Summary Lecture 1 (glossery: see App. B, SG)

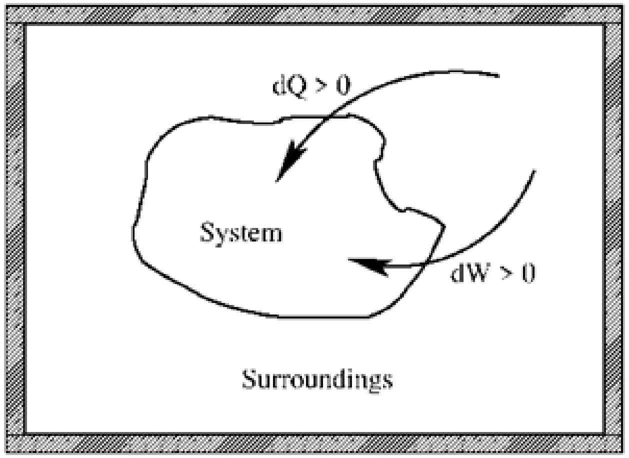
- **First law: conservation of energy**

$$dU = dW + dQ$$

$$\Delta U = \int dU = W + Q$$

$$\oint dU = 0$$

U is a state function



Reversible process

- Mechanical work

$$W = -\int P_{\text{ext}}\, dV \overset{\downarrow}{=} -\int P\, dV$$

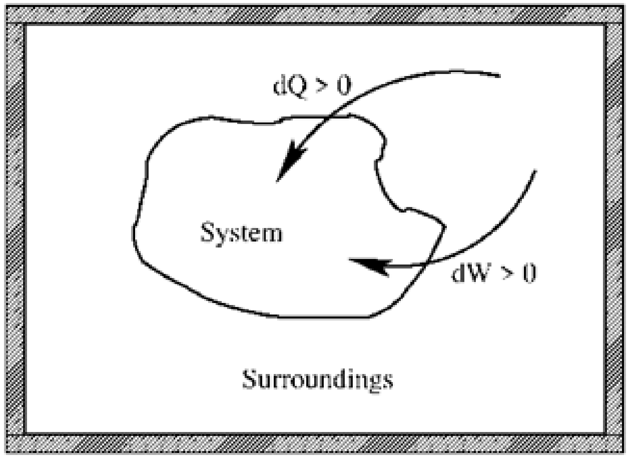
- Perfect gas

$$PV = nRT$$ Equation of state

- Perfect atomic gas

$$U = \frac{3}{2} nRT = \frac{3}{2} PV$$

Summary Lecture 2 (second law and entropy)



Second law:

for any spontaneous process

$$\boxed{dS_{\text{tot}} = dS + dS_{\text{sur}} \geq 0}$$

$$\boxed{dS \equiv \frac{dQ^{\text{rev}}}{T}}$$

S is a state function, so independent of path

Alternative form: Clausius inequality:

$$\boxed{dQ \leq TdS} \quad \begin{cases} \boxed{dQ^{\text{rev}} = TdS} & \textbf{Reversible process} \\ \boxed{dQ^{\text{irr}} < TdS} & \textbf{Irreversible process} \end{cases}$$

Summary Lecture 2 (alternative energy functions)

Internal energy	$\boxed{U}$
Enthalpy	$\boxed{H \equiv U + PV}$
Helmholtz free energy	$\boxed{A \equiv U - TS}$
Gibbs free energy	$\boxed{G \equiv H - TS}$

State functions

$$\boxed{dU = TdS - PdV} \Rightarrow \boxed{dU\big|_V = TdS}$$

$$\boxed{dH = TdS + VdP} \Rightarrow \boxed{dH\big|_P = TdS}$$

$$\boxed{dA = -SdT - PdV} \Rightarrow \boxed{dA\big|_{T,V} = 0}$$

$$\boxed{dG = -SdT + VdP} \Rightarrow \boxed{dG\big|_{T,P} = 0}$$

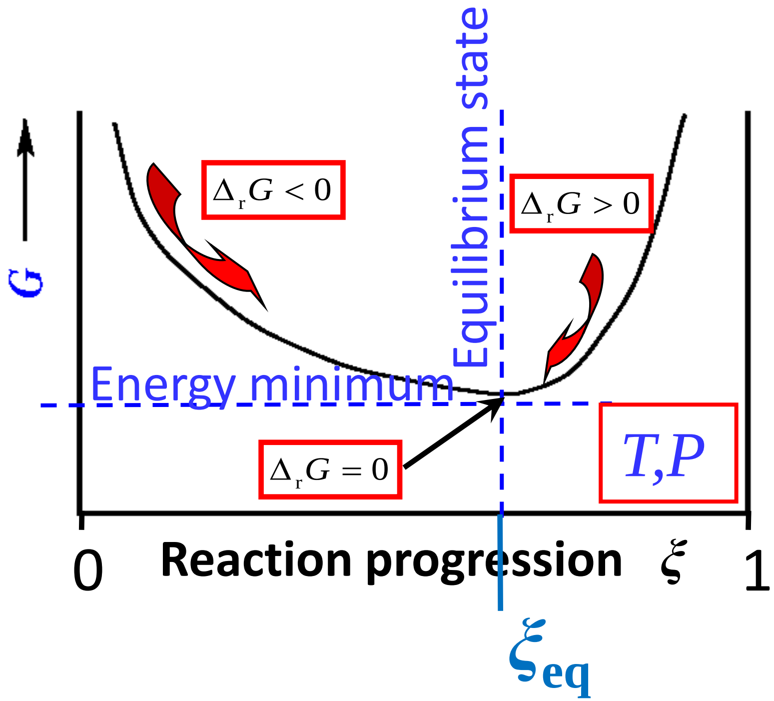
Heat capacities

$$\boxed{C_V \equiv \left(\frac{\delta U}{\delta T}\right)\bigg|_V} \quad \boxed{C_P \equiv \left(\frac{\delta H}{\delta T}\right)\bigg|_P}$$

Summary Lecture 3 (chemical equilibria)

Second law→ $\boxed{dG\big|_{P,T} \le 0}$

$$\Delta_r G \equiv \left(\frac{\partial G}{\partial \xi}\right)_{P,T}$$

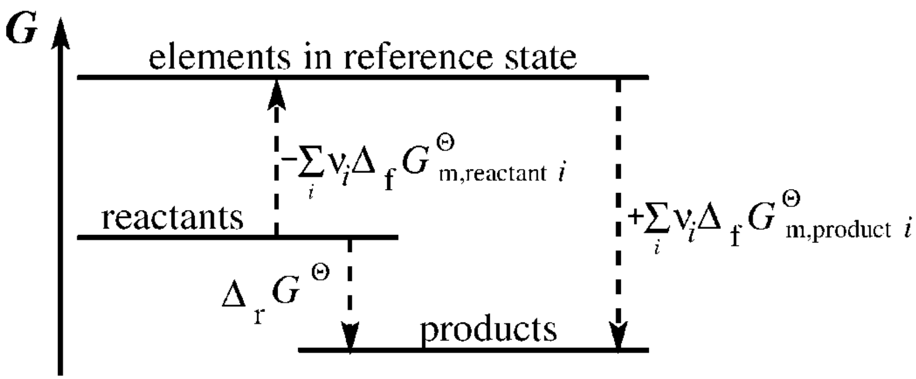


$$\Delta_r G = \Delta_r G^{\Theta} + RT \ln Q$$

$\Delta_r G$	reaction
$\Delta_r G < 0$	→
$\Delta_r G > 0$	←
$\Delta_r G = 0$	↔

$$\Delta_r G^{\Theta} = \sum_i \nu_i \Delta_f G^{\Theta}_{m,i} \quad \Rightarrow \quad K = \exp\left[-\frac{\Delta_r G^{\Theta}}{RT}\right]$$

Summary Lecture 3 (formation energies)



$$\Delta_f G^{\Theta}_{m,i} = \Delta_f H^{\Theta}_{m,i} - T\Delta_f S^{\Theta}_{m,i}$$

At constant, chosen T

For all ellements in their reference states at T $\Delta_f G^{\Theta}_{m,i} \equiv 0$

For all ellements in their reference states at T $\Delta_f H^{\Theta}_{m,i} \equiv 0$

For gaseous mixtures

Partial pressure

$$P_i \equiv x_i P$$

Mole fraction

$$x_i \equiv \frac{n_i}{n} = \frac{n_i}{\sum_j n_j}$$

For perfect gas mixtures

$$Q = \prod_i \left(\frac{P_i}{P^{\Theta}}\right)^{\nu_i}$$

Summary Lecture 4 (activity)

For general systems:

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

$$\boxed{\Delta_r G = \Delta_r G^\Theta + RT \ln Q}$$

$$\boxed{Q = \prod_i a_i^{\nu_i}}$$

$$\boxed{\Delta_r G^\Theta = \sum_i \nu_i \Delta_f G_{m,i}^\Theta}$$

$$\boxed{\Delta_r G^\Theta = \sum_i \nu_i \mu_i^\Theta}$$

$P^\Theta \equiv 1\,\text{bar};\ a_i^\Theta = 1;\ i^\Theta \text{is pure}$

$$\boxed{a_i = \frac{P_i}{P^\Theta}}$$ **For perfect gas mixtures**

$$\boxed{a_l \approx 1}$$ **For pure liquids**

$$\boxed{a_s \approx 1}$$ **For pure solids**

$$\boxed{a_i = \gamma_i^{(c)} \frac{c_i}{c^\Theta}}$$ **with** $$\boxed{c^\Theta \equiv 1\,\text{mol/L}}$$

$$\boxed{a_i = \gamma_i^{(b)} \frac{b_i}{b^\Theta}}$$ **with** $$\boxed{b^\Theta \equiv 1\,\text{mol/kg}}$$

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

$$\boxed{\text{pH} \equiv \text{-log}\ a_{\text{H}^+}}$$

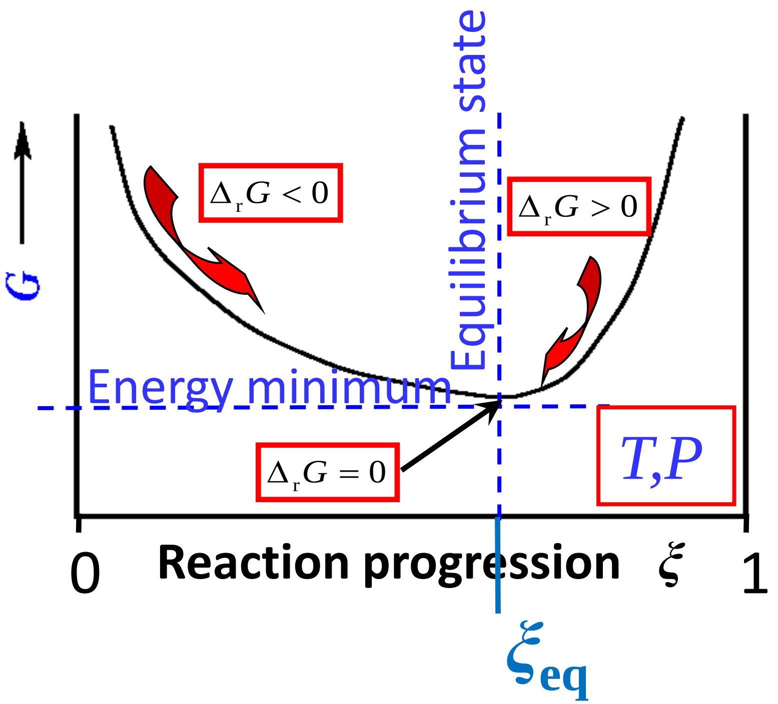
Summary Lecture 4 (electrochemistry)

$$\Delta_r G = \Delta_r G^{\Theta} + RT \ln Q$$

$$\Delta_r G = -\nu F E$$

$$E = E^{\Theta} - \frac{RT}{\nu F} \ln Q$$

Nernst equation

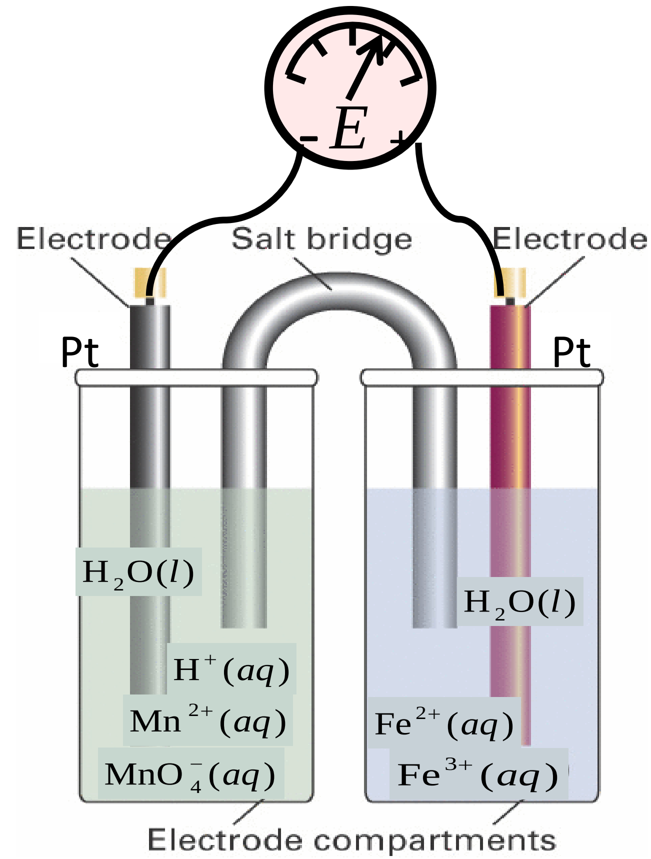


reaction

$\Delta_r G < 0$ $E > 0$

$\Delta_r G > 0$ $E < 0$

$\Delta_r G = 0$ $E = 0$



Summary Lecture 4 (electrochemistry)

$$\boxed{\Delta_f G^{\ominus}_{H^+(aq)} = \Delta_f H^{\ominus}_{H^+(aq)} \equiv 0 \text{ for all } T}$$

$$\boxed{E^{\ominus}_{2H^+/H_2} \equiv 0 \text{ for all } T}$$

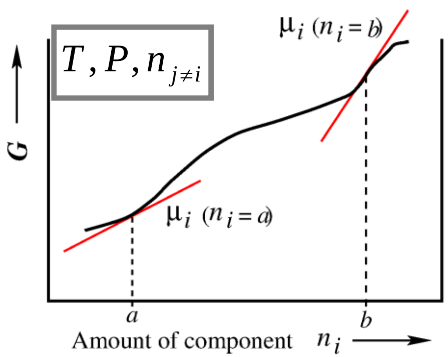
$$\boxed{\mathrm{pH} \equiv -{}^{10}\log a_{H^+} \approx -{}^{10}\log\left[H^+\right]}$$

Lecture 5: Solutions and colligative processes

Lecture 5: Solutions and mixing processes

Solutions or mixtures with NO chemical reactions:

still $\boxed{dn_i \neq 0}$ $\boxed{dG = VdP - SdT + \sum_i \mu_i dn_i}$



with $\boxed{\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}} \equiv \mu_i^\Theta + RT\ln a_i}$

For perfect gas mixtures $\boxed{a_i = \frac{P_i}{P^\Theta}}$ $\Rightarrow$ $\boxed{\mu_i = \mu_i^\Theta + RT\ln\frac{P_i}{P^\Theta}}$

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

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

Lecture 5: Solutions and mixing processes

Solutions or mixtures with NO chemical reactions:

still $\boxed{dn_i \neq 0}$ $\boxed{dG = VdP - SdT + \sum_i \mu_i dn_i}$

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

Standard state Θ for component *i*

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

$\boxed{a_i \equiv 1}$

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

Lecture 5: Solutions and mixing processes

Importance of the chemical potential:

1) Equilibrium between phases

$$H_2O(l) \leftrightarrow H_2O(s)$$

$$@1\,\text{bar},\ 273.15\ \text{K}$$

$$\Rightarrow \quad dG = VdP - SdT + \mu_l dn_l + \mu_s dn_s$$

Lecture 5: Solutions and mixing processes

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1) Equilibrium between phases

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$$dG = VdP - SdT + \mu_l dn_l + \mu_s dn_s$$

2nd law: in equilibrium:

$$dG\big|_{P,T} = 0$$

$$dG\big|_{P,T} = \mu_l dn_l + \mu_s dn_s = (\mu_l - \mu_s) dn_l = 0$$

$$dn_s = -dn_l$$

Lecture 5: Solutions and mixing processes

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1) Equilibrium between phases

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$$dn_s = -dn_l$$

in equilibrium: $\boxed{\mu_l = \mu_s}$

Lecture 5: Solutions and mixing processes

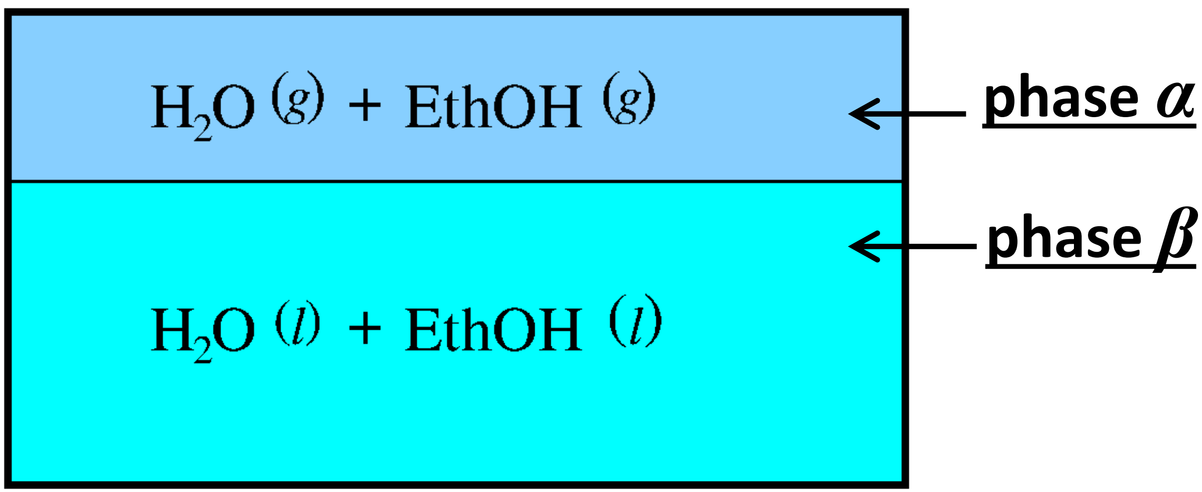
Importance of the chemical potential: (Study guide p.16)

1) **Equilibrium between phases**

$$H_2O(\alpha) \leftrightarrow H_2O(\beta)$$

in equilibrium: $$\boxed{\mu_\alpha = \mu_\beta}$$

2) **Equilibrium between phases of component *i* in mixtures**



in equilibrium: $$\boxed{\mu_{i,\alpha} = \mu_{i,\beta}}$$

Lecture 5: Solutions and mixing processes

Importance of the chemical potential: (Study guide p.16)

1) Equilibrium between phases

$$\boxed{H_2O(\alpha) \leftrightarrow H_2O(\beta)}$$

in equilibrium: $\boxed{\mu_\alpha = \mu_\beta}$

2) Equilibrium between phases of component *i* in mixtures

in equilibrium: $\boxed{\mu_{i,\alpha} = \mu_{i,\beta}}$

3) For a general mixture of two or more components A, B, · · · :

$$\boxed{G\Big|_{P,T}^{\alpha} = \int_0^{n_A} \mu_{A,\alpha} dn_{A,\alpha} + \int_0^{n_B} \mu_{B,\alpha} dn_{B,\alpha} + \cdots = \mu_{A,\alpha} \int_0^{n_A} dn_{A,\alpha} + \mu_{B,\alpha} \int_0^{n_B} dn_{B,\alpha} + \cdots}$$

$$\boxed{dG\Big|_{P,T}^{\alpha} = \mu_{A,\alpha} dn_{A,\alpha} + \mu_{B,\alpha} dn_{B,\alpha} + \cdots}$$

***G* is a state function**

Lecture 5: Solutions and mixing processes

Importance of the chemical potential: (Study guide p.16)

1) Equilibrium between phases

$$\mathrm{H_2O}(\alpha) \leftrightarrow \mathrm{H_2O}(\beta)$$

in equilibrium: $\boxed{\mu_\alpha = \mu_\beta}$

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in equilibrium: $\boxed{\mu_{i,\alpha} = \mu_{i,\beta}}$

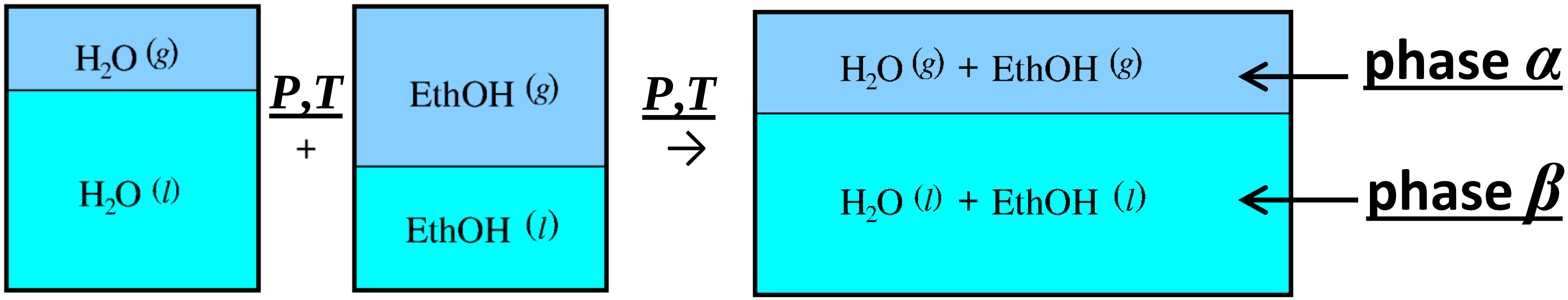
3) For a general mixture of two or more components A, B, · · · :

$$G\Big|_{P,T}^{\alpha} = \mu_{\mathrm{A},\alpha} \int_0^{n_\mathrm{A}} dn_{\mathrm{A},\alpha} + \mu_{\mathrm{B},\alpha} \int_0^{n_\mathrm{B}} dn_{\mathrm{B},\alpha} + \cdots$$

$$\Rightarrow \quad \boxed{G\Big|_{P,T}^{\alpha} = \mu_{\mathrm{A},\alpha} \mathrm{n}_{\mathrm{A},\alpha} + \mu_{\mathrm{B},\alpha} \mathrm{n}_{\mathrm{B},\alpha} + \cdots = \sum_i \mu_{i,\alpha} \mathrm{n}_{i,\alpha}}$$

Lecture 5: Solutions and mixing processes

The process of mixing two or more components @ *P,T*



$$\boxed{G\Big|_{P,T}^{\alpha} = \sum_i \mu_{i,\alpha}\,\mathrm{n}_{i,\alpha}}$$

Initial:

$$G^{\alpha}_{\text{initial}} = n_{\mathrm{A},\alpha}\left(\mu^{\Theta}_{\mathrm{A},\alpha} + RT\ln a_{\mathrm{A},\alpha}\right) + n_{\mathrm{B},\alpha}\left(\mu^{\Theta}_{\mathrm{B},\alpha} + RT\ln a_{B,\alpha}\right)$$

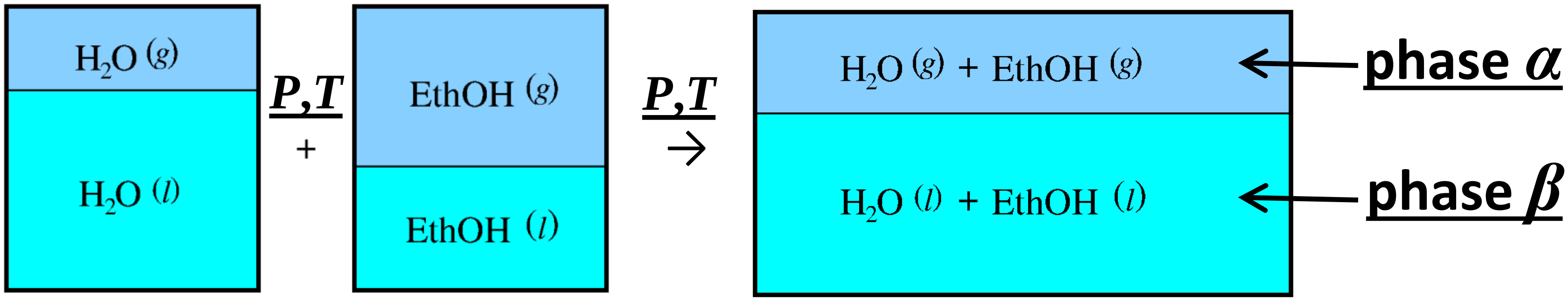
α: pure perfect gases @ *P*

Initial:

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

Lecture 5: Solutions and mixing processes

The process of mixing two or more components @ *P,T*



Final:

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

Initial:

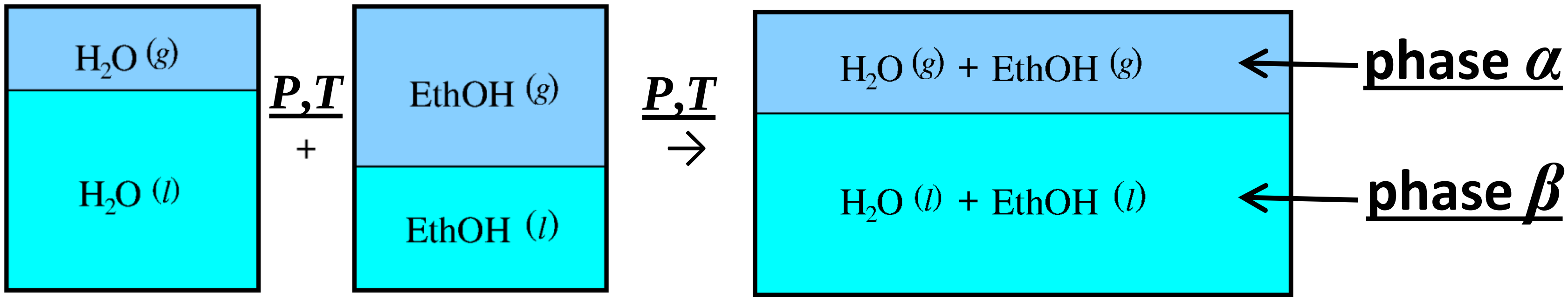
$$G^{g}_{\text{initial}} = n_{\text{A},g}\left(\mu^{\ominus}_{\text{A},g} + RT\ln\frac{P}{P^{\ominus}}\right) + n_{\text{B},g}\left(\mu^{\ominus}_{\text{B},g} + RT\ln\frac{P}{P^{\ominus}}\right)$$

—

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

Lecture 5: Solutions and mixing processes

The process of mixing two or more components @ *P,T*



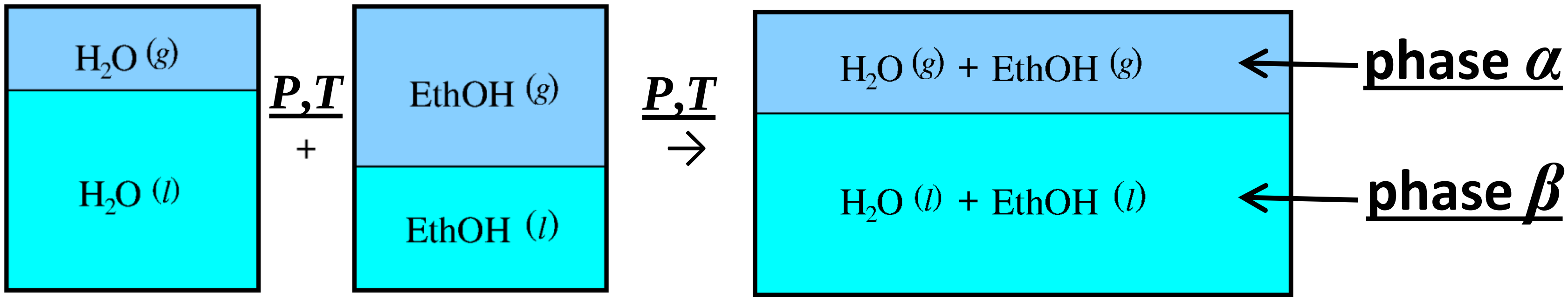
$$\Delta_{\text{mix}} G^{g} = G^{g}_{\text{final}} - G^{g}_{\text{initial}} = n_{\text{A},g} RT \ln \frac{P_{\text{A}}}{P} + n_{\text{B},g} RT \ln \frac{P_{\text{B}}}{P}$$

$$\Delta_{\text{mix}} G^{g} = RT \left(n_{\text{A},g} \ln \frac{n_{\text{A}}}{n} + n_{\text{B},g} \ln \frac{n_{\text{B}}}{n} \right)$$ **as** $\frac{P_i}{P} \equiv \frac{n_i}{n}$

$$\Delta_{\text{mix}} G^{g} = nRT \left(x_{\text{A},g} \ln x_{\text{A},g} + x_{\text{B},g} \ln x_{\text{B},g} \right)$$ **as** $x_{i,\alpha} \equiv \frac{n_{i,\alpha}}{n}$

Lecture 5: Solutions and mixing processes

The process of mixing two or more components @ P,T



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

$$\boxed{@T:\ \Delta_{\text{mix}} G^{g} = \Delta_{\text{mix}} H^{g} - T\Delta_{\text{mix}} S^{g}}$$

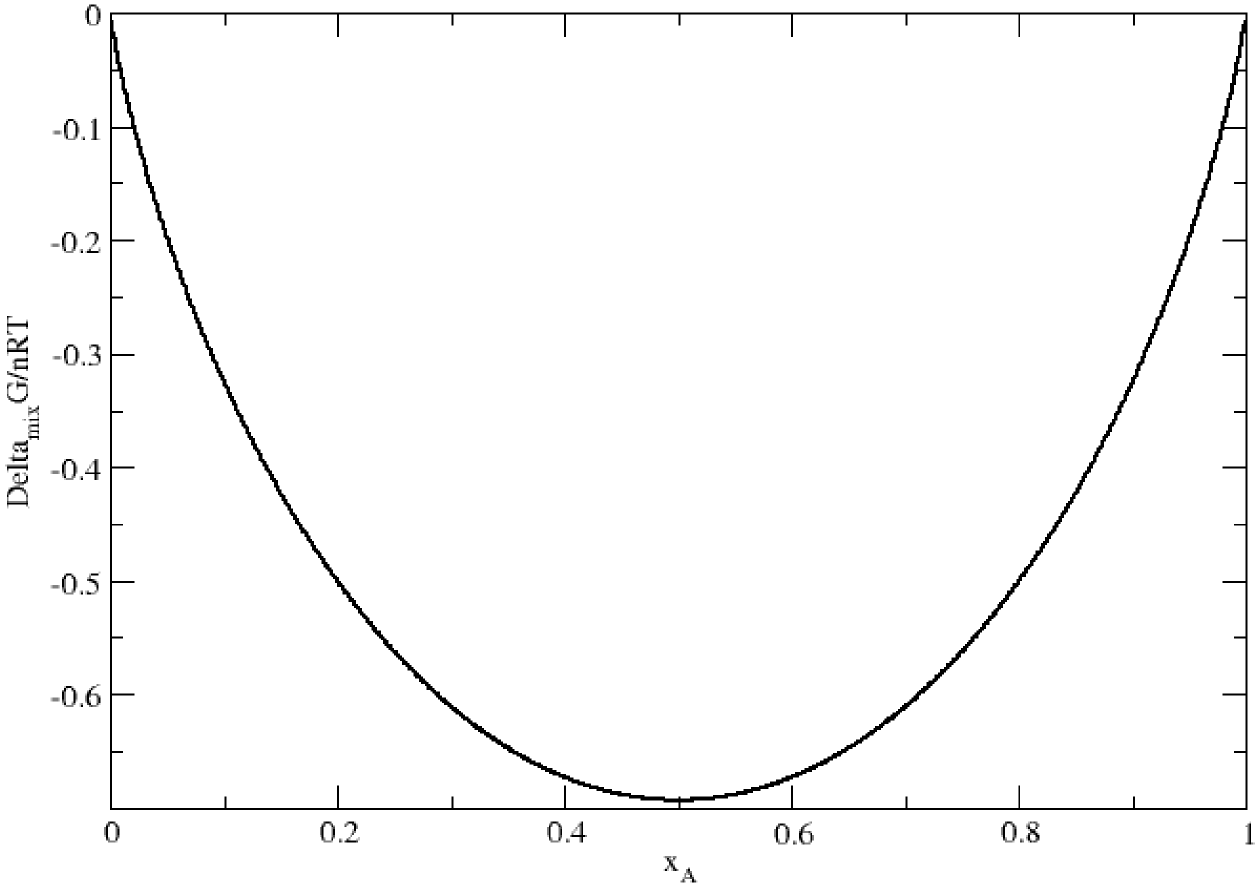
Perfect gas mixing

$$\left\{\begin{array}{l} \boxed{\Delta_{\text{mix}} S = -nR\left(x_{\text{A}} \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}}\right)} \\ \boxed{\Delta_{\text{mix}} H = 0} \end{array}\right.$$

Lecture 5: Solutions and mixing processes

Perfect gas mixing

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

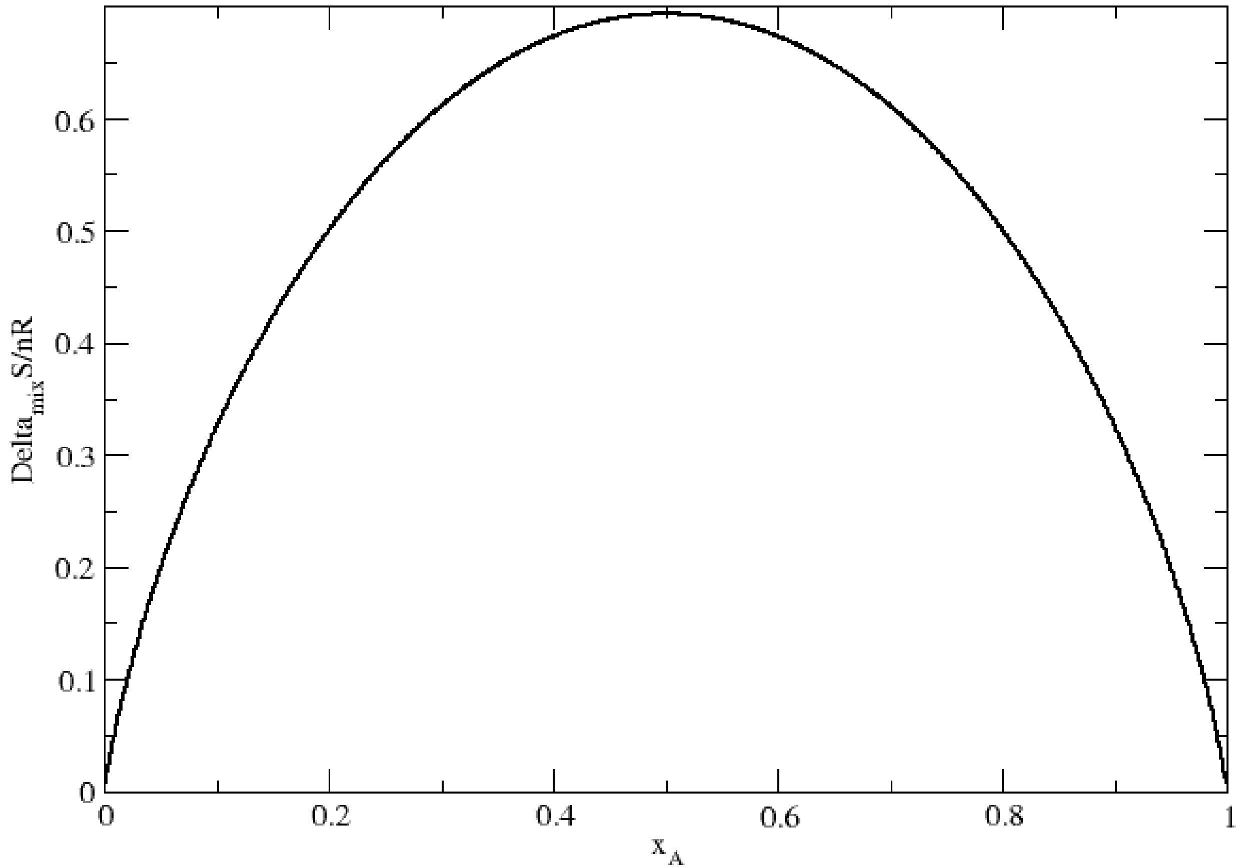


Lecture 5: Solutions and mixing processes

Perfect gas mixing

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

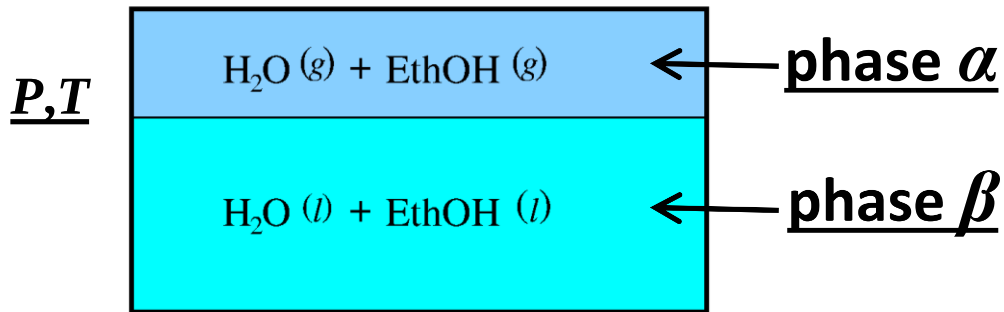
$$\boxed{\Delta_{\text{mix}} H = 0}$$



2nd law: Mixing is spontaneous, towards increasing entropy

Lecture 5: Solutions and mixing processes

The process of mixing two or more components @ P,T



Equilibrium $\Leftrightarrow$ $\boxed{\mu_{i,\alpha} = \mu_{i,\beta}}$

$$\boxed{\mu_{\text{A},g} = \mu_{\text{A},l}}$$

$$\boxed{\mu_{\text{B},g} = \mu_{\text{B},l}}$$

$$\mu_{\text{A},g} = \mu_{\text{A}}^{\Theta} + RT\ln\frac{P_{\text{A}}}{P^{\Theta}} = \mu_{\text{A},l}$$

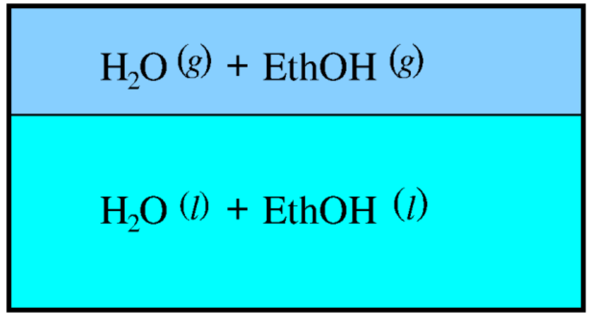
(similar for B)

perfect gas

Lecture 5: Solutions and mixing processes

The process of mixing two or more components @ P,T

P,T



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

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

(* pure A)

−

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

(similar for B)

Lecture 5: Solutions: Ideal solutions (Raoult)

The process of mixing two or more components @ *P,T*

(Study guide p.17-18)

P,T

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

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

$$\boxed{\underbrace{\mu_{A,l} = \mu^*_{A,l}}_{\text{liquid}} + RT \ln \underbrace{\frac{P_A}{P^*_A}}_{\text{gas}}}$$

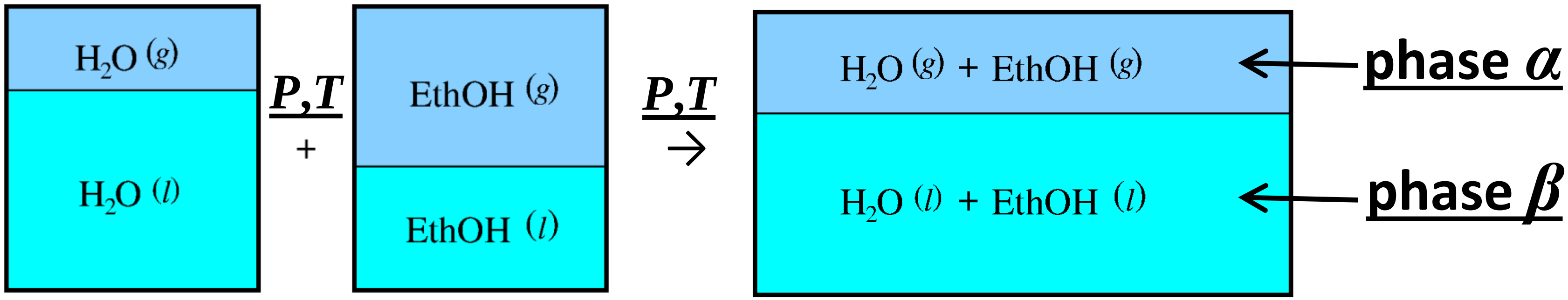
(similar for B)

Special case: $\boxed{P_A = x_{A,l} P^*_A}$ **and** $\boxed{P_B = x_{B,l} P^*_B}$

Ideal solution or Raoult's law

Lecture 5: Solutions: Ideal solutions (Raoult)

The process of mixing two or more components @ *P,T*



Special case:

$$\boxed{\underbrace{\mu_{A,l} = \mu^*_{A,l}}_{\text{liquid}} + RT \ln \underbrace{x_{A,l}}_{\text{liquid}}}$$

(similar for B)

$$\boxed{P_A = x_{A,l} P_A^*}$$

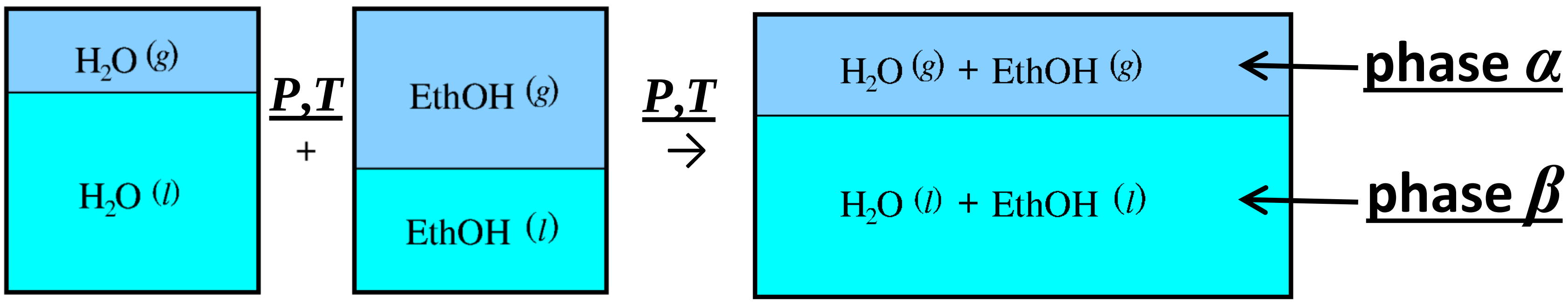
$$\boxed{P_B = x_{B,l} P_B^*}$$

Ideal solution or Raoult's law

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

Lecture 5: Solutions: Ideal solutions (Raoult)

The process of mixing two or more components @ P,T



$$\Delta_{\mathrm{mix},l}G = \left(n_{\mathrm{A},l}\mu_{\mathrm{A},l} + n_{\mathrm{B},l}\mu_{\mathrm{B},l}\right) - \left(n_{\mathrm{A},l}\mu^*_{\mathrm{A},l} + n_{\mathrm{B},l}\mu^*_{\mathrm{B},l}\right)$$

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

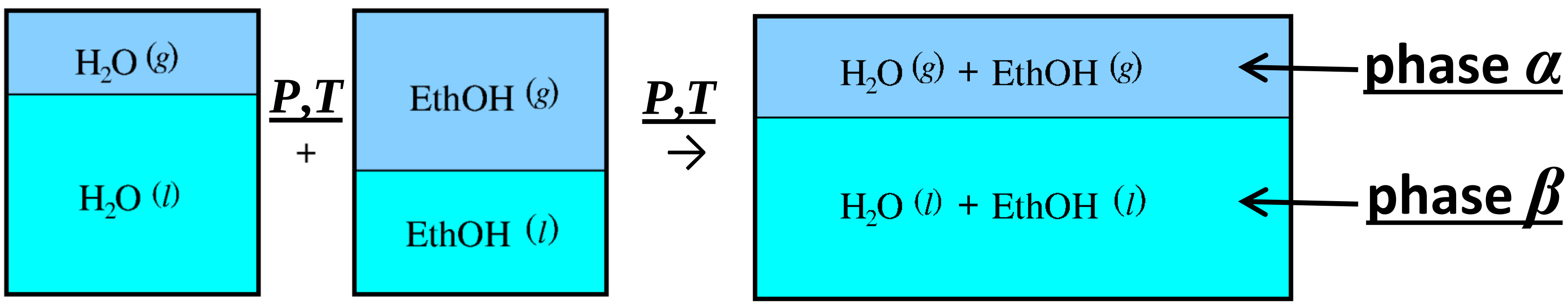
Similar to the perfect gas case:

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

Ideal solution or Raoult's law

Lecture 5: Solutions: Ideal solutions (Raoult)

The process of mixing two or more components @ *P,T*



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

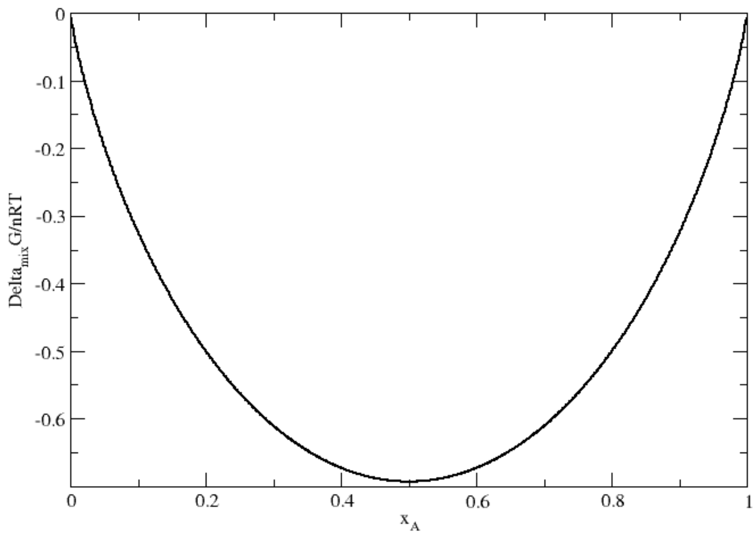
$$\left\{ \begin{array}{l} \boxed{\Delta_{\mathrm{mix},l} G = nRT\left(x_{\mathrm{A},l} \ln x_{\mathrm{A},l} + x_{\mathrm{B},l} \ln x_{\mathrm{B},l}\right)} \\ \boxed{\Delta_{\mathrm{mix},l} S = -nR\left(x_{\mathrm{A}} \ln x_{\mathrm{A},l} + x_{\mathrm{B}} \ln x_{\mathrm{B},l}\right)} \end{array} \right.$$

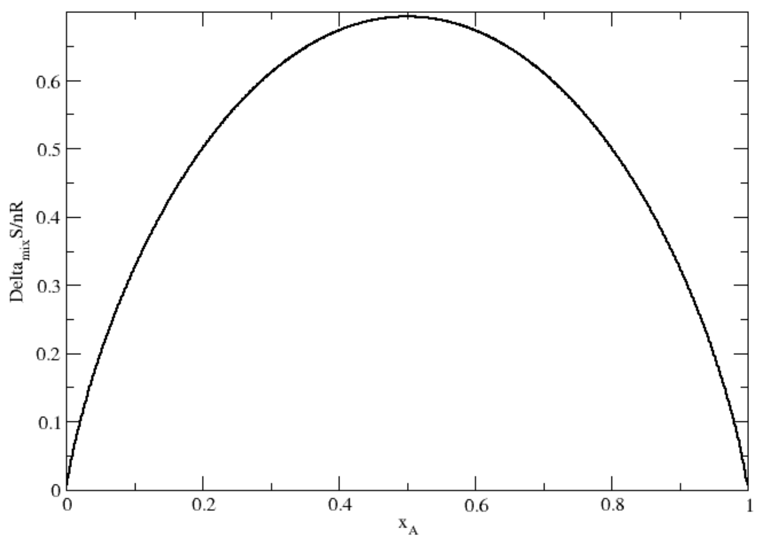
and $\boxed{\Delta_{\mathrm{mix},l} H = 0}$

Ideal solution or Raoult's law

Lecture 5: Solutions: Ideal solutions (Raoult)

The process of mixing two or more components @ *P*,*T*



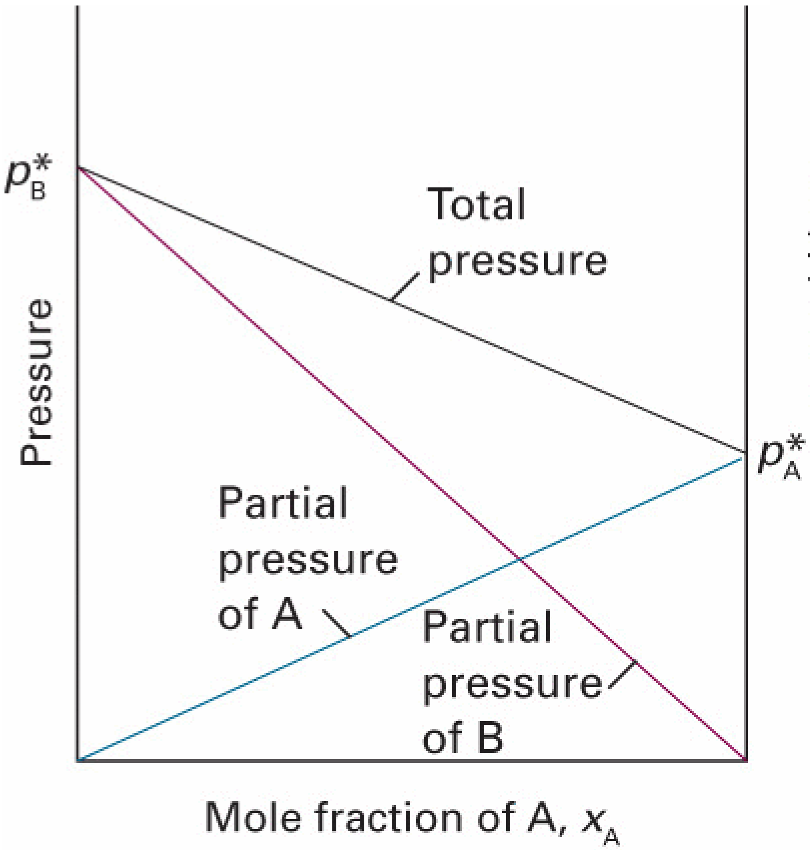


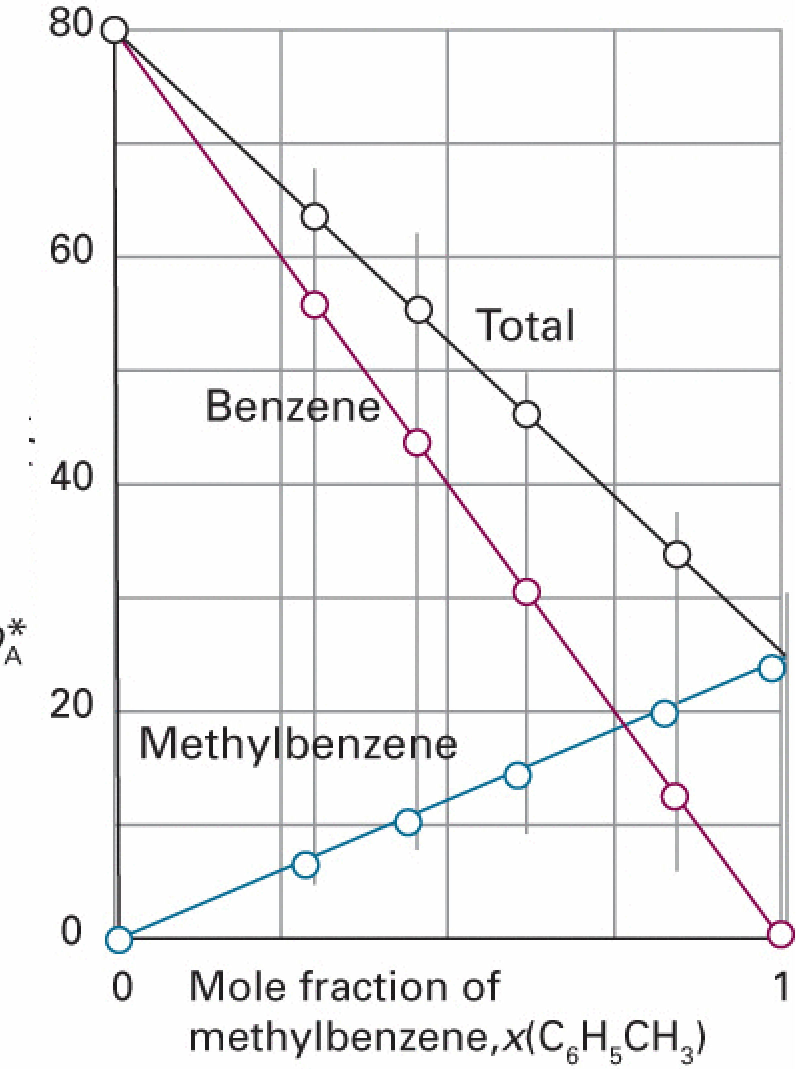
$$\begin{cases} \boxed{\Delta_{\text{mix},l} G = nRT\left(x_{\text{A},l} \ln x_{\text{A},l} + x_{\text{B},l} \ln x_{\text{B},l}\right)} \\ \boxed{\Delta_{\text{mix},l} S = -nR\left(x_{\text{A}} \ln x_{\text{A},l} + x_{\text{B}} \ln x_{\text{B},l}\right)} \end{cases}$$ **and** $\boxed{\Delta_{\text{mix},l} H = 0}$

Ideal solution or Raoult's law **(Study guide p.17-18)**

Lecture 5: Solutions: Ideal solutions (Raoult)

Raoult's law



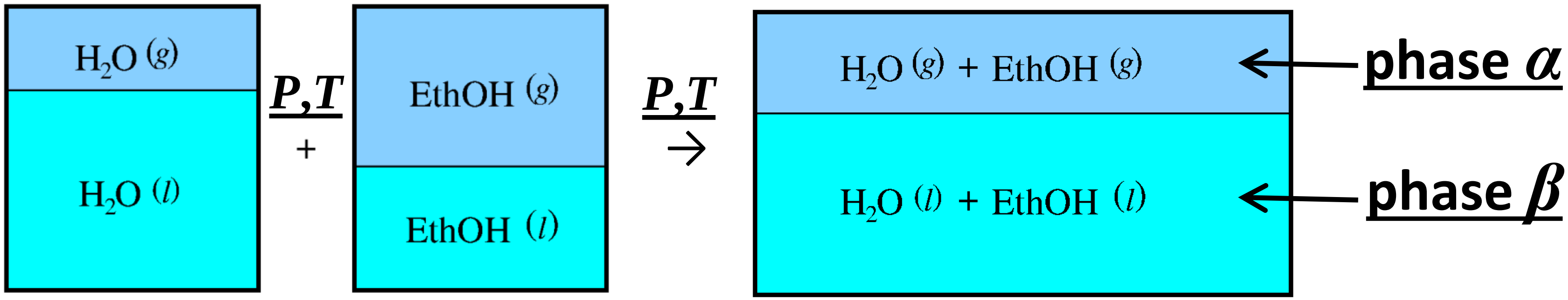


$$\boxed{P_j^g = x_j^l P_j^{*,g}}$$ **Raoult**

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

Lecture 5: Solutions: Real solutions

The process of mixing two or more components @ *P,T*



$$\Delta_{\mathrm{mix},l} G = G_{\mathrm{final},l} - G_{\mathrm{initial},l} = \left(n_{\mathrm{A},l}\mu_{\mathrm{A},l} + n_{\mathrm{B},l}\mu_{\mathrm{B},l}\right) - \left(n_{\mathrm{A},l}\mu^*_{\mathrm{A},l} + n_{\mathrm{B},l}\mu^*_{\mathrm{B},l}\right)$$

$$\mu_{\mathrm{A},l} = \mu^*_{\mathrm{A},l} + RT\ln a_{\mathrm{A},l}$$ **(similar for B)**

$$\Delta_{\mathrm{mix},l} G = n_{\mathrm{A},l} RT\ln a_{\mathrm{A},l} + n_{\mathrm{B},l} RT\ln a_{\mathrm{B},l}$$

$$\Delta_{\mathrm{mix},l} G = nRT\left(x_{\mathrm{A},l}\ln a_{\mathrm{A},l} + x_{\mathrm{B},l}\ln a_{\mathrm{B},l}\right)$$ **(real solutions)**

Lecture 5: Solutions: Colligative properties

Lecture 5: Solutions: Colligative properties

Colligative properties:

Effects due to the presence of a mixture in the liquid phase in equilibrium with a

-Freezing point depression
-Boiling point elevation
-Osmosis
-Solubility

solid phase
gas phase
pure liquid
dissolved solute

Lecture 5: Solutions: Colligative properties

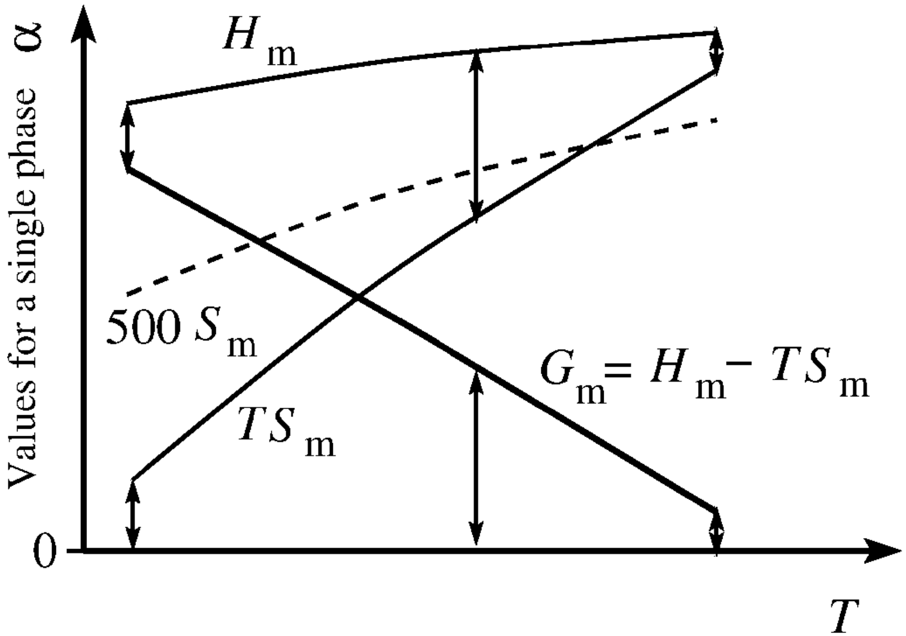
Effects due to the presence of a mixture in the liquid phase in equilibrium with a

solid phase
gas phase

-Freezing point depression
-Boiling point elevation

Lecture 5: Solutions: Colligative properties

Pure compound

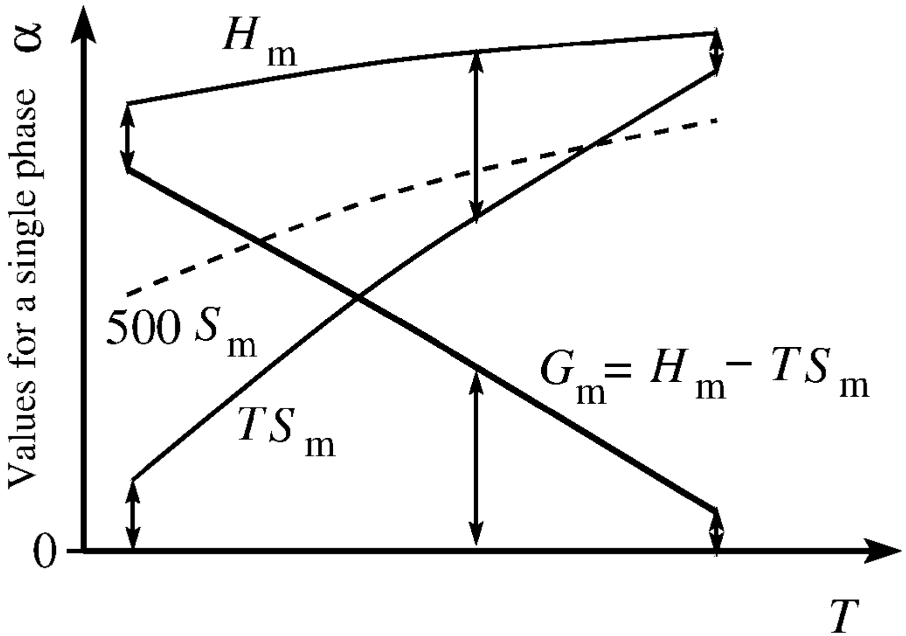


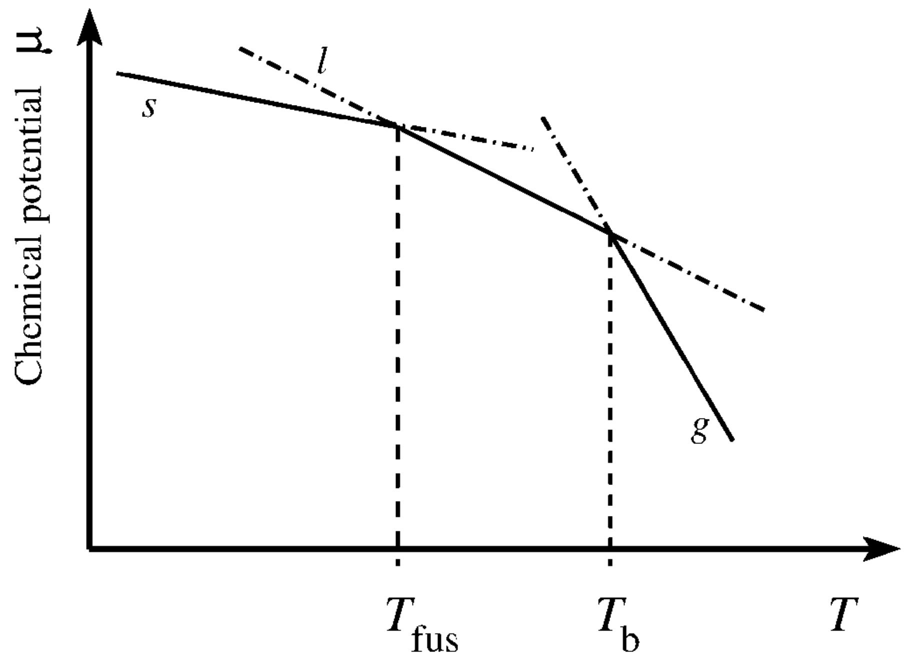
$$H_{m,\alpha}(T) \approx H_{m,\alpha} \text{ and } S_{m,\alpha}(T) \approx S_{m,\alpha}$$

$$dG_{m,\alpha}(T) \approx H_{m,\alpha} - S_{m,\alpha} dT$$

Lecture 5: Solutions: Colligative properties

Pure compound





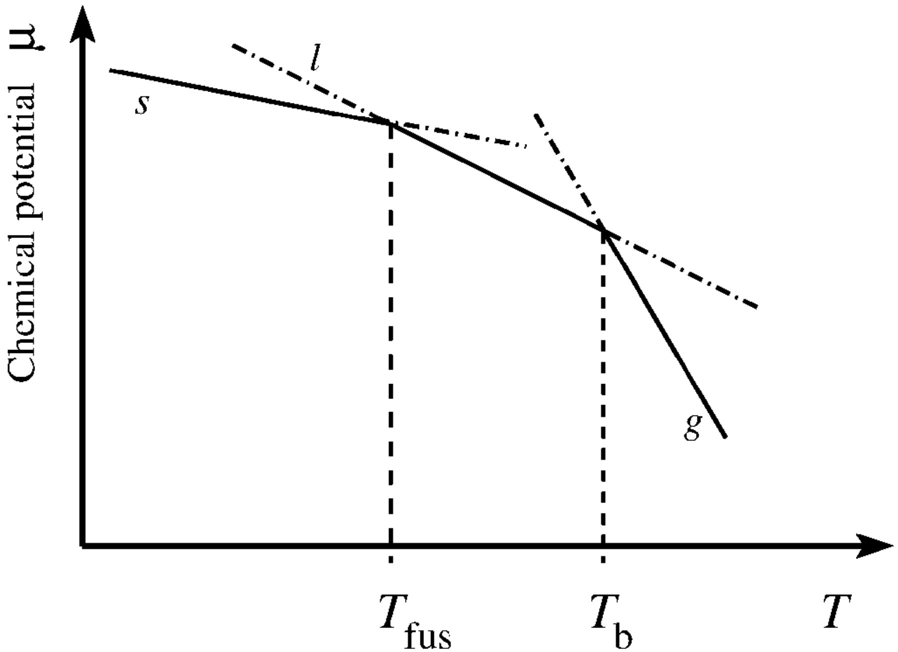
$$H_{m,\alpha}(T) \approx H_{m,\alpha} \text{ and } S_{m,\alpha}(T) \approx S_{m,\alpha}$$

$$dG_{m,\alpha}(T) \approx H_{m,\alpha} - S_{m,\alpha} dT$$

$$d\mu_\alpha^* = dG_{m,\alpha}^* \approx H_{m,\alpha}^* - S_{m,\alpha}^* dT$$

(* pure α) **(α = s, l, g)**

Lecture 5: Solutions: Colligative properties



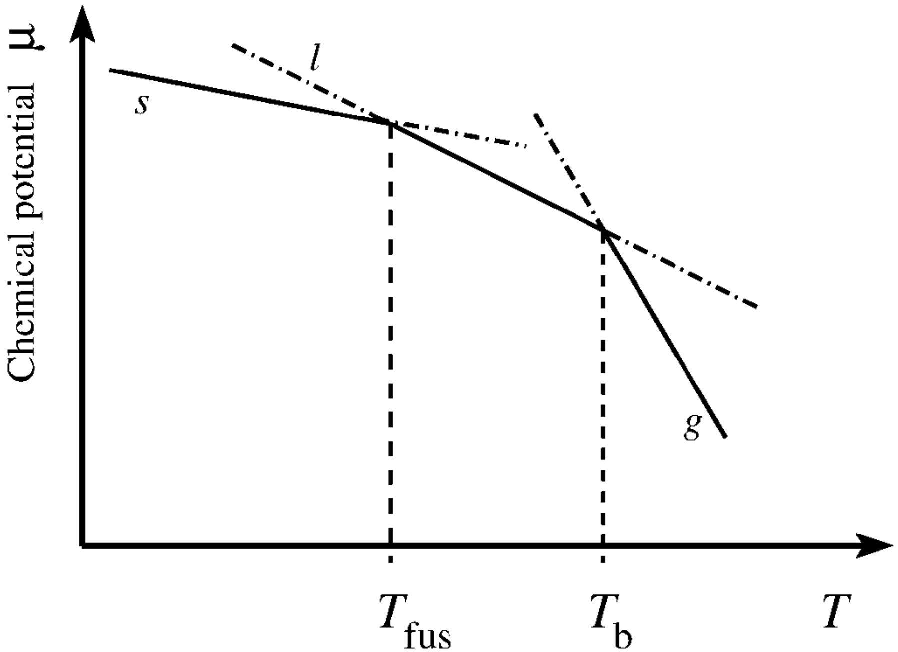
$$\boxed{d\mu_{\alpha}^{*} = dG_{\mathrm{m},\alpha}^{*} \approx H_{\mathrm{m},\alpha}^{*} - S_{\mathrm{m},\alpha}^{*}\, dT}$$

$$(\boldsymbol{\alpha} = \mathbf{s, l, g})$$

$$\boxed{S_{\mathrm{m},s} < S_{\mathrm{m},l} < S_{\mathrm{m},g}}$$

Entropy is a measure for amount of freedom of the movement of molecules

Lecture 5: Solutions: Colligative properties



$$d\mu_\alpha^* = dG_{\mathrm{m},\alpha}^* \approx H_{\mathrm{m},\alpha}^* - S_{\mathrm{m},\alpha}^* \, dT$$

(α = s, l, g)

$$S_{\mathrm{m},s} < S_{\mathrm{m},l} < S_{\mathrm{m},g}$$

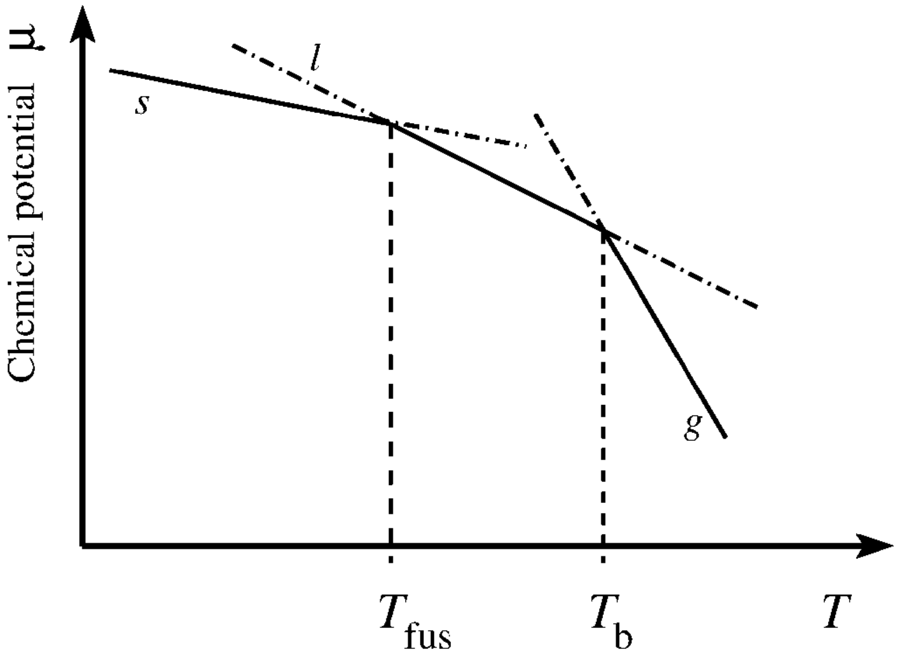
Add a solute to only the solvent

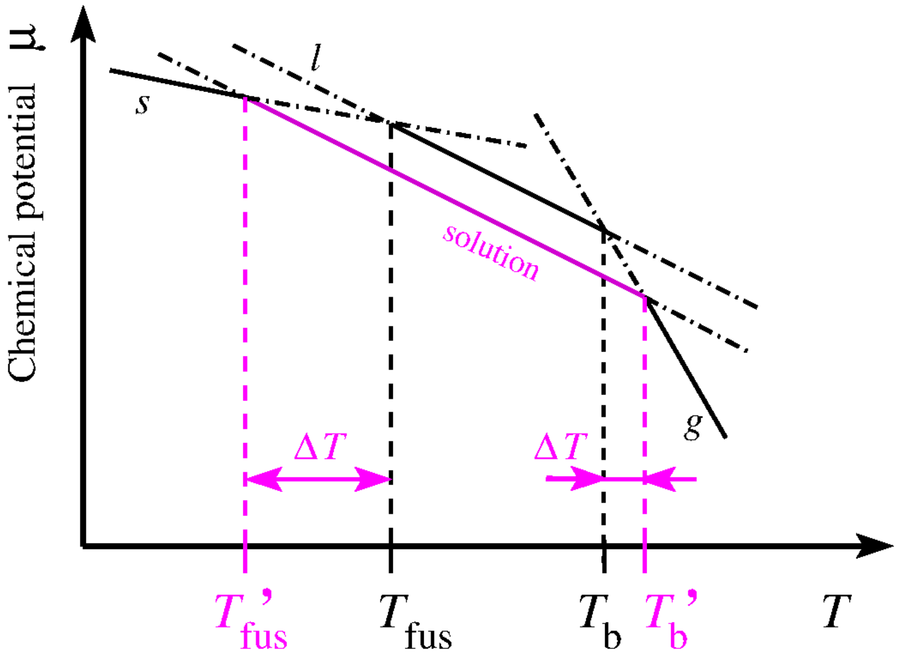
→phase g stays pure

→phase s stays pure

→phase l becomes a solution

Lecture 5: Solutions: Colligative properties





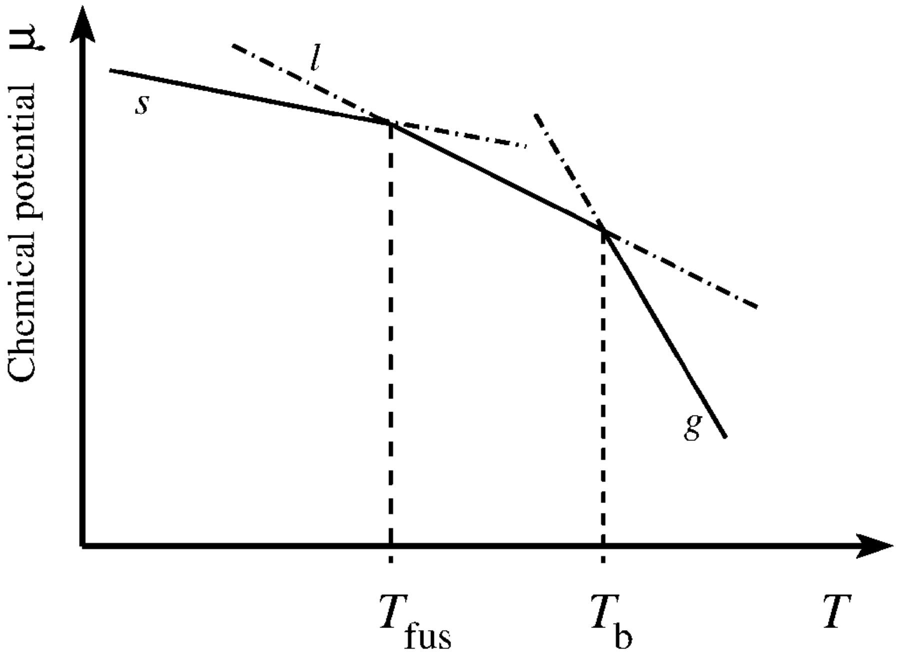
$$\boxed{d\mu^*_\alpha = dG^*_{m,\alpha} \approx H^*_{m,\alpha} - S^*_{m,\alpha}\, dT}$$

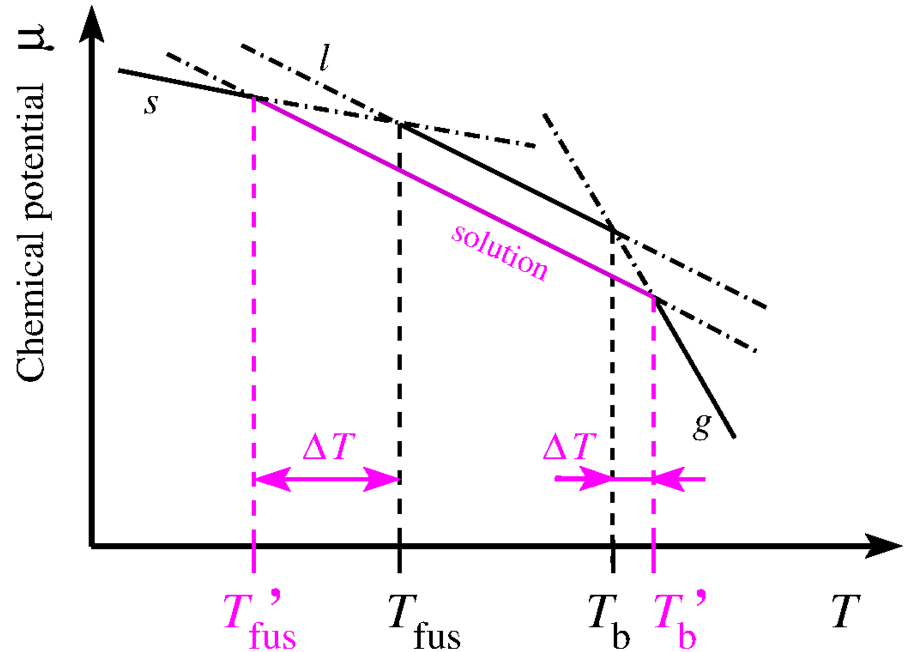
$$\boxed{\mu_s = \mu^*_s}$$

$$\boxed{\mu_g = \mu^*_g}$$

$$(\boldsymbol{\alpha} = \mathbf{s, l, g})$$

Lecture 5: Solutions: Colligative properties





$$\boxed{d\mu^*_{\alpha} = dG^*_{\mathrm{m},\alpha} \approx H^*_{\mathrm{m},\alpha} - S^*_{\mathrm{m},\alpha}\, dT}$$

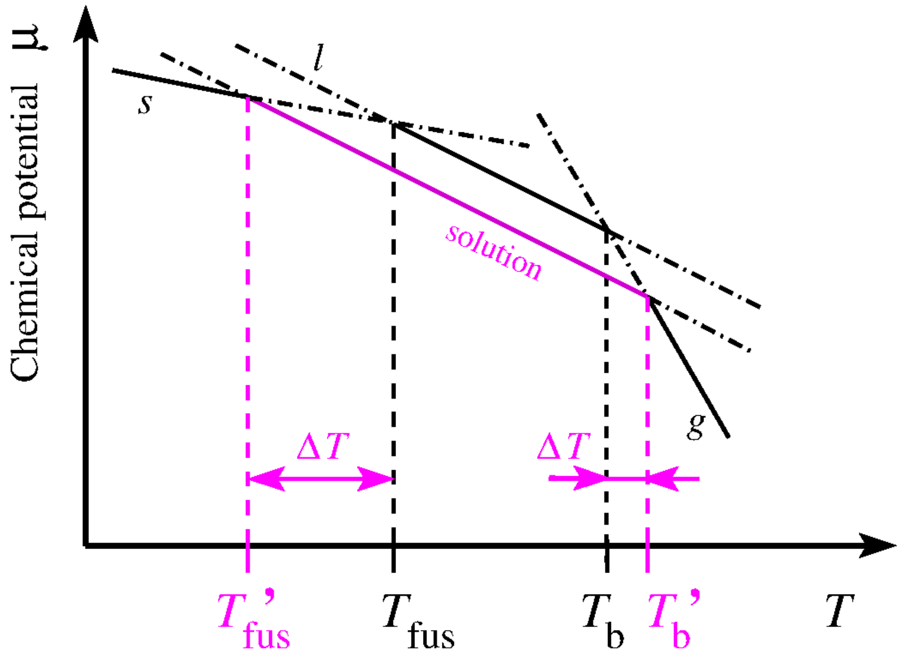
($\boldsymbol{\alpha}$ = s, l, g)

$$\boxed{\mu_s = \mu^*_s} \qquad \boxed{\mu_g = \mu^*_g}$$

$$\boxed{\mu_{\mathrm{A},l} = \mu^*_{\mathrm{A},l} + RT \ln a_{\mathrm{A},l}}$$

Real mixture of A and B

Lecture 5: Solutions: Colligative properties

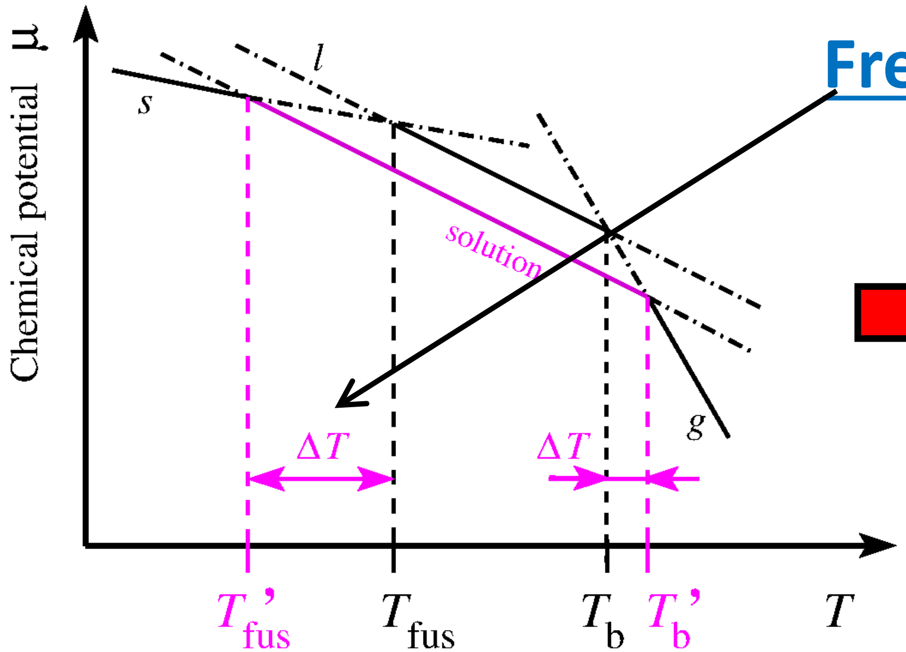


$$\mu_{A,l} = \mu^*_{A,l} + RT \ln a_{A,l}$$

A is the solvent

B is the solute

Lecture 5: Solutions: Colligative properties



Freezing point depression

New equilibrium: $@\,T'_{\mathrm{A,fus}}$

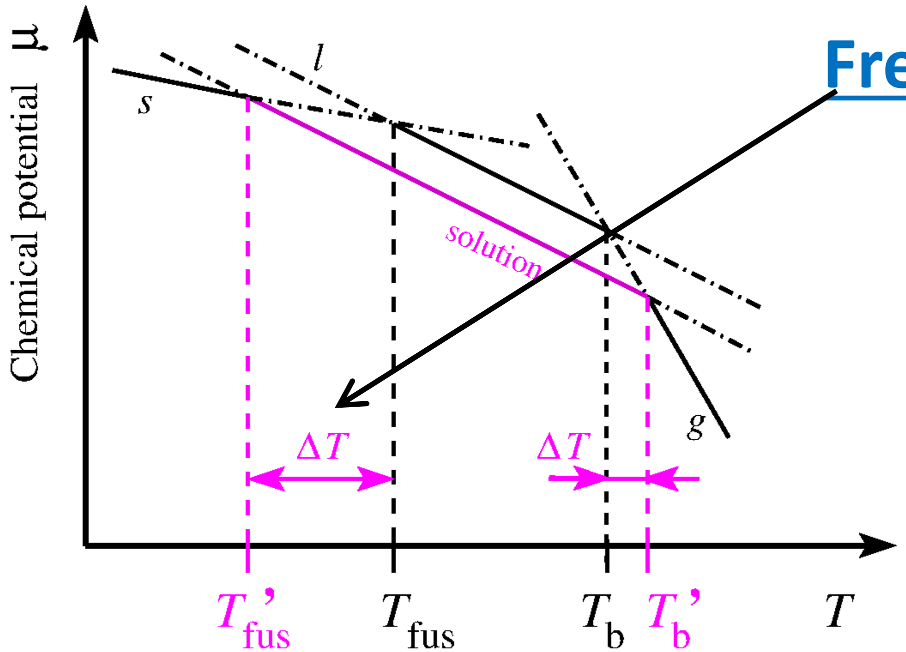
$$\boxed{\mu_l = \mu_s = \mu_s^*} \quad @\,T'_{\mathrm{A,fus}}$$

$$\boxed{\mu_{\mathrm{A},l} = \mu^*_{\mathrm{A},l} + RT \ln a_{\mathrm{A},l}}$$

A is the solvent

B is the solute

Lecture 5: Solutions: Colligative properties



Freesing point depression

New equilibrium: $@\,T'_{\mathrm{A,fus}}$

$$\boxed{\mu_l = \mu_s = \mu_s^*} \quad @\,T'_{\mathrm{A,fus}}$$

$$\boxed{\mu^*_{\mathrm{A},s} = \mu^*_{\mathrm{A},l} + RT'_{\mathrm{A,fus}} \ln a_{\mathrm{A},l}}$$

$$@\,T'_{\mathrm{A,fus}}$$

$$\boxed{G^*_{\mathrm{m,A},s} - G^*_{\mathrm{m,A},l} = RT'_{\mathrm{A,fus}} \ln a_{\mathrm{A},l}}$$

$$\left({}^*\text{pure phase} \rightarrow \mu^*_{\mathrm{A},\alpha} = G^*_{\mathrm{m,A},\alpha}\right)$$

$$\boxed{\mu_{\mathrm{A},l} = \mu^*_{\mathrm{A},l} + RT \ln a_{\mathrm{A},l}}$$

A is the solvent

B is the solute

Lecture 5: Solutions: Colligative properties

$$\boxed{G^*_{\mathrm{m,A},s} - G^*_{\mathrm{m,A},l} = RT'_{\mathrm{A,fus}} \ln a_{\mathrm{A},l}} \quad @\, T'_{\mathrm{A,fus}}$$

$$\boxed{\left(H^*_{\mathrm{m,A},s} - T'_{\mathrm{A,fus}} S^*_{\mathrm{m,A},s}\right) - \left(H^*_{\mathrm{m,A},l} - T'_{\mathrm{A,fus}} S^*_{\mathrm{m,A},l}\right) = RT'_{\mathrm{A,fus}} \ln a_{\mathrm{A},l}} \quad @\, T'_{\mathrm{A,fus}}$$

$$\Rightarrow \boxed{\Delta_{\mathrm{fus}} H^*_{\mathrm{m,A}} - T'_{\mathrm{A,fus}} \Delta_{\mathrm{fus}} S^*_{\mathrm{m,A}} = -RT'_{\mathrm{A,fus}} \ln a_{\mathrm{A},l}} \quad @\, T'_{\mathrm{A,fus}}$$

Lecture 5: Solutions: Colligative properties

$$\boxed{\Delta_{\text{fus}} H^{*}_{\text{m,A}} - T^{'}_{\text{A,fus}} \Delta_{\text{fus}} S^{*}_{\text{m,A}} = -RT^{'}_{\text{A,fus}} \ln a_{\text{A},l}} \quad @\, T^{'}_{\text{A,fus}}$$

For the pure compound:

$$\boxed{\Delta_{\text{fus}} H^{*}_{\text{m,A}} - T^{*}_{\text{A,fus}} \Delta_{\text{fus}} S^{*}_{\text{m,A}} = \Delta_{\text{fus}} G^{*}_{\text{m,A}} = 0} \quad @\, T^{*}_{\text{A,fus}}$$

$$\Rightarrow \boxed{\Delta_{\text{fus}} S^{*}_{\text{m,A}} = \frac{\Delta_{\text{fus}} H^{*}_{\text{m,A}}}{T^{*}_{\text{A,fus}}}}$$

Lecture 5: Solutions: Colligative properties

$$\boxed{\Delta_{\text{fus}} H^*_{\text{m,A}} - T'_{\text{A,fus}} \Delta_{\text{fus}} S^*_{\text{m,A}} = -RT'_{\text{A,fus}} \ln a_{\text{A},l}} \quad @\, T'_{\text{A,fus}}$$

For the pure compound:

$$\boxed{\Delta_{\text{fus}} H^*_{\text{m,A}} - T^*_{\text{A,fus}} \Delta_{\text{fus}} S^*_{\text{m,A}} = \Delta_{\text{fus}} G^*_{\text{m,A}} = 0} \quad @\, T^*_{\text{A,fus}}$$

$$\Rightarrow \boxed{\Delta_{\text{fus}} S^*_{\text{m,A}} = \frac{\Delta_{\text{fus}} H^*_{\text{m,A}}}{T^*_{\text{A,fus}}}}$$

$$\boxed{\Delta_{\text{fus}} H^*_{\text{m,A}}(T'_{\text{A,fus}}) \approx \Delta_{\text{fus}} H^*_{\text{m,A}}(T^*_{\text{A,fus}})}$$

$$\boxed{\Delta_{\text{fus}} S^*_{\text{m,A}}(T'_{\text{A,fus}}) \approx \Delta_{\text{fus}} S^*_{\text{m,A}}(T^*_{\text{A,fus}})}$$

$$\Rightarrow \boxed{\Delta_{\text{fus}} S^*_{\text{m,A}} \approx \frac{\Delta_{\text{fus}} H^*_{\text{m,A}}}{T^*_{\text{A,fus}}}} \quad @\, T'_{\text{A,fus}}$$

Lecture 5: Solutions: Colligative properties

$$\boxed{\Delta_{\text{fus}} H^{*}_{\text{m,A}} - T^{'}_{\text{A,fus}} \Delta_{\text{fus}} S^{*}_{\text{m,A}} = -RT^{'}_{\text{A,fus}} \ln a_{\text{A},l}} \quad @\, T^{'}_{\text{A,fus}}$$

$$\boxed{\Delta_{\text{fus}} S^{*}_{\text{m,A}} \approx \frac{\Delta_{\text{fus}} H^{*}_{\text{m,A}}}{T^{*}_{\text{A,fus}}}} \quad @\, T^{'}_{\text{A,fus}}$$

$$\Rightarrow \boxed{\frac{\Delta_{\text{fus}} H^{*}_{\text{m,A}}}{R}\left(\frac{1}{T^{'}_{\text{A,fus}}} - \frac{1}{T^{*}_{\text{A,fus}}}\right) \approx -\ln a_{\text{A},l}}$$

Lecture 5: Solutions: Colligative properties

$$\boxed{\Delta_{\text{fus}} H^*_{\text{m,A}} - T'_{\text{A,fus}} \Delta_{\text{fus}} S^*_{\text{m,A}} = -RT'_{\text{A,fus}} \ln a_{\text{A},l}} \quad @T'_{\text{A,fus}}$$

$$\boxed{\Delta_{\text{fus}} S^*_{\text{m,A}} \approx \frac{\Delta_{\text{fus}} H^*_{\text{m,A}}}{T^*_{\text{A,fus}}}} \quad @T'_{\text{A,fus}}$$

$$\boxed{\frac{\Delta_{\text{fus}} H^*_{\text{m,A}}}{R}\left(\frac{1}{T'_{\text{A,fus}}} - \frac{1}{T^*_{\text{A,fus}}}\right) \approx -\ln a_{\text{A},l} \approx -\ln x_{\text{A},l} = -\ln\left(1 - x_{\text{B},l}\right)}$$

Assume ideal solution

Lecture 5: Solutions: Colligative properties

$$\boxed{\Delta_{\text{fus}} H^{*}_{\text{m,A}} - T'_{\text{A,fus}} \Delta_{\text{fus}} S^{*}_{\text{m,A}} = -RT'_{\text{A,fus}} \ln a_{\text{A},l}} \quad @\, T'_{\text{A,fus}}$$

$$\boxed{\Delta_{\text{fus}} S^{*}_{\text{m,A}} \approx \frac{\Delta_{\text{fus}} H^{*}_{\text{m,A}}}{T^{*}_{\text{A,fus}}}} \quad @\, T'_{\text{A,fus}}$$

$$\Rightarrow \boxed{\frac{\Delta_{\text{fus}} H^{*}_{\text{m,A}}}{R}\left(\frac{1}{T'_{\text{A,fus}}} - \frac{1}{T^{*}_{\text{A,fus}}}\right) \approx -\ln\left(1 - x_{\text{B},l}\right) \approx x_{\text{B},l}}$$

Lecture 5: Solutions: Colligative properties

$$\boxed{\Delta_{\text{fus}} H^{*}_{\text{m,A}} - T'_{\text{A,fus}} \Delta_{\text{fus}} S^{*}_{\text{m,A}} = -RT'_{\text{A,fus}} \ln a_{\text{A},l}} \quad @\, T'_{\text{A,fus}}$$

$$\boxed{\Delta_{\text{fus}} S^{*}_{\text{m,A}} \approx \frac{\Delta_{\text{fus}} H^{*}_{\text{m,A}}}{T^{*}_{\text{A,fus}}}} \quad @\, T'_{\text{A,fus}}$$

$$\Rightarrow \boxed{\frac{\Delta_{\text{fus}} H^{*}_{\text{m,A}}}{R}\left(\frac{1}{T'_{\text{A,fus}}} - \frac{1}{T^{*}_{\text{A,fus}}}\right) \approx -\ln\left(1 - x_{\text{B},l}\right) \approx x_{\text{B},l}}$$

Let's work this out in detail

Lecture 5: Solutions: Colligative properties

$$\boxed{\Delta_{\text{fus}} H^{*}_{\text{m,A}} - T^{'}_{\text{A,fus}} \Delta_{\text{fus}} S^{*}_{\text{m,A}} = -RT^{'}_{\text{A,fus}} \ln a_{\text{A},l}} \quad @\, T^{'}_{\text{A,fus}}$$

$$\boxed{\Delta_{\text{fus}} S^{*}_{\text{m,A}} \approx \frac{\Delta_{\text{fus}} H^{*}_{\text{m,A}}}{T^{*}_{\text{A,fus}}}} \quad @\, T^{'}_{\text{A,fus}}$$

$$\Rightarrow \boxed{\frac{\Delta_{\text{fus}} H^{*}_{\text{m,A}}}{R} \left(\frac{1}{T^{'}_{\text{A,fus}}} - \frac{1}{T^{*}_{\text{A,fus}}} \right) \approx -\ln\left(1 - x_{\text{B},l}\right) \approx x_{\text{B},l}}$$

$$\Rightarrow \boxed{\frac{\Delta_{\text{fus}} H^{*}_{\text{m,A}}}{R} \left(\frac{T^{*}_{\text{A,fus}} - T^{'}_{\text{A,fus}}}{T^{'}_{\text{A,fus}} T^{*}_{\text{A,fus}}} \right) \approx -\ln\left(1 - x_{\text{B},l}\right) \approx x_{\text{B},l}}$$

$$\Rightarrow \boxed{\frac{\Delta_{\text{fus}} H^{*}_{\text{m,A}}}{R} \left(\frac{T^{*}_{\text{A,fus}} - T^{'}_{\text{A,fus}}}{T^{*2}_{\text{A,fus}}} \right) \approx -\ln\left(1 - x_{\text{B},l}\right) \approx x_{\text{B},l}}$$

Lecture 5: Solutions: Colligative properties

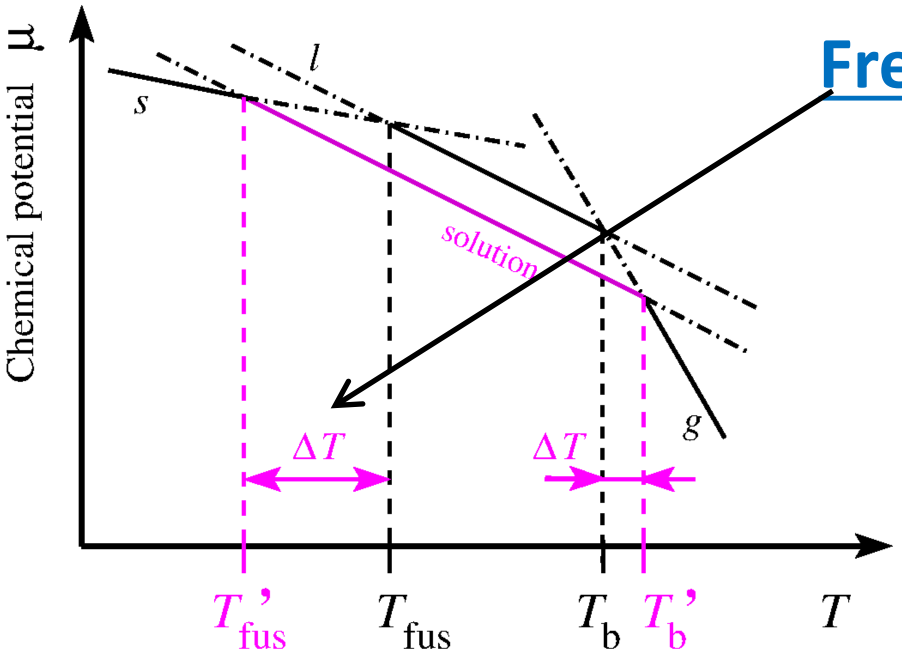
$$\boxed{\frac{\Delta_{\text{fus}} H^{*}_{\text{m, A}}}{R}\left(\frac{T^{*}_{\text{A,fus}} - T^{'}_{\text{A,fus}}}{T^{*2}_{\text{A,fus}}}\right) \approx -\ln\left(1 - x_{\text{B},l}\right) \approx x_{\text{B},l}}$$

Freezing point depression

$$\boxed{\Delta T \equiv T^{*}_{\text{A,fus}} - T^{'}_{\text{A,fus}}}$$

$$\Rightarrow \quad \boxed{\Delta T \approx \frac{R T^{*2}_{\text{A,fus}}}{\Delta_{\text{fus}} H^{*}_{\text{m, A}}} x_{\text{B}}}$$

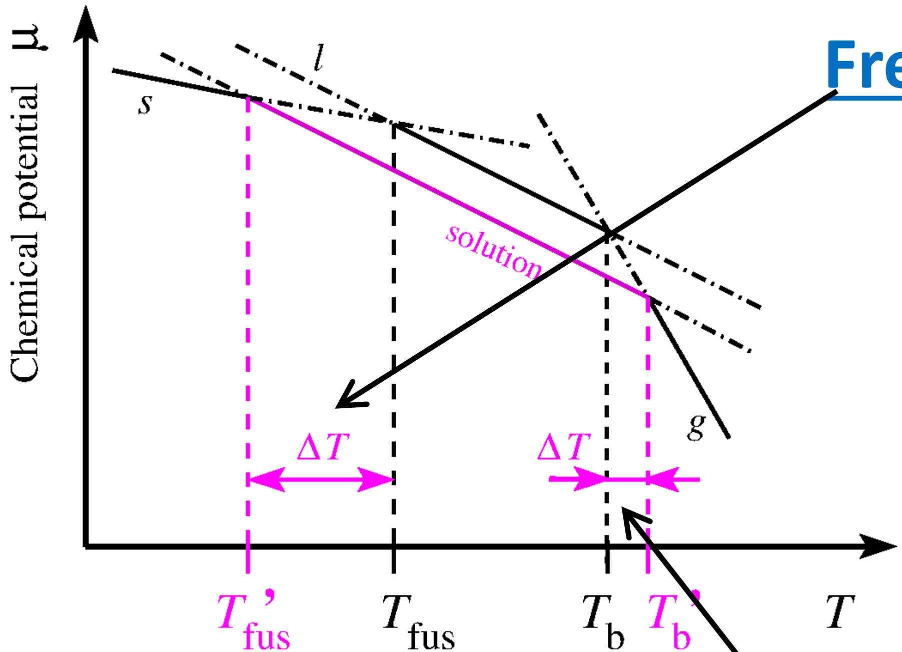
Lecture 5: Solutions: Colligative properties



Freezing point depression

$$\boxed{\Delta T \approx \frac{RT^{*2}_{\mathrm{A,fus}}}{\Delta_{\mathrm{fus}} H^{*}_{\mathrm{m,A}}} x_{\mathrm{B}}}$$

Lecture 5: Solutions: Colligative properties



Freezing point depression

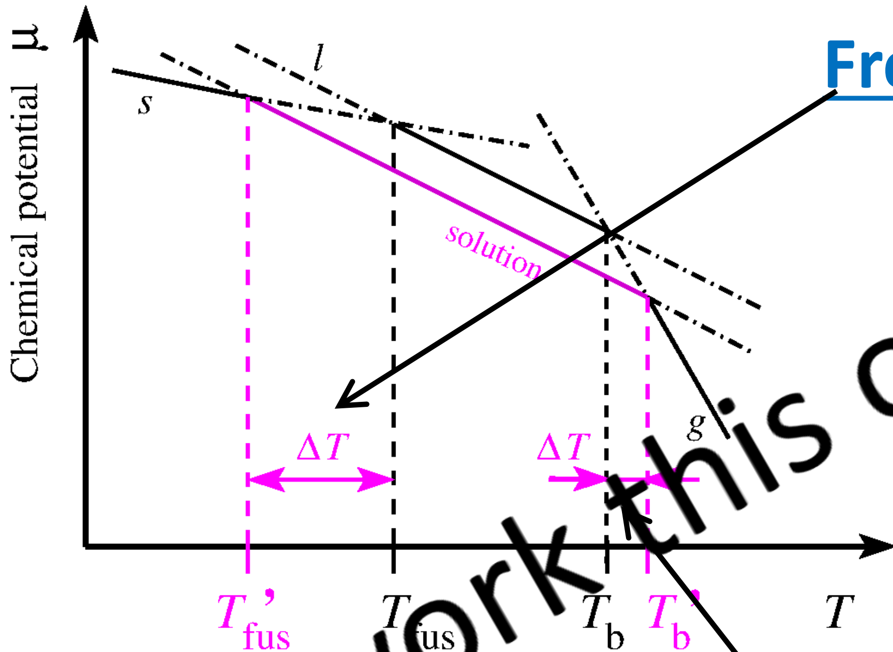
$$\boxed{\Delta T \approx \frac{RT^{*2}_{\mathrm{A,fus}}}{\Delta_{\mathrm{fus}} H^{*}_{\mathrm{m,A}}} x_{\mathrm{B}}}$$

Analogously:

$$\boxed{\Delta T \approx \frac{RT^{*2}_{\mathrm{A,vap}}}{\Delta_{\mathrm{vap}} H^{*}_{\mathrm{m,A}}} x_{\mathrm{B}}}$$

Boiling point elevation

Lecture 5: Solutions: Colligative properties



Freezing point depression

$$\Delta T \approx \frac{R T^{*2}_{\mathrm{A,fus}}}{\Delta_{\mathrm{fus}} H^{*}_{\mathrm{m,A}}} x_{\mathrm{B}}$$

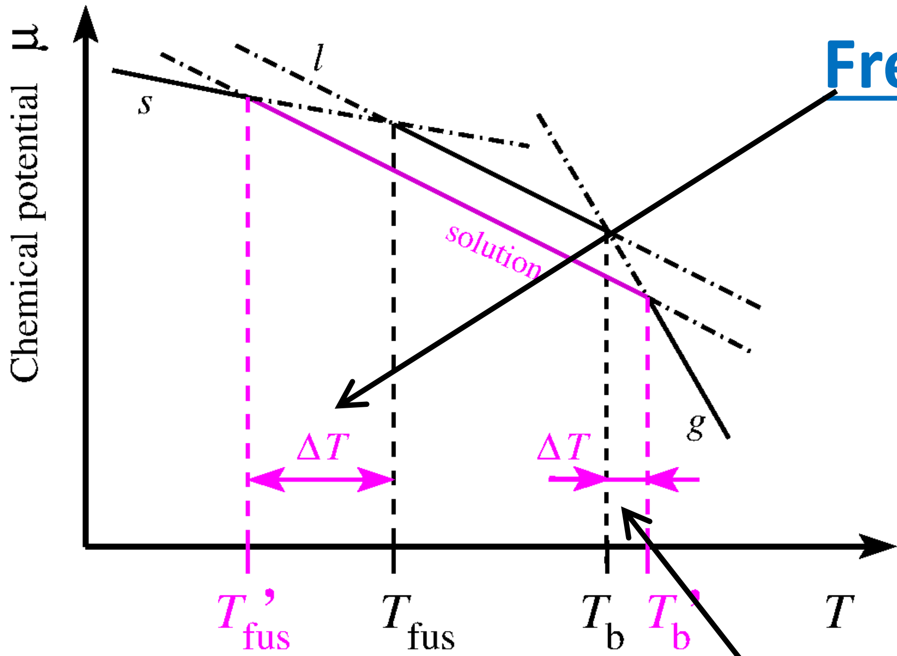
Analogously:

$$\Delta T \approx \frac{R T^{*2}_{\mathrm{A,vap}}}{\Delta_{\mathrm{vap}} H^{*}_{\mathrm{m,A}}} x_{\mathrm{B}}$$

Boiling point elevation

Let's work this out in detail

Lecture 5: Solutions: Colligative properties



Freezing point depression

$$\boxed{\Delta T \approx \frac{RT^{*2}_{\mathrm{A,fus}}}{\Delta_{\mathrm{fus}} H^{*}_{\mathrm{m,A}}} x_{\mathrm{B}}}$$

Analogously:

$$\boxed{\Delta T \approx \frac{RT^{*2}_{\mathrm{A,vap}}}{\Delta_{\mathrm{vap}} H^{*}_{\mathrm{m,A}}} x_{\mathrm{B}}}$$

Boiling point elevation

Assumptions made:

→phase g stays pure

→phase s stays pure

→phase l becomes an *ideal* solution: $a_l \approx x_l$

→$\Delta_{\mathrm{trs}}H$, $\Delta_{\mathrm{trs}}S$ independent of T

Lecture 5: Solutions: Colligative properties

Colligative properties:

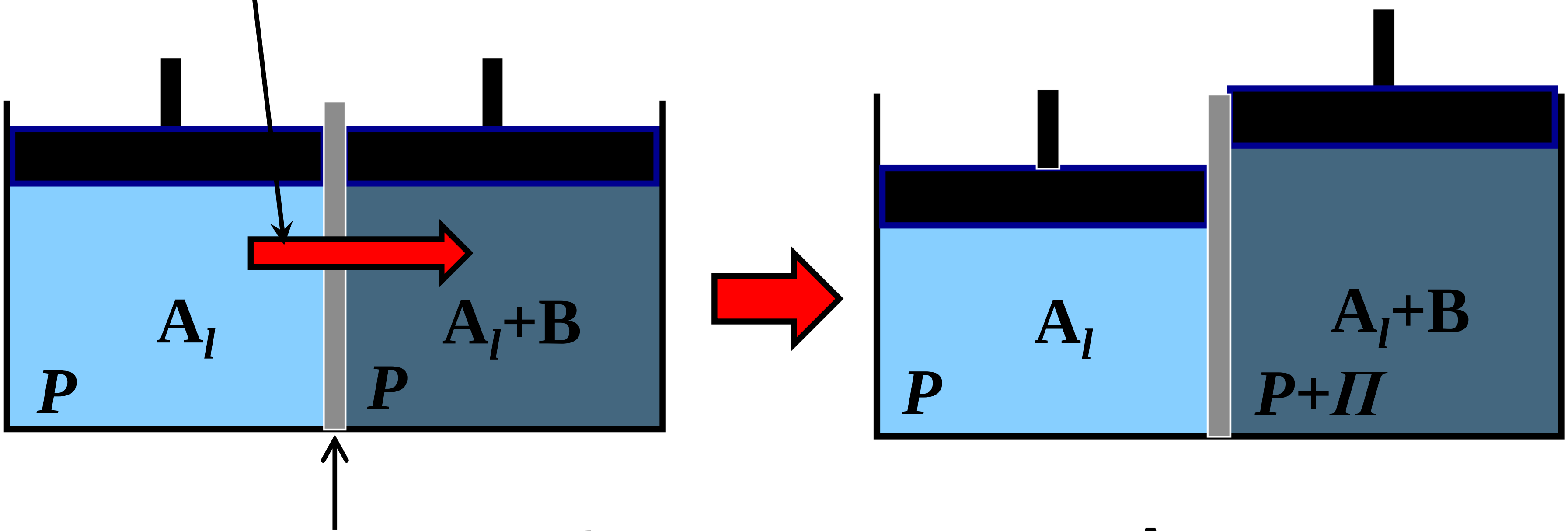
Effects due to the presence of a mixture in the liquid phase in equilibrium with a

- **-Freezing point depression**
- **-Boiling point elevation**
- **-Osmosis**
- **-Solubility**

solid phase
gas phase
pure liquid
dissolved solute

Lecture 5: Solutions: Colligative properties

Osmosis → **Gain in entropy (2nd law)**



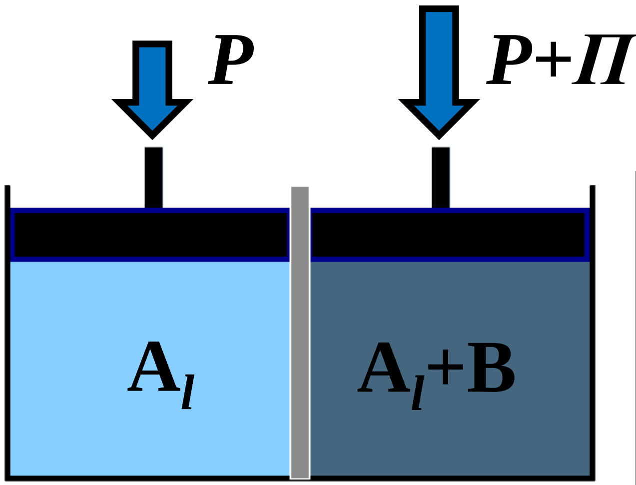
Semipermeable membrane
- **Permeable for solvent A**
- **Impermeable for solute B**

Π is the osmotic pressure

Equilibrium:

$$\boxed{\mu^*_{A,l}(P) = \mu_{A,l}(x_A, P+\Pi)}$$

Lecture 5: Solutions: Colligative properties



Osmosis

Equilibrium:

$$\mu^*_{\mathrm{A},l}(P) = \mu_{\mathrm{A},l}(x_\mathrm{A}, P+\Pi)$$
$$= \mu^*_{\mathrm{A},l}(P+\Pi) + RT\ln a_\mathrm{A}$$
$$= \mu^*_{\mathrm{A},l}(P) + \int_P^{P+\Pi} V^*_{\mathrm{A,m}}\, dP + RT\ln a_\mathrm{A}$$

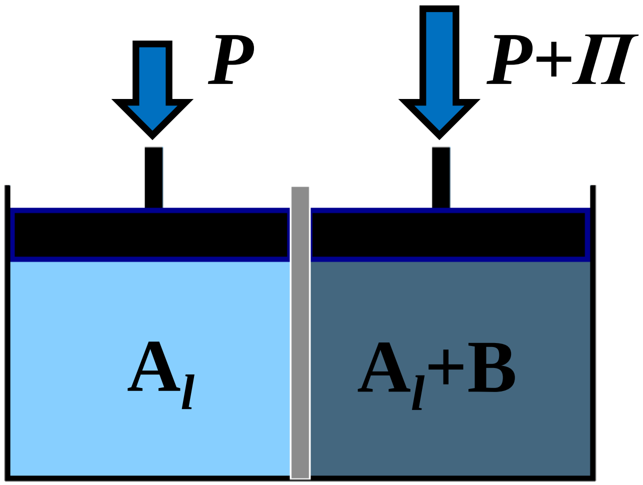
$$-RT\ln a_\mathrm{A} = \int_P^{P+\Pi} V^*_{\mathrm{A,m}}\, dP \approx V^*_{\mathrm{A,m}} \int_P^{P+\Pi} P = V^*_{\mathrm{A,m}}\, \Pi$$

A is the solvent

B is the solute

liquid ≈ incompressible

Lecture 5: Solutions: Colligative properties



Osmosis

Equilibrium:

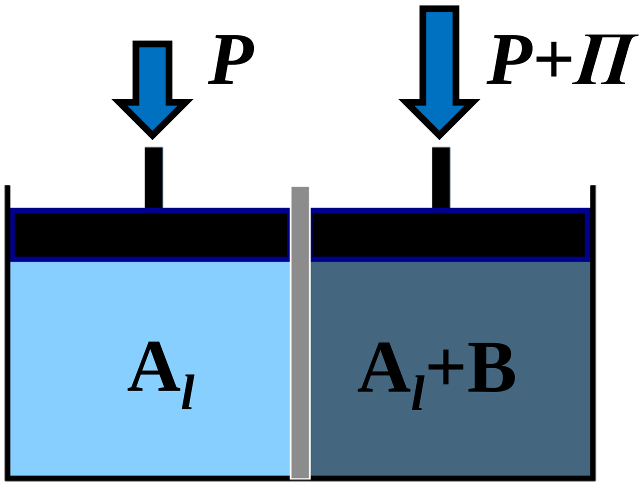
$$-RT\ln a_{\mathrm{A}} \approx V^{*}_{\mathrm{A,m}}\int_{P}^{P+\Pi} dP = V^{*}_{\mathrm{A,m}}\,\Pi$$

$$\boxed{\Pi \approx -\frac{RT}{V^{*}_{\mathrm{A,m}}}\ln a_{\mathrm{A}}}$$

A is the solvent

B is the solute

Lecture 5: Solutions: Colligative properties



Osmosis

Equilibrium:

$$-RT\ln a_{\mathrm{A}} \approx V^*_{\mathrm{A,m}} \int_P^{P+\Pi} P = V^*_{\mathrm{A,m}}\,\Pi$$

$$\boxed{\Pi \approx -\frac{RT}{V^*_{\mathrm{A,m}}}\ln a_{\mathrm{A}}}$$

Ideal solution

$$\Pi \approx -\frac{RT}{V^*_{\mathrm{A,m}}}\ln x_{\mathrm{A}} \approx \frac{RT}{V^*_{\mathrm{A,m}}}x_{\mathrm{B}} \approx \frac{RTn_B}{V^*_{\mathrm{A,m}}n_A} \approx RT[B]$$

$$\boxed{\Pi \approx RT[\mathrm{B}]}$$

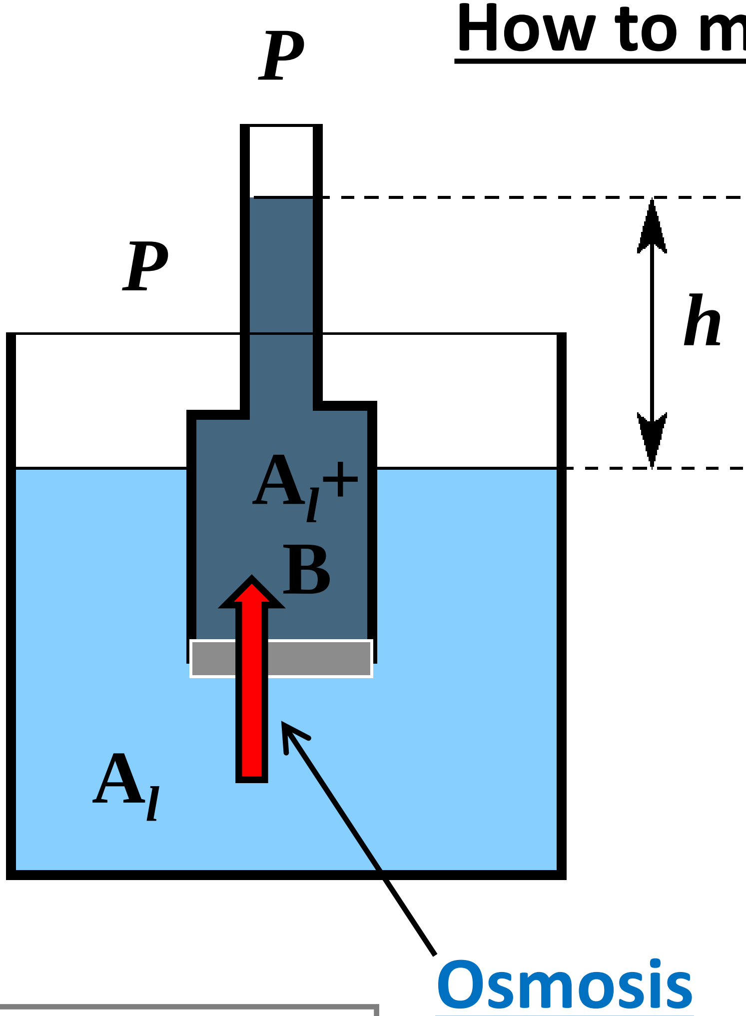
Van 't Hoff equation

A is the solvent

B is the solute

Lecture 5: Solutions: Colligative properties

How to measure Π ?



Equilibrium:

$$\boxed{\rho g h = \Pi = -\frac{RT}{V^*_{\mathrm{A,m}}} \ln a_{\mathrm{A}}}$$

Solution mass density ρ

$$\boxed{\rho g h = \Pi \approx RT[\mathrm{B}]}$$

Van 't Hoff

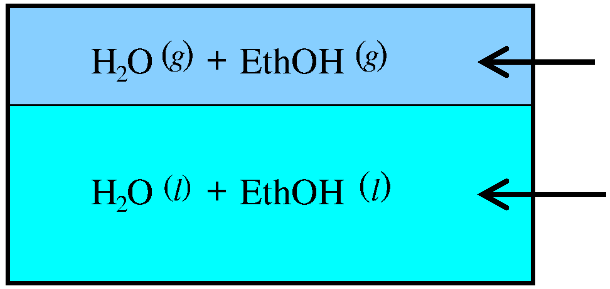
A is the solvent

B is the solute

Summary Lecture 5 (solutions)

Summary Lecture 5: solutions or mixtures

Equilibrium between phases of component *i* in mixtures



phase α

phase β

in equilibrium: $\boxed{\mu_{i,\alpha} = \mu_{i,\beta}}$

$$\boxed{G\big|_{P,T} = \sum_i \mu_i n_i}$$

Real phase mixing

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

Perfect gas mixing

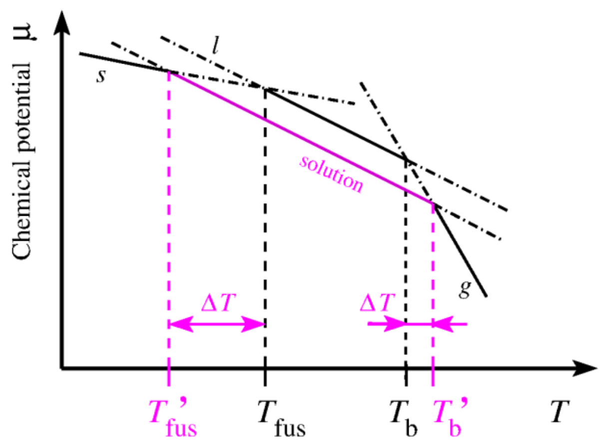
Ideal solution (Raoult)

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

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

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

Summary Lecture 5: colligative properties



Freezing point depression

Boiling point elevation

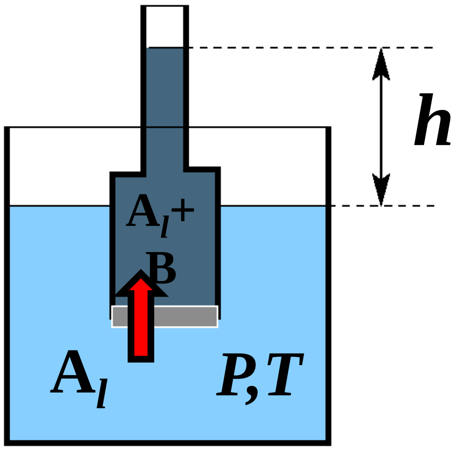
$$\Delta T \approx -\frac{RT^{*2}_{\mathrm{A,fus}}}{\Delta_{\mathrm{fus}} H^{*}_{\mathrm{m,A}}} \ln a_{\mathrm{A}}$$

$$\Delta T \approx -\frac{RT^{*2}_{\mathrm{A,vap}}}{\Delta_{\mathrm{vap}} H^{*}_{\mathrm{m,A}}} \ln a_{\mathrm{A}}$$

Ideal solution:

$$\Delta T \approx \frac{RT^{*2}_{\mathrm{A,fus}}}{\Delta_{\mathrm{fus}} H^{*}_{\mathrm{m,A}}} x_{\mathrm{B}}$$

$$\Delta T \approx \frac{RT^{*2}_{\mathrm{A,vap}}}{\Delta_{\mathrm{vap}} H^{*}_{\mathrm{m,A}}} x_{\mathrm{B}}$$



Osmosis

$$\rho g h = \Pi = -\frac{RT}{V^{*}_{\mathrm{A,m}}} \ln a_{\mathrm{A}}$$

Ideal solution:

$$\rho g h = \Pi \approx RT[\mathrm{B}]$$