Ravnoteža kapljevina-krutina

Ravnoteža kapljevina-krutina

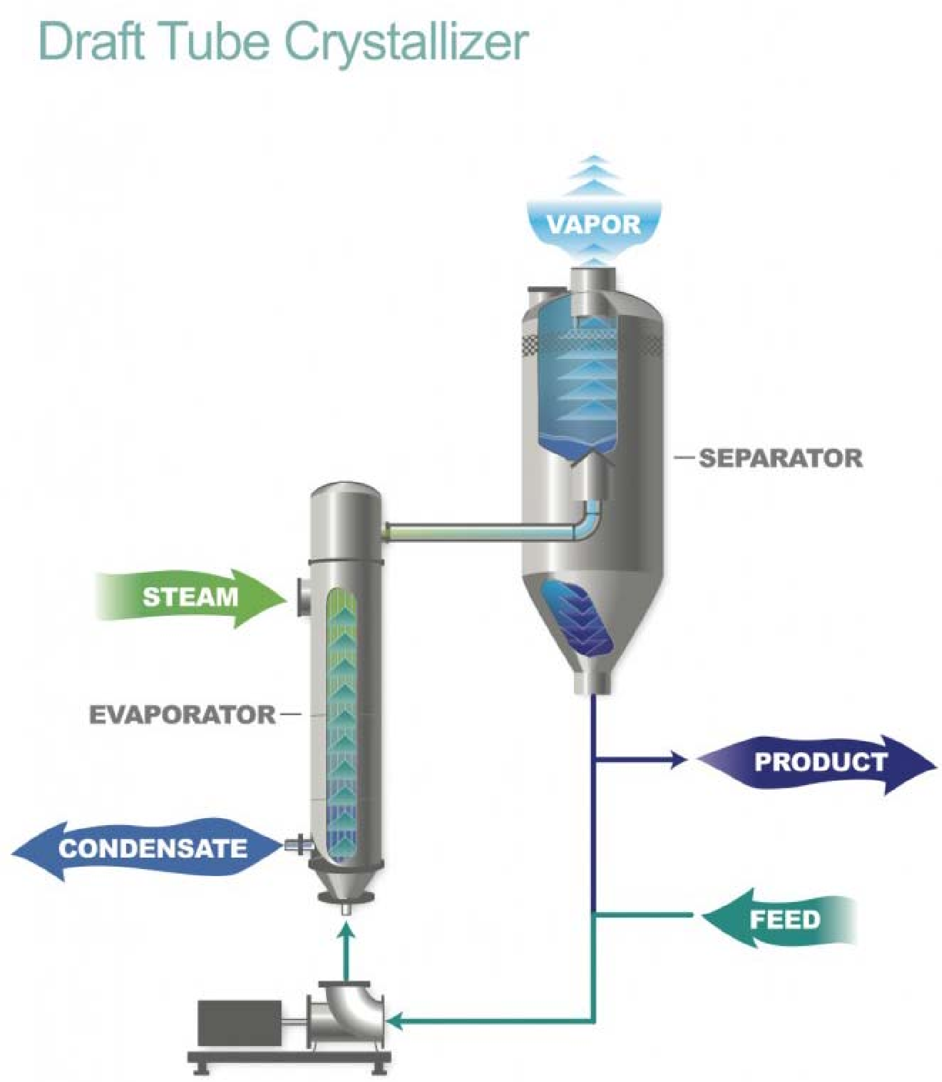
Fazna ravnoteža

Nema kemijskih ili
elektrokemijskih procesa

Industrijska praksa

Kristalizacija

Metalurški procesi



Uvjeti fazne ravnoteže

Prvi zakon termodinamike – bilančne jednadžbe

$$\sum_{i=1}^{nk} n_i^{\mathrm{F}} = \sum_{i=1}^{nk} n_i^{\mathrm{L}} + \sum_{i=1}^{nk} n_i^{\mathrm{S}}$$

Ukupna bilanca tvari

$$n^{\mathrm{F}} z_i^{\mathrm{F}} = n^{\mathrm{L}} x_i^{\mathrm{L}} + n^{\mathrm{S}} x_i^{\mathrm{S}}$$

Bilanca po komponentama

$$\sum_{i=1}^{nk} x_i^{\mathrm{L}} = 1 \qquad \sum_{i=1}^{nk} x_i^{\mathrm{S}} = 1$$

Bilanca po fazama

$$H^{\mathrm{F}} = H^{\mathrm{S}} + H^{\mathrm{L}}$$

Bilanca energije za izolirani sustav

Uvjeti fazne ravnoteže

Drugi zakon termodinamike

$S = \max.$ $dS = 0$ Izolirani sustav

Ekvivalentni uvjeti za dvofazne, višekomponentne sustave

$$T^{\mathrm{L}} = T^{\mathrm{S}}$$

$$p^{\mathrm{L}} = p^{\mathrm{S}}$$

$$\mu_i^{\mathrm{L}} = \mu_i^{\mathrm{S}}$$

Jednadžba fazne ravnoteže

$$\mu_i^{\mathrm{L}} = \mu_i^{\mathrm{S}}$$

Jednakost kemijskih potencijala

$$\left(\mu_i^{\mathrm{L}} - \mu_i^{\mathrm{S}}\right)_T = RT \ln \frac{\hat{f}_i^{\mathrm{L}}}{\hat{f}_i^{\mathrm{S}}} = 0$$

Preko parcijalnih fugacitivnosti

$$\hat{f}_i^{\mathrm{L}} = \hat{f}_i^{\mathrm{S}}$$

Jednakost parcijalnih fugacitivnosti

$$a_i = \frac{\hat{f}_i^{\mathrm{L}}}{f_i^{\mathrm{L}\circ}} \quad a_i = \frac{\hat{f}_i^{\mathrm{S}}}{f_i^{\mathrm{S}\circ}}$$

Uvođenje aktivnosti

$$a_i = \gamma_i x_i$$

Uvođenje koeficijenta aktivnosti

$$x_i^{\mathrm{L}} \gamma_i^{\mathrm{L}} f_i^{\mathrm{L}\circ} = x_i^{\mathrm{S}} \gamma_i^{\mathrm{S}} f_i^{\mathrm{S}\circ}$$

Ravnotežna jednadžba

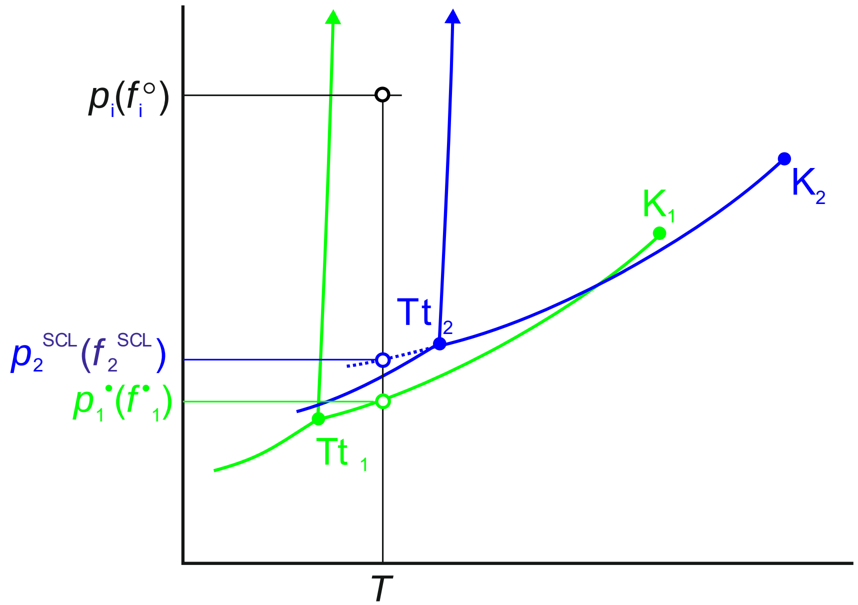
Jednadžba fazne ravnoteže

NA STRANI KAPLJEVITE FAZE

Za komponentu koja pri temperaturi i tlaku sustava može postojati kao kapljevina (otapalo)

$$f_i^{L\circ} = f_i^{\bullet} \exp\left[\int_{p_i^{\bullet}}^{p} \frac{v_i^L}{RT} dp\right]$$

$$f_i^{\bullet} = \varphi_i^{\bullet} p_i^{\bullet} \qquad \varphi_i^{\bullet} = 1$$



Standardna fugacitivnost (čiste) kapljevine

Potrebno:
Ravnotežni tlak para
Molarni volumen kapljevine
Jednadžba stanja ?!

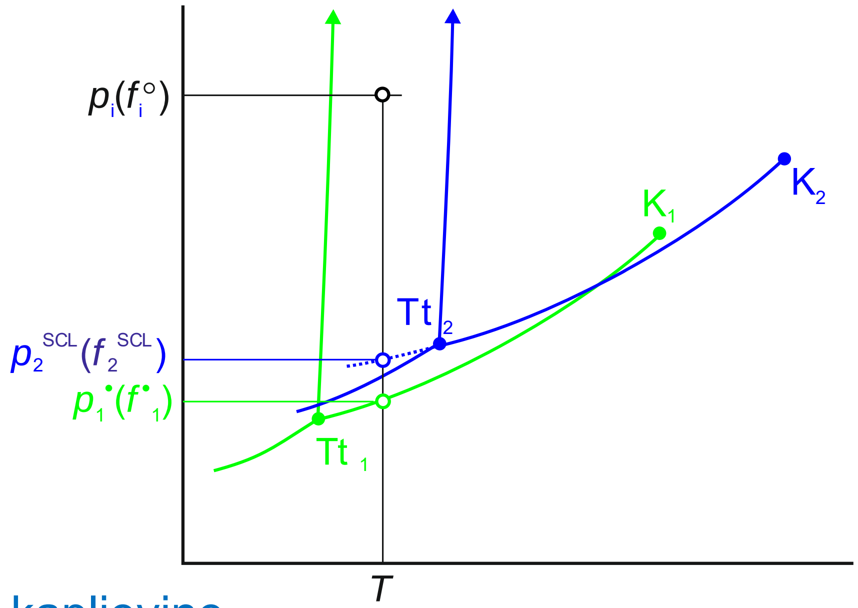
Jednadžba fazne ravnoteže

NA STRANI KAPLJEVITE FAZE

Za komponentu koja pri temperaturi i tlaku sustava ne može postojati kao kapljevina (otopljena krutina)

$$f_i^{\mathrm{SCL}\,\circ} = f_i^{\bullet} \exp\left[\int_{p_i^{\bullet}}^{p} \frac{v_i^{\mathrm{L}}}{RT}\, dp\right]$$

$$f_i^{\bullet} = \varphi_i^{\bullet} p_i^{\bullet} \qquad \varphi_{\mathrm{i}}^{\bullet} = 1$$



Standardna fugacitivnost (čiste) pothlađene kapljevine (sub-cooled, SCL)

Potrebno:

Hipotetski ravnotežni tlak para

Hipotetski molarni volumen kapljevine

Jednadžba stanja ?!

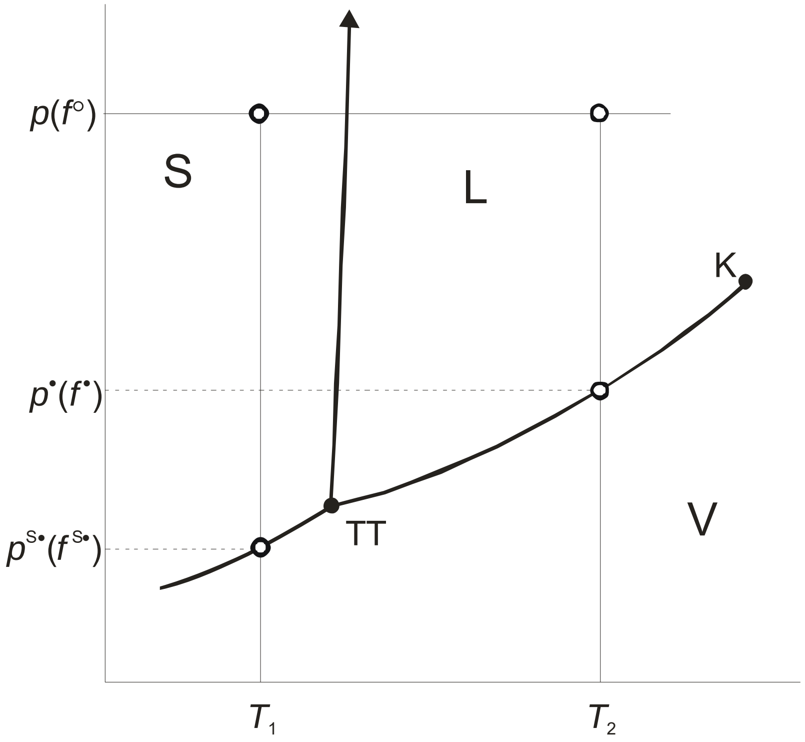
Jednadžba fazne ravnoteže

NA STRANI ČVRSTE FAZE

Za komponentu koja pri temperaturi i tlaku sustava postoji kao krutina (neotopljeni kristali)

$$f_i^{S\circ} = f_i^{\bullet} \exp\left[\int_{p_i^{\bullet}}^{p} \frac{v_i^{S}}{RT} dp \right]$$

$$f_i^{\bullet} = \varphi_i^{\bullet} p_i^{S\bullet} \qquad \varphi_i^{\bullet} = 1$$



Standardna fugacitivnost (čiste) krutine

Potrebno:
Ravnotežni tlak para sublimacije ?
Molarni volumen krutine
Jednadžba stanja ?!

https://www.youtube.com/watch?v=jX9pskbKSw0

https://www.youtube.com/watch?v=A2qBnlxWhZQ

https://answers.yahoo.com/question/index?qid=20090322154450AAFeKHy

https://www.youtube.com/watch?v=TEIzO6tpSfQ

Jednadžba fazne ravnoteže

NA STRANI ČVRSTE FAZE

Za komponentu koja pri temperaturi i tlaku sustava postoji kao krutina (neotopljeni kristali)

$$\ln \frac{f_i^{S\circ}}{f_{tt,i}} = \int_{p_{tt,i}}^{p} \frac{v_i^{S}}{RT} dp + \int_{T_{tt,i}}^{T} \frac{h_i^{V,id} - h_i^{S}}{RT^2} dT$$

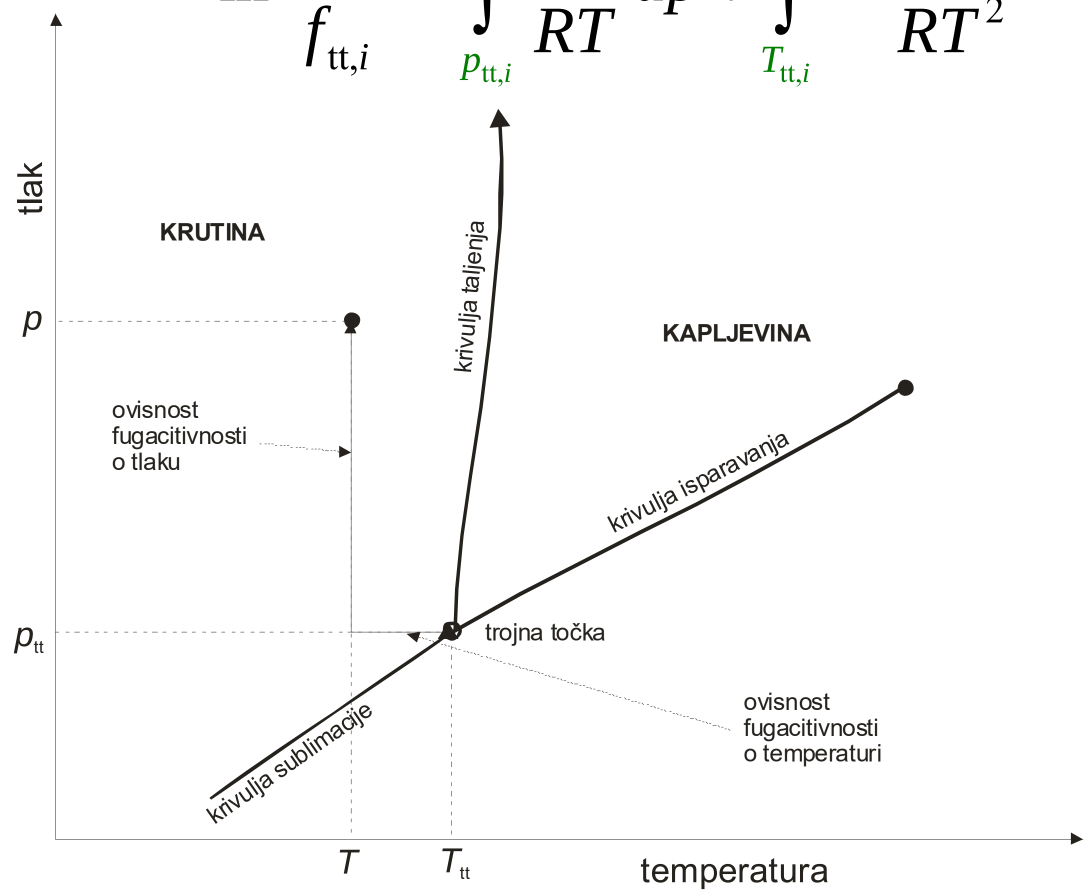
Standardna fugacitivnost (čiste) krutine

Potrebno:
Temperatura trojne točke
Tlak trojne točke
Fugacitivnost trojne točke = ?
Molarni volumen krutine
Entalpija sublimacije

$$h_i^{V,id} - h_i^{S} \approx \Delta h_i^{subl}$$

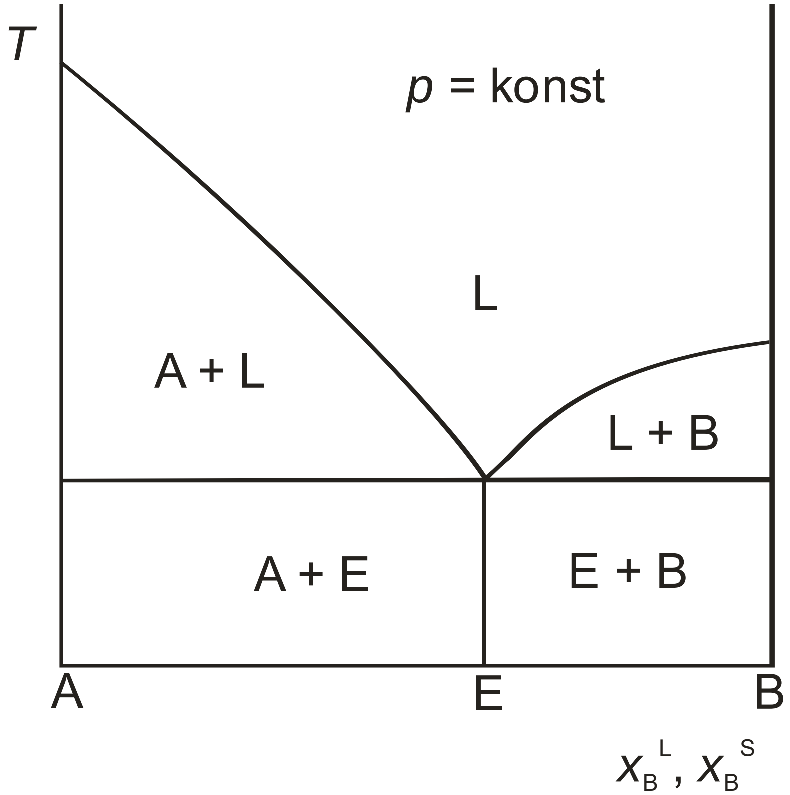
$$\Delta H_i^{subl} \approx \Delta H_i^{talj} + \Delta H_i^{isp}$$

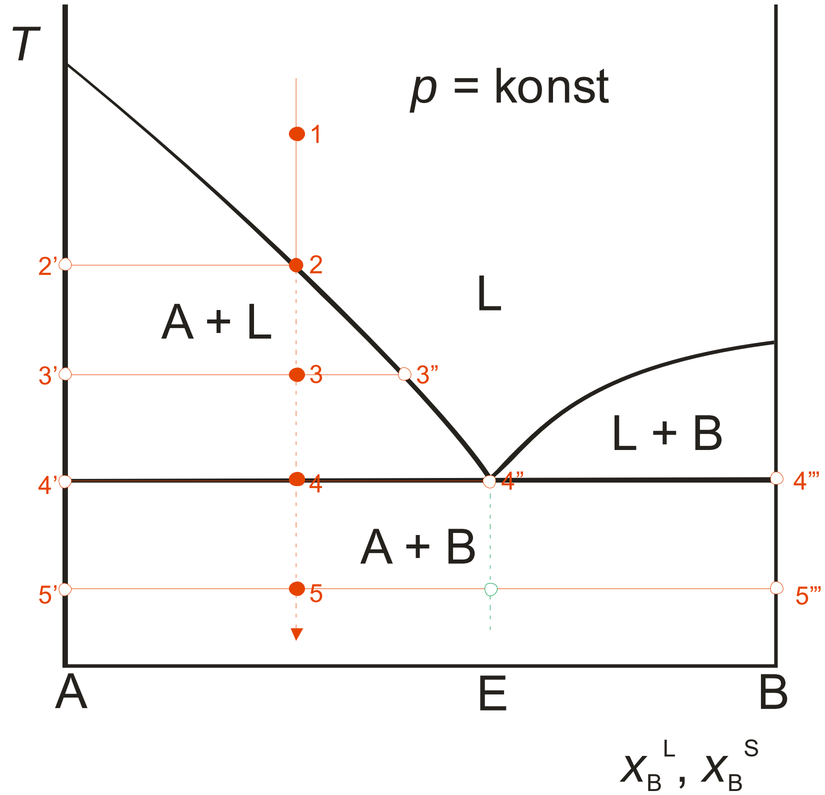
$$f_{tt,i} \approx p_{tt,i}$$



Fazni dijagrami

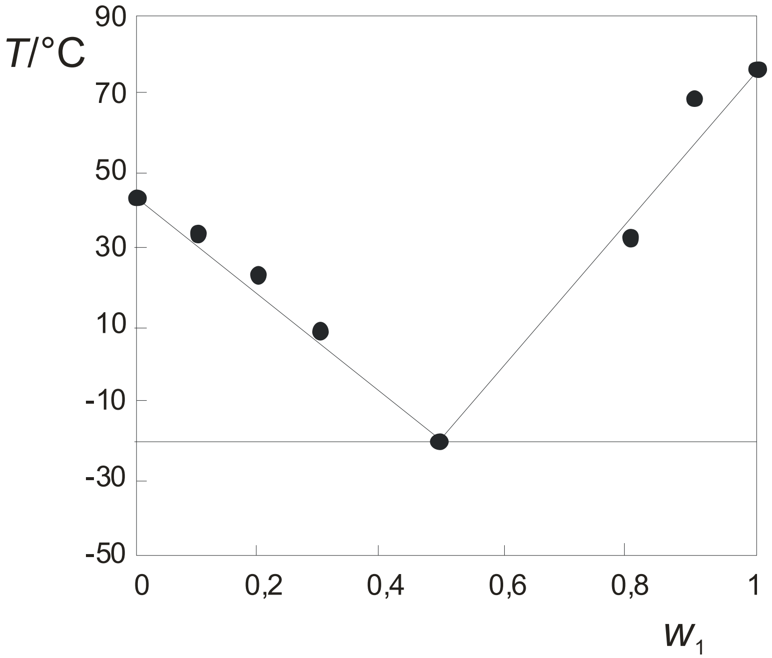
Potpuna nemješljivost





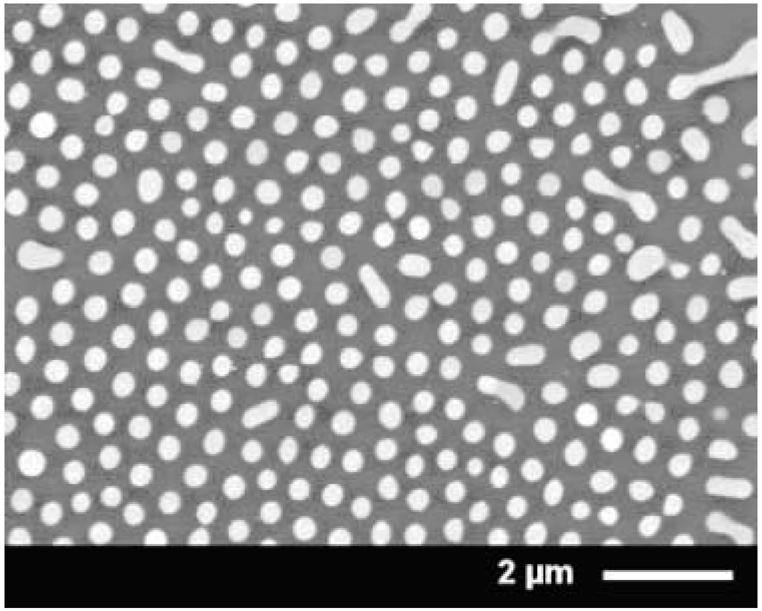
Fazni dijagrami

Potpuna nemješljivost



ibuprofen(1) – metil-nikotinat(2), 10325 Pa, US Patent 6841161

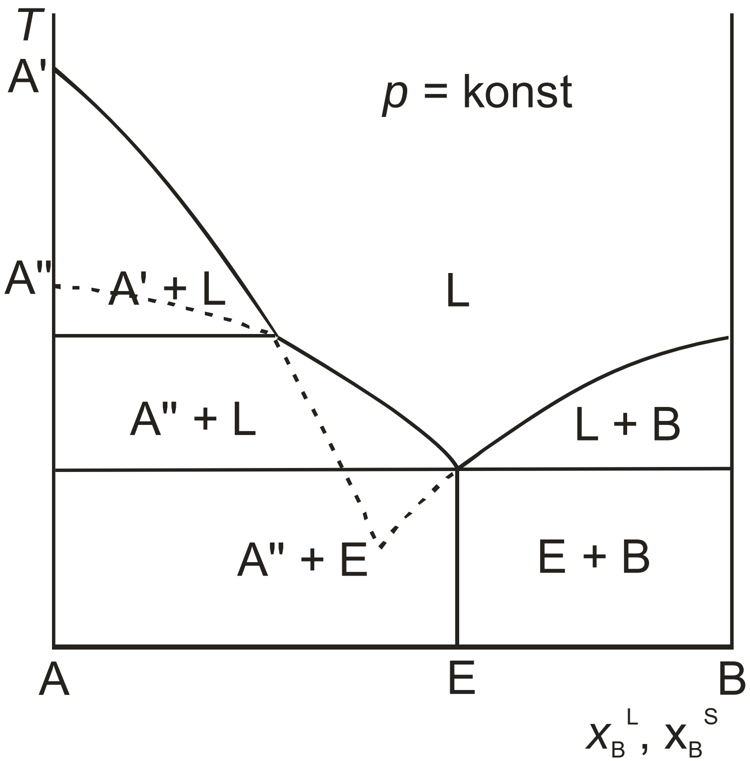
Eutektik

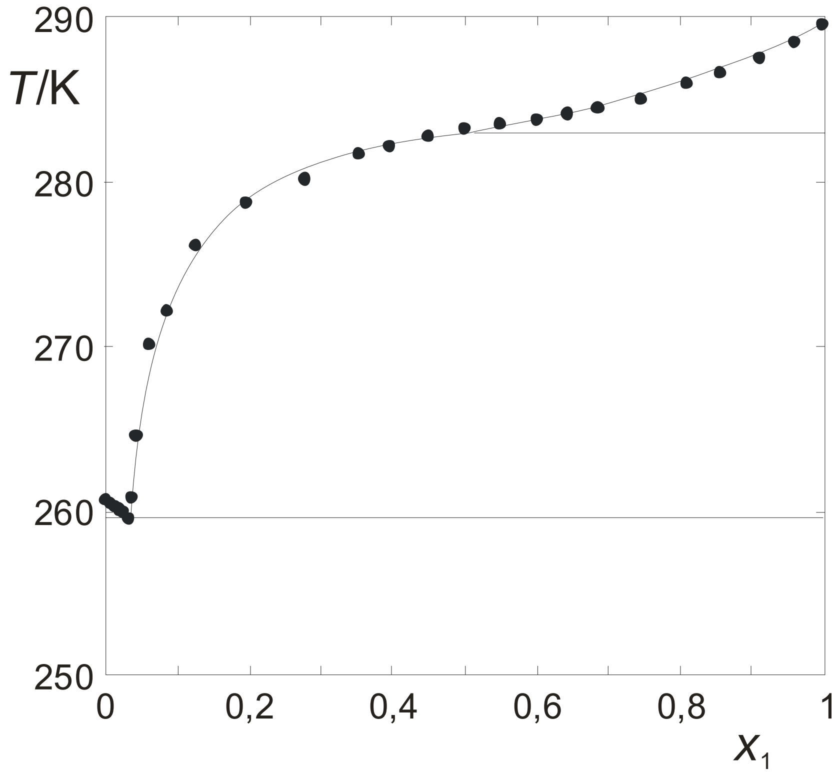


Nb (81.8%) – Si (18.2%) legura
Nb svijetla područja
Nb_3Si tamna područja

Fazni dijagrami

Potpuna nemješljivost, dvije kristalne modifikacije

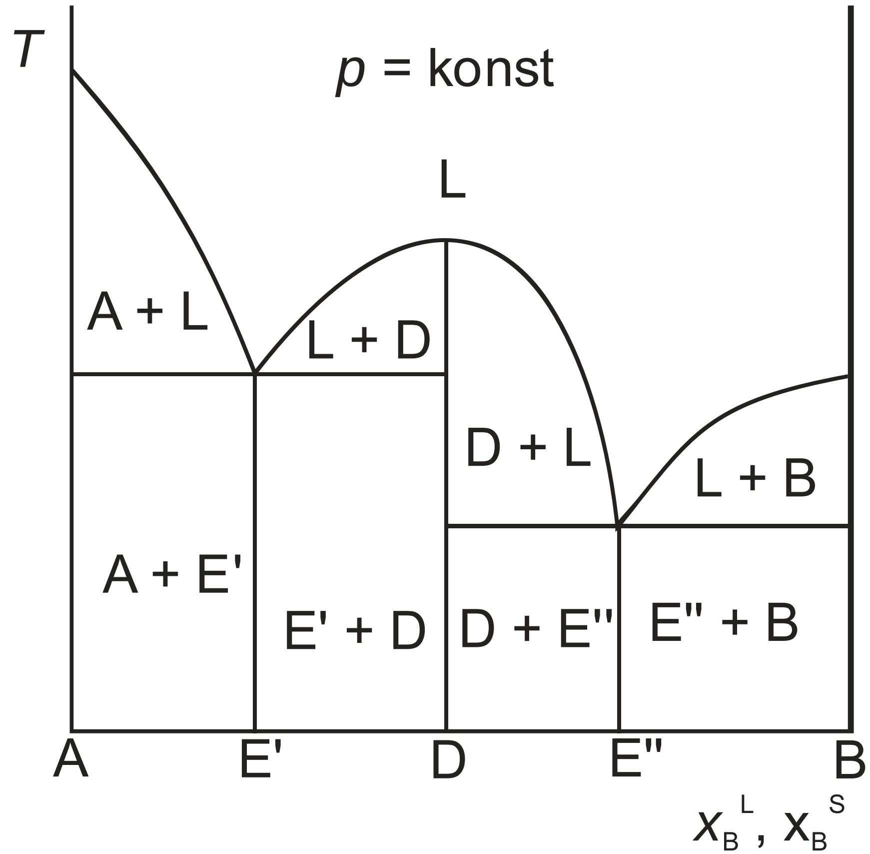


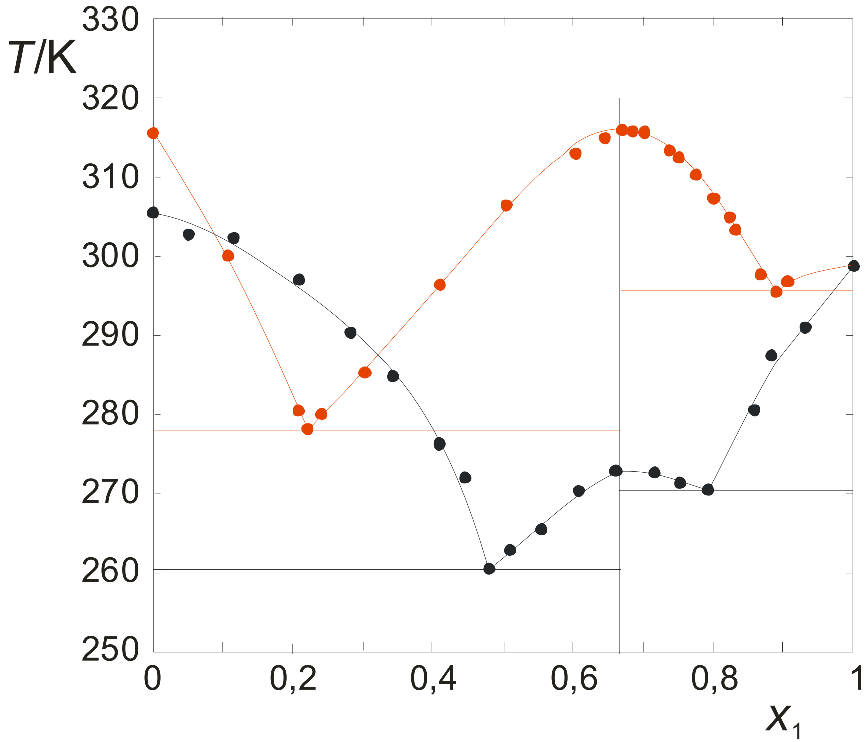


undekan-1-ol(1) i benzonitril(2), U. Domańska i M. Marciniak

Fazni dijagrami

Potpuna nemješljivost, međumolekulski spoj, dva eutektika

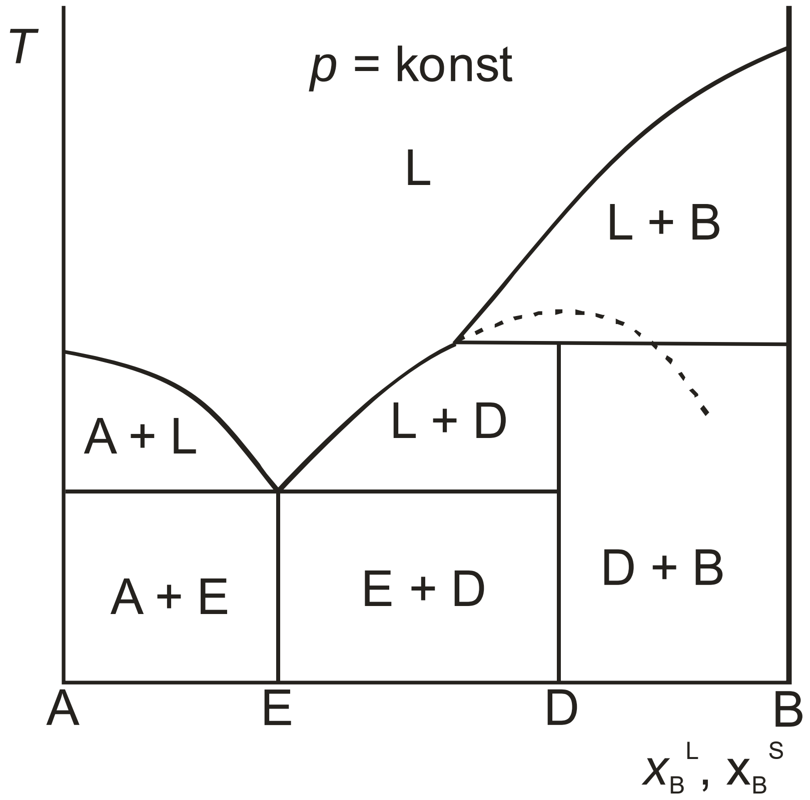


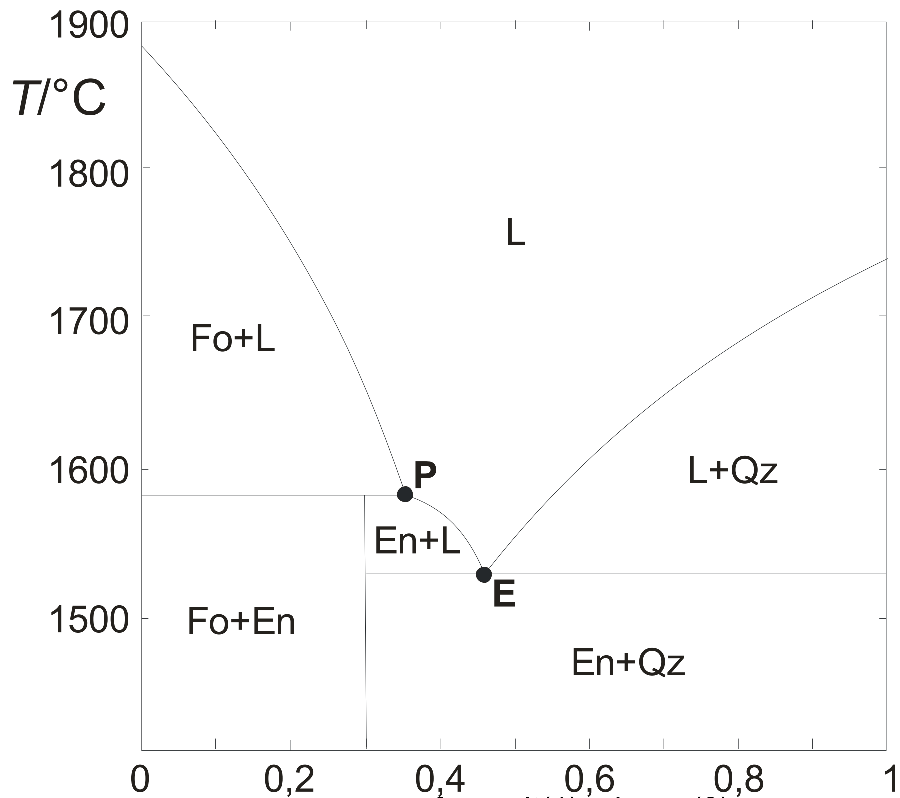


terc-butanol(1) – *m*-klorofenol(2)
terc-butanol(1) – *p*-klorofenol(2)
T.-M. Her i suradnici

Fazni dijagrami

Potpuna nemješljivost, međumolekulski spoj, eutektik, peritektik, peritektička transformacija (reakcija), nekongruentno taljenje

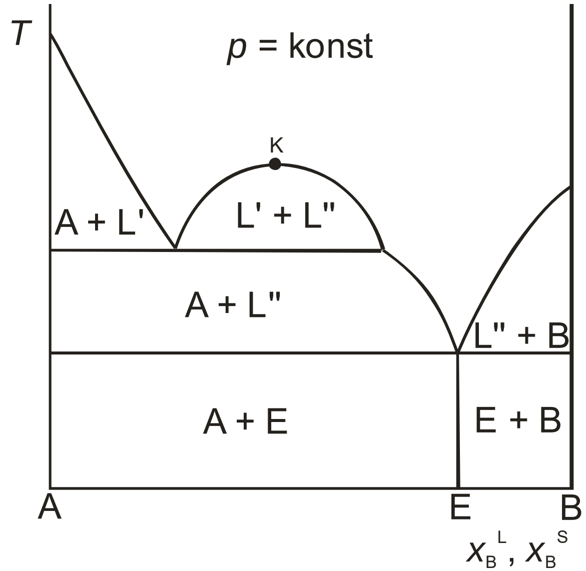


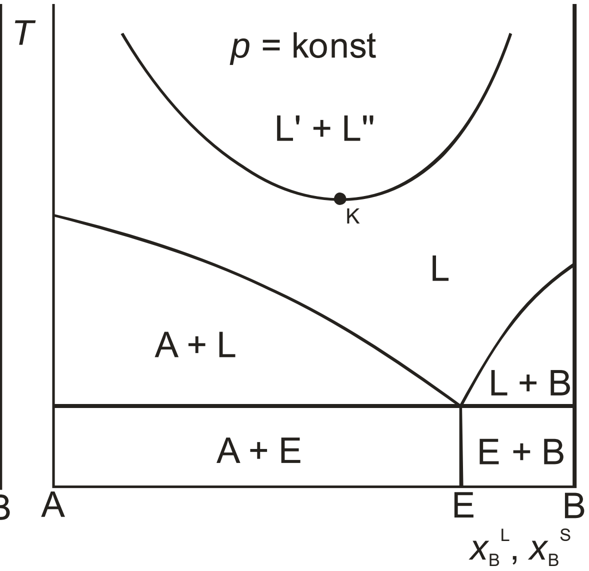


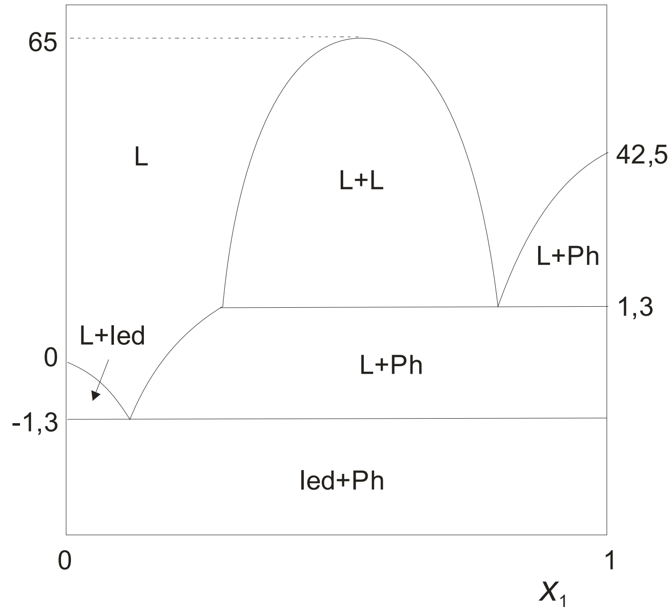
forsterit(1) – kvarc(2)
forsterit (Fo, Mg_2SiO_4)
enstatit (En, $MgSiO_3$)
kvarc (Qz, SiO_2)

Fazni dijagrami

Djelimična mješljivost u kapljevitoj fazi



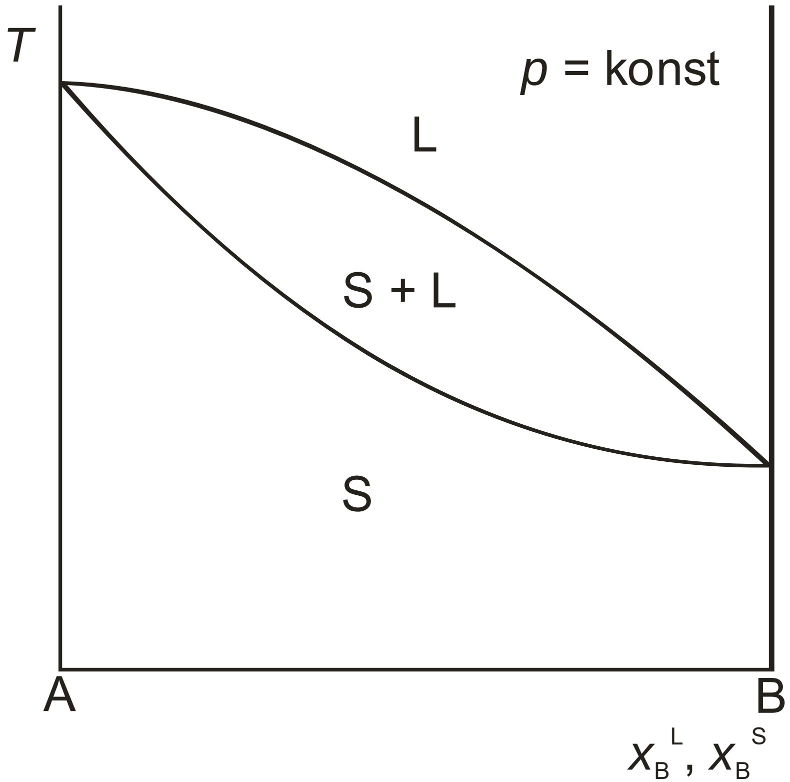


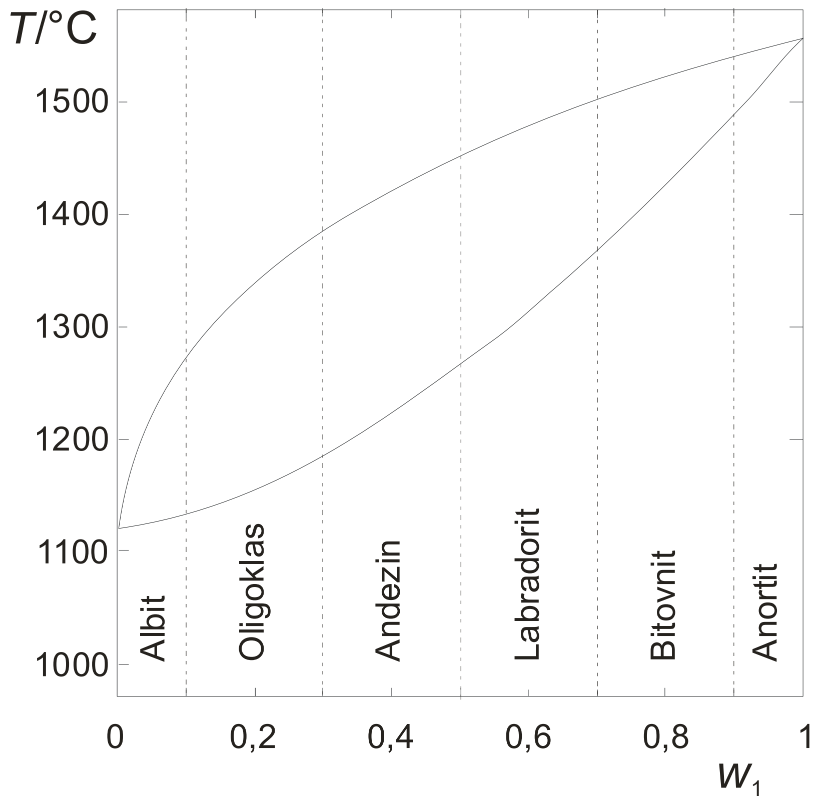


fenol(1) – voda(2)

Fazni dijagrami

Potpuna mješljivost u kapljevitoj i krutoj fazi



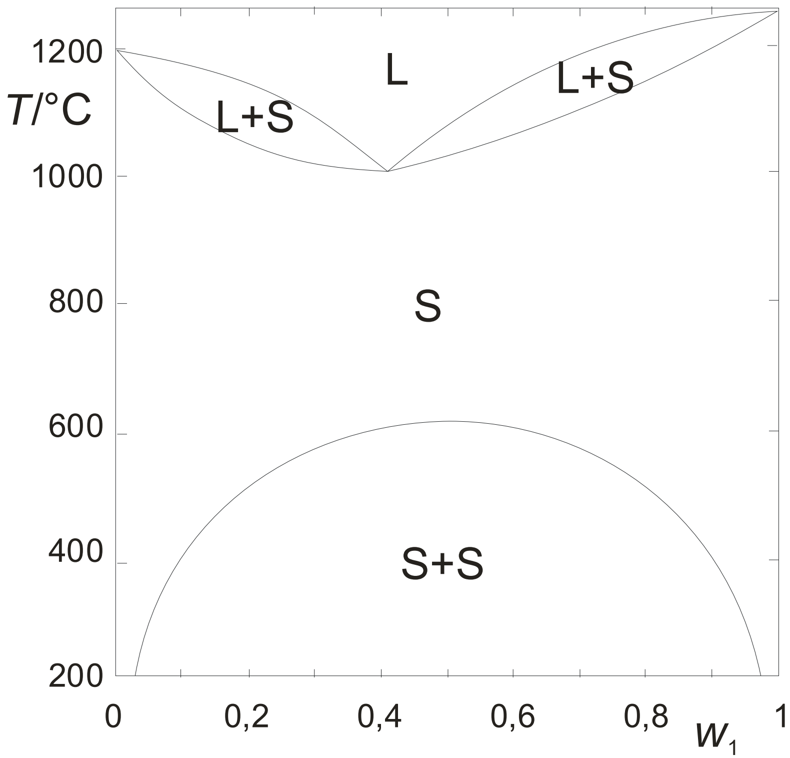


anortit($CaAl_2Si_2O_8$, 1) – albit($NaAlSi_3O_8$, 2)

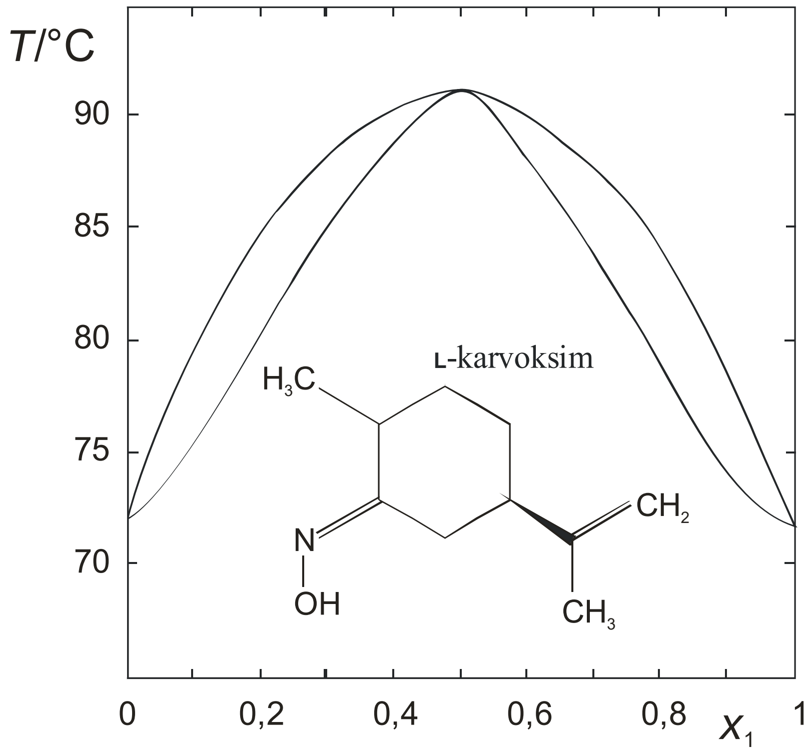
Fazni dijagrami

Potpuna mješljivost u kapljevitoj i krutoj fazi

Minimum ili maksimum tališta ("azeotropija")



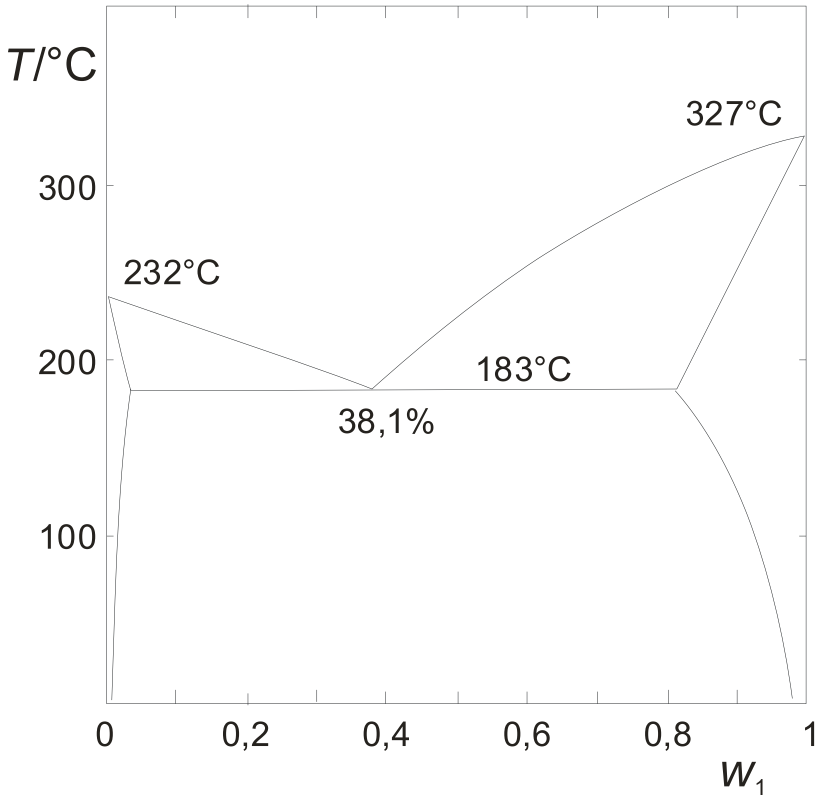
ortoklas($KAlSi_3O_8$, 1) – albit($NaAlSi_3O_8$, 2)



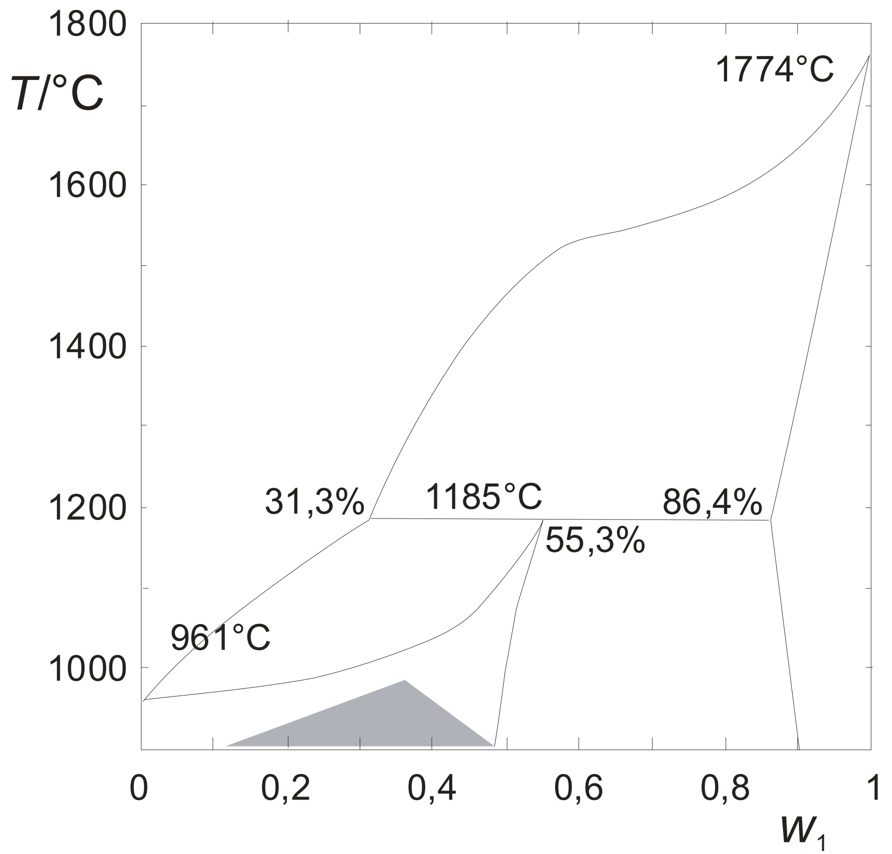
L-karvoksim(1) – **D**-karvoksim(1)

Fazni dijagrami

Djelimična mješljivost u krutoj fazi



olovo(1) – kositar(2)



platina(1) – srebro(2)

Topljivost krutina

Jednadžba ravnoteže $\hat{f}_i^{\,\mathrm{L}} = \hat{f}_i^{\,\mathrm{S}}$

$$\hat{f}_2^{\,\mathrm{L}} = \hat{f}_2^{\,\mathrm{S}}$$

Otopljena tvar

Standardno stanje čiste pothlađene kapljevine $\hat{f}_2^{\,\mathrm{L}} = x_2^{\mathrm{L}} \gamma_2^{\mathrm{L}} f_2^{\,\mathrm{SCL}\circ}$ $\hat{f}_2^{\,\mathrm{S}} = f_2^{\,\mathrm{S}}$ Krutina je čista tvar

$$x_2^{\mathrm{L}} = \frac{1}{\gamma_2^{\mathrm{L}}} \cdot \frac{f_2^{\,\mathrm{S}}}{f_2^{\,\mathrm{SCL}\circ}}$$

Jednadžba topljivosti

$$f_2^{\,\mathrm{SCL}\circ} = \varphi_2^{\mathrm{SCL}\bullet} p_2^{\mathrm{SCL}\bullet} \exp\left[\int_{p_2^{\mathrm{SCL}\bullet}}^{p} \frac{v_2^{\mathrm{L}}}{RT} dp \right]$$

Kapljevina

$$f_2^{\,\mathrm{S}} = \varphi_2^{\mathrm{S}\bullet} p_2^{\mathrm{S}\bullet} \exp\left[\int_{p_2^{\mathrm{S}\bullet}}^{p} \frac{v_2^{\mathrm{S}}}{RT} dp \right]$$

Krutina

Topljivost krutina

$$f_2^{\mathrm{SCL}\circ} = \varphi_2^{\mathrm{SCL}\bullet} p_2^{\mathrm{SCL}\bullet} \exp\left[\frac{v_2^{\mathrm{L}}\left(p - p_2^{\mathrm{SCL}\bullet}\right)}{RT}\right] \qquad f_2^{\mathrm{S}} = \varphi_2^{\mathrm{S}\bullet} p_2^{\mathrm{S}\bullet} \exp\left[\frac{v_2^{\mathrm{S}}\left(p - p_2^{\mathrm{S}\bullet}\right)}{RT}\right]$$

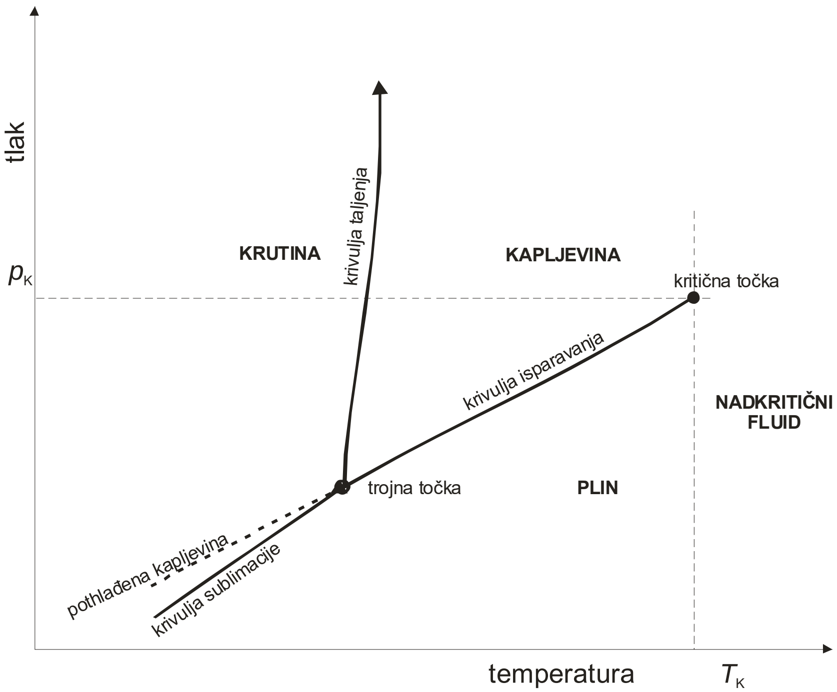
$PF_2^{\mathrm{SCL}} \rightarrow 1$ Zanemarivanje Poyntingova faktora $PF_2^{\mathrm{S}} \rightarrow 1$

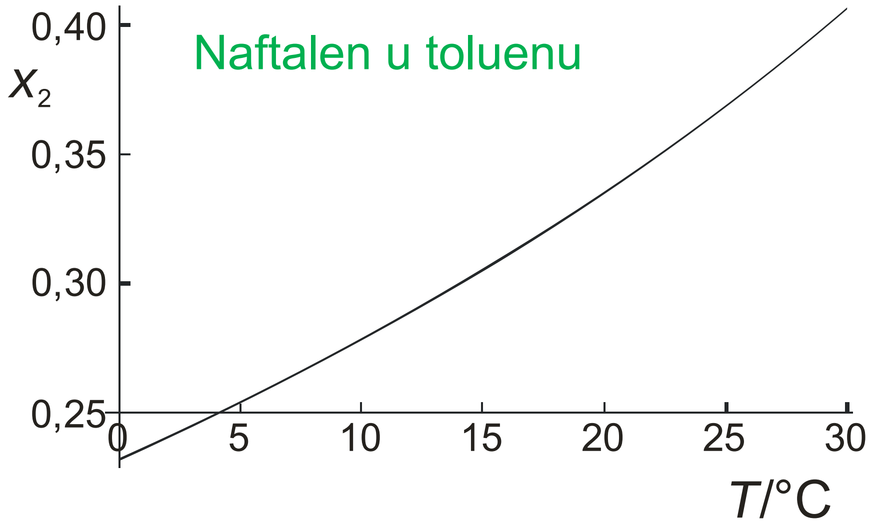
$\varphi_2^{\mathrm{S}\bullet} \rightarrow 1$ Idealna Parna faza $\varphi_2^{\mathrm{SCL}\bullet} \rightarrow 1$

$$x_2^{\mathrm{L}} = \frac{1}{\gamma_2^{\mathrm{L}}} \cdot \frac{p_2^{\mathrm{S}\bullet}}{p_2^{\mathrm{SCL}\bullet}}$$

Jednadžba topljivosti

Topljivost krutina





$$\log\left(p_2^{\mathrm{SCL}\bullet}/\mathrm{bar}\right) = 4{,}13555 - \frac{1733{,}710}{T + 201{,}859 - 273{,}15}$$

$$\log\left(p_2^{\mathrm{S}\bullet}/\mathrm{bar}\right) = 8{,}583 - \frac{3733{,}9}{T}$$

Topljivost krutina

$$x_2^{\mathrm{L}} = \frac{1}{\gamma_2^{\mathrm{L}}} \cdot \frac{f_2^{\mathrm{S}}}{f_2^{\mathrm{SCL}\circ}}$$

Jednadžba topljivosti

$$d \ln f = \frac{v}{RT} dp - \frac{h - h^{\circ}}{RT^2} dT$$

$$d \ln f_2^{\mathrm{S}} = \frac{v_2^{\mathrm{S}}}{RT} dp - \frac{h_2^{\mathrm{S}} - h_2^{\circ}}{RT^2} dT$$ Krutina

$$d \ln f_2^{\mathrm{SCL}\circ} = \frac{v_2^{\mathrm{SCL}\circ}}{RT} dp - \frac{h_2^{\mathrm{SCL}\circ} - h_2^{\circ}}{RT^2} dT$$ Pothlađena kapljevina

$$d \ln \frac{f_2^{\mathrm{S}}}{f_2^{\mathrm{SCL}\circ}} = \frac{h_2^{\mathrm{SCL}\circ} - h_2^{\mathrm{S}}}{RT^2} dT - \frac{v_2^{\mathrm{SCL}\circ} - v_2^{\mathrm{S}}}{RT} dp$$

Molarna entalpija taljenja

Molarni volumen taljenja

Topljivost krutina

$$h_2^{\mathrm{SCL}\circ} - h_2^{\mathrm{S}} \approx \Delta h_{2,\mathrm{tt}}^{\mathrm{talj}} + \Delta c_{p2,\mathrm{tt}}^{\mathrm{talj}} \left(T - T_{\mathrm{tt}}\right)$$

$$d\ln\frac{f_2^{\mathrm{S}}}{f_2^{\mathrm{SCL}\circ}} = \frac{\Delta h_{2,\mathrm{tt}}^{\mathrm{talj}} + \Delta c_{p2,\mathrm{tt}}^{\mathrm{talj}}\left(T - T_{\mathrm{tt}}\right)}{RT^2}dT - \frac{\Delta v_2^{\mathrm{talj}}}{RT}dp$$

Nakon integriranja:

$$\ln\frac{f_2^{\mathrm{S}}}{f_2^{\mathrm{SCL}\circ}} = \frac{\Delta h_{2,\mathrm{tt}}^{\mathrm{talj}}}{R}\left(\frac{1}{T_{\mathrm{tt}}} - \frac{1}{T}\right) - \frac{\Delta c_{p2,\mathrm{tt}}^{\mathrm{talj}}}{R}\left(\ln\frac{T_{\mathrm{tt}}}{T} - \frac{T_{\mathrm{tt}}}{T} + 1\right) - \frac{\Delta v_2^{\mathrm{talj}}}{RT}\left(p - p_{\mathrm{tt}}\right)$$

$$x_2^{\mathrm{L}} = \frac{1}{\gamma_2^{\mathrm{L}}}\cdot\frac{\Delta h_{2,\mathrm{tt}}^{\mathrm{talj}}}{R}\left(\frac{1}{T_{\mathrm{tt}}} - \frac{1}{T}\right) - \frac{\Delta c_{p2,\mathrm{tt}}^{\mathrm{talj}}}{R}\left(\ln\frac{T_{\mathrm{tt}}}{T} - \frac{T_{\mathrm{tt}}}{T} + 1\right) - \frac{\Delta v_2^{\mathrm{talj}}}{RT}\left(p - p_{\mathrm{tt}}\right)$$

$$\frac{\Delta v_2^{\mathrm{talj}}}{RT}\left(p - p_{\mathrm{tt}}\right) \approx 0$$

$$\Delta c_{p2,\mathrm{tt}}^{\mathrm{talj}} \approx 0$$

Potrebno poznavati:

- model koeficijenta aktivnosti
- trojnu točku (tlak i temperaturu)
- entalpiju taljenja (Δ) u trojnoj točki
- toplinski kapacitet taljenja (Δ) u trojnoj točki
- volumen taljenja (Δ) u trojnoj točki

Topljivost krutina

Potrebno poznavati:
- model koeficijenta aktivnosti
- trojnu točku (tlak i temperaturu)
- entalpiju taljenja (Δ) u trojnoj točki

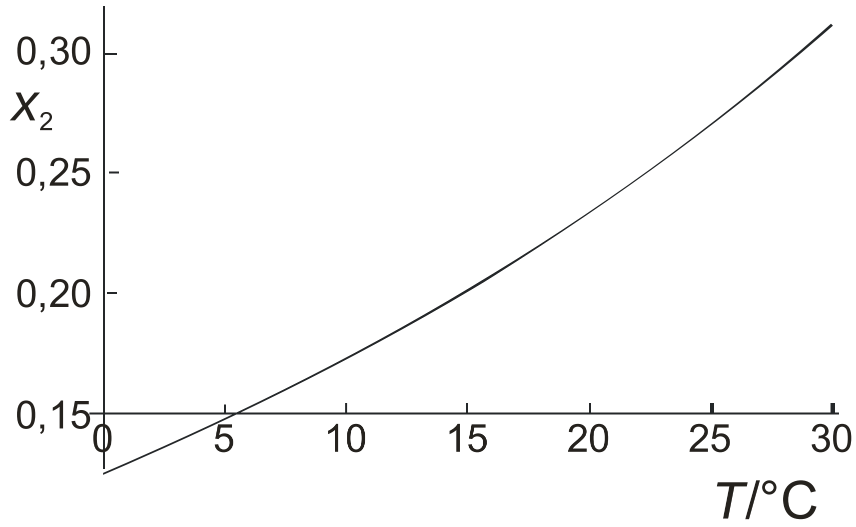
$$x_2 = \frac{1}{\gamma_2}\exp\left[\frac{\Delta h_{2,\mathrm{tt}}^{\mathrm{talj}}}{R}\left(\frac{1}{T_{\mathrm{tt}}} - \frac{1}{T}\right)\right]$$

Potrebno poznavati:
- talište pri atmosferskom tlaku
- entalpiju taljenja (Δ) pri atm. tlaku

$$x_2 = \exp\left[\frac{\Delta h_2^{\mathrm{talj}}}{R}\left(\frac{1}{T^{\mathrm{talj}}} - \frac{1}{T}\right)\right]$$

Schröderova jednadžba (1893)
Za idealne otopine

Naftalen u toluenu
Model Scatchard-Hildebrand



$$x_2 = \exp\left[\frac{\Delta h_{2,\mathrm{tt}}^{\mathrm{talj}}}{R}\left(\frac{1}{T_{\mathrm{tt}}} - \frac{1}{T}\right) - \frac{v_2^{\mathrm{L}}}{RT}(\delta_1 - \delta_2)^2\left(1 + \frac{v_2^{\mathrm{L}}}{v_1^{\mathrm{L}}}\cdot\frac{x_2}{1-x_2}\right)^{-2}\right]$$

Ravnoteža taljenja

$$x_i^{\mathrm{L}}\gamma_i^{\mathrm{L}} f_i^{\mathrm{L}\circ} = x_i^{\mathrm{S}}\gamma_i^{\mathrm{S}} f_i^{\mathrm{S}\circ}$$

Ravnotežna jednadžba
za obje komponente

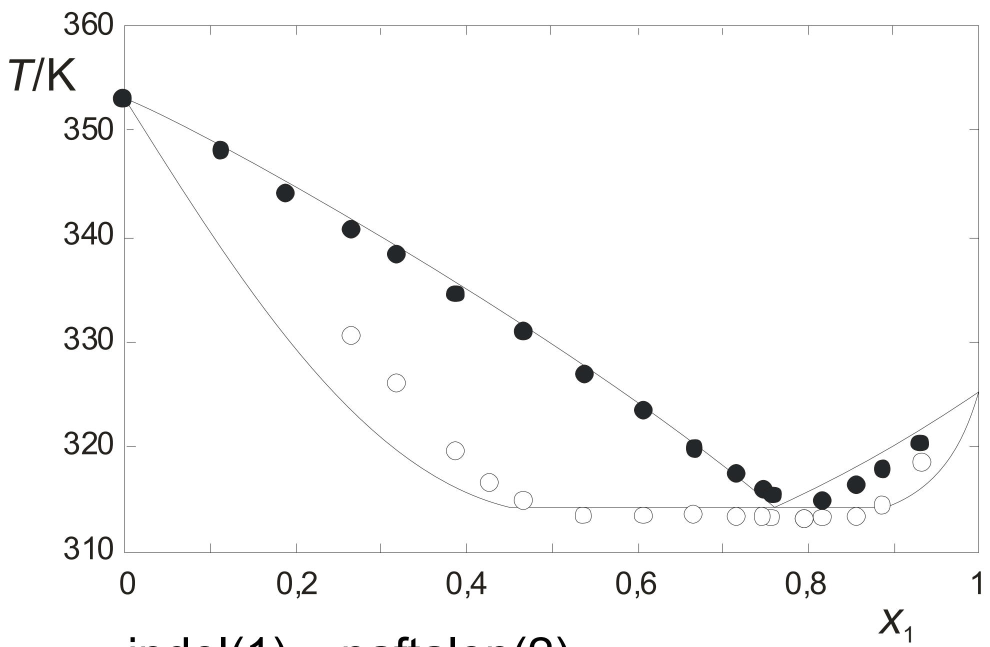
$$\ln\frac{x_i^{\mathrm{L}}\gamma_i^{\mathrm{L}}}{x_i^{\mathrm{S}}\gamma_i^{\mathrm{S}}} = \ln\frac{f_i^{\mathrm{S}\circ}}{f_i^{\mathrm{SCL}\circ}}$$

$$\ln\frac{f_i^{\mathrm{S}\circ}}{f_i^{\mathrm{SCL}\circ}} = \frac{\Delta h_{i,\mathrm{tt}}^{\mathrm{talj}}}{R}\left(\frac{1}{T_{i,\mathrm{tt}}}-\frac{1}{T}\right) - \frac{\Delta c_{pi,\mathrm{tt}}^{\mathrm{talj}}}{R}\left(\ln\frac{T_{i,\mathrm{tt}}}{T}-\frac{T_{i,\mathrm{tt}}}{T}+1\right) - \frac{\Delta v_i^{\mathrm{talj}}}{RT}\left(p-p_{i,\mathrm{tt}}\right)$$

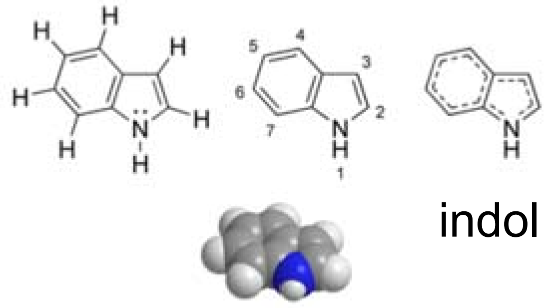
$$\ln\frac{\gamma_i^{\mathrm{L}}x_i^{\mathrm{L}}}{\gamma_i^{\mathrm{S}}x_i^{\mathrm{S}}} = \frac{\Delta h_i^{\mathrm{talj}}}{R}\left(\frac{1}{T_i^{\mathrm{talj}}}-\frac{1}{T}\right)$$

Jednadžba slična Schröderovoj
Vrijedi za neidealne otopine

Ravnoteža taljenja



indol(1) – naftalen(2)



Landolt-Börnstein, Vol. 6, Aufl., Bd.II/2c, Springer, Berlin, 1964.

Model Margules

$$\ln \frac{\gamma_1^L x_1^L}{\gamma_1^S x_1^S} = \frac{\Delta h_1^{talj}}{R}\left(\frac{1}{T_1^{talj}} - \frac{1}{T}\right)$$

$$\ln \frac{\gamma_2^L x_2^L}{\gamma_2^S x_2^S} = \frac{\Delta h_2^{talj}}{R}\left(\frac{1}{T_2^{talj}} - \frac{1}{T}\right)$$

$$x_1^L + x_2^L = 1$$

$$x_1^S + x_2^S = 1$$

Eutektički uvjeti

$$\ln \frac{\gamma_1^{L} x_1^{L}}{\gamma_1^{S} x_1^{S}} = \frac{\Delta h_1^{talj}}{R}\left(\frac{1}{T_1^{talj}} - \frac{1}{T}\right)$$

$$\ln \frac{\gamma_2^{L} x_2^{L}}{\gamma_2^{S} x_2^{S}} = \frac{\Delta h_i^{talj}}{R}\left(\frac{1}{T_2^{talj}} - \frac{1}{T}\right)$$

$$x_1^{L} = \exp\left[\frac{\Delta h_1^{talj}}{R}\left(\frac{1}{T_1^{talj}} - \frac{1}{T}\right)\right]$$

$$x_2^{L} = \exp\left[\frac{\Delta h_2^{talj}}{R}\left(\frac{1}{T_2^{talj}} - \frac{1}{T}\right)\right]$$

Schröderove jednadžbe

Potpuna nemješljivost u krutini

$$\ln\left(\gamma_1^{L} x_1^{L}\right) = \frac{\Delta h_1^{talj}}{R}\left(\frac{1}{T_1^{talj}} - \frac{1}{T}\right)$$

$$\ln\left(\gamma_2^{L} x_2^{L}\right) = \frac{\Delta h_2^{talj}}{R}\left(\frac{1}{T_2^{talj}} - \frac{1}{T}\right)$$

$$T = \left(\frac{1}{T_1^{talj}} - \frac{R \ln x_1^{L}}{\Delta h_1^{talj}}\right)^{-1}$$

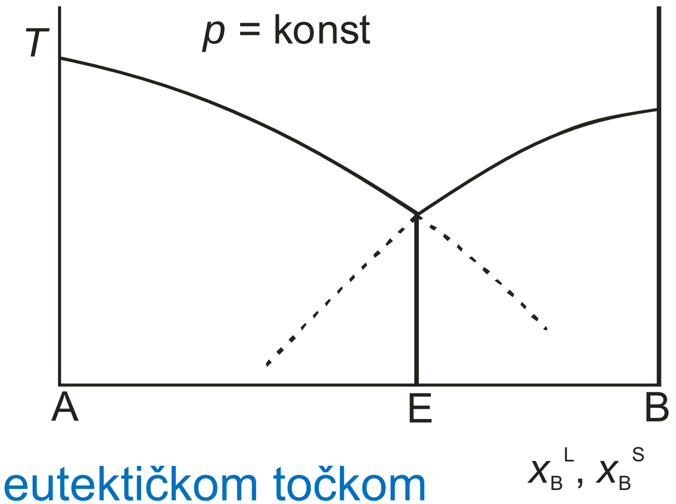
$$T = \left(\frac{1}{T_2^{talj}} - \frac{R \ln x_2^{L}}{\Delta h_2^{talj}}\right)^{-1}$$

Jednadžbe tališta u dvokomponentnom sustavu

Idealne otopine

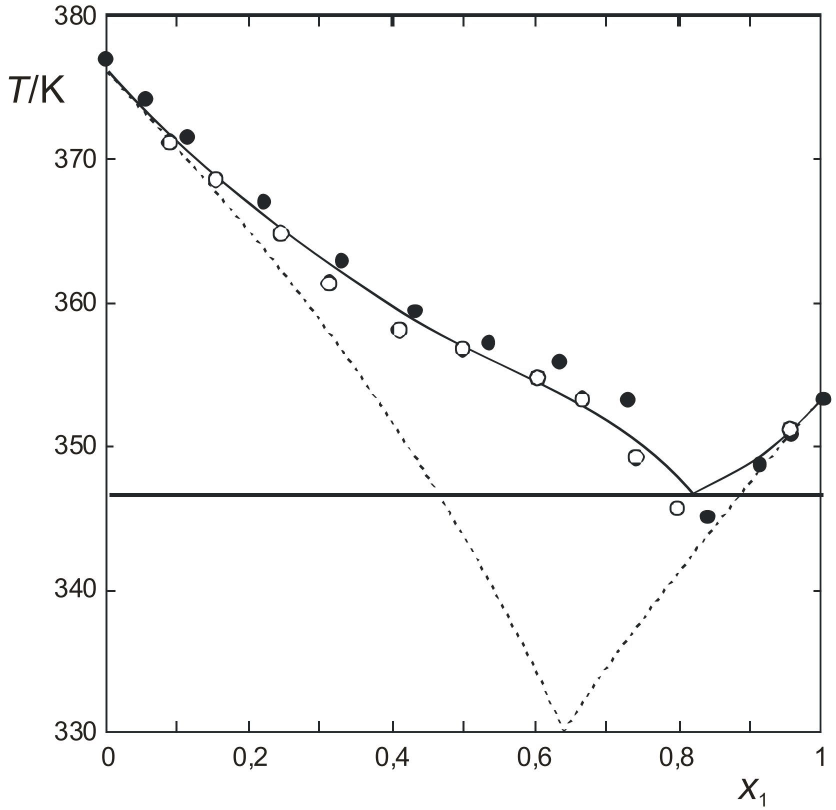
$$\ln x_1^{L} = \frac{\Delta h_1^{talj}}{R}\left(\frac{1}{T_1^{talj}} - \frac{1}{T}\right)$$

$$\ln x_1^{L} = \frac{\Delta h_i^{talj}}{R}\left(\frac{1}{T_2^{talj}} - \frac{1}{T}\right)$$



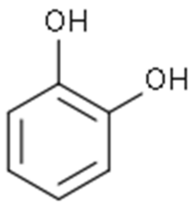
Dijagram s eutektičkom točkom

Eutektički uvjeti



naftalen(1) – katehol(2)

Landolt-Börnstein, Vol. 6, Aufl., Bd.II/2c, Springer, Berlin, 1964.



katehol

Jednadžbe tališta
u dvokomponentnom
sustavu

$$\ln\left(\gamma_1^{L} x_1^{L}\right) = \frac{\Delta h_1^{\text{talj}}}{R}\left(\frac{1}{T_1^{\text{talj}}} - \frac{1}{T}\right)$$

$$\ln\left(\gamma_2^{L} x_2^{L}\right) = \frac{\Delta h_2^{\text{talj}}}{R}\left(\frac{1}{T_2^{\text{talj}}} - \frac{1}{T}\right)$$

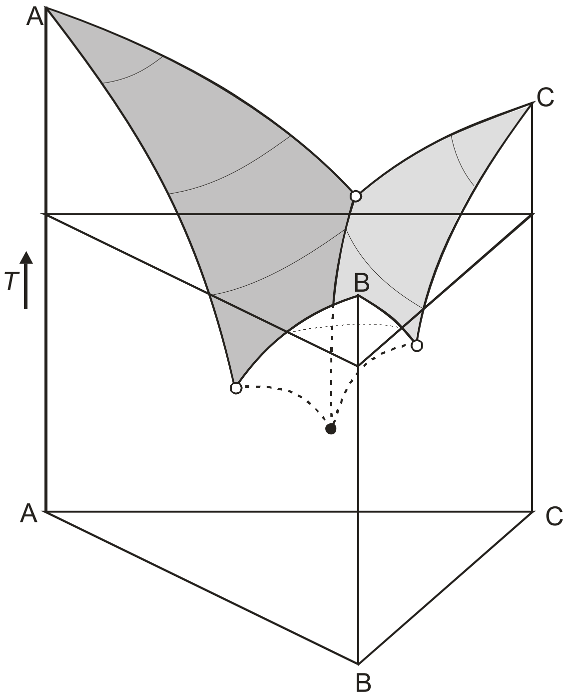
$$x_1^{L} + x_2^{L} = 1$$

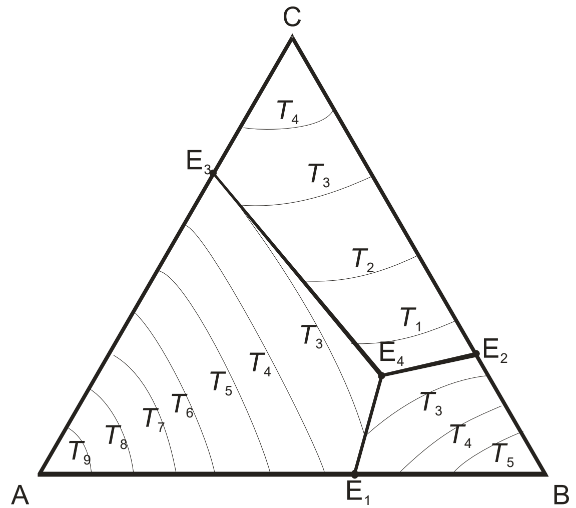
Model NRTL

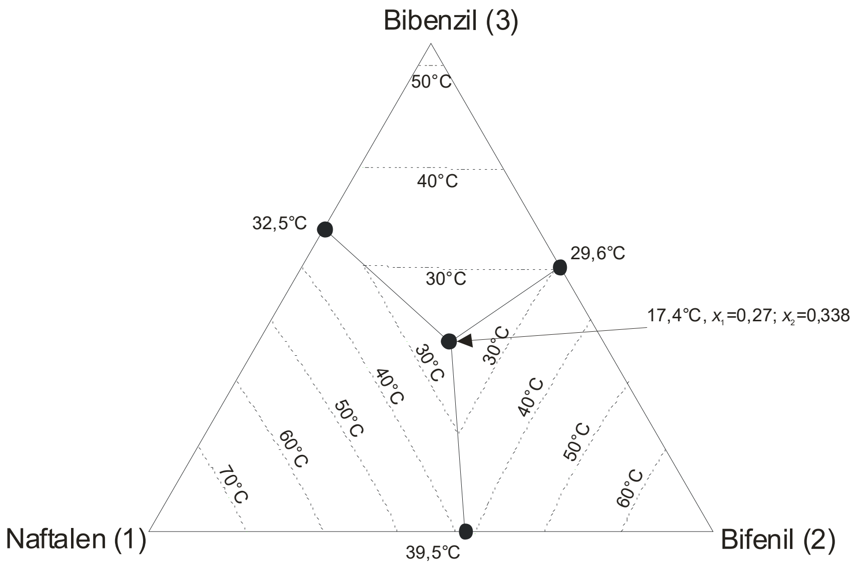
Eutektički uvjeti

Ternarni eutektik

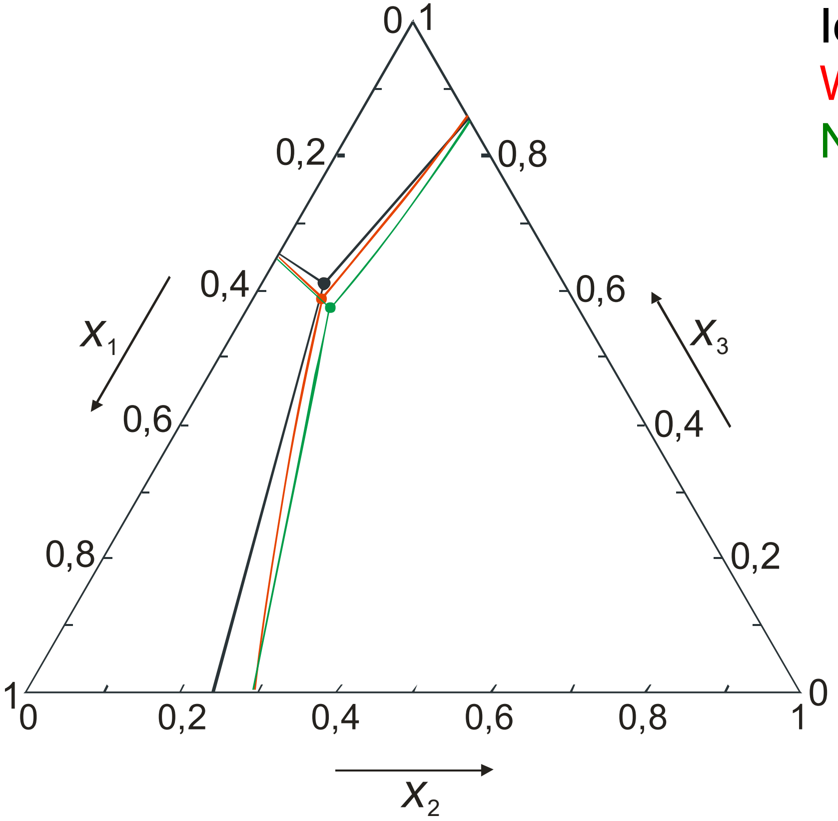
Eutektički kanal







Eutektički uvjeti



Idealna otopina
Wilson
NRTL

$$x_1 = \frac{1}{\gamma_1^{\mathrm{L}}(x_1, x_2)} \exp\left[\frac{\Delta h_1^{\mathrm{talj}}}{R}\left(\frac{1}{T_1^{\mathrm{talj}}} - \frac{1}{T^{\mathrm{e}}}\right)\right]$$

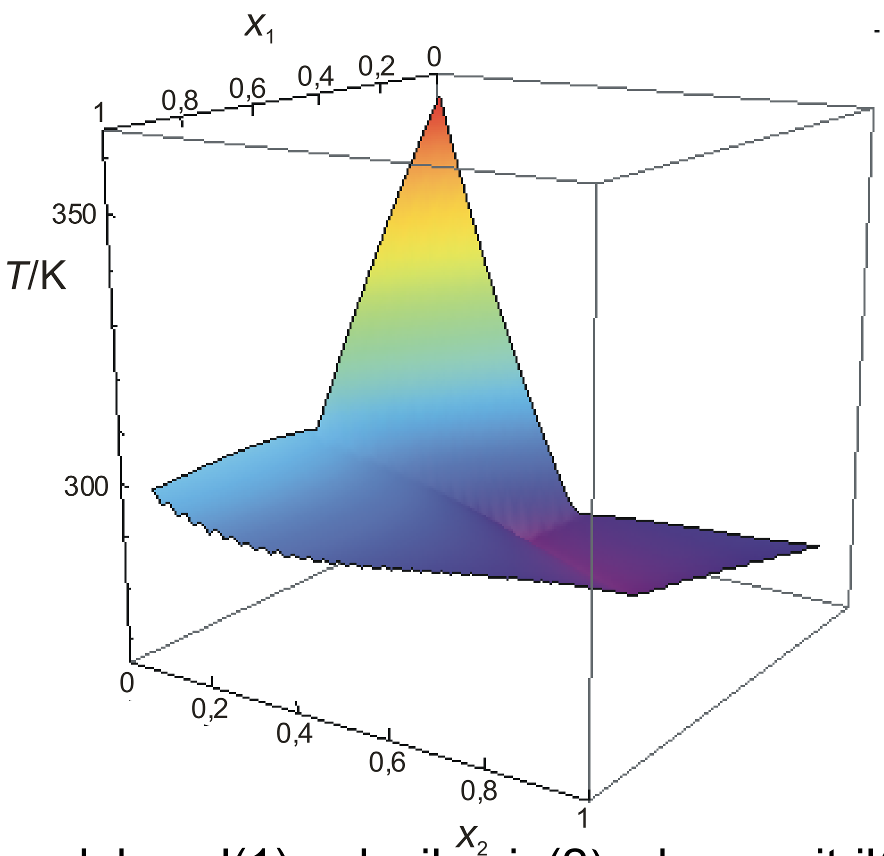
$$x_2 = \frac{1}{\gamma_2^{\mathrm{L}}(x_1, x_2)} \exp\left[\frac{\Delta h_2^{\mathrm{talj}}}{R}\left(\frac{1}{T_2^{\mathrm{talj}}} - \frac{1}{T^{\mathrm{e}}}\right)\right]$$

$$1 - x_1 - x_2 = \frac{1}{\gamma_3^{\mathrm{L}}(x_1, x_2)} \exp\left[\frac{\Delta h_3^{\mathrm{talj}}}{R}\left(\frac{1}{T_3^{\mathrm{talj}}} - \frac{1}{T^{\mathrm{e}}}\right)\right]$$

p-metoksifenol(1) – katehol(2) – *p*-krezol(3)

Ho-mu Lin, Yu-Hsing Chou, Fu-Li Wu, Ming-Jer Lee

Eutektički uvjeti

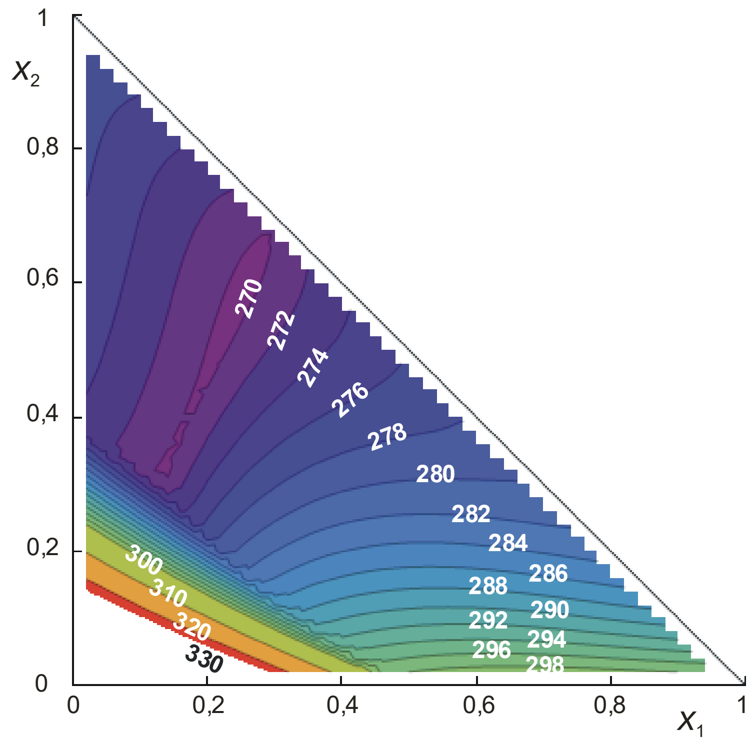


n-dekanol(1) – decilamin(2) – benzonitril(3)

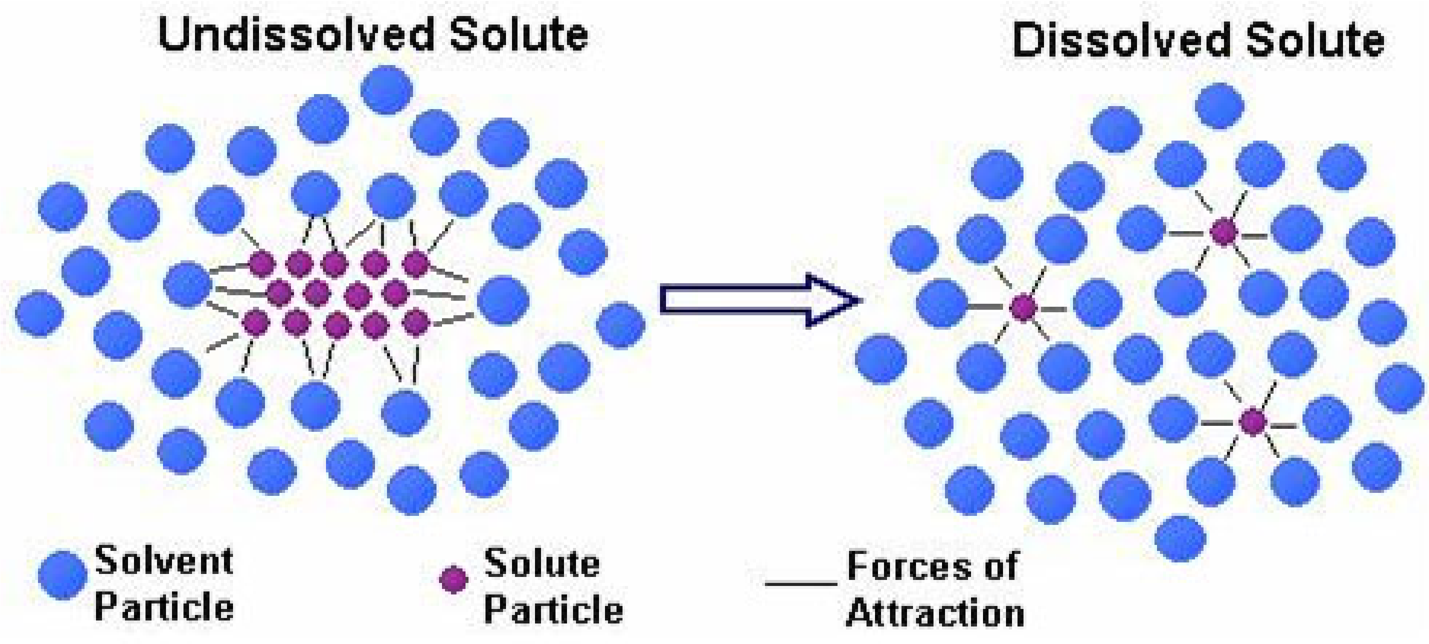
U. Domańska i M. Marciniak

$$x_i = \frac{1}{\gamma_i^{\mathrm{L}}} \exp\left[\frac{\Delta h_i^{\mathrm{talj}}}{R} \left(\frac{1}{T_i^{\mathrm{talj}}} - \frac{1}{T} \right) - \frac{\Delta c_{pi}^{\mathrm{talj}}}{R} \left(\ln \frac{T}{T_i^{\mathrm{talj}}} + \frac{T_i^{\mathrm{talj}}}{T} - 1 \right) \right]$$

$$T = \max\left(T_i\right)$$

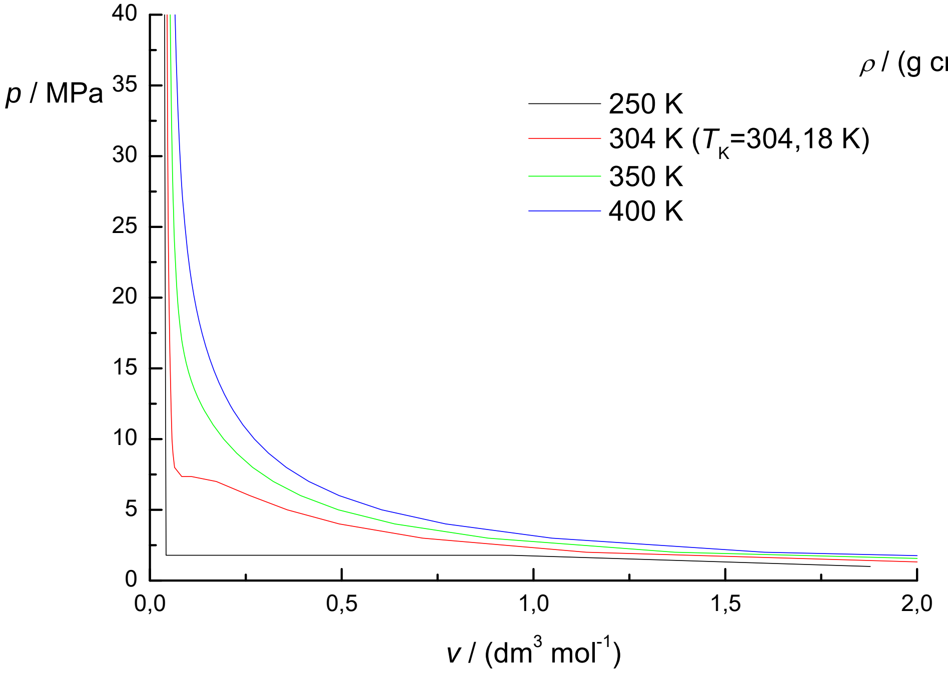


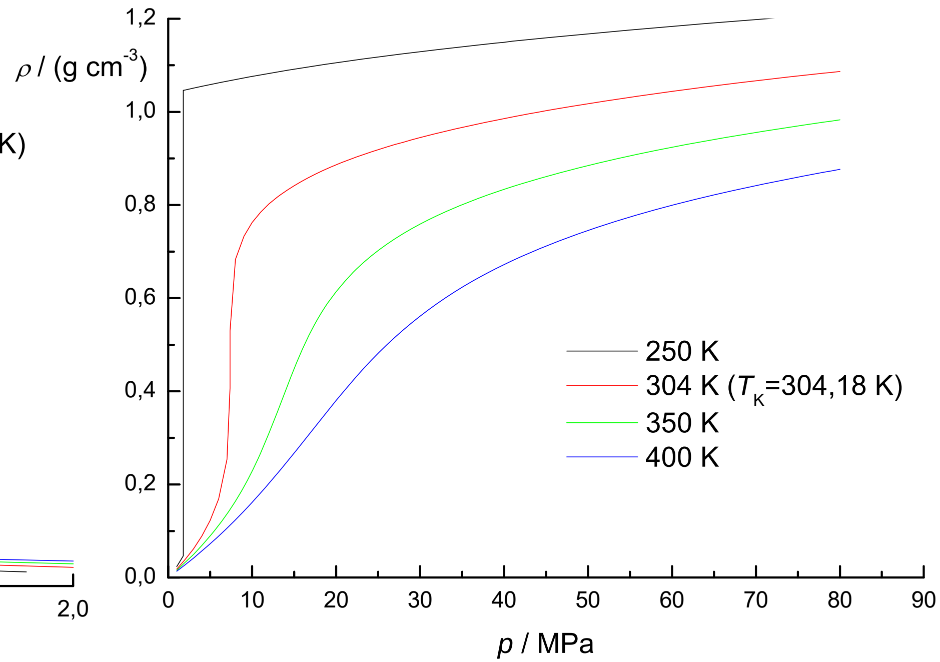
Ravnoteža plin-krutina

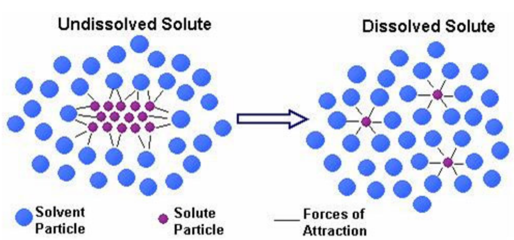


Ravnoteža plin-krutina

Nadkritični fluidi kao otapala







Velika gustoća – velika moć otapanja
Nema granice faza – bolja kinetika nego u kapljevinama
Niska temperatura – podobno za termolabilne ekstrakte
Laka *downstream* separacija
Nedostatak – slaba topljivost
Nedostatak – visoka cijena

Ravnoteža plin-krutina

Topljivost u nadkritičnom fluidu

$$\hat{f}_2^{\mathrm{SF}} = \hat{f}_2^{\mathrm{S}}$$

Jednadžba ravnoteže

Otopina $\hat{f}_2^{\mathrm{SF}} = y_2^{\mathrm{SF}} \hat{\varphi}_2^{\mathrm{SF}} p$

$\hat{f}_2^{\mathrm{S}} = f_2^{\mathrm{S}}$ Čista krutina

Topljivost krutine u plinu

$$y_2^{\mathrm{SF}} = \frac{1}{\hat{\varphi}_2^{\mathrm{SF}}} \cdot \frac{f_2^{\mathrm{S}}}{p}$$

$$f_2^{\mathrm{S}} = \varphi_2^{\bullet} p_2^{\bullet} \exp\left[\frac{v_2^{\mathrm{S}}\left(p - p_2^{\bullet}\right)}{RT}\right]$$

Fugacitivnost čiste krutine

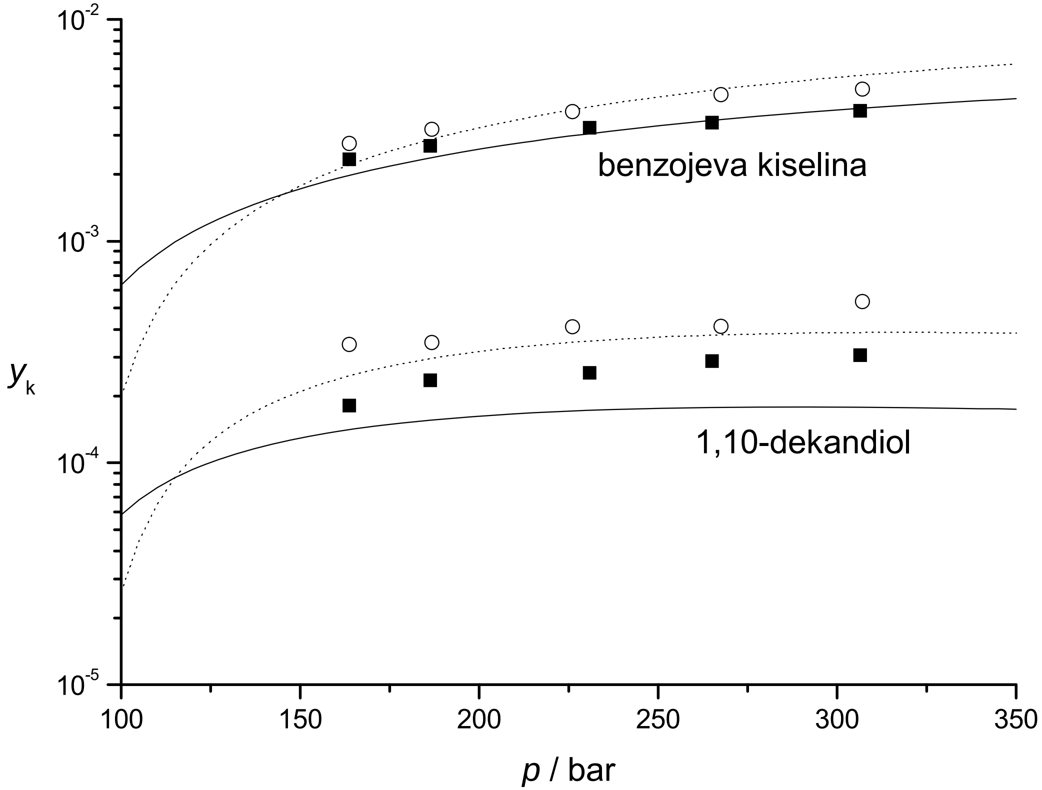
Topljivost krutine u plinu

$$y_2^{\mathrm{SF}} = \frac{\varphi_2^{\bullet} p_2^{\bullet}}{\hat{\varphi}_2^{\mathrm{SF}} p} \exp\left[\frac{v_2^{\mathrm{S}}\left(p - p_2^{\bullet}\right)}{RT}\right]$$

$$y_2^{\mathrm{SF}} = \frac{p_2^{\bullet}}{\hat{\varphi}_2^{\mathrm{SF},\infty} p} \exp\left[\frac{p v_2^{\mathrm{S}}}{RT}\right]$$

Pojednostavljenje

Ravnoteža plin-krutina



CO_2(1) – benzojeva kiselina(2) – 1,10-dekandiol(3)

M. Mukhopadhyay i G. V. Raghuram Rao – pravila miješanja

E. H. Chimovitz i K. J. Pennisi – podaci