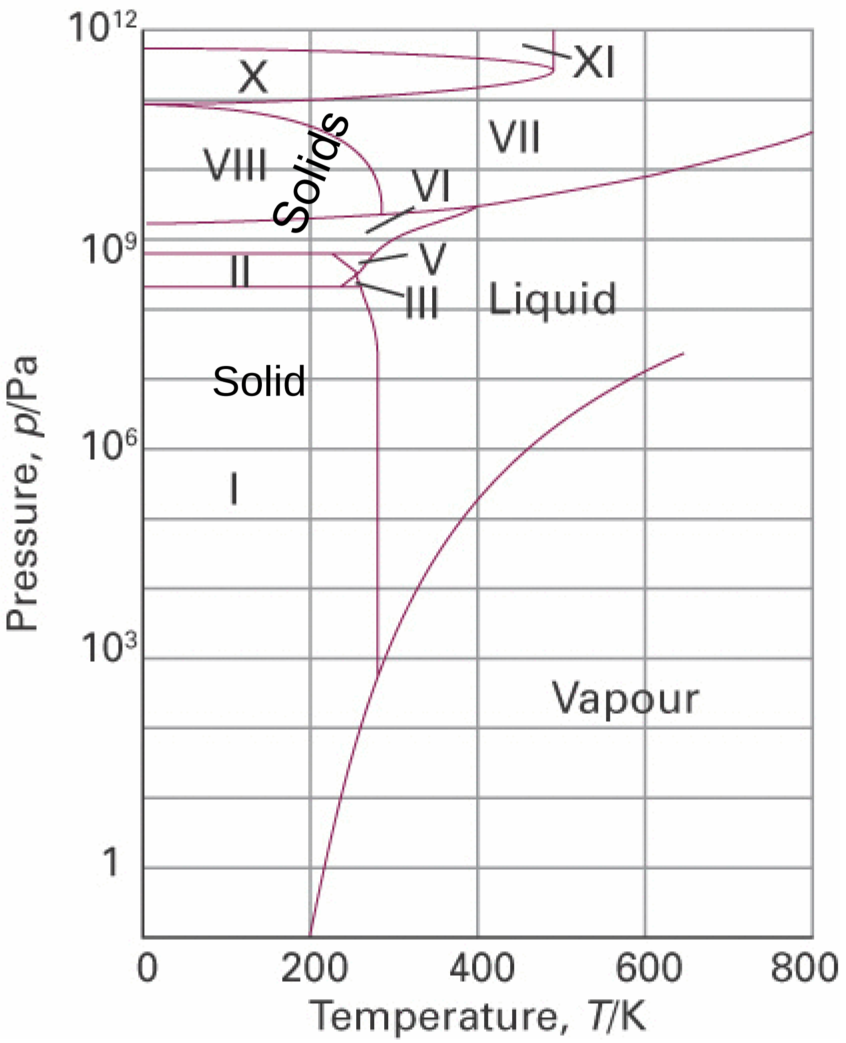
Phase diagrams and phase transitions of unary systems



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

- •Thermodynamics *vs* kinetics
- •Metastable phases

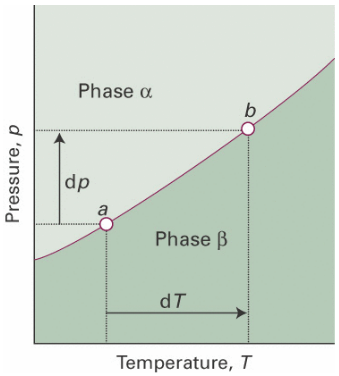
(**Equilibrium**) Phase Diagram of a **pure** compound

Phase boundary lines in phase diagrams of unary systems

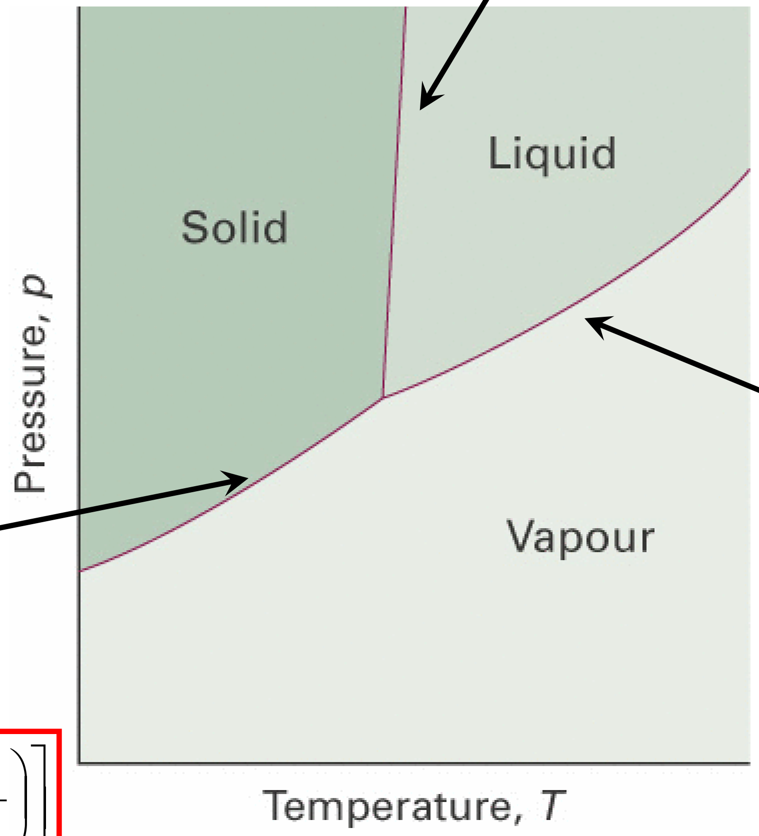
$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{trs}} S}{\Delta_{\mathrm{trs}} V} = \frac{\Delta_{\mathrm{trs}} H}{T_{\mathrm{trs}} \Delta_{\mathrm{trs}} V}$$

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

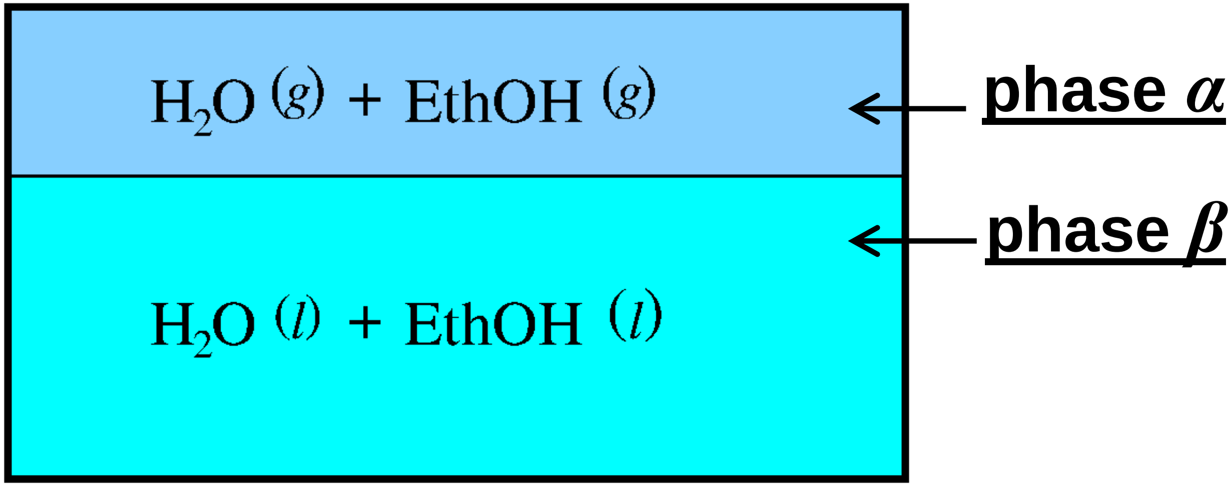
Phase diagrams: multicomponent phases

Importance of the chemical potential:

Equilibrium between phases of a single component

in equilibrium: $\boxed{H_2O(\alpha) \leftrightarrow H_2O(\beta)} \longrightarrow \boxed{\mu_\alpha = \mu_\beta}$

Equilibrium between phases of components *i* in mixtures



$H_2O\ (g) + \text{EthOH}\ (g)$

$H_2O\ (l) + \text{EthOH}\ (l)$

phase *α*

phase *β*

in equilibrium: $\boxed{\mu_{i,\alpha} = \mu_{i,\beta}} \left\{ \begin{array}{l} \textbf{phases } \alpha, \beta \\ \textbf{components } i \end{array} \right.$

Lecture 3: mixtures of compounds

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

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

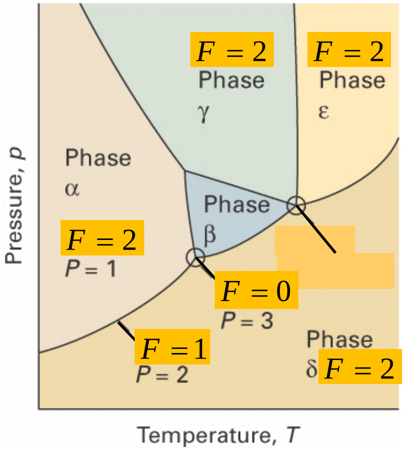
$$\boxed{F = C - P + 2}$$

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

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

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

$C = 1; F = ?$



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

Phase diagrams of mixtures of compounds

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

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

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

P, T

 # components in each phase: $\boxed{F = C + 2}$

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

Phase diagrams of mixtures of compounds

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

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

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

$$\boxed{\sum_i x_i = \sum_i \frac{n_i}{n} = \frac{1}{n}\sum_i n_i = \frac{n}{n} = 1} \Rightarrow \boxed{F = C - 1 + 2}$$

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

all components in each phase: $\boxed{F = P(C-1) + 2}$

Phase diagrams of mixtures of compounds

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

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

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

Equilibrium condition:

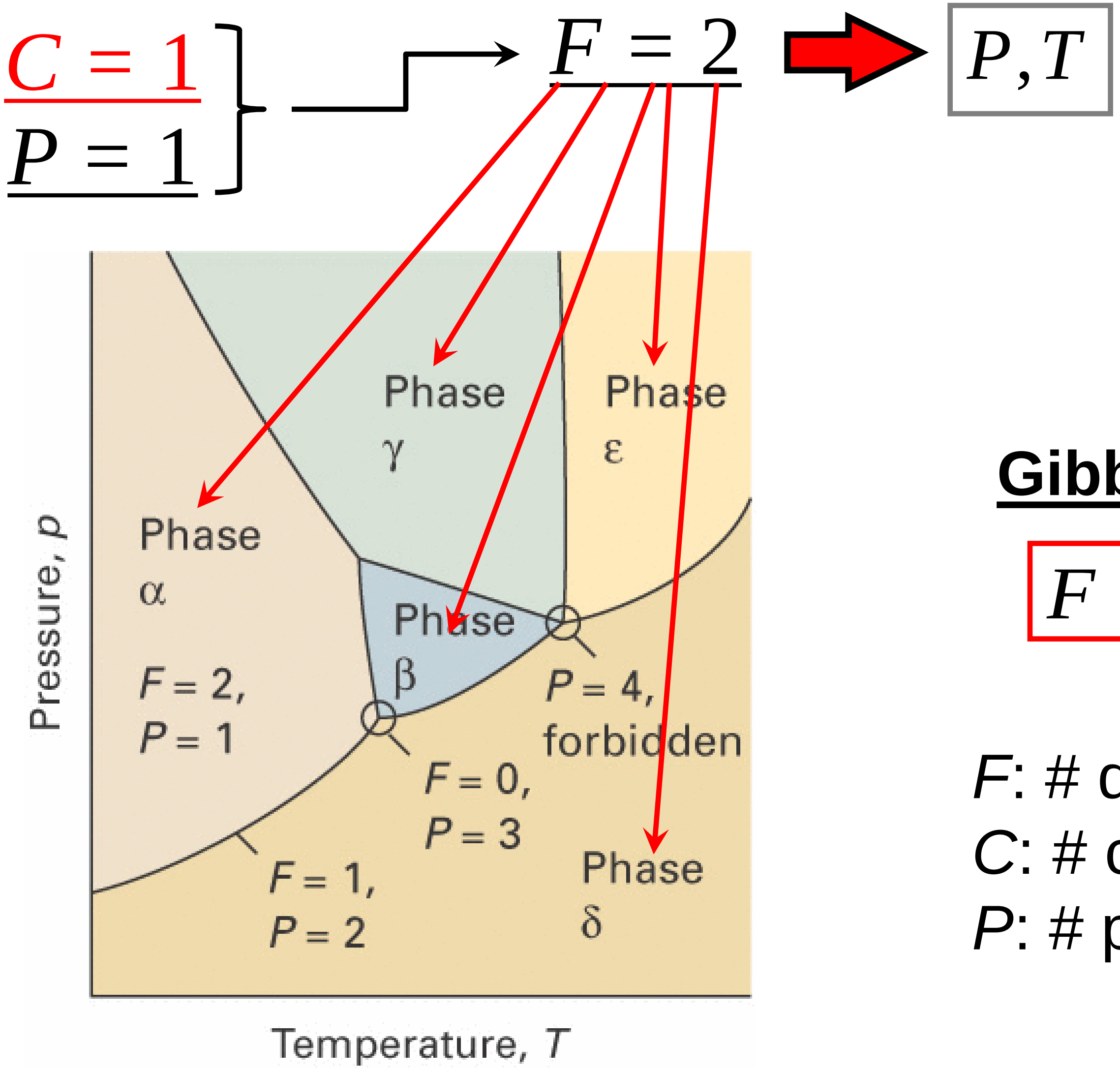
$$\mu_i^{\alpha} = \mu_i^{\beta} \text{ for } i = 1,\dots, C \text{ and } \alpha, \beta = 1,\dots, P$$

$$\left.\begin{array}{l} \mu_1^{\alpha} = \mu_1^{\beta} = \mu_1^{\gamma} = \dots\dots\dots\dots\dots = \mu_1^{P} \\ \mu_2^{\alpha} = \mu_2^{\beta} = \mu_2^{\gamma} = \dots\dots\dots\dots\dots = \mu_2^{P} \\ \quad\;\; . \qquad\; . \qquad\; . \qquad\qquad\qquad\quad . \\ \quad\;\; . \qquad\; . \qquad\; . \qquad\qquad\qquad\quad . \\ \mu_C^{\alpha} = \mu_C^{\beta} = \mu_C^{\gamma} = \dots\dots\dots\dots\dots = \mu_C^{P} \end{array}\right\}$$

$(P-1)C$ conditions

$$\boxed{F = P(C-1)+2-(P-1)C = C-P+2}$$

Phase diagrams of unary systems



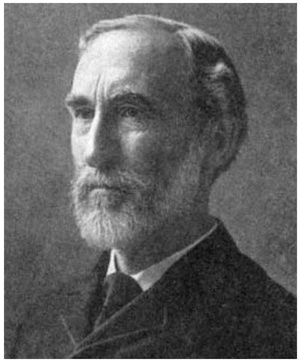
$C = 1$

$P = 1$

$F = 2$

$\boxed{P, T}$

unary phase diagram



Gibbs phase rule

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

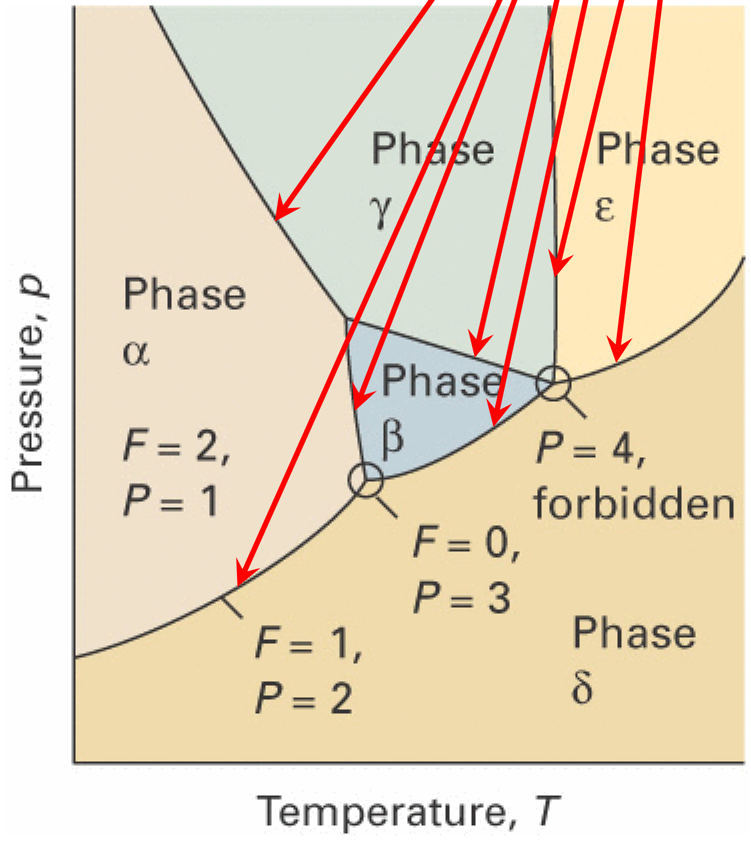
F: # degrees of freedom
C: # components
P: # phases

Phase diagrams of unary systems

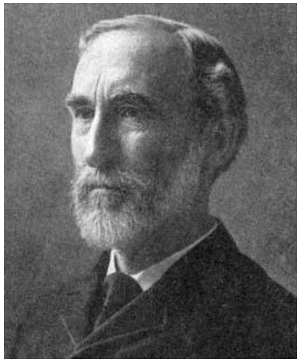
$C = 1$

$P = 2$

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



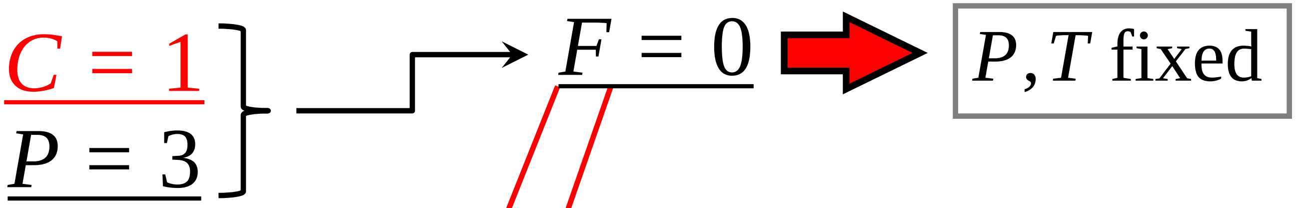
unary phase diagram



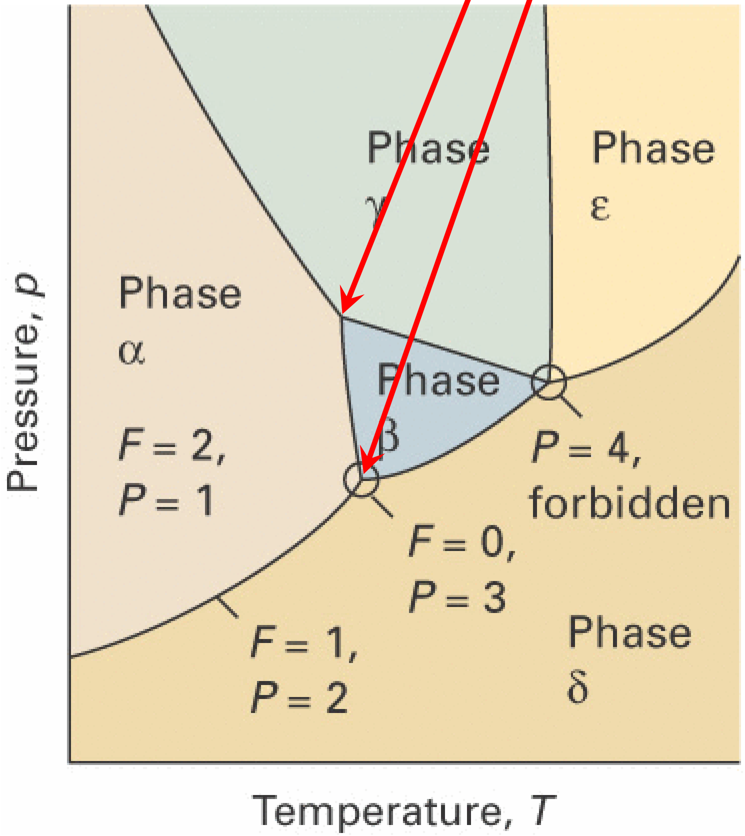
Gibbs phase rule

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

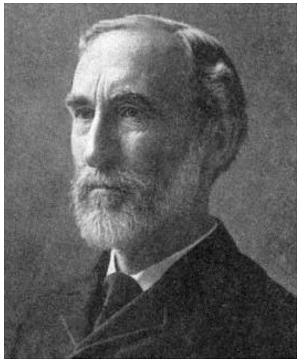
Phase diagrams of unary systems



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



unary phase diagram

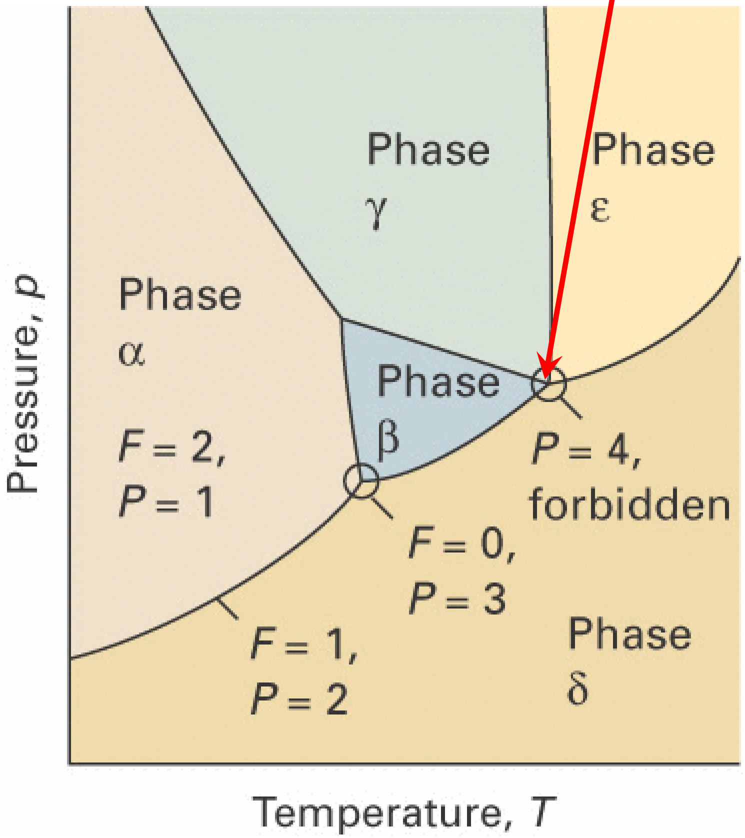


Gibbs phase rule

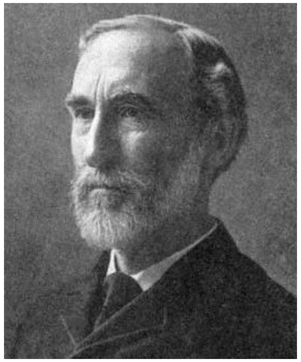
$$\boxed{F = C - P + 2}$$

Phase diagrams of unary systems

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



unary phase diagram

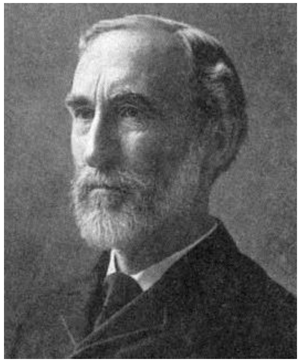


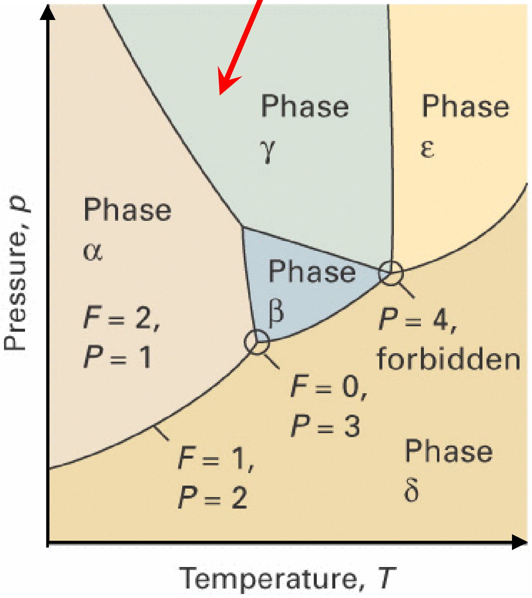
Gibbs phase rule

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

Phase diagrams of binary systems

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



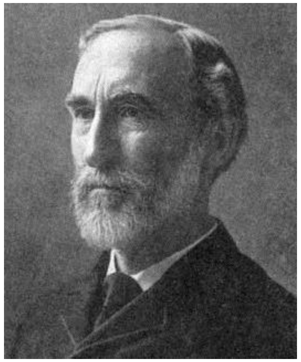


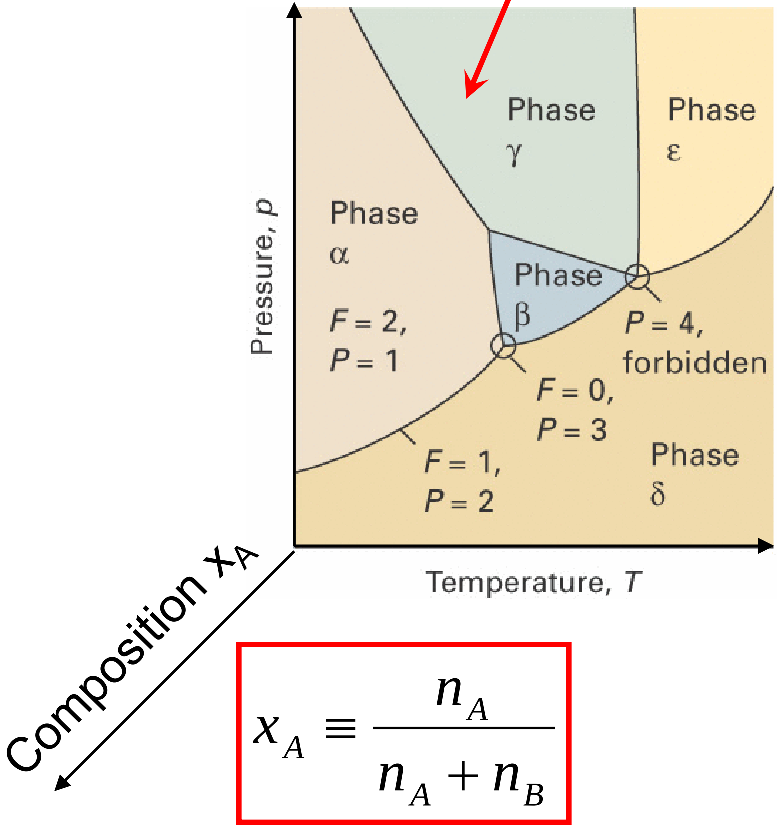
Gibbs phase rule

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

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

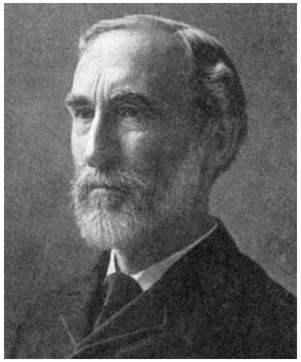
$$\boxed{F = C - P + 2}$$

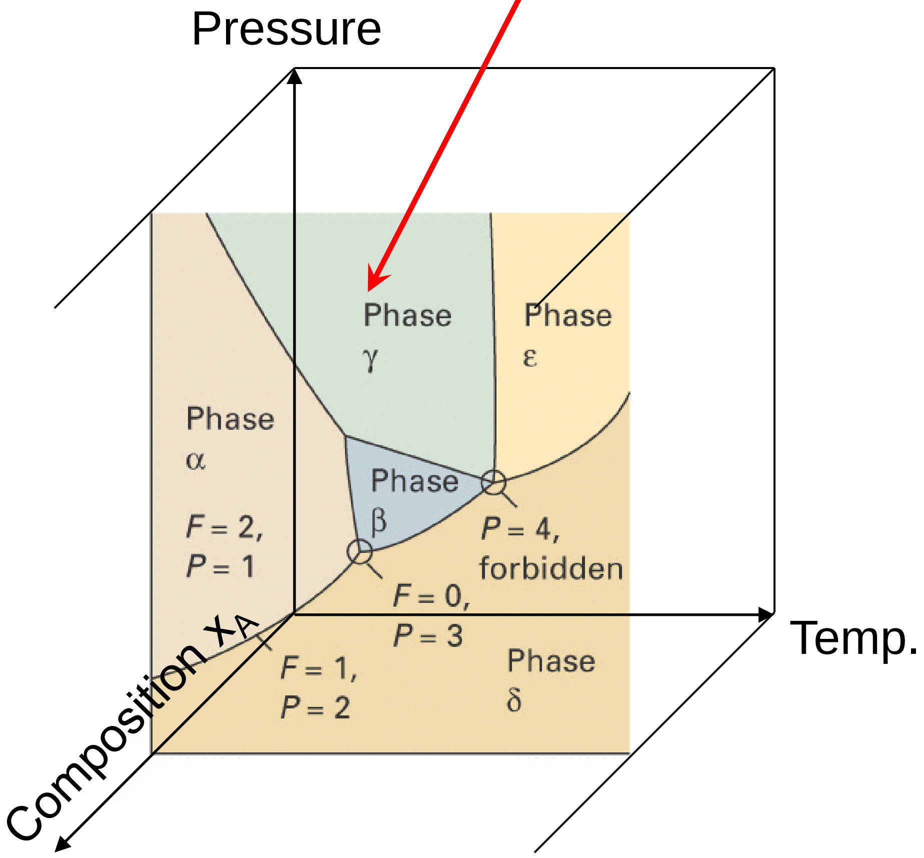
$$\boxed{x_A \equiv \frac{n_A}{n_A + n_B}}$$

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

Phase diagrams of binary systems

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





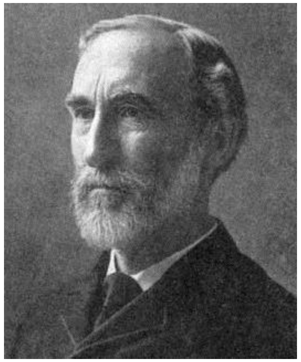
Gibbs phase rule

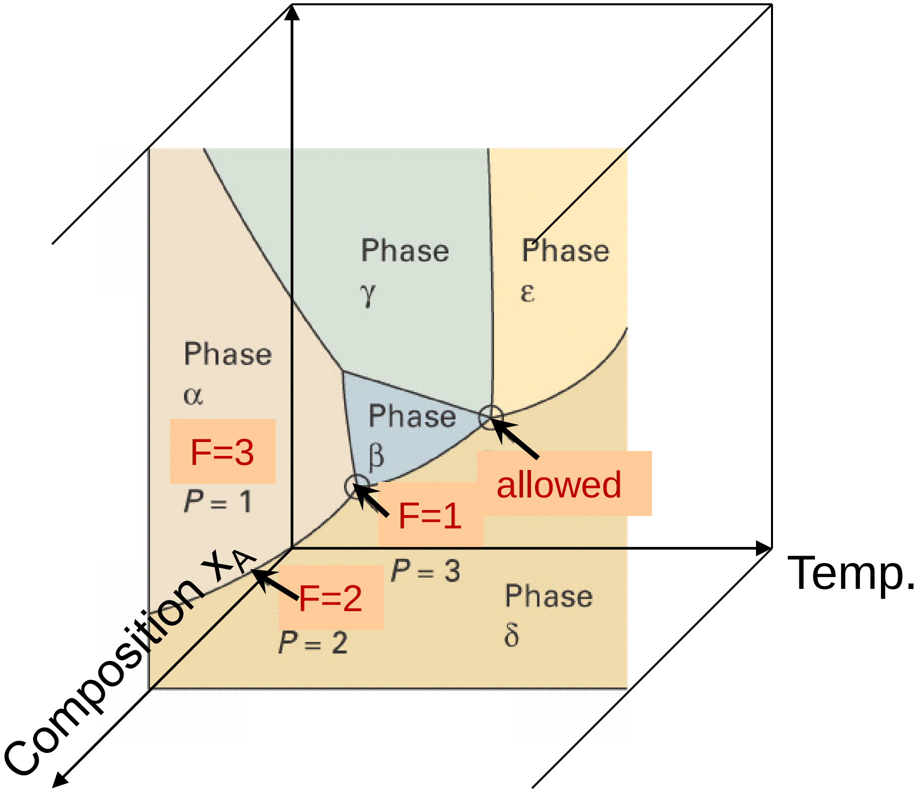
$$\boxed{F = C - P + 2}$$

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

Phase diagrams of binary systems

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





Gibbs phase rule

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

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

Partial molar quantities in mixtures

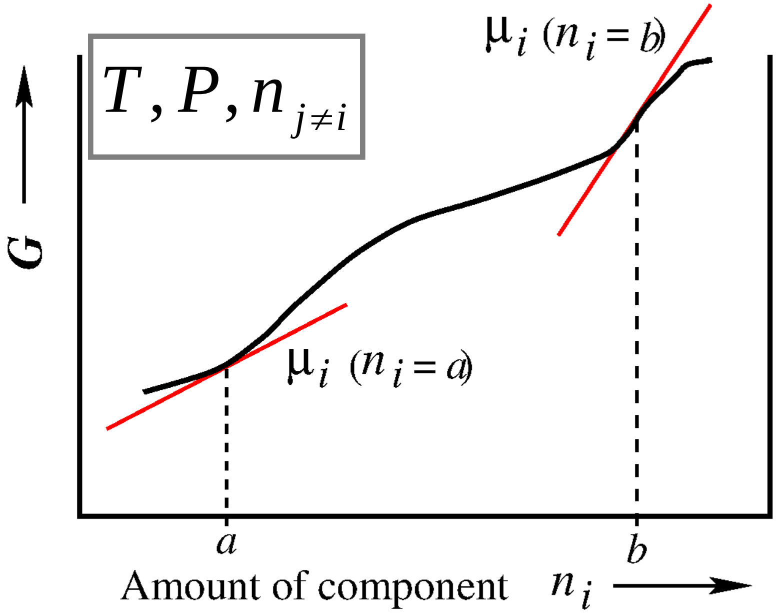
Partial molar quantities in mixtures

The chemical potential of a component *i* in mixtures

(Study guide p.11-13)

mixture → $\boxed{dn_i \neq 0}$

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$



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

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

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

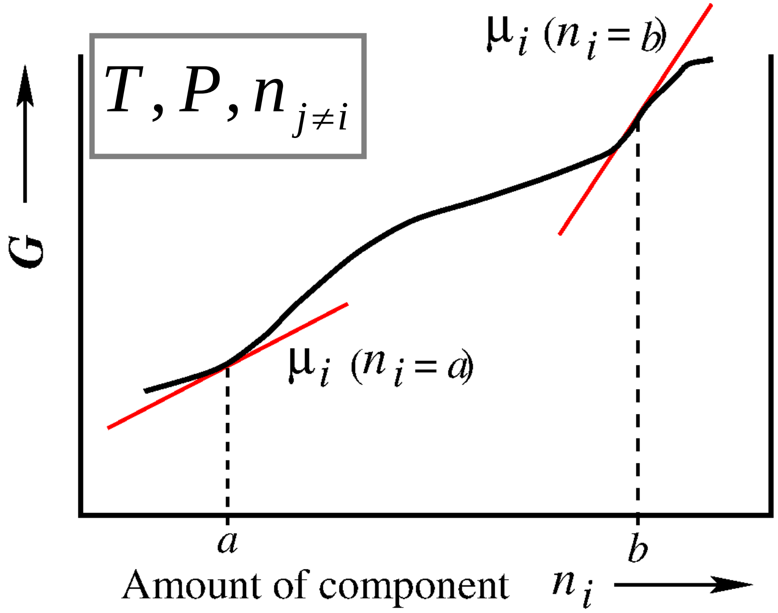
μ_i: the chemical potential is a partial molar quantity

Partial molar quantities: Chemical potential

The chemical potential of a component *i* in mixtures

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

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



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

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

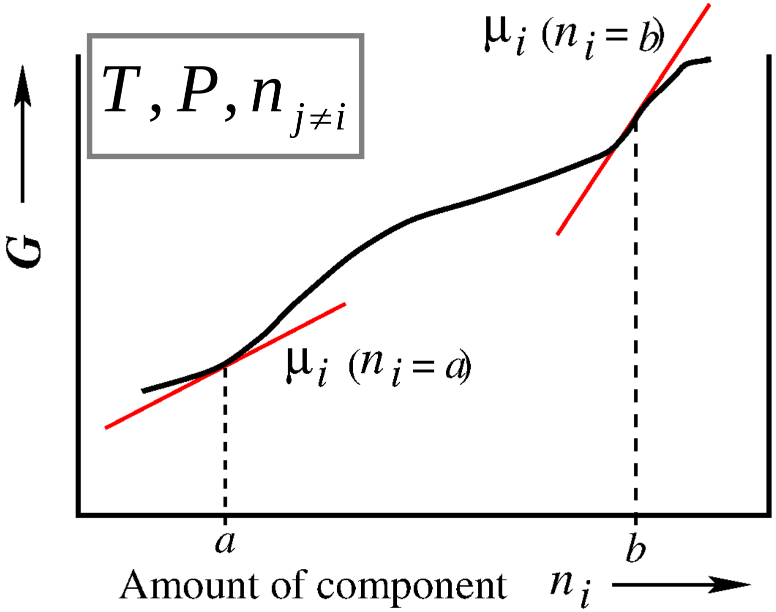
For pure solids $\boxed{a_s \approx 1}$ ⇒ $\boxed{\mu_s \approx \mu_s^\Theta}$

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*

$$\boxed{P^{\Theta} \equiv 1\,\text{bar}}$$

$$\boxed{a_i \equiv 1}$$

$$\boxed{\text{component } i \text{ is pure}}$$

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
(-)

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

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

Molarity
(mol/L)

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

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

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

Molality
(mol/kg)

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

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

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

example

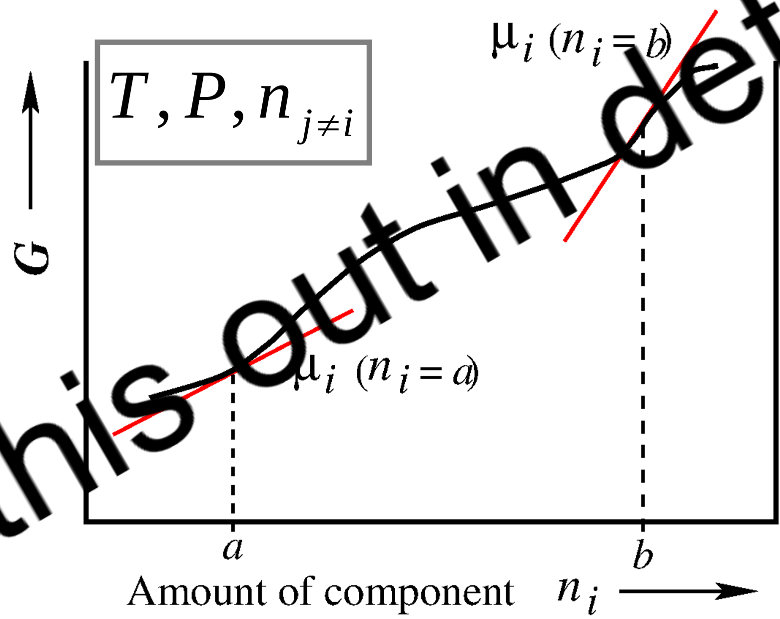
$$\boxed{\text{pH} \equiv -\log a_{\text{H}^+} = -\log \frac{c_{\text{H}^+}}{c^{\Theta}} - \log \gamma_{\text{H}^+}}$$

Partial molar quantities: Chemical potential

The chemical potential of a component *i* in mixtures

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

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



Let's work this out in detail

$$G\big|_{P,T}^{\alpha} = \mu_{\mathrm{A}}^{\alpha}\mathrm{n}_{\mathrm{A}}^{\alpha} + \mu_{\mathrm{B}}^{\alpha}\mathrm{n}_{\mathrm{B}}^{\alpha} + \cdots = \sum_i \mu_i^{\alpha}\mathrm{n}_i^{\alpha}$$

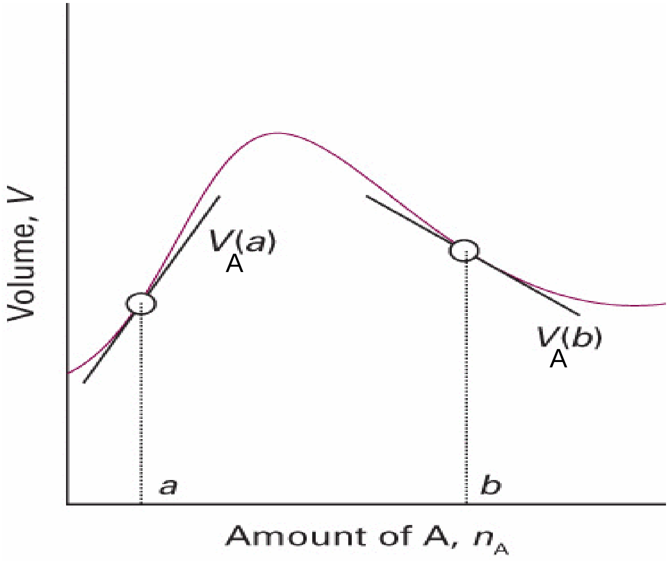
binary systems $$G\big|_{P,T}^{\alpha} = \mu_{\mathrm{A}}^{\alpha}\mathrm{n}_{\mathrm{A}}^{\alpha} + \mu_{\mathrm{B}}^{\alpha}\mathrm{n}_{\mathrm{B}}^{\alpha}$$ **for phase α**

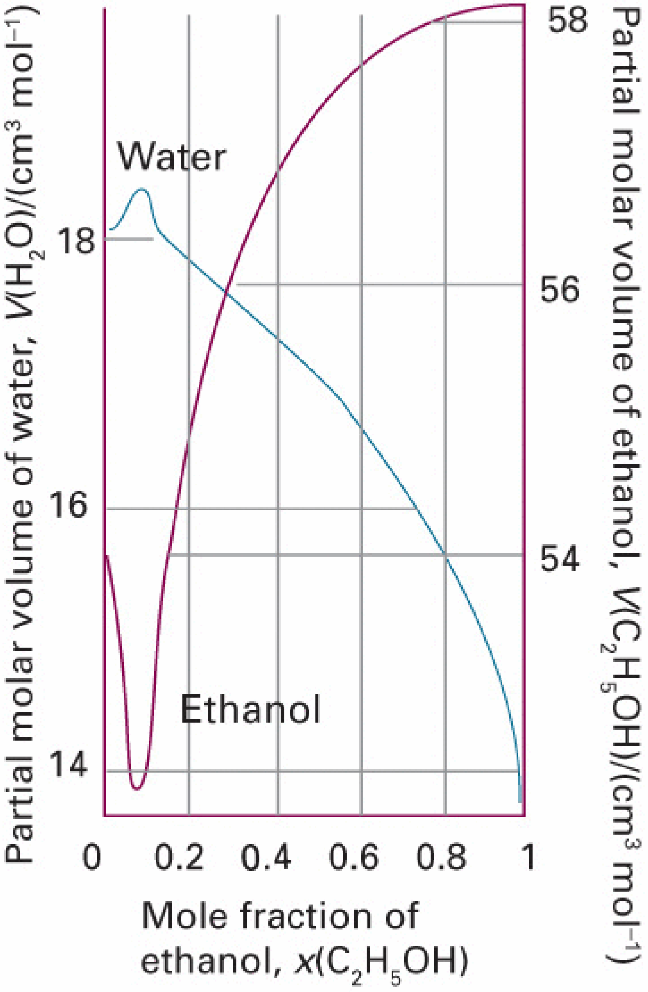
(Study guide p.13)

Partial molar quantities: Partial molar volume

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

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



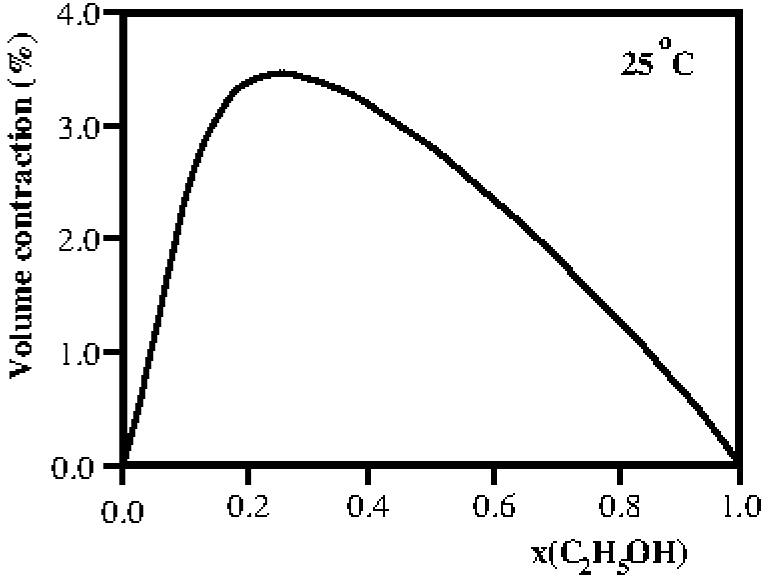


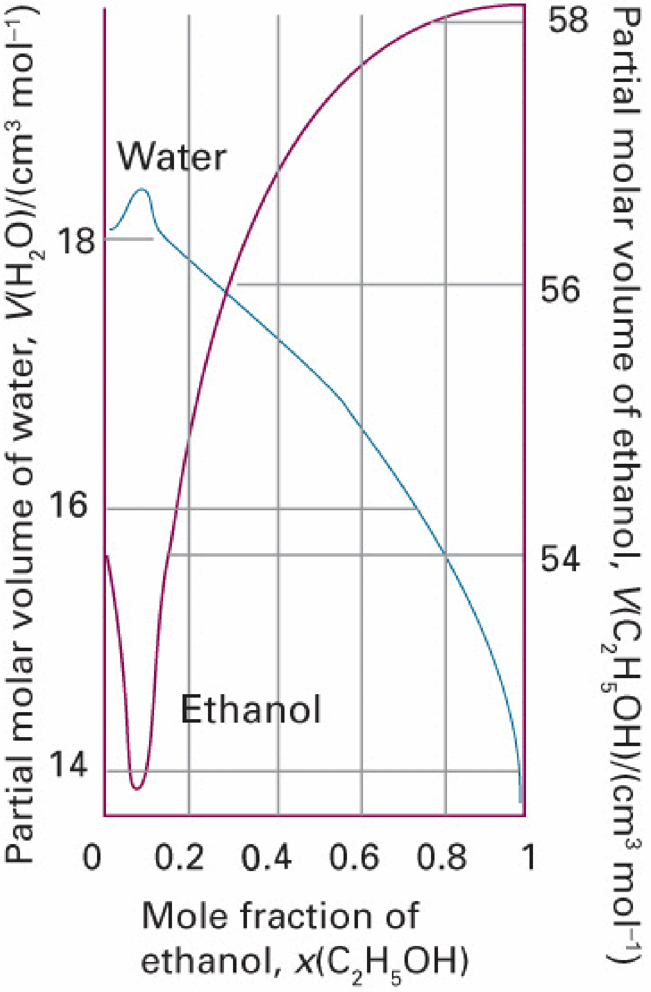
binary systems $$V^{\alpha}_{P,T} = V^{\alpha}_{A} n^{\alpha}_{A} + V^{\alpha}_{B} n^{\alpha}_{B}$$ **for phase α**

Partial molar quantities: Partial molar volume

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

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





binary systems $\boxed{V^{\alpha}_{P,T} = V^{\alpha}_{A} n^{\alpha}_{A} + V^{\alpha}_{B} n^{\alpha}_{B}}$ **for phase α**

Partial molar quantities: Partial molar volume

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

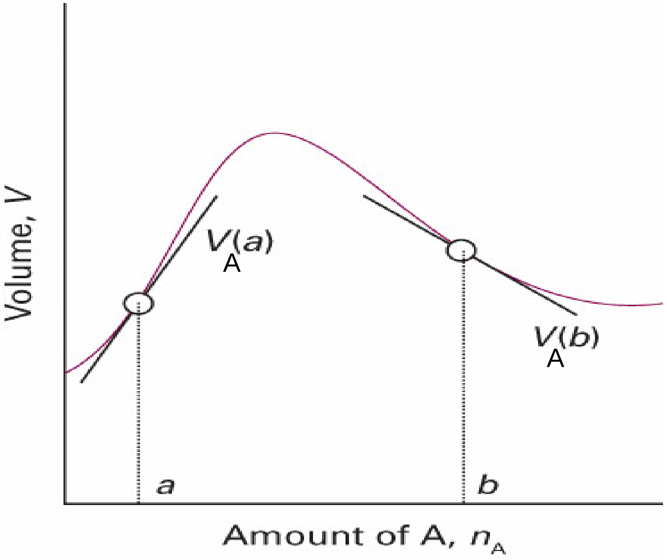
$$\boxed{V_i = \left(\frac{\partial V}{\partial n_i}\right)_{P,T,n_{j\neq i}}}$$

binary systems

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

for phase α

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



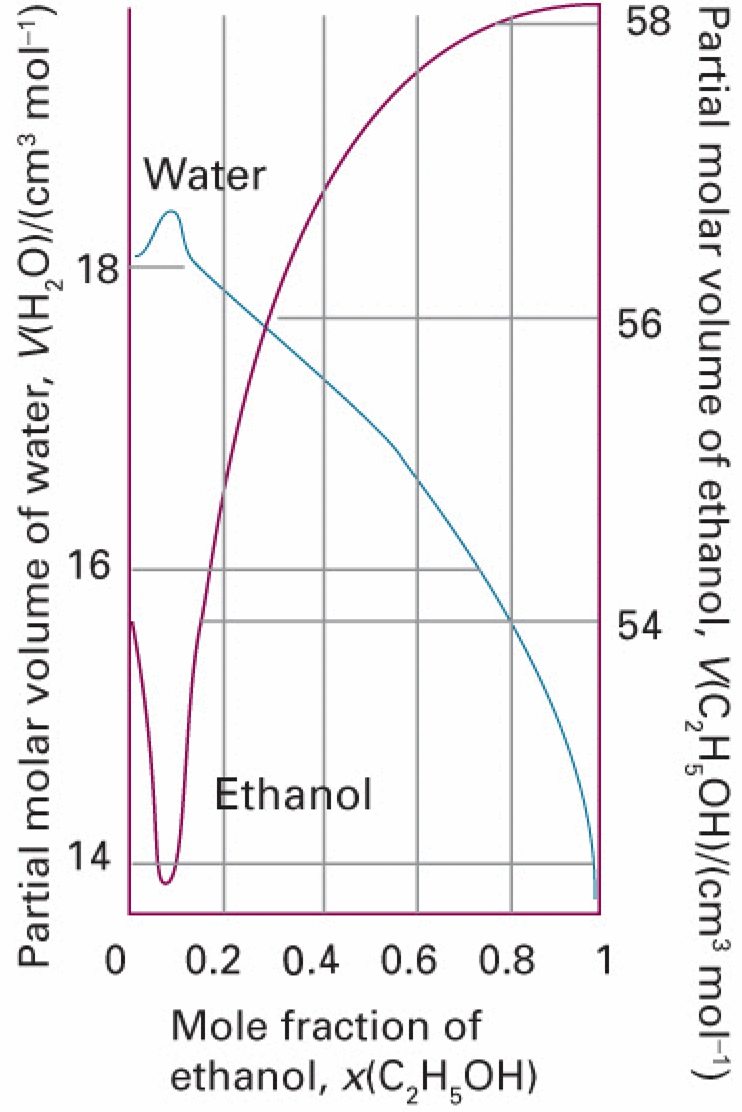
for each phase

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

(molar volume)

Exercise 10-11

Partial molar quantities: Gibbs-Duhem equation



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

$$\boxed{V = V_A n_A + V_B n_B}$$

$$\boxed{dV = V_A dn_A + V_B dn_B}$$

$$\boxed{dV = V_A dn_A + V_B dn_B + n_A dV_A + n_B dV_B}$$

$$\boxed{\sum_i n_i dV_i = 0} \quad \boxed{0 = n_A dV_A + n_B dV_B}$$

Gibbs-Duhem equation

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

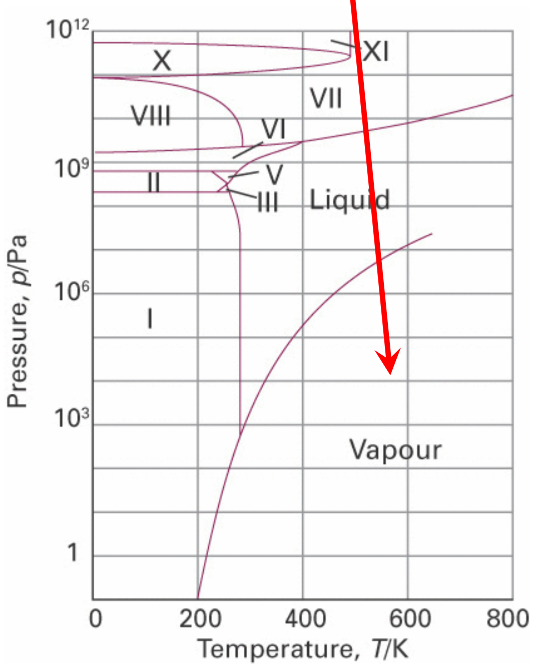
(for any state function)

Mixing processes of perfect gases:binary mixture

(Study guide p.14-16)

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

$$\underbrace{\boxed{\overset{P,T}{H_2O\,(g)}}\;+\;\boxed{\overset{P,T}{\text{EthOH}\,(g)}}}_{\textbf{initial pure compounds}}\;\rightarrow\;\underbrace{\boxed{\overset{P,T}{H_2O\,(g)+\text{EthOH}\,(g)}}}_{\textbf{final mixture}}$$



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

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

Unary phase diagram: *P* = 1

Mixing processes of perfect gases:binary mixture

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

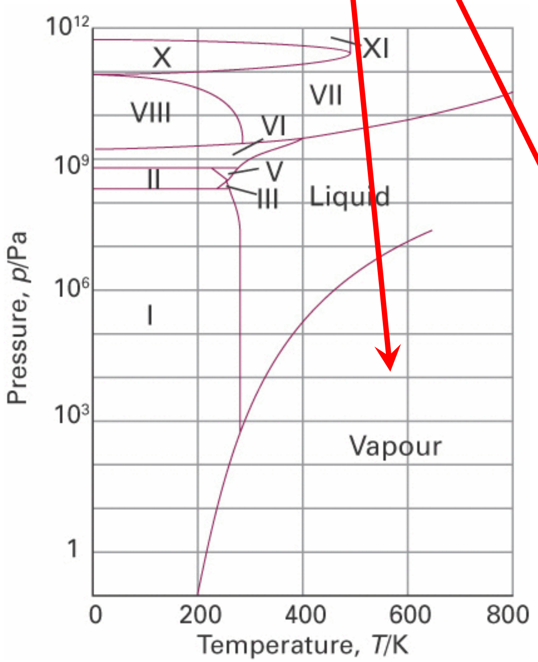
$H_2O\,(g)$ P,T + $EthOH\,(g)$ P,T → $H_2O\,(g) + EthOH\,(g)$ P,T

$$P = P_A + P_B$$

(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:

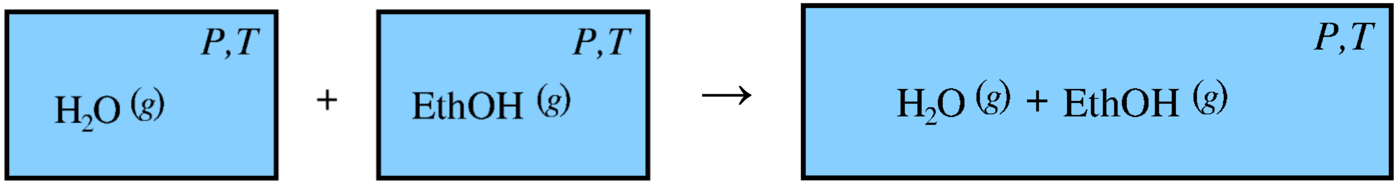
$$G^g_{\text{initial}} = n_{\text{A},g}\left(\mu^{\Theta}_{\text{A},g} + RT\ln\frac{P}{P^{\Theta}}\right) + n_{\text{B},g}\left(\mu^{\Theta}_{\text{B},g} + RT\ln\frac{P}{P^{\Theta}}\right)$$

$-$

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

Mixing processes of perfect gases: binary mixture

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



P,T

$H_2O\,(g)$

$+$

P,T

$\mathrm{EthOH}\,(g)$

$\rightarrow$

P,T

$H_2O\,(g) + \mathrm{EthOH}\,(g)$

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

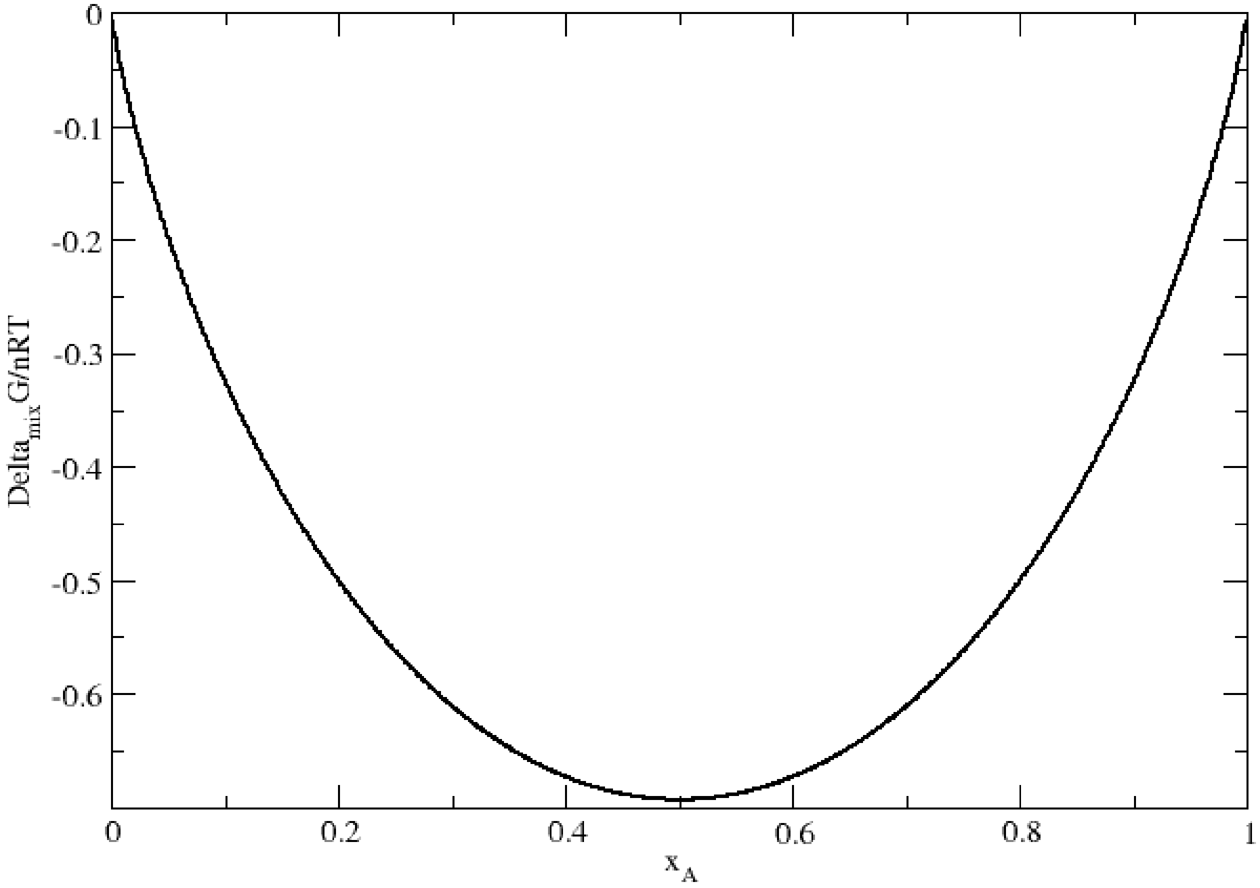
Mole fraction $$x_i = \frac{n_i}{n} \equiv \frac{P_i}{P}$$

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

Mixing processes of perfect gases:binary mixture

Perfect gas mixing

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



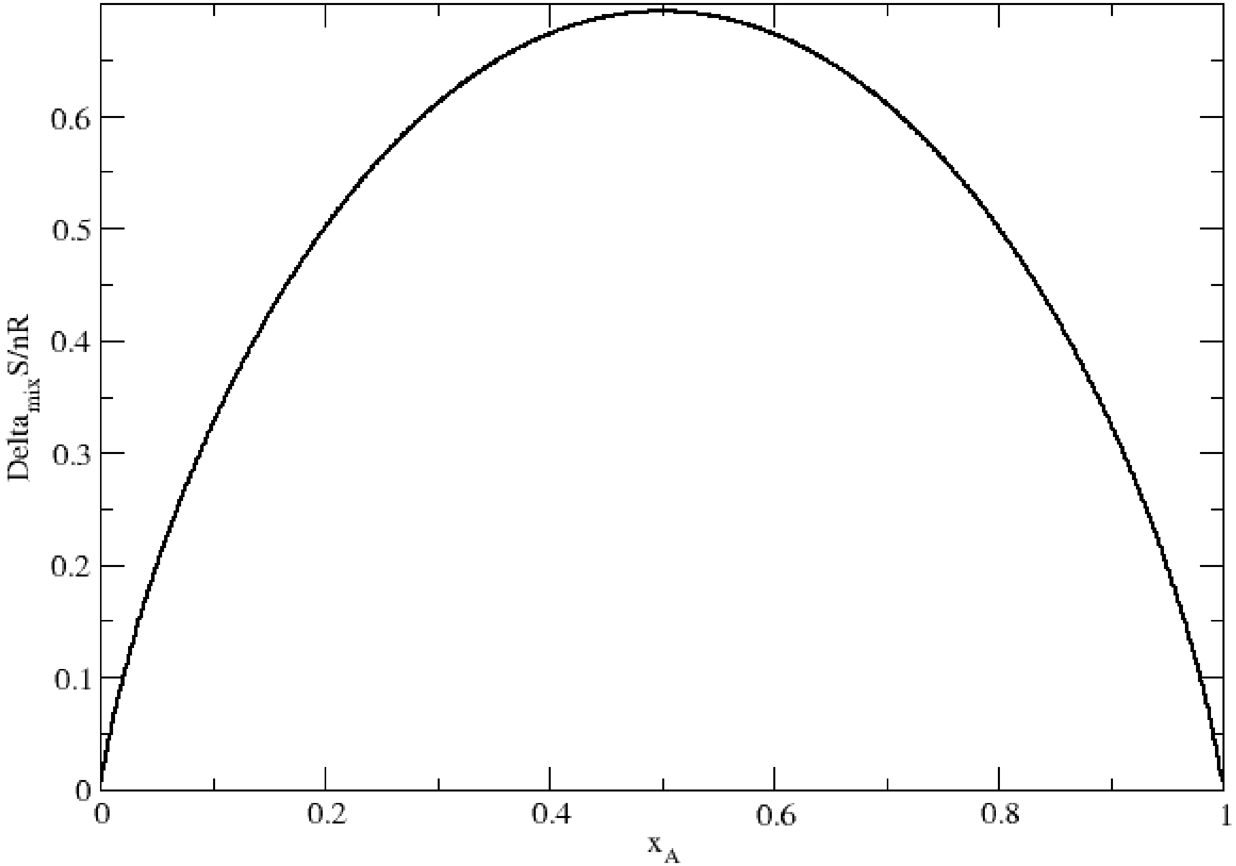
Mixing processes of perfect gases:binary mixture

Perfect gas mixing

$$\Delta_{\text{mix}} G\Big|_{T} = \Delta_{\text{mix}} H - T\Delta_{\text{mix}} S$$

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

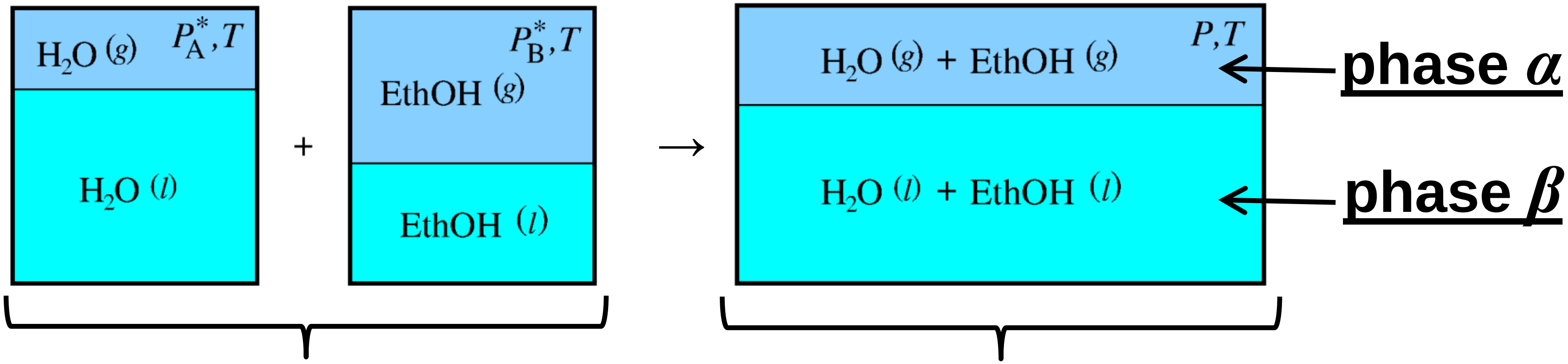
$$\Delta_{\text{mix}} H = 0$$



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



$H_2O\,(g)$ P_A^*, T

$H_2O\,(l)$

+

P_B^*, T $EthOH\,(g)$

$EthOH\,(l)$

$\rightarrow$

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

$H_2O\,(l) + EthOH\,(l)$

phase α

phase β

initial pure compounds

final mixture

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

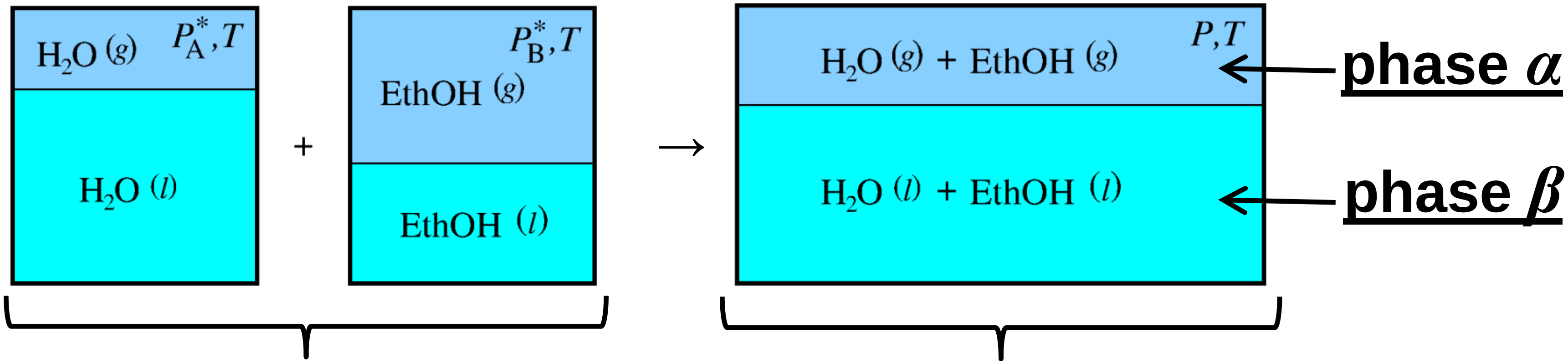
vapor pressure

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

(* : pure compound)

Solutions and mixing processes:binary mixture

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



$H_2O\ (g)$ P_A^*, T

$H_2O\ (l)$

+

P_B^*, T $EthOH\ (g)$

$EthOH\ (l)$

→

P, T

$H_2O\ (g) + EthOH\ (g)$ ← **phase α**

$H_2O\ (l) + EthOH\ (l)$ ← **phase β**

initial pure compounds

final mixture

vapor pressures

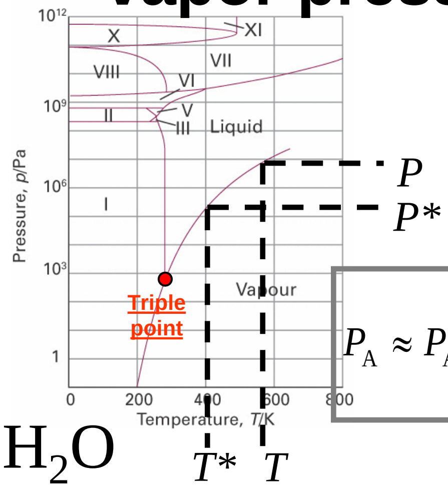
$$\boxed{P_A^*(T)}$$

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

vapor pressure

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

(* : pure compound)



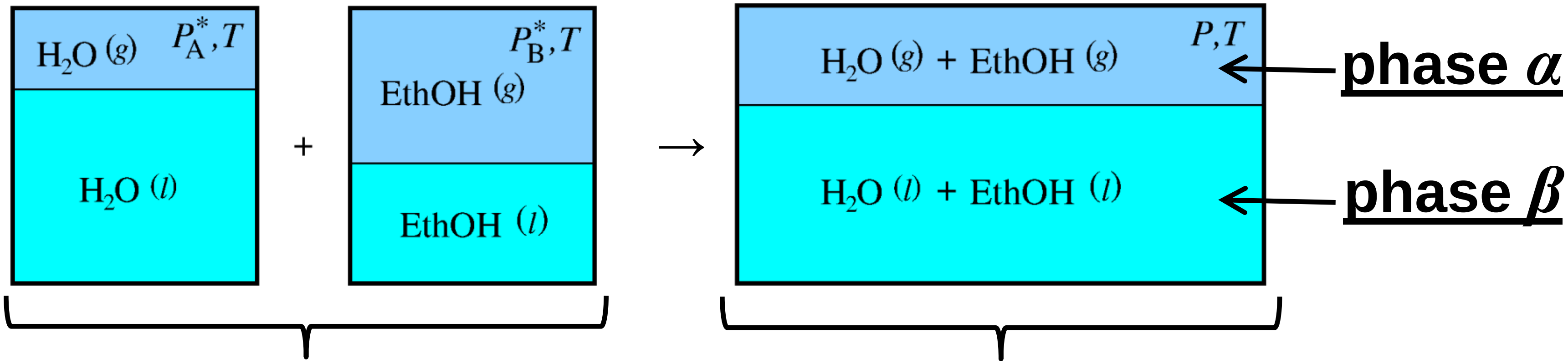
Clausius-Clapeyron

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

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

Solutions and mixing processes:binary mixture

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



initial pure compounds

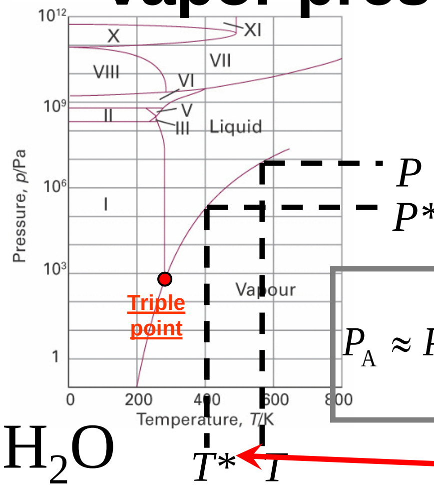
final mixture

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

vapor pressure

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

(* : pure compound)



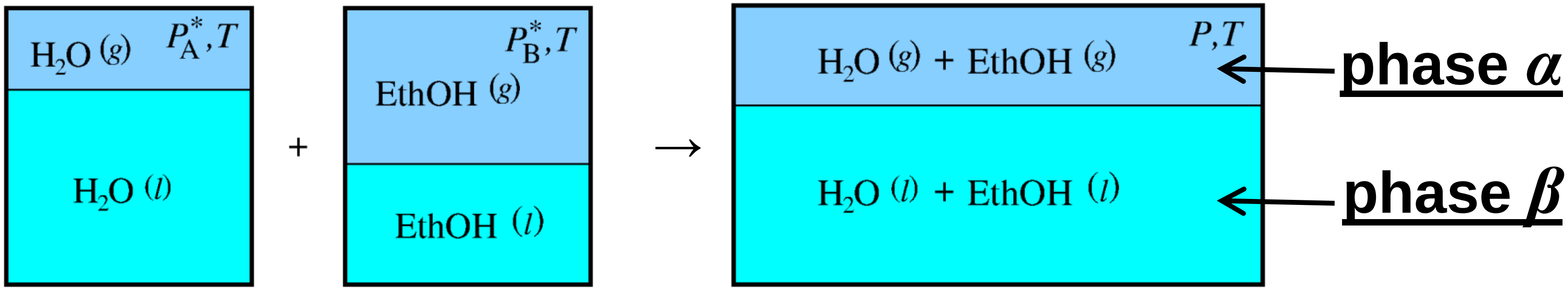
Clausius-Clapeyron

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

(* : reference T,P)

Solutions and mixing processes: binary mixture

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



$H_2O\ (g)$ P_A^*, T

$H_2O\ (l)$

+

EthOH (g) P_B^*, T

EthOH (l)

→

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

$H_2O\ (l)$ + EthOH (l)

phase *α*

phase *β*

phase *α* $$G\Big|_{P,T}^{\alpha} = \sum_i \mu_{i,\alpha} n_{i,\alpha} = \mu_{\mathrm{A},\alpha} n_{\mathrm{A},\alpha} + \mu_{\mathrm{B},\alpha} n_{\mathrm{B},\alpha}$$ **(sim. phase *β*)**

(slide 18: def. of μ) →

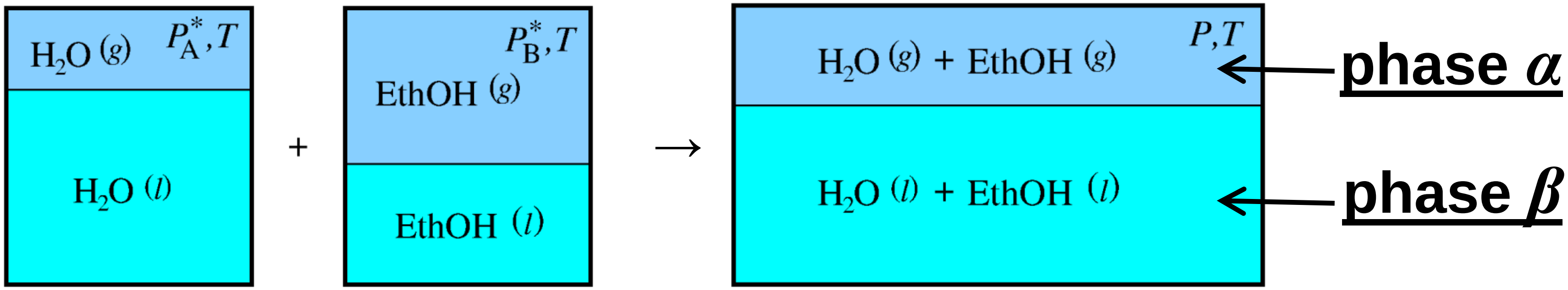
Initial: $$G_{\mathrm{initial}}^{\alpha} = n_{\mathrm{A},\alpha}\left(\mu_{\mathrm{A},\alpha}^{\Theta} + RT \ln a_{\mathrm{A},\alpha}^{*}\right) + n_{\mathrm{B},\alpha}\left(\mu_{\mathrm{B},\alpha}^{\Theta} + RT \ln a_{\mathrm{B},\alpha}^{*}\right)$$

(* : initial phases are pure; before mixing)

(Note: Θ per definition for pure compound)

Solutions and mixing processes: binary mixture

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



$H_2O\,(g)$ P_A^*, T

$H_2O\,(l)$

$+$

P_B^*, T $\text{EthOH}\,(g)$

$\text{EthOH}\,(l)$

$\rightarrow$

P, T

$H_2O\,(g) + \text{EthOH}\,(g)$ ← **phase *α***

$H_2O\,(l) + \text{EthOH}\,(l)$ ← **phase *β***

phase *α*

Final:

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

Initial:

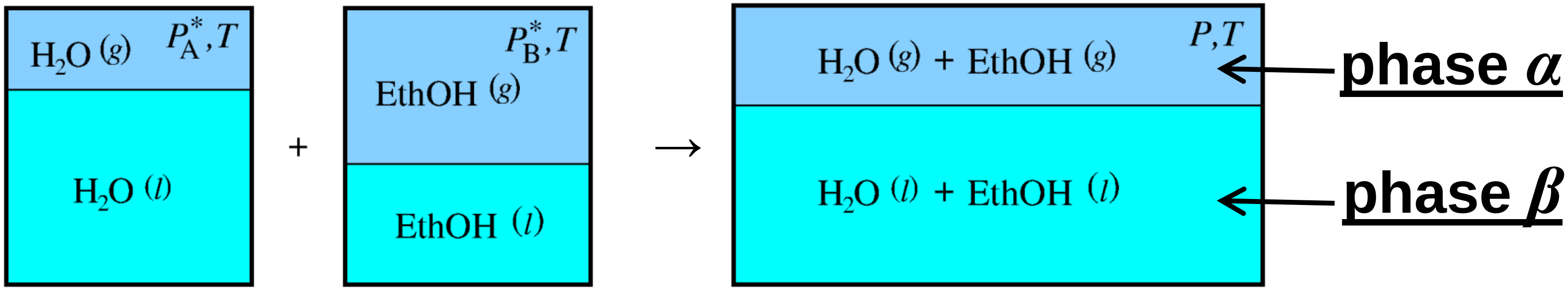
$$\boxed{G^{\alpha}_{\text{initial}} = n_{A,\alpha}\left(\mu^{\ominus}_{A,\alpha} + RT\ln a^{*}_{A,\alpha}\right) + n_{B,\alpha}\left(\mu^{\ominus}_{B,\alpha} + RT\ln a^{*}_{B,\alpha}\right)}$$

$-$

$$\boxed{\Delta_{\text{mix}}G^{\alpha} = G^{\alpha}_{\text{final}} - G^{\alpha}_{\text{initial}} = n_{A,\alpha}RT\ln\frac{a_{A,\alpha}}{a^{*}_{A,\alpha}} + n_{B,\alpha}RT\ln\frac{a_{B,\alpha}}{a^{*}_{B,\alpha}}}$$

Solutions and mixing processes: binary mixture

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


$H_2O\,(g)$ P_A^*, T

$H_2O\,(l)$

+

P_B^*, T EthOH (g)

EthOH (l)

→

P, T $H_2O\,(g)$ + EthOH (g) ← **phase α**

$H_2O\,(l)$ + EthOH (l) ← **phase β**

phase α

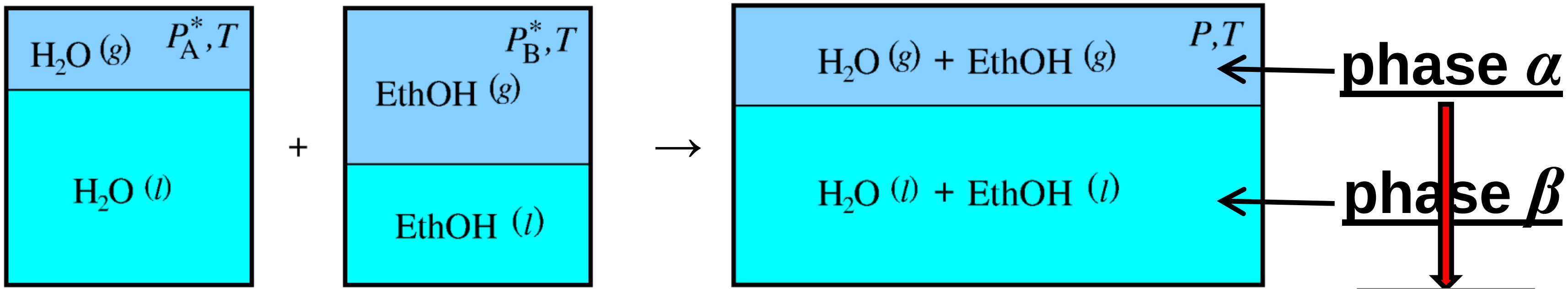
$$\boxed{\Delta_{\text{mix}} G^{\alpha} = G^{\alpha}_{\text{final}} - G^{\alpha}_{\text{initial}} = n_{A,\alpha} RT \ln \frac{a_{A,\alpha}}{a^*_{A,\alpha}} + n_{B,\alpha} RT \ln \frac{a_{B,\alpha}}{a^*_{B,\alpha}}}$$

$$\Rightarrow \boxed{\Delta_{\text{mix}} G^{\alpha} = n_{\alpha} RT \left(x_{A,\alpha} \ln \frac{a_{A,\alpha}}{a^*_{A,\alpha}} + x_{B,\alpha} \ln \frac{a_{B,\alpha}}{a^*_{B,\alpha}} \right)}$$

(similar for phase β)

Solutions and mixing processes: gas phase α

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



$$\boxed{\alpha = g}$$

$$\boxed{\Delta_{\text{mix}} G^{\alpha} = n_{\alpha} RT \left(x_{A,\alpha} \ln \frac{a_{A,\alpha}}{a^*_{A,\alpha}} + x_{B,\alpha} \ln \frac{a_{B,\alpha}}{a^*_{B,\alpha}} \right)}$$

initial: pure perfect gases ➡ $$\boxed{a^*_{i,\alpha} = \frac{P^*_{i,g}}{P^{\Theta}}}$$

final: mixed perfect gases @ P ➡ $$\boxed{a_{i,\alpha} = \frac{P_{i,g}}{P^{\Theta}}}$$

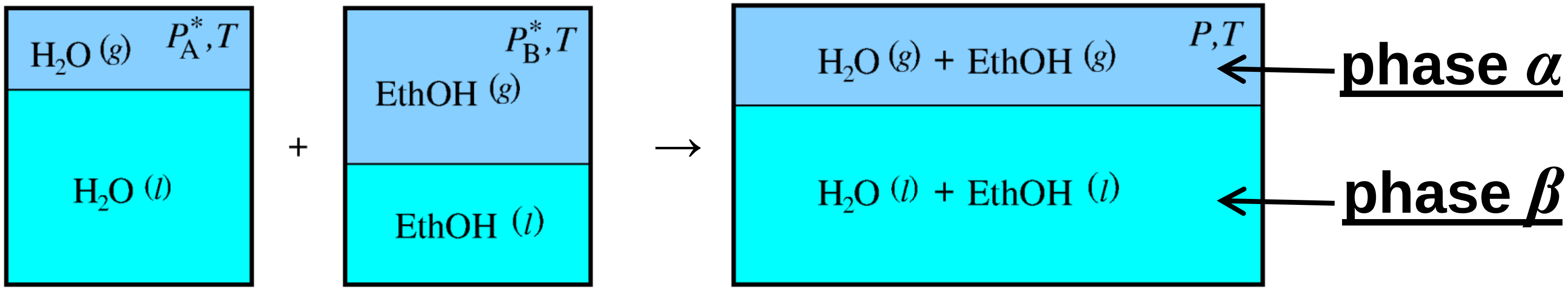
$$\left(P_{A,g} + P_{B,g} = P \right)$$

$$\boxed{n_{\alpha} = n_g}$$

➡

Solutions and mixing processes: gas phase α

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



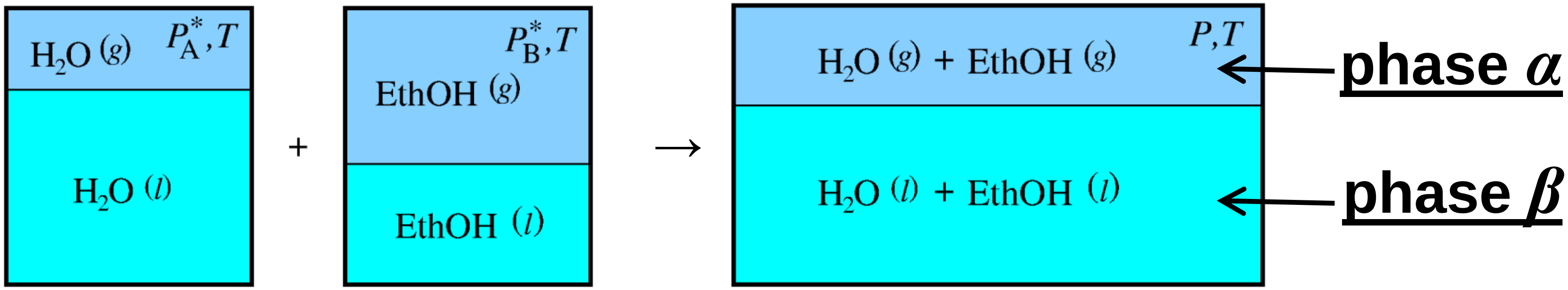
$$\boxed{\Delta_{\text{mix}} G^{g} = n_{g} RT\left(x_{\text{A},g} \ln \frac{P_{\text{A}}}{P_{\text{A}}^{*}} + x_{\text{B},g} \ln \frac{P_{\text{B}}}{P_{\text{B}}^{*}} \right)}$$

Note: $\boxed{\frac{P_{\text{A}}}{P_{\text{A}}^{*}} \neq x_{\text{A}}}$ and $\boxed{\frac{P_{\text{B}}}{P_{\text{B}}^{*}} \neq x_{\text{B}}}$ like in slide 30!

What about phase β (liquid)?

Solutions and mixing processes: gas phase α

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



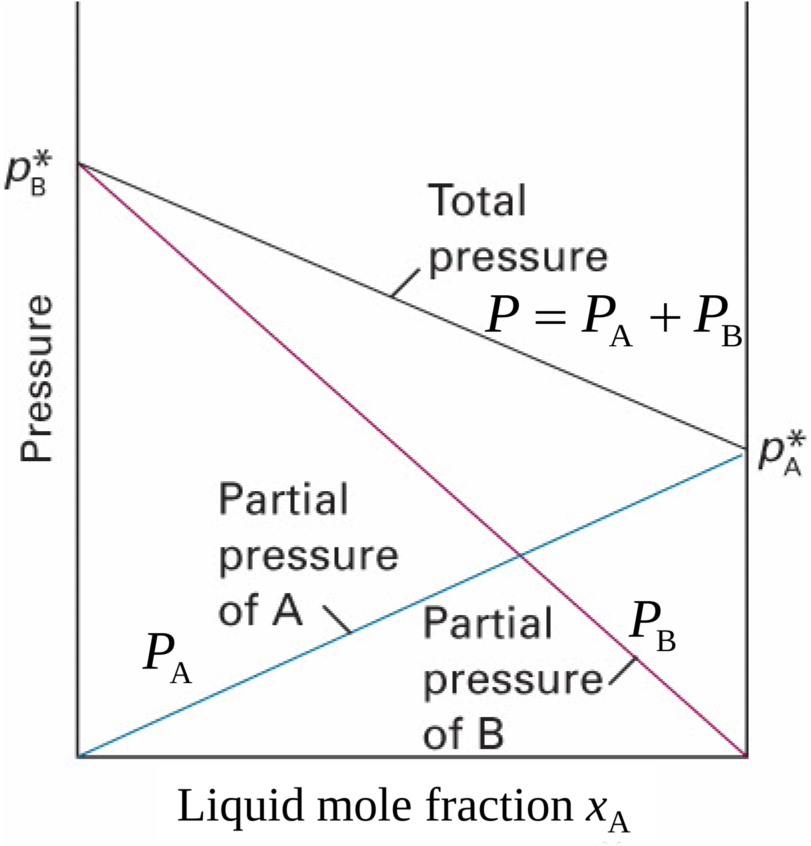
$$\Delta_{\text{mix}} G^g = n_g RT \left(x_{A,g} \ln \frac{P_A}{P_A^*} + x_{B,g} \ln \frac{P_B}{P_B^*} \right)$$

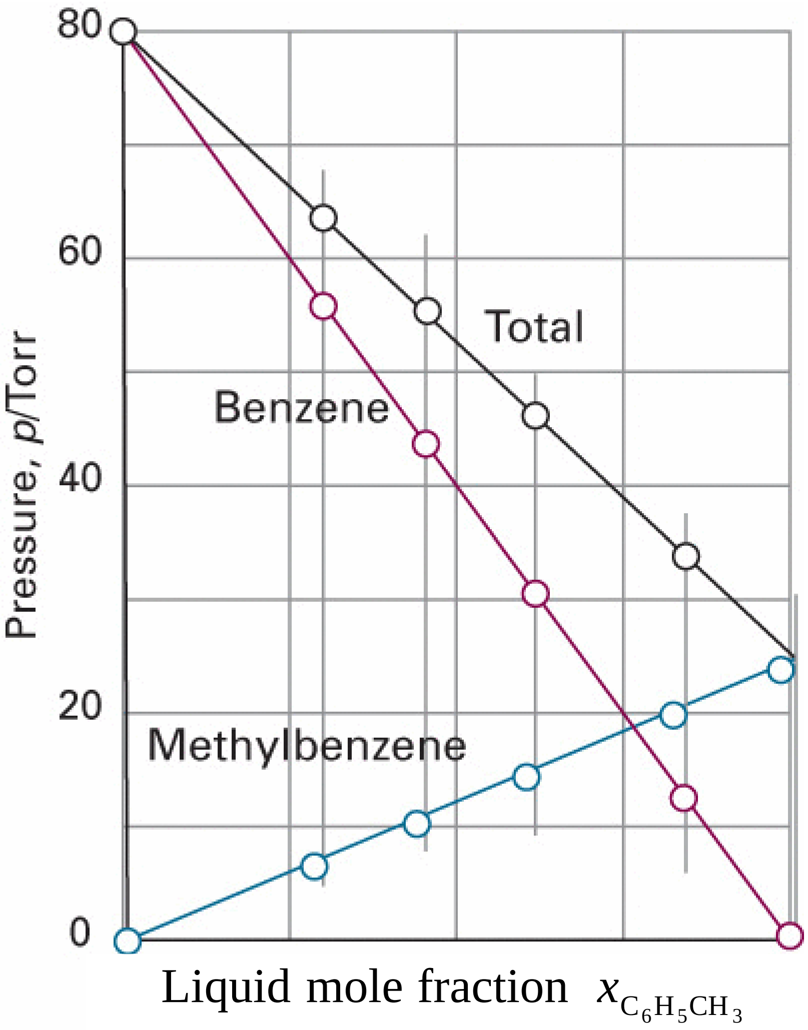
Raoult's law: Ideal solutions:

$$\underset{\text{vapor}}{P_{i,g}} = \underset{\text{liquid}}{x_{i,l}} \underset{\text{vapor}}{P_{i,g}^*}$$

Solutions: Ideal solutions (Raoult)

Raoult's law





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

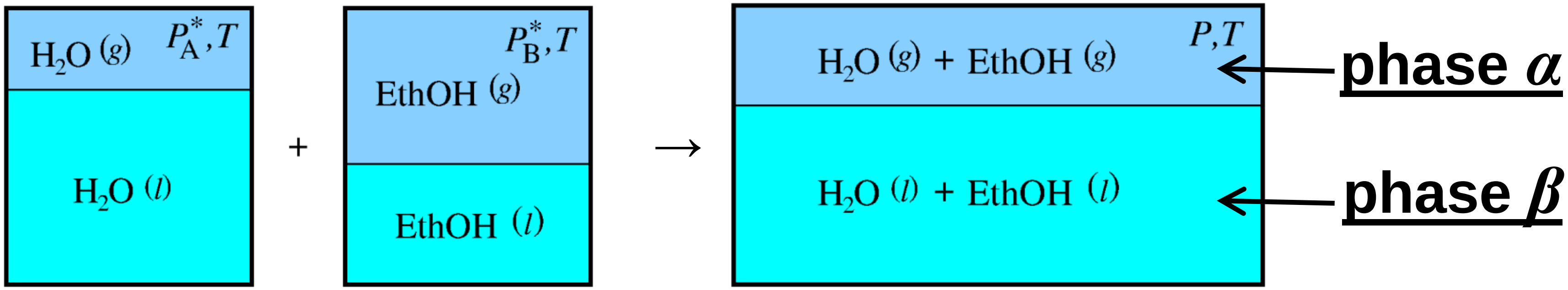
Raoult

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

Dalton

Solutions and mixing processes: gas phase α

The process of mixing two or more components @ T



H_2O (g) P_A^*, T

H_2O (l)

+

P_B^*, T

EthOH (g)

EthOH (l)

→

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

H_2O (l) + EthOH (l)

phase α

phase β

$$\Delta_{\text{mix}} G^{g} = n_{g} RT \left(x_{\text{A},g} \ln \frac{P_{\text{A}}}{P_{\text{A}}^{*}} + x_{\text{B},g} \ln \frac{P_{\text{B}}}{P_{\text{B}}^{*}} \right)$$

Raoult’s law: Ideal solutions: $$\boxed{P_{i,g} = x_{i,l} P_{i,g}^{*}}$$

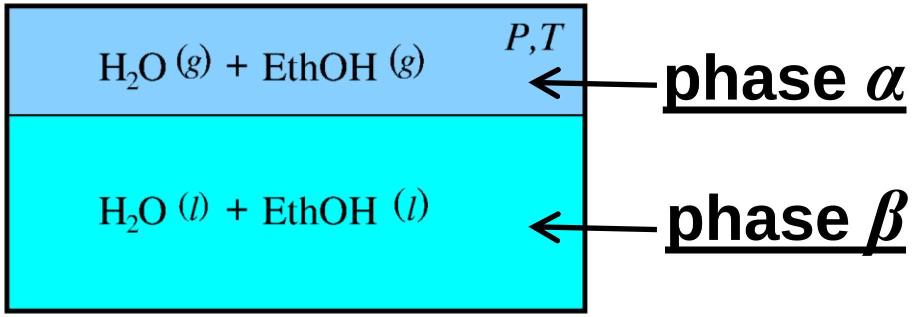
$$\Rightarrow \boxed{\Delta_{\text{mix}} G^{g} = n_{g} RT \left(x_{\text{A},g} \ln x_{\text{A},l} + x_{\text{B},g} \ln x_{\text{B},l} \right)}$$

(Note the mixture of *g* and *l* parameters)

(different from the gas mixture in single gas phase situation)

Solutions and mixing processes: liquid phase β

The process of mixing two or more components @ T



P,T

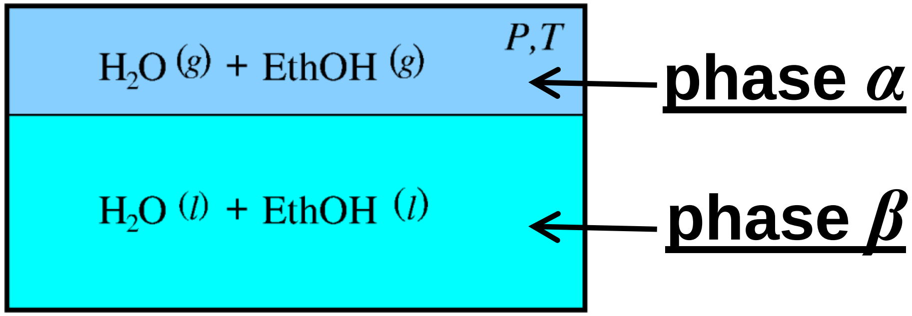
$H_2O\,(g) + \text{EthOH}\,(g)$ ← **phase α**

$H_2O\,(l) + \text{EthOH}\,(l)$ ← **phase β**

$$\textbf{Equilibrium} \Longleftrightarrow \boxed{\mu_{i,\alpha} = \mu_{i,\beta}} \quad \begin{cases} \boxed{\mu_{\mathrm{A},g} = \mu_{\mathrm{A},l}} \\ \boxed{\mu_{\mathrm{B},g} = \mu_{\mathrm{B},l}} \end{cases}$$

Solutions and mixing processes: liquid phase β

The process of mixing two or more components @ T



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

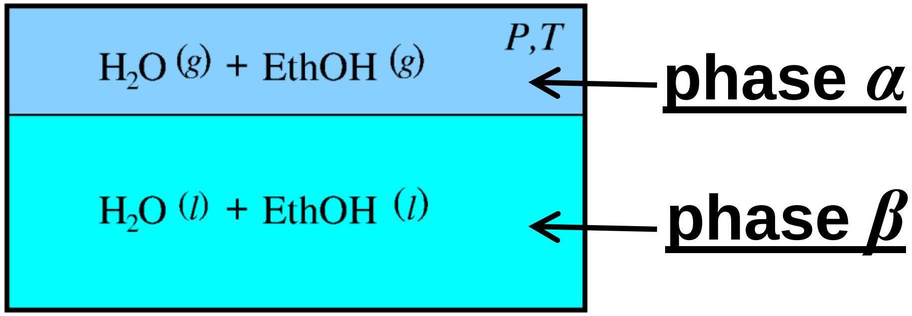
$$\boxed{\mu^{*}_{A,g} = \mu^{*}_{A,l}} \Rightarrow \boxed{\mu^{*}_{A,g} = \mu^{\Theta}_{A,g} + RT\ln\frac{P^{*}_A}{P^{\Theta}} = \mu^{*}_{A,l}}$$

$$\Rightarrow \boxed{RT\ln\frac{P_A}{P^{*}_A} = \mu_{A,l} - \mu^{*}_{A,l}}$$

(similar for B)

Solutions and mixing processes: liquid phase β

The process of mixing two or more components @ T



$$\boxed{RT \ln \frac{P_A}{P_A^*} = \mu_{A,l} - \mu_{A,l}^*}$$

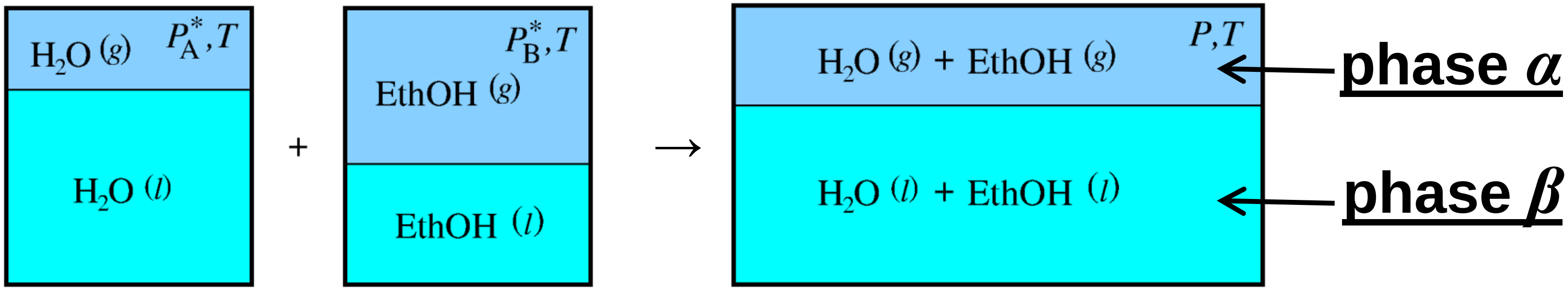
Raoult's law: Ideal solutions: $\boxed{P_{i,g} = x_{i,l} P_{i,g}^*}$

$$\boxed{RT \ln x_{A,l} = \mu_{A,l} - \mu_{A,l}^*}$$

Ideal solutions: $\boxed{\mu_{A,l} = \mu_{A,l}^* + RT \ln x_{A,l}}$ **(similar for B)**

Solutions: Ideal solutions (Raoult) liquid phase β

The process of mixing two or more components @ T



$$\boxed{\Delta_{\text{mix},l} G = \underbrace{\left(n_{\text{A},l}\mu_{\text{A},l} + n_{\text{B},l}\mu_{\text{B},l}\right)}_{\text{final mixture}} - \underbrace{\left(n_{\text{A},l}\mu^*_{\text{A},l} + n_{\text{B},l}\mu^*_{\text{B},l}\right)}_{\text{initial pure compounds}}}$$

Ideal solution: $\boxed{\mu_{\text{A},l} = \mu^*_{\text{A},l} + RT \ln x_{\text{A},l}}$ **(similar for B)**

Similar to the perfect gas case:

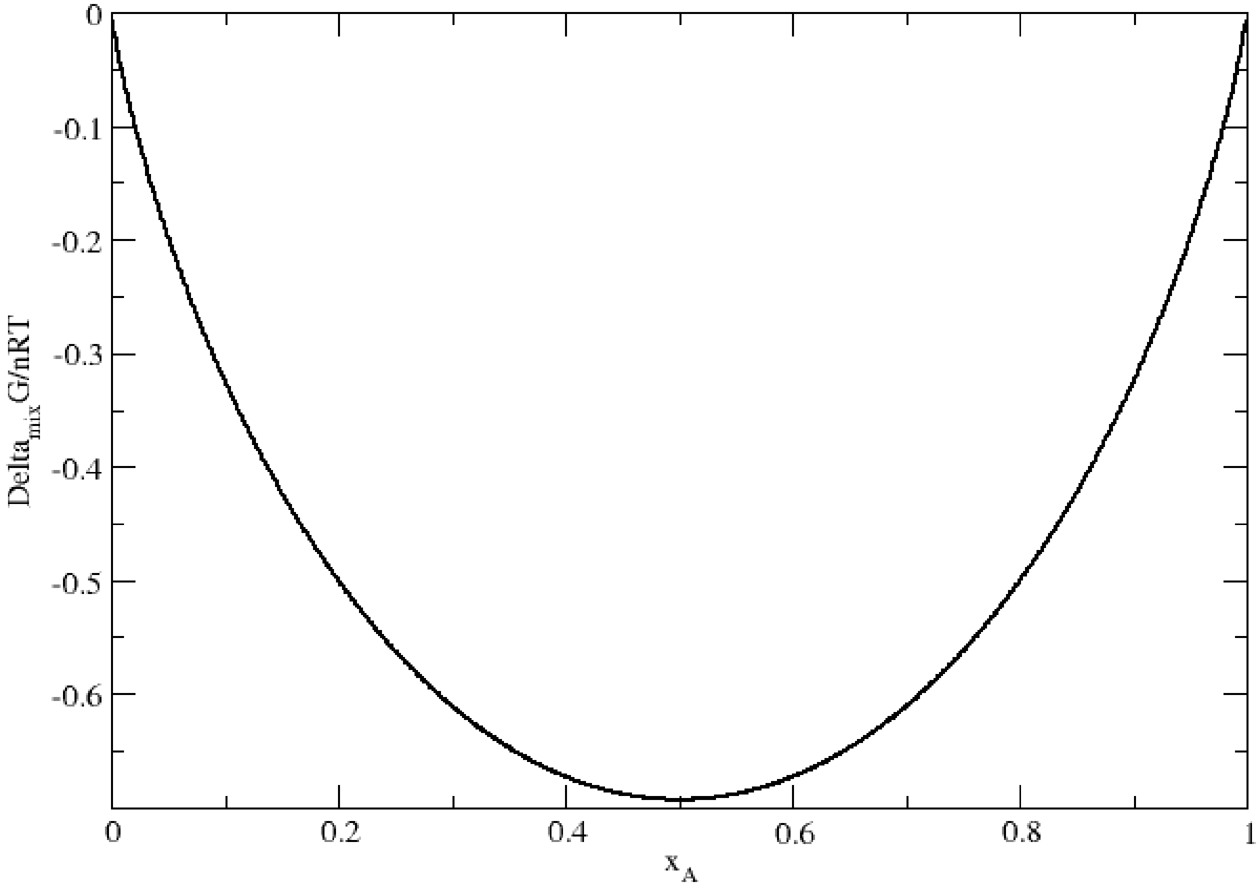
$$\boxed{\Delta_{\text{mix},l} G = n_l RT \left(x_{\text{A},l} \ln x_{\text{A},l} + x_{\text{B},l} \ln x_{\text{B},l}\right)}$$

Ideal solution (of the liquid)

Solutions: Ideal solutions (Raoult) liquid phase β

Ideal liquid mixing

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

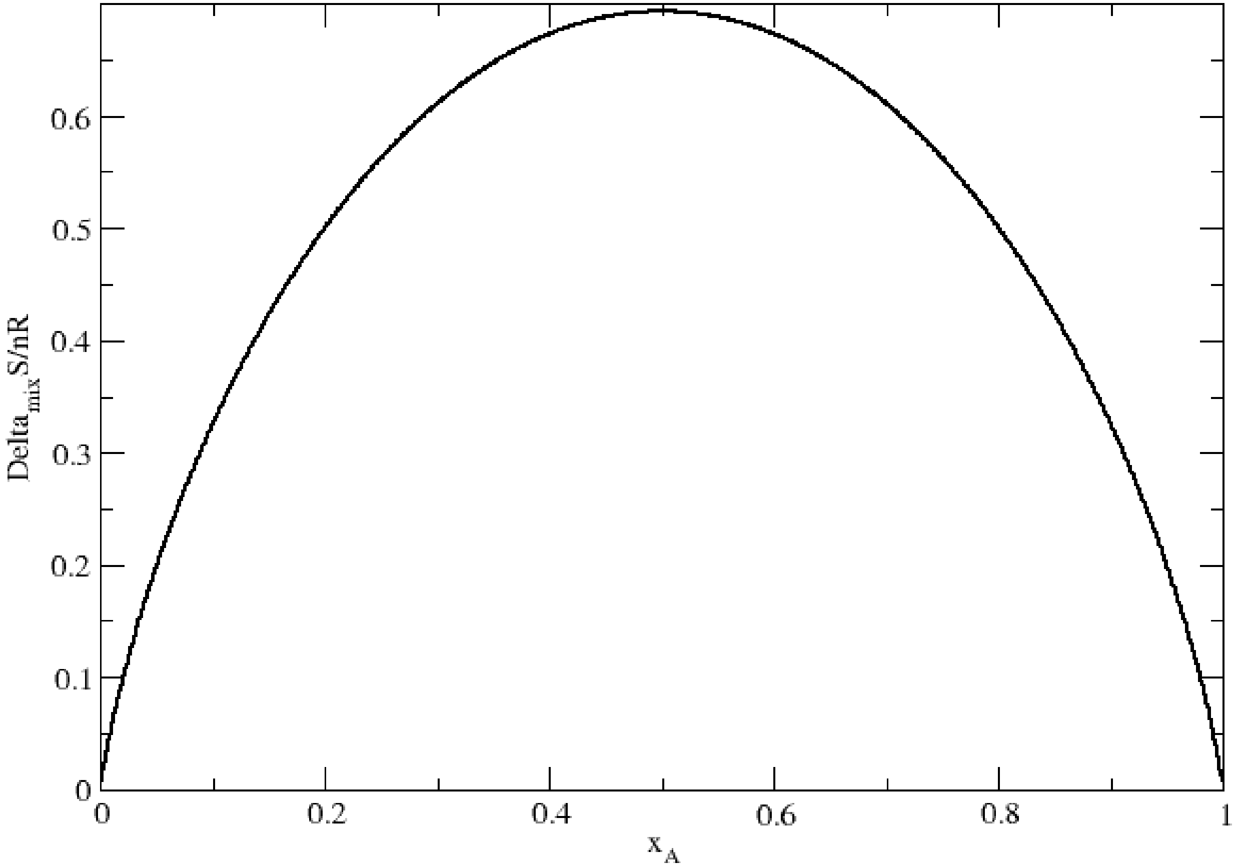


Solutions: Ideal solutions (Raoult) liquid phase β

Ideal liquid mixing

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

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



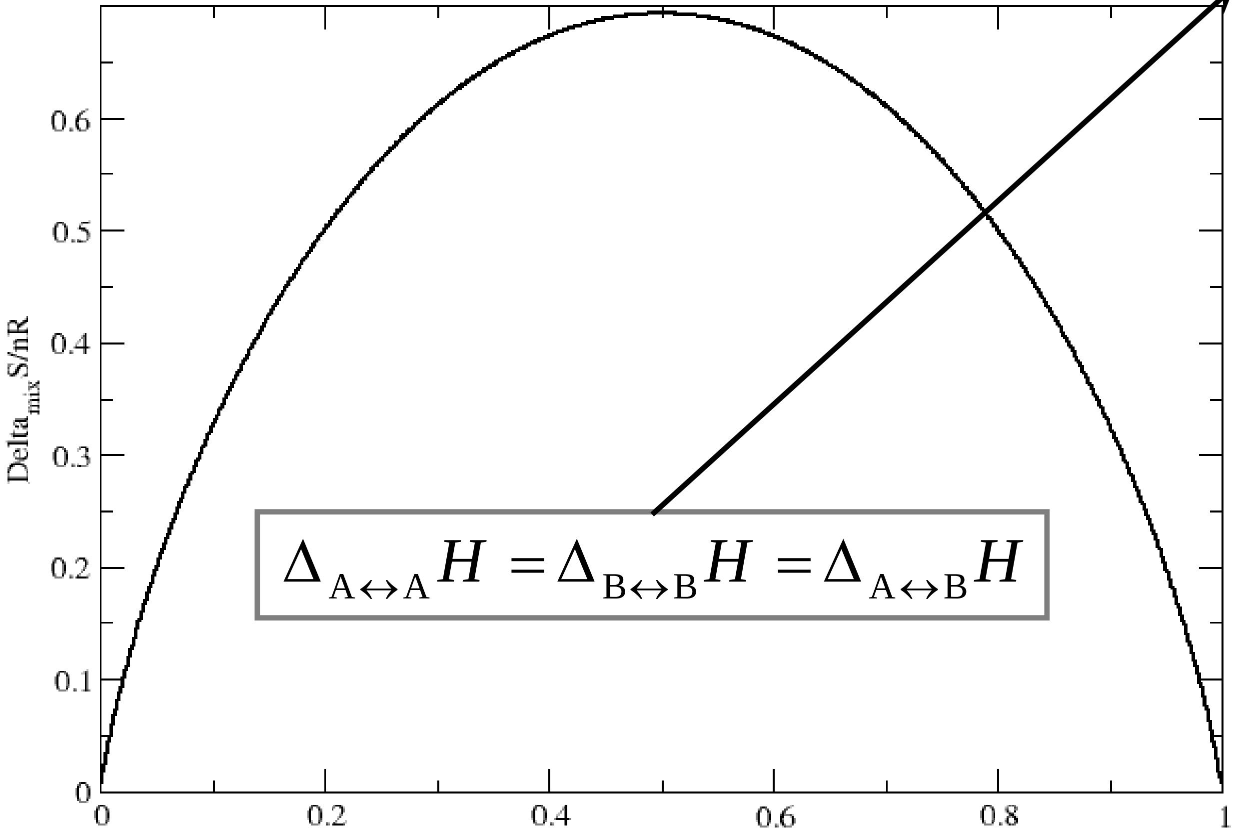
2nd law: Mixing is spontaneous, towards increasing entropy

Solutions: Ideal solutions (Raoult) liquid phase β

Ideal liquid mixing

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

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

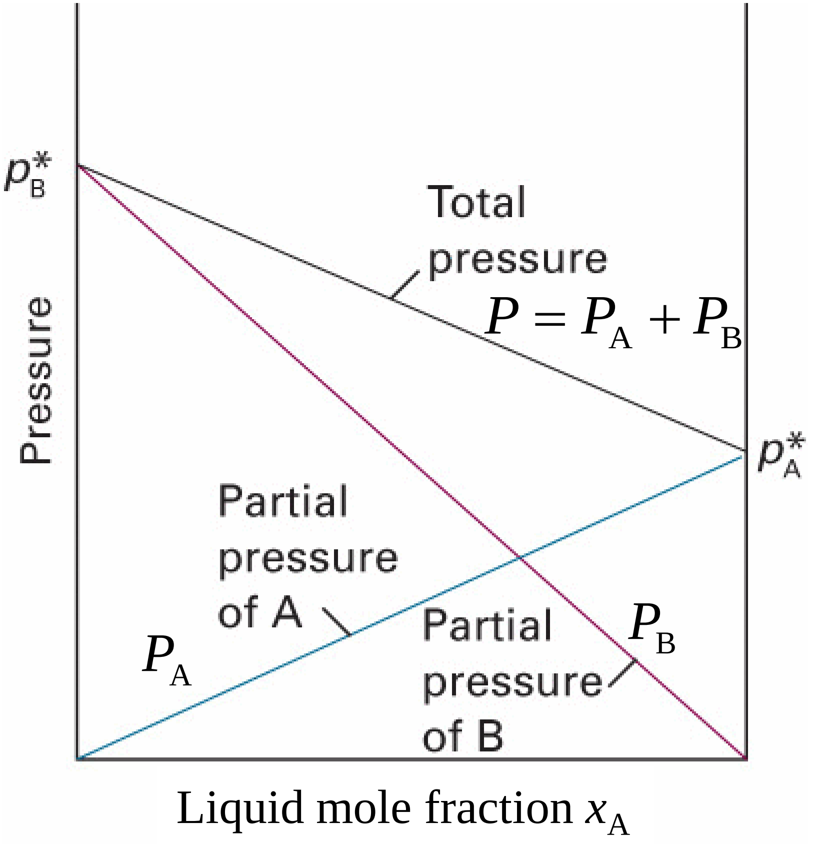


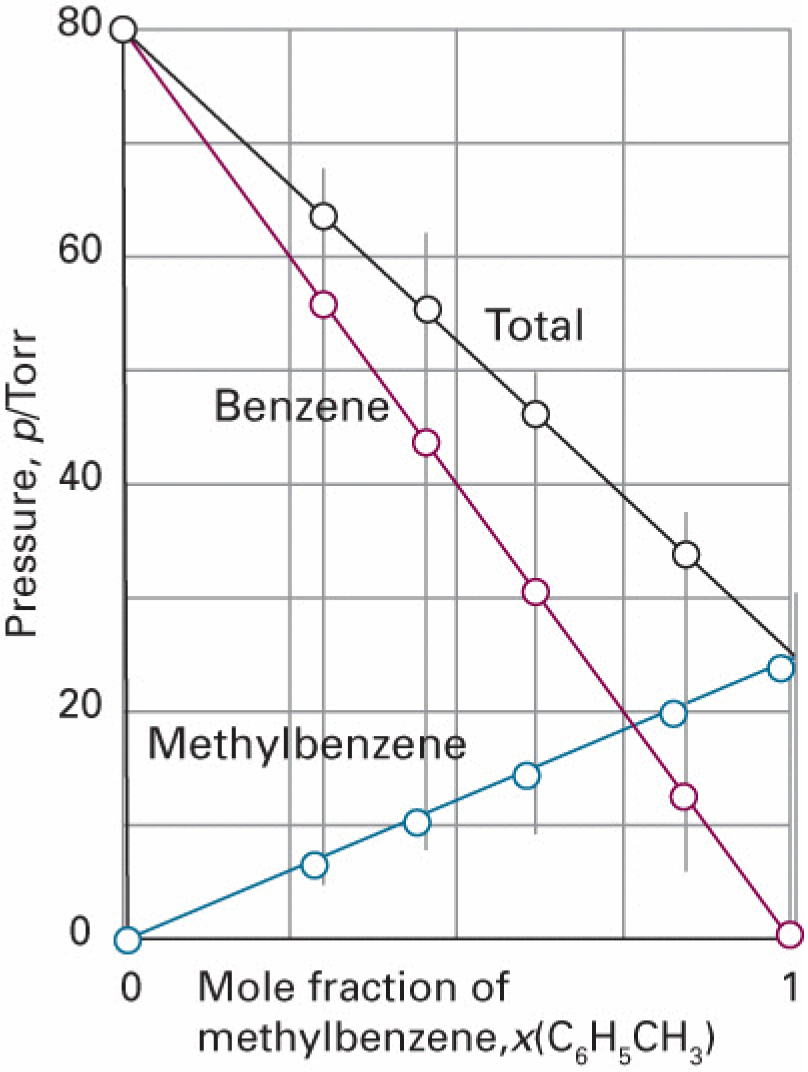
$$\boxed{\Delta_{\text{A}\leftrightarrow\text{A}} H = \Delta_{\text{B}\leftrightarrow\text{B}} H = \Delta_{\text{A}\leftrightarrow\text{B}} H}$$

2nd law: Mixing is spontaneous, towards increasing entropy

(Study guide p.14-16)

Solutions: Ideal solutions (Raoult) liquid phase β





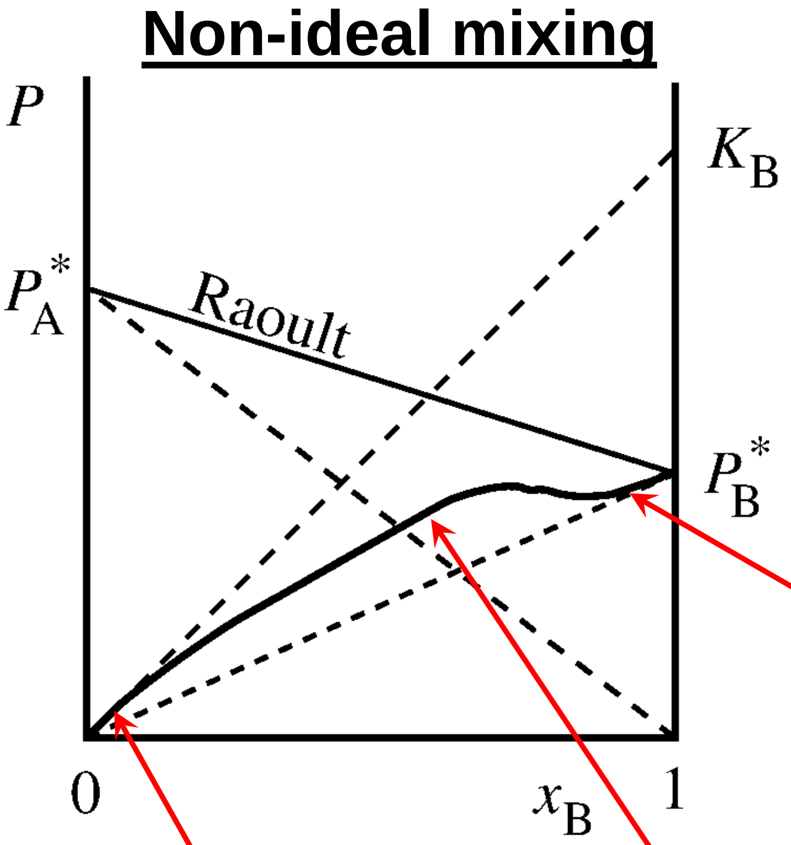
Ideal mixing (Raoult)

Exercise 12

$$\boxed{P_A = x_A P_A^*}$$

$$\boxed{P_B = x_B P_B^*}$$

Solutions: Ideal-dilute solutions liquid phase β



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

Ideal-dilute solutions:

Henry constant K_B

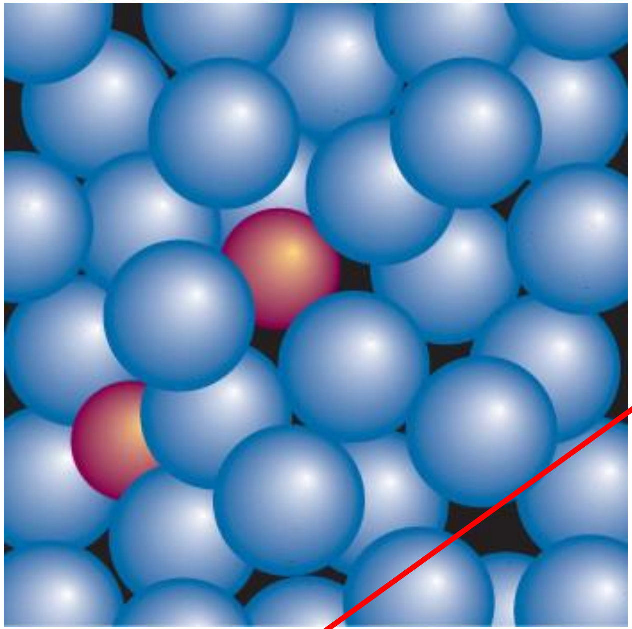
almost pure solvent B

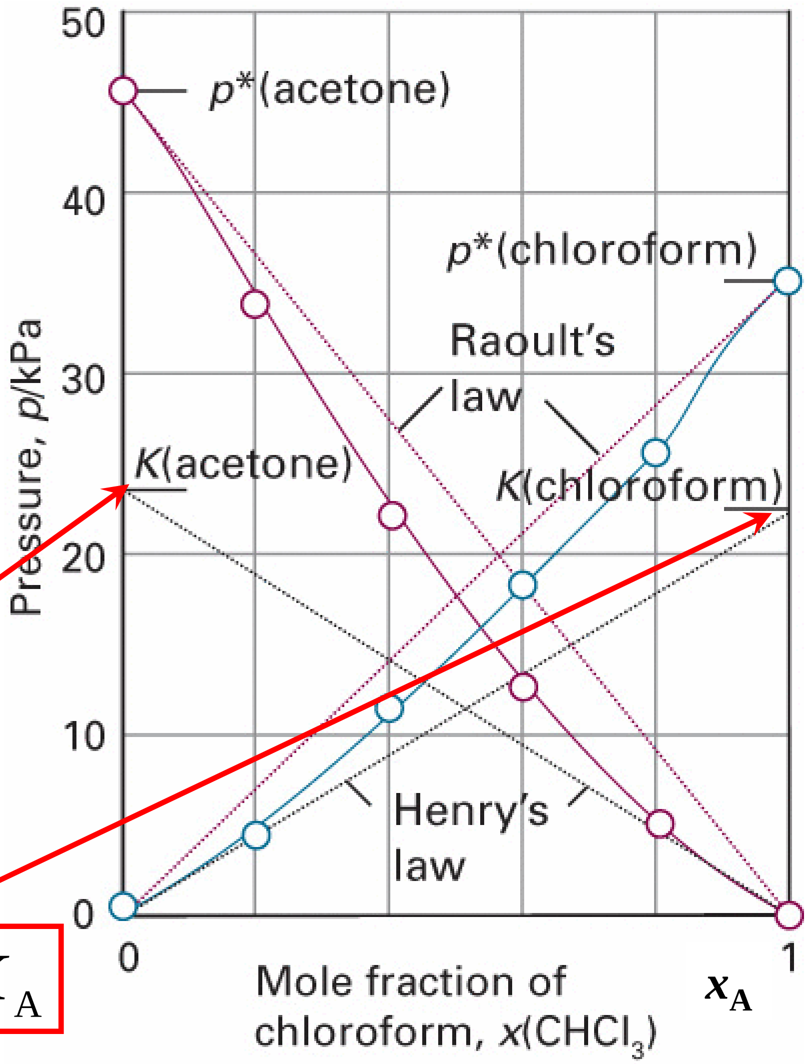
solute B expelled from solution

very low concentration of solute B

Solutions: Ideal-dilute solutions liquid phase β

Non-ideal mixing





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

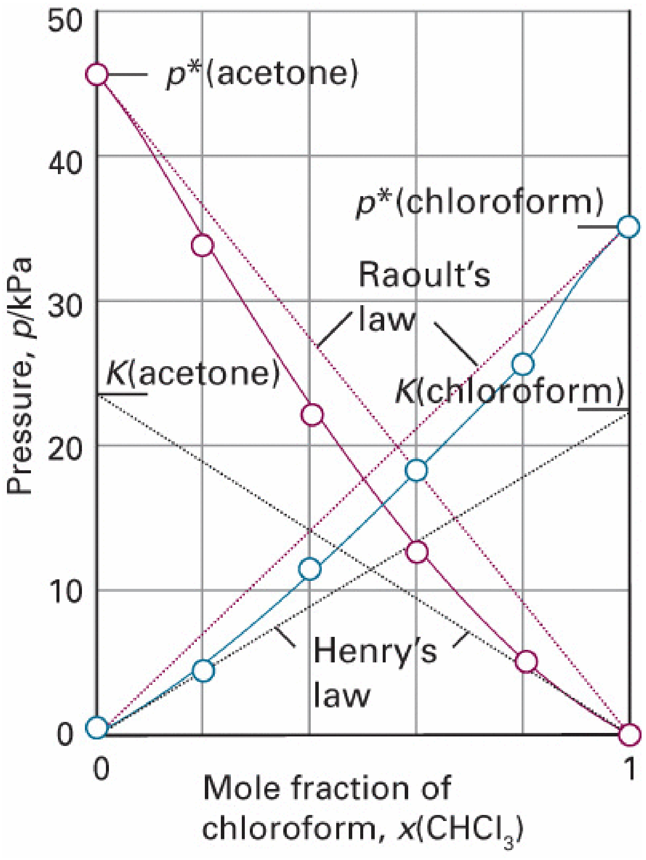
$$\boxed{P_A = x_A K_A}$$

Ideal-dilute solutions: Henry constant K_B

Exercise 13

Solutions: Ideal-dilute solutions liquid phase β

Non-ideal mixing



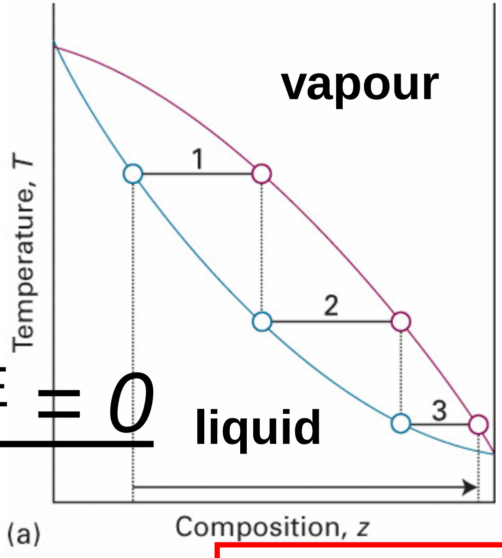
(Excess functions)

$$\left\{ \begin{array}{l} \boxed{S^{\mathrm{E}} = \Delta_{\mathrm{mix}} S - \Delta_{\mathrm{mix}} S^{\mathrm{ideal}}} \\ \boxed{H^{\mathrm{E}} = \Delta_{\mathrm{mix}} H - \Delta_{\mathrm{mix}} H^{\mathrm{ideal}} = \Delta_{\mathrm{mix}} H} \end{array} \right.$$

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

Temperature-composition diagrams

ideal solutions

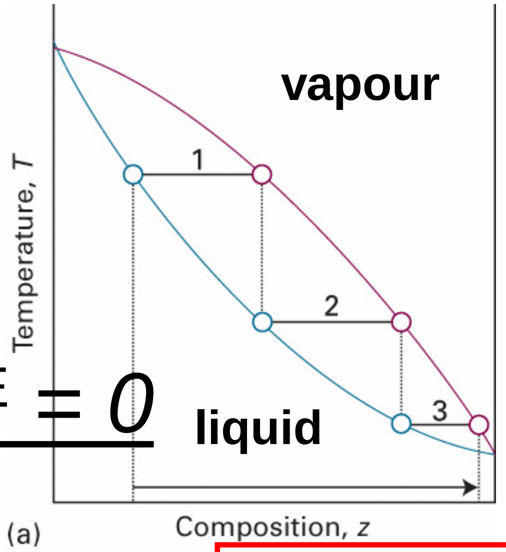


$G^{E} = 0$

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

Temperature-composition diagrams

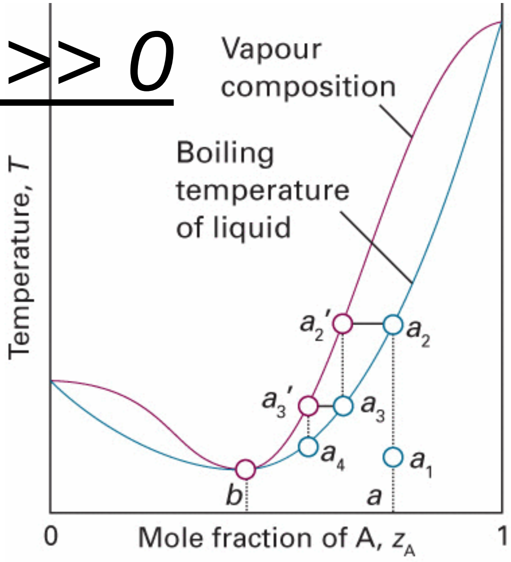
ideal solutions



$G^E = 0$

vapour

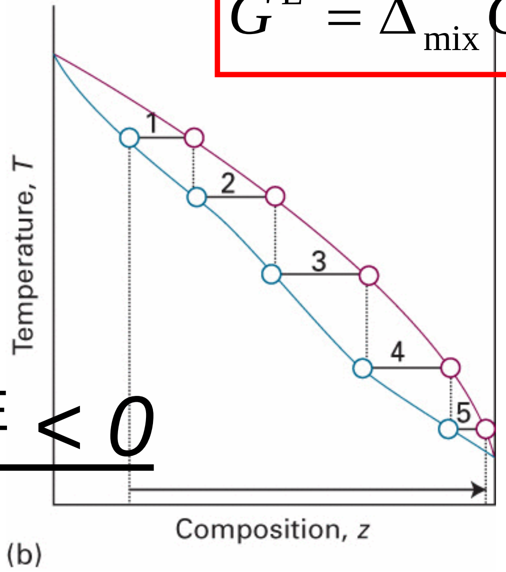
liquid



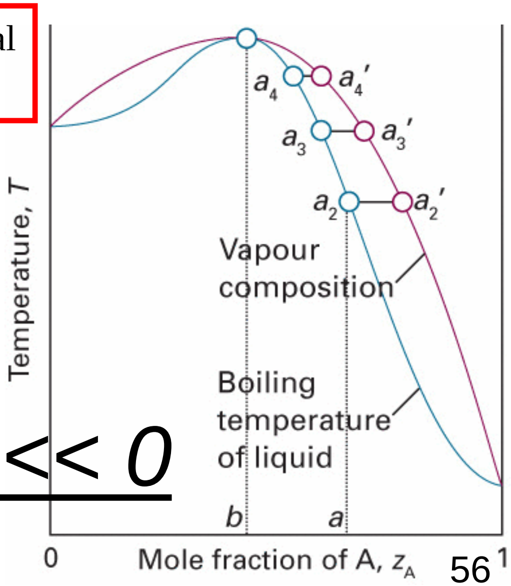
$G^E >> 0$

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

Non-ideal solutions



$G^E < 0$

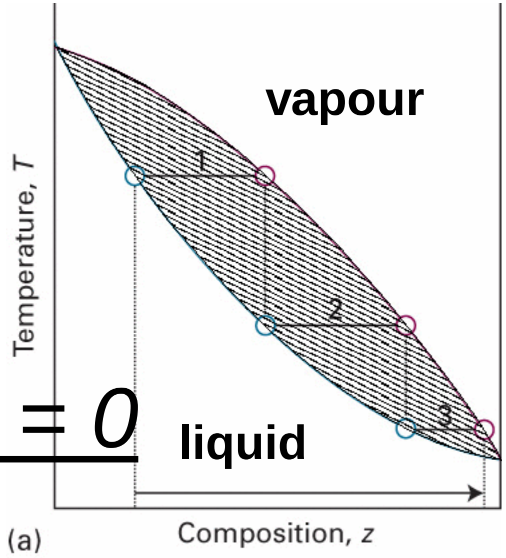


$G^E << 0$

Temperature-composition diagrams

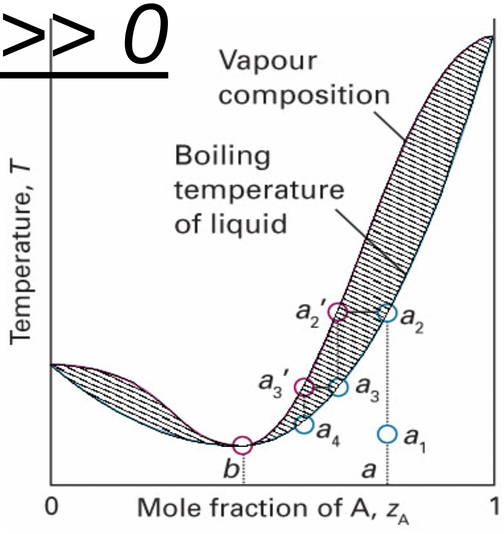
ideal solutions

$G^E = 0$



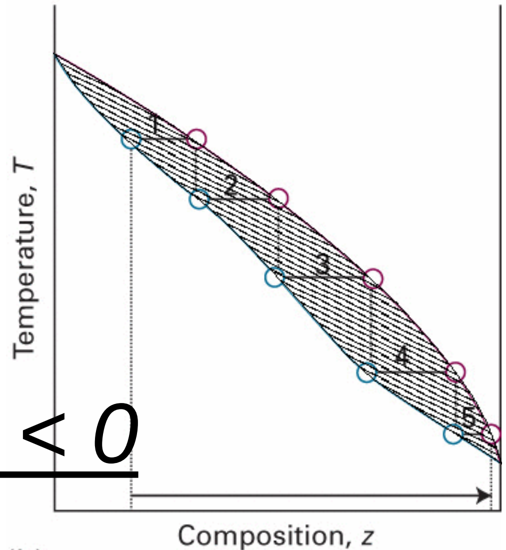
(a)

$G^E >> 0$



Non-ideal solutions

$G^E < 0$



(b)

$G^E << 0$