Osnove termodinamike realnih otopina

Idealna otopina = ?

- Otopina – dvo- ili višekomponentni kondenzirani sustav
- Idealna otopina = stvar dogovora
- Idealno miješanje – proces nastajanja idealne otopine
- Usporedba termodinamičkih svojstava nastale otopine sa svojstvima komponenata
- Promatrat će se miješanje dviju kapljevina !!!!!!!!!

Idealna otopina

Idealni volumen

$$V^{\mathrm{id}} = V_1 + V_2$$

$$v^{\mathrm{id}} = x_1 v_1 + x_2 v_2$$

Idealna entalpija

$$H^{\mathrm{id}} = H_1 + H_2$$

$$h^{\mathrm{id}} = x_1 h_1 + x_2 h_2$$

Gibbsova energija miješanja
(idealno miješanje je spontan proces)

$$G^{\mathrm{id}} < G_1 + G_2$$

$$G^{\mathrm{id}} = H^{\mathrm{id}} - TS^{\mathrm{id}}$$

$$S^{\mathrm{id}} > 0$$

Idealna entropija

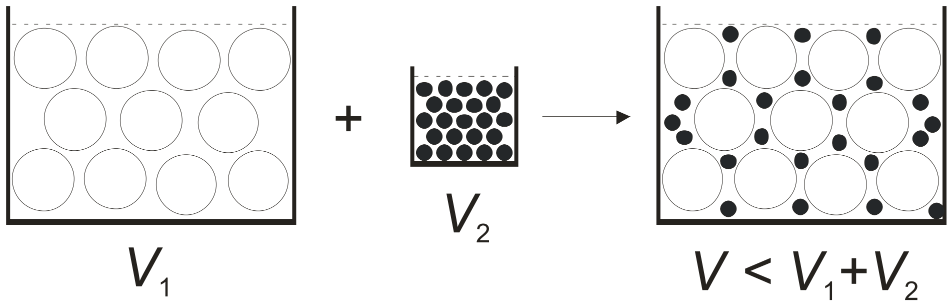
$$S^{\mathrm{id}} = S_1 + S_2 - R\left(n_1 \ln x_1 + n_2 \ln x_2\right)$$

$$s^{\mathrm{id}} = x_1 s_1 + x_2 s_2 - R\left(x_1 \ln x_1 + x_2 \ln x_2\right)$$

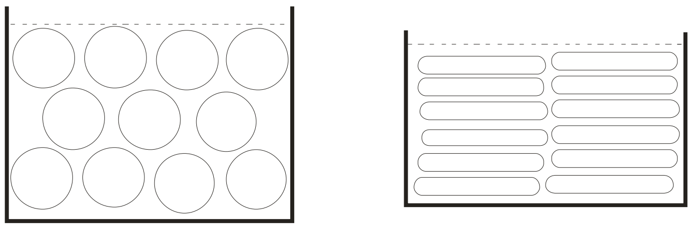
$$g^{\mathrm{id}} = x_1 g_1 + x_2 g_2 + RT\left(x_1 \ln x_1 + x_2 \ln x_2\right)$$

Uzroci neidealnosti volumena

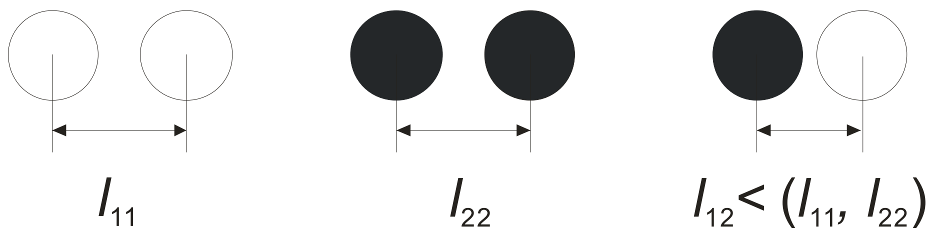
Razlika u veličini čestica



Razlika u obliku čestica

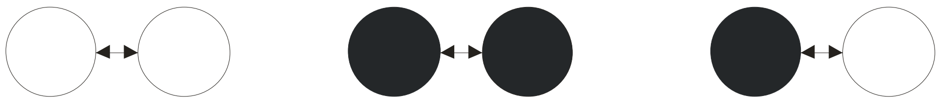


Međudjelovanja



Uzroci neidealnosti entalpije

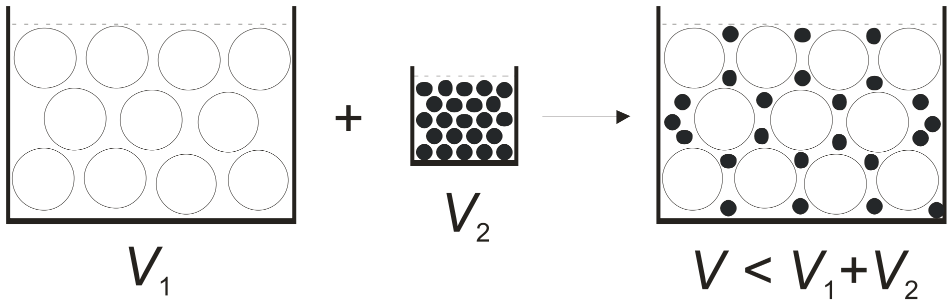
Međudjelovanja



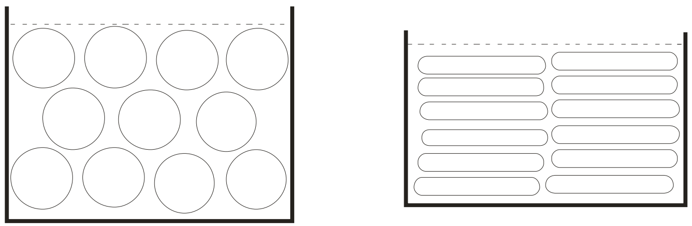
ε_{11} ε_{22} $2\varepsilon_{12} \neq \varepsilon_{11}+\varepsilon_{22}$

Uzroci neidealnosti entropije

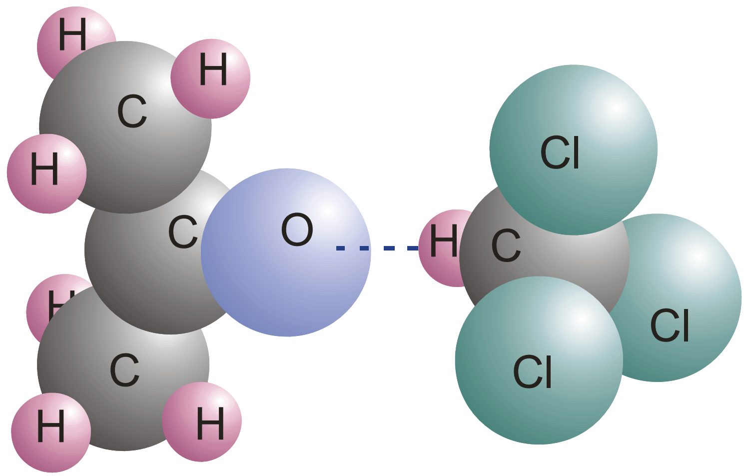
Razlika u veličini čestica



Razlika u obliku čestica



Međudjelovanja



Idealno miješanje (zaključak)

- Proces nastajanja idealne otopine
- Idealna otopina nastaje miješanjem dviju komponenata čije su molekule SLIČNE VELIČINE, SLIČNOGA OBLIKA I SLIČNIH MEĐUDJELOVANJA
- Slično se otapa u sličnome!
- Radi se o otopinama (smjesama) dviju kapljevina !!!!!!!!!

Idealno miješanje (zaključak)

- Dogovorena definicija idealne otopine ne vrijedi za asimetrične sustave, tj. otopine plinova ili krutina u kapljevinama !!!

$$v^{\mathrm{id}} = x_1 v_1^{\mathrm{L}} + x_2 v_2^{\mathrm{L}}$$

$$h^{\mathrm{id}} = x_1 h_1^{\mathrm{L}} + x_2 h_2^{\mathrm{L}}$$

$$s^{\mathrm{id}} = x_1 s_1^{\mathrm{L}} + x_2 s_2^{\mathrm{L}} - R\left(x_1 \ln x_1 + x_2 \ln x_2\right)$$

ZAŠTO ?

- Što s nesimetričnim sustavima? Koja je definicija idealne otopine za npr. otopine plinova u kapljevinama ili otopine krutina u kapljevinama?

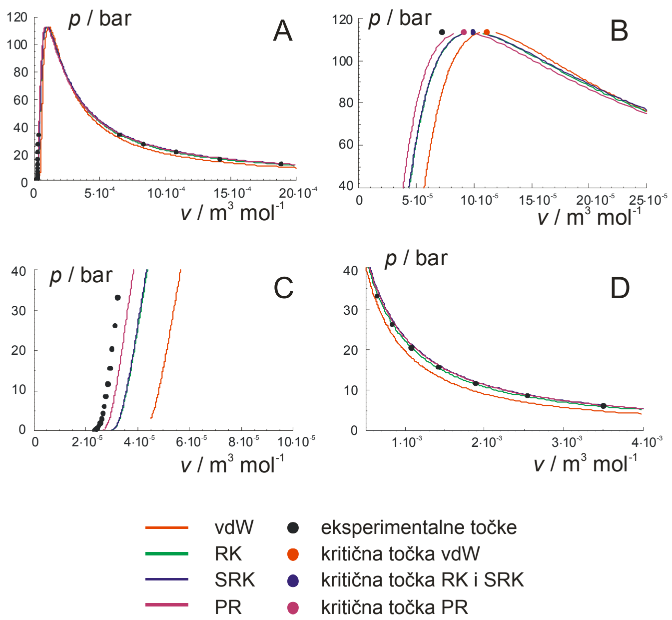
Opis otopina jednadžbama stanja

Mogu li se termodinamičke veličine kapljevina izračunati jednadžbama stanja ?

$$v^3 - v^2\left(b+\frac{RT}{p}\right)+v\left(\frac{a}{p}\right)-\frac{ab}{p}=0$$

$$h = h_{\mathrm{ref}} + \int_{T^\circ}^{T} c_p^{\mathrm{id}}\, dT + RT(z-1) + \int_{\infty}^{v} \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]dv$$

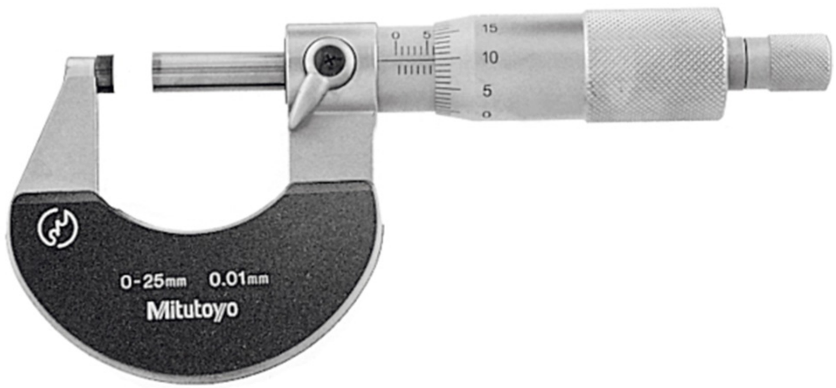
$$s = s_{\mathrm{ref}} + \int_{T^\circ}^{T} \frac{c_p^{\mathrm{id}}}{T}\, dT + R\ln\frac{v}{v^\circ} + \int_{\infty}^{v} \left[\left(\frac{\partial p}{\partial T}\right)_v - \frac{R}{v}\right]dv$$



Ima li to uopće smisla ?

Opis otopina jednadžbama stanja

Mogu li se termodinamičke veličine kapljevina izračunati jednadžbama stanja ?



Ima li to uopće smisla ?

Veličine miješanja

$$V^{\mathrm{M}} = V - \left(V_1 + V_2\right)$$

$$v^{\mathrm{M}} = v - \left(x_1 v_1 + x_2 v_1\right)$$

$$H^{\mathrm{M}} = H - \left(H_1 + H_2\right)$$

$$h^{\mathrm{M}} = h - \left(x_1 h_1 + x_2 h_2\right)$$

$$S^{\mathrm{M}} = S - \left(S_1 + S_2\right)$$

$$s^{\mathrm{M}} = s - \left(x_1 s_1 + x_2 s_2\right)$$

$$G^{\mathrm{M}} = G - \left(G_1 + G_2\right)$$

$$g^{\mathrm{M}} = g - \left(x_1 g_1 + x_2 g_2\right)$$

$$Y^{\mathrm{M}} = Y - \left(Y_1 + Y_2\right)$$

$$y^{\mathrm{M}} = y - \left(x_1 y_1 + x_2 y_2\right)$$

$$y^{\mathrm{M}} = y - \sum x_i y_i$$

Veličine miješanja određuju se eksperimentom !

Stanje nakon miješanja minus stanje prije miješanja

Veličine miješanja
pri idealnom miješanju

$$V^{\mathrm{M}} = V - (V_1 + V_2)$$

$$V^{\mathrm{M,id}} = (V_1 + V_2) - (V_1 + V_2) = 0$$

$$v^{\mathrm{M,id}} = 0$$

$$H^{\mathrm{M}} = H - (H_1 + H_2)$$

$$V^{\mathrm{M,id}} = (H_1 + H_2) - (H_1 + H_2) = 0$$

$$h^{\mathrm{M,id}} = 0$$

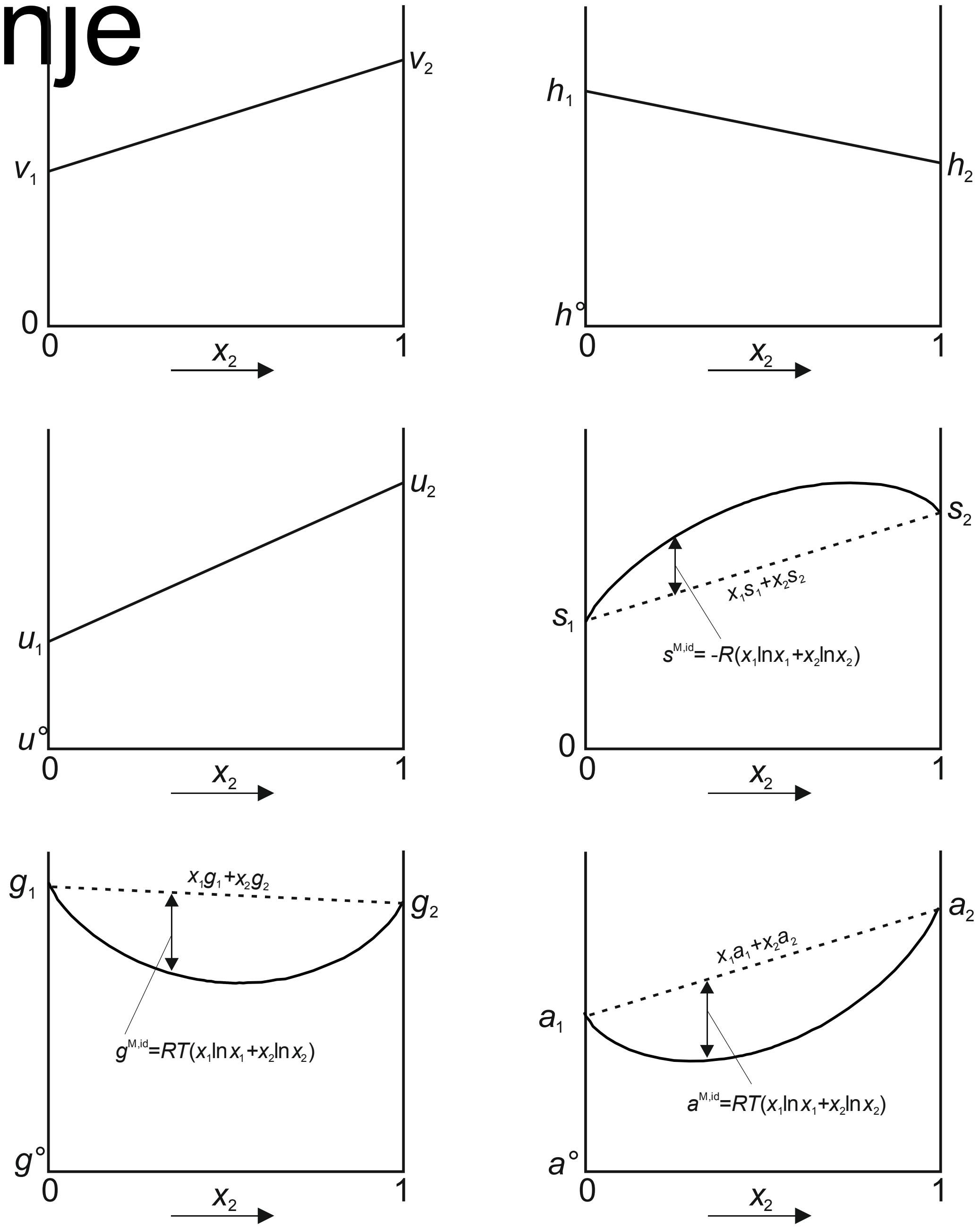
$$S^{\mathrm{M}} = S - (S_1 + S_2)$$

$$S^{\mathrm{M,id}} = \left[S_1 + S_2 - R(n_1 \ln x_1 + n_2 \ln x_2)\right] - (S_1 + S_2) = -R(n_1 \ln x_1 + n_2 \ln x_2)$$

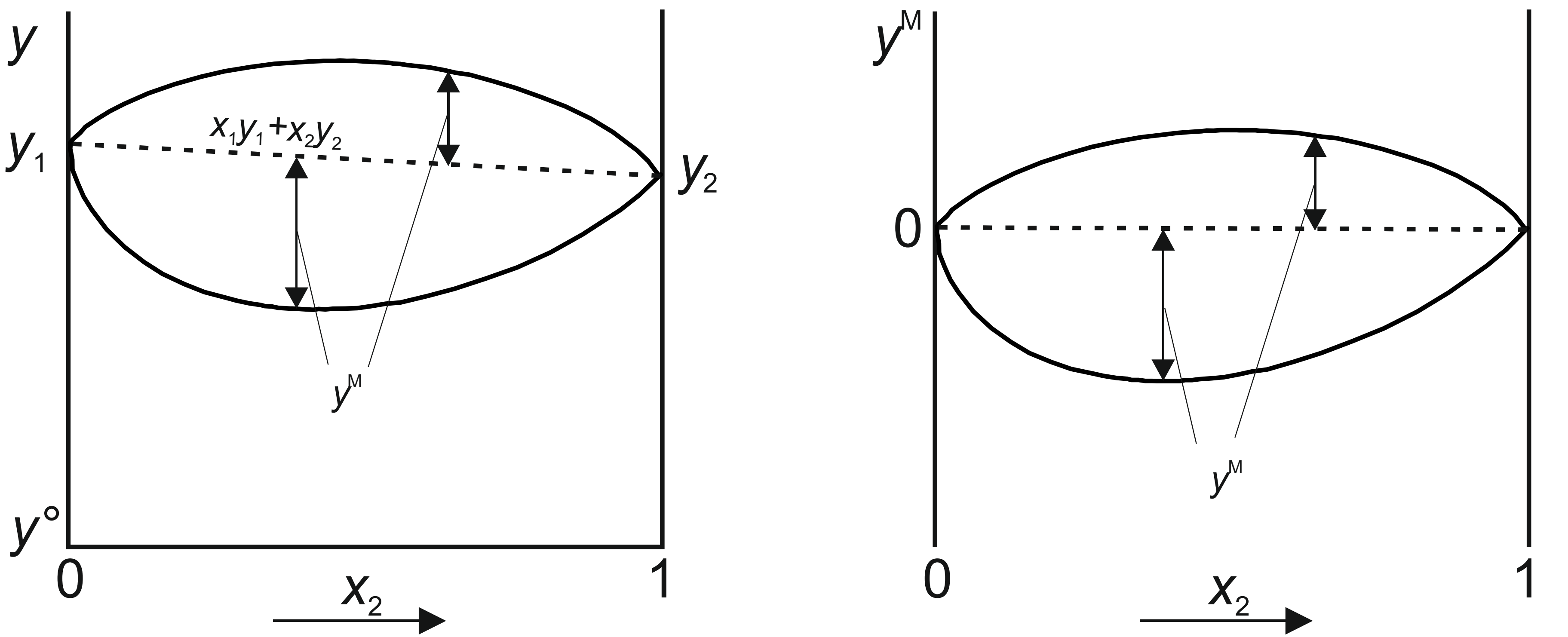
$$s^{\mathrm{M,id}} = -R\sum x_i \ln x_i$$

Idealno miješanje (zaključak)

Veličina	Iznos promjene
v_M^{id}	0
u_M^{id}	0
h_M^{id}	0
s_M^{id}	$-R\sum x_i \ln x_i$
g_M^{id}	$RT\sum x_i \ln x_i$
a_M^{id}	$RT\sum x_i \ln x_i$



Veličine miješanja
pri realnom miješanju



Ekscesne veličine

$$V^{\text{ex}} = V - V^{\text{id}} \qquad H^{\text{ex}} = H - H^{\text{id}} \qquad S^{\text{ex}} = S - S^{\text{id}}$$

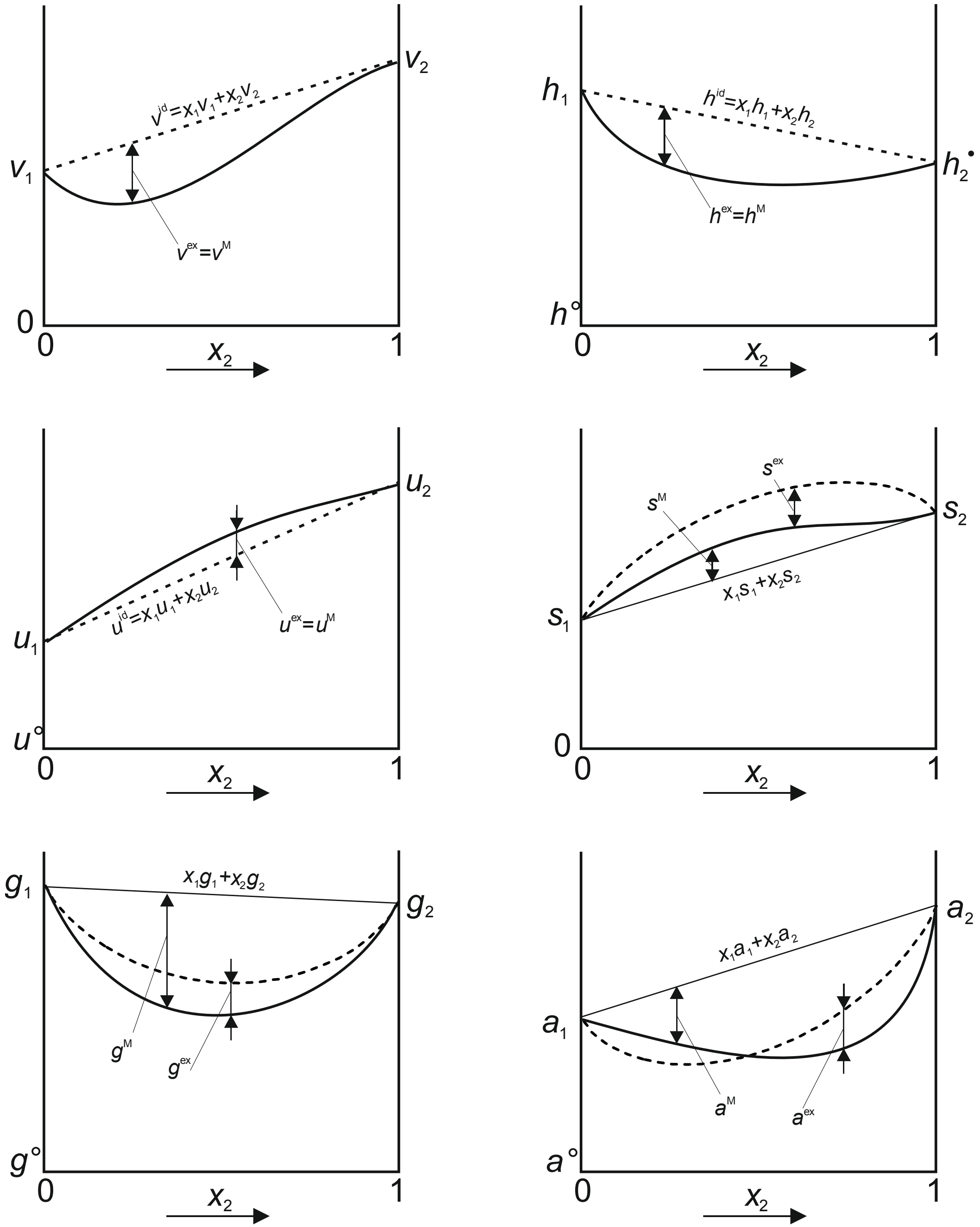
$$v^{\text{ex}} = v - v^{\text{id}} \qquad h^{\text{ex}} = h - h^{\text{id}} \qquad s^{\text{ex}} = s - s^{\text{id}}$$

$$Y^{\text{ex}} = Y - Y^{\text{id}}$$

$$y^{\text{ex}} = y - y^{\text{id}}$$

Iznos ekscesnih veličina ovisi o izboru idealne otopine !
Radi se o razlici mjerene (mjerljive) veličine i zamišljene (dogovorene veličine)

Stanje nakon realnog miješanja minus stanje nakon (zamišljenog) idealnog miješanja



Ekscesne veličine

Uz dogovorenu definiciju idealne otopine

$v^{ex}=v^{M}$

$h^{ex}=h^{M}$

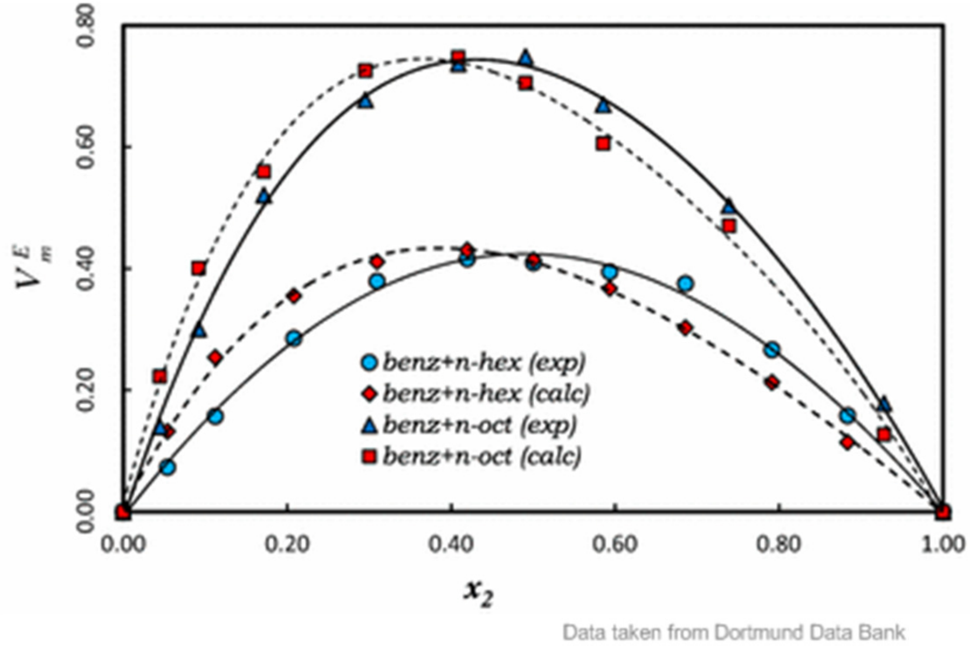
$u^{ex}=u^{M}$

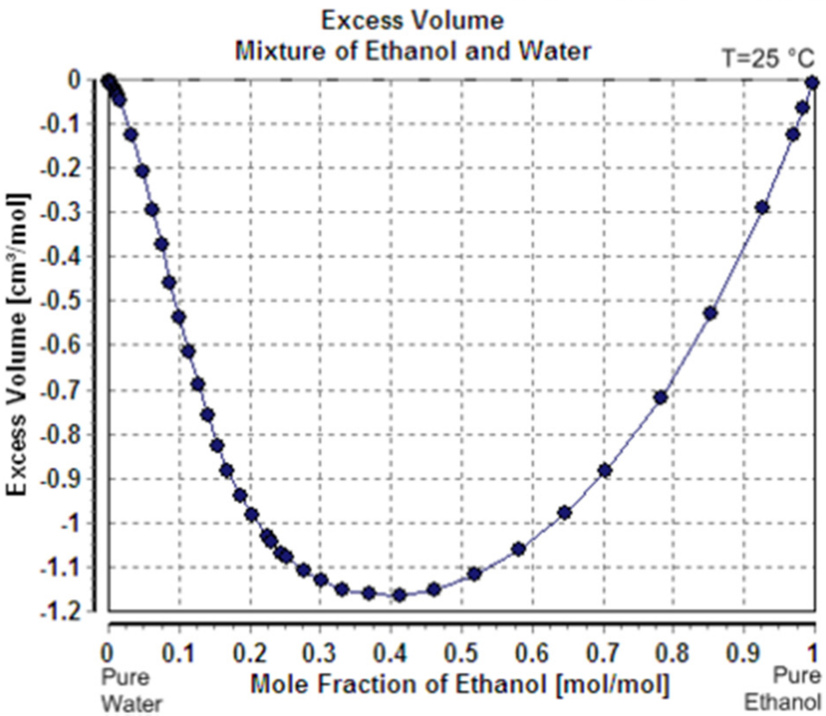
$s^{ex}\neq s^{M}$

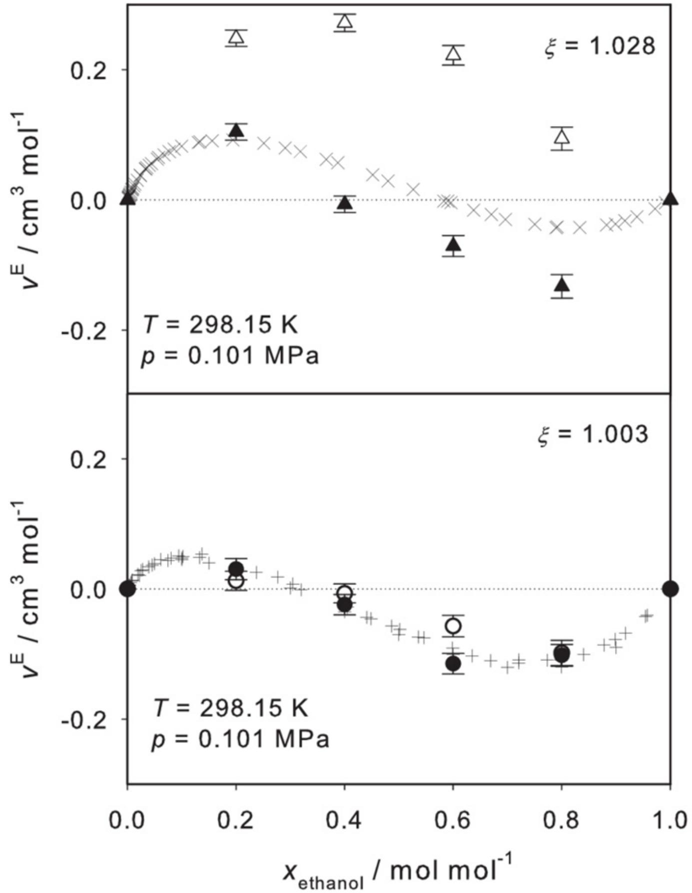
$g^{ex}\neq g^{M}$

$a^{ex}\neq a^{M}$

Ekscesne veličine

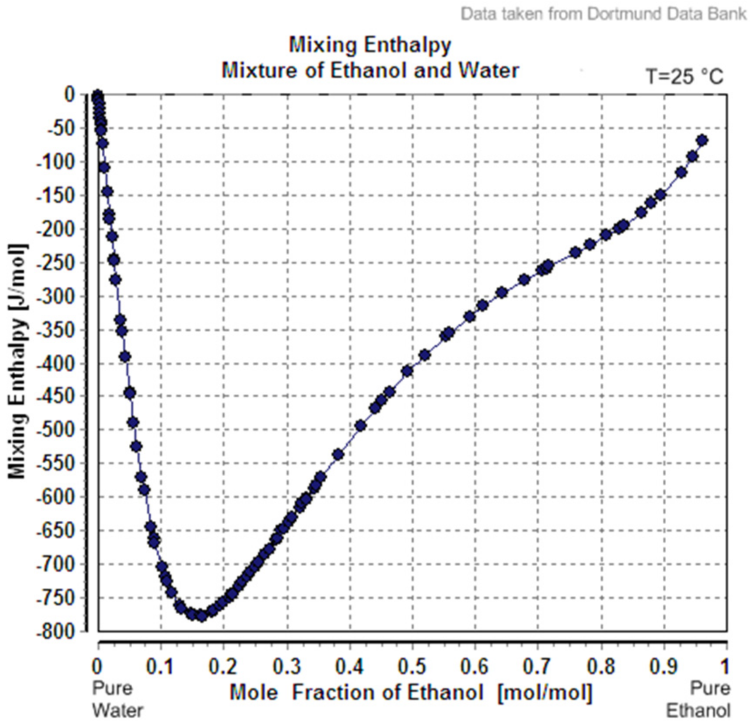


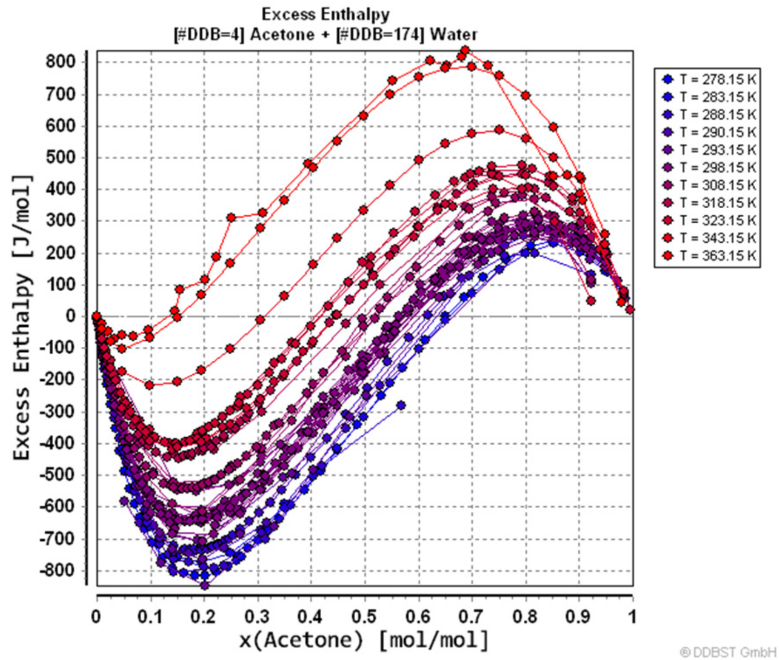


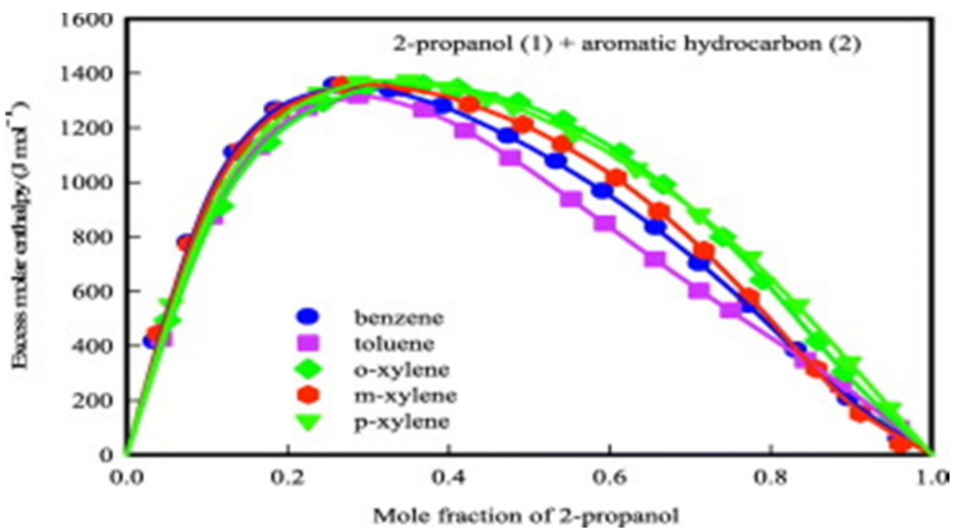


Etanol – benzen
Etanol – toluen

Ekscesne veličine







Ekscesne veličine

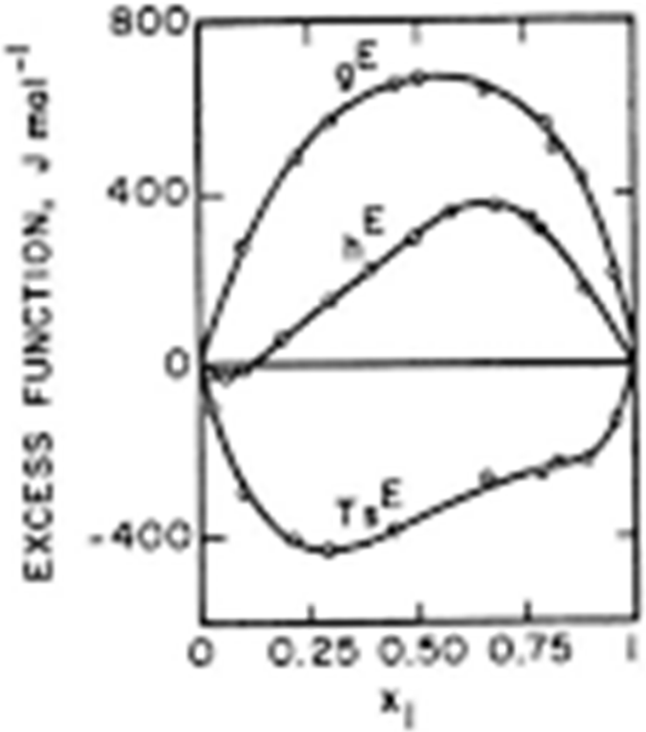


Figure 6-8 Excess functions for the acetic acid (1)/water (2) system at 25°C (R. Haase *et al.*, 1973, *Z. Naturforschung*, 28a: 1740).

Parcijalne molarne veličine

Formalno značenje

$$V = \mathrm{f}(p, T, n_1, n_2)$$

$$dV = \left(\frac{\partial V}{\partial p}\right)_{T,n_1,n_2} dp + \left(\frac{\partial V}{\partial T}\right)_{p,n_1,n_2} dT + \left(\frac{\partial V}{\partial n_1}\right)_{p,T,n_2} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{p,T,n_1} dn_2$$

$$dV = \left(\frac{\partial V}{\partial n_1}\right)_{p,T,n_2} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{p,T,n_1} dn_2$$

$$\bar{v}_1 = \left(\frac{\partial V}{\partial n_1}\right)_{p,T,n_2}$$

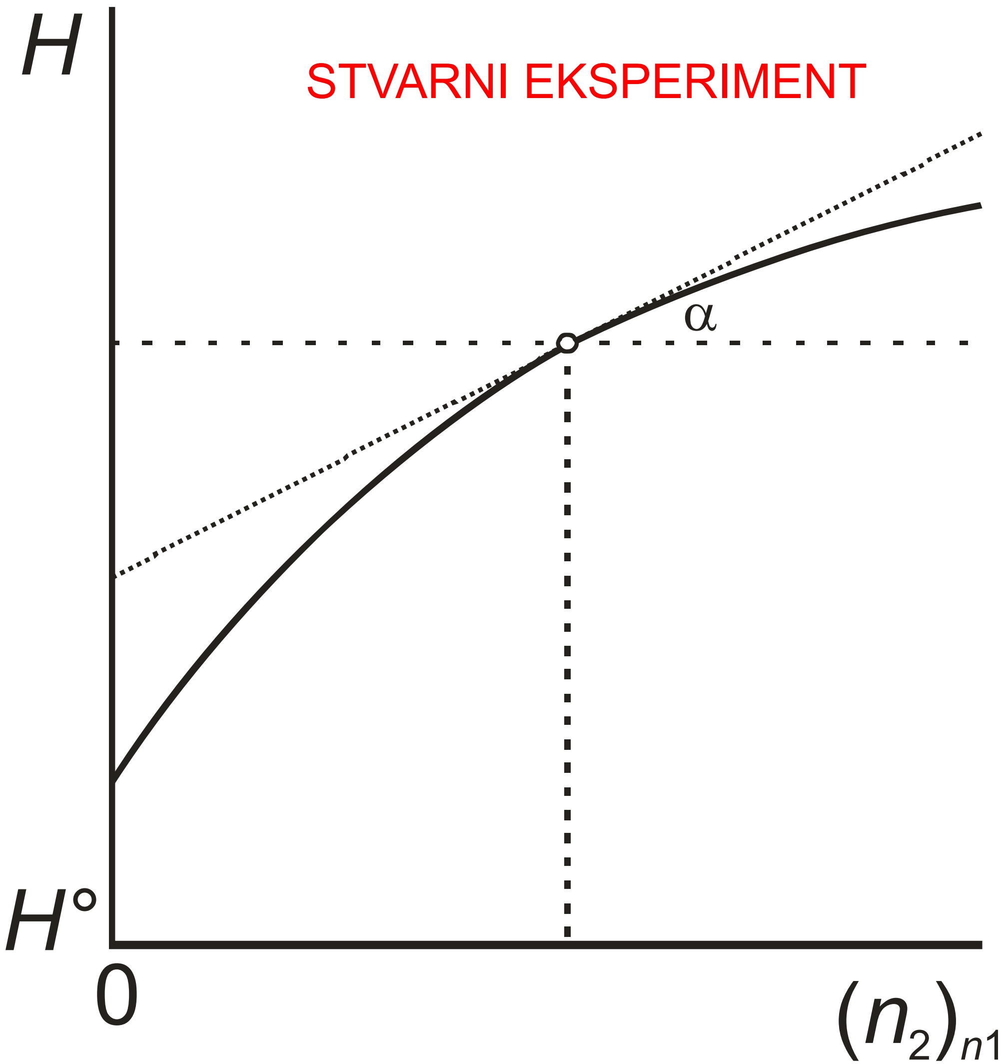
$$\bar{v}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{p,T,n_1}$$

Određivanje PMV – 1

Metoda tangente

$$\bar{h}_i = \left(\frac{\partial H}{\partial n_i}\right)_{p,T,n_{j\neq i}}$$

$$\bar{h}_2 = \left(\frac{\partial H}{\partial n_2}\right)_{p,T,n_1}$$



Parcijalne molarne veličine

Idealne otopine

$$V^{\mathrm{id}} = n_1 v_1 + n_2 v_2$$

$$v^{\mathrm{id}} = x_1 v_1 + x_2 v_2$$

Realne otopine
Formalna analogija

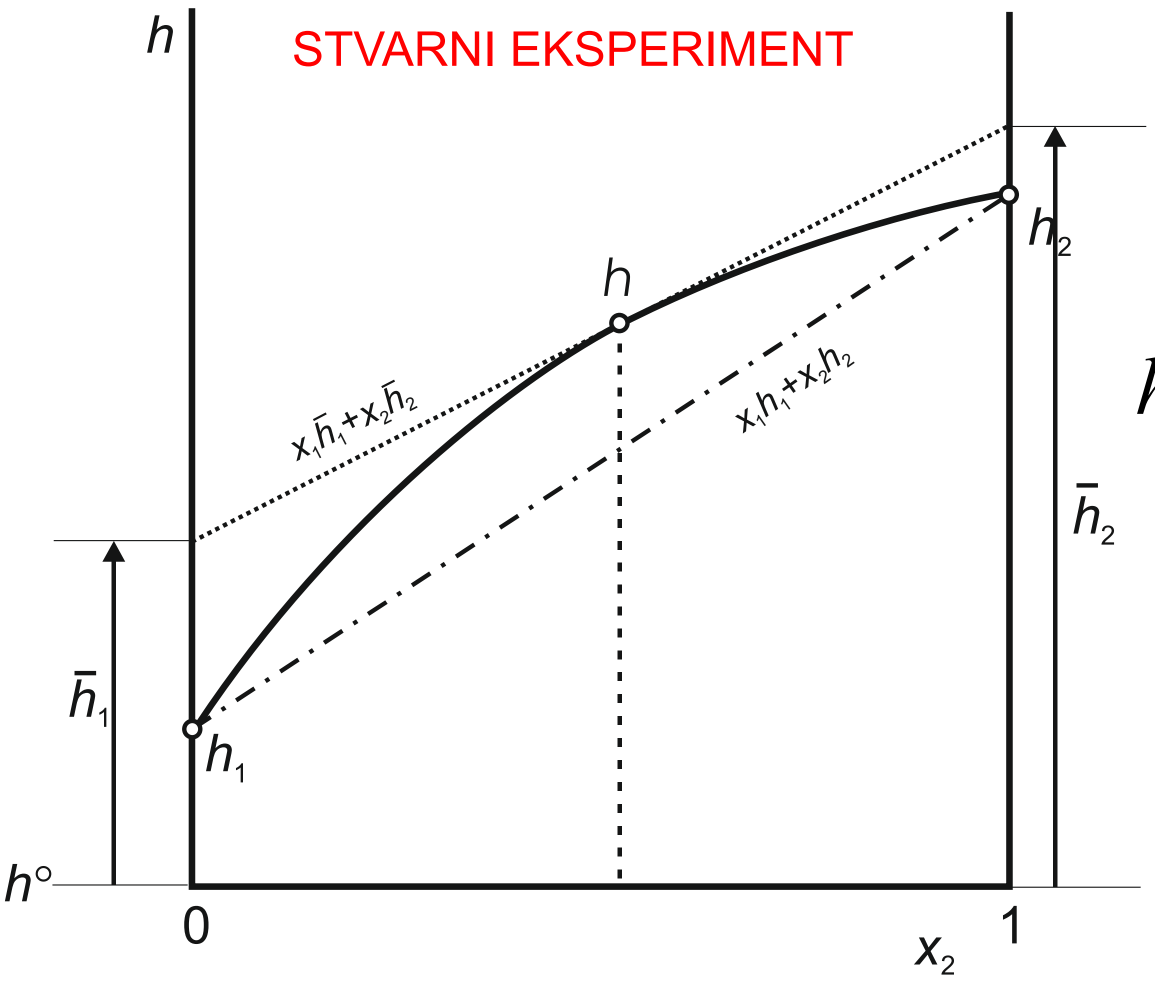
$$V = n_1 \overline{v}_1 + n_2 \overline{v}_2$$

$$v = x_1 \overline{v}_1 + x_2 \overline{v}_2$$

Koliki dio realne otopine „otpada" na pojedinu komponentu

Određivanje PMV – 2

Metoda odsječka (intercepta)



$$h = x_1\bar{h}_1 + x_2\bar{h}_2$$

$$x_1 = 1 - x_2$$

$$h = \bar{h}_1 + x_2\left(\bar{h}_2 - \bar{h}_1\right)$$

Parcijalne molarne veličine

$\bar{y}_\mathrm{i} = \left(\dfrac{\partial Y}{\partial n_\mathrm{i}}\right)_{p,T,n_{\mathrm{j}\neq\mathrm{i}}}$
$Y = \sum n_i \bar{y}_i$
$y = \sum x_i \bar{y}_i$
$\bar{y}_\mathrm{i} = y - \sum_{\mathrm{k}\neq\mathrm{i}} x_\mathrm{k} \left(\dfrac{\partial y}{\partial x_\mathrm{k}}\right)_{p,T,x_{\mathrm{j}\neq\mathrm{i,k}}}$

$$\bar{h}_\mathrm{i} = \bar{u}_\mathrm{i} + p\bar{v}_\mathrm{i}$$

$$\bar{g}_\mathrm{i} = \bar{h}_\mathrm{i} - T\bar{s}_\mathrm{i}$$

$$\frac{\partial(\bar{g}_\mathrm{i}/T)}{\partial T} = -\frac{\bar{h}_\mathrm{i}}{T^2}$$

$$\left(\frac{\partial \bar{h}_\mathrm{i}}{\partial T}\right)_p = \bar{c}_{p,\mathrm{i}}$$

Parcijalne molarne veličine miješanja i parcijalne molarne ekscesne veličine

$$V^{\mathrm{M}} = V - (V_1 + V_2)$$

$$v^{\mathrm{M}} = v - (x_1 v_1 + x_2 v_2)$$

$$v^{\mathrm{M}} = x_1 \overline{v}_1 + x_2 \overline{v}_2 - (x_1 v_1 + x_2 v_2)$$

$$V^{\mathrm{ex}} = V - V^{\mathrm{id}}$$

$$v^{\mathrm{ex}} = v - (x_1 v_1 + x_2 v_2)$$

$$v^{\mathrm{ex}} = x_1 \overline{v}_1 + x_2 \overline{v}_2 - (x_1 v_1 + x_2 v_2)$$

$$Y^{\mathrm{M}} = \sum n_{\mathrm{i}} (\overline{y}_{\mathrm{i}} - y_{\mathrm{i}})$$

$$y^{\mathrm{M}} = \sum x_{\mathrm{i}} (\overline{y}_{\mathrm{i}} - y_{\mathrm{i}})$$

Parcijalne molarne veličine miješanja

$$y^{\mathrm{M}} = \sum x_{\mathrm{i}} \overline{y}_{\mathrm{i}}^{\mathrm{M}}$$

$$\overline{y}_{\mathrm{i}}^{\mathrm{M}} = \overline{y}_{\mathrm{i}} - y_{\mathrm{i}}$$

Parcijalne molarne ekscesne veličine

$$y^{\mathrm{ex}} = \sum x_{\mathrm{i}} \overline{y}_{\mathrm{i}}^{\mathrm{ex}} \qquad \overline{v}_{\mathrm{i}}^{\mathrm{ex}} = \overline{v}_{\mathrm{i}} - v_{\mathrm{i}} = \overline{v}_{\mathrm{i}}^{\mathrm{M}}$$

$$\overline{a}_{\mathrm{i}}^{\mathrm{ex}} = \overline{a}_{\mathrm{i}} - a_{\mathrm{i}} - RT \ln x_{\mathrm{i}} \neq \overline{a}_{\mathrm{i}}^{\mathrm{M}}$$

Gibbs-Duhemova jednadžba

Totalni diferencijal

$$dV = n_1 d\bar{v}_1 + n_2 d\bar{v}_2 + \bar{v}_1 dn_1 + \bar{v}_2 dn_2$$

Definicija

$$dV = \bar{v}_1 dn_1 + \bar{v}_2 dn_2$$

Gibbs-Duhem

$$n_1 d\bar{v}_1 + n_2 d\bar{v}_2 = 0$$

$$x_1 d\bar{v}_1 + x_2 d\bar{v}_2 = 0$$

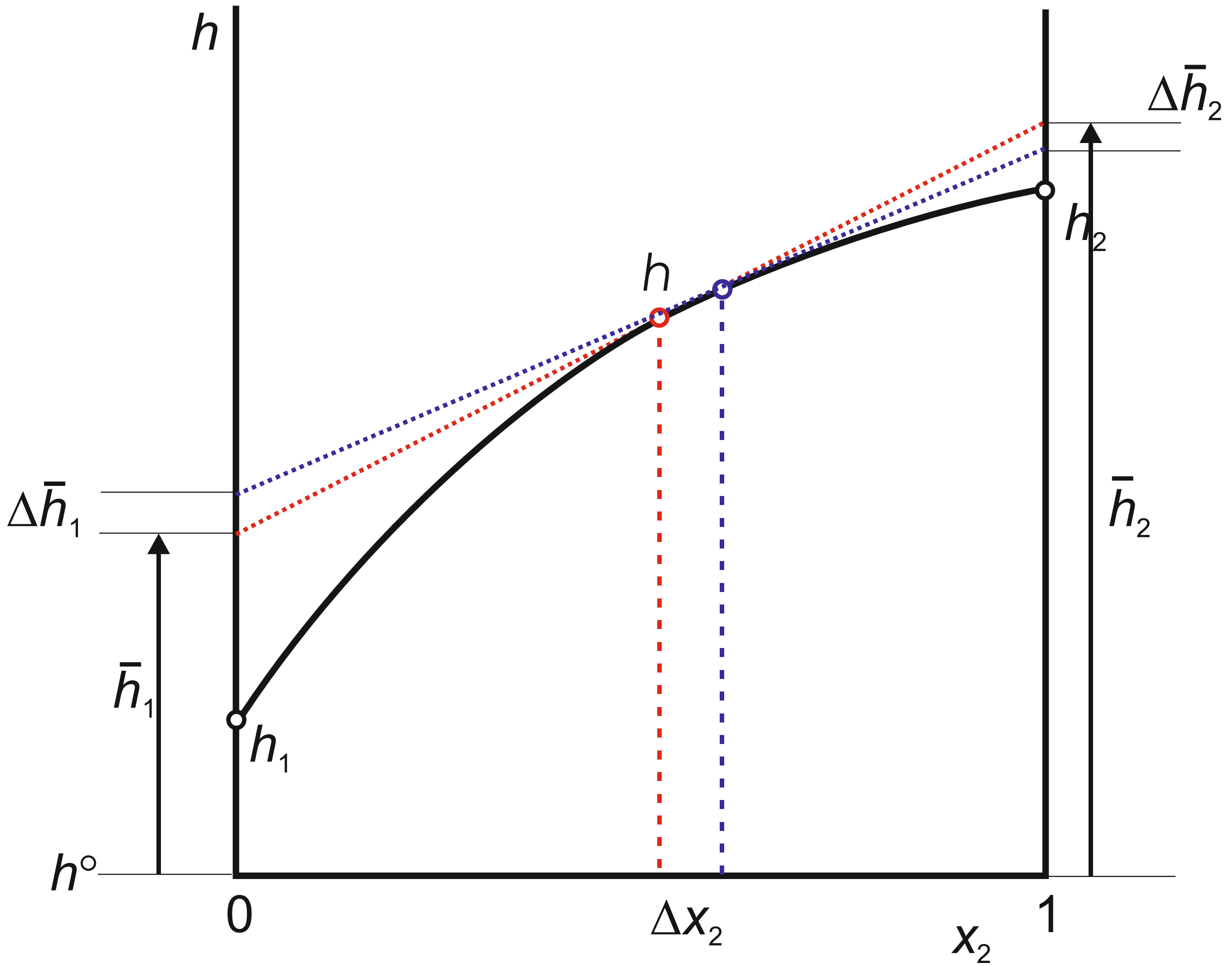
Višekomponentni sustavi

$$\sum n_\mathrm{i} d\bar{y}_\mathrm{i} = 0$$

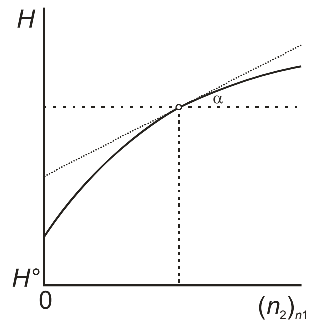
$$\sum x_\mathrm{i} d\bar{y}_\mathrm{i} = 0$$

Gibbs-Duhemova jednadžba

Međuovisnost parcijalnih molarnih veličina



Primjena



$$x_1 d\bar{h}_1 + x_2 d\bar{h}_2 = 0$$

$$d\bar{h}_1 = -\frac{x_2}{x_1} d\bar{h}_2$$

$$\lim_{x_1 \to 1} \bar{h}_1 = h_1$$

$$\bar{h}_1 = h_1 - \int_{\bar{h}_2(x_2=0)}^{\bar{h}_2} \frac{x_2}{x_1} d\bar{h}_2$$

Aktivnost i standardna stanja

- Što je aktivnost čistih plinova ?
- Kako mjeriti aktivnost molekula u čistim plinovima ?
- Prirodna mjera aktivnosti ?

IDEALNI PLINOVI

$$(dg)_T = RTd\ln p$$

REALNI PLINOVI

Fugacitivnost $$(dg)_T = RTd\ln f$$

Standardno stanje

$$g = g^\circ + RT\ln\frac{p}{p^\circ} \qquad a = \frac{p}{p^\circ}$$

$$g = g^\circ + RT\ln\frac{f}{f^\circ} \qquad a = \frac{f}{f^\circ}$$

Lewis

Standardno stanje – stanje čistog plina pri temperaturi T
i referentnom tlaku $p°$ (1 bar)
Definicija se upotpunjuje odgovarajućim iznosom entalpije

Parcijalne fugacitivnosti

Idealna plinska smjesa

Smjesa dvaju ili više plinova koja ne mora biti idealni plin, ali jest idealna otopina, sukladno dogovorenoj definiciji idealne otopine

$$v^{\mathrm{M,id}} = 0$$

$$h^{\mathrm{M,id}} = 0$$

$$s^{\mathrm{M,id}} = -R\sum y_i \ln y_i$$

$$\overline{v}_{\mathrm{i}} = v_{\mathrm{i}}$$

Za čisti plin fugacitivnost se uspoređuje s tlakom:

$$\ln\frac{f}{p} = \frac{\left(g - g^{\circ}\right)}{RT} = \frac{1}{RT}\int_0^p \left(v - \frac{RT}{p}\right) dp$$

Za plinsku smjesu parcijalna fugacitivnost uspoređuje se s parcijalnim tlakom:

$$\ln\frac{\hat{f}_{\mathrm{i}}}{p_{\mathrm{i}}} = \frac{\left(\overline{g}_{\mathrm{i}} - \overline{g}_{\mathrm{i}}^{\mathrm{id}}\right)}{RT} = \frac{1}{RT}\int_0^p \left(\overline{v}_{\mathrm{i}} - \overline{v}_{\mathrm{i}}^{\mathrm{id}}\right) dp$$

Parcijalni koeficijent fugacitivnosti

$$\hat{\varphi}_{\mathrm{i}} = \frac{\hat{f}_{\mathrm{i}}}{y_{\mathrm{i}}\, p}$$

$$\ln\frac{\hat{f}_{\mathrm{i}}}{y_{\mathrm{i}}\, p} = \frac{\left(\overline{g}_{\mathrm{i}} - \overline{g}_{\mathrm{i}}^{\mathrm{id}}\right)}{RT} = \frac{1}{RT}\int_0^p \left(\overline{v}_{\mathrm{i}} - \frac{RT}{p}\right) dp$$

Aktivnost i standardna stanja

- Što je aktivnost komponente u plinskoj smjesi ?
- Kako mjeriti aktivnost molekula komponenata u plinskim smjesama ? Elektrodni potencijal ?
- Prirodna mjera aktivnosti ?

IDEALNE PLINSKE SMJESE

$$\left(d\bar{g}_i\right)_T = RTd\ln p_i$$

$$\left(d\mu_i\right)_T = RTd\ln p_i$$

REALNE PLINSKE SMJESE

Parcijalna fugacitivnost

$$\left(d\bar{g}_i\right)_T = RTd\ln \hat{f}_i$$

KEMIJSKI POTENCIJAL

$$\left(d\mu_i\right)_T = RTd\ln \hat{f}_i$$

$$\mu_i = \mu_i^\circ + RT\ln\frac{p_i}{p^\circ} \qquad a_i = \frac{p_i}{p^\circ}$$

$$\mu_i = \mu_i^\circ + RT\ln\frac{\hat{f}_i}{f^\circ} \qquad a_i = \frac{\hat{f}_i}{f^\circ}$$

Lewis

Standardno stanje – stanje čistog plina pri temperaturi *T* i referentnom tlaku *p*° (1 bar)
Definicija se upotpunjuje odgovarajućim iznosom entalpije

Standardno stanje

Aktivnost i standardna stanja

Čiste kapljevine i krutine

- Aktivnost čistih kapljevina i krutina po definiciji iznosi 1
- jer se kao standardno stanje odabire stanje čiste kapljevine, odnosno krutine pri temperaturi T i tlaku sustava p

$$g = g^\circ + RT \ln \frac{f}{f^\circ}$$

Fugacitivnost pri temperaturi i tlaku sustava)

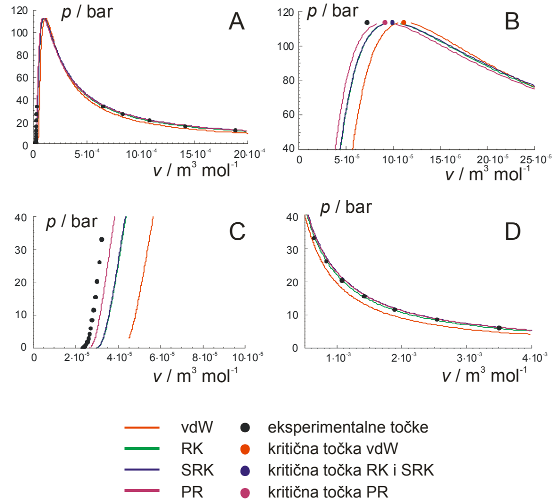
Fugacitivnost u standardnom stanju (pri temperaturi i tlaku sustava)

$$a = \frac{f}{f^\circ}$$

$$a = 1$$

Kolika je fugacitivnost čiste kapljevine, odnosno krutine (kapljevine, odnosno krutine u standardnom stanju) ?

$$\ln \varphi = \ln \frac{v}{v-b} + \frac{a\alpha(T)}{bRT} \ln \frac{v}{v+b} + (z-1) - \ln z$$



Fugacitivnost čiste kapljevine ili krutine

- Vrijednosti fugacitivnosti kapljevine (krutine) moraju biti konzistentne s onima u plinskoj fazi
- Fugacitivnost plina računa se jednadžbom stanja
- Fugacitivnost kapljevine (krutine) računa se iz eksperimentalnog podatka o gustoći kapljevine (krutine)

$$g^{\mathrm{L}} = g^{\mathrm{V}}$$

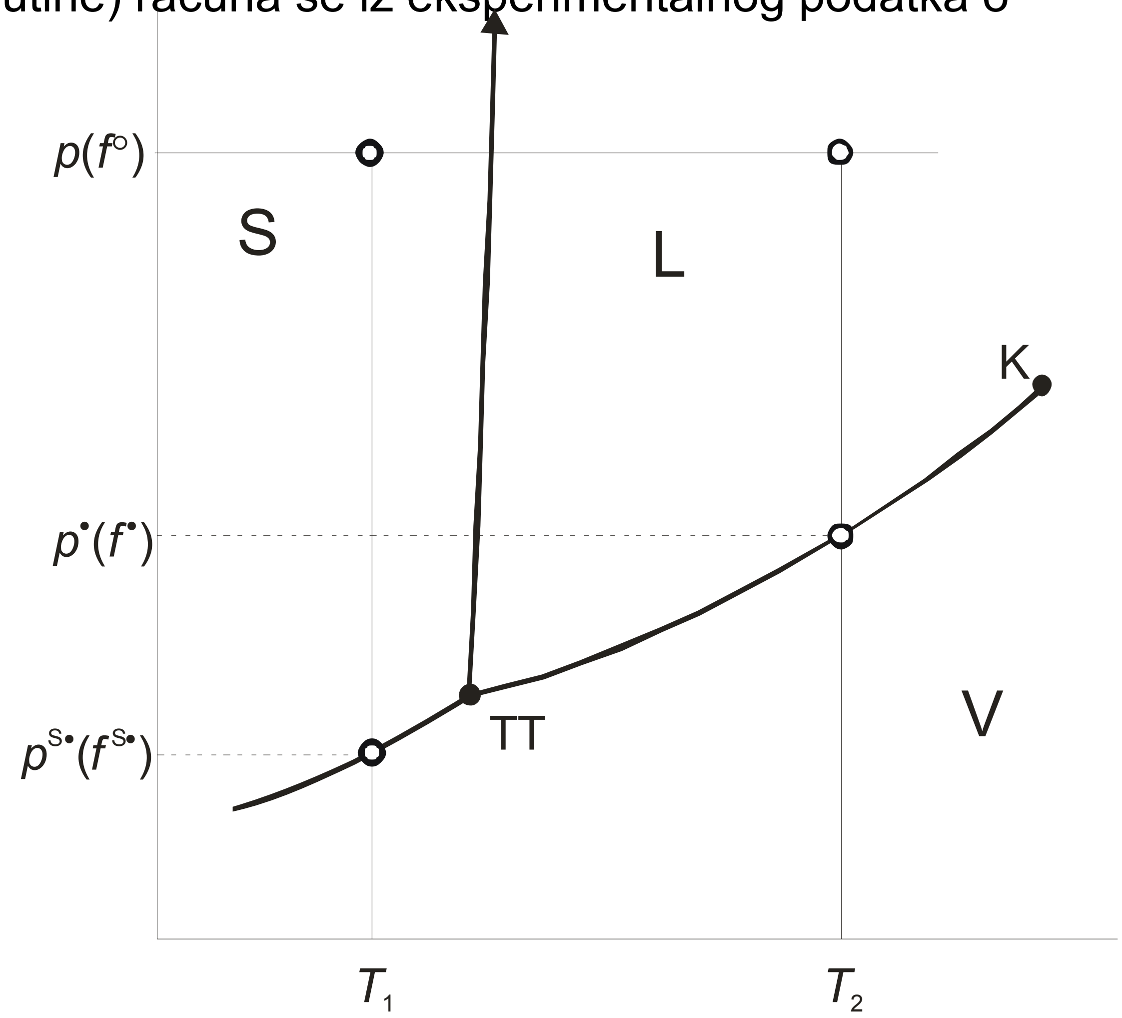
$$f^{\mathrm{L}} = f^{\mathrm{V}} = f^{\bullet}$$

$$RTd\ln f = vdp$$

$$\int_{f^{\bullet}}^{f^{\circ}} d\ln f = \frac{1}{RT}\int_{p^{\bullet}}^{p} v^{\mathrm{L}} dp$$

$$f^{\circ} = f^{\bullet}\exp\left(\frac{1}{RT}\int_{p^{\bullet}}^{p} v^{\mathrm{L}} dp\right)$$

$$f^{\bullet} = \varphi^{\bullet} p^{\bullet} \qquad v^{\mathrm{L}} = \frac{M}{\rho}$$



Fugacitivnost čiste kapljevine ili krutine

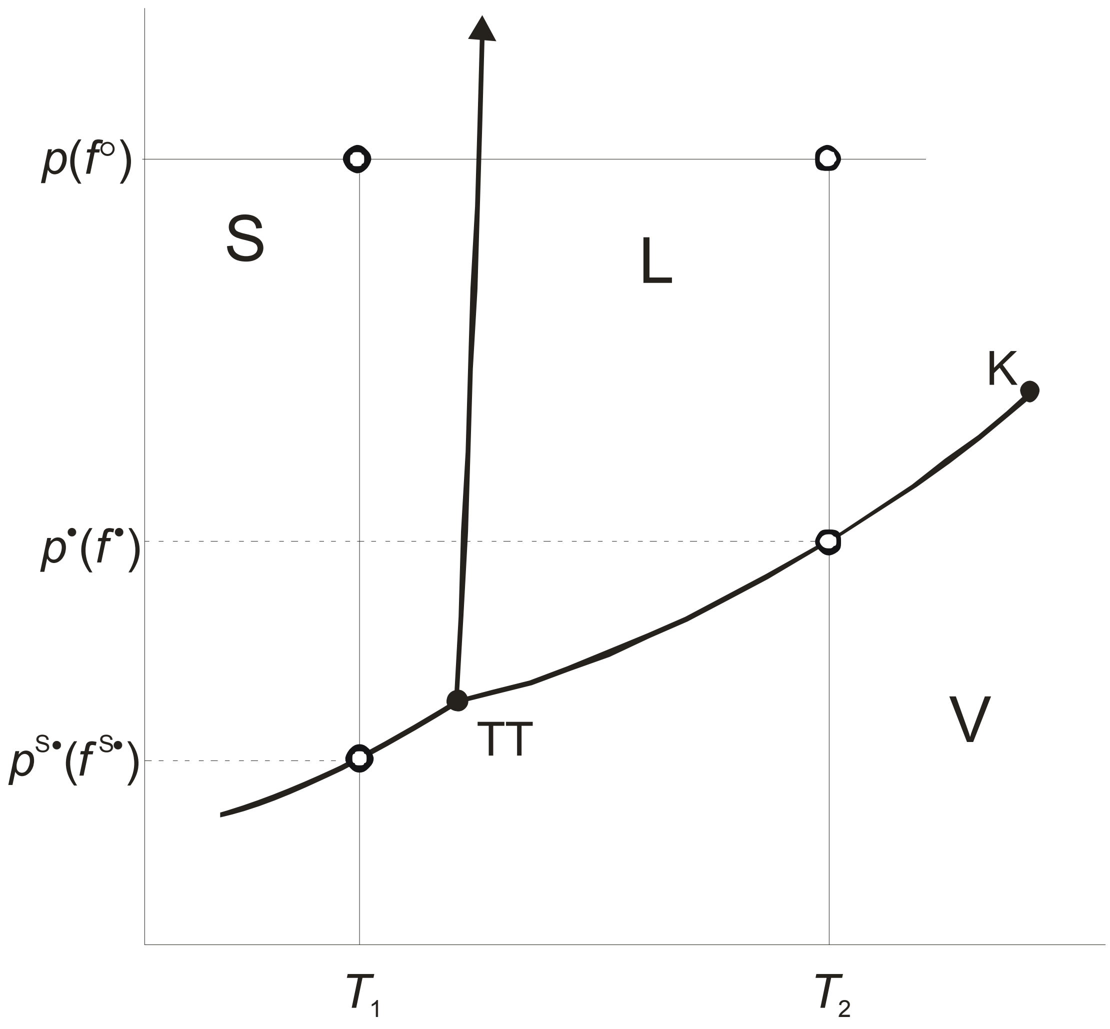
Poyntingov faktor

$$PF = \exp\left[\frac{v^{L}\left(p - p^{\bullet}\right)}{RT}\right]$$

Krutina

$$f^{\circ} = f^{S\bullet} \exp\left(\frac{1}{RT}\int_{p^{S\bullet}}^{p} v^{S} dp\right) =$$

$$= \varphi^{S\bullet} p^{S\bullet} \exp\left[\frac{v^{S}\left(p - p^{S\bullet}\right)}{RT}\right]$$



Aktivnost i standardna stanja

Smjese kapljevina (otopine)

- Što je aktivnost komponente u kapljevitoj smjesi ?
- Kako mjeriti aktivnost molekula komponenata u kapljevitim smjesama ? Elektrodni potencijal ? Osmotski tlak? Povišenje vrelišta ? Sniženje ledišta ? Tlak para ?

- U idealnim otopinama u jednadžbe ide množinski udio komponente, u realnima aktivnost komponente !!!!

- Aktivnost komponente u otopini stoga je manje-više izravno povezana s njenim množinskim udjelom $\rightarrow$ za čistu tvar aktivnost je 1, a kad komponente nema u sustavu aktivnost je 0 !!!

Aktivnost i standardna stanja

Smjese kapljevina (otopine)

- Formalne jednadžbe su slične kao i za smjese plinova !!!

$$\mu_i = \mu_i^\circ + RT\ln\frac{p_i}{p^\circ} \qquad a_i = \frac{p_i}{p^\circ} \qquad \mu_i = \mu_i^\circ + RT\ln\frac{\hat{f}_i}{f^\circ} \qquad a_i = \frac{\hat{f}_i}{f^\circ}$$

Veza aktivnosti i množinskog udjela je "racionalni" koeficijent aktivnosti

$$\gamma_i = \frac{a_i}{x_i} \qquad \hat{f}_i = \gamma_i x_i f_i^\circ$$

γ_i > 1 znači da je aktivnost veća od množinskog udjela → mjereno svojstvo ukazuje na to da mu komponenta više pridonosi od očekivanoga sukladno sastavu otopine

Za idealne otopine ili idealne plinske smjese:
Vrijedi tzv. Lewis-Randallovo pravilo

$$\gamma_i = 1 \qquad \hat{f}_i = x_i f_i^\circ$$

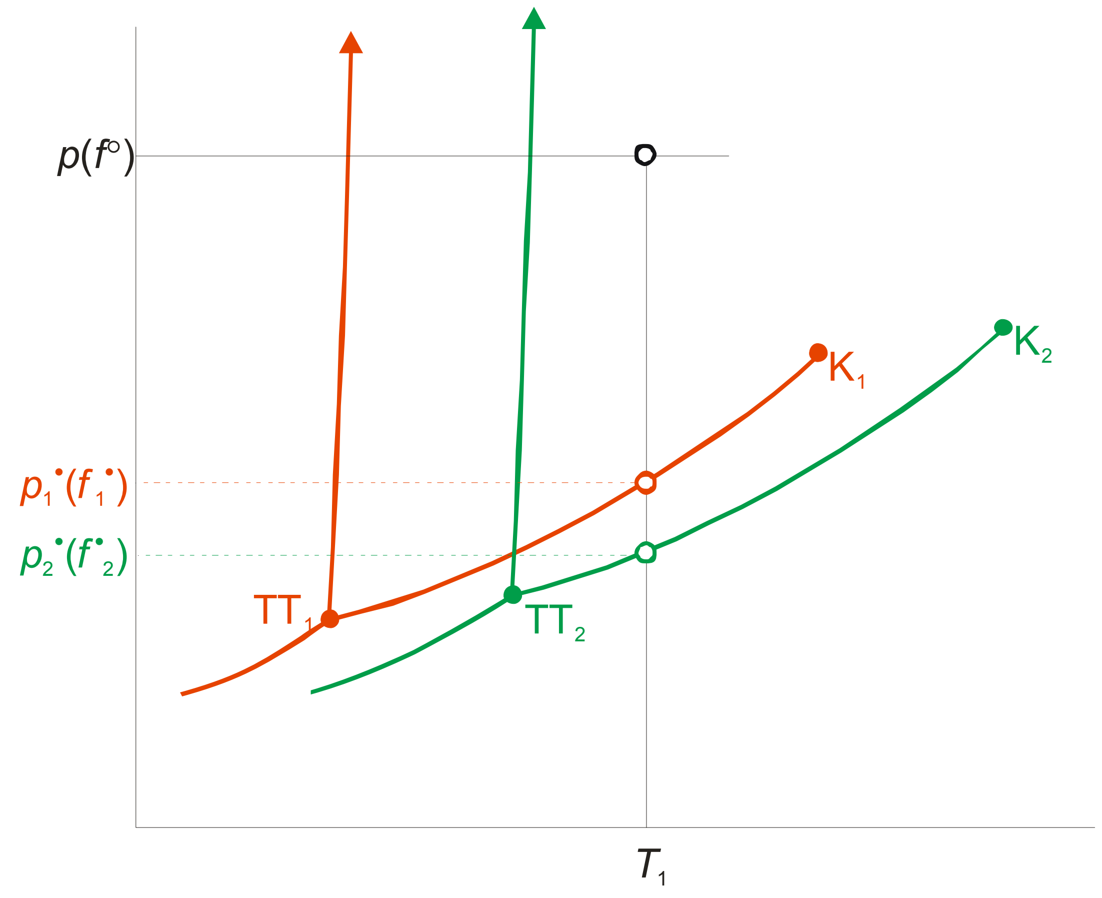
$$\hat{f}_i = y_i f_i^\circ \qquad \hat{\varphi}_i = \varphi_i^\circ$$

$$v^{M} = 0$$

Standardne fugacitivnosti komponenata u otopinama (smjesama) dviju kapljevina

Standardno stanje – čista kapljevina pri temperaturi i tlaku sustava

$$f_{\mathrm{i}}^{\circ} = f_{\mathrm{i}}^{\bullet} \exp\left(\frac{1}{RT}\int_{p_{\mathrm{i}}^{\bullet}}^{p} v_{\mathrm{i}}^{\mathrm{L}}\, dp\right)$$



Aktivnosti komponenata u otopinama (smjesama) dviju kapljevina

Standardno stanje – čista kapljevina pri temperaturi sustava i ravnotežnom tlaku

Iz definicije aktivnosti i koeficijenta aktivnosti:

Realne otopine

$$\hat{f}_i = \gamma_i x_i f_i^\circ$$

Idealne otopine

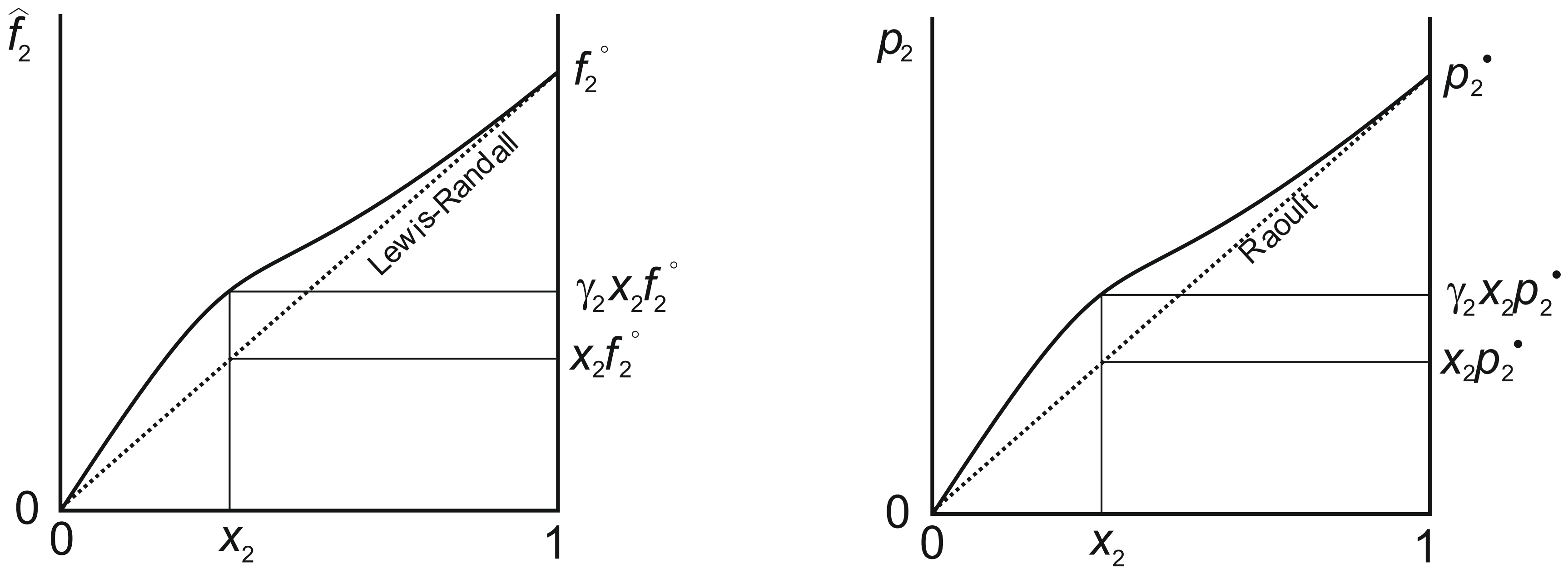
$$\hat{f}_i = x_i f_i^\circ$$

Ako je Poyntingov faktor ≈ 1

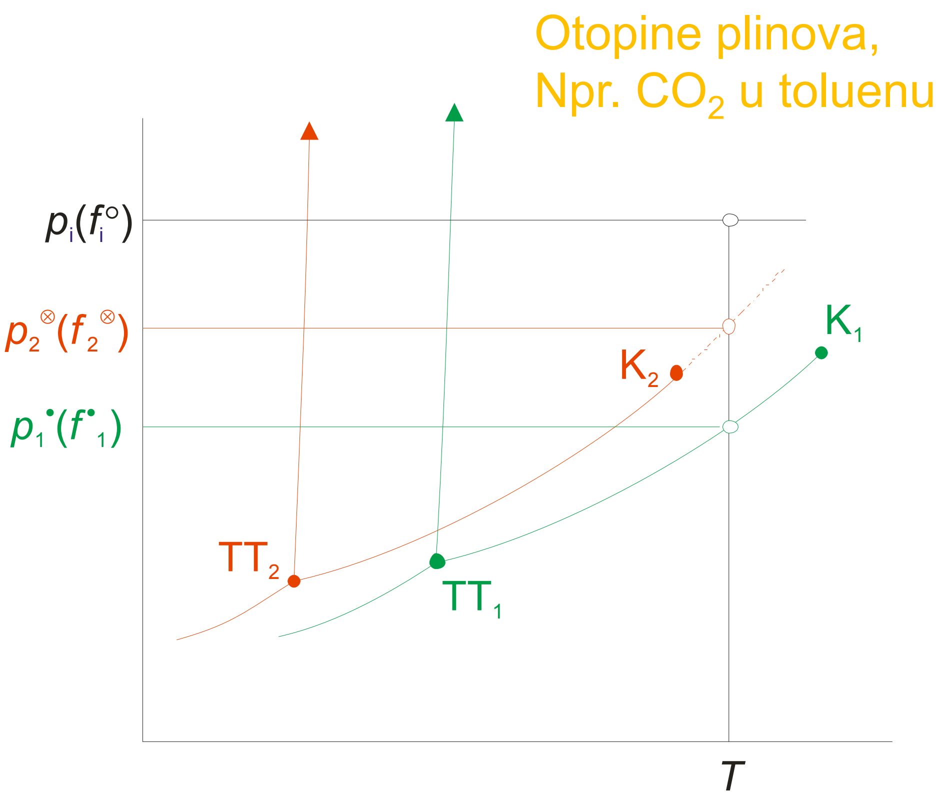
Ako je tlak nizak: $f_i^\circ \approx f_i^\bullet = \varphi_i^\bullet p_i^\bullet \approx p_i^\bullet$

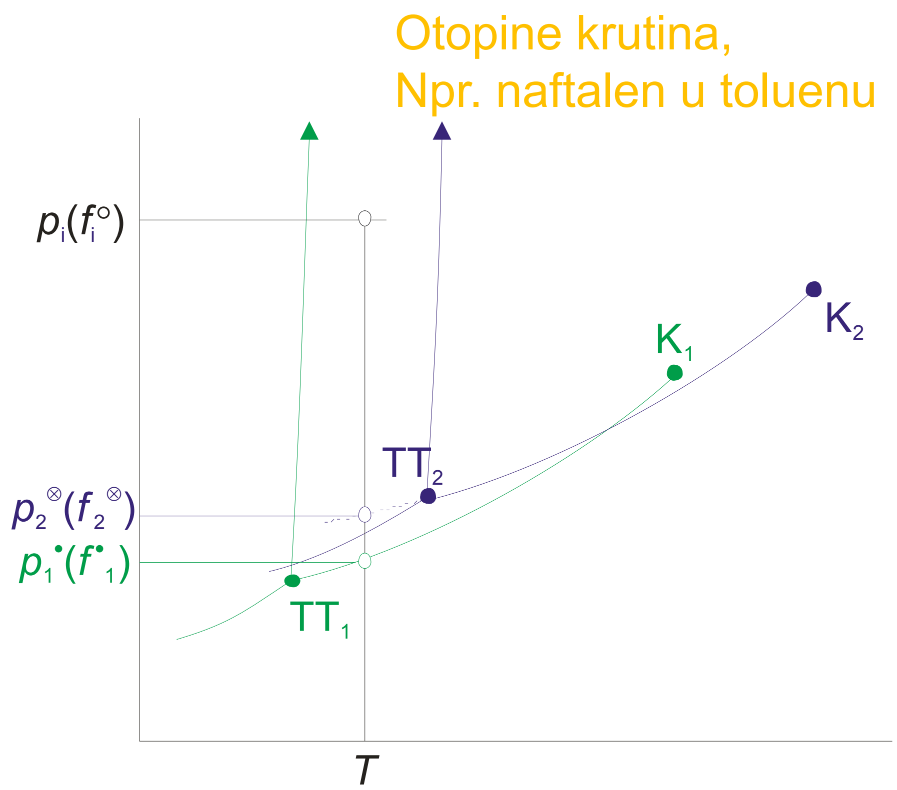
$$\hat{f}_i = \hat{\varphi}_i p_i \approx p_i$$

$$p_i = \gamma_i x_i p_i^\bullet \qquad p_i = x_i p_i^\bullet$$



Standardne fugacitivnosti komponenata u asimetričnim otopinama





Ekstrapolacijski postupci

$$f_2^\circ = f_2^\bullet \exp\left(\frac{1}{RT}\int_{p_2^\bullet}^{p} v_2^{\mathrm{L}}\,dp\right)$$

$$f_2^\circ = f_2^\otimes \exp\left(\frac{1}{RT}\int_{p_2^\otimes}^{p} v_2^{\mathrm{L}\otimes}\,dp\right) \qquad v_2^{\mathrm{L}\otimes} = ?$$

Otopine plinova ili krutina u kapljevinama

Odstupanja od Henryjeva zakona
za realne otopine

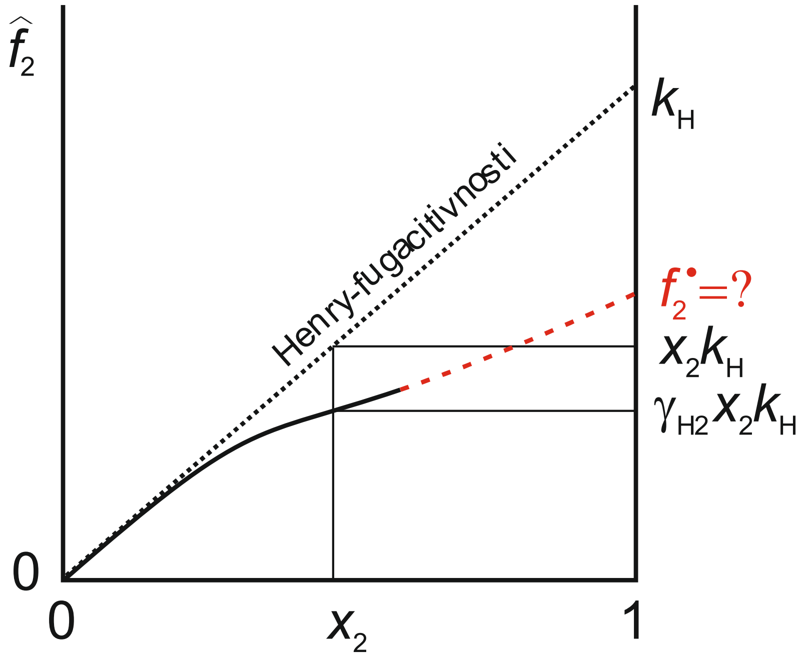
Henryjev zakon

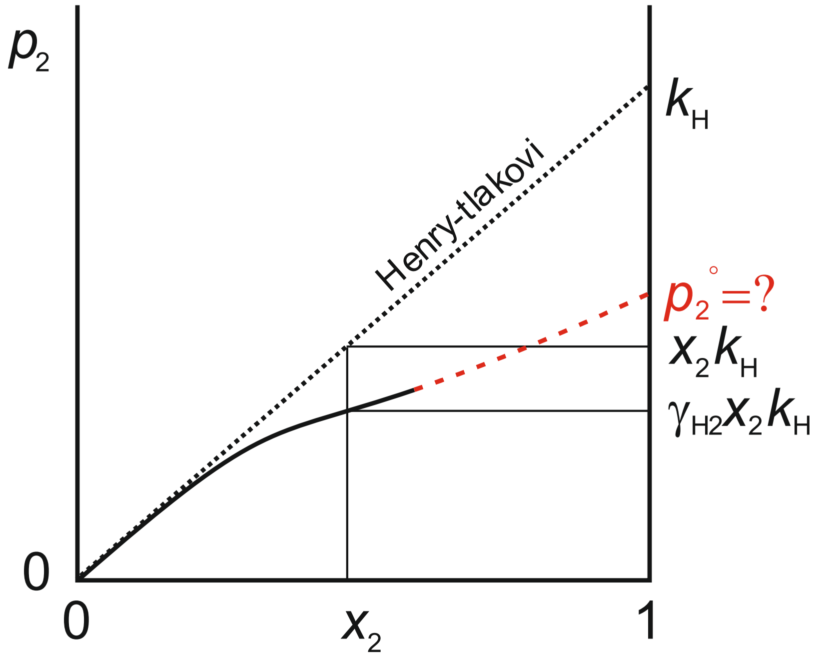
$$p_2 = x_2 k_{\mathrm{H}}$$

$$\hat{f}_2 = x_2 k_{\mathrm{H}}$$

Aktivnost otopljene tvari u asimetričnim otopinama

Realne otopine	Idealne otopine	Realne otopine	Idealne otopine
$\hat{f}_2 = \gamma_{H2} x_2 k_H$	$\hat{f}_2 = x_2 k_H$	$p_2 = \gamma_{H2} x_2 k_H$	$p_2 = x_2 k_H$





NOVA DEFINICIJA IDEALNE OTOPINE !!!

Nova (asimetrična) definicija idealne otopine

- Otopina se vlada idealno u vrlo razrijeđenom području
- Parcijalna fugacitivnost (parcijalni tlak otapala) razmjeran je njegovu množinskom udjelu – slijedi Raoultov zakon
- Topljivost plina razmjerna je njegovu parcijalnom tlaku iznad otopine – slijedi Henryjev zakon
- Mikroskopski gledano, u idealnoj otopini otapanje molekula plina (ili krutine) ne remeti interakcije molekula otapala;
- Interakcije molekula otopljene tvari zanemarive su!

Kemijski potencijal – parcijalna molarna Gibbsova energija

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

Parcijalna molarna Gibbsova energija

Središnja veličina kemijsko inženjerske termodinamike

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{s,v,n_{j\neq i}}$$

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{s,p,n_{j\neq i}}$$

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

Jesu kemijski potencijali,
ali nisu parcijalne molarne veličine
(tlak i temperatura nisu konstantni)

Promjena entropije pri idealnom miješanju iz kemijskih potencijala

$$g = x_1\mu_1 + x_2\mu_2$$

$$\mu_i = \mu_i^\circ + RT\ln a_i$$

$$\mu_i = g_i + RT\ln a_\mathrm{i}$$

Standardno stanje – čista tvar

$$g^\mathrm{M} = g - x_1 g_1 - x_2 g_2 =$$
$$= x_1\left(g_1 + RT\ln a_1\right) + x_2\left(g_2 + RT\ln a_2\right) - x_1 g_1 - x_2 g_2 =$$
$$= RT\left(x_1\ln a_1 + x_2\ln a_2\right)$$

$$g^\mathrm{M} = RT\sum x_\mathrm{i}\ln a_\mathrm{i}$$

$$g^\mathrm{M} = RT\sum x_\mathrm{i}\ln\left(x_\mathrm{i}\gamma_\mathrm{i}\right)$$

Veza aktivnosti i koeficijenta aktivnosti

$$g^\mathrm{M,id} = RT\sum x_\mathrm{i}\ln x_\mathrm{i}$$

Iz opće termodinamike $s^\mathrm{M,id} = -\left(\frac{\partial g^\mathrm{M,id}}{\partial T}\right)_p$

$$s^\mathrm{M,id} = -R\sum x_\mathrm{i}\ln x_\mathrm{i}$$

Logaritam aktivnosti i logaritam koeficijenta aktivnosti kao PMV

Metoda odsječka za Gibbsovu energiju

$$\frac{g^{\mathrm{M}}}{RT} = \sum x_i \ln a_i \qquad \frac{g^{\mathrm{ex}}}{RT} = \sum x_i \ln \gamma_i$$

OBRAZAC: $v = \sum x_i \bar{v}_i$

$$h = \sum x_i \bar{h}_i$$

$$s^{\mathrm{M}} = \sum x_i s_i^{\mathrm{M}}$$

Logaritam aktivnosti i logaritam koeficijenta aktivnosti su PMV