

Fázové rovnováhy a směsi

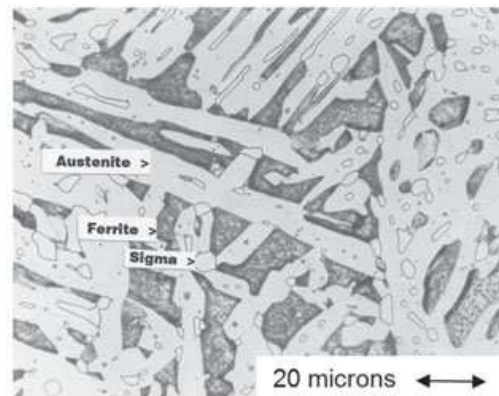
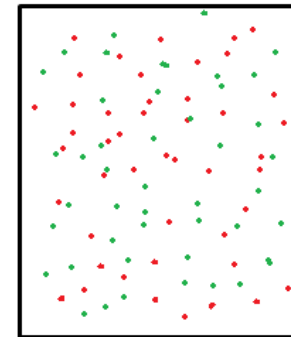
- 4. Fázové rovnováhy a směsi
 - Fázové diagramy čistých látek. 4.1.1 Pojem fáze, fázový přechod, kritéria fázové stability. Závislost chemického potenciálu na teplotě a tlaku, změna teploty tání s tlakem. 4.1.2 Fázový diagram čisté látky, Gibbsovo fázové pravidlo, koexistenční křivky. Typy fázových přechodů.
 - 4.2 Jednoduché směsi. Popis složení v termodynamice. Parciální molární objemy složek ve směsi (příklad vody a ethanolu). Parciální molární Gibbsova funkce – chemický potenciál. 4.2.1 Směsi plynů. Gibbsova energie mísení ideálních plynů, složení páry z Daltonova zákona. 4.2.2 Směsi kapalin. Ideální roztok, tlak nasycené páry pro směs (příklad benzen-toluen), Raoultův zákon, Henryho zákon. Gibbsova energie mísení kapalin, dodatkové funkce. Koligativní vlastnosti roztoků: Ebulioskopický a kryoskopický efekt, osmotický tlak.
 - 4.3 Fázové diagramy dvousložkových systémů. Binární ideální roztok: interpretace fázových diagramů, pákové pravidlo, destilace směsí.
 - 4.4 Reálné roztoky. Aktivita, molární zlomek a aktivitní koeficient složky v roztoku. Elektrolyty. Střední aktivitní koeficient elektrolytu. Debye-Hückelův limitní zákon.

4.1 Fázové diagramy čistých látek

fáze, počet fází P



Roztok



Disperze

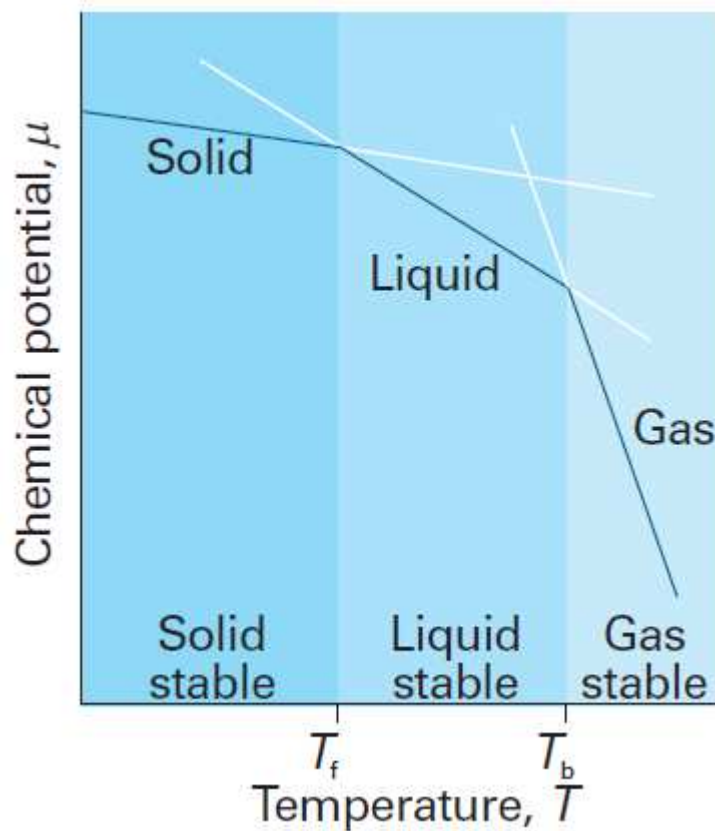


Figure 6. 2209 Weld Metal Annealed 96 hours at 1040°C.

*D. J. Kotecki Soldag. insp. 15 (4)
(Oct. / Dec. 2010) São Paulo*

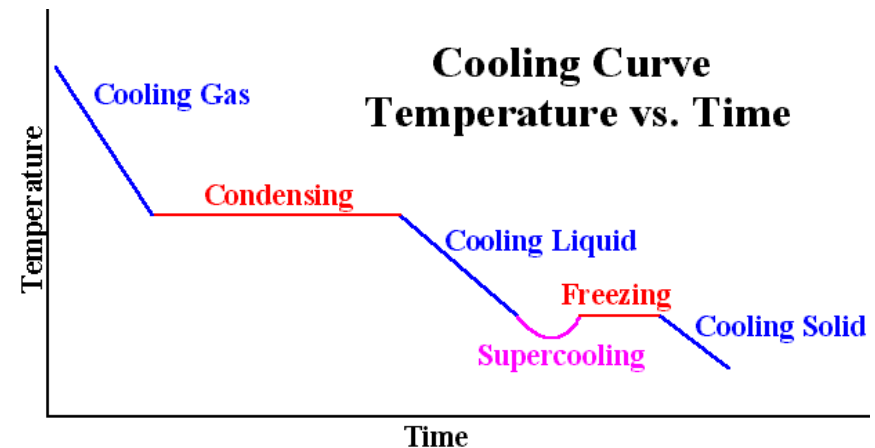
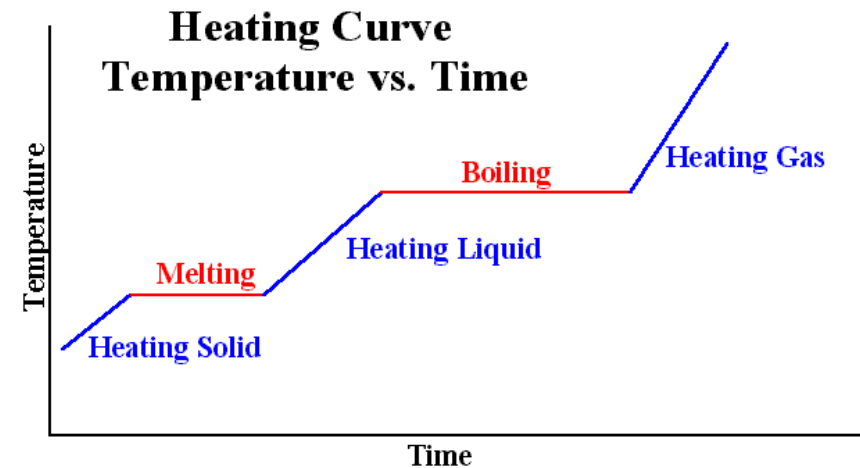
4.1 Fázové diagramy čistých látek

fázové přechody



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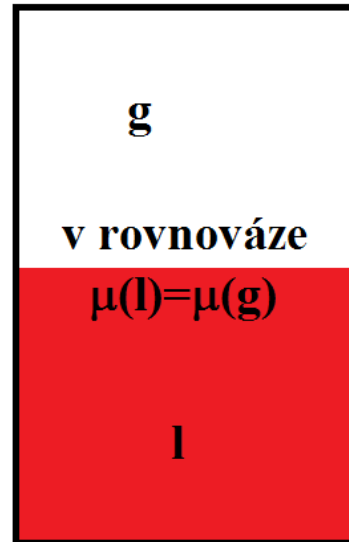
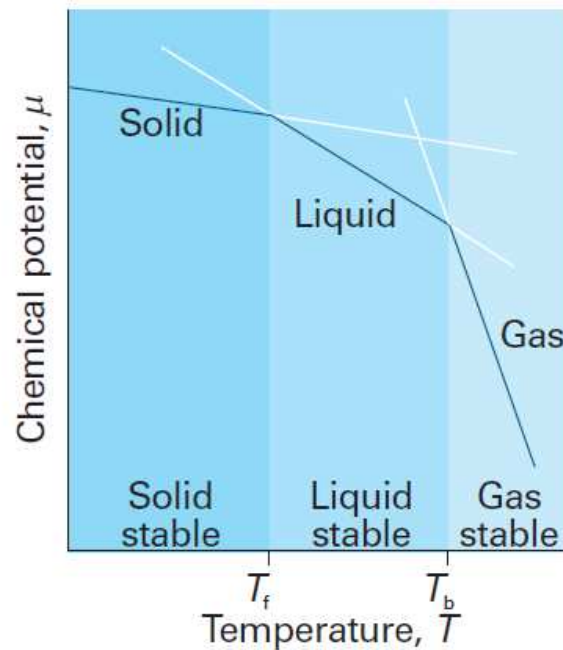
určení fázového přechody



http://people.uwplatt.edu/~sundin/114/l114_34.htm

4.1 Fázové diagramy čistých látek

rychlost fázového přechodu
kritéria fázové stability



přeměna n molů látky
a z fáze f_1 na fázi f_2

$$-\mu_{A,f_1} dn = \mu_{A,f_2} dn$$

$$dG = \mu_{A,f_2} dn - \mu_{A,f_1} dn = \\ = (\mu_{A,f_2} - \mu_{A,f_1}) dn$$

$$a) \mu_{A,f_2} = \mu_{A,f_1}$$

$$dG = 0$$

$$b) \mu_{A,f_2} > \mu_{A,f_1}$$

$$dG > 0$$

$$c) \mu_{A,f_2} < \mu_{A,f_1}$$

$$dG < 0$$

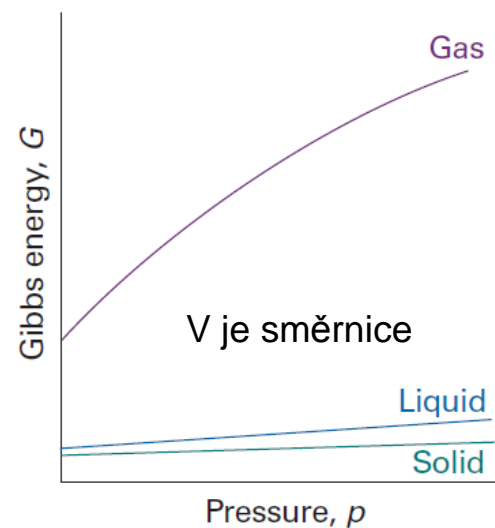
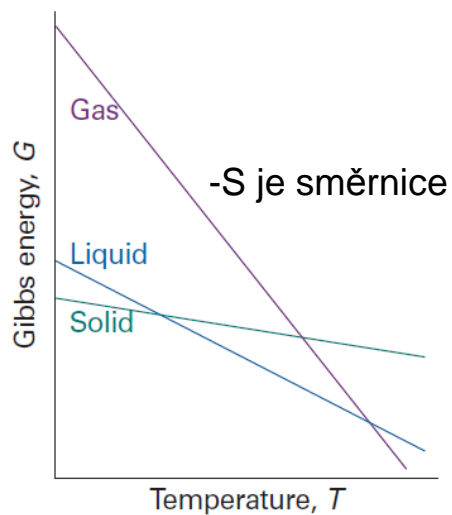
4.1 Fázové diagramy čistých látek

závislost μ na T a p

$$dG_m = V_m dp - S_m dT$$

$$-S_m = \left(\frac{\partial G_m}{\partial T} \right)_p = \left(\frac{\partial \mu}{\partial T} \right)_p$$

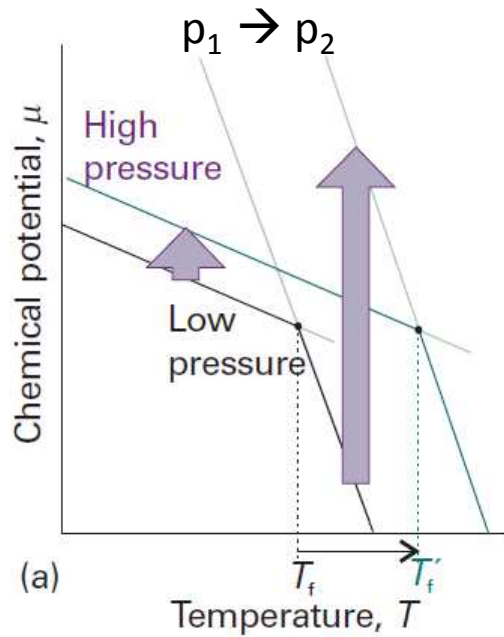
$$V_m = \left(\frac{\partial G_m}{\partial p} \right)_T = \left(\frac{\partial \mu}{\partial p} \right)_T$$



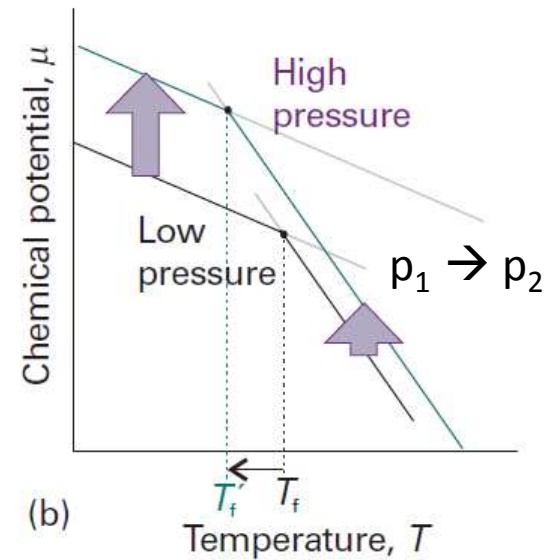
4.1 Fázové diagramy čistých látek

vliv p na T_t $d\mu = V_m dp - S_m dT$
 $d\mu = V_m dp$ $T = \text{konst.}$

$V_m(s) < V_m(l)$

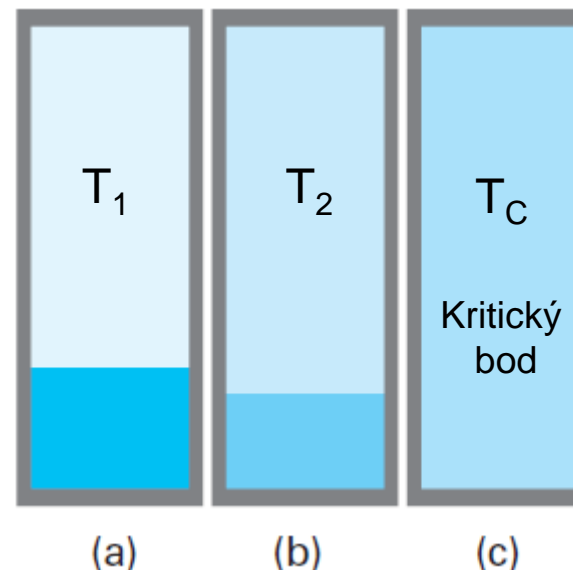
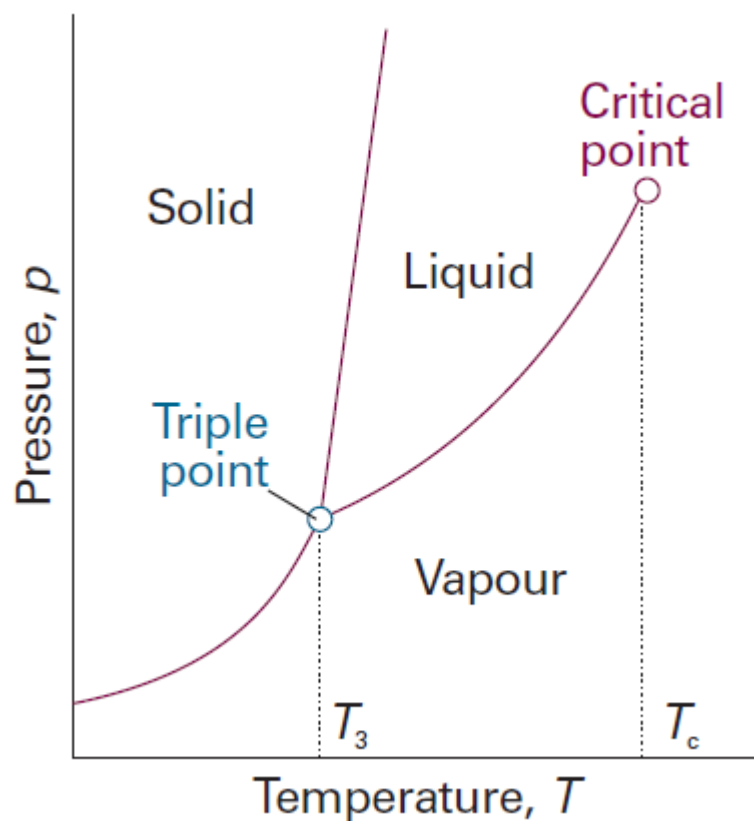


$V_m(s) > V_m(l)$ pro vodu



4.1 Fázové diagramy čistých látek

fázový diagram
koexistenční křivky



$$T_1 < T_2 < T_c$$

fázové pravidlo

$$F = C - P + 2$$

F ... počet stupňů volnosti

C ... počet složek

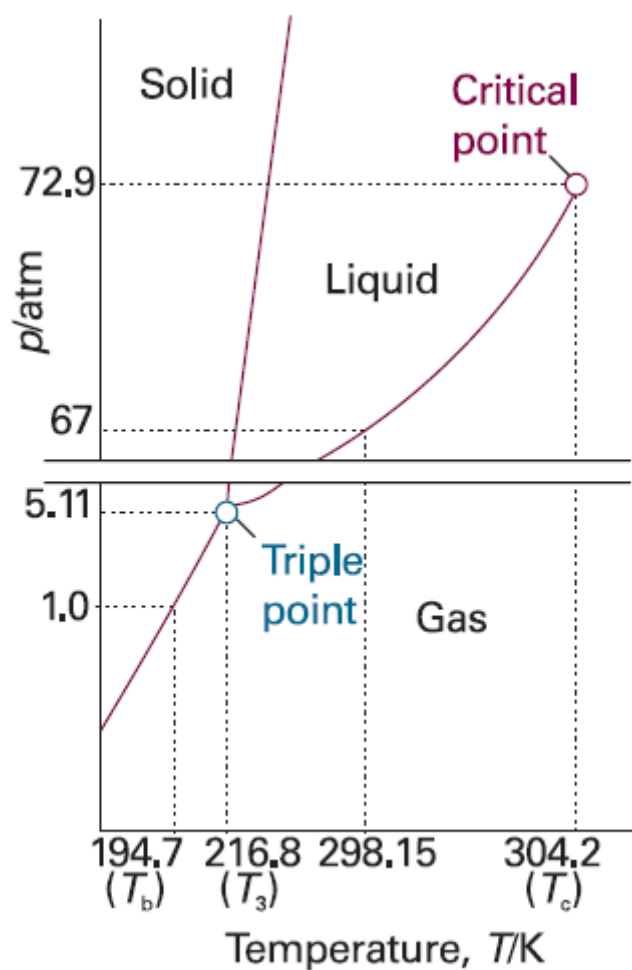
P ... počet fází

4.1 Fázové diagramy čistých látek

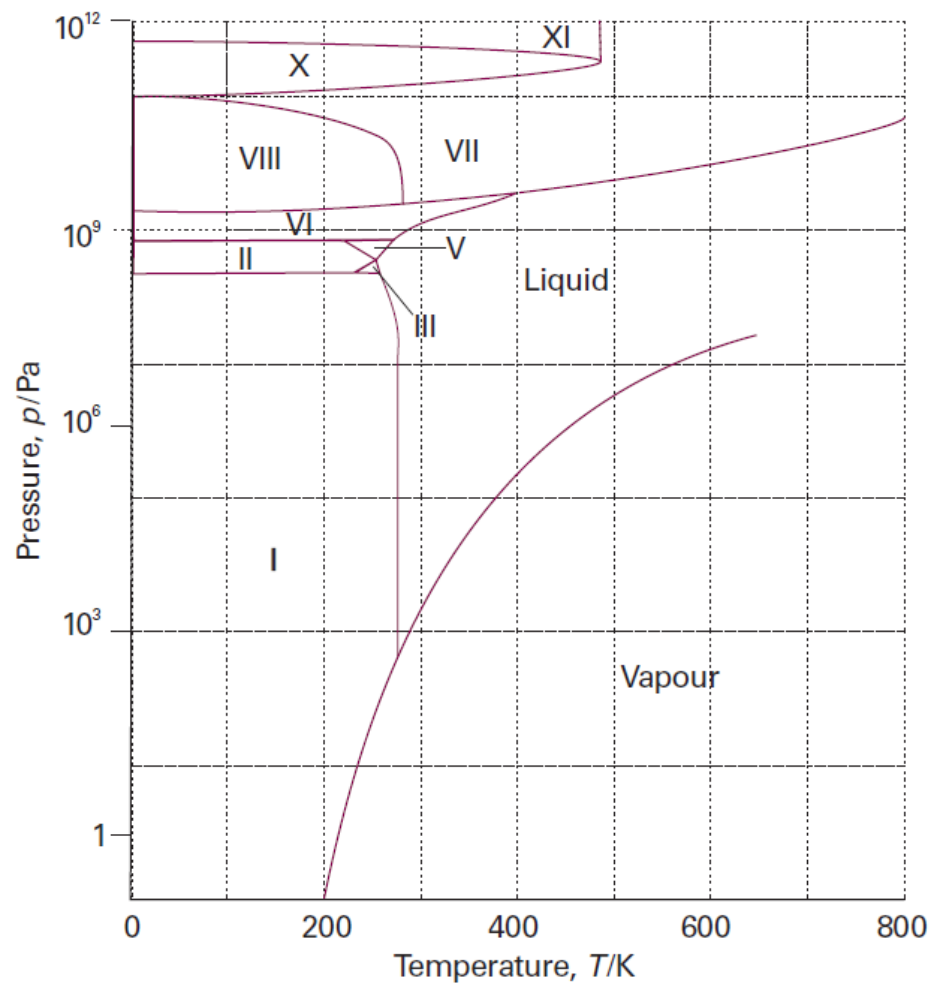
Látka	$T_t / ^\circ\text{C}$	$T_v / ^\circ\text{C}$	$T_v - T_t / ^\circ\text{C}$
H ₂ Te	-4	-49	45
H ₂ Se	-42	-64	22
H ₂ S	-62	-84	22
H ₂ O	+100	0	100

4.1 Fázové diagramy čistých látek

CO₂

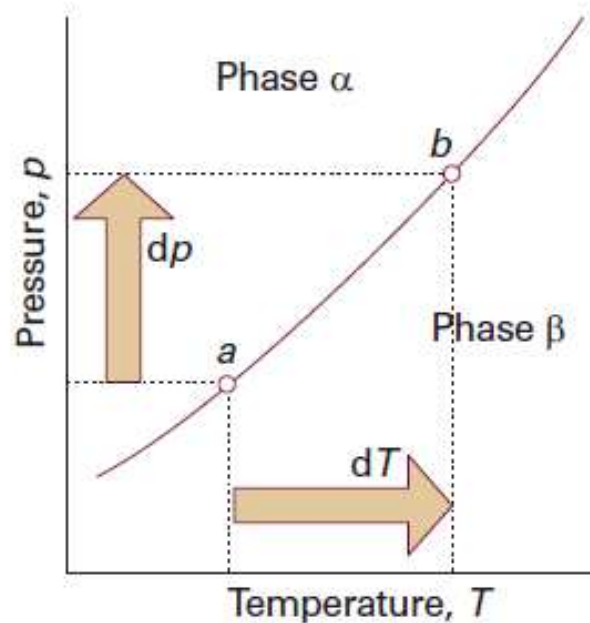


H₂O



4.1 Fázové diagramy čistých látek

koexistenční křivky



$$\mu(f_1, T, p) = \mu(f_2, T, p)$$

$$d\mu(f_1) = d\mu(f_2)$$

$$dG_m = V_m dp - S_m dT$$

$$V_m(f_1)dp - S_m(f_1)dT = V_m(f_2)dp - S_m(f_2)dT$$

$$S_m(f_2)dT - S_m(f_1)dT = V_m(f_2)dp - V_m(f_1)dp$$

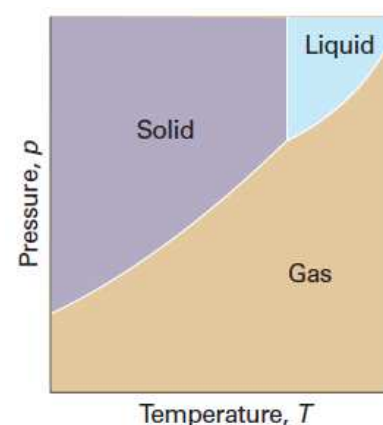
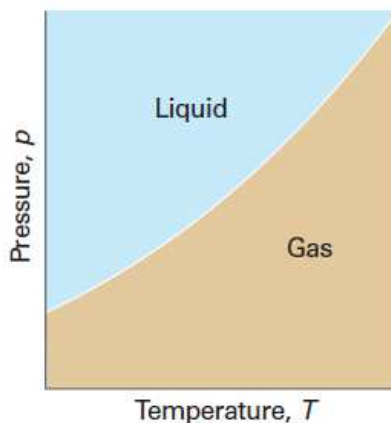
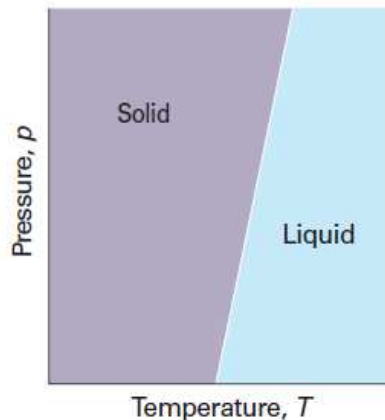
$$\Delta S_m dT = \Delta V_m dp$$

$$\frac{\Delta S_m}{\Delta V_m} = \frac{dp}{dT}$$

Clapeyronova rovnice

4.1 Fázové diagramy čistých látek

koexistenční křivky



$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

$$dp = \frac{\Delta_t S_m}{\Delta_t V_m} dT = \frac{\Delta_t H_m}{T \Delta_t V_m} dT \quad / \int$$

$$p_2 - p_1 = \int_{T_1}^{T_2} \frac{\Delta_t H_m}{T \Delta_t V_m} dT = \frac{\Delta_t H_m}{\Delta_t V_m} \int_{T_1}^{T_2} \frac{1}{T} dT$$

$$\Delta p = \frac{\Delta_t H_m}{\Delta_t V_m} \ln \frac{T_2}{T_1}$$

$$\frac{dp}{dT} = \frac{\Delta_v S_m}{\Delta_v V_m} = \frac{\Delta_v H_m}{T * nRT / p} = \frac{\Delta_v H_m p}{1RT^2}$$

$$\frac{1}{p} \frac{dp}{dT} = \frac{\Delta_v H_m}{RT^2}$$

$$\frac{1}{x} dx = d \ln x$$

$$\frac{d \ln p}{dT} = \frac{\Delta_v H_m}{RT^2}$$

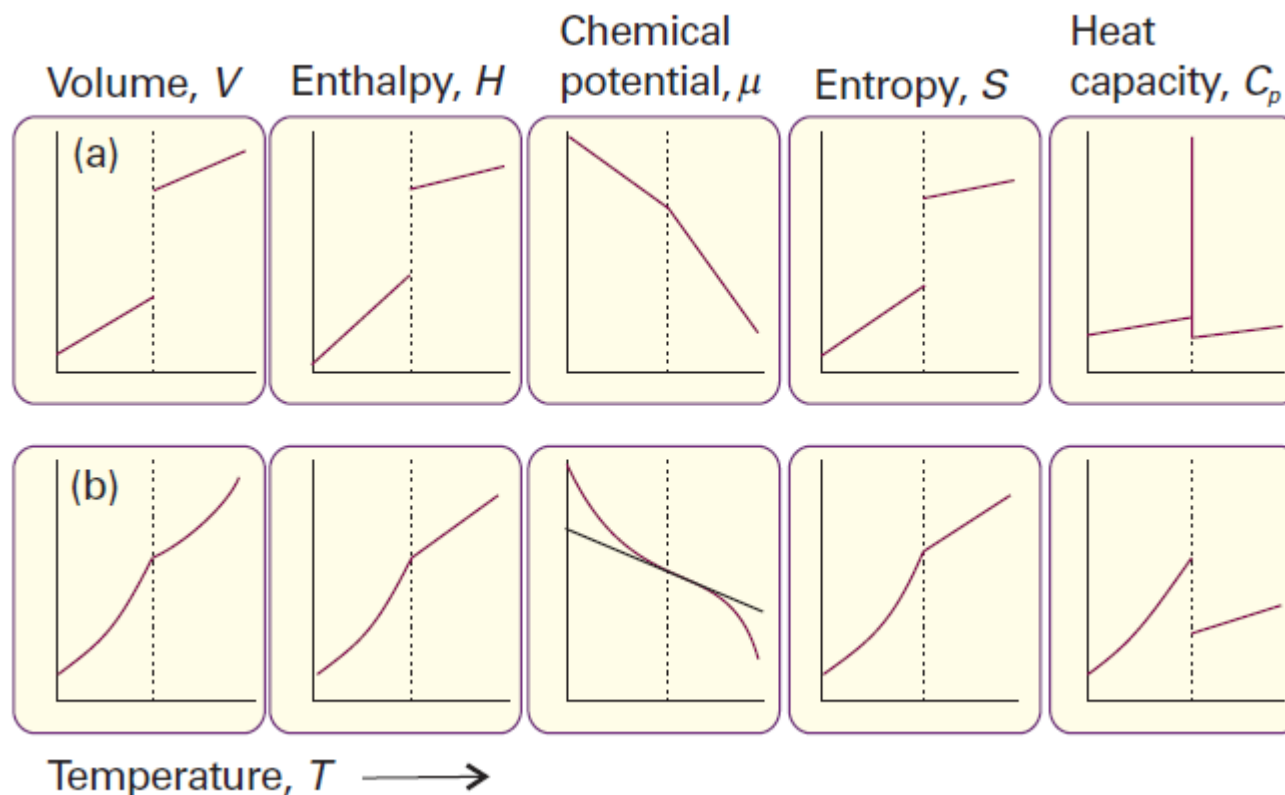
$$\Delta_s H_m = \Delta_t H_m + \Delta_v H_m$$

$$\frac{d \ln p}{dT} = \frac{\Delta_s H_m}{RT^2}$$

Clausiova-
Clapeyronova rovnice

4.1 Fázové diagramy čistých látek

typy fázových přechodů



The changes in thermodynamic properties accompanying (a) first-order and (b) second-order phase transitions.

4.1 Fázové diagramy čistých látek

typy fázových přechodů

λ přechod

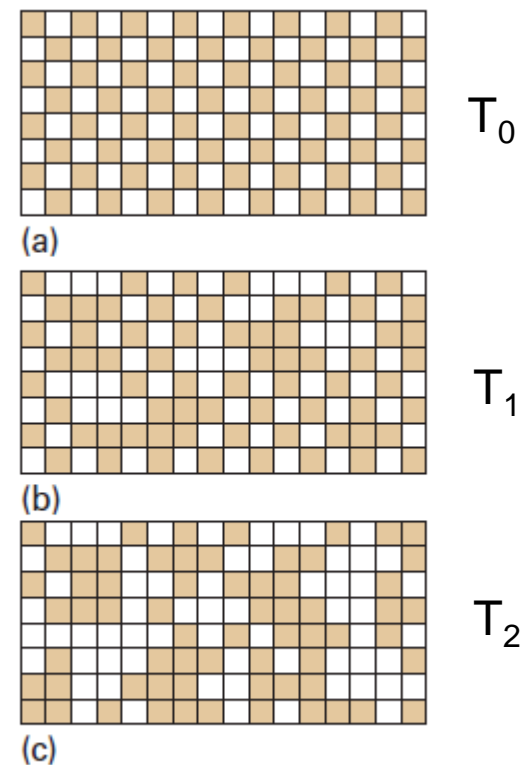
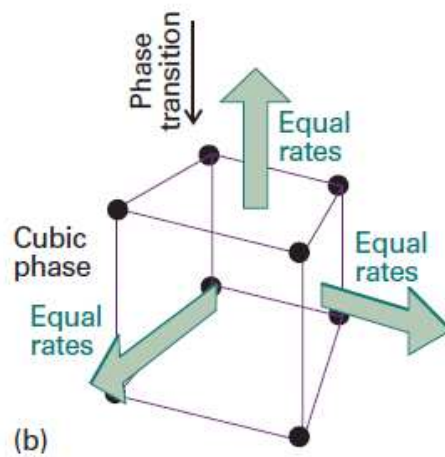
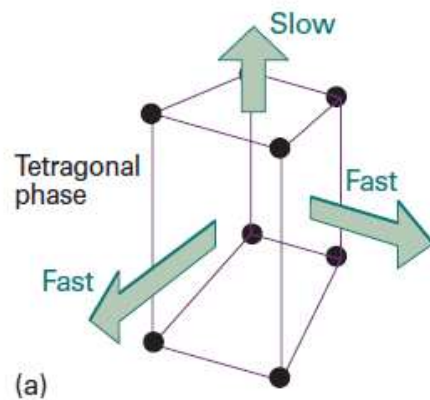
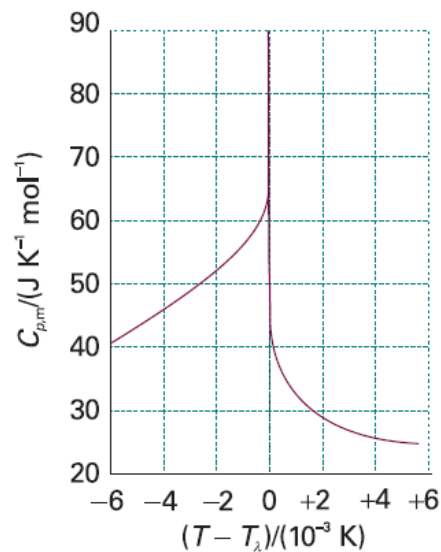


Fig. 4.19 An order–disorder transition.

$$T_0 < T_1 < T_2$$

4.2 Jednoduché směsi

předpoklady

- binární směs
- neinteragující složky $\Delta_{\text{mis}}H=0$
- $x_A+x_B = 1$

parciální molární objem

$$\bar{V}_j = \left(\frac{\partial V}{\partial n_j} \right)_{p,T,n'}$$

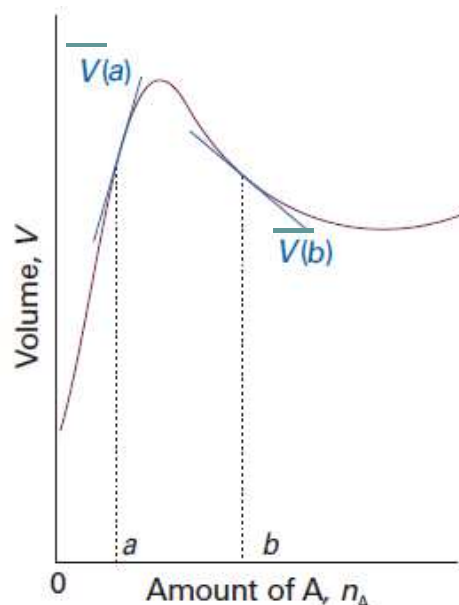
- je fcí. složení

$$dV_{(p,T=\text{konst.})} = \left(\frac{\partial V}{\partial n_A} \right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B} \right)_{p,T,n_A} dn_B =$$

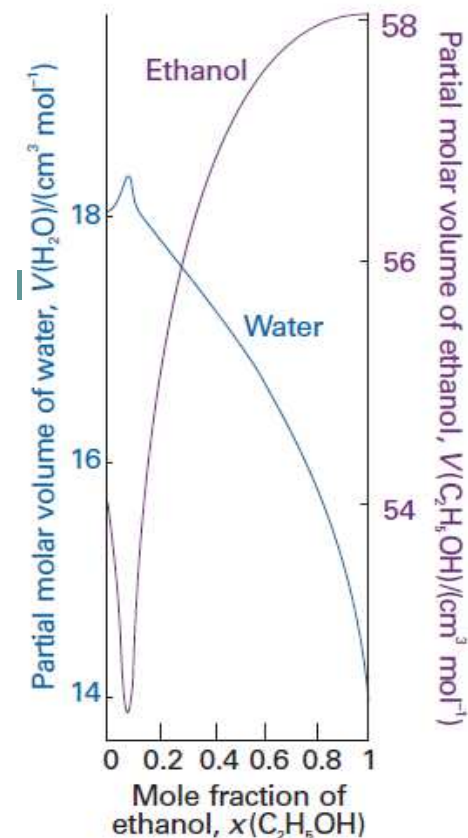
$$= \bar{V}_A dn_A + \bar{V}_B dn_B$$

$$V - 0 = \int_0^{n_A} \bar{V}_A dn_A + \int_0^{n_B} \bar{V}_B dn_B =$$

$$V = \bar{V}_A n_A + \bar{V}_B n_B$$

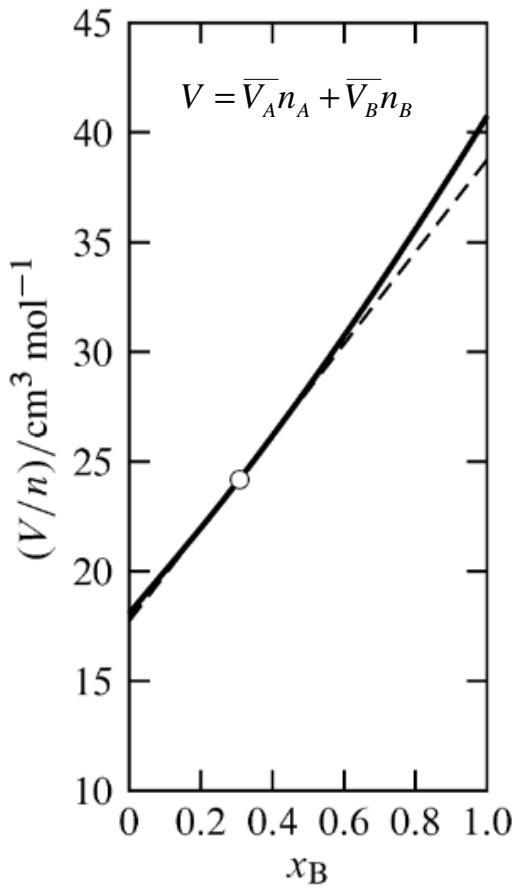


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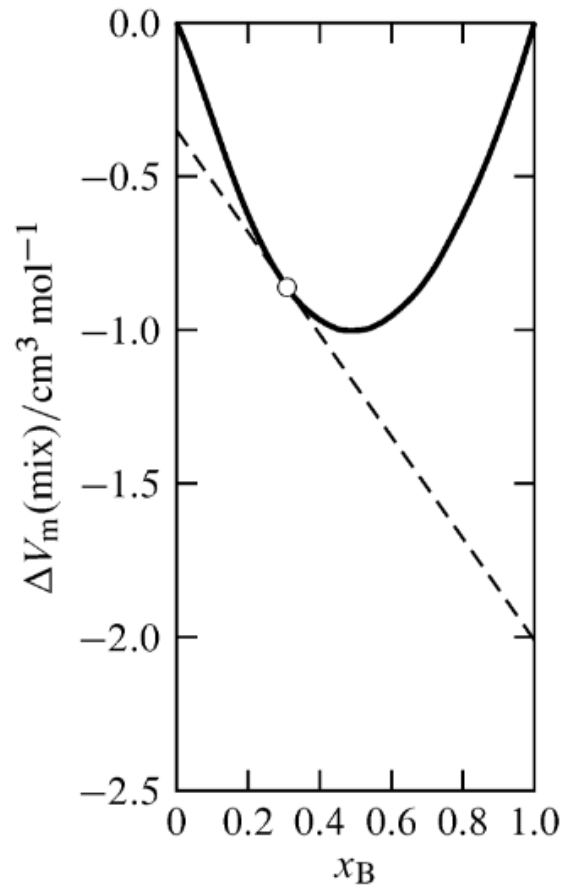


Parciální molární objemy vody a ethanolu při teplotě 25 °C. Všimněte si různých stupnic (voda po levé straně, ethanol vpravo).

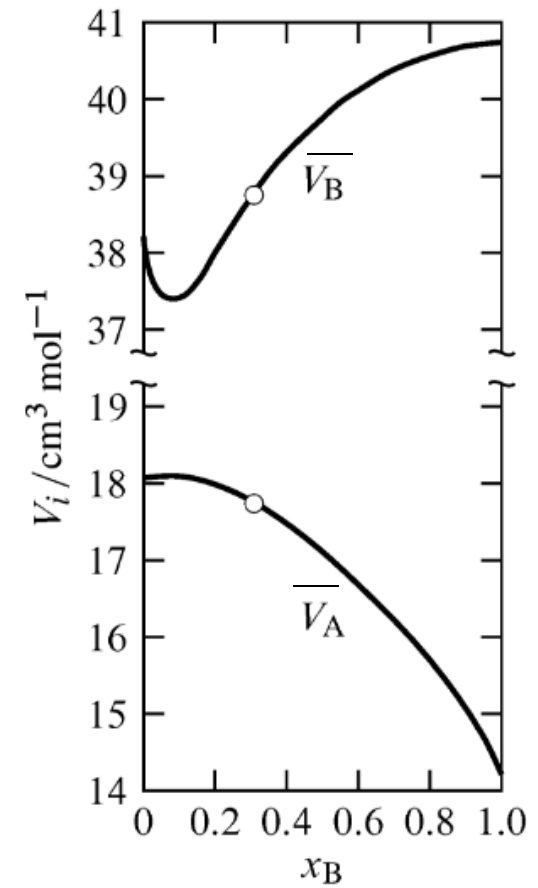
4.2 Jednoduché směsi



(a)



(b)



(c)

Mixtures of water (A) and methanol (B) at 25 °C and 1bar (based on data in George C. Benson and Osamu Kiyohara, *J. Solution Chem.*, **9**, 791–804, 1980).

(a) Mean molar volume as a function of x_B . The dashed line is the tangent to the curve at $x_B=0.307$.

(b) Molar volume of mixing as a function of x_B . The dashed line is the tangent to the curve at $x_B=0.307$.

(c) Partial molar volumes as functions of x_B . The points at $x_B=0.307$ (open circles) are obtained from the intercepts of the dashed line in either (a) or (b). 15

4.2 Jednoduché směsi

parciální molární Gibbsova energie

- je fcí. složení

$$\mu_j = \bar{G}_j = \left(\frac{\partial G}{\partial n_j} \right)_{p,T,n'}$$

$$\begin{aligned} dG_{(p,T=\text{konst.})} &= \left(\frac{\partial G}{\partial n_A} \right)_{p,T,n_B} dn_A + \left(\frac{\partial G}{\partial n_B} \right)_{p,T,n_A} dn_B = \\ &= \bar{G}_A dn_A + \bar{G}_B dn_B \end{aligned}$$

$$dG_{(p,T=\text{konst.})} = \mu_A dn_A + \mu_B dn_B$$

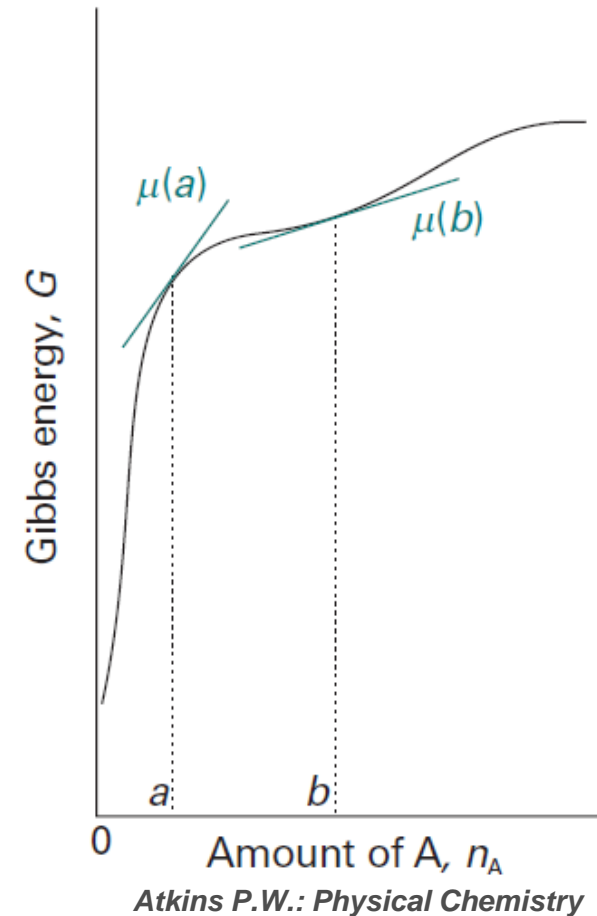
obecně

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \dots$$

fundamentální rovnice

$$dG = dw_{add,max}$$

$$dw_{add,max} = \mu_A dn_A + \mu_B dn_B$$



4.2 Jednoduché směsi

Gibbsova-Duhemova rovnice

$$dG_{(p,T=\text{konst.})} = \mu_A dn_A + \mu_B dn_B$$

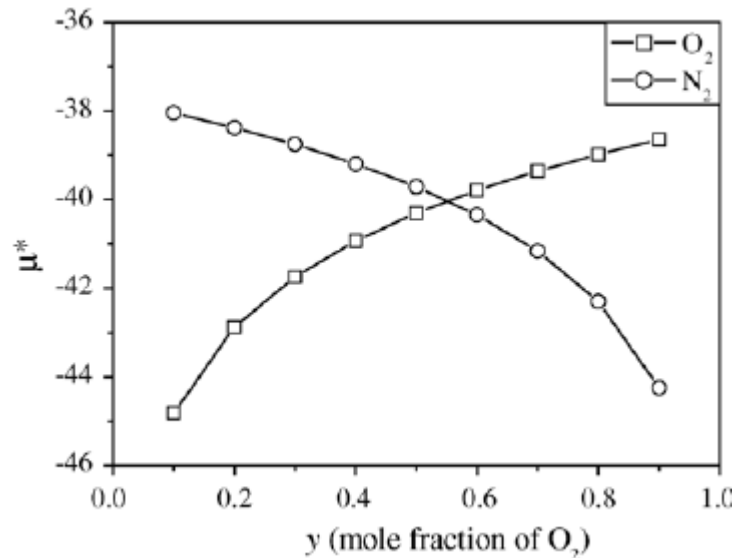
$$G_{(p,T=\text{konst.})} = \mu_A n_A + \mu_B n_B = \mu_A dn_A + \mu_B dn_B$$

$$dG_{(p,T=\text{konst.})} = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$$

$$0 = n_A d\mu_A + n_B d\mu_B$$

$$0 = \sum_i n_i d\mu_i$$

Gibbsova-Duhemova rovnice



Reduced chemical potential of species *i* as a function of the composition for N₂/O₂ mixture at 303 K. The pressure of permeate side is fixed at 1.0501 MPa

S.-M. Wang et al. / Journal of Membrane Science 271 (2006) 140–150

4.2 Jednoduché směsi

μ a U, H, A

fundamentální rovnice

$$dU = TdS - PdV + \sum_j \mu_j dn_j$$

$$dA = -SdT - PdV + \sum_j \mu_j dn_j$$

$$dH = TdS + VdP + \sum_j \mu_j dn_j$$

$$dG = -SdT + VdP + \sum_j \mu_j dn_j$$

parciální molární G, A, H, U

$$\mu_j = \bar{G}_j = \left(\frac{\partial G}{\partial n_j} \right)_{p,T,n'}$$

$$\mu_j = \bar{H}_j = \left(\frac{\partial H}{\partial n_j} \right)_{S,p,n'}$$

$$\mu_j = \bar{A}_j = \left(\frac{\partial A}{\partial n_j} \right)_{T,V,n'}$$

$$\mu_j = \bar{U}_j = \left(\frac{\partial U}{\partial n_j} \right)_{S,V,n'}$$

4.2.1 Směsi plynů

a) ČISTÝ I.G.

$$\mu_j = \left(\frac{\partial G}{\partial n_j} \right)_{p,T,n'} = \left(\frac{\partial n_j G_m}{\partial n_j} \right)_{p,T,n'} = G_m$$

změna μ s tlakem

$$dG = Vdp - SdT$$

$$dG = Vdp \quad T = \text{konst.}$$

$$dG = \frac{nRT}{p} dp$$

$$G - G^0 = \int_{p^0}^p \frac{nRT}{p} dp = nRT \int_{p^0}^{p_2} \frac{1}{p} dp = nRT \ln \frac{p}{p^0}$$

$$G_m = G_m^0 + RT \ln \frac{p}{p^0}$$
$$\mu = \mu^0 + RT \ln \frac{p}{p^0}$$

$$\frac{p}{p^0} = p_{rel} \quad \dots \text{relativní tlak}$$

μ^0 standardní chem. potenciál čistého
plynu pro $p = 10^5$ Pa

4.2.1 Směsi plynů

b) SMĚS I.G. A a B

oddělené plyny

$$\mu_A = \mu_A^0 + RT \ln \frac{p}{p^0}$$

$$G(i) = n_A \bar{G}_A + n_B \bar{G}_B = n_A \mu_A + n_B \mu_B$$

$$G(i) = n_A \bar{G}_A + n_B \bar{G}_B = n_A \left(\mu_A^0 + RT \ln \frac{p}{p^0} \right) + n_B \left(\mu_B^0 + RT \ln \frac{p}{p^0} \right)$$

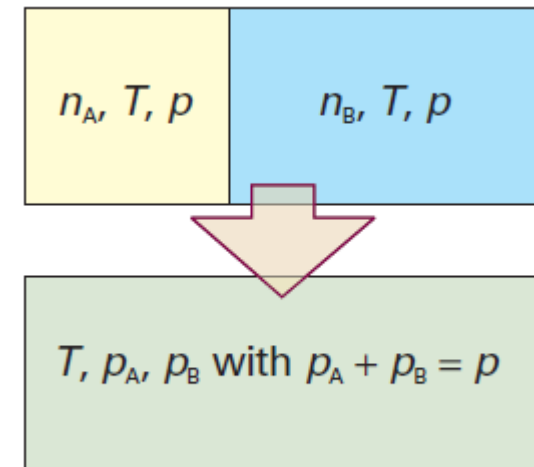
směs

parciální tlaky plynů ve směsi jsou \bar{p}_A a \bar{p}_B

$$\mu_A = \mu_A^0 + RT \ln \frac{\bar{p}_A}{p^0}$$

$$G(f) = n_A \mu_A + n_B \mu_B$$

$$G(f) = n_A \left(\mu_A^0 + RT \ln \frac{\bar{p}_A}{p^0} \right) + n_B \left(\mu_B^0 + RT \ln \frac{\bar{p}_B}{p^0} \right)$$



4.2.1 Směsi plynů

c) GIBBSOVA ENERGIE MÍSENÍ

$$G(i) = n_A(\mu_A^0 + RT \ln \frac{p}{p^0}) + n_B(\mu_B^0 + RT \ln \frac{p}{p^0})$$

$$G(f) = n_A(\mu_A^0 + RT \ln \frac{\bar{p}_A}{p^0}) + n_B(\mu_B^0 + RT \ln \frac{\bar{p}_B}{p^0})$$

$$\Delta_{mix} G = G(f) - G(i) = n_A(RT \ln \frac{\bar{p}_A}{p^0} - RT \ln \frac{p}{p^0}) + n_B(RT \ln \frac{\bar{p}_B}{p^0} - RT \ln \frac{p}{p^0})$$

$$\Delta_{mix} G = n_A(RT \ln \frac{\bar{p}_A}{p^0} \frac{p^0}{p}) + n_B(RT \ln \frac{\bar{p}_B}{p^0} \frac{p^0}{p})$$

$$\Delta_{mix} G = n_A(RT \ln \frac{\bar{p}_A}{p}) + n_B(RT \ln \frac{\bar{p}_B}{p})$$

$$n_A = n x_A$$

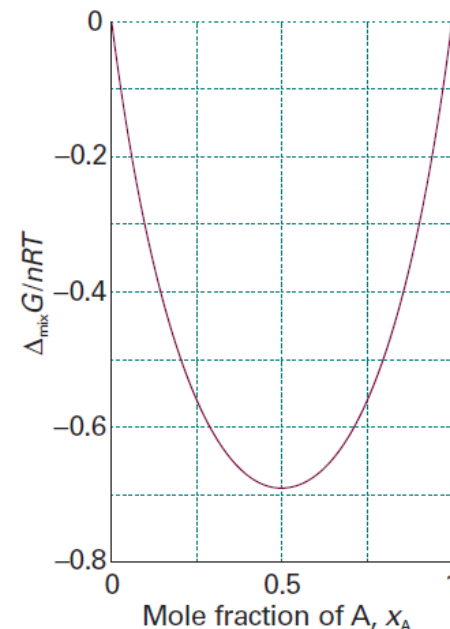
$$x_A(g) = \frac{\bar{p}_A}{p}$$

z experimentů

Daltonův zákon

$$\Delta_{mix} G = x_A n(RT \ln x_A) + x_B n(RT \ln x_B)$$

$$\Delta_{mix} G = nRT(x_A \ln x_A + x_B \ln x_B)$$



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4.2.1 Směsi plynů

d) ENTROPIE MÍSENÍ

$$dG = Vdp - SdT$$

$$dG = -SdT \quad p = \text{konst.}$$

$$-S = \left(\frac{dG}{dT} \right)_{p,n}$$

$$\Delta_{mix} S = - \left(\frac{\partial \Delta_{mix} G}{\partial T} \right)_{p,n_A,n_B} = - \left(\frac{nRT(x_A \ln x_A + x_B \ln x_B)}{T} \right)_{p,n_A,n_B}$$

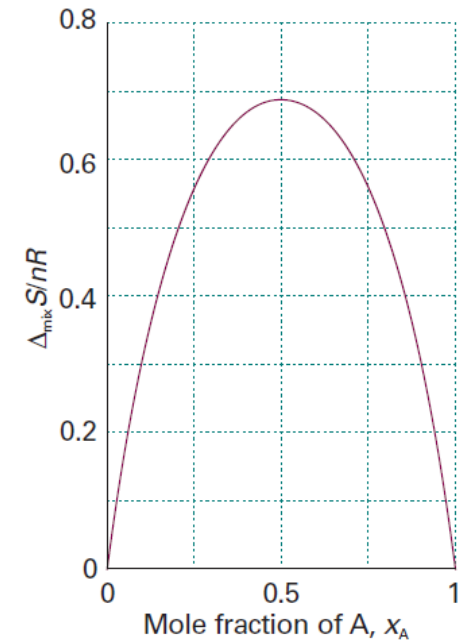
$$\Delta_{mix} S = -nR(x_A \ln x_A + x_B \ln x_B)$$

e) ENTHALPIE MÍSENÍ

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

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

$$\Delta_{mix} H = 0 \quad \text{pro i.g.}$$



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4.2.1 Směsi kapalin

A. ideální roztok oddělené

$$p_A^* \qquad p_B^*$$

$$\mu_A^*(l) = \mu_A^*(g) \qquad \mu_B^*(l) = \mu_B^*(g)$$

$$\mu_A^*(l) = \mu_A^*(g) = \mu_A^0(g) + RT \ln \frac{p_A^*}{p^0}$$

směs

$$p = \bar{p}_A + \bar{p}_B$$

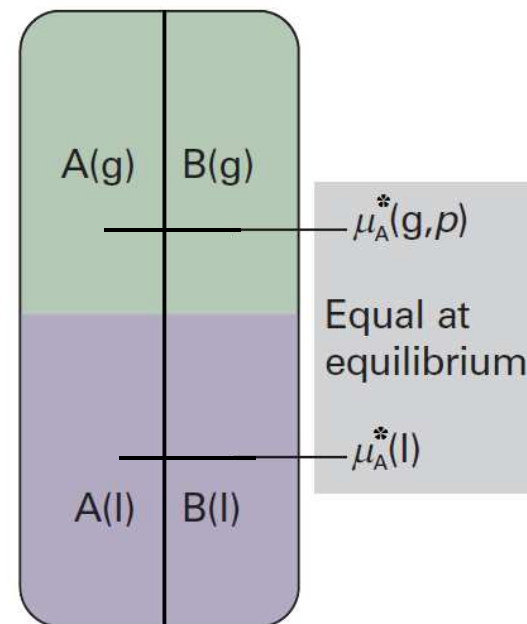
$$\bar{p}_A = p_A^* x_A$$

$$\mu_A(l) = \mu_A(g) \qquad \mu_B(l) = \mu_B(g)$$

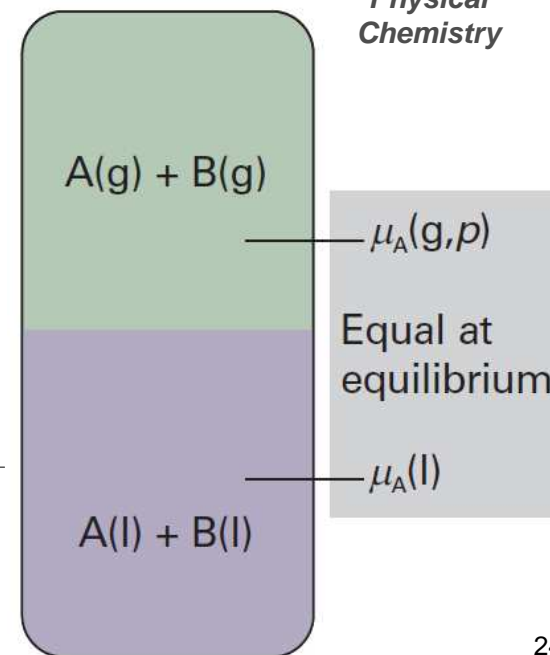
$$\mu_A(l) = \mu_A(g) = \mu_A^0(g) + RT \ln \frac{\bar{p}_A}{p^0}$$

$$\mu_A(l) = \mu_A^*(l) - RT \ln \frac{p_A^*}{p^0} + RT \ln \frac{\bar{p}_A}{p^0} = \mu_A^*(l) + RT \ln \frac{\bar{p}_A}{p^0} \frac{p^0}{p_A^*}$$

$$\mu_A(l) = \mu_A^*(l) + RT \ln \frac{\bar{p}_A}{p_A^*}$$



*Physical
Chemistry*

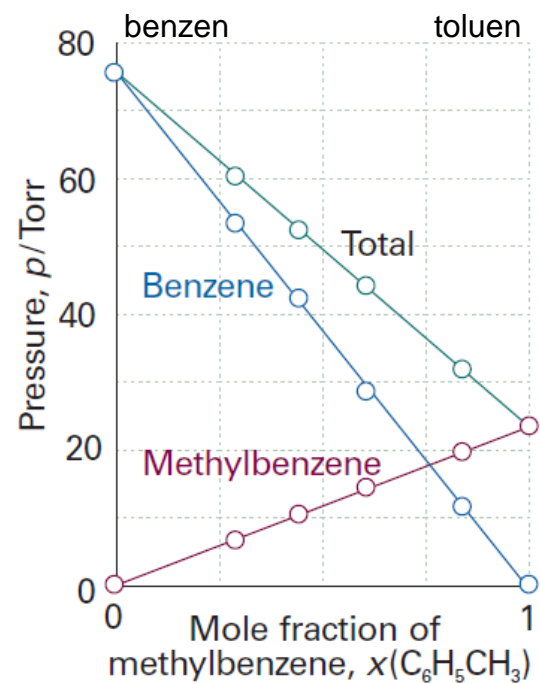
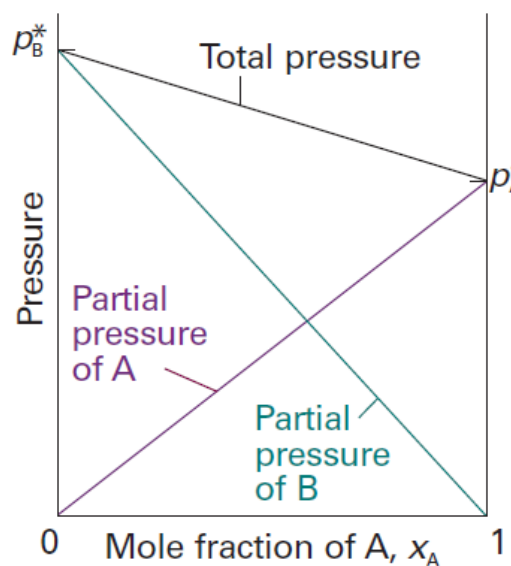


4.2.1 Směsi kapalin

Raoultův zákon

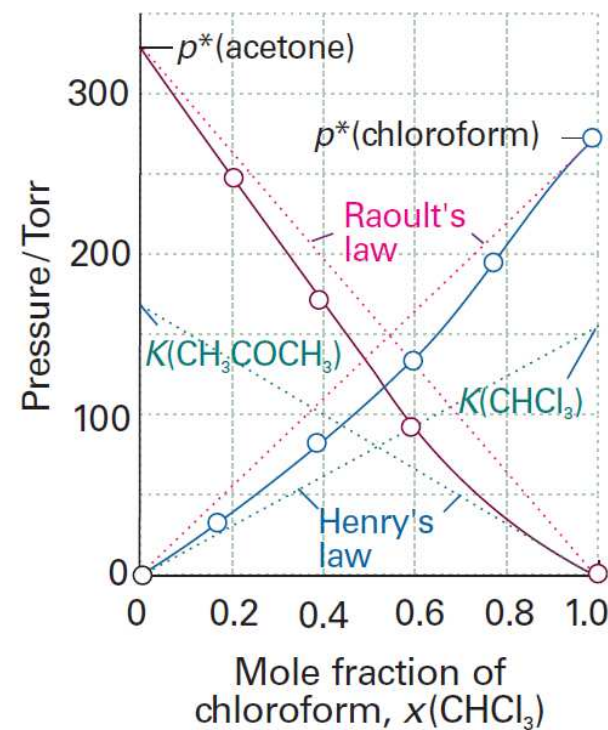
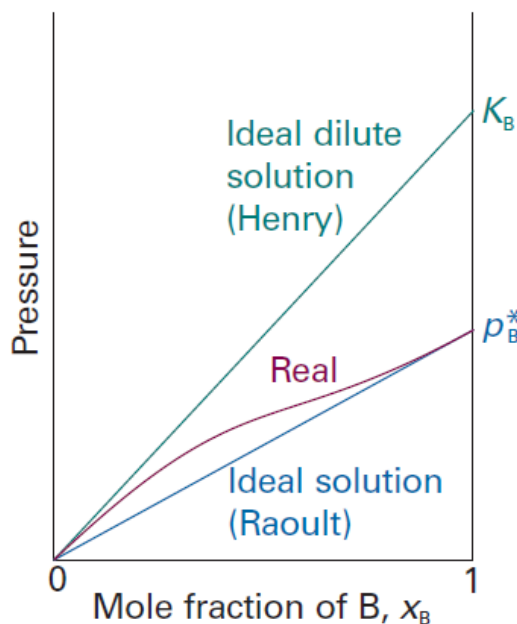
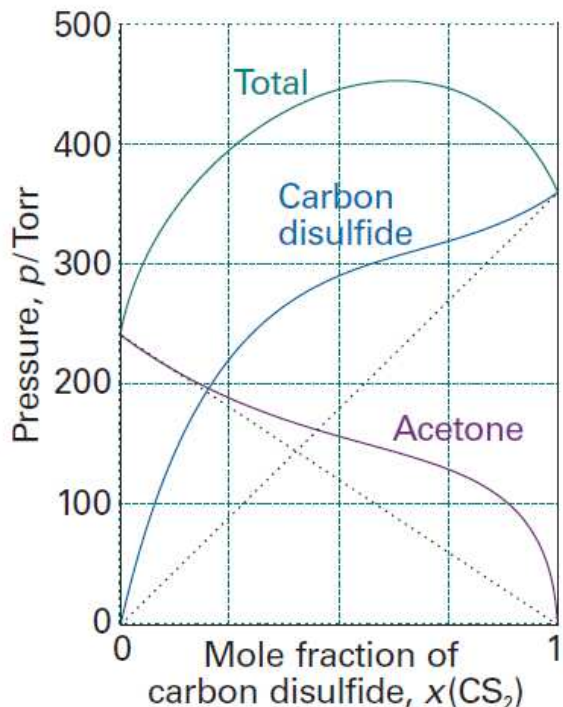
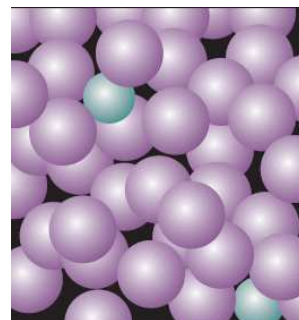
$$\frac{\bar{p}_A}{p_A^*} = x_A(l)$$

$$\mu_A(l) = \mu_A^*(l) + RT \ln \frac{\bar{p}_A}{p_A^*} = \mu_A^*(l) + RT \ln x_A$$



4.2.1 Směsi kapalin

B. odchyly od Raoultova zákona



ideálně zředěné roztoky

~~$$\frac{p_A}{x_A} = p_A^*$$~~

$$\frac{p_A}{x_A} = K_B$$

Henryho zákon

4.2.1 Směsi kapalin

TERMODYNAMIKA MÍSENÍ KAPALIN ad A. ideální roztoky

$$G(i) = n_A \mu_A^*(l) + n_B \mu_B^*(l)$$

$$G(f) = n_A \mu_A(l) + n_B \mu_B(l) =$$

$$= n_A \left(\mu_A^*(l) + RT \ln \frac{\bar{p}_A}{p_A^*} \right) + n_B \left(\mu_B^*(l) + RT \ln \frac{\bar{p}_B}{p_B^*} \right) =$$

$$= n_A (\mu_A^*(l) + RT \ln x_A) + n_B (\mu_B^*(l) + RT \ln x_B)$$

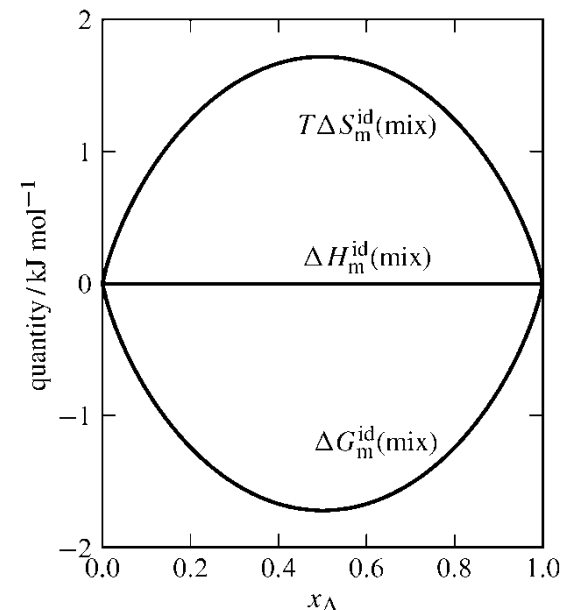
$$\Delta_{mix} G = n_A (\mu_A^*(l) + RT \ln x_A) + n_B (\mu_B^*(l) + RT \ln x_B) - n_A \mu_A^*(l) - n_B \mu_B^*(l) =$$

$$= n_A (RT \ln x_A) + n_B (RT \ln x_B) = n x_A (RT \ln x_A) + n x_B (RT \ln x_B) =$$

$$= nRT (x_A \ln x_A + x_B \ln x_B)$$

$$\Delta_{mix} S = -\frac{\Delta_{mix} G}{T} = -\frac{nRT (x_A \ln x_A + x_B \ln x_B)}{T} = -nR (x_A \ln x_A + x_B \ln x_B)$$

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



https://chem.libretexts.org/Textbook_Maps/Physical_and_Theoretical_Chemistry_Textbook_Maps/DeVoe%27s_%22Thermodynamics_and_Chemistry%22/11%3A_Reactions_and_Other_Chemical_Processes/11.1_Mixing_Processes

4.2.1 Směsi kapalin

TERMODYNAMIKA MÍSENÍ KAPALIN

ad B. reálné roztoky

- změny objemu
- změny interakcí
- změny entropie

$$\bar{V}_i$$

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

dodatkové funkce

$$\Delta X^E = \Delta X^{real} - \Delta X^{ideal}$$

$$\Delta S^E = \Delta S^{real} - \Delta S^{ideal}$$

$$\Delta H^E = \Delta H^{real} - \Delta H^{ideal} = \Delta H^{real} - 0 = \Delta H^{real}$$

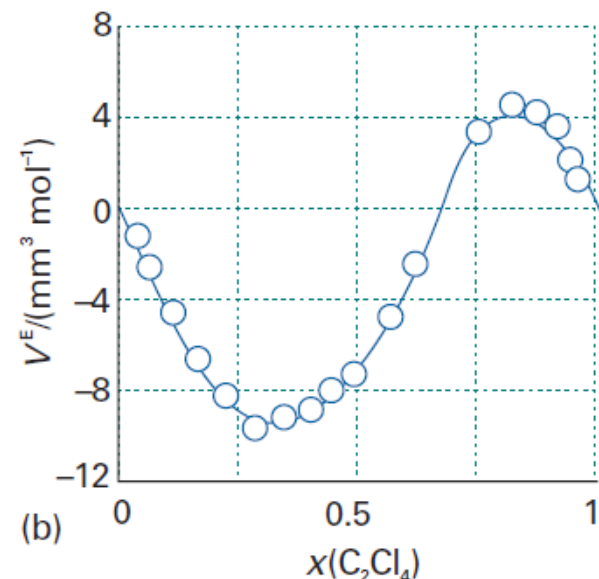
$$\Delta V^E = \Delta V^{real} - \Delta V^{ideal} = \Delta V^{real} - 0 = \Delta V^{real}$$

$$\Delta G^E = \Delta H^E - T\Delta S^E$$

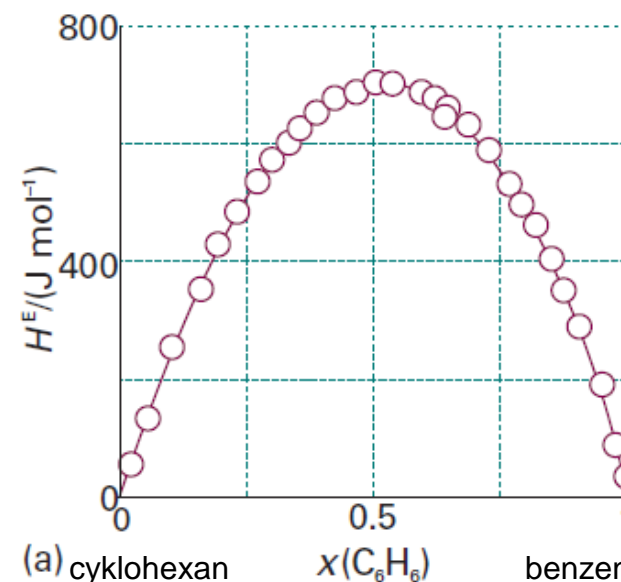
regulární roztok

$$\Delta H^E \neq 0 \quad \Delta S^E = 0$$

reálný roztok



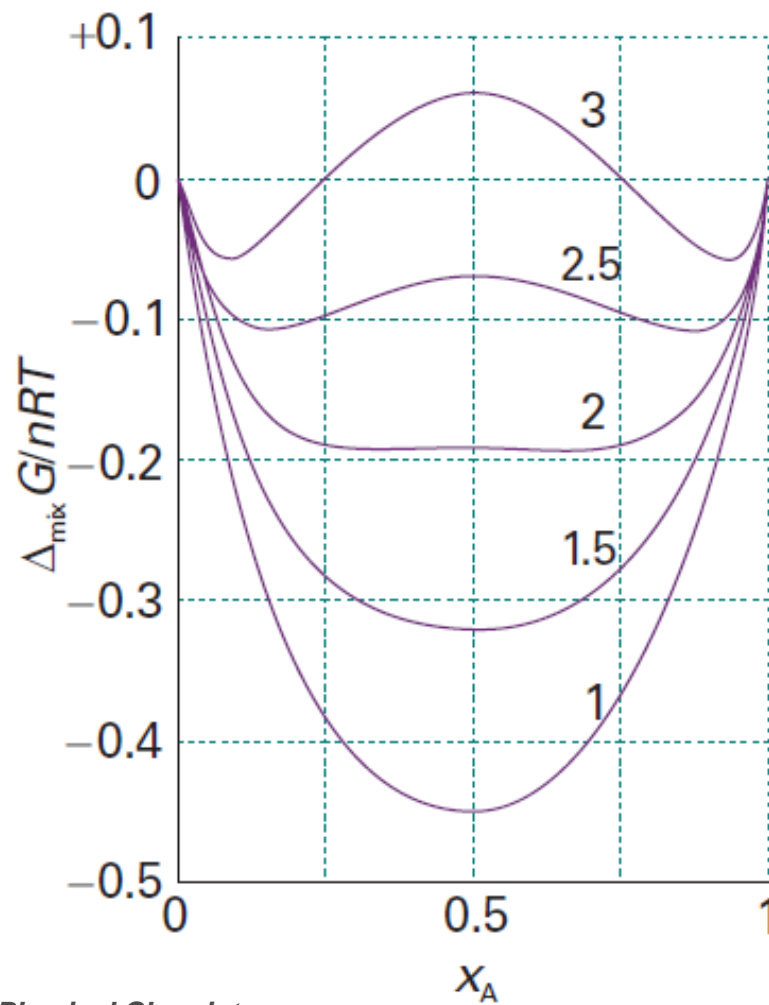
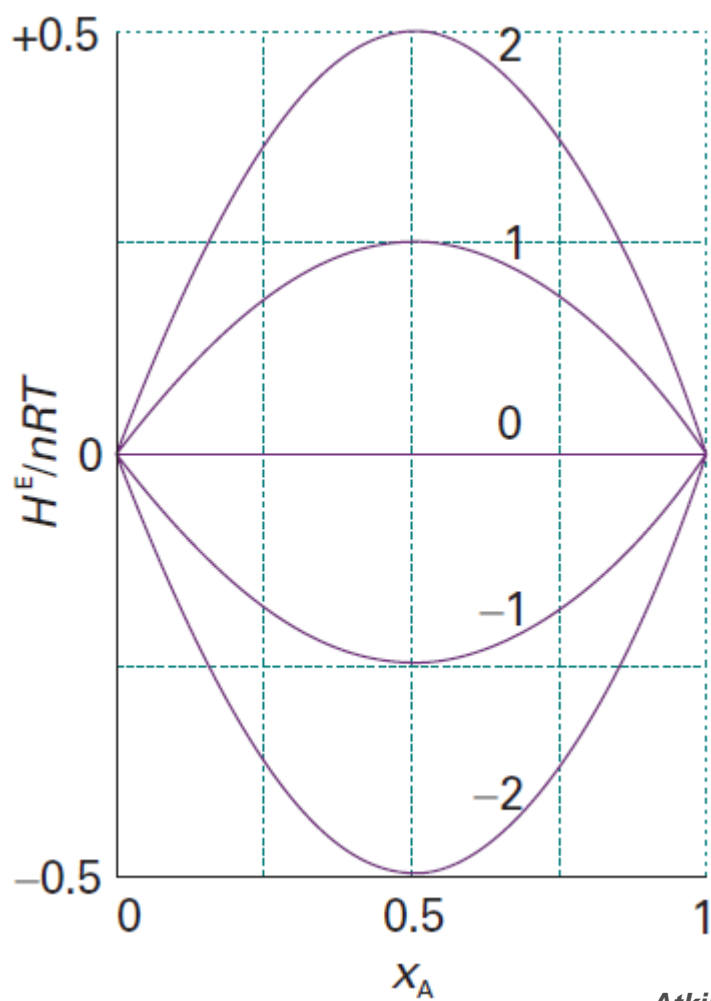
tetrachloroethene/cyclopentane



(a) cyklohexan $x(\text{C}_6\text{H}_6)$ benzen

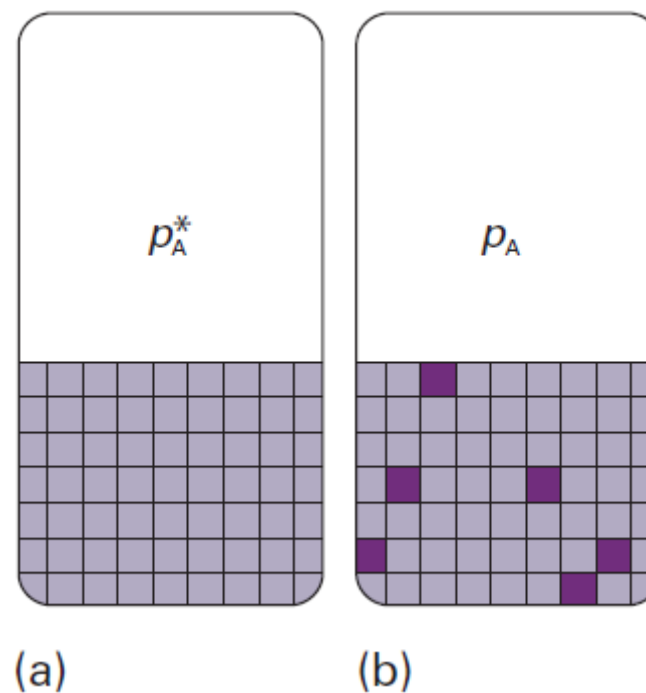
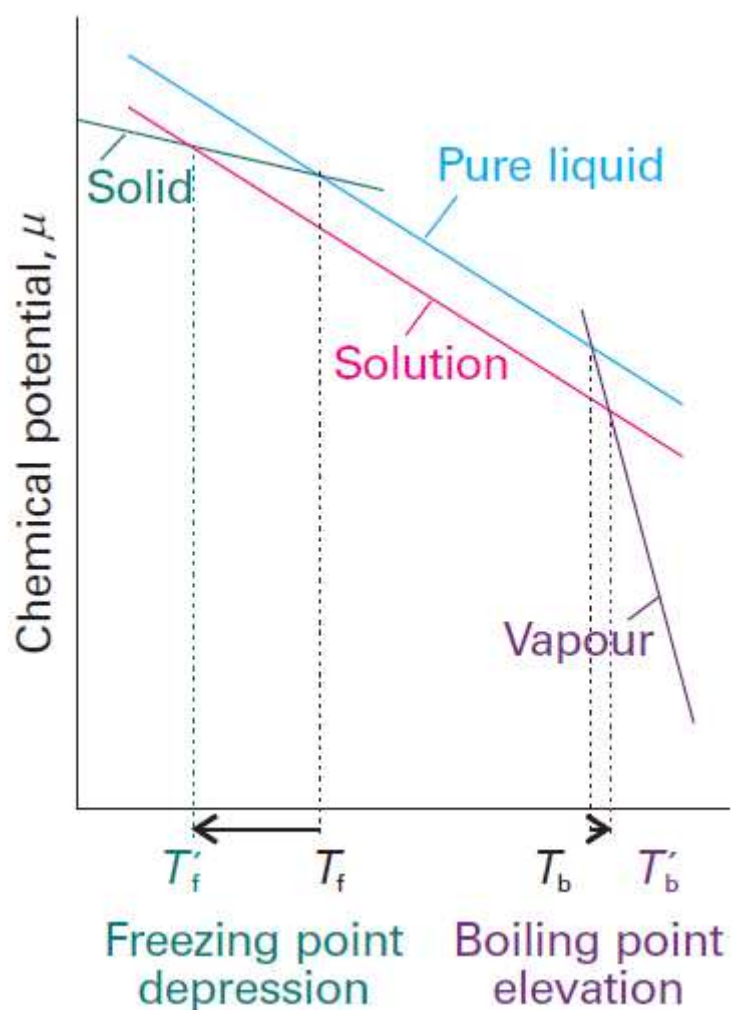
4.2.1 Směsi kapalin

TERMODYNAMIKA MÍSENÍ KAPALIN ad B. reálné roztoky



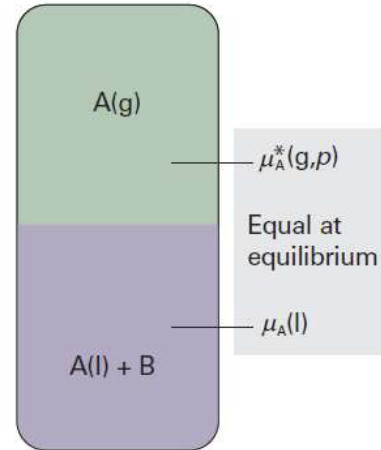
4.2.1 Směsi kapalin

koligativní vlastnosti



4.2.1 Směsi kapalin

ebulioskopie



$$\mu_A^*(g) = \mu_A(l) = \mu_A^*(l) + RT \ln x_A$$

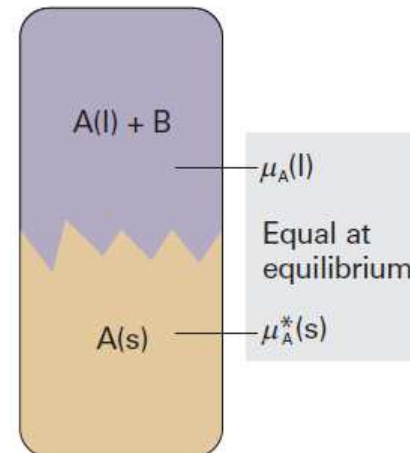
$$\frac{\mu_A^*(g) - \mu_A^*(l)}{RT} = \ln x_A$$

$$\frac{\Delta_v G}{RT} = \ln x_A$$

$$\Delta T_v \cong \frac{RT^{*2}}{\Delta_v H} x_B = K_B m_B$$

m_B ... molalita [mol/kg]

kryoskopie



$$\mu_A(l) = \mu_A^*(l) + RT \ln x_A = \mu_A^*(s)$$

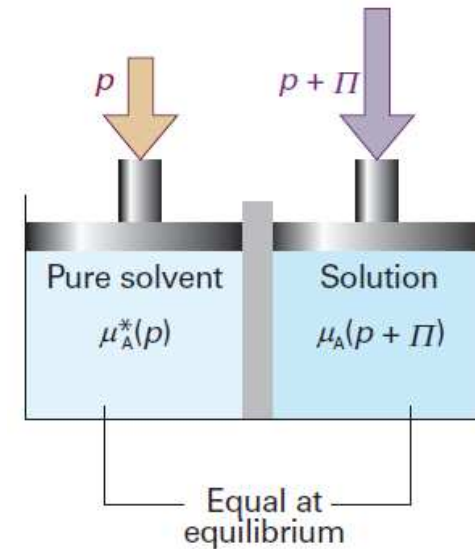
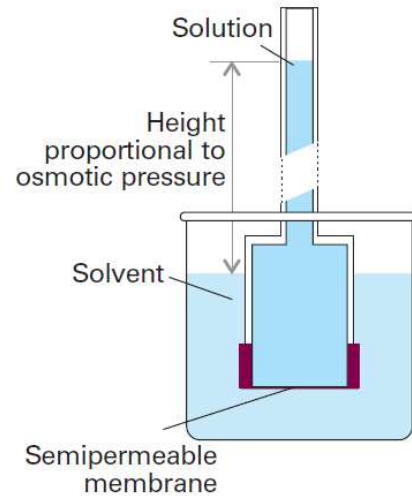
$$\ln x_A = \frac{\mu_A^*(s) - \mu_A^*(l)}{RT} = -\frac{\Delta_t G}{RT}$$

$$\Delta T_t \cong \frac{RT^{*2}}{\Delta_t H} x_B = K_T m_B$$

ΔT_t ... pokles teploty tání

4.2.1 Směsi kapalin

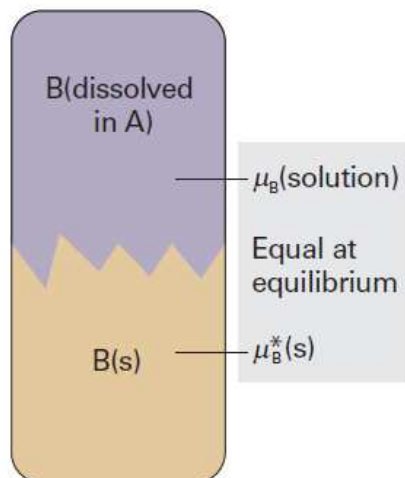
osmóza



$$\Pi = c_B RT$$

$$\Pi = c_B RT (1 + Bc_B + \dots)$$

rozpustnost látky B v látce A



$$\mu_B(\text{rozt.}) = \mu_B^*(l) + RT \ln x_B(l) = \mu_B^*(s)$$

$$\ln x_B(l) = \frac{\mu_B^*(s) - \mu_B^*(l)}{RT} = -\frac{\Delta_t G_B}{RT}$$

$$\ln x_B(l) = \frac{\Delta_t H_B}{R} \left(\frac{1}{T_{t,B}} - \frac{1}{T} \right)$$

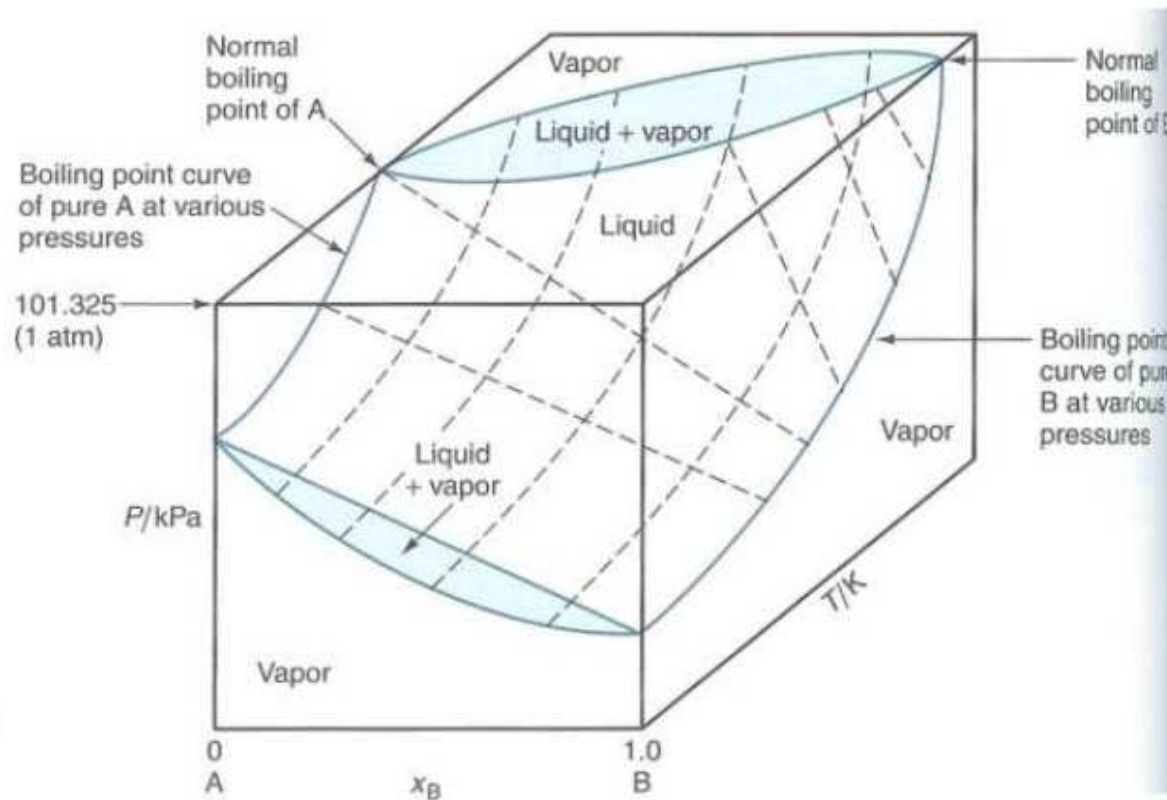
B... rozpouštěná látka

4.3 Fáz. diag. binárních systémů

Gibbsovo fázové pravidlo

$$F = C - P + 2$$

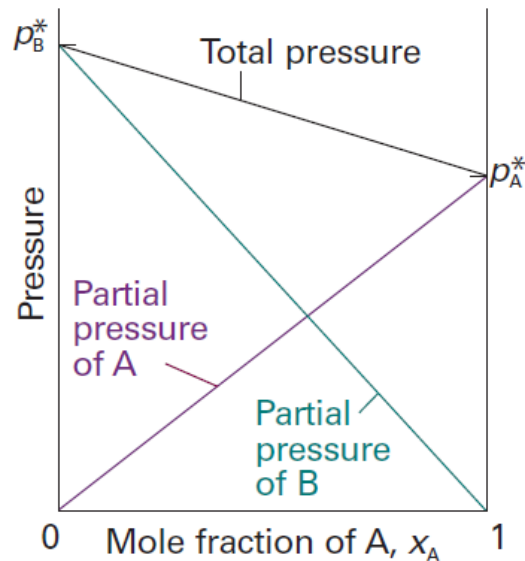
$$x_A, x_B$$



4.3 Fáz. diag. binárních systémů

A) p-x diagram

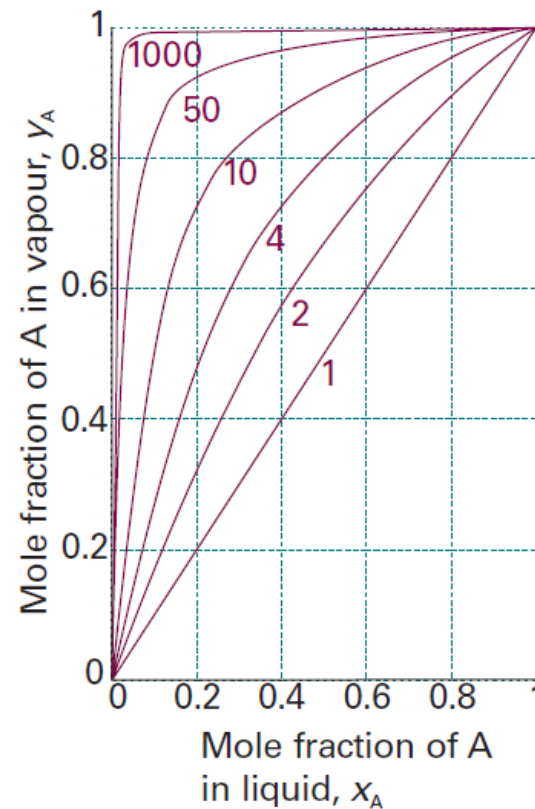
Raoultův zákon



$$\frac{\bar{p}_A}{p_A^*} = x_A(l)$$

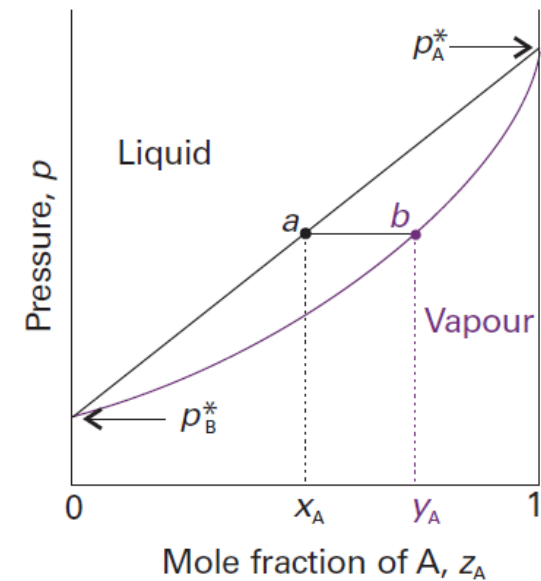
$$\frac{\bar{p}_B}{p_B^*} = x_B(l)$$

Daltonův zákon



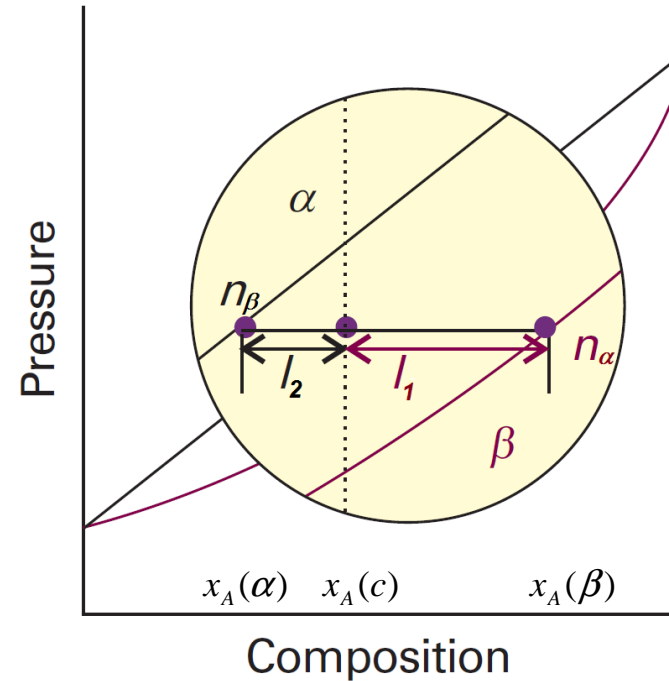
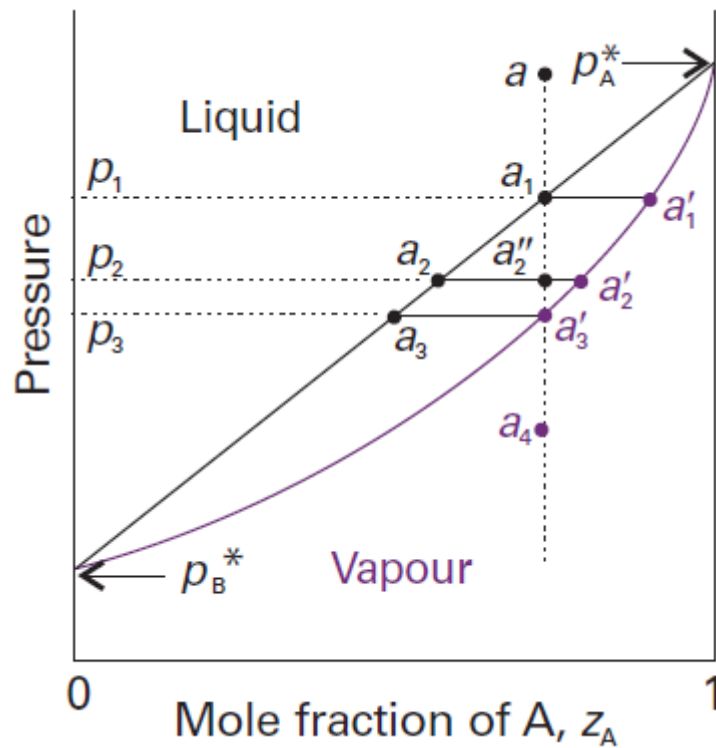
$$\frac{\bar{p}_A}{p} = x_A(g)$$

$$\frac{\bar{p}_B}{p} = x_B(g)$$



4.3 Fáz. diag. binárních systémů

interpretace fázových diagramů



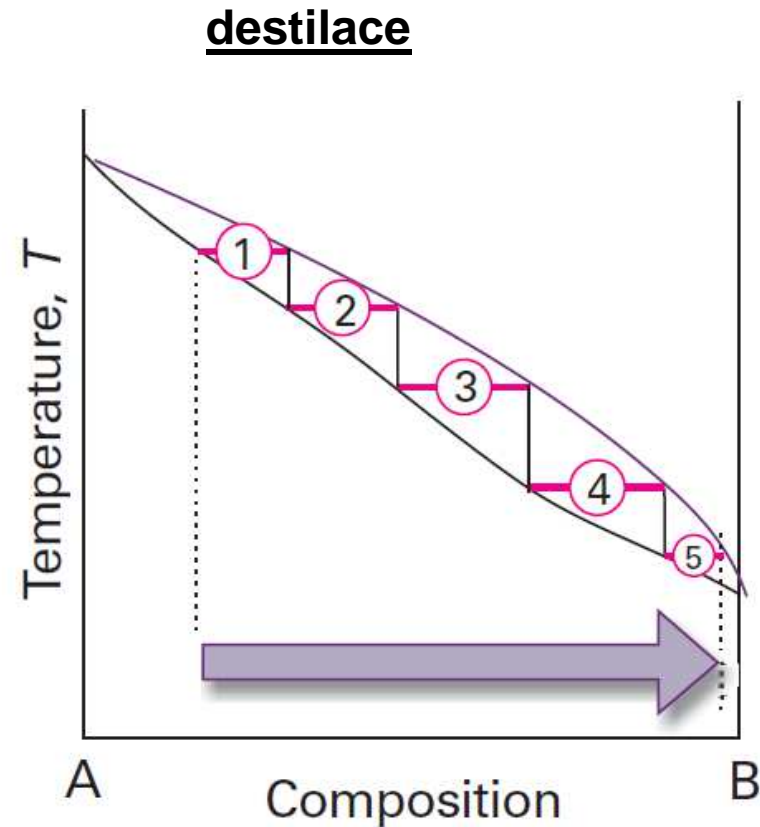
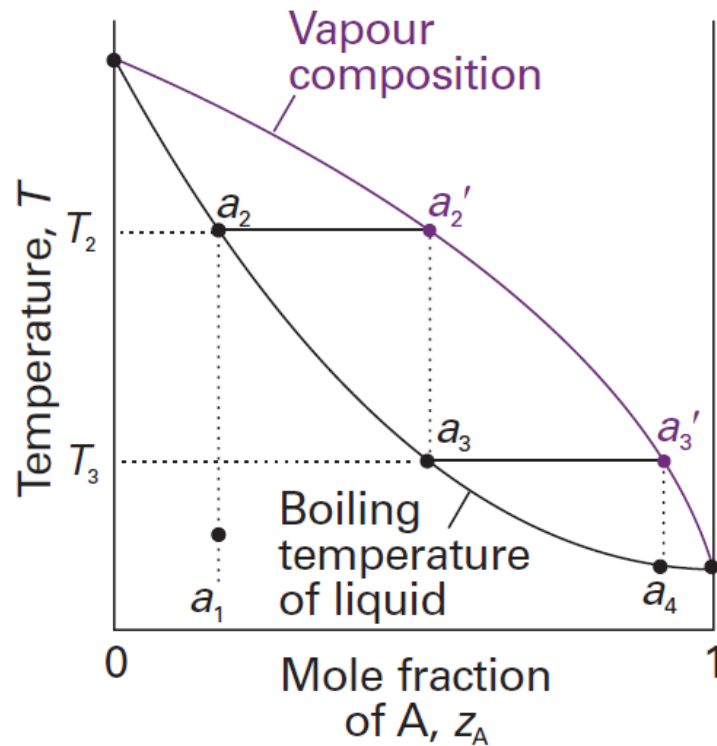
pákové pravidlo

$$\frac{l_1}{l_2} = \frac{n_\alpha}{n_\beta} = \frac{x_A(\beta) - x_A(c)}{x_A(c) - x_A(\alpha)}$$

$$n_\alpha l_2 = n_\beta l_1$$

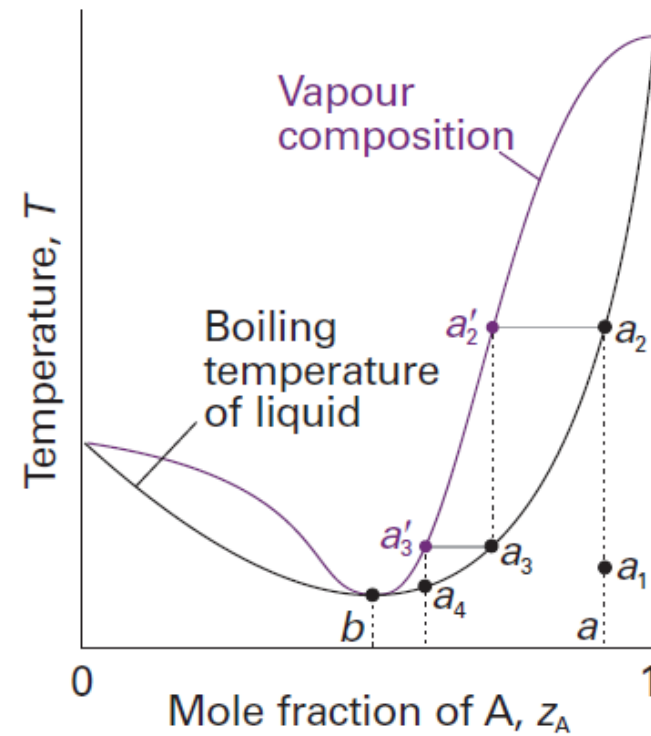
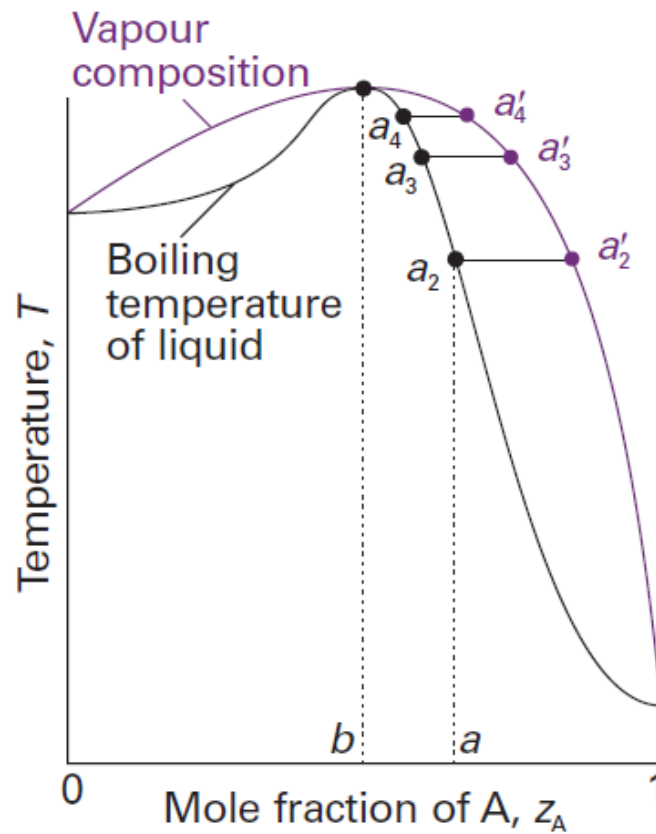
4.3 Fáz. diag. binárních systémů

B) T-x diagram



4.3 Fáz. diag. binárních systémů

B) T-x diagram azeotropy



4.3 Fáz. diag. binárních systémů

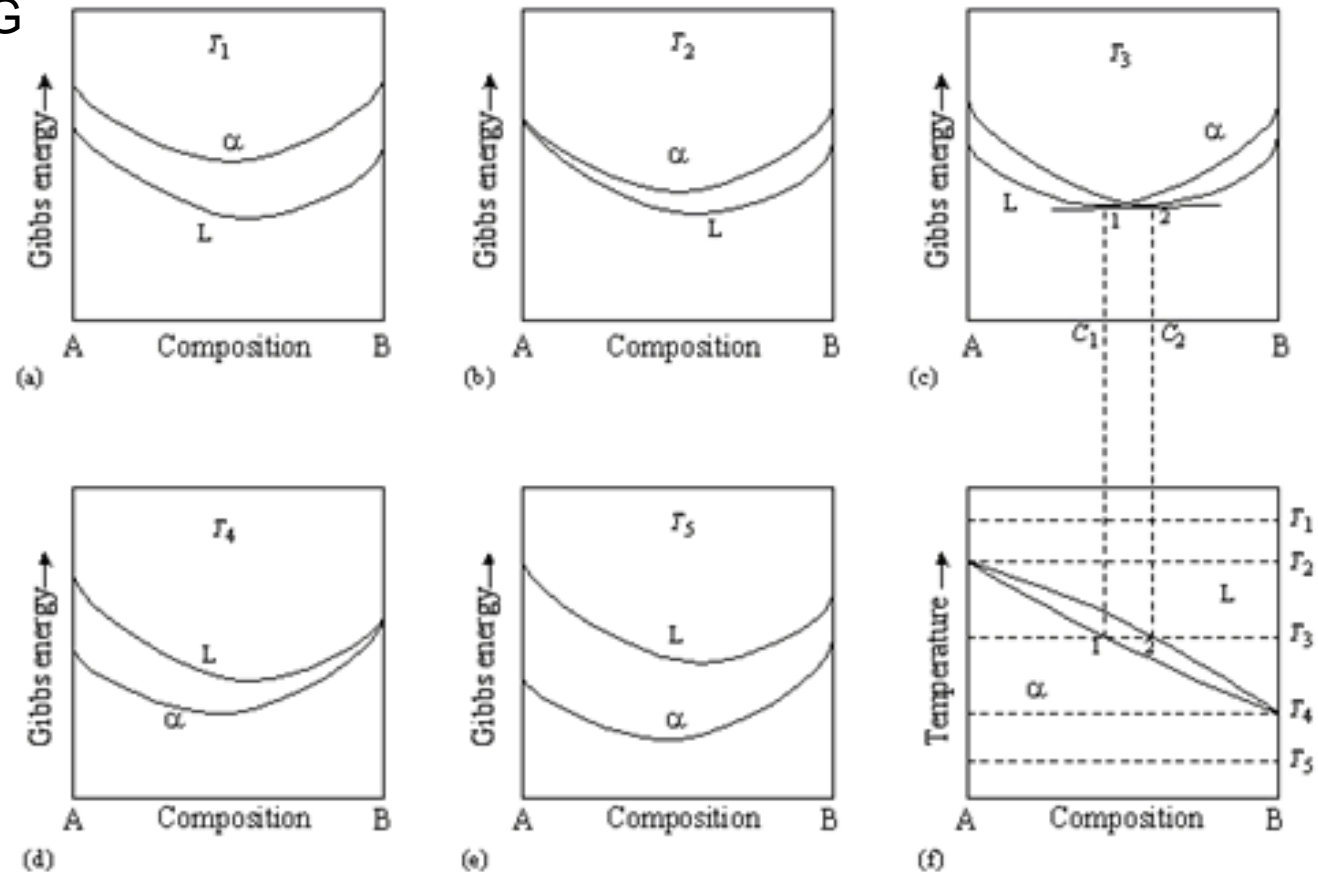
hledání rovnováhy

1. rovnost chemických potenciálů

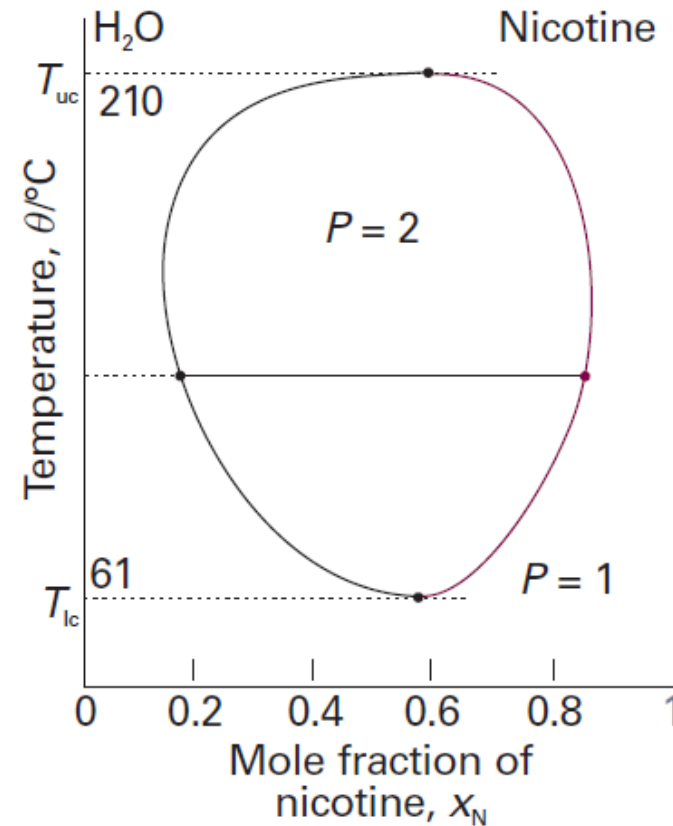
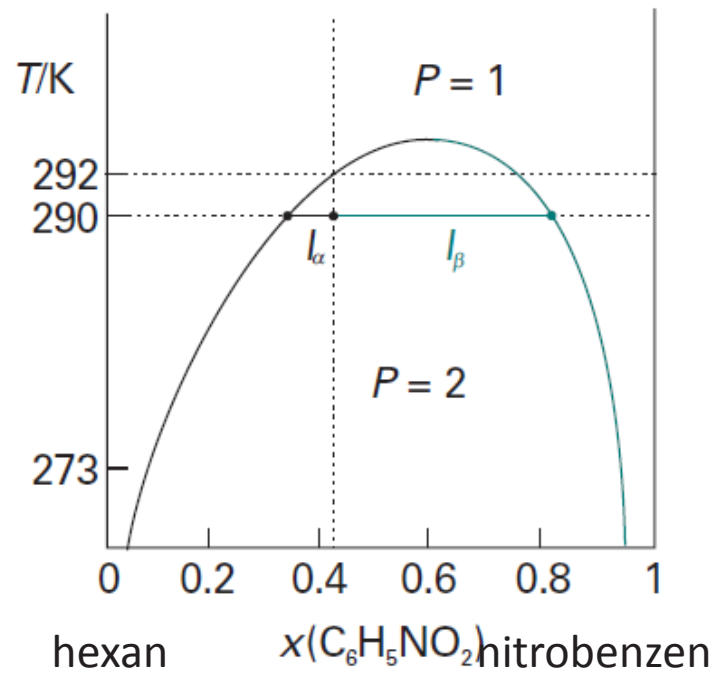
$$\mu_A(\alpha) = \mu_A(\beta)$$

2. minimalizací G

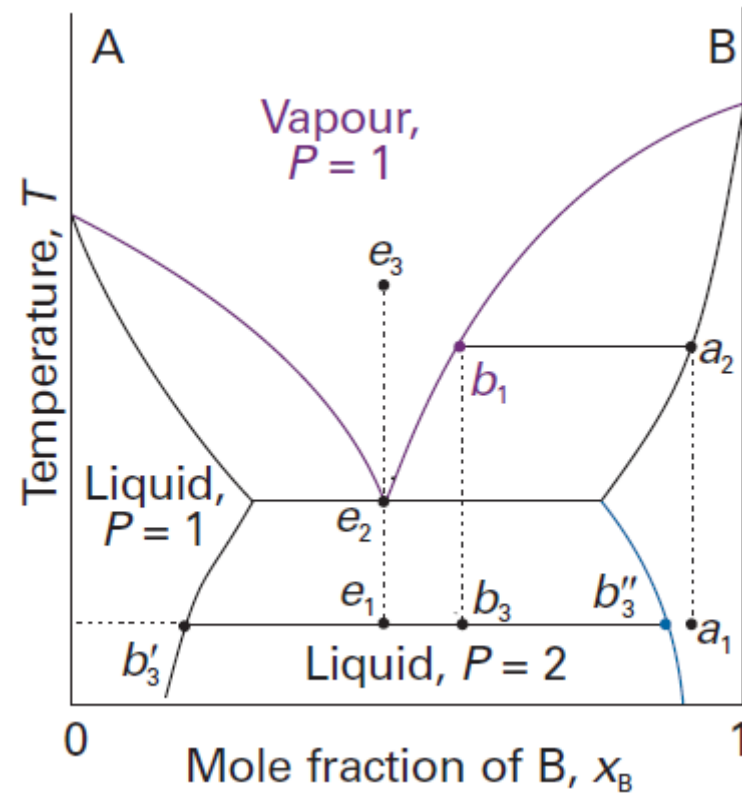
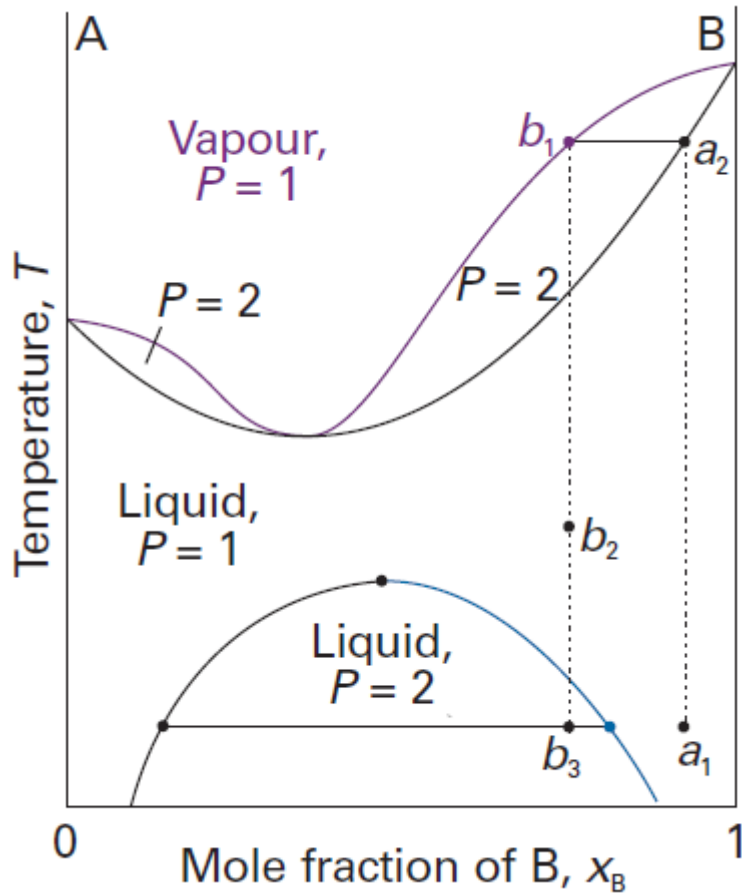
$$\Delta G_{tot} = 0$$



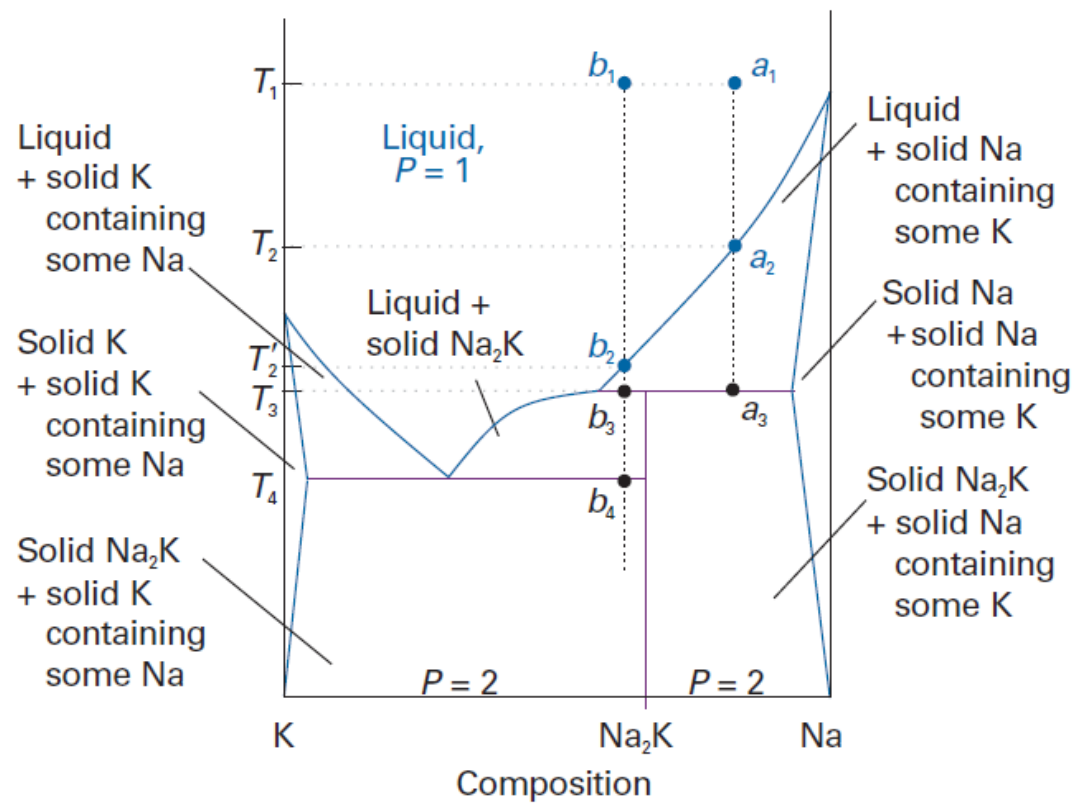
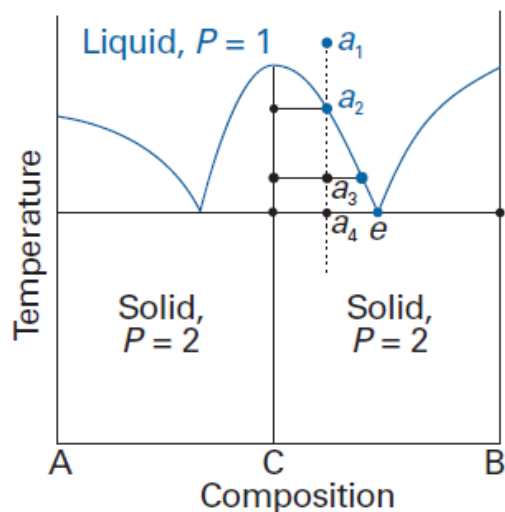
4.3 Fáz. diag. binárních systémů



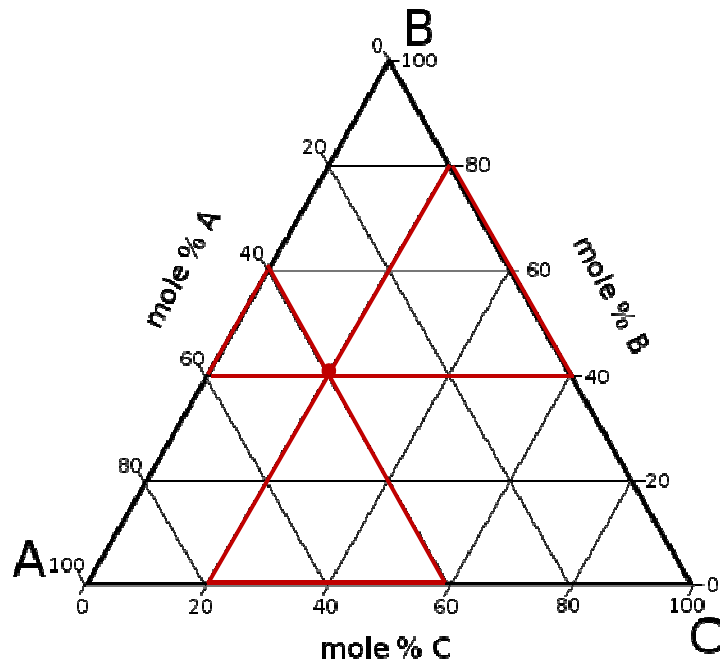
4.3 Fáz. diag. binárních systémů



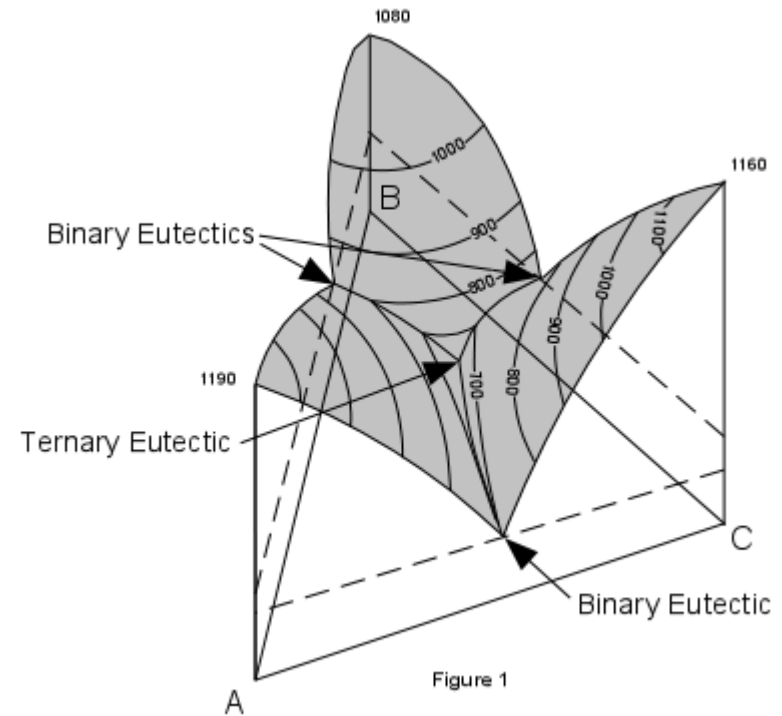
4.3 Fáz. diag. binárních systémů



4.3 Fáz. diag. ternárních systémů



https://en.wikipedia.org/wiki/Talk%3APhase_diagram



<http://www.tulane.edu/~sanelson/eens212/ternaryphdiag.htm>

4.3 Fáz. diag. ternárních systémů

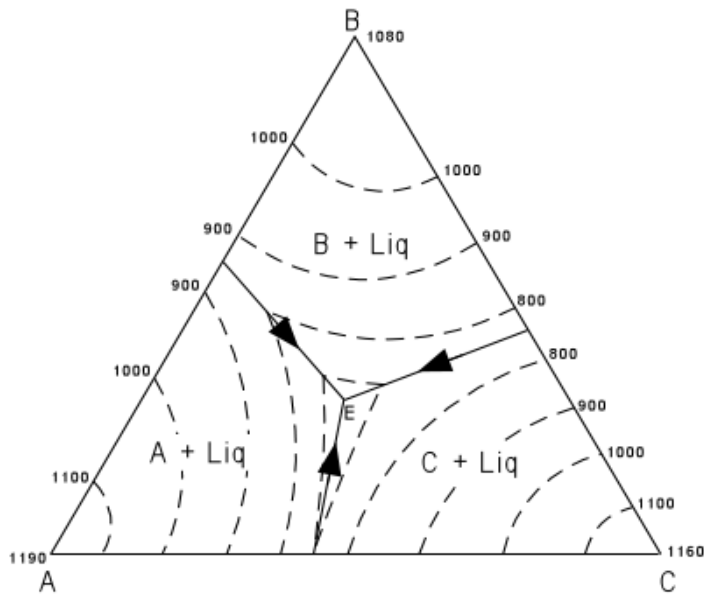
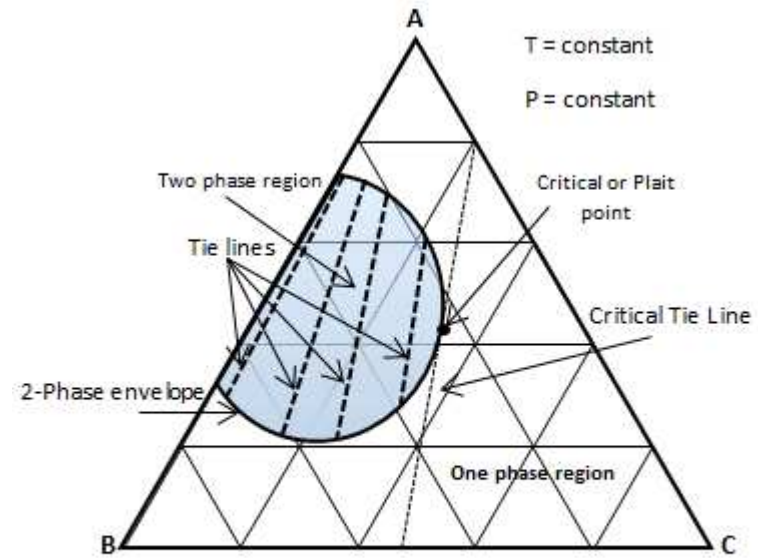


Figure 2



(a). ternary phase diagram for a system of components A, B, C with limited miscibility

<http://www.tulane.edu/~sanelson/eens212/ternaryphdiag.htm>

<http://perminc.com/resources/fundamentals-of-fluid-flow-in-porous-media/chapter-5-miscible-displacement/fluid-phase-behavior/tertiary-diagram/>

4.4 Reálné roztoky - aktivity

aktivita rozpouštědla

$$\mu_A(l) = \mu_A^*(l) + RT \ln \frac{\bar{p}_A}{p_A^*}$$

$$\frac{\bar{p}_A}{p_A^*} = x_A = a_A \quad \text{Raoultův zákon pro i.g.}$$

obecně

$$a_A = x_A \gamma_A$$

$$\mu_A(l) = \mu_A^*(l) + RT \ln a_A = \mu_A^*(l) + RT \ln x_A + RT \ln \gamma_A$$

standardní stav – čisté rozpouštědlo při $p=10^5$ Pa

4.4 Reálné roztoky - aktivity

aktivita rozpuštěné látky

a) ideální zředěný roztok

$$\bar{p}_B = x_B K_B$$

$$\begin{aligned}\mu_B(l) &= \mu_B^*(l) + RT \ln \frac{\bar{p}_B}{p_B^*} = \mu_B^*(l) + RT \ln \frac{K_B x_B}{p_B^*} = \\ &= \mu_B^*(l) + RT \ln \frac{K_B}{p_B^*} + RT \ln x_B =\end{aligned}$$

$$\mu_B(l) = \mu_B^0(l) + RT \ln x_B$$

b) reálný roztok

$$\mu_B(l) = \mu_B^0(l) + RT \ln a_B = \mu_B^0(l) + RT \ln x_B + RT \ln \gamma_B$$

míšení

$$\begin{aligned}\Delta_{mix} G &= nRT(x_A \ln a_A + x_B \ln a_B) = \\ &= nRT(x_A \ln x_A + x_B \ln x_B) + nRT(x_A \ln \gamma_A + x_B \ln \gamma_B) = \\ &= \Delta_{mix} G^{ideal} + \Delta_{mix} G^{real}\end{aligned}$$

4.4 Reálné roztoky - aktivita

Table 5.3 Standard states

Component	Basis	Standard state	Activity	Limits
Solid or liquid		Pure	$a = 1$	
Solvent	Raoult	Pure solvent	$a = p/p^*, a = \gamma x$	$\gamma \rightarrow 1$ as $x \rightarrow 1$ (pure solvent)
Solute	Henry	(1) A hypothetical state of the pure solute	$a = p/K, a = \gamma x$	$\gamma \rightarrow 1$ as $x \rightarrow 0$
		(2) A hypothetical state of the solute at molality b^\ominus	$a = \gamma b/b^\ominus$	$\gamma \rightarrow 1$ as $b \rightarrow 0$

In each case, $\mu = \mu^\ominus + RT \ln a$.

Atkins P.W.: Physical Chemistry

$a = \text{bezrozm. koncentrace} * \gamma$

$$a_{i,x} = x_i \gamma_{i,x}$$

$$a_{i,m} = \frac{m_i}{m^0} \gamma_{i,m}$$

$$a_{i,c} = \frac{c_i}{c^0} \gamma_{i,c}$$

4.4 Reálné roztoky - aktivity

aktivita iontů v roztoku

látka M_1X_1 v roztoku

kationt μ_+ $G_m = 1\mu_+ + 1\mu_-$

aniont μ_- $G_m^{id} = \mu_+^{id} + \mu_-^{id}$

$$G_m^{real} = \mu_+^{id} + \mu_-^{id} + RT \ln \gamma_+ + RT \ln \gamma_- = G_m^{id} + RT \ln \gamma_+ \gamma_-$$

$$\gamma_{\pm} = \sqrt{\gamma_+ \gamma_-}$$

$$\mu_+ = \mu_+^{id} + RT \ln \gamma_{\pm}$$

$$\mu_- = \mu_-^{id} + RT \ln \gamma_{\pm}$$

látka M_pX_q

$$G_m^{real} = p\mu_+ + q\mu_- = G_m^{id} + pRT \ln \gamma_+ + qRT \ln \gamma_-$$

$$p + q = s$$

$$\gamma_{\pm} = \sqrt[s]{\gamma_+^p \gamma_-^q}$$

$$\mu_+ = \mu_+^{id} + RT \ln \gamma_{\pm}$$

$$\mu_- = \mu_-^{id} + RT \ln \gamma_{\pm}$$

4.4 Reálné roztoky - aktivity

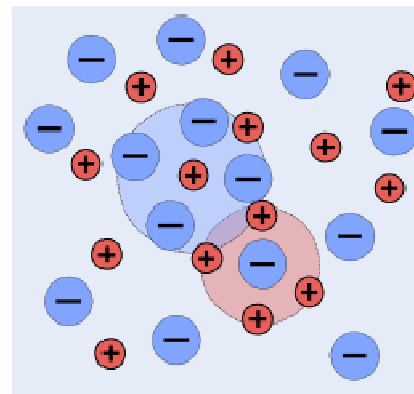
Debye-Hückelův limitní zákon

- pro velmi nízké koncentrace

$$\log \gamma_{\pm} = - |Z_+ Z_-| A \sqrt{I}$$

A=0,509 pro H₂O roztok při 25°C

$$I = \frac{1}{2} \sum_i Z_i^2 \frac{m_i}{m^0}$$



iontová
atmosféra
snižuje chemický
potenciál iontu

Debye-Hückelův rozšířený zákon

$$\log \gamma_{\pm} = \frac{- |Z_+ Z_-| A \sqrt{I}}{1 + B \sqrt{I}} + C I$$

