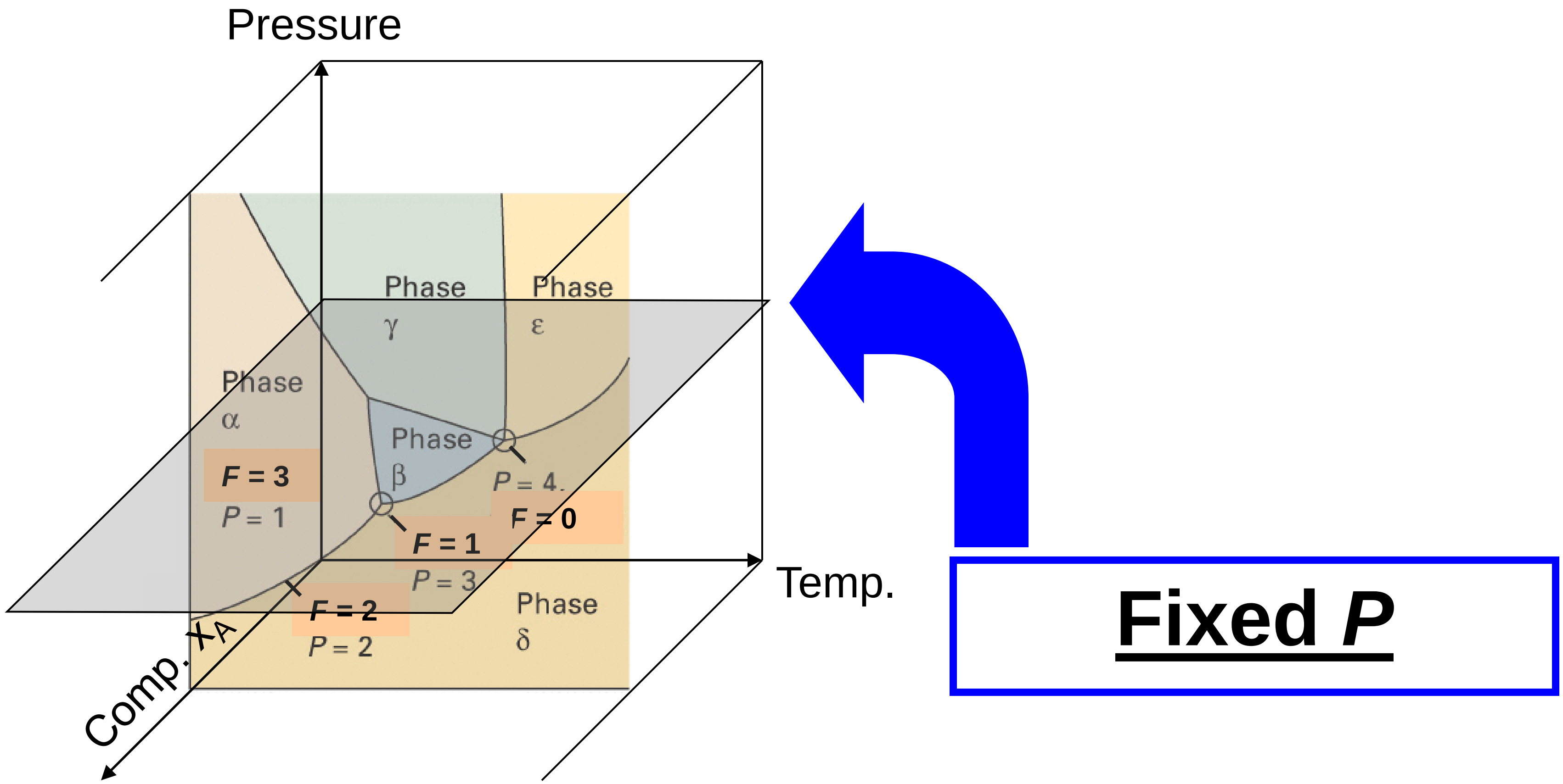
Pressure-composition diagrams

Fixed *T*





Temperature-composition diagrams



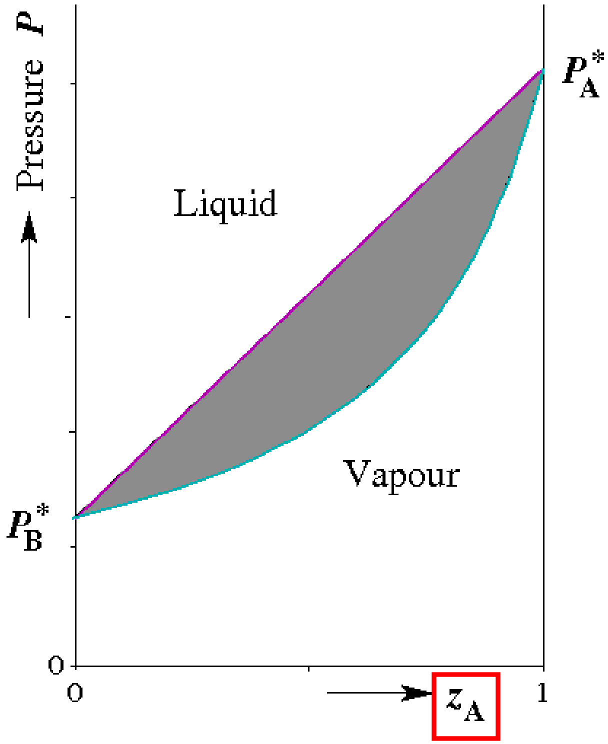
Temperature-composition diagrams

Pressure-composition diagrams

Ideal solution

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

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



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

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

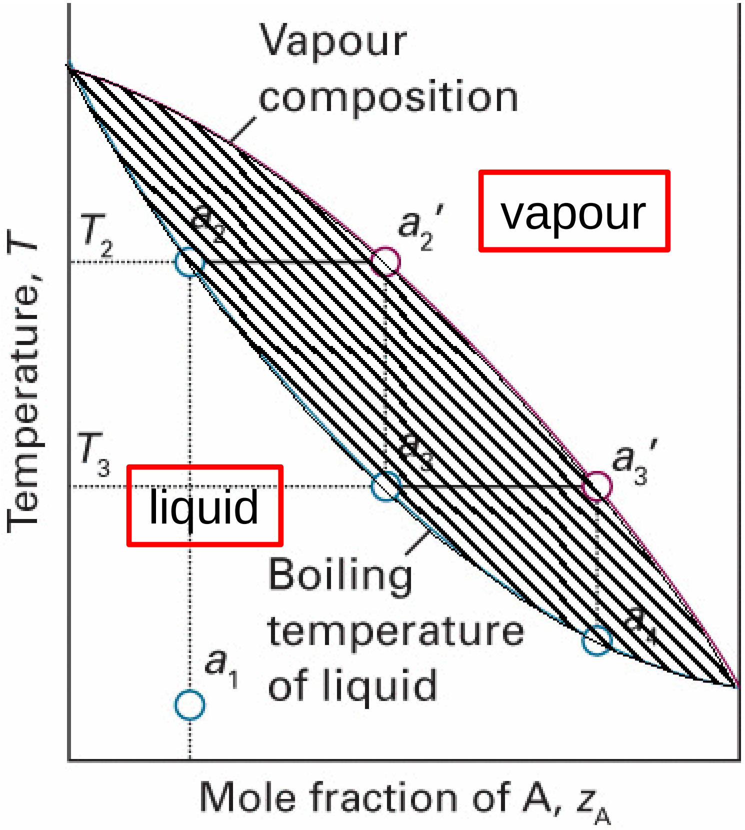
Fixed *T*

Temperature-composition diagrams

Ideal solution

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

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



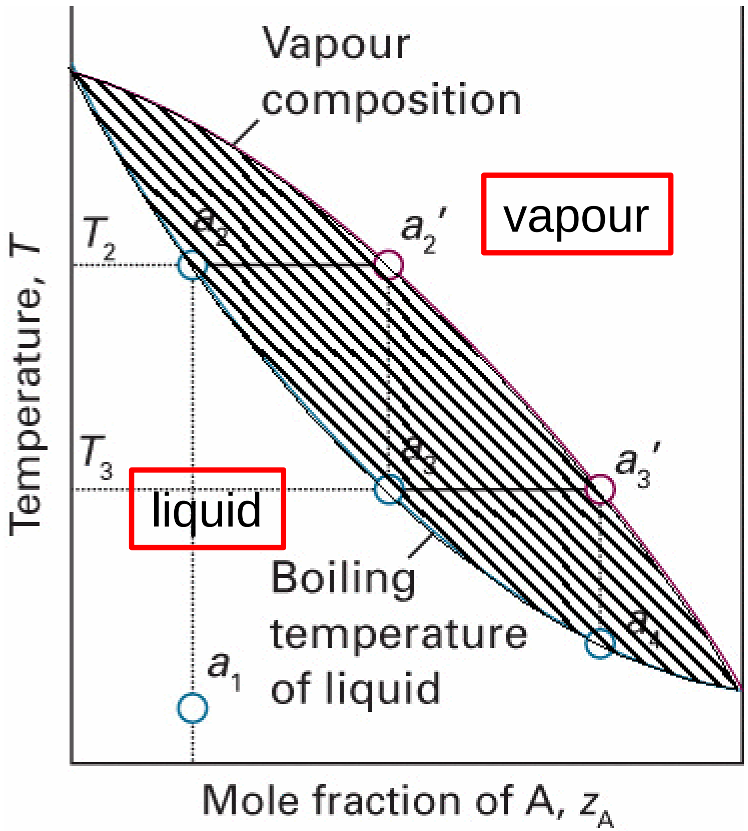
Fixed *P*

Temperature-composition diagrams

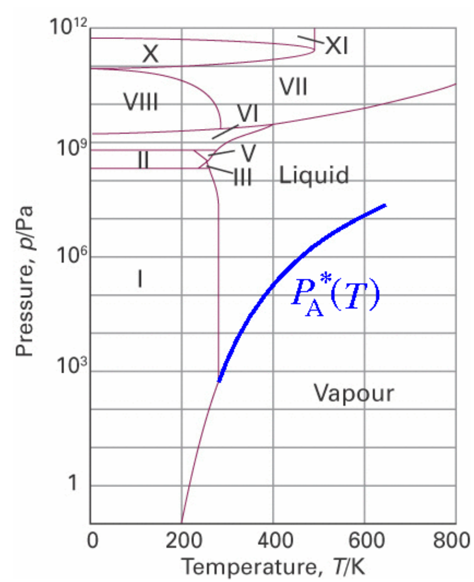
Ideal solution

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

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



Fixed *P*



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

(Clapeyron)

(P,T)-diagram

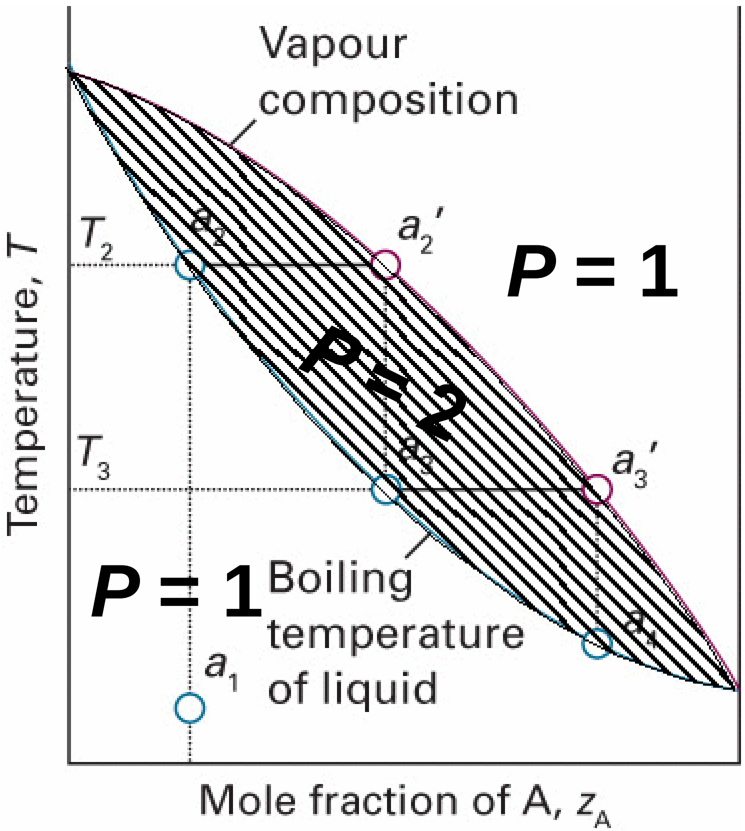
Component A

Temperature-composition diagrams

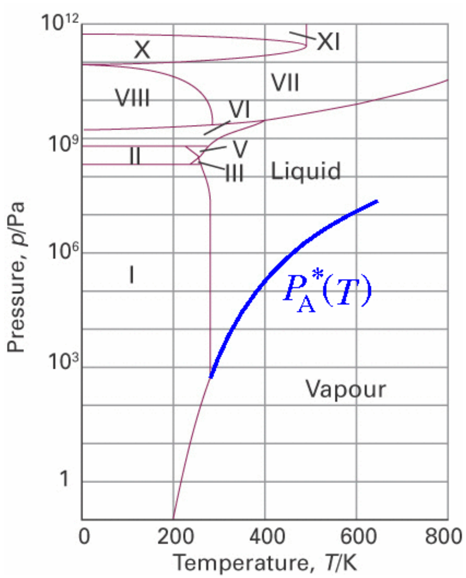
Ideal solution

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

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



Fixed *P*



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

(Clapeyron)

(P,T)-diagram

Component A

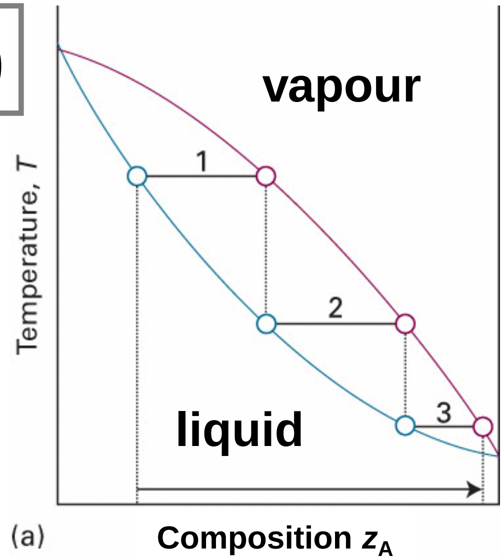
$$F = C - P + 2$$

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

C = 2 Temperature-composition diagrams

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

ideal solution



Excess Gibbs free energy

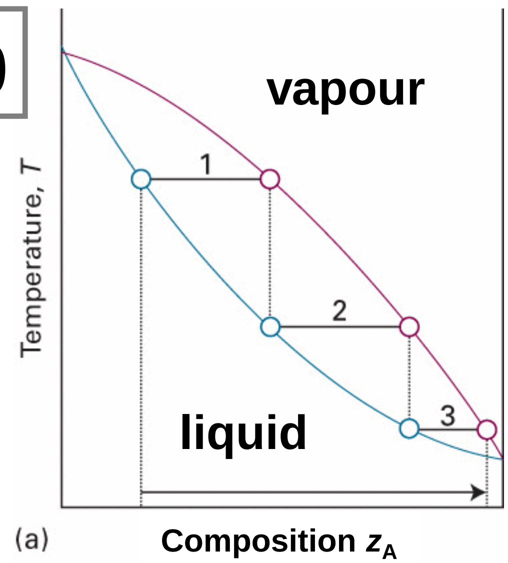
$$G^{\mathrm{E}} \equiv \Delta_{\mathrm{mix}} G - \Delta_{\mathrm{mix}} G^{\mathrm{ideal}}$$

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

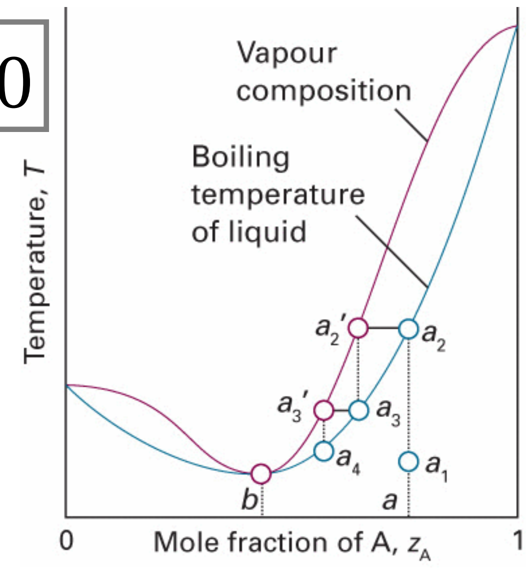
C = 2 Temperature-composition diagrams

$G^{E} = 0$

ideal solution

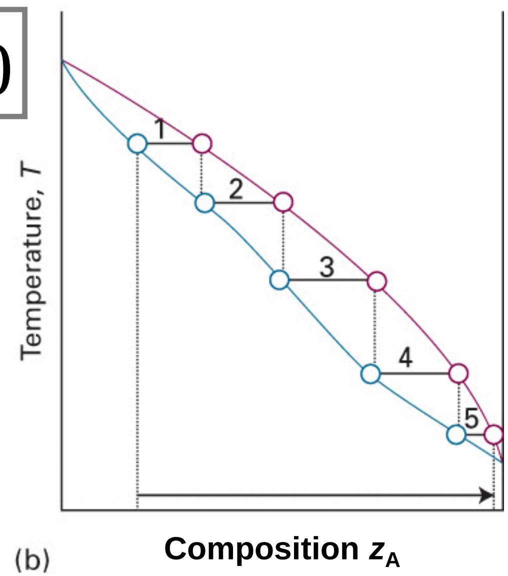


$G^{E} >> 0$

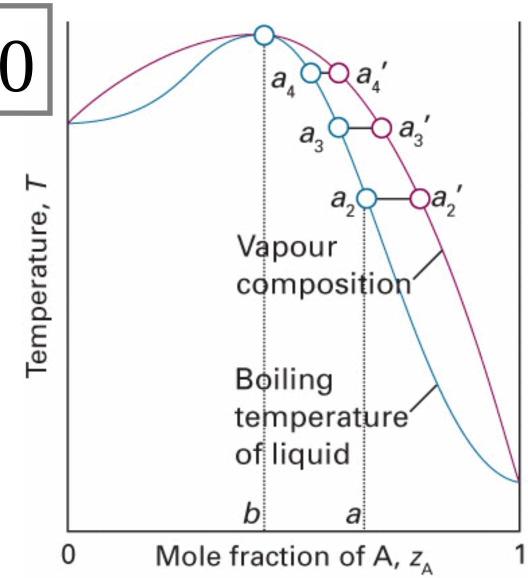


$G^{E} < 0$

non-ideal solutions



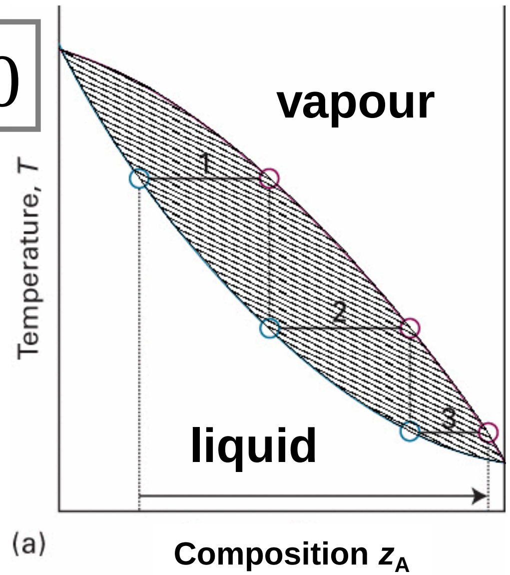
$G^{E} << 0$



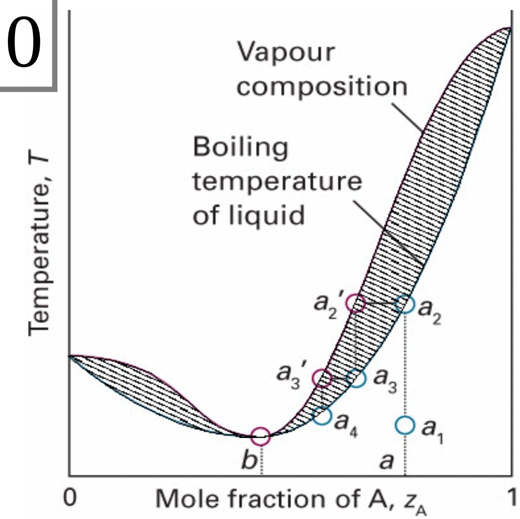
C = 2 Temperature-composition diagrams

$G^E = 0$

ideal solution

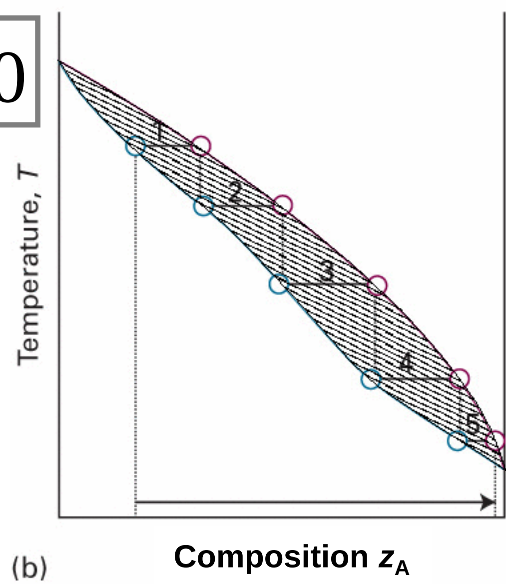


$G^E >> 0$

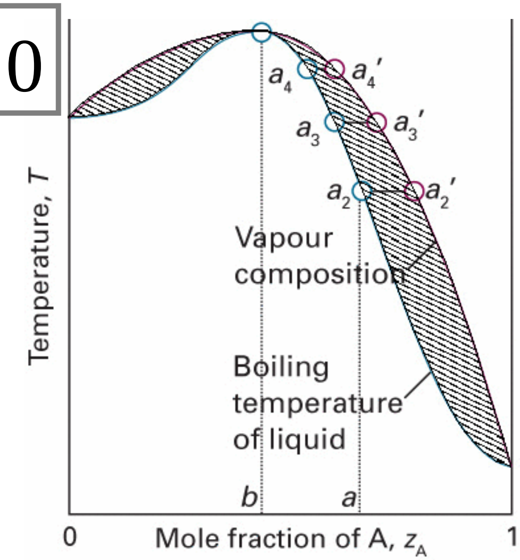


$G^E < 0$

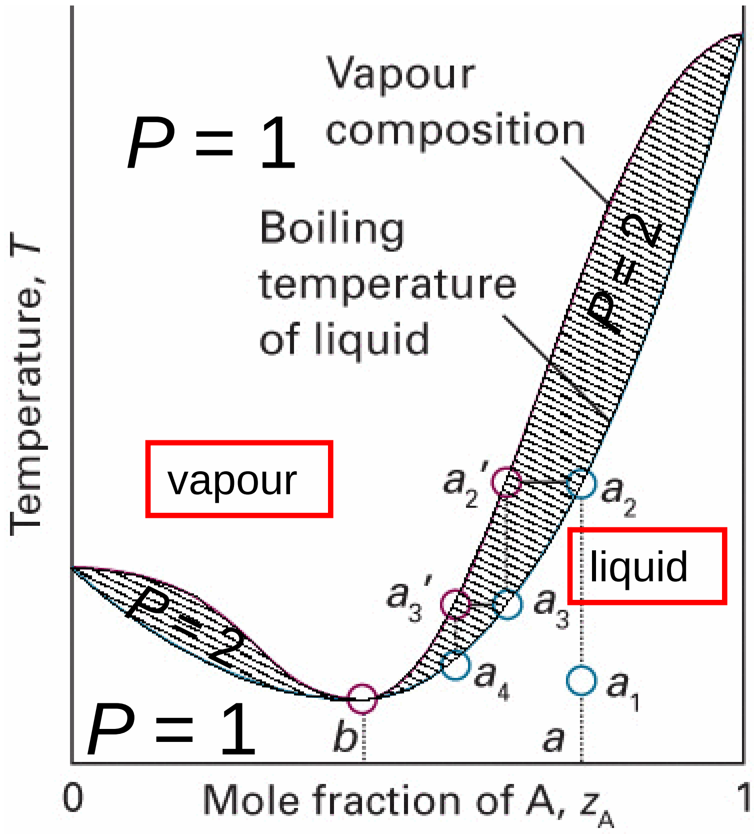
non-ideal solutions

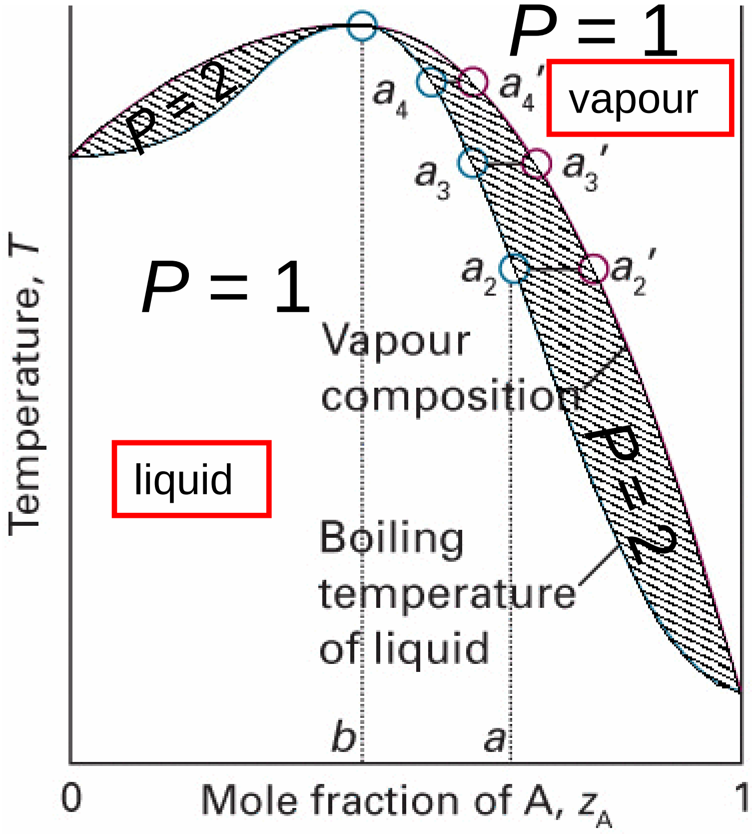


$G^E << 0$



C = 2 Temperature-composition diagrams





Low boiling azeotrope

High boiling azeotrope

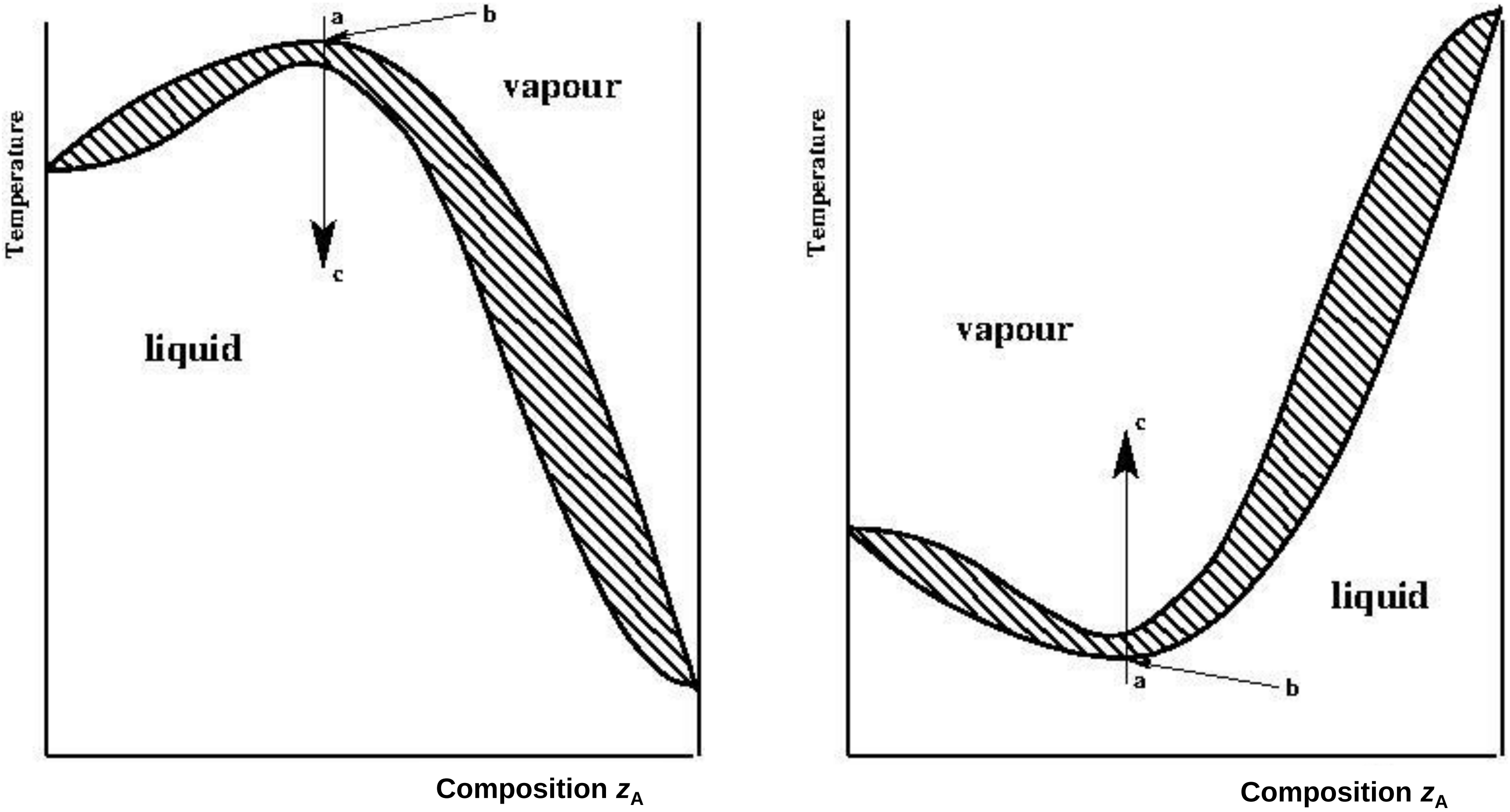
H_2O/Eth: 4 wgt%H_2O @ 78°C

H_2O/HCl: 80 wgt%H_2O @ 108.6°C

Exercise 16

C = 2

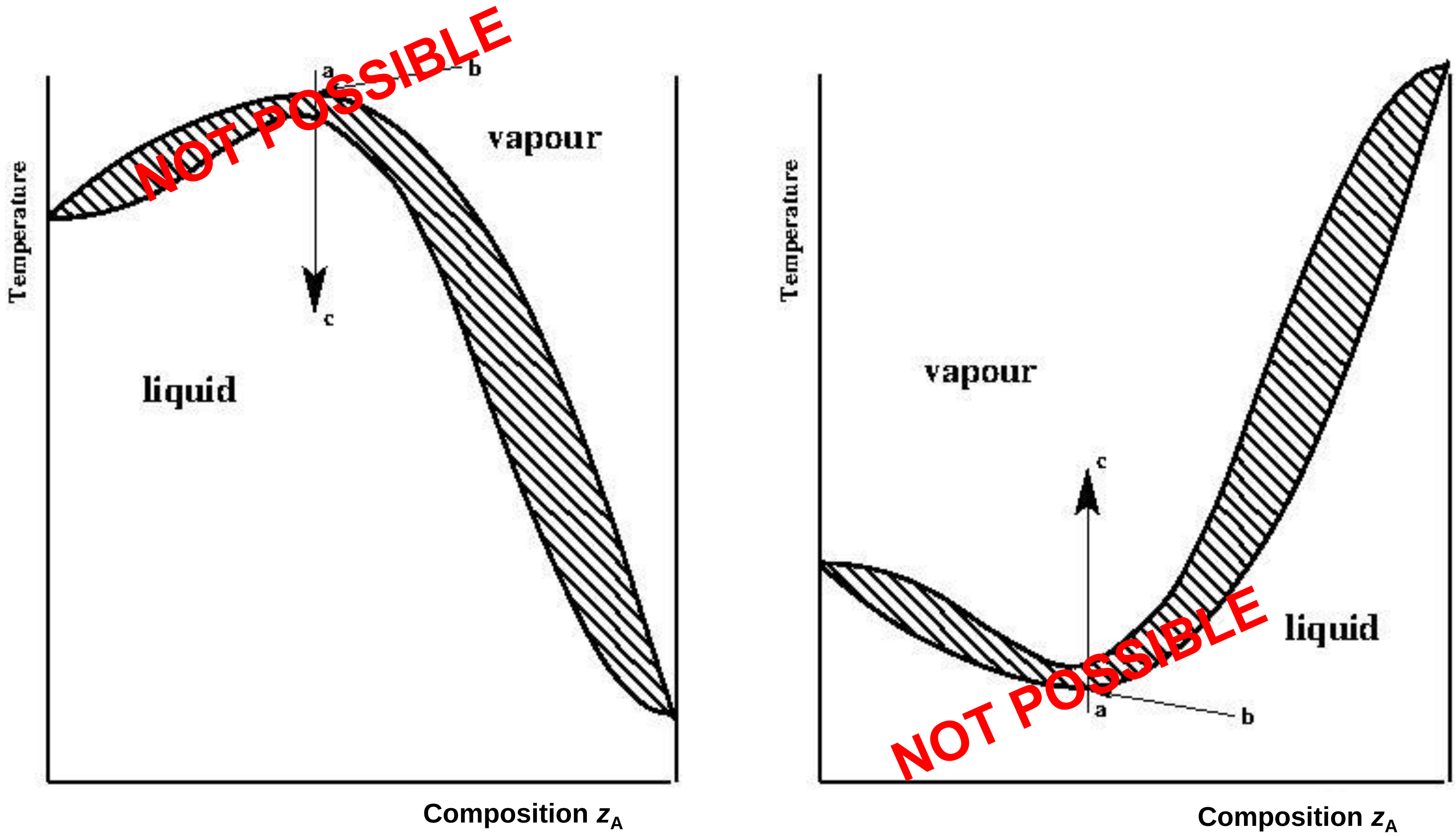
Impossible azeotropes



would lead to g-g separation

C = 2

Impossible azeotropes



would lead to g-g separation

Exess functions

Exess functions

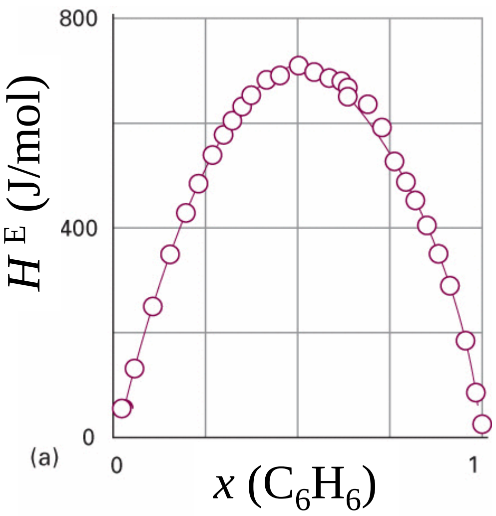
Non-ideal mixing

(Excess functions)

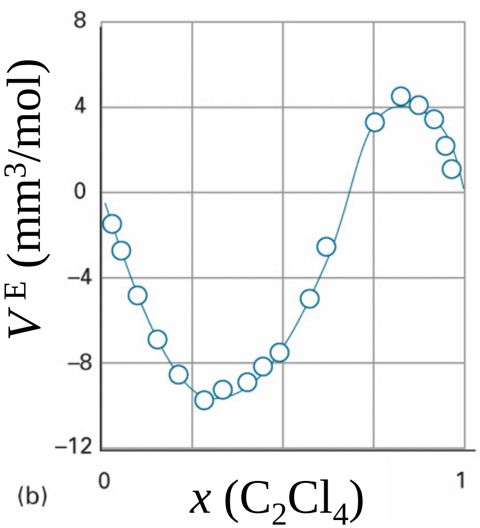
$$S^{E} \equiv \Delta_{mix} S - \Delta_{mix} S^{ideal}$$

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

Benzene/cyclohexane



Cl_4ethene/cyclopentene



$$G^{E} = H^{E} - TS^{E}$$

		Ideal	Regular	Quasi regular
S^{E}		=0	=0	≠0
H^{E}		=0	≠0	≠0

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

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

Exess functions

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

Regular solution

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

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

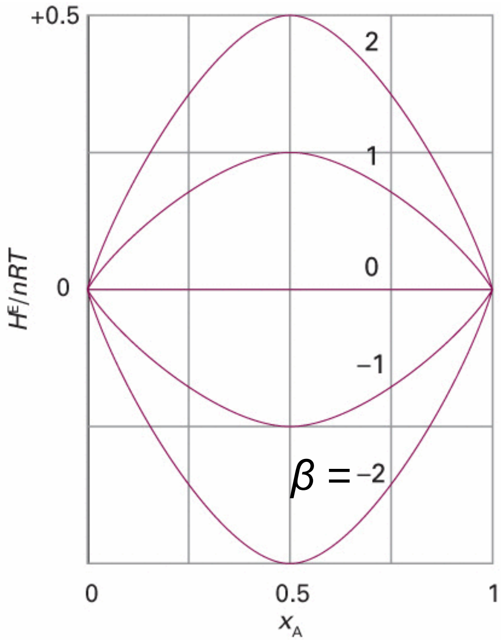
(Regular solution: $H^E \neq 0$) (Regular solution: $S^E = 0$)

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

Exess functions

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

Regular solution



$$-T \; \Delta_{mix}S \qquad = \qquad \Delta_{mix}G$$

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

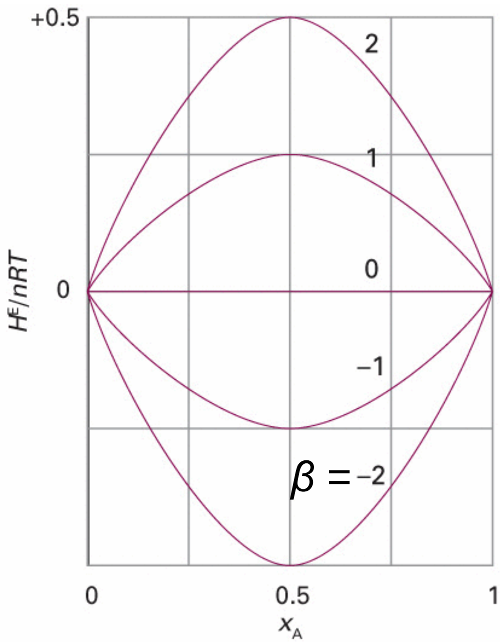
(Regular solution: $H^{E} \neq 0$)

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

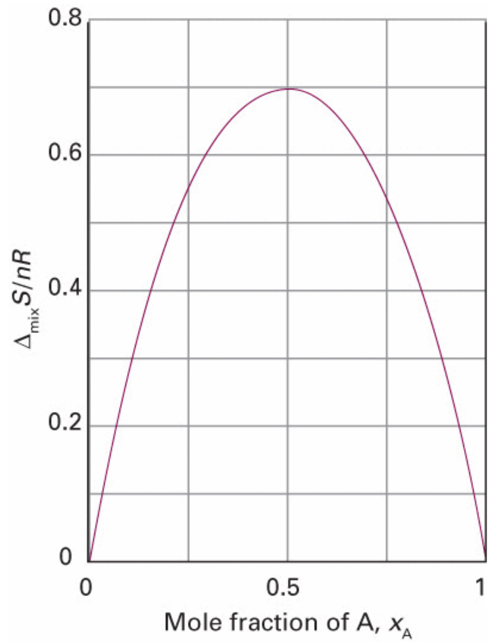
Exess functions

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

Regular solution



-T



=

$$\Delta_{mix}G$$

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

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

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

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

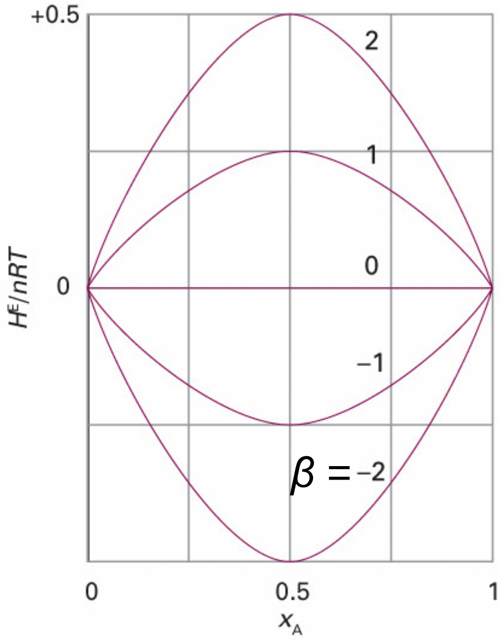
$$H^E = \Delta_{mix}H$$

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

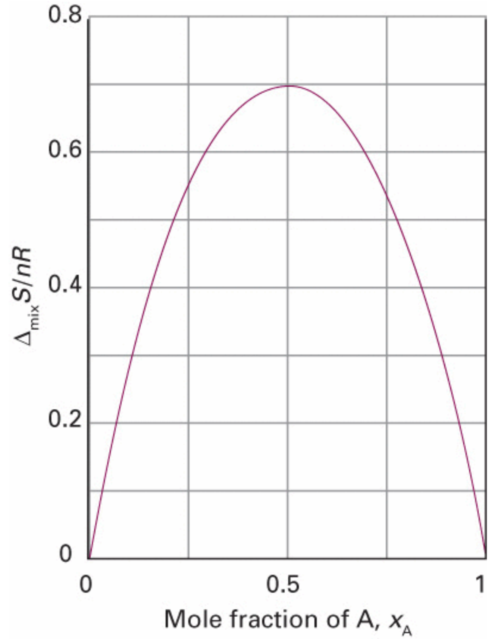
Exess functions

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

Regular solution



-T



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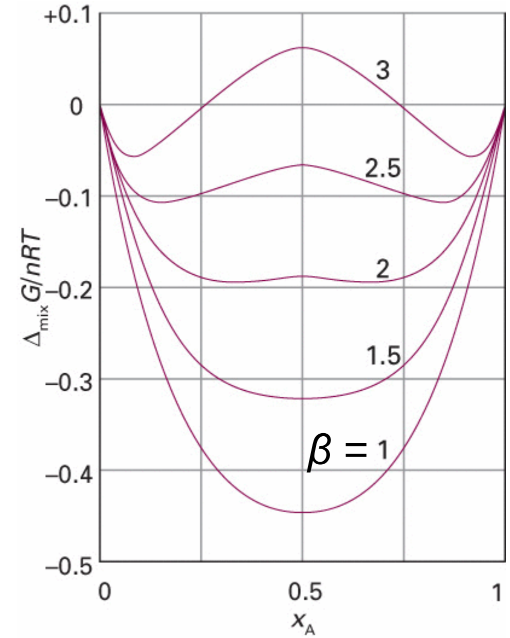


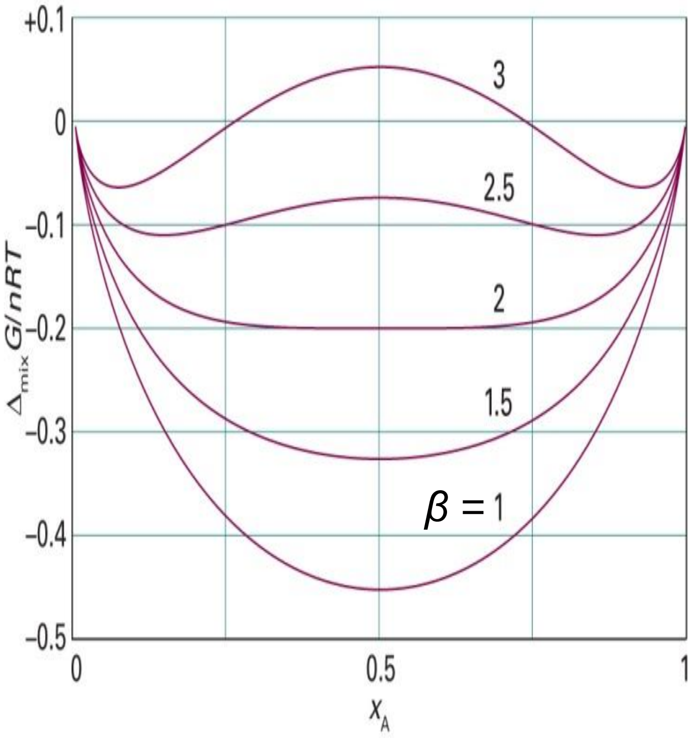
$$H^E = n\beta RT x_A x_B$$

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

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

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

Liquid-liquid separation for Regular solution



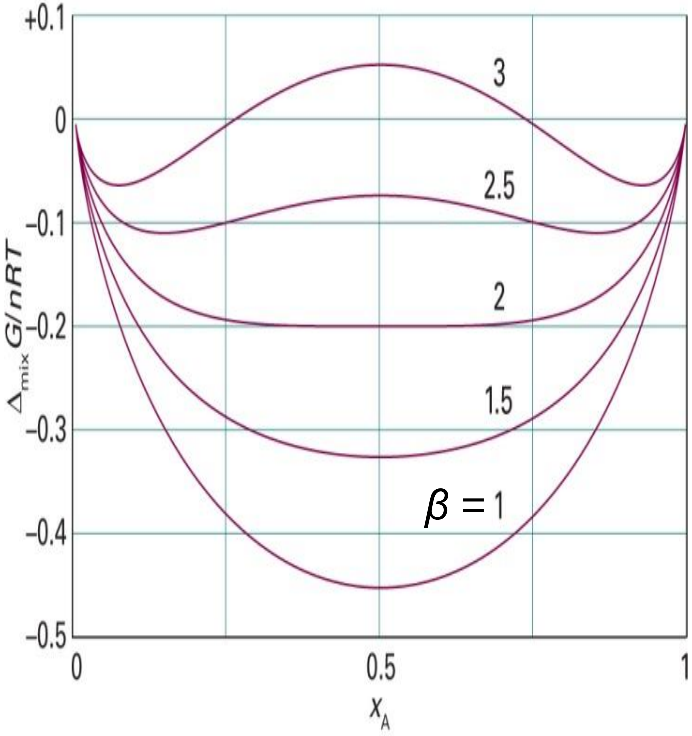
$$H^E = n\beta RT x_A x_B$$

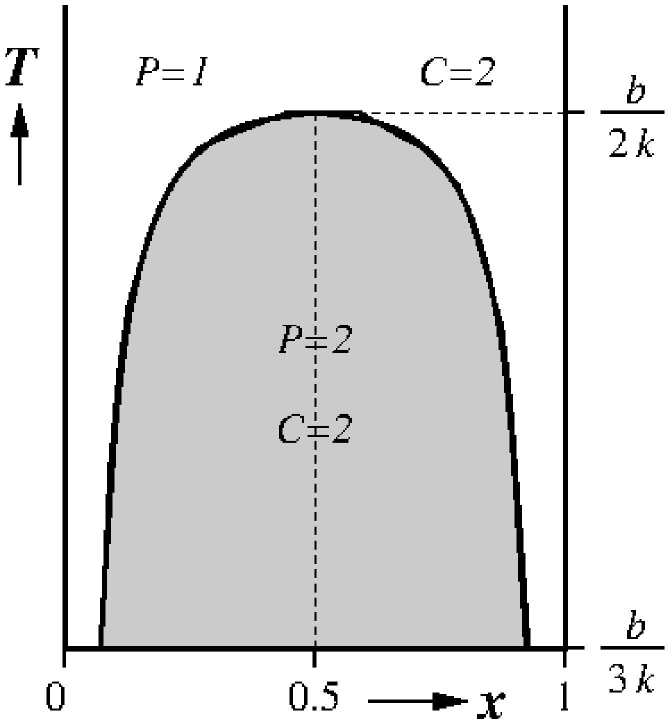
Model regular solution

$$\beta = \frac{b}{kT}$$

$$T = \frac{b}{\beta k}$$

Liquid-liquid separation for Regular solution





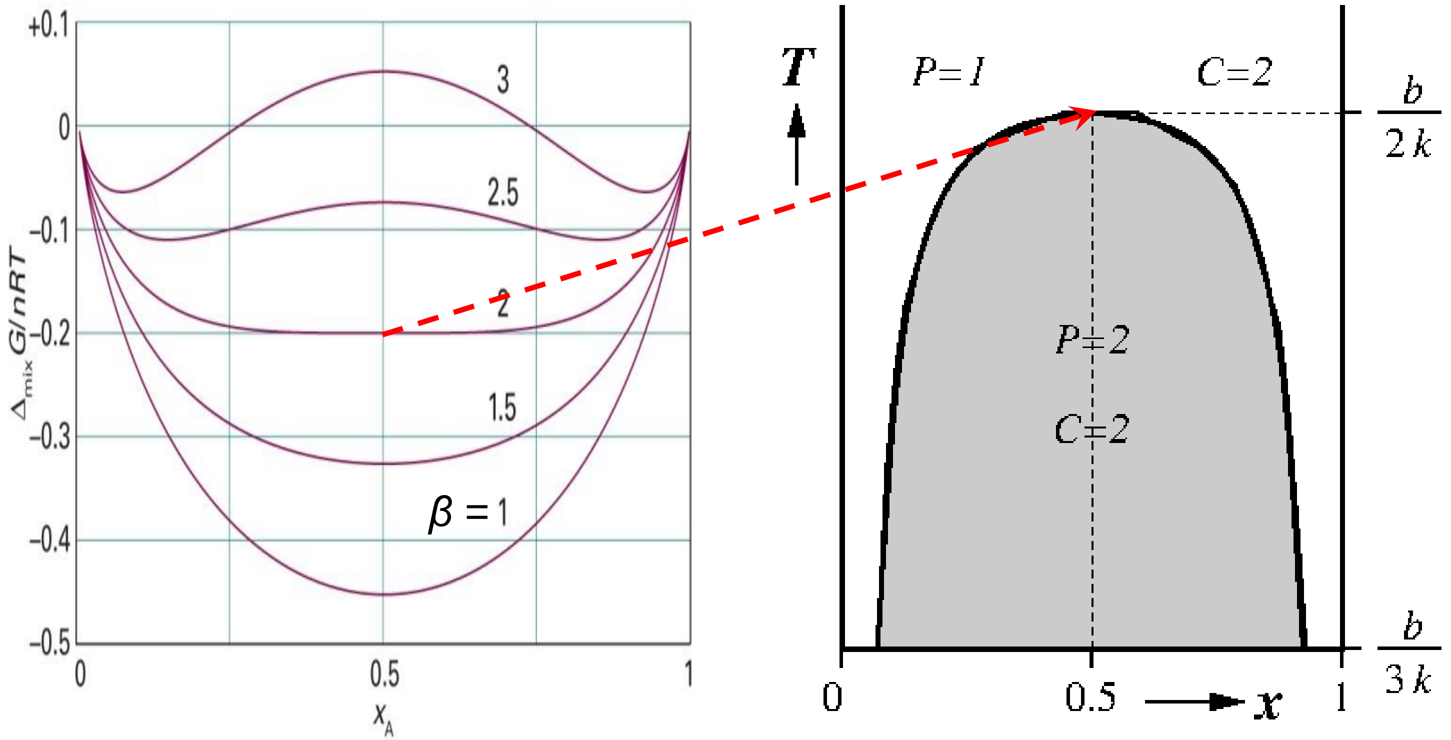
$$H^E = n\beta RT x_A x_B$$

Model regular solution

$$\beta = \frac{b}{kT}$$

$$T = \frac{b}{\beta k}$$

Liquid-liquid separation for Regular solution



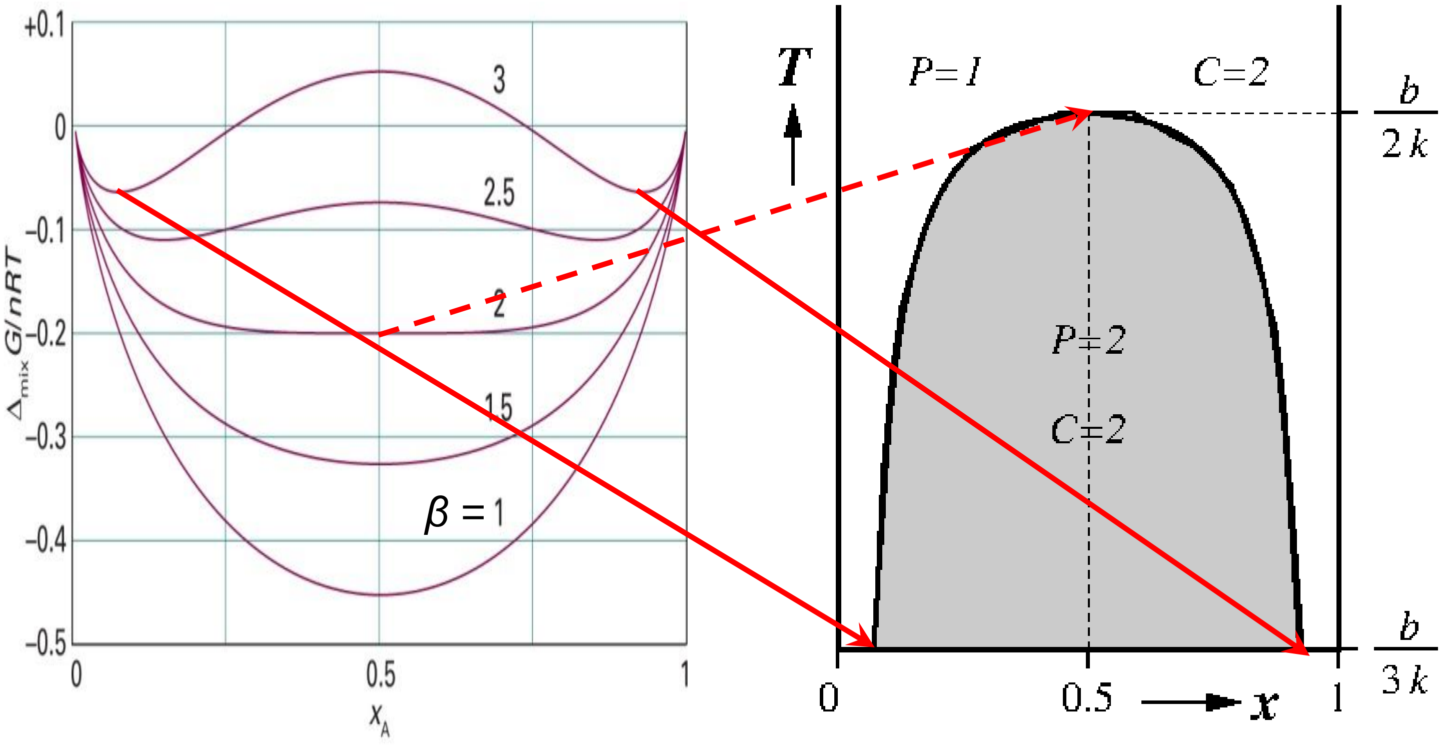
$$H^E = n\beta RT x_A x_B$$

Model regular solution

$$\beta = \frac{b}{kT}$$

$$T = \frac{b}{\beta k}$$

Liquid-liquid separation for Regular solution



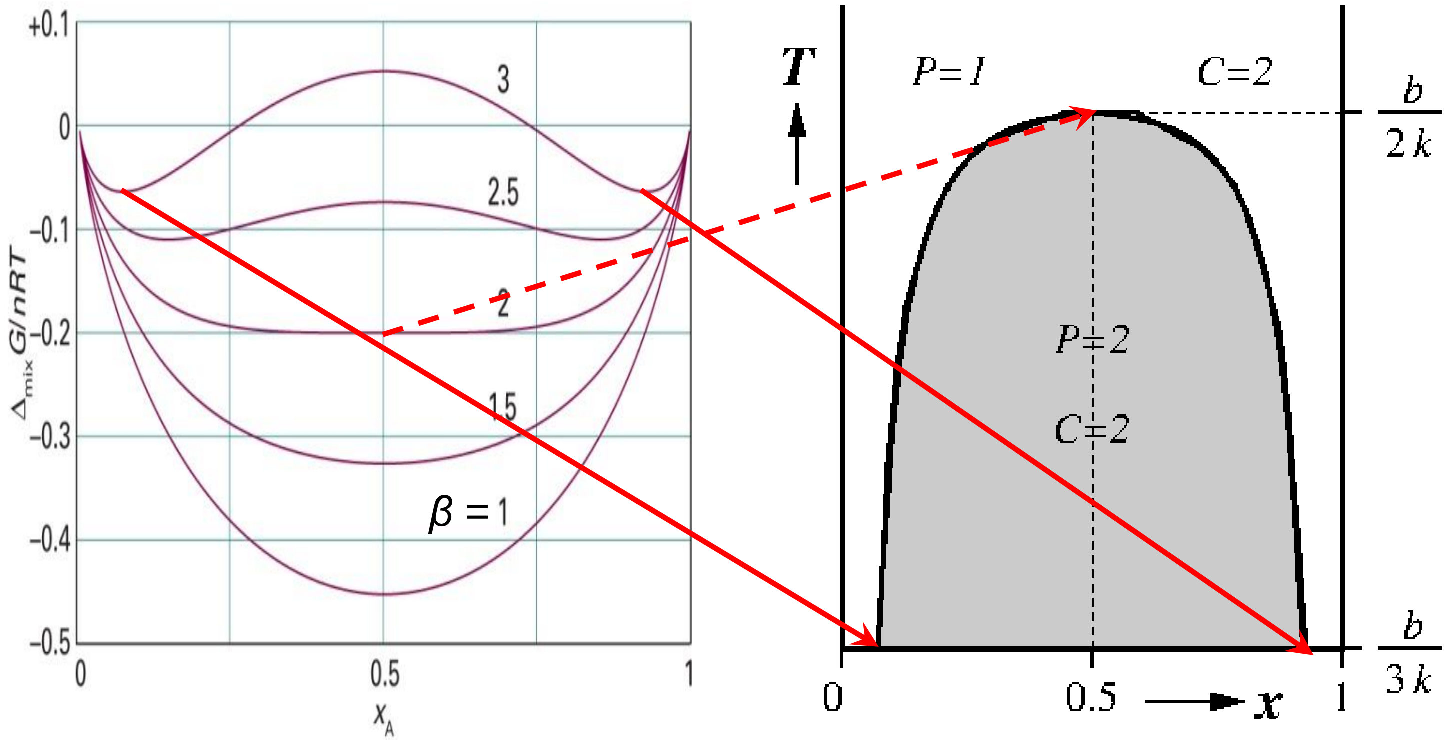
$$H^{E} = n\beta RTx_{A}x_{B}$$

Model regular solution

$$\beta = \frac{b}{kT}$$

$$T = \frac{b}{\beta k}$$

Liquid-liquid separation for Regular solution



Liquid-liquid separation

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

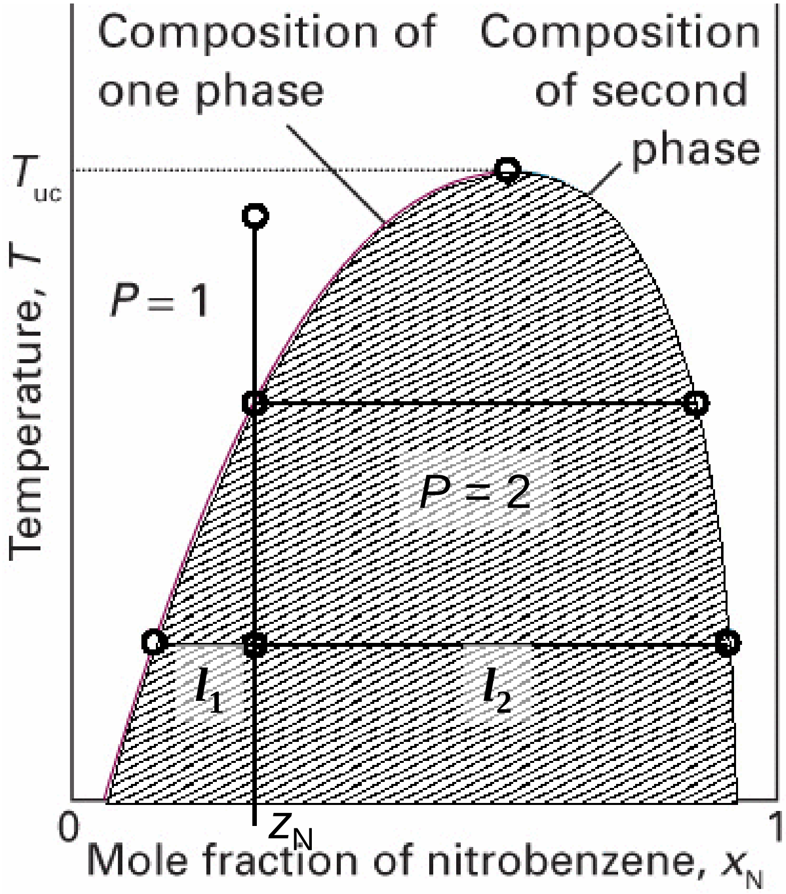
Model regular solution

$$\beta = \frac{b}{kT}$$

$$T = \frac{b}{\beta k}$$

Exercise 17

Liquid-liquid separation for quasi regular solution

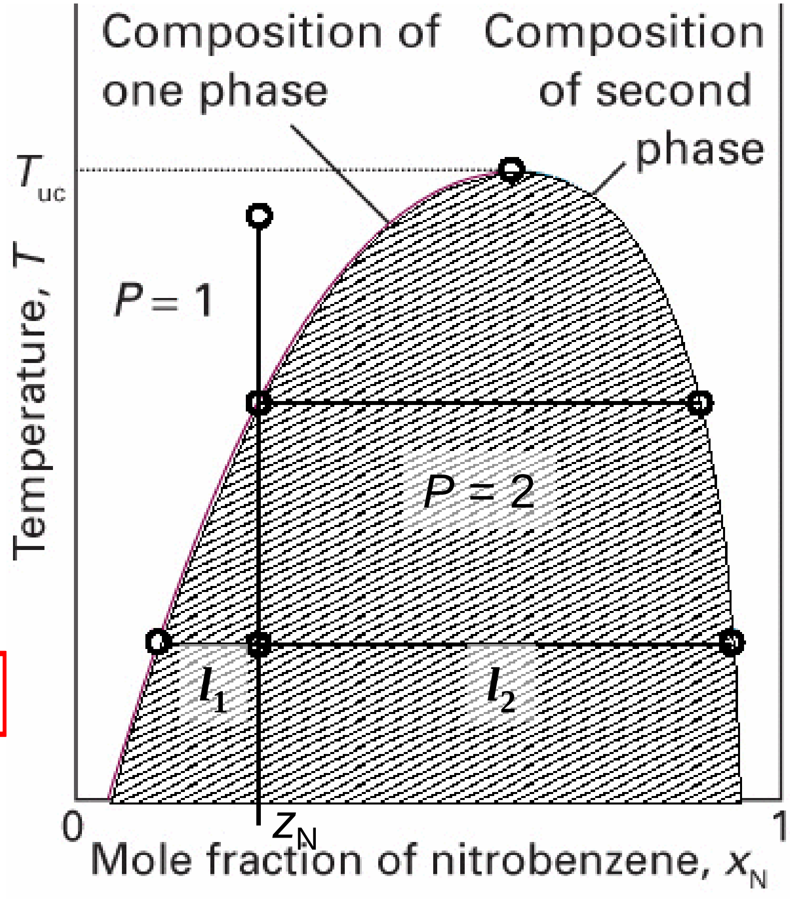


Nitrobenzene in hexane

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

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

Liquid-liquid separation for quasi regular solution



Nitrobenzene in hexane

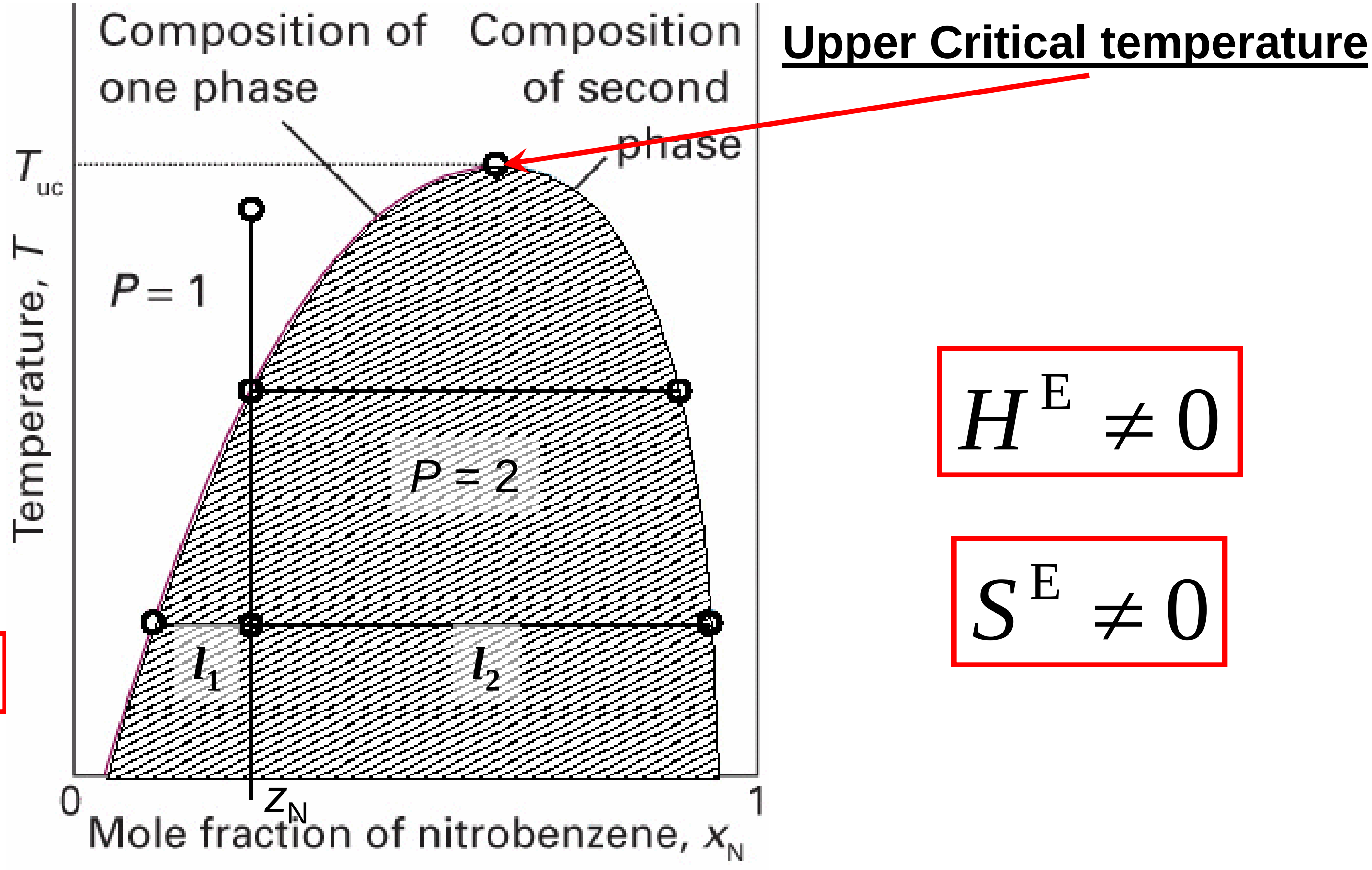
$$n_1 l_1 = n_2 l_2$$

Lever rule

$$H^E \neq 0$$

$$S^E \neq 0$$

Liquid-liquid separation for quasi regular solution



$$n_1 l_1 = n_2 l_2$$

Lever rule

$$H^E \neq 0$$

$$S^E \neq 0$$

Nitrobenzene in hexane