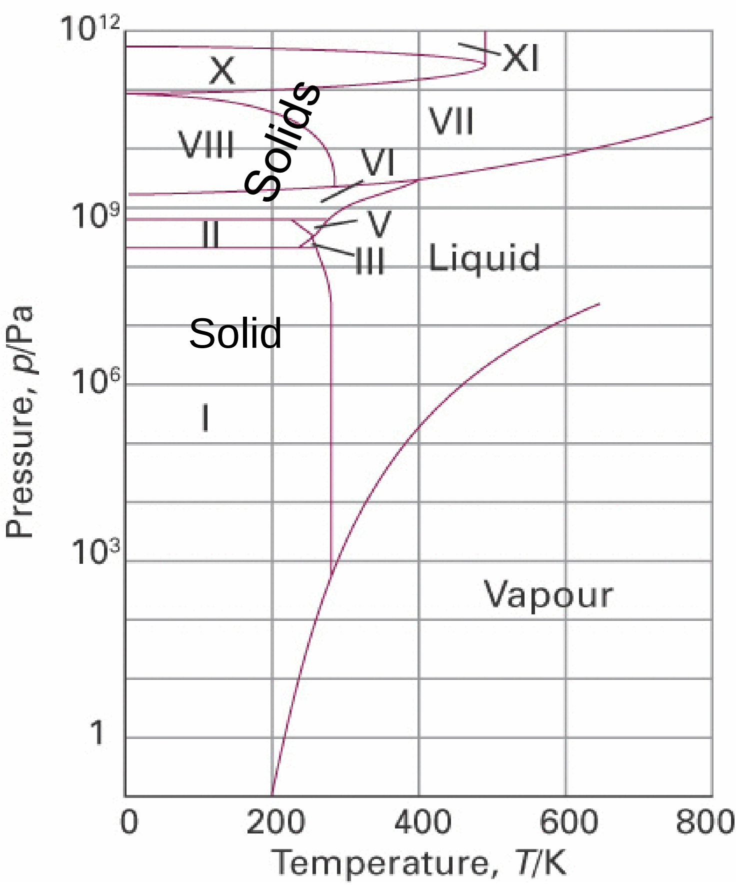
Summary of Lecture 2

Phase diagrams and phase transitions of unary systems



(**Equilibrium**) Phase Diagram H_2O

- Phase transitions
- Phase boundaries
- Phase transition temperature
- Melting point
- Boiling point
- Triple point
- Critical point
- Polymorphic forms

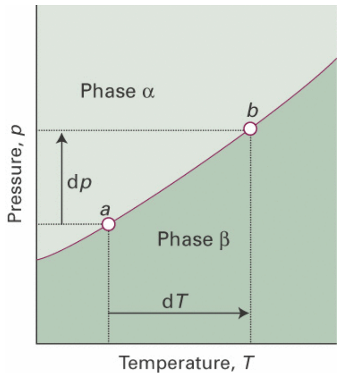
- Thermodynamics *vs* kinetics
- Metastable phases

Phase boundary lines in phase diagrams of unary systems

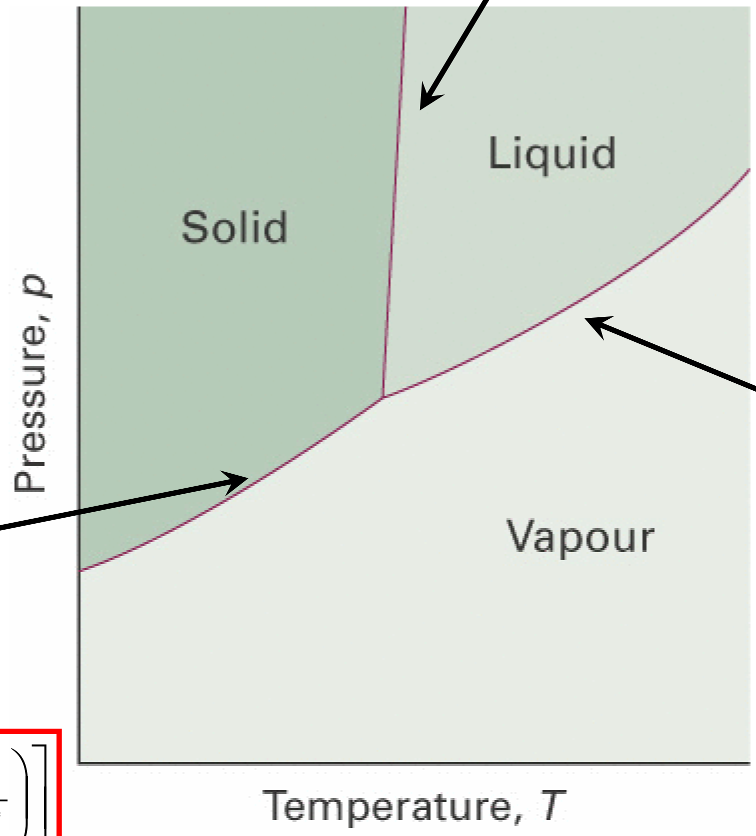
$$\frac{\mathrm{d}P}{\mathrm{d}T}=\frac{\Delta_{\mathrm{trs}}S}{\Delta_{\mathrm{trs}}V}=\frac{\Delta_{\mathrm{trs}}H}{T_{\mathrm{trs}}\Delta_{\mathrm{trs}}V}$$

Clapeyron

$$\frac{\mathrm{d}P}{\mathrm{d}T}=\frac{\Delta_{\mathrm{fus}}H}{T_{\mathrm{fus}}\Delta_{\mathrm{fus}}V}$$



$$P\approx P^{*}+\frac{\Delta_{\mathrm{fus}}H}{\Delta_{\mathrm{fus}}V}\ln\frac{T}{T^{*}}\approx P^{*}+\frac{\Delta_{\mathrm{fus}}H}{T^{*}\Delta_{\mathrm{fus}}V}\left(T-T^{*}\right)$$



$$\frac{\mathrm{d}P}{\mathrm{d}T}=\frac{\Delta_{\mathrm{vap}}H}{T_{\mathrm{vap}}\Delta_{\mathrm{vap}}V}$$

$$\frac{\mathrm{d}\ln P}{\mathrm{d}T}\approx\frac{\Delta_{\mathrm{vap}}H}{\mathrm{R}T^{2}}$$

$$P\approx P^{*}\exp\left[-\frac{\Delta_{\mathrm{vap}}H}{\mathrm{R}}\left(\frac{1}{T}-\frac{1}{T^{*}}\right)\right]$$

$$\frac{\mathrm{d}P}{\mathrm{d}T}=\frac{\Delta_{\mathrm{sub}}H}{T_{\mathrm{sub}}\Delta_{\mathrm{sub}}V}$$

$$\frac{\mathrm{d}\ln P}{\mathrm{d}T}\approx\frac{\Delta_{\mathrm{sub}}H}{\mathrm{R}T^{2}}$$

$$P\approx P^{*}\exp\left[-\frac{\Delta_{\mathrm{sub}}H}{\mathrm{R}}\left(\frac{1}{T}-\frac{1}{T^{*}}\right)\right]$$

Clausius-Clapeyron

Lecture 3: mixtures of compounds

Lecture 3: mixtures of compounds

Components (compounds): $\boxed{1,2,3,\ldots\ldots\ldots, C}$

Molarity (mol/L):

$$\boxed{c_i = \frac{\#\,\text{mol solute } i}{\text{volume } V \text{ solution}} = \frac{n_i}{V}}$$

Molality (mol/kg):

$$\boxed{b_i = \frac{\#\,\text{mol solute } i}{\text{mass } m \text{ solvent}} = \frac{n_i}{m}}$$

Mole fraction ():

$$\boxed{x_i = \frac{\#\,\text{mol solute } i}{\text{total }\#\,\text{mol in solution}} = \frac{n_i}{\sum_j n_j} = \frac{n_i}{n}}$$

$$\boxed{\sum_i x_i = \sum_i \frac{n_i}{n} = \frac{1}{n}\sum_i n_i = \frac{n}{n} = 1}$$

Phase diagrams of mixtures of compounds

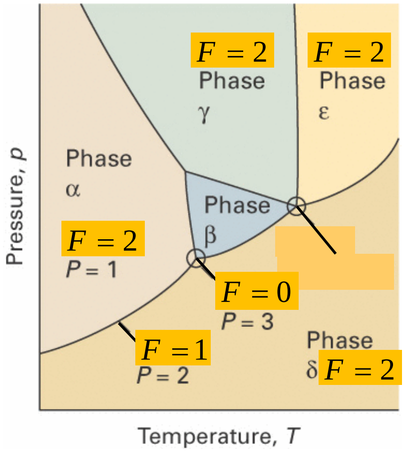
Gibbs Phase Rule $\boxed{F = C - P + 2}$

 # independent intensive variables: $\boxed{F}$

 # components (compounds): $\boxed{C}$

 # phases in mutual equilibrium: $\boxed{P}$

Unary system: C = 1:



$$\begin{cases} F = 2: P, T \text{ free to choose} \\ F = 1: P(T) \text{ or } T(P) \\ F = 0: P, T \text{ fixed values of compound} \end{cases}$$

Phase diagrams of mixtures of compounds

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

 # independent intensive variables: $\boxed{F}$

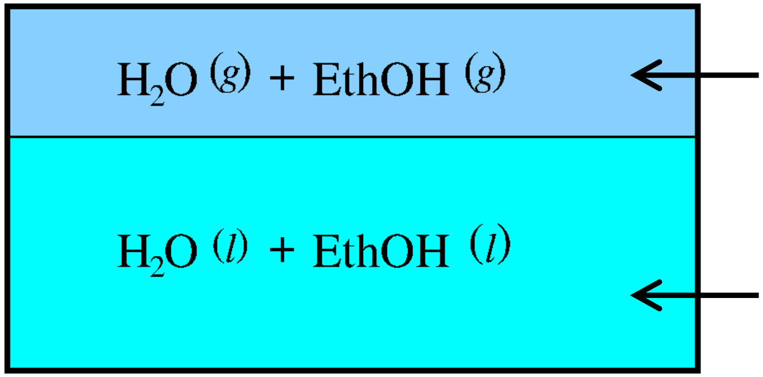
 # components (compounds): $\boxed{C}$

 # phases in mutual equilibrium: $\boxed{P}$

intensive variables T, P, x_i^α

$$\boxed{x_i^\alpha \equiv \frac{n_i^\alpha}{\sum_{j=1}^{C} n_j^\alpha}}$$

mole fraction of component *i* in phase *α*



$H_2O\,(g)$ + $EthOH\,(g)$ ← $T, P, x^g_{H_2O}, x^g_{EthOH}$

$H_2O\,(l)$ + $EthOH\,(l)$ ← $T, P, x^l_{H_2O}, x^l_{EthOH}$

Phase diagrams of mixtures of compounds

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

 # independent intensive variables: $\boxed{F}$

 # components (compounds): $\boxed{C}$

However:

$$\boxed{\sum_{i=1}^{C} x_i^\alpha = \sum_{i=1}^{C} \frac{n_i^\alpha}{n^\alpha} = \frac{1}{n^\alpha}\sum_{i=1}^{C} n_i^\alpha = \frac{n^\alpha}{n^\alpha} = 1} \Rightarrow \boxed{C-1}$$

free x values for each phase

 # phases in mutual equilibrium: $\boxed{P}$

⇒ **Total of free variables:** $\boxed{F = P\left(C-1\right) + \overset{P,T}{\overset{\downarrow}{2}}}$

Phase diagrams of mixtures of compounds

$C-1$ **independent x_i per phase**

***T,P* for all phases**

$$F = P(C-1)+2$$

However: Equilibrium conditions:

$$\mu_i^\alpha = \mu_i^\beta \text{ for } i = 1,\ldots, C \text{ and } \alpha,\beta = 1,\ldots,P$$

$$\begin{array}{ccccccc}
\mu_1^\alpha & = \mu_1^\beta & = \mu_1^\gamma & = & \ldots\ldots\ldots\ldots\ldots\ldots & = & \mu_1^P \\
\mu_2^\alpha & = \mu_2^\beta & = \mu_2^\gamma & = & \ldots\ldots\ldots\ldots\ldots\ldots & = & \mu_2^P \\
. & . & . & & & & . \\
. & . & . & & & & . \\
\mu_C^\alpha & = \mu_C^\beta & = \mu_C^\gamma & = & \ldots\ldots\ldots\ldots\ldots\ldots & = & \mu_C^P
\end{array}$$

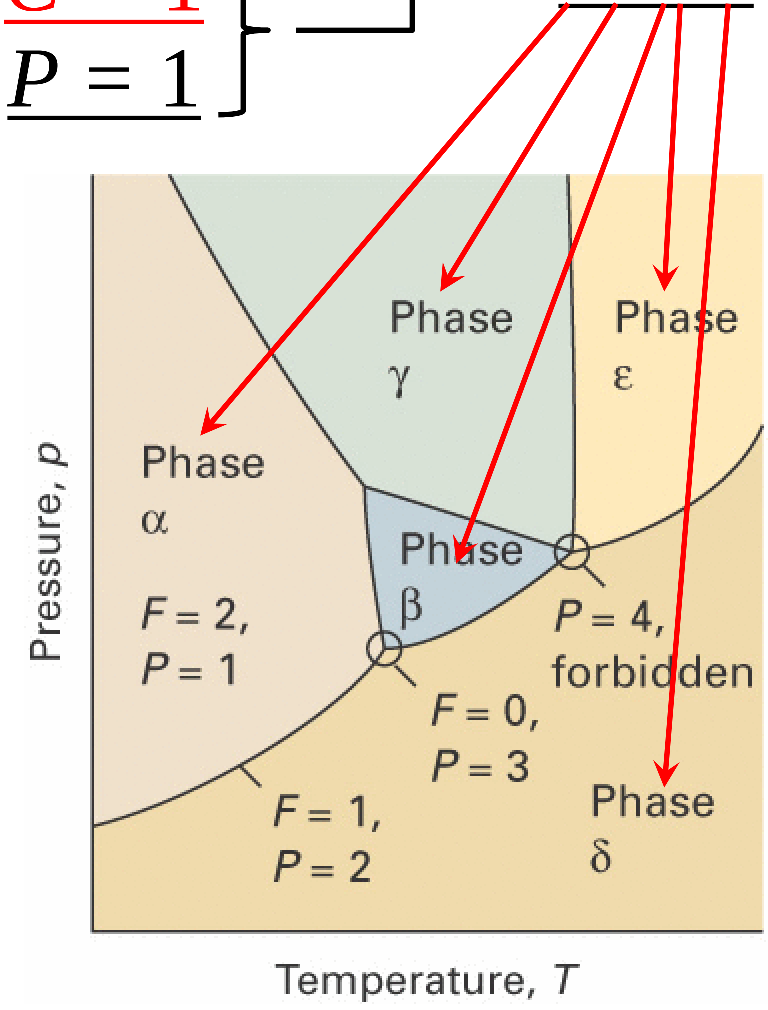
$(P-1)C$ conditions

$$F = P(C-1)+2-(P-1)C = C-P+2$$

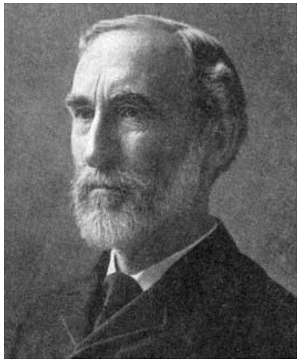
Gibbs phase rule $\boxed{F = C-P+2}$

Phase diagrams of unary systems

$$\left.\begin{array}{l}\underline{C = 1}\\ \underline{P = 1}\end{array}\right\} \rightarrow \underline{F = 2} \Rightarrow \boxed{P, T}$$



unary phase diagram



Gibbs phase rule

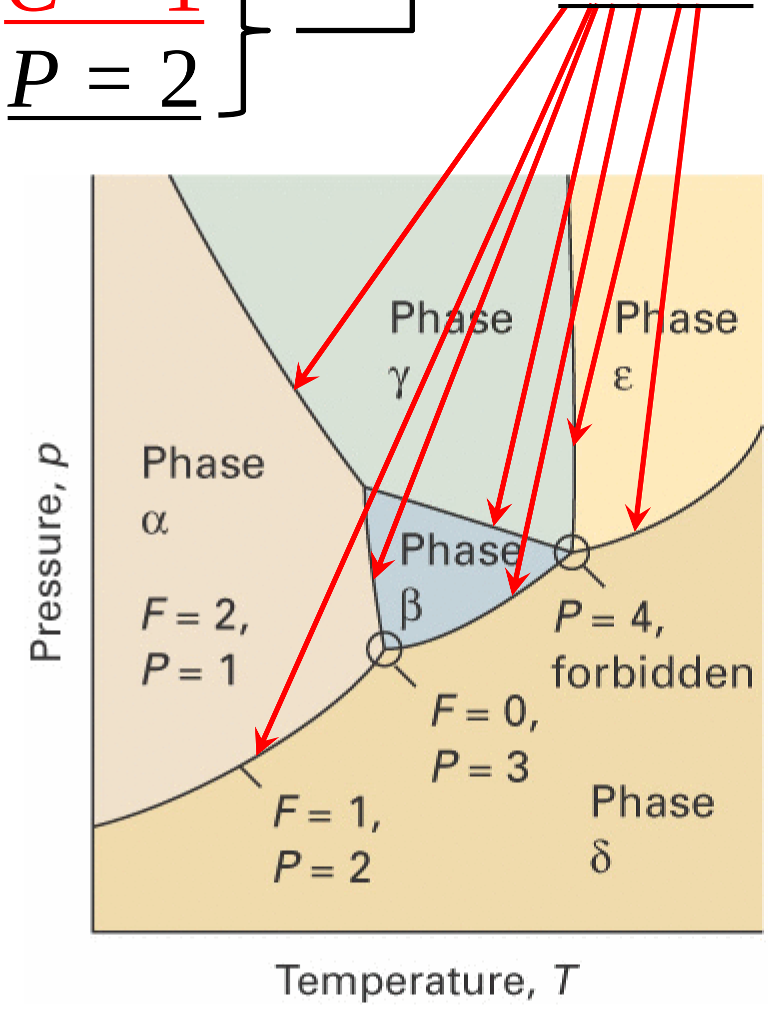
$$\boxed{F = C - P + 2}$$

F: # degrees of freedom
C: # components
P: # phases

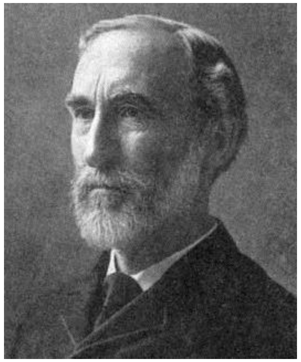
Phase diagrams of unary systems

$C = 1$
$P = 2$

$F = 1$ ⟹ $\boxed{P(T) \text{ or } T(P)}$



unary phase diagram

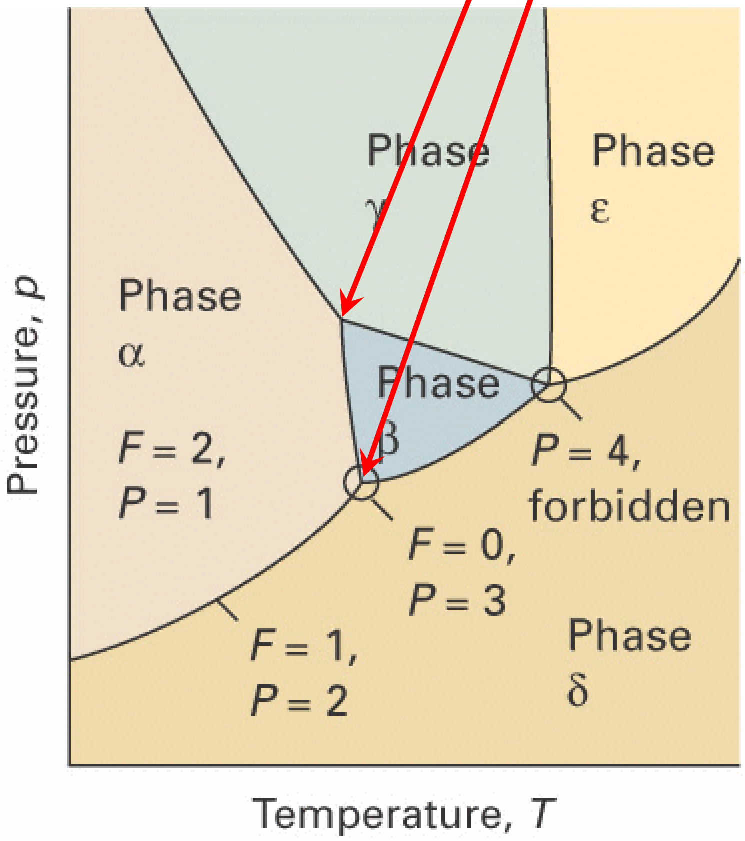


Gibbs phase rule

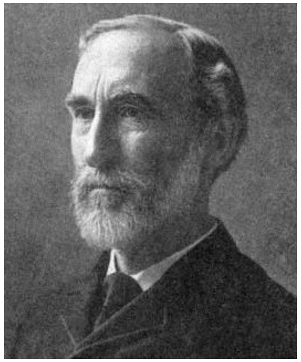
$$\boxed{F = C - P + 2}$$

Phase diagrams of unary systems

$$\left.\begin{array}{l} C = 1 \\ P = 3 \end{array}\right\} \longrightarrow F = 0 \Rightarrow \boxed{P, T \text{ fixed}}$$



unary phase diagram

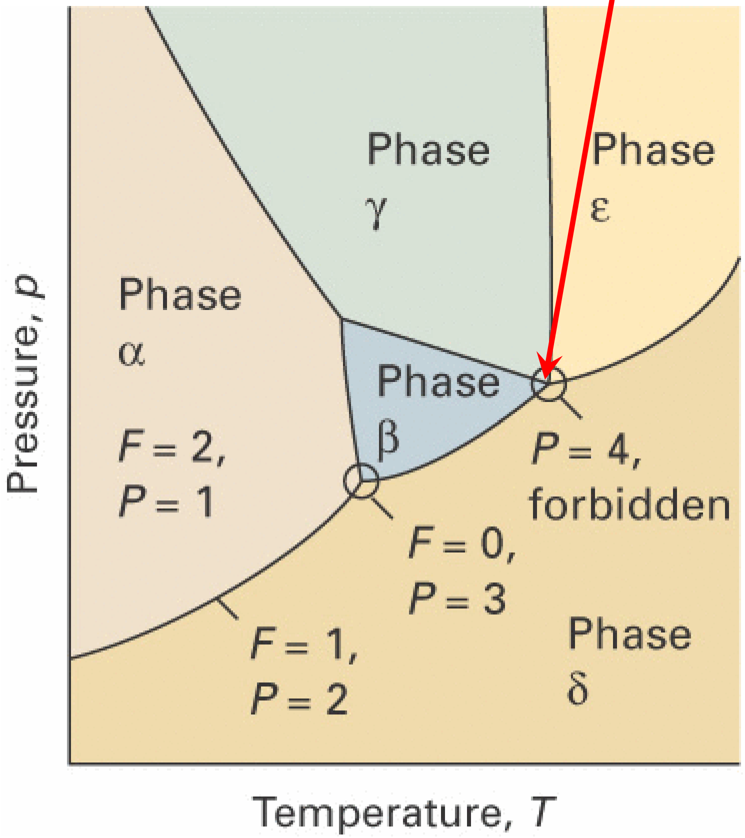


Gibbs phase rule

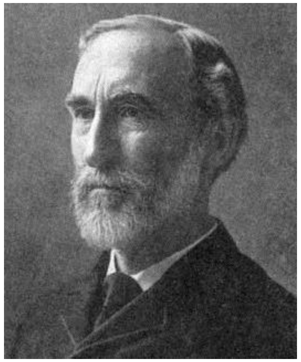
$$\boxed{F = C - P + 2}$$

Phase diagrams of unary systems

$$\cancel{\left.\begin{array}{l}\underline{C = 1}\\ \underline{P = 4}\end{array}\right\}} \rightarrow \cancel{\underline{F = -1}}$$



unary phase diagram

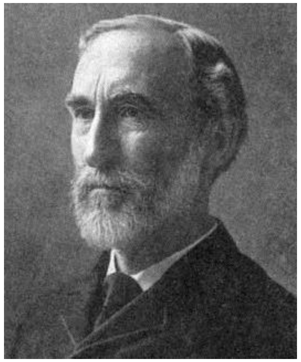


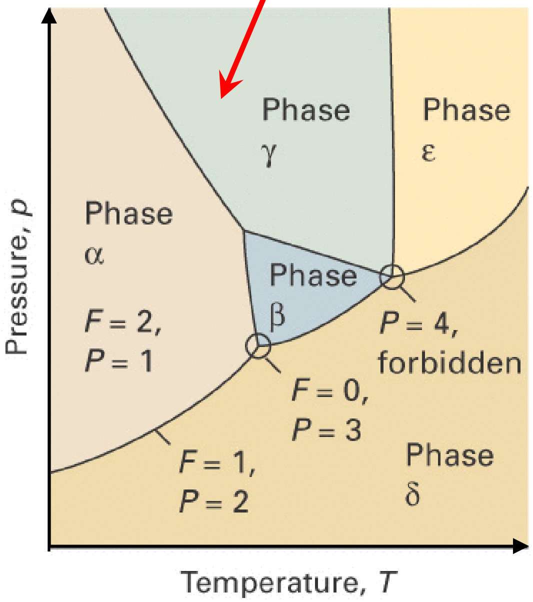
Gibbs phase rule

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

Phase diagrams of binary systems

$$\left.\begin{array}{l}\underline{C = 2}\\ \underline{P = 1}\end{array}\right\} \Rightarrow \underline{F = 3}$$



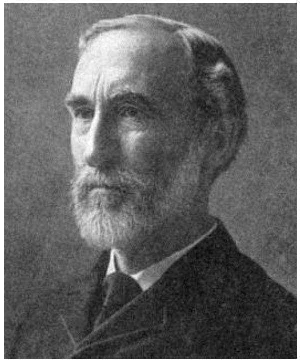


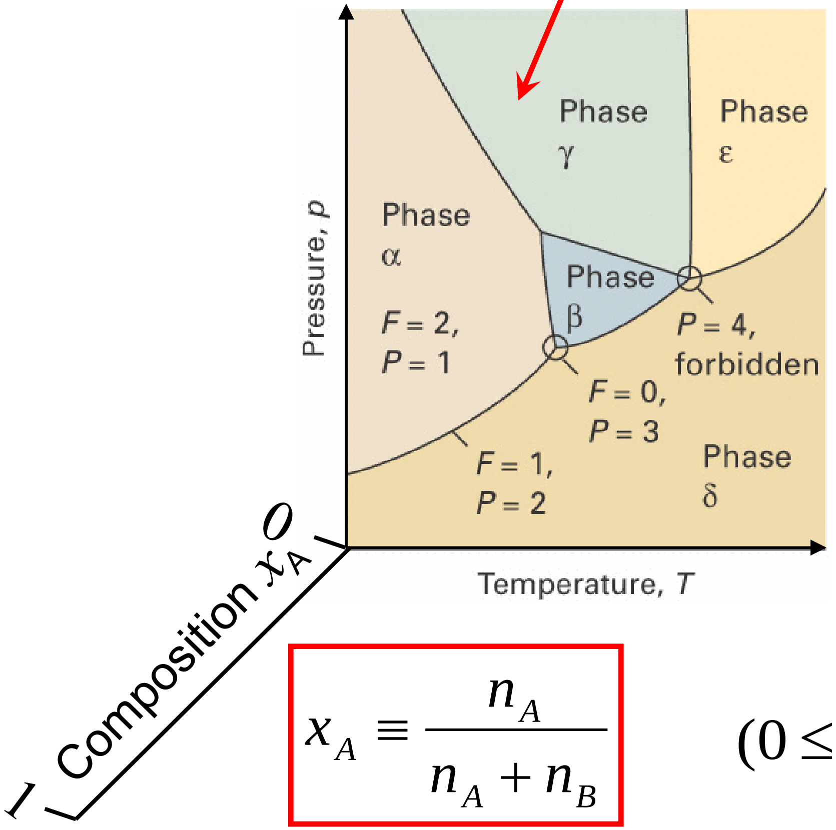
Gibbs phase rule

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

Phase diagrams of binary systems

$$\left.\begin{array}{l} \underline{C = 2} \\ \underline{P = 1} \end{array}\right\} \Rightarrow \underline{F = 3}$$





Gibbs phase rule

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

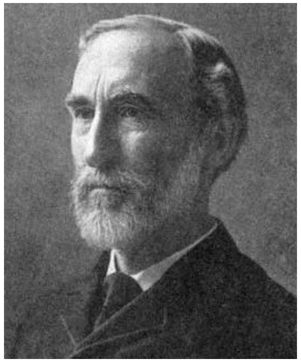
$$\boxed{x_A \equiv \frac{n_A}{n_A + n_B}}$$

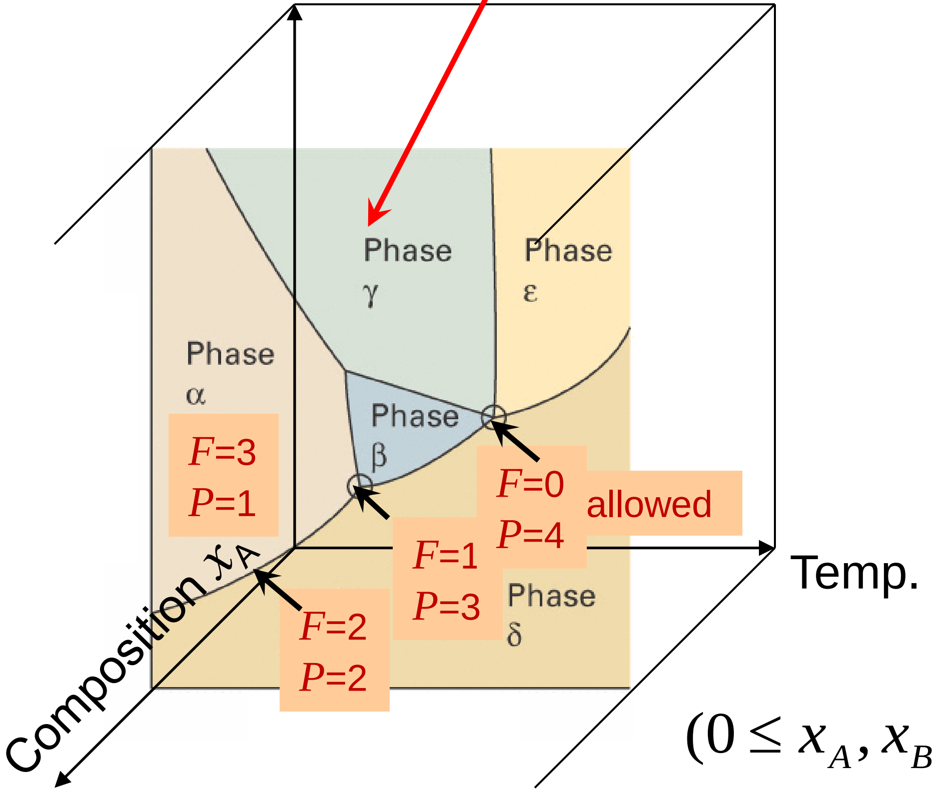
$$(0 \le x_A, x_B \le 1)$$

$$\boxed{x_A + x_B = 1}$$

Phase diagrams of binary systems

$$\left.\begin{array}{l} \underline{C = 2} \\ \underline{P = 1} \end{array}\right\} \Rightarrow \underline{F = 3}$$





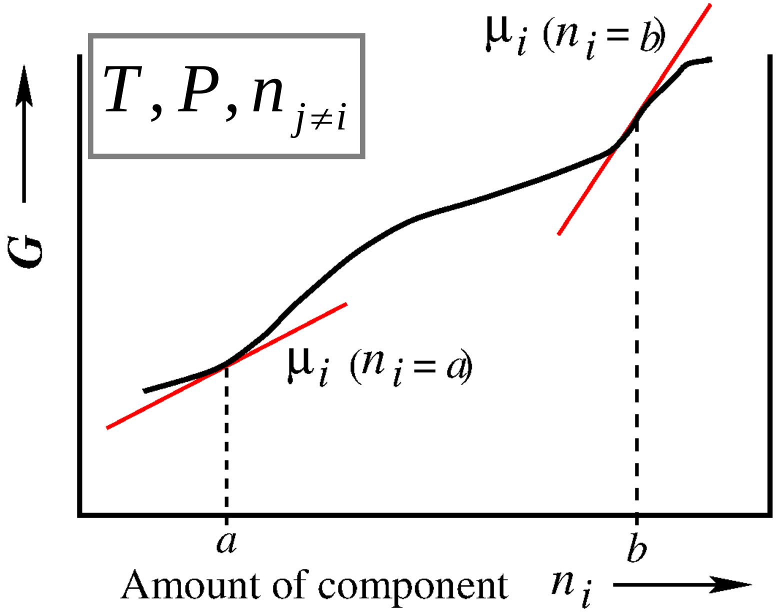
Gibbs phase rule

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

$$(0 \le x_A, x_B \le 1) \qquad \boxed{x_A + x_B = 1}$$

Partial molar quantities in mixtures

The chemical potential of a component *i* in mixtures (Study guide p.11-13)



Partial molar quantities in mixtures

The chemical potential of a component *i* in mixtures

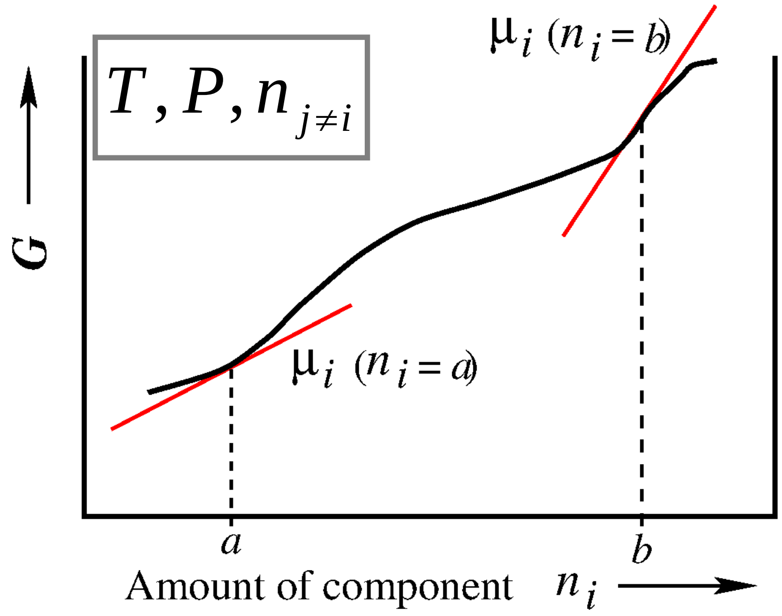
(Study guide p.11-13)

mixture → $\boxed{dn_i \neq 0}$

$$\boxed{dG = -SdT + VdP + \sum_i \mu_i dn_i}$$

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

$$\boxed{\mu_i \equiv \mu_i^{\Theta} + RT \ln a_i}$$



a_i: the activity of component *i* in the mixture

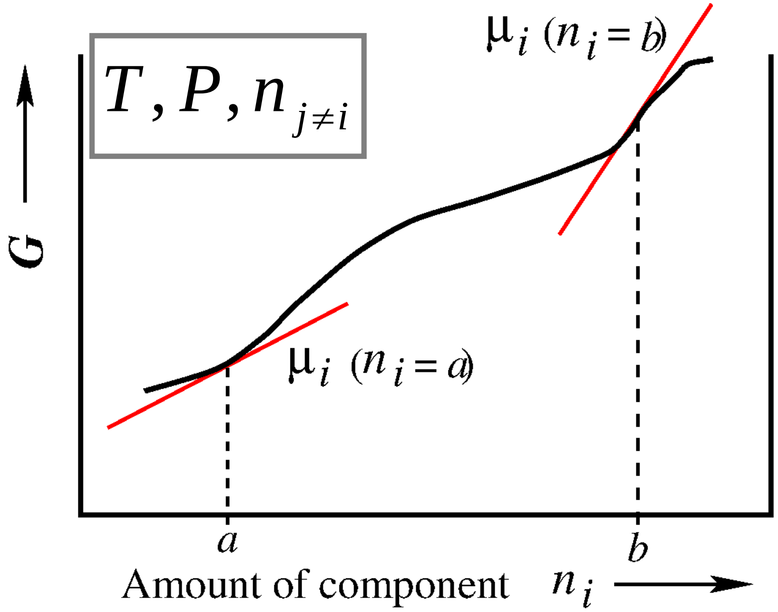
Equilibrium *P* phases $\boxed{\mu_i^{\alpha} = \mu_i^{\beta} = \ldots}$ $\left\{ \begin{array}{l} \textbf{phases } \alpha, \beta, \ldots \\ \textbf{components } i \end{array} \right.$

Partial molar quantities: Chemical potential

The chemical potential of a component *i* in mixtures

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

$$\mu_i \equiv \mu_i^{\Theta} + RT\ln a_i$$



$$G\Big|_{P,T}^{\alpha} = \mu_A^{\alpha} n_A^{\alpha} + \mu_B^{\alpha} n_B^{\alpha} + \cdots = \sum_i \mu_i^{\alpha} n_i^{\alpha}$$

binary systems $$G\Big|_{P,T}^{\alpha} = \mu_A^{\alpha} n_A^{\alpha} + \mu_B^{\alpha} n_B^{\alpha}$$ **for phase α**

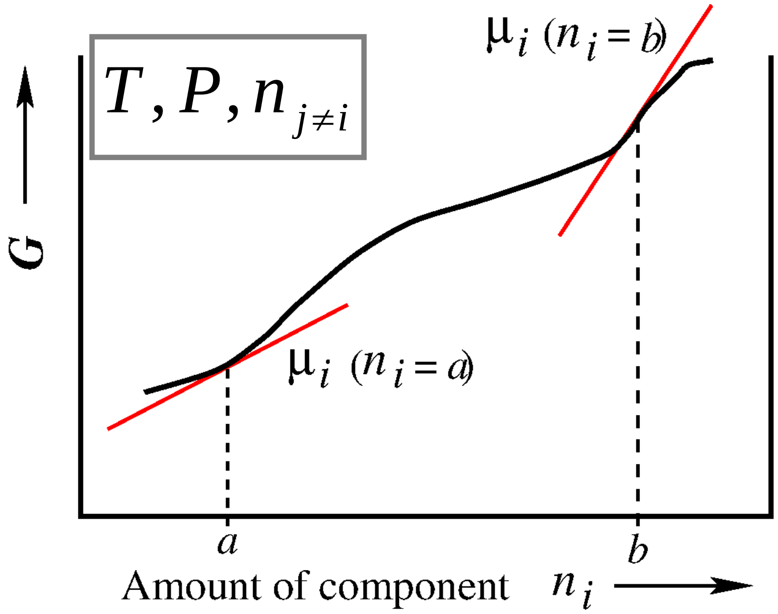
(Study guide p.13)

Partial molar quantities: Chemical potential

The chemical potential of a component *i* in mixtures

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

$$\boxed{\mu_i \equiv \mu_i^\Theta + RT\ln a_i}$$



Standard state Θ for component *i*

$$\left\{\begin{array}{l}\boxed{P^\Theta \equiv 1\,\mathrm{bar}}\\ \boxed{a_i \equiv 1}\\ \boxed{\text{component } i \text{ is pure}}\end{array}\right.$$

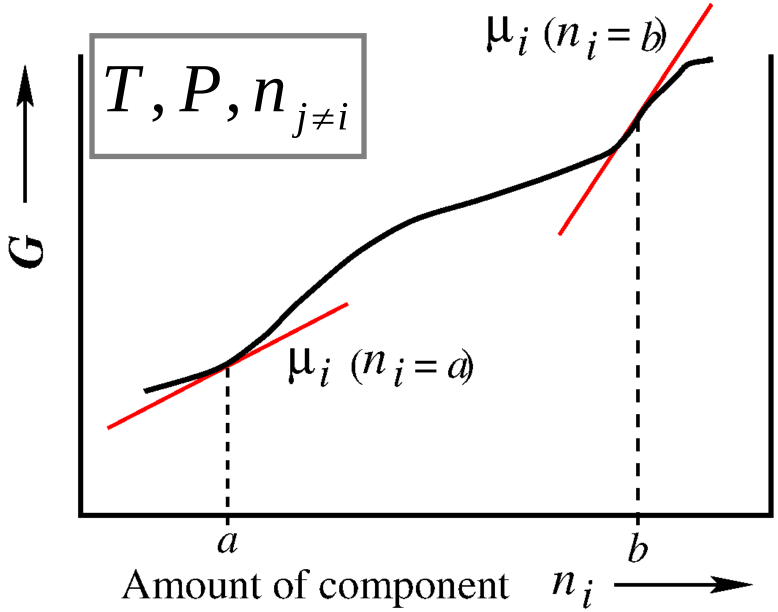
Note: there is no T^Θ

Partial molar quantities: Chemical potential

μ_i: the chemical potential is a partial molar quantity

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

$$\boxed{\mu_i \equiv \mu_i^{\Theta} + RT\ln a_i}$$



Perfect gases $\boxed{a_i = \frac{P_i}{P^{\Theta}}}$ $\Rightarrow$ $\boxed{\mu_i = \mu_i^{\Theta} + RT\ln\frac{P_i}{P^{\Theta}}}$

For pure liquids $\boxed{a_l \approx 1}$ $\Rightarrow$ $\boxed{\mu_l \approx \mu_l^{\Theta}}$

For pure solids $\boxed{a_s \approx 1}$ $\Rightarrow$ $\boxed{\mu_s \approx \mu_s^{\Theta}}$

Partial molar quantities: Chemical potential

Activity and activity coefficient

$$\boxed{\mu_i \equiv \mu_i^{\Theta} + RT \ln a_i = \mu_i^{\Theta} + RT \ln x_i + RT \ln \gamma_i^{(x)}}$$

(Mole fraction example)

Mole fraction
(-)

$$x_i = \frac{\#\,\mathrm{mol\ solute}\ i}{\mathrm{total\ \#\ mol\ in\ solution}} = \frac{n_i}{n}$$

$$a_i = \gamma_i^{(x)} x_i$$

Molarity
(mol/L)

$$c_i = \frac{\#\,\mathrm{mol\ solute}\ i}{\mathrm{volume}\ V\ \mathrm{solution}} = \frac{n_i}{V}$$

$$a_i = \gamma_i^{(c)} \frac{c_i}{c^{\Theta}}$$

$$c^{\Theta} \equiv 1\,\mathrm{mol/L}$$

Molality
(mol/kg)

$$b_i = \frac{\#\,\mathrm{mol\ solute}\ i}{\mathrm{mass}\ m\ \mathrm{solvent}} = \frac{n_i}{m}$$

$$a_i = \gamma_i^{(b)} \frac{b_i}{b^{\Theta}}$$

$$b^{\Theta} \equiv 1\,\mathrm{mol/kg}$$

example

$$\boxed{\mathrm{pH} \equiv -\log a_{\mathrm{H}^+} = -\log \frac{c_{\mathrm{H}^+}}{c^{\Theta}} - \log \gamma_{\mathrm{H}^+}^{(c)}}$$

Partial molar quantities: Partial molar volume

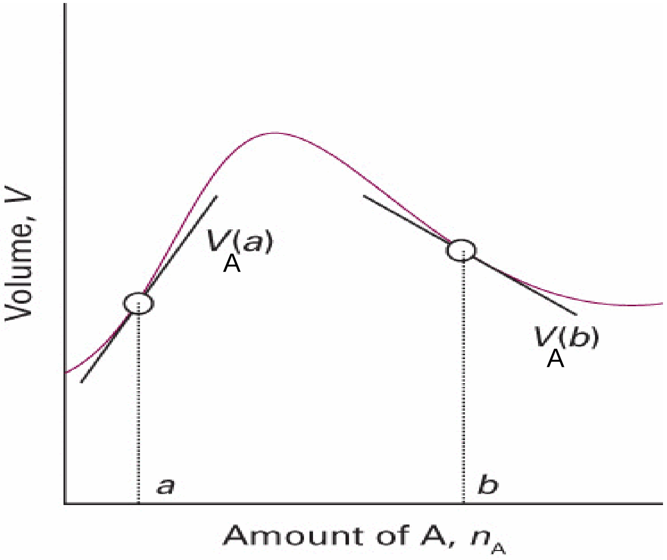
The partial molar volume of a component *i* in mixtures

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

binary systems

$$V^{\alpha}_{P,T} = V^{\alpha}_{\mathrm{A}}\mathrm{n}^{\alpha}_{\mathrm{A}} + V^{\alpha}_{\mathrm{B}}\mathrm{n}^{\alpha}_{\mathrm{B}}$$

for phase α



$$V^{\alpha}_{\mathrm{m},P,T} = \frac{V^{\alpha}_{P,T}}{n^{\alpha}} = V^{\alpha}_{\mathrm{A}}x^{\alpha}_{\mathrm{A}} + V^{\alpha}_{\mathrm{B}}x^{\alpha}_{\mathrm{B}}$$

for each phase

$$V_{\mathrm{m},P,T} = V_{\mathrm{A}}x_{\mathrm{A}} + V_{\mathrm{B}}x_{\mathrm{B}}$$

(molar volume)

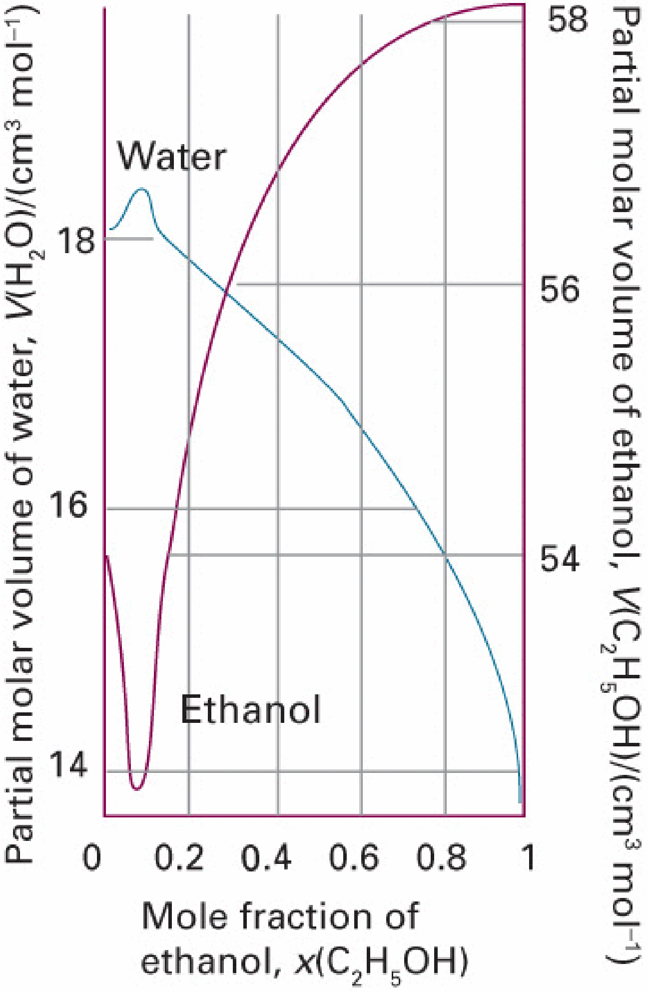
Exercise 10

Partial molar quantities: Partial molar volume

The partial molar volumes of an Ethanol/H_2O mixture

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

Eth. and H_2O mix well in liquid phase



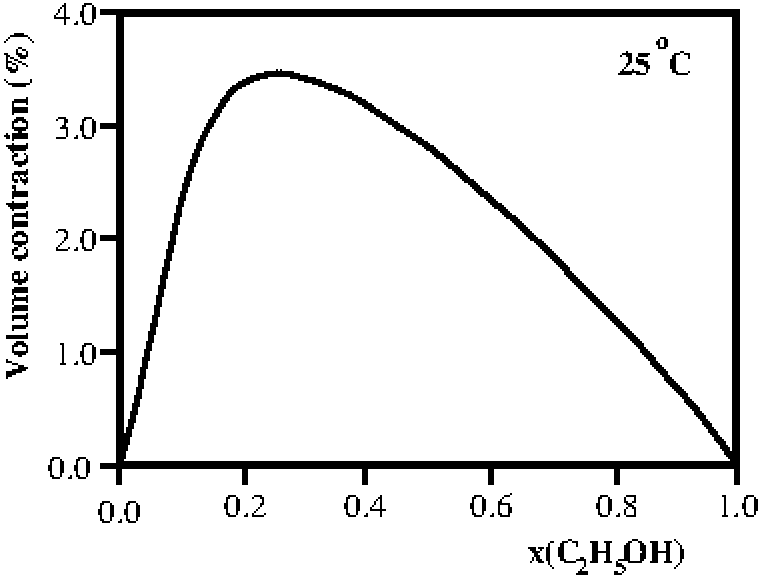
binary system $\boxed{V^l_{P,T} = V^l_{\text{Eth}}\,\text{n}^l_{\text{Eth}} + V^l_{H_2O}\,\text{n}^l_{H_2O}}$ **in liquid phase**

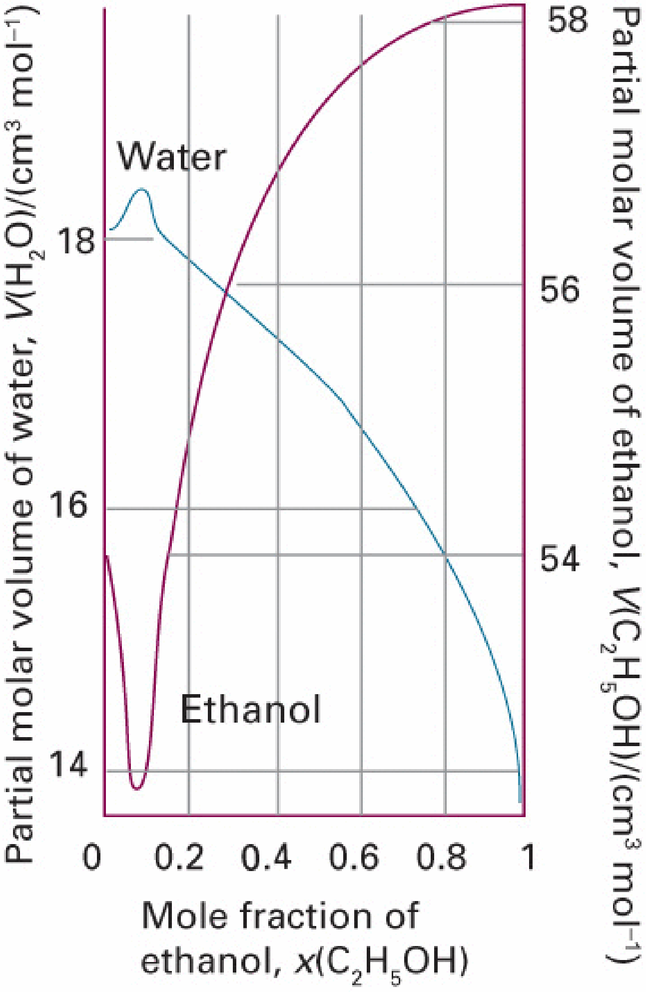
Partial molar quantities: Partial molar volume

The partial molar volumes of an Ethanol/H_2O mixture

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

Eth. and H_2O mix well in liquid phase





binary system $\boxed{V^l_{P,T} = V^l_{\mathrm{Eth}}\, \mathrm{n}^l_{\mathrm{Eth}} + V^l_{\mathrm{H_2O}}\, \mathrm{n}^l_{\mathrm{H_2O}}}$ **in liquid phase**

Partial molar quantities: Gibbs-Duhem equation

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

$$V\Big|_{T,P} = V_\mathrm{A} n_\mathrm{A} + V_\mathrm{B} n_\mathrm{B}$$

$$\mathrm{d}V\Big|_{T,P} = V_\mathrm{A}\mathrm{d}n_\mathrm{A} + V_\mathrm{B}\mathrm{d}n_\mathrm{B}$$

$$\mathrm{d}V\Big|_{T,P} = V_\mathrm{A}\mathrm{d}n_\mathrm{A} + V_\mathrm{B}\mathrm{d}n_\mathrm{B} + n_\mathrm{A}\mathrm{d}V_\mathrm{A} + n_\mathrm{B}\mathrm{d}V_\mathrm{B}$$

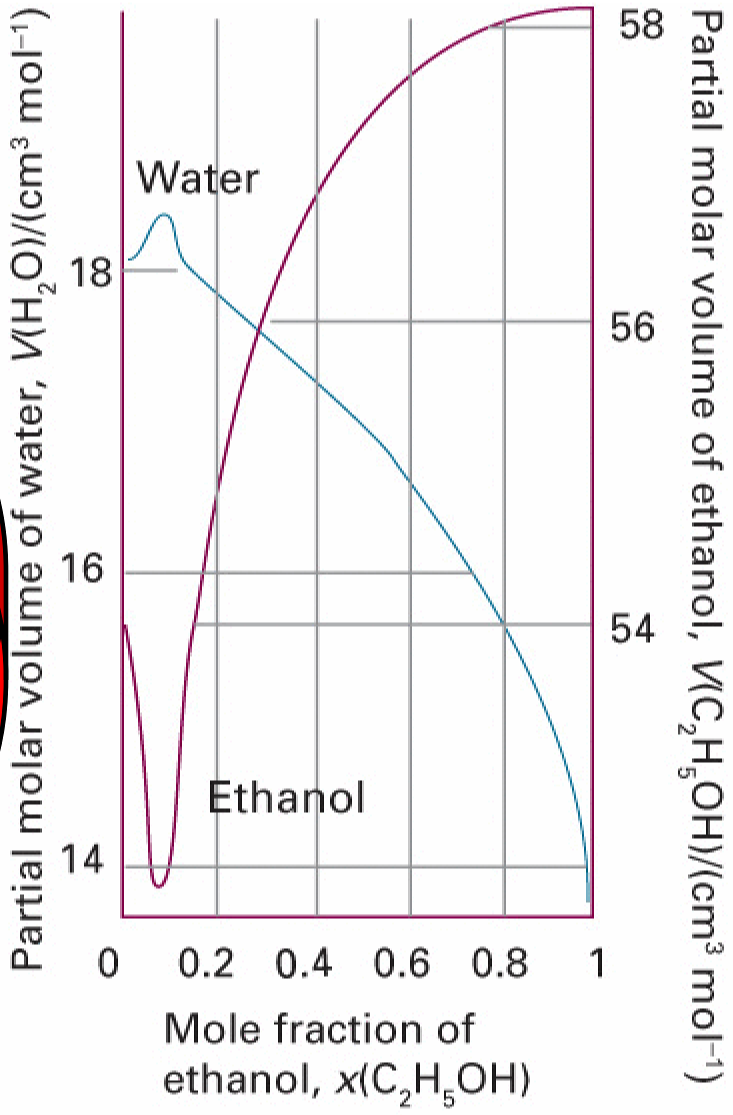
$$\sum_i n_i \mathrm{d}V_i = 0$$

$$0 = n_\mathrm{A}\mathrm{d}V_\mathrm{A} + n_\mathrm{B}\mathrm{d}V_\mathrm{B}$$

Gibbs-Duhem equation

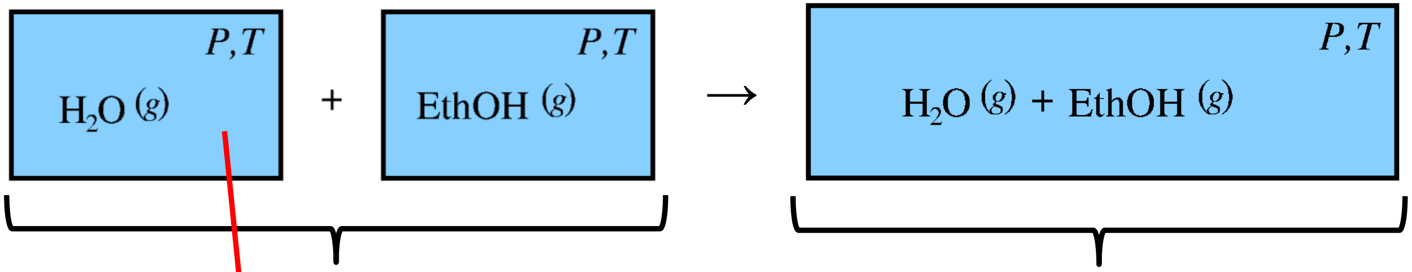
$$\sum_i n_i \mathrm{d}\mu_i = 0$$

(for any state function)



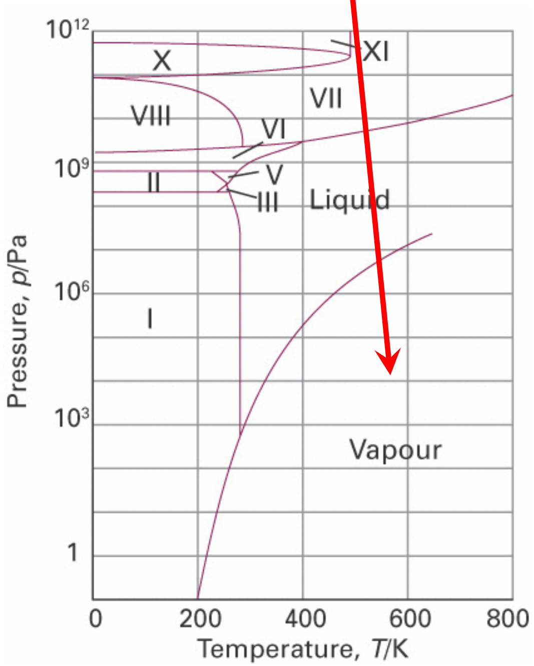
Mixing processes of perfect gases:binary mixture

The process of mixing two components @ *P,T* in gas phase



P,T — H_2O (g) + P,T — EthOH (g) → P,T — H_2O (g) + EthOH (g)

initial pure compounds **final mixture**



μ is a partial molar quantity of G, so:

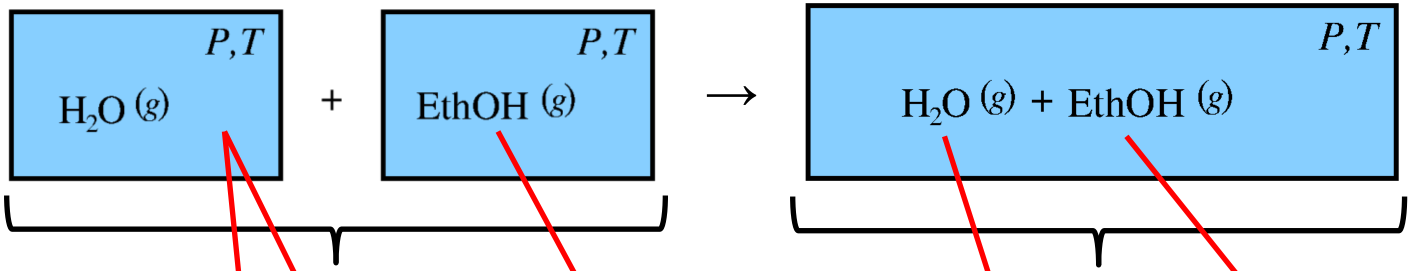
$$\boxed{G\Big|_{P,T}^{g} = \sum_i \mu_{i,g} n_{i,g} = \mu_{\mathrm{A},g} n_{\mathrm{A},g} + \mu_{\mathrm{B},g} n_{\mathrm{B},g}}$$

$$\boxed{\mu_{i,g} = \mu^{\Theta}_{i,g} + RT \ln a_{i,g}}$$

Unary phase diagram: $P = 1$

Mixing processes of perfect gases:binary mixture

The process of mixing two components @ P,T in gas phase



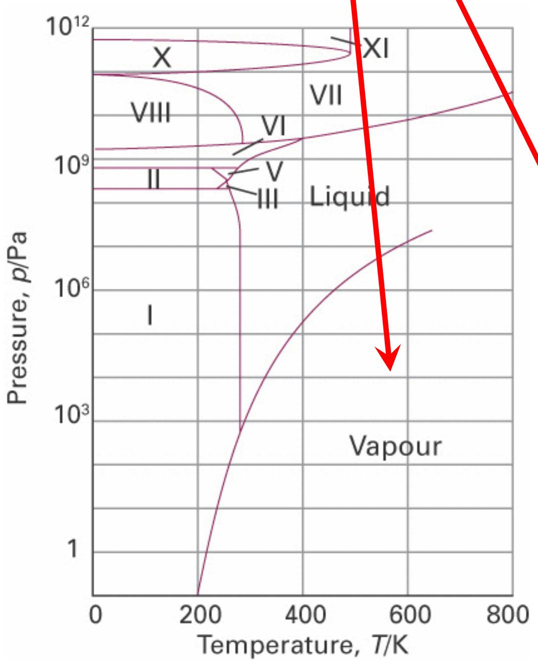
P,T $H_2O\,(g)$ + P,T EthOH (g) → P,T $H_2O\,(g)$ + EthOH (g)

$P = P_A + P_B$

(Dalton)

initial pure compounds

final mixture



$$a_{B,g} = \frac{P}{P^{\Theta}}$$

$$a_{A,g} = \frac{P}{P^{\Theta}}$$

$$a_{A,g} = \frac{P_A}{P^{\Theta}}$$

$$a_{B,g} = \frac{P_B}{P^{\Theta}}$$

Perfect gases

$$\mu_{i,g} = \mu^{\Theta}_{i,g} + RT \ln a_{i,g}$$

$$\boxed{G\Big|^{g}_{P,T} = \mu_{A,g} n_{A,g} + \mu_{B,g} n_{B,g}}$$

Mixing processes of perfect gases:binary mixture

The process of mixing two components @ *P,T* in gas phase

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

Final:

$$G^g_{\text{final}} = n_{\text{A},g}\left(\mu^{\Theta}_{\text{A},g} + RT\ln\frac{P_{\text{A}}}{P^{\Theta}}\right) + n_{\text{B},g}\left(\mu^{\Theta}_{\text{B},g} + RT\ln\frac{P_{\text{B}}}{P^{\Theta}}\right)$$

Initial:

$$G^g_{\text{initial}} = n_{\text{A},g}\left(\mu^{\Theta}_{\text{A},g} + RT\ln\frac{P}{P^{\Theta}}\right) + n_{\text{B},g}\left(\mu^{\Theta}_{\text{B},g} + RT\ln\frac{P}{P^{\Theta}}\right)$$

$$-$$

$$\Delta_{\text{mix}}G^g \equiv G^g_{\text{final}} - G^g_{\text{initial}} = n_{\text{A},g}RT\ln\frac{P_{\text{A}}}{P} + n_{\text{B},g}RT\ln\frac{P_{\text{B}}}{P}$$

Mixing processes of perfect gases:binary mixture

The process of mixing two components @ *P,T* in gas phase

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

$$\boxed{\Delta_{\text{mix}} G^{g} = n_{\text{A},g} RT \ln \frac{P_{\text{A}}}{P} + n_{\text{B},g} RT \ln \frac{P_{\text{B}}}{P}}$$

$$\boxed{\frac{P_i}{P} \equiv \frac{n_i^g}{n^g} = x_i^g}$$ **(mole fraction)**

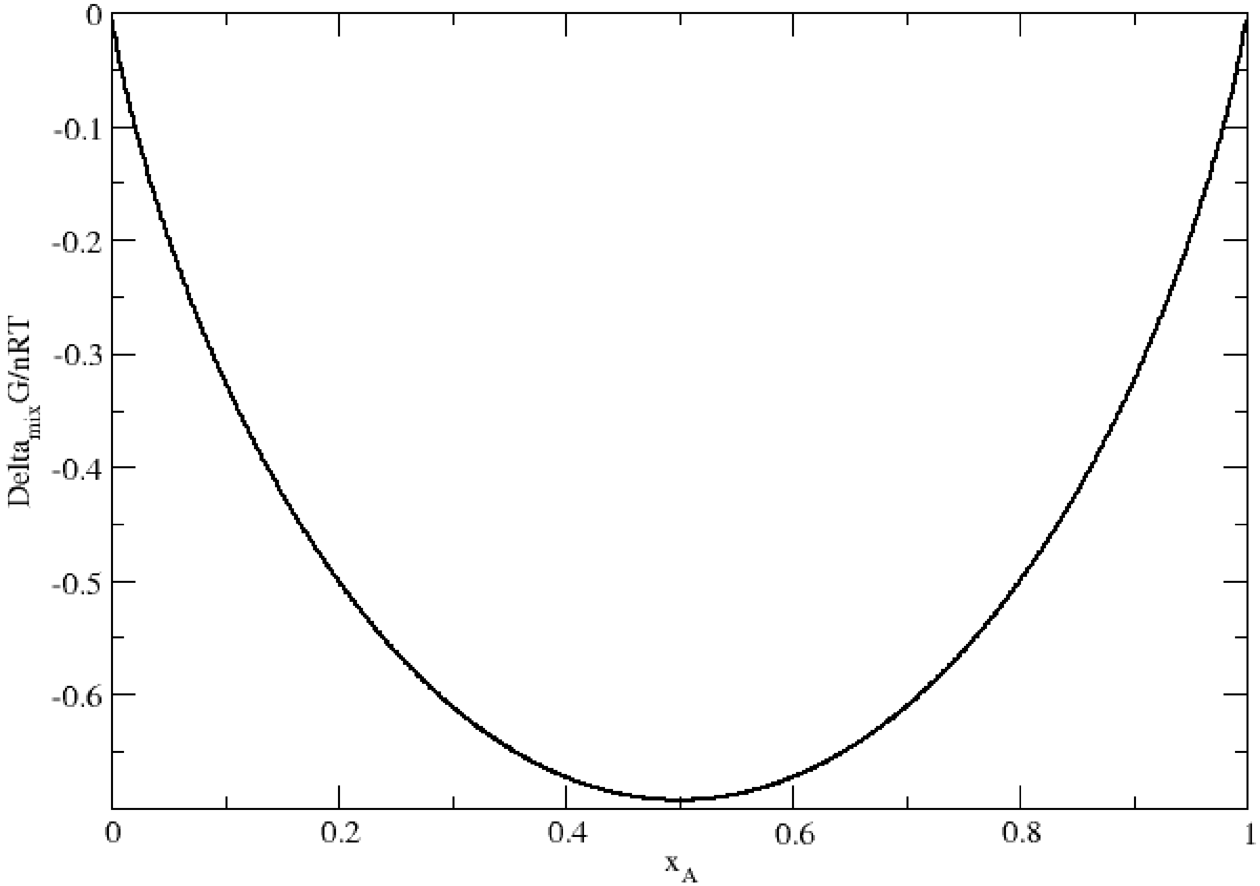
in this system there is only vapour so we write

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

Mixing processes of perfect gases:binary mixture

Perfect gas mixing

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



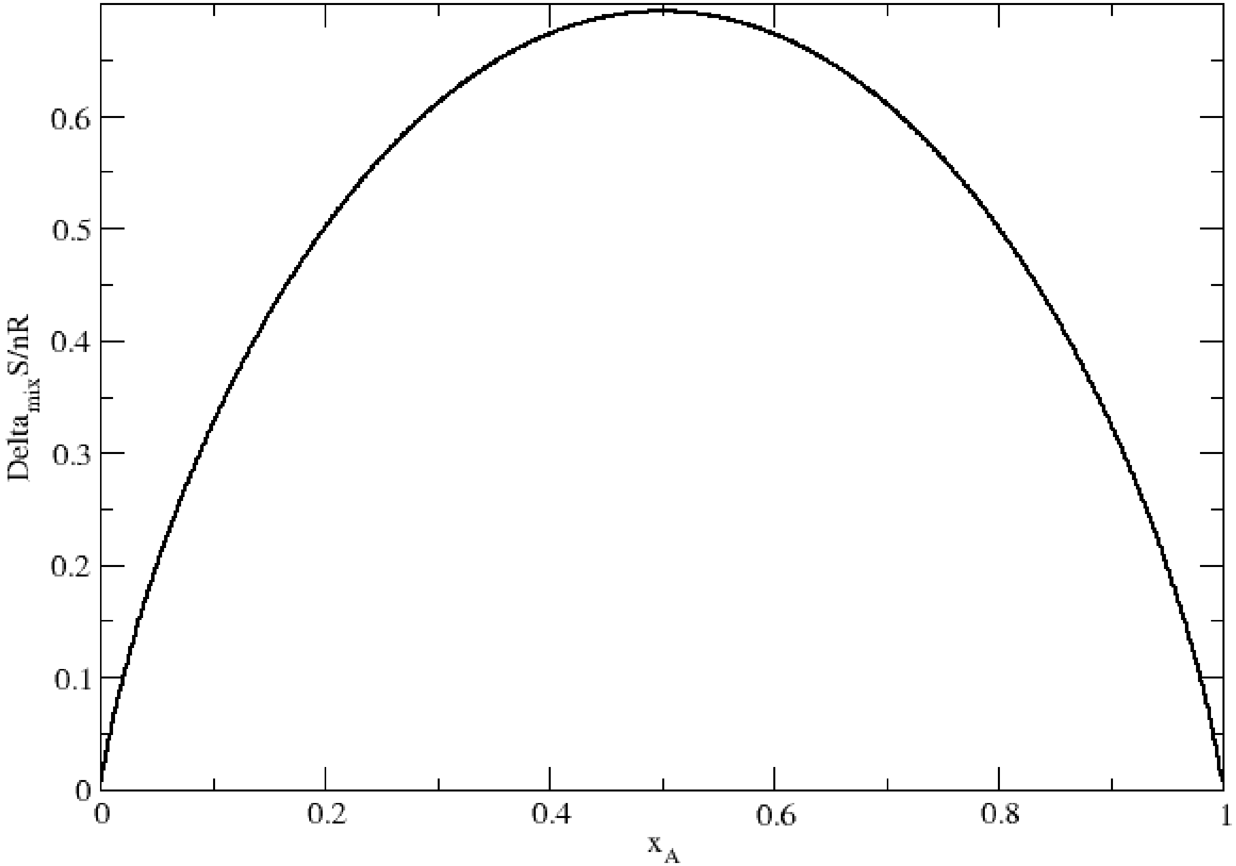
Mixing processes of perfect gases: binary mixture

Perfect gas mixing

$$\Delta_{\text{mix}} G\big|_T = \Delta_{\text{mix}} H - T\Delta_{\text{mix}} S$$

$$\Delta_{\text{mix}} S = -nR\left(x_{\text{A}} \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}}\right)$$

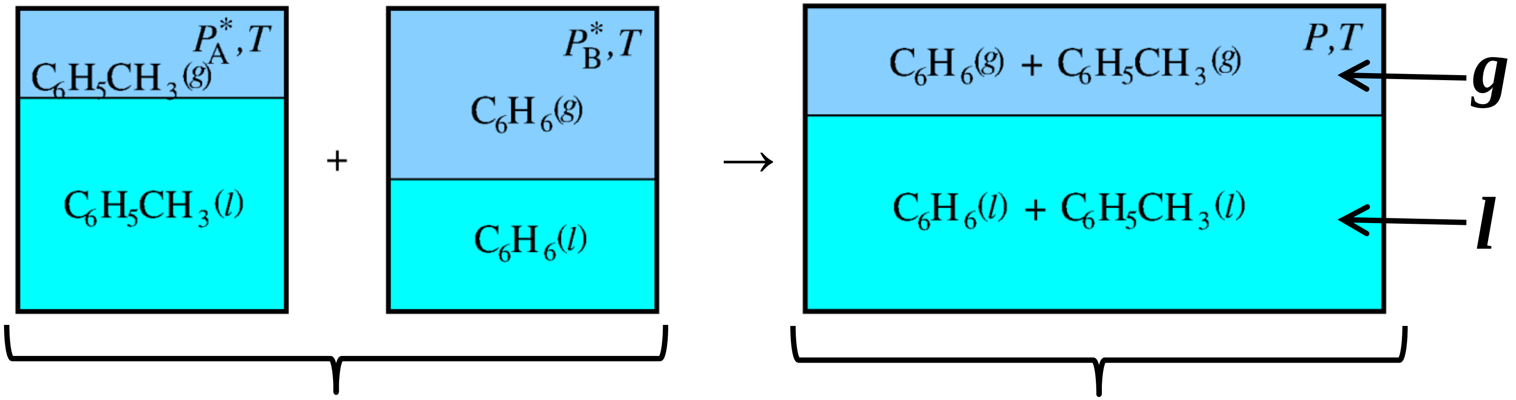
$$\Delta_{\text{mix}} H = 0$$



2nd law: Mixing is spontaneous, towards increasing entropy

Solutions and mixing processes: binary mixture

The process of mixing two components @ T in l, g phases



initial pure compounds

vapor pressures $\boxed{P_A^*(T)}$

$\boxed{P_B^*(T)}$

final mixture

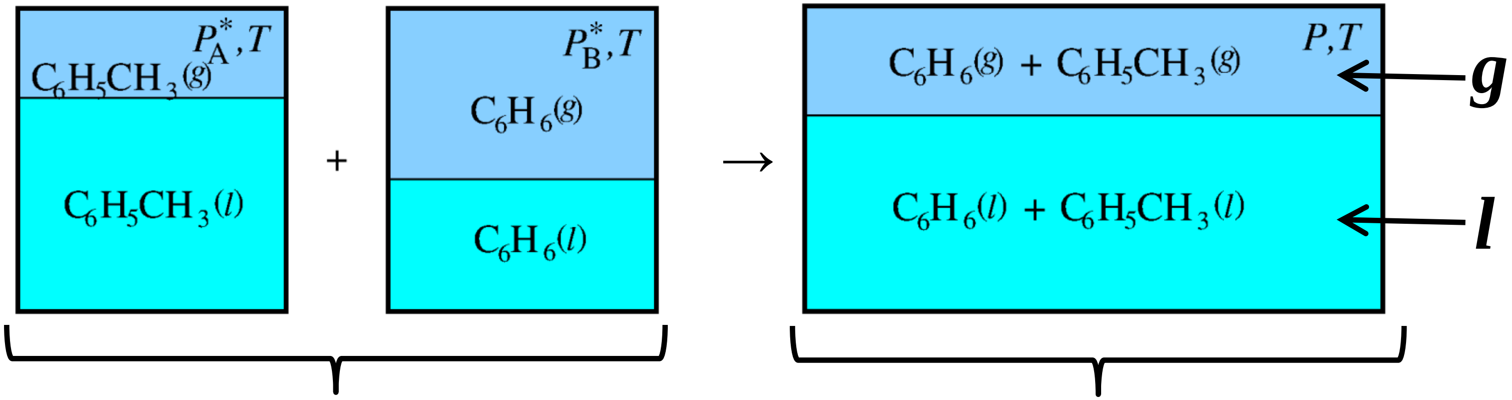
vapor pressure

$$\boxed{P(T) = P_A(T) + P_B(T)}$$

(* : pure compound)

Solutions and mixing processes: binary mixture

The process of mixing two components @ *T* in *l*, *g* phases



P_A^*, T

$C_6H_5CH_3(g)$

$C_6H_5CH_3(l)$

+

P_B^*, T

$C_6H_6(g)$

$C_6H_6(l)$

→

P, T

$C_6H_6(g) + C_6H_5CH_3(g)$

$C_6H_6(l) + C_6H_5CH_3(l)$

g

l

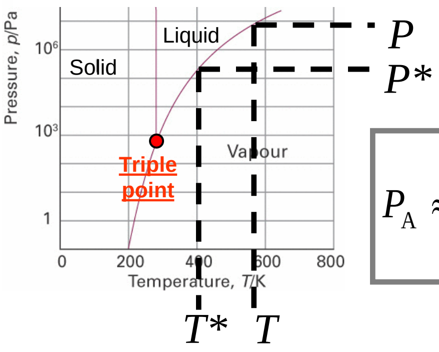
initial pure compounds

final mixture

vapor pressures $\boxed{P_A^*(T)}$ $\boxed{P_B^*(T)}$

vapor pressure

$$\boxed{P(T) = P_A(T) + P_B(T)}$$



Clausius-Clapeyron

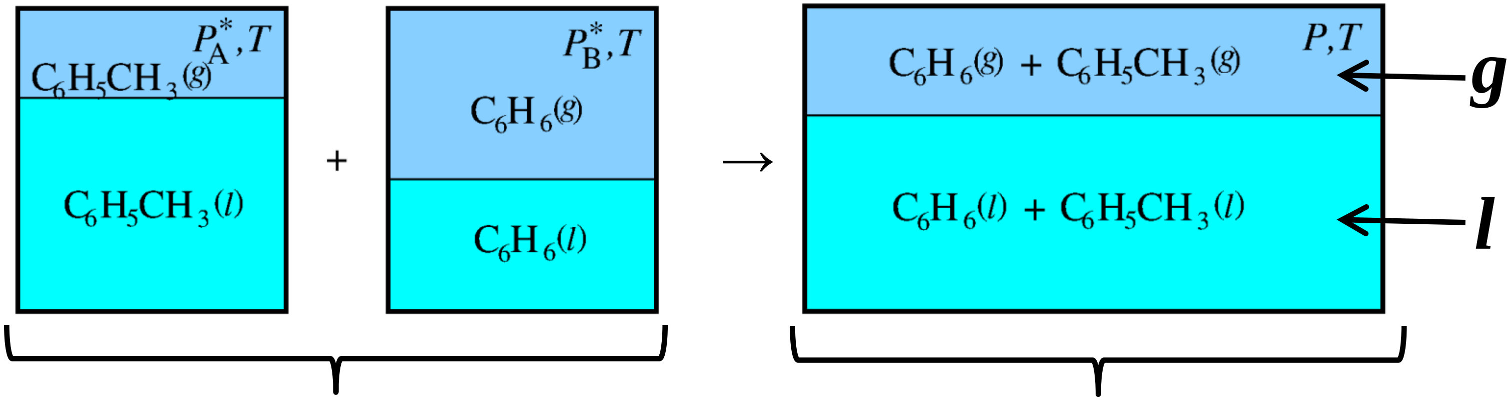
$$\boxed{P_A \approx P_A^* \exp\left[-\frac{\Delta_{\text{vap}} H_A}{R}\left(\frac{1}{T} - \frac{1}{T_A^*}\right)\right]}$$

(* : pure compound)

(* : reference *T*,*P*)

Solutions and mixing processes:binary mixture

The process of mixing two components @ *T* in *l*, *g* phases



P_A^*, T

$C_6H_5CH_3(g)$

$C_6H_5CH_3(l)$

+

P_B^*, T

$C_6H_6(g)$

$C_6H_6(l)$

→

P, T

$C_6H_6(g) + C_6H_5CH_3(g)$

$C_6H_6(l) + C_6H_5CH_3(l)$

g

l

initial pure compounds

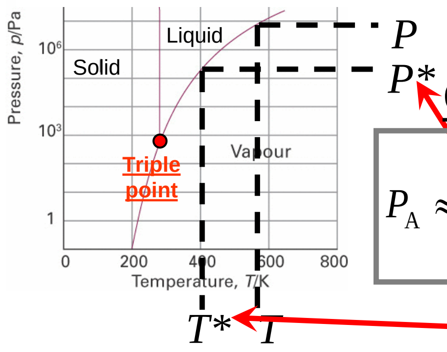
final mixture

vapor pressures $\boxed{P_A^*(T)}$ $\boxed{P_B^*(T)}$

vapor pressure

$$\boxed{P(T) = P_A(T) + P_B(T)}$$

(* : pure compound)



Clausius-Clapeyron

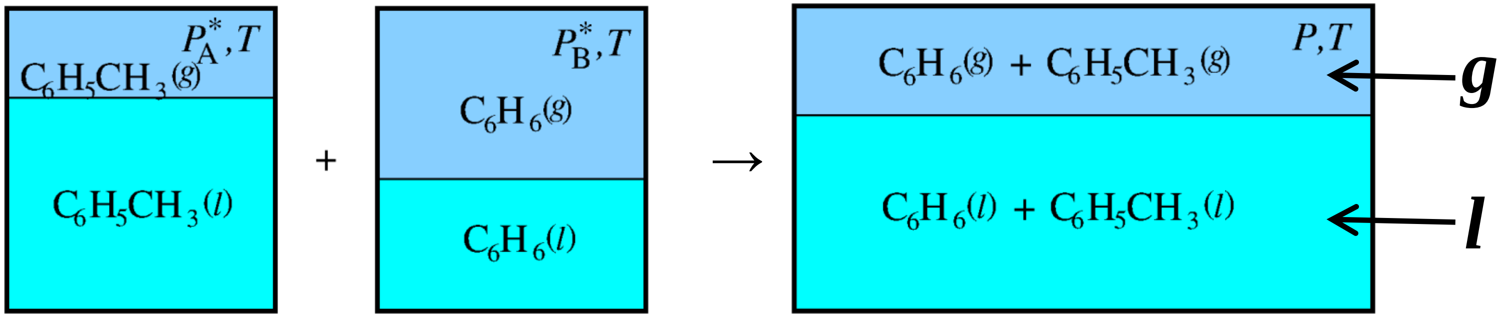
$$\boxed{P_A \approx P_A^* \exp\left[-\frac{\Delta_{vap}H_A}{R}\left(\frac{1}{T}-\frac{1}{T_A^*}\right)\right]}$$

Don't confuse * and *

(* : reference *T*,*P*)

Solutions and mixing processes:binary mixture

The process of mixing two components @ *T* in *l*, *g* phases



P_A^*, T

$C_6H_5CH_3(g)$

$C_6H_5CH_3(l)$

+

P_B^*, T

$C_6H_6(g)$

$C_6H_6(l)$

→

P, T

$C_6H_6(g) + C_6H_5CH_3(g)$ ← **g**

$C_6H_6(l) + C_6H_5CH_3(l)$ ← **l**

phase *α*

$$\boxed{G\Big|_{P,T}^{g} = \sum_i \mu_{i,g} n_{i,g} = \mu_{A,g} n_{A,g} + \mu_{B,g} n_{B,g}}$$

(sim. phase *l*)

(slide 17: def. of μ)

Initial:

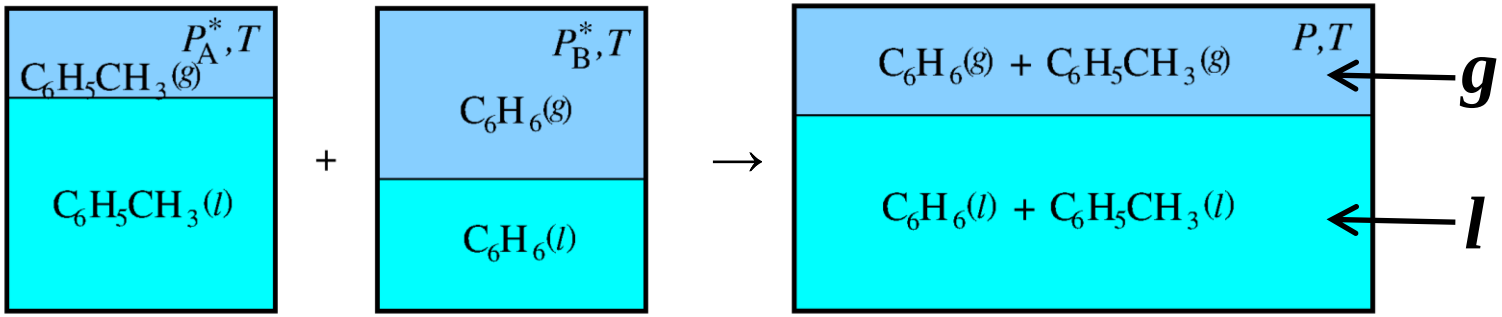
$$\boxed{G_{\text{initial}}^{g} = n_{A,g}\left(\mu_{A,g}^{\Theta} + RT \ln a_{A,g}^{*}\right) + n_{B,g}\left(\mu_{B,g}^{\Theta} + RT \ln a_{B,g}^{*}\right)}$$

(* : initial phases are pure; before mixing)

(Note: Θ per definition for pure compound; slide 18)

Solutions and mixing processes:binary mixture

The process of mixing two components @ *T* in *l*, *g* phases



phase *g*

Final:

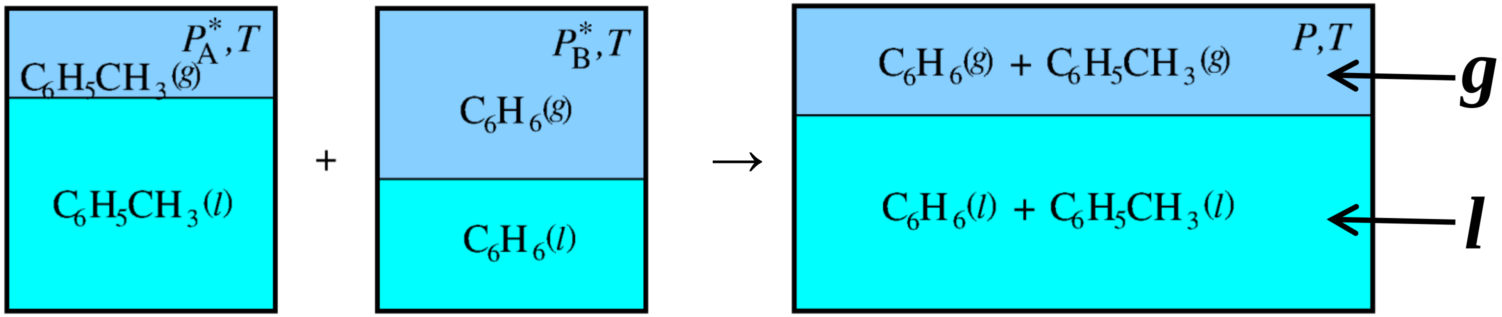
$$\boxed{G^g_{\text{final}} = n_{A,g}\left(\mu^{\Theta}_{A,g} + RT\ln a_{A,g}\right) + n_{B,g}\left(\mu^{\Theta}_{B,g} + RT\ln a_{B,g}\right)}$$

Initial:

$$\boxed{G^g_{\text{initial}} = n_{A,g}\left(\mu^{\Theta}_{A,g} + RT\ln a^*_{A,g}\right) + n_{B,g}\left(\mu^{\Theta}_{B,g} + RT\ln a^*_{B,g}\right)}$$

Solutions and mixing processes: binary mixture

The process of mixing two components @ T in l, g phases



phase α

Final:

$$G^{g}_{\text{final}} = n^{f}_{A,g}\left(\mu^{\ominus}_{A,g} + RT\ln a_{A,g}\right) + n^{f}_{B,g}\left(\mu^{\ominus}_{B,g} + RT\ln a_{B,g}\right)$$

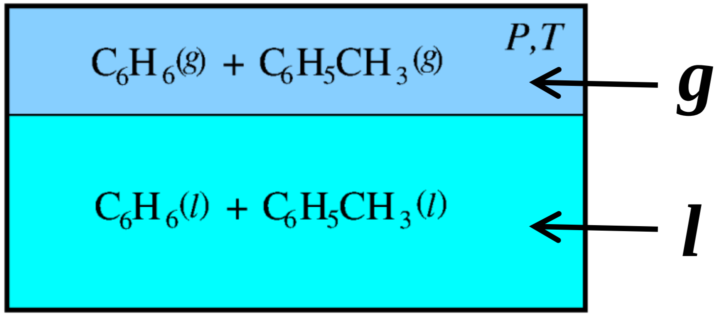
Initial:

$$G^{g}_{\text{initial}} = n^{i}_{A,g}\left(\mu^{\ominus}_{A,g} + RT\ln a^{*}_{A,g}\right) + n^{i}_{B,g}\left(\mu^{\ominus}_{B,g} + RT\ln a^{*}_{B,g}\right)$$

Problem: in general $n_{A,l}, n_{A,g}$ **and** $n_{B,l}, n_{B,g}$ **will change on mixing**

Solutions and mixing processes:binary mixture

The process of mixing two components @ *T* in *l*, *g* phases



P,T

$C_6H_6(g) + C_6H_5CH_3(g)$ ← ***g***

$C_6H_6(l) + C_6H_5CH_3(l)$ ← ***l***

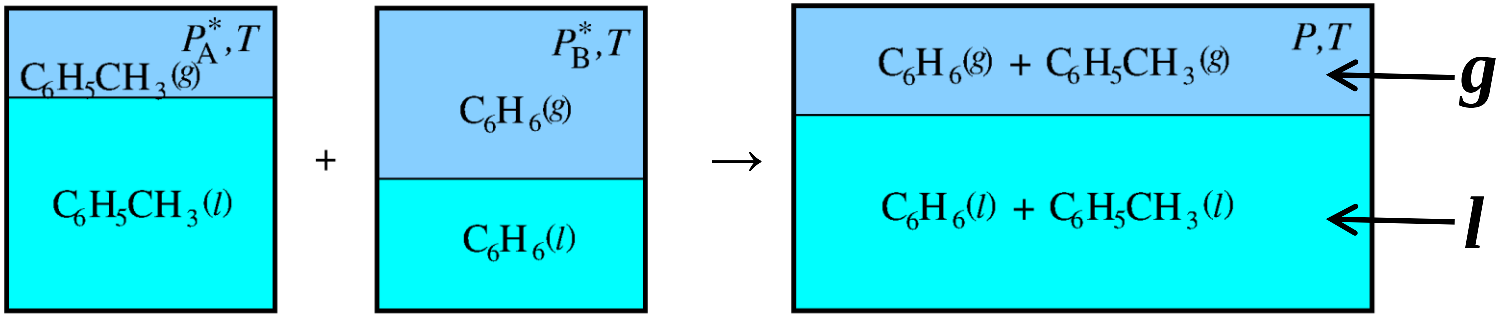
alternative approach:

Equilibrium ⟺ $\boxed{\mu_{i,g} = \mu_{i,l}}$

$$\left\{\begin{array}{l} \boxed{\mu_{\mathrm{A},g} = \mu_{\mathrm{A},l}} \\ \boxed{\mu_{\mathrm{B},g} = \mu_{\mathrm{B},l}} \end{array}\right.$$

Solutions and mixing processes: binary mixture

The process of mixing two components @ *T* in *l*, *g* phases



Final: $\mu_{A,g} = \mu_{A,l}$ ⇒

$$\mu_{A,g} = \mu^{\Theta}_{A,g} + RT \ln \frac{P_A}{P^{\Theta}} = \mu_{A,l} \equiv \mu_A$$

Initial: $\mu^*_{A,g} = \mu^*_{A,l}$ ⇒

$$\mu^*_{A,g} = \mu^{\Theta}_{A,g} + RT \ln \frac{P^*_A}{P^{\Theta}} = \mu^*_{A,l} \equiv \mu^*_A$$

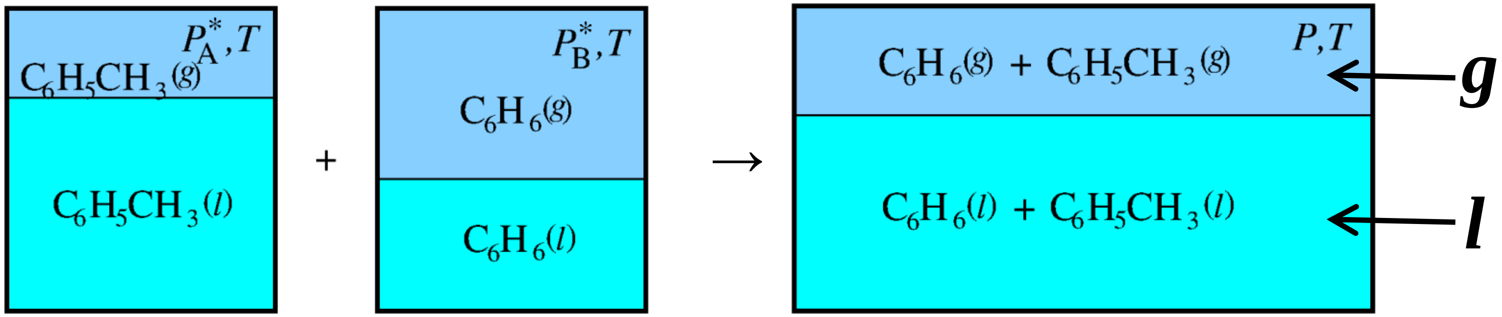
⇒

$$RT \ln \frac{P_A}{P^*_A} = \mu_A - \mu^*_A$$

(similar for B)

Solutions and mixing processes:binary mixture

The process of mixing two components @ *T* in *l*, *g* phases

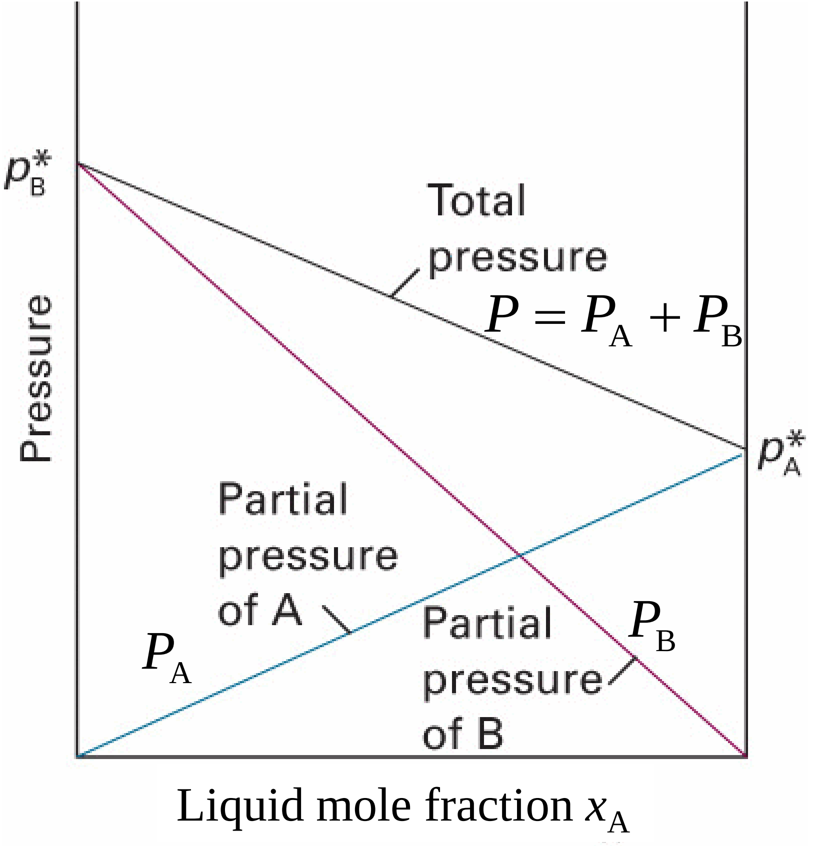


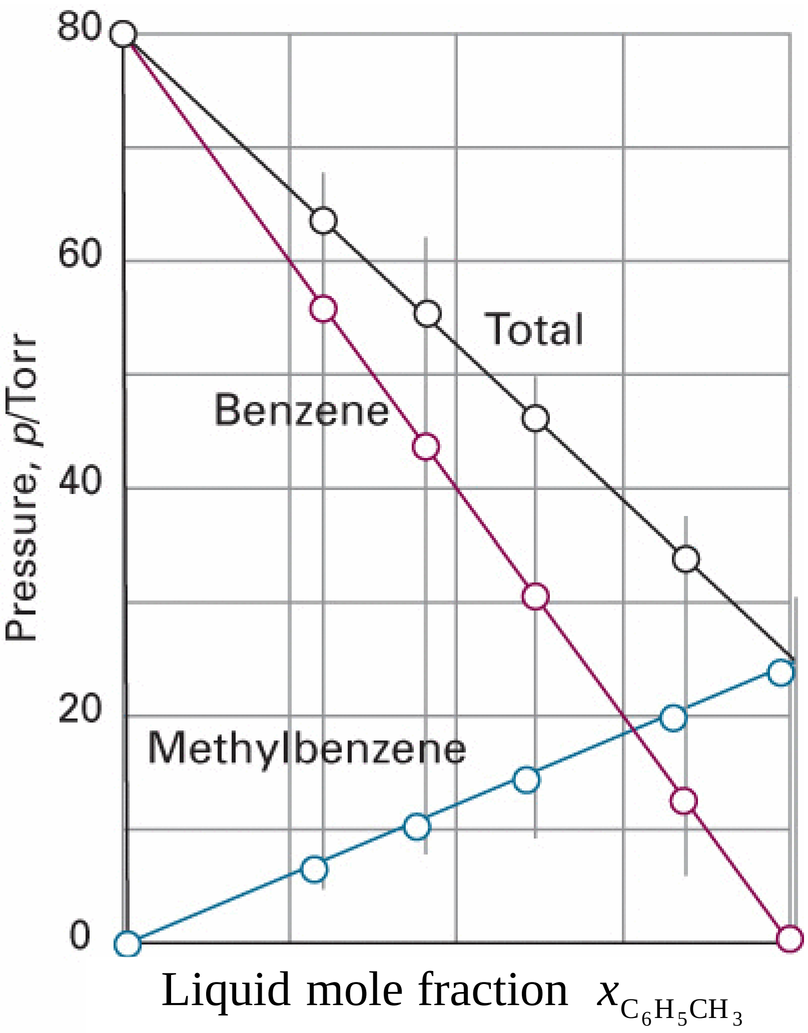
$$\boxed{\mu_A = \mu_A^* + RT \ln \frac{P_A}{P_A^*}} \qquad \boxed{\mu_B = \mu_B^* + RT \ln \frac{P_B}{P_B^*}}$$

Note, in general: $\boxed{\frac{P_A}{P_A^*} \neq x_A}$ and $\boxed{\frac{P_B}{P_B^*} \neq x_B}$ like in slide 29!

Special solutions: Ideal solutions (Raoult)

Raoult's law





$$\boxed{P_{i,g} = x_{i,l} P_{i,g}^*}$$

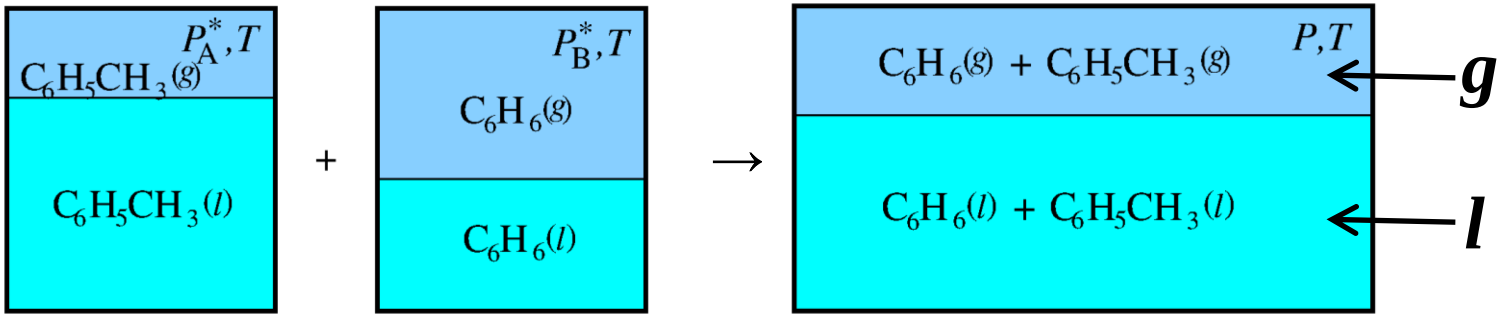
Raoult

$$\boxed{P = P_A + P_B}$$

Dalton

Solutions and mixing processes:binary mixture

The process of mixing two components @ *T* in *l*, *g* phases



P_A^*, T $C_6H_5CH_3(g)$ / $C_6H_5CH_3(l)$ + P_B^*, T $C_6H_6(g)$ / $C_6H_6(l)$ → P, T $C_6H_6(g) + C_6H_5CH_3(g)$ ← *g* / $C_6H_6(l) + C_6H_5CH_3(l)$ ← *l*

$$\boxed{\mu_A = \mu_A^* + RT \ln \frac{P_A}{P_A^*}}$$

$$\boxed{\mu_B = \mu_B^* + RT \ln \frac{P_B}{P_B^*}}$$

Special case:

Raoult's law: Ideal solutions:

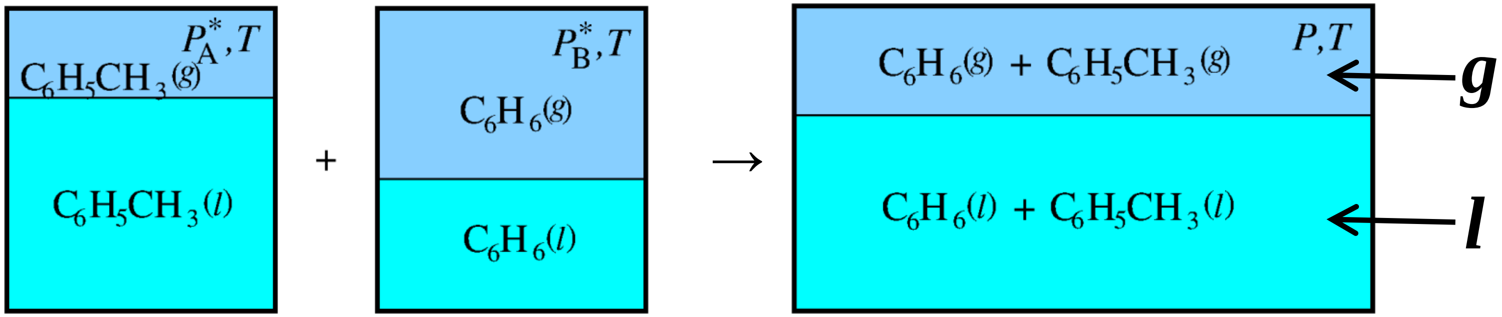
$$\boxed{P_{i,g} = x_{i,l} P_{i,g}^*}$$

vapor **vapor**

liquid

Solutions and mixing processes:binary mixture

The process of mixing two components @ T in l, g phases



Raoult's law: Ideal solutions:

Final:

$$\boxed{G_{\text{final}} = n_A\left(\mu_A^* + RT\ln x_A\right) + n_B\left(\mu_B^* + RT\ln x_B\right)}$$

Initial:

$$\boxed{G_{\text{initial}} = n_A\mu_A^* + n_B\mu_B^*}$$

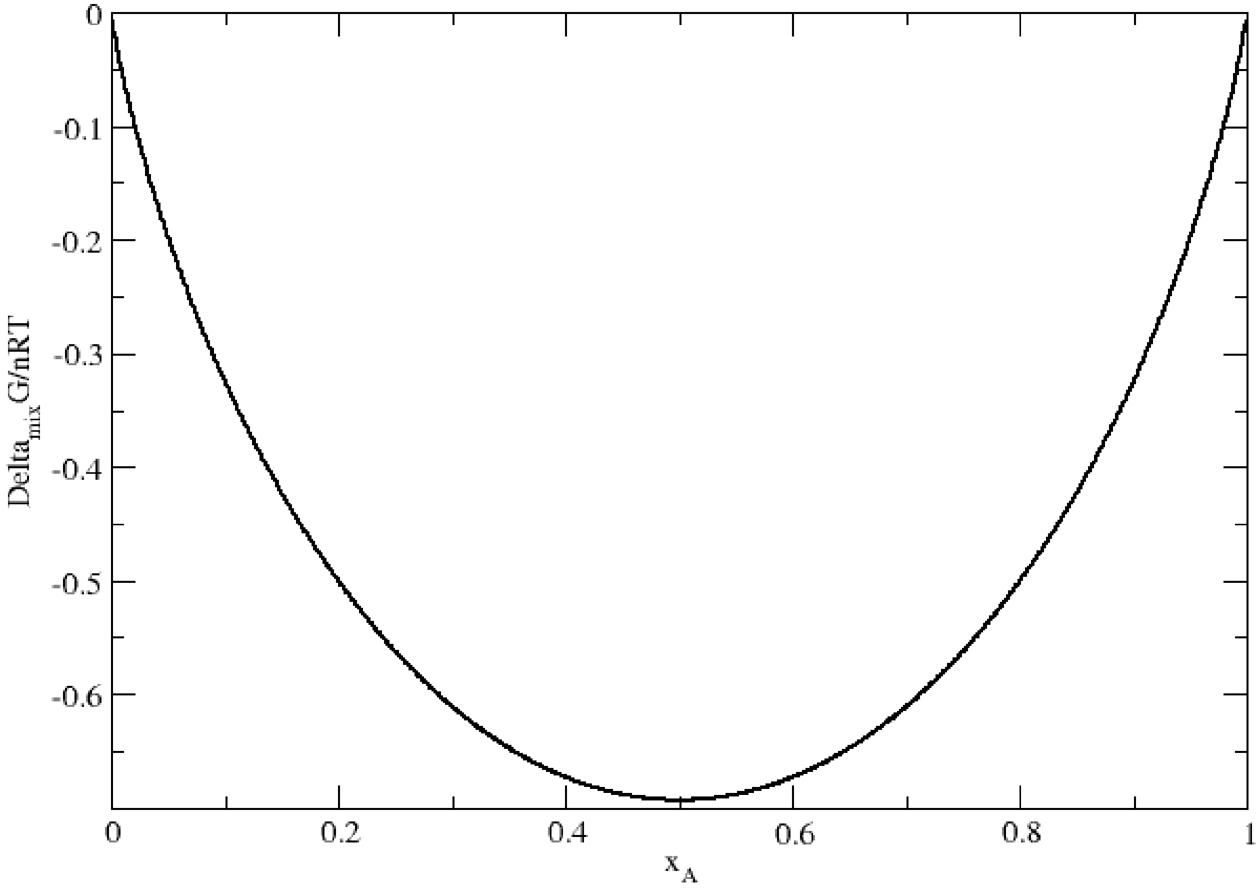
$$\boxed{\Delta_{\text{mix}}G = G_{\text{final}} - G_{\text{initial}} = nRT\left(x_A\ln x_A + x_B\ln x_B\right)}$$

Gibbs free energy of mixing for ideal solutions

Solutions: Ideal solutions (Raoult)

Ideal liquid mixing

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

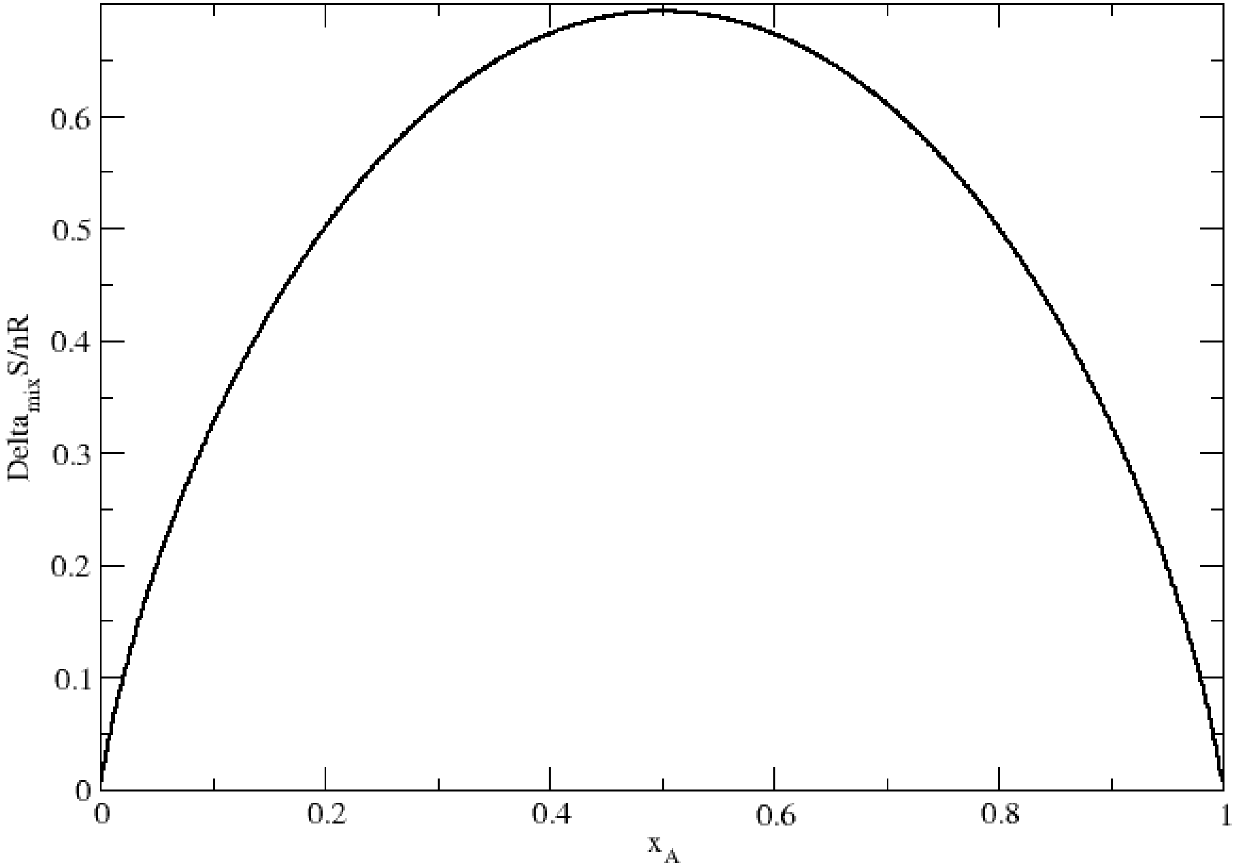


Solutions: Ideal solutions (Raoult)

Ideal liquid mixing

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

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



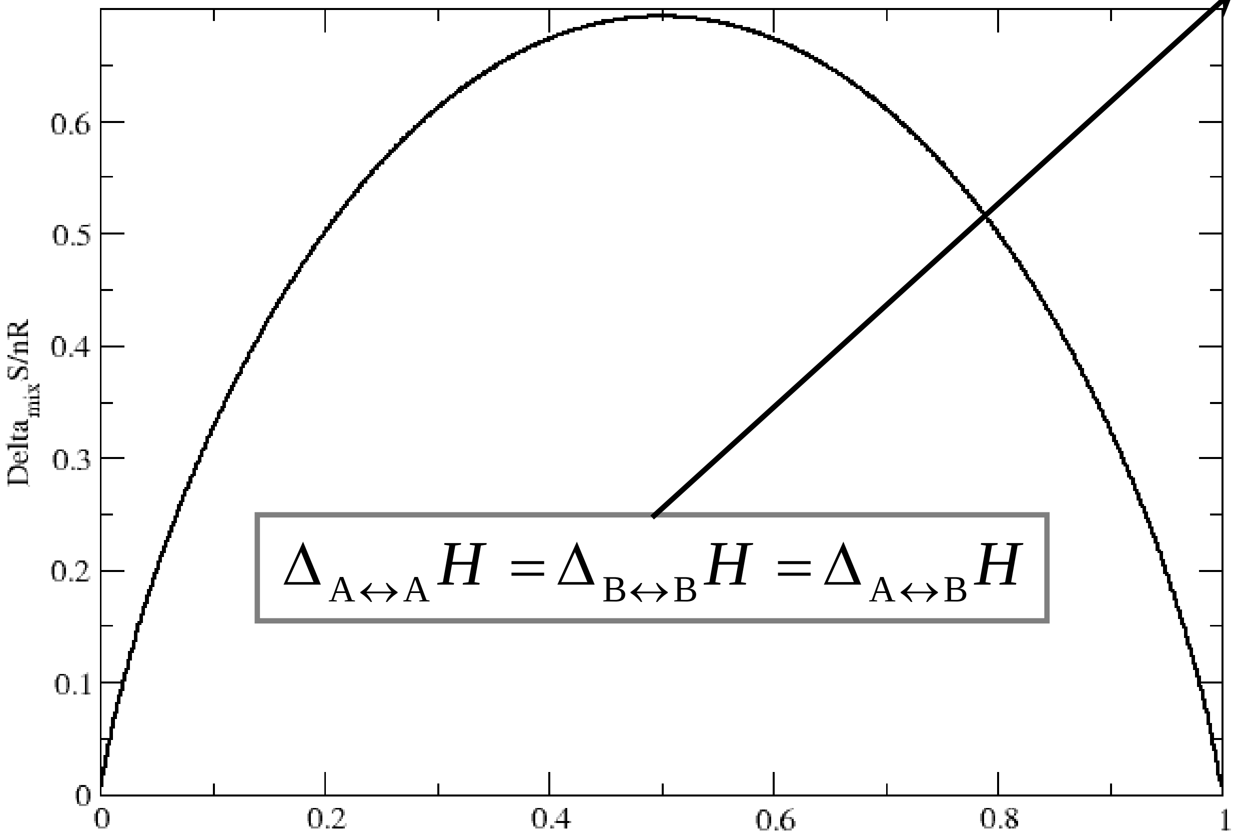
2nd law: Mixing is spontaneous, towards increasing entropy

Solutions: Ideal solutions (Raoult)

Ideal liquid mixing

$$\Delta_{\text{mix}} S = -nR\left(x_{\text{A}} \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}}\right)$$

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

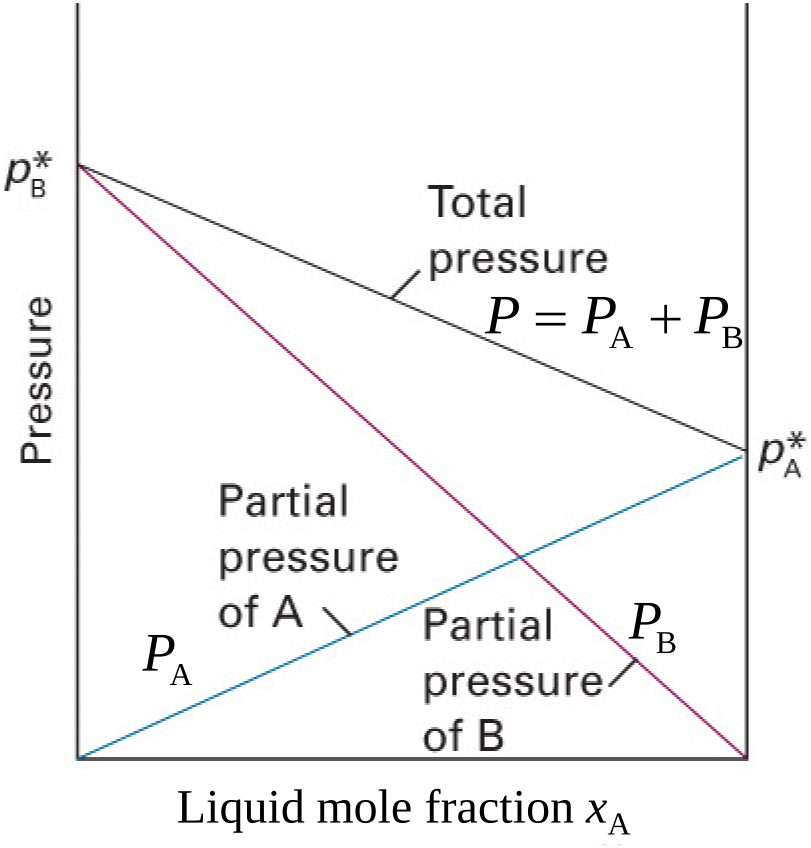


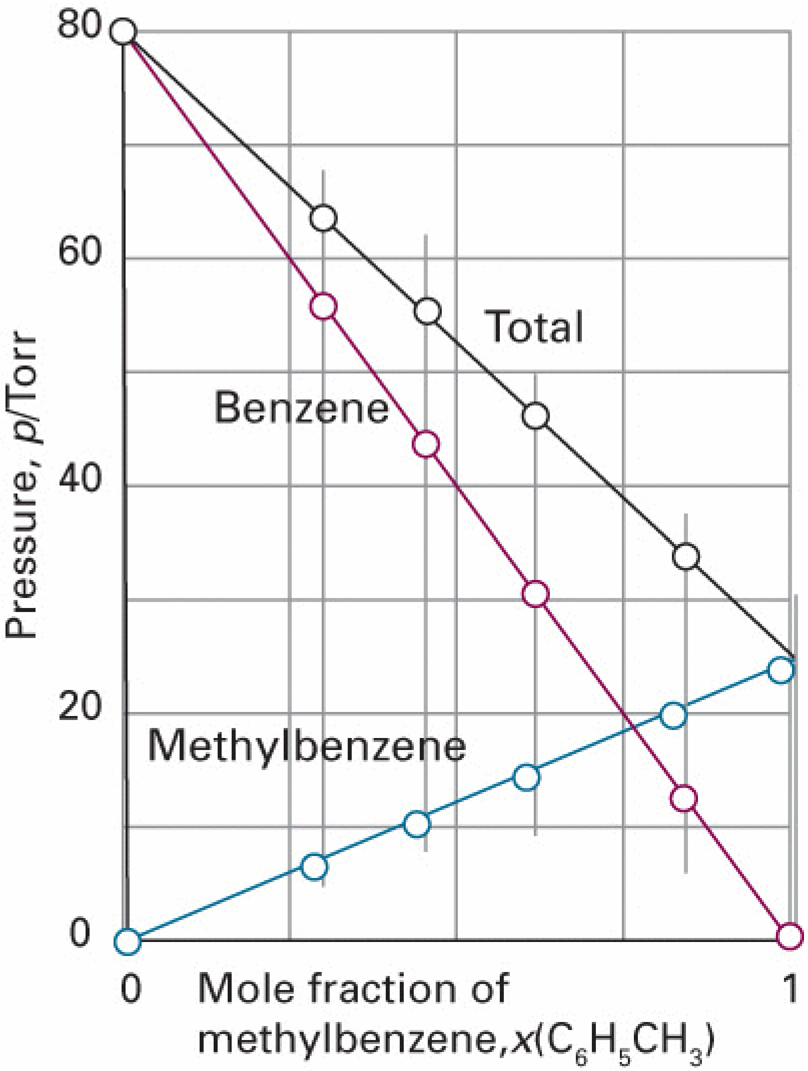
$$\Delta_{\text{A}\leftrightarrow\text{A}} H = \Delta_{\text{B}\leftrightarrow\text{B}} H = \Delta_{\text{A}\leftrightarrow\text{B}} H$$

2nd law: Mixing is spontaneous, towards increasing entropy

(Study guide p.14-17)

Solutions: Ideal solutions (Raoult)





Ideal mixing (Raoult)

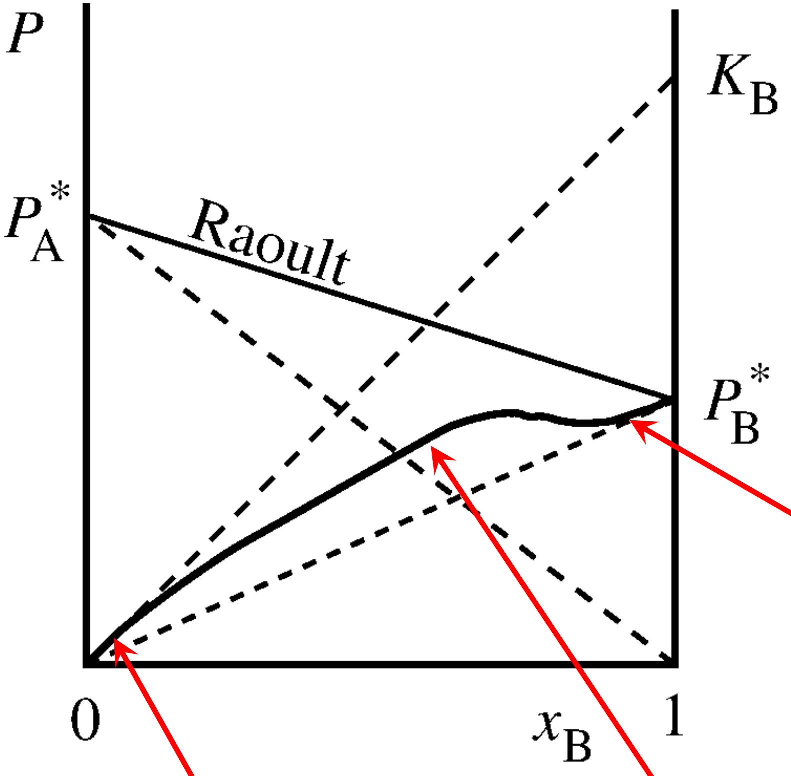
Exercise 11

$$P_A = x_A P_A^*$$

$$P_B = x_B P_B^*$$

Solutions: Ideal-dilute solutions

Non-ideal mixing



$$\boxed{P_B = x_B K_B}$$

Ideal-dilute solutions:

Henry constant K_B

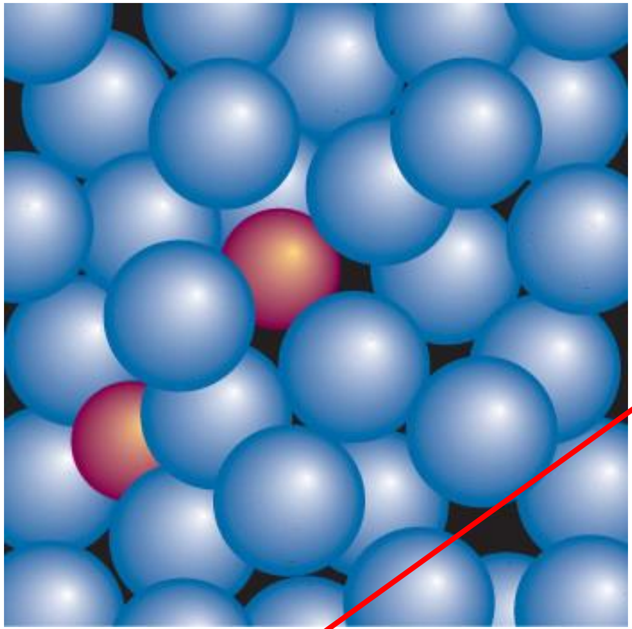
almost pure solvent B

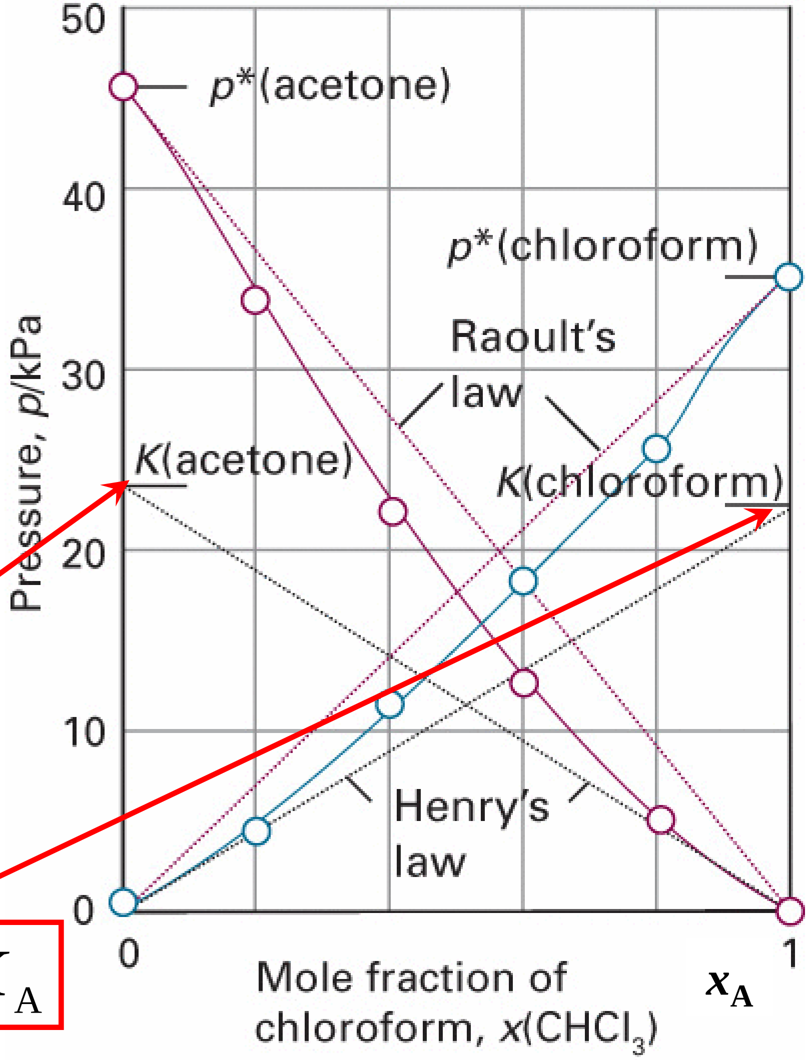
solute B expelled from solution

very low concentration of solute B

Solutions: Ideal-dilute solutions

Non-ideal mixing





$$\boxed{P_B = x_B K_B}$$

$$\boxed{P_A = x_A K_A}$$

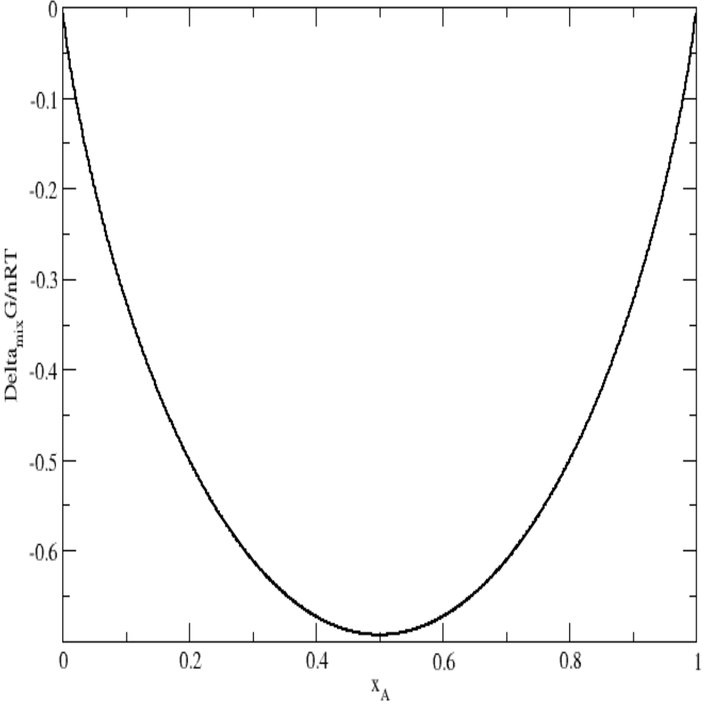
Ideal-dilute solutions: Henry constant K_B

Exercise 13

Solutions: Real solutions

ideal mixing

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

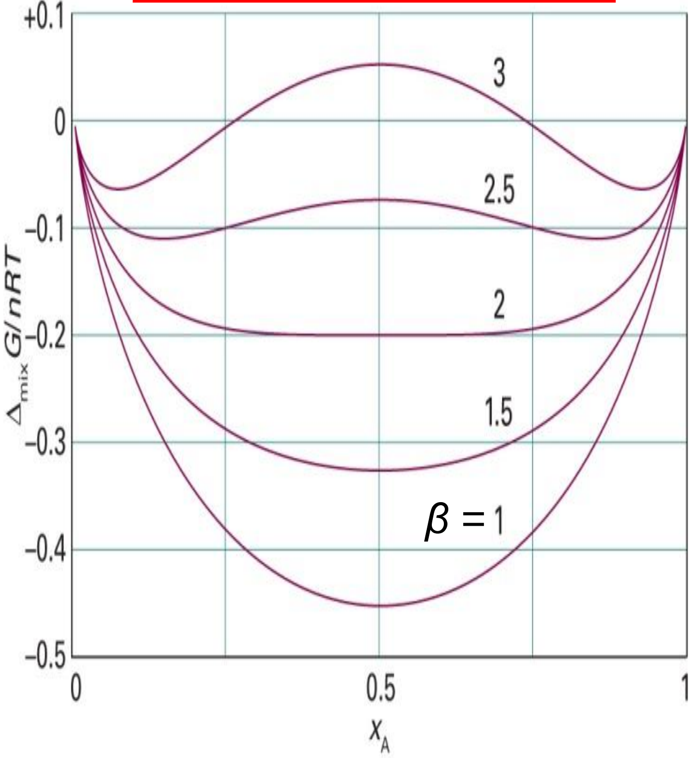


$$\Delta_{mix} G = nRT\left[x_A \ln x_A + x_B \ln x_B\right]$$

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

Non-ideal mixing

$$\Delta_{mix} H = n\beta RT x_A x_B$$



Solutions: Real solutions

Non-ideal mixing

$$\Delta_{mix} H = n\beta RTx_A x_B$$

(Excess functions)

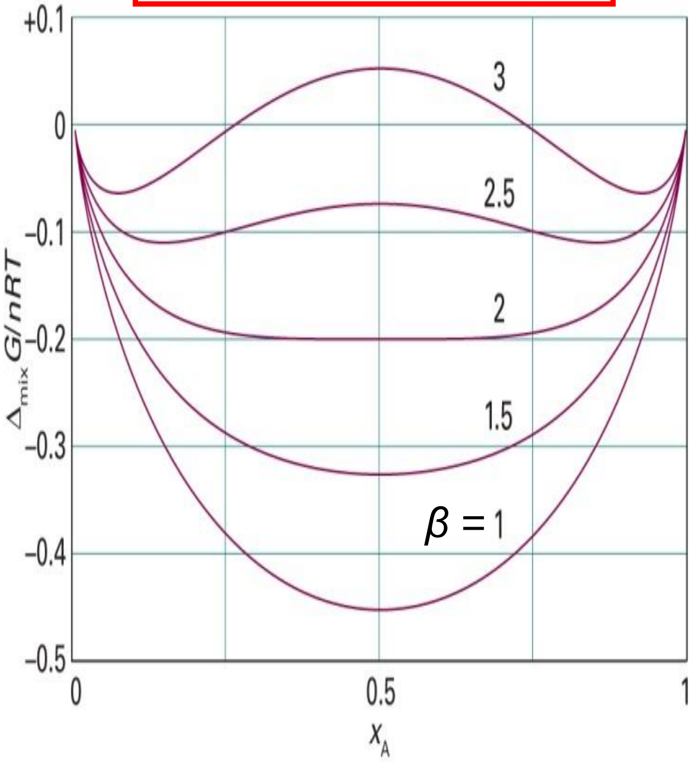
$$G^E \equiv \Delta_{mix} G - \Delta_{mix} G^{ideal}$$

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

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

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

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

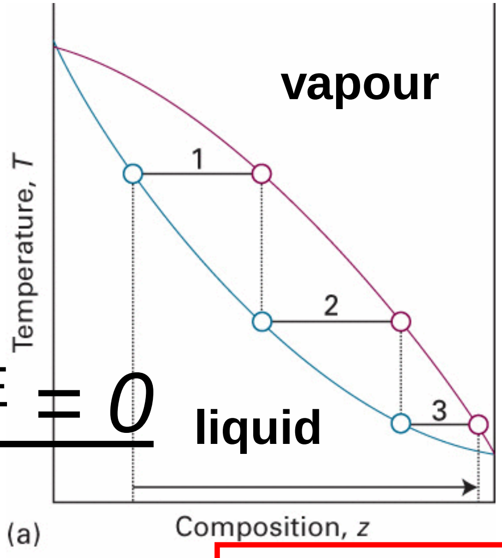


Exercise 12

Temperature-composition diagrams

Temperature-composition diagrams

ideal solutions

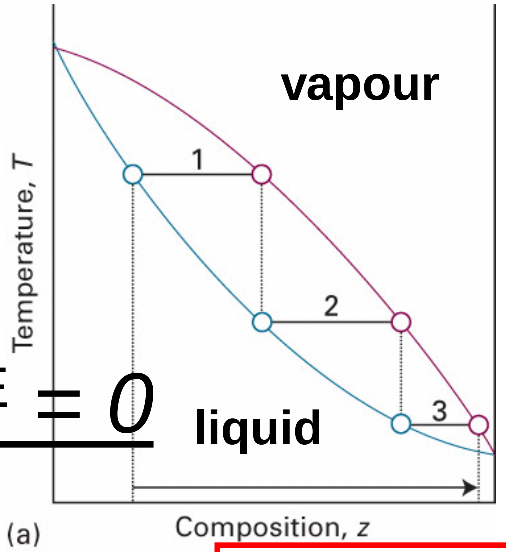


$G^E = 0$

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

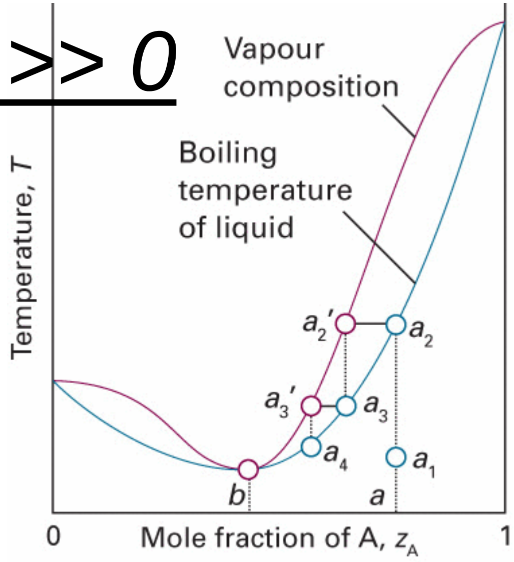
Temperature-composition diagrams

ideal solutions



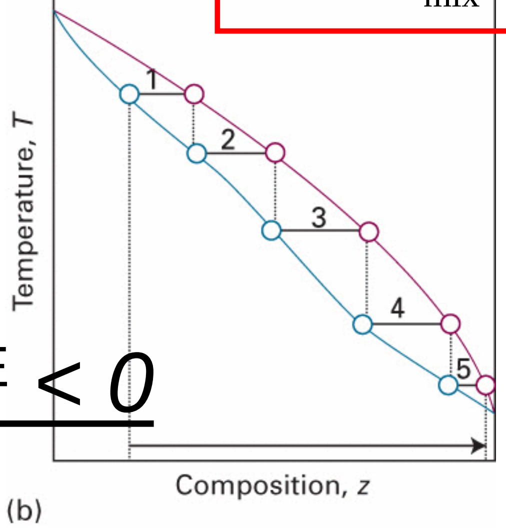
$G^{E} = 0$

$G^{E} >> 0$



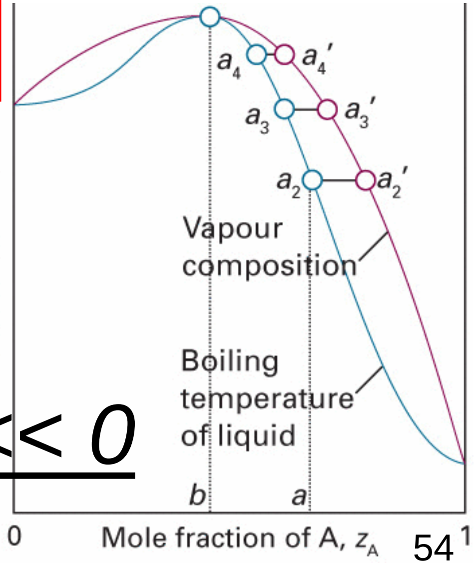
$$G^{E} = \Delta_{mix} G - \Delta_{mix} G^{ideal}$$

Non-ideal solutions



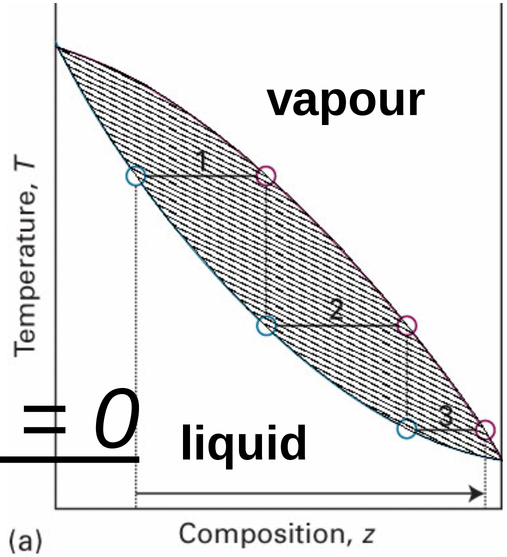
$G^{E} < 0$

$G^{E} << 0$



Temperature-composition diagrams

ideal solutions

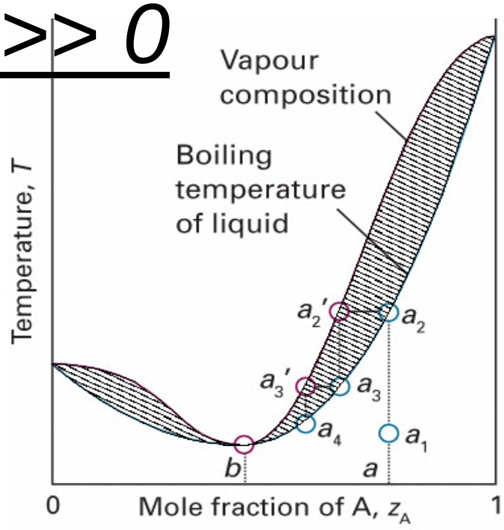


vapour

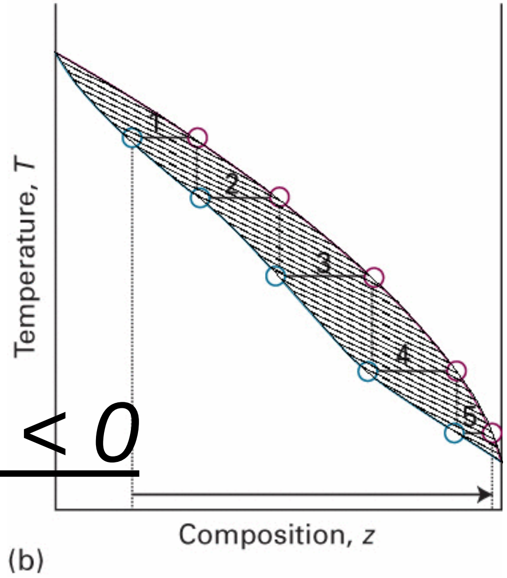
liquid

$G^E = 0$

$G^E >> 0$



Non-ideal solutions



$G^E < 0$

$G^E << 0$