Ravnoteža kapljevina-kapljevina

Ravnoteža kapljevina-kapljevina

Fazna ravnoteža

Nema kemijskih ili elektrokemijskih procesa

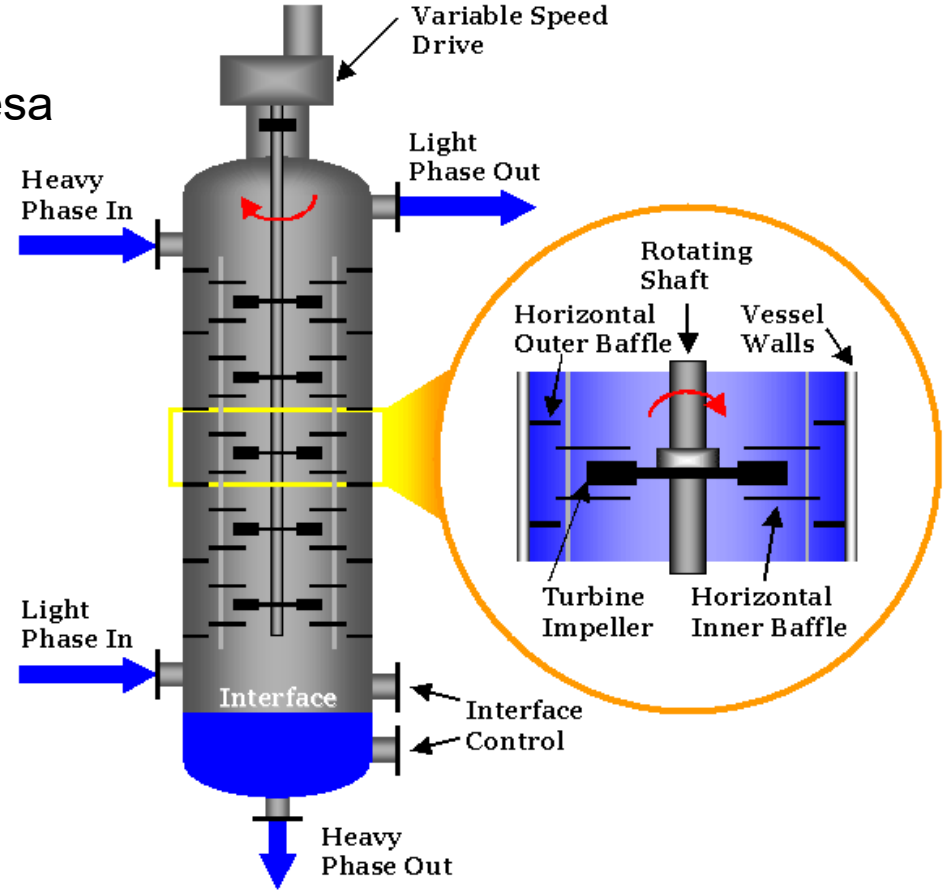
Industrijska praksa

Razdvajanje smjesa na komponente

Jednokratna i višekratna ekstrakcija

Kontinuirana kolonska ekstrakcija

Heterogena azeotropna destilacija



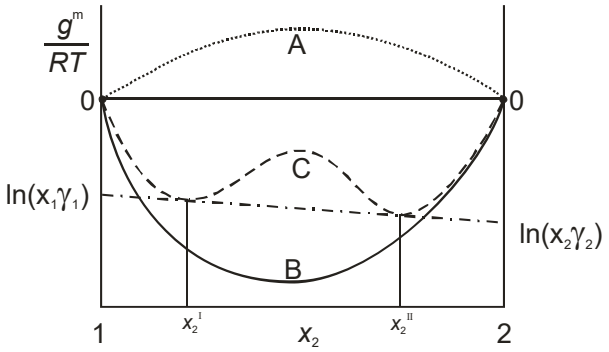
Fizikalnokemijske osnove

Kemijski potencijal

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

Metoda odsječka

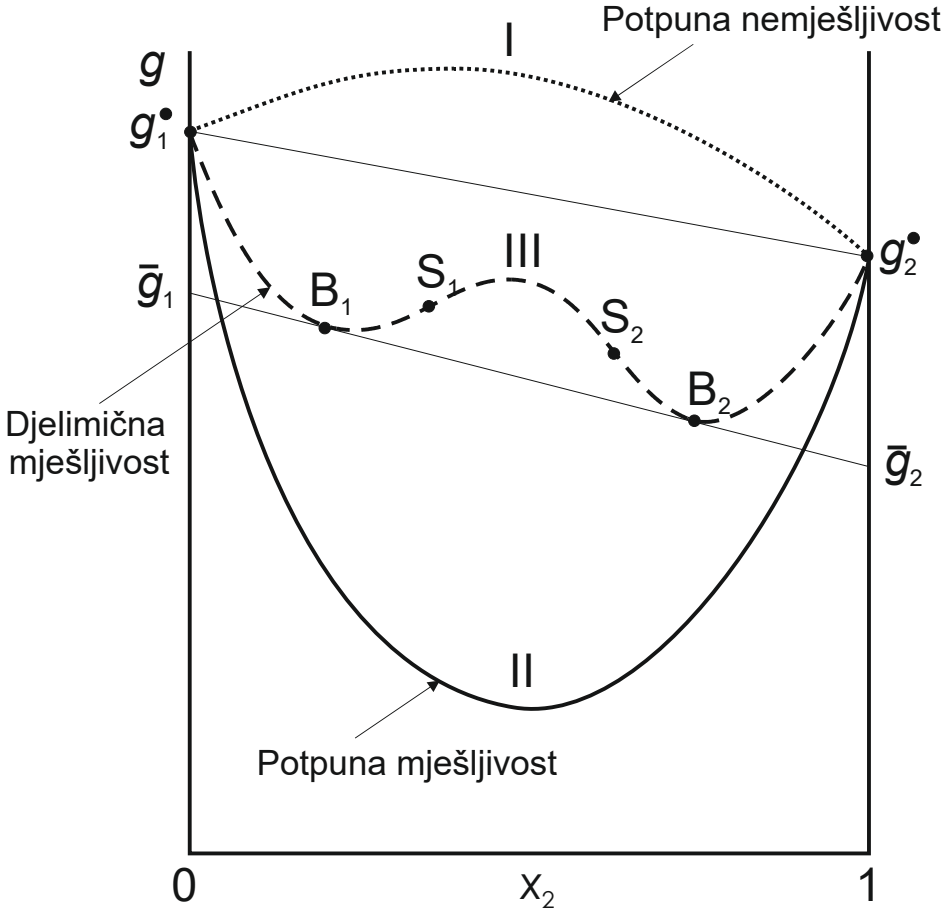
$$\mu_i = \bar{g}_i = g + (1 - x_i)\frac{\partial g}{\partial x_i}$$



Gibbsova energija miješanja

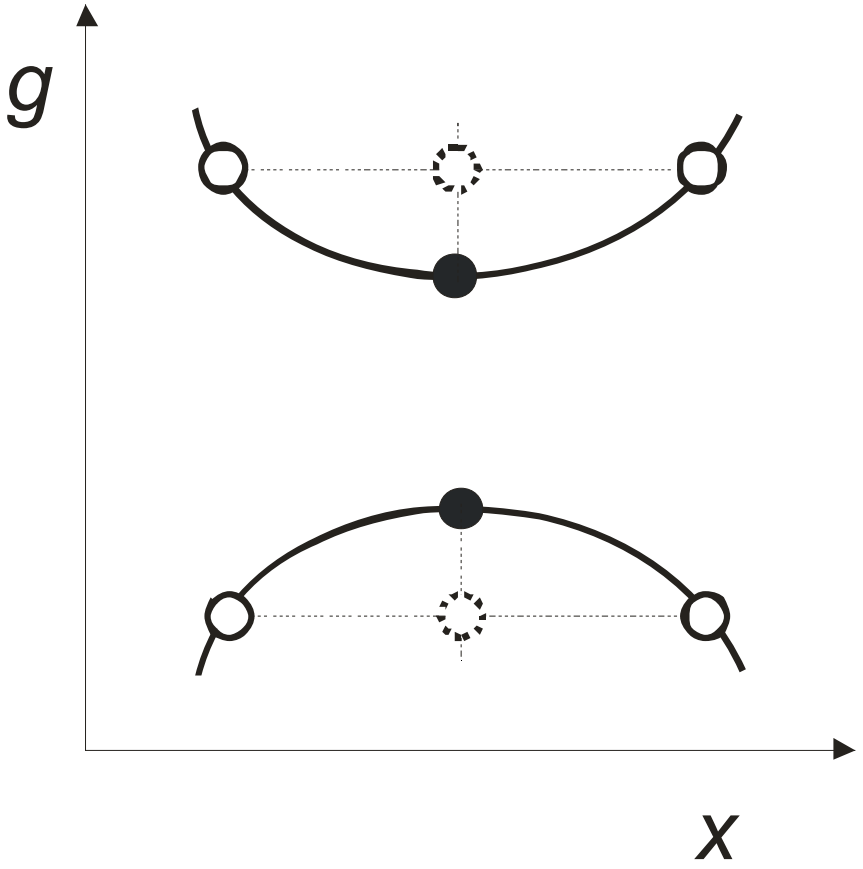
Uvjet ravnoteže – jednakost aktivnosti

Jednakost kemijskih potencijala u dvokomponentnim sustavima

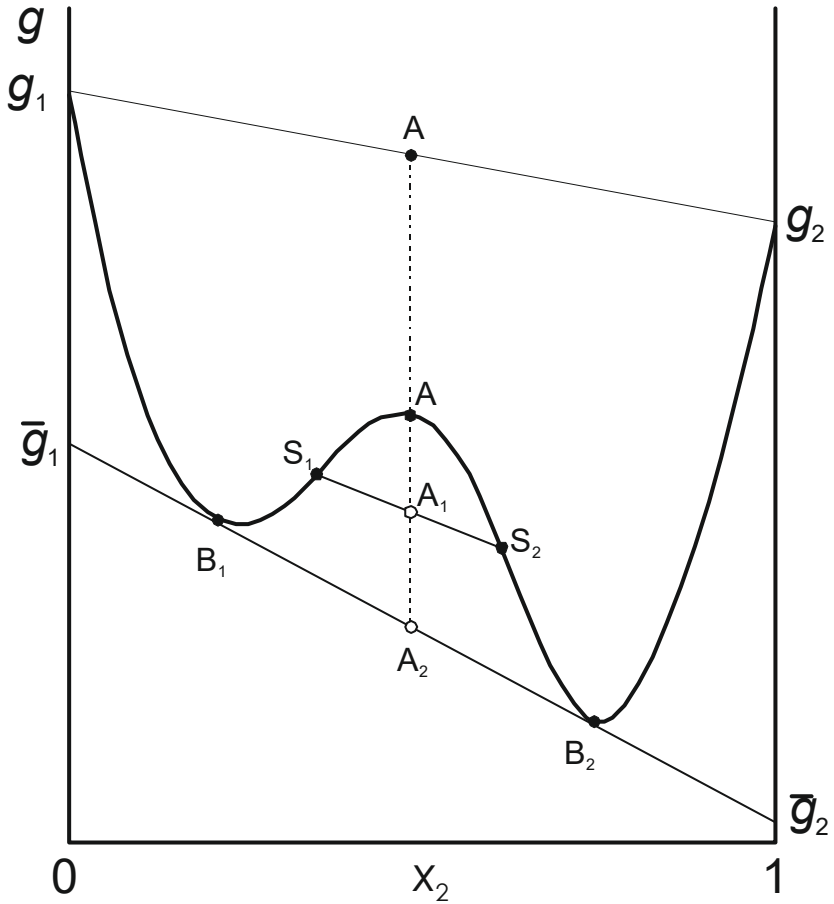


Fizikalnokemijske osnove

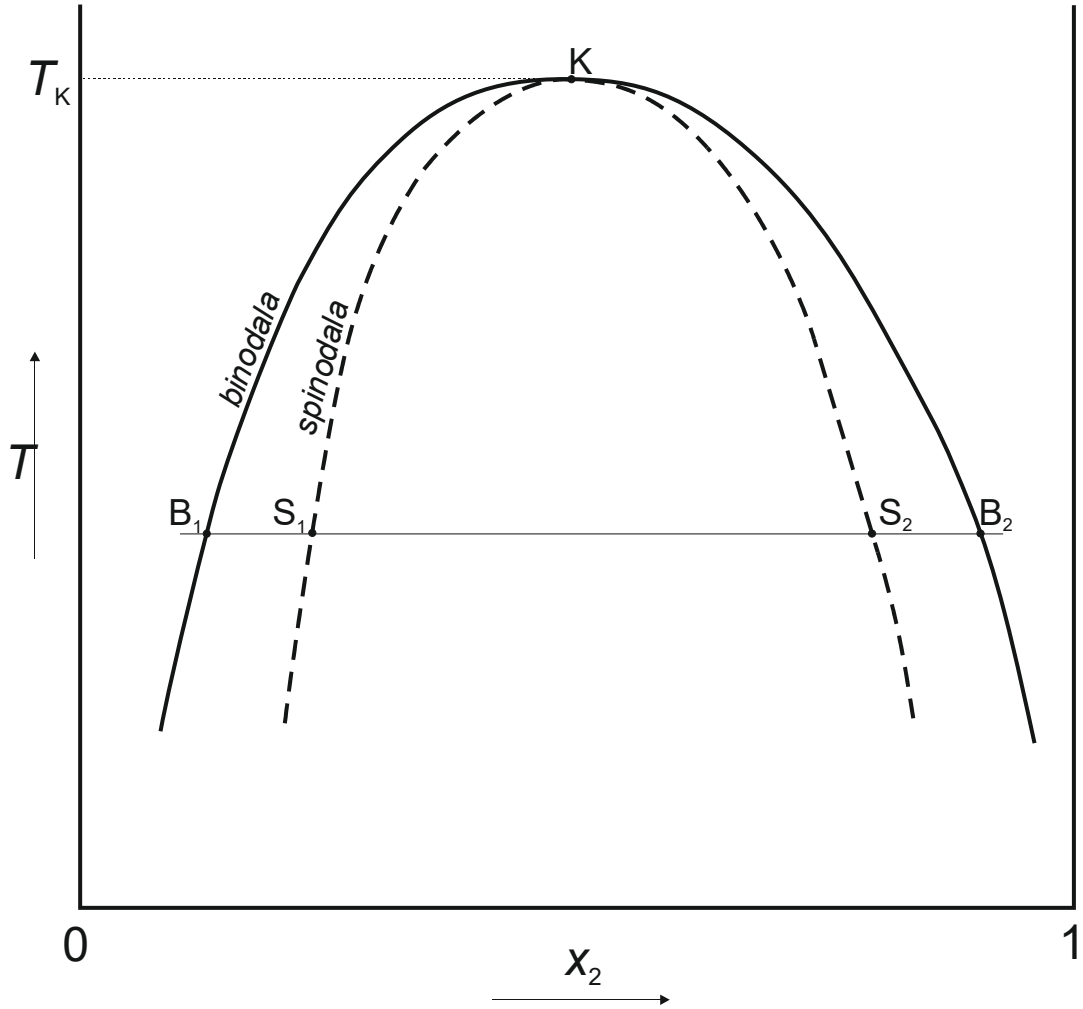
Nestabilno i metastabilno područje



Snižavanje Gibbsove energije



Fizikalnokemijske osnove



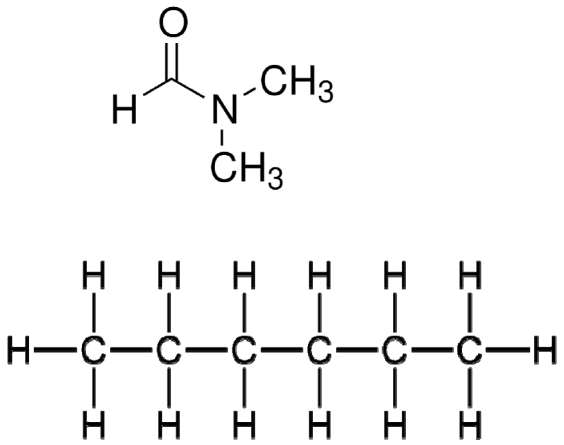
Ovisnost ravnotežnih sastava o temperaturi

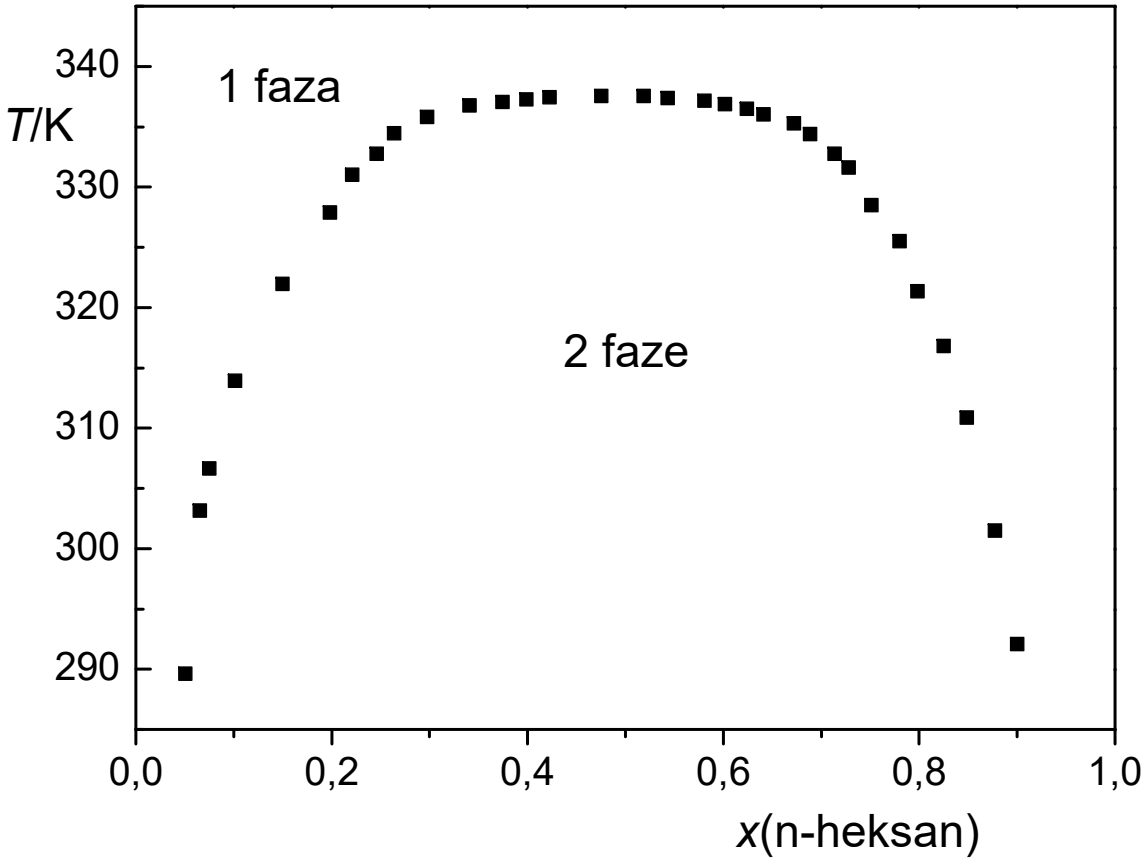
Kritična temperatura otopine

Binodalna i spinodalna krivulja

Fazni dijagrami

Ovisnost ravnotežnih sastava o temperaturi

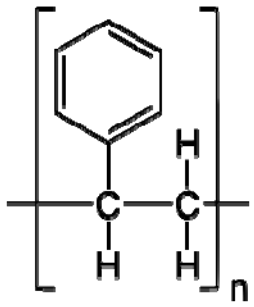


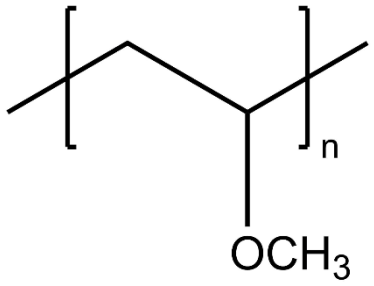


Dimetilformamid – *n*-heksan, Matsuda i suradnici

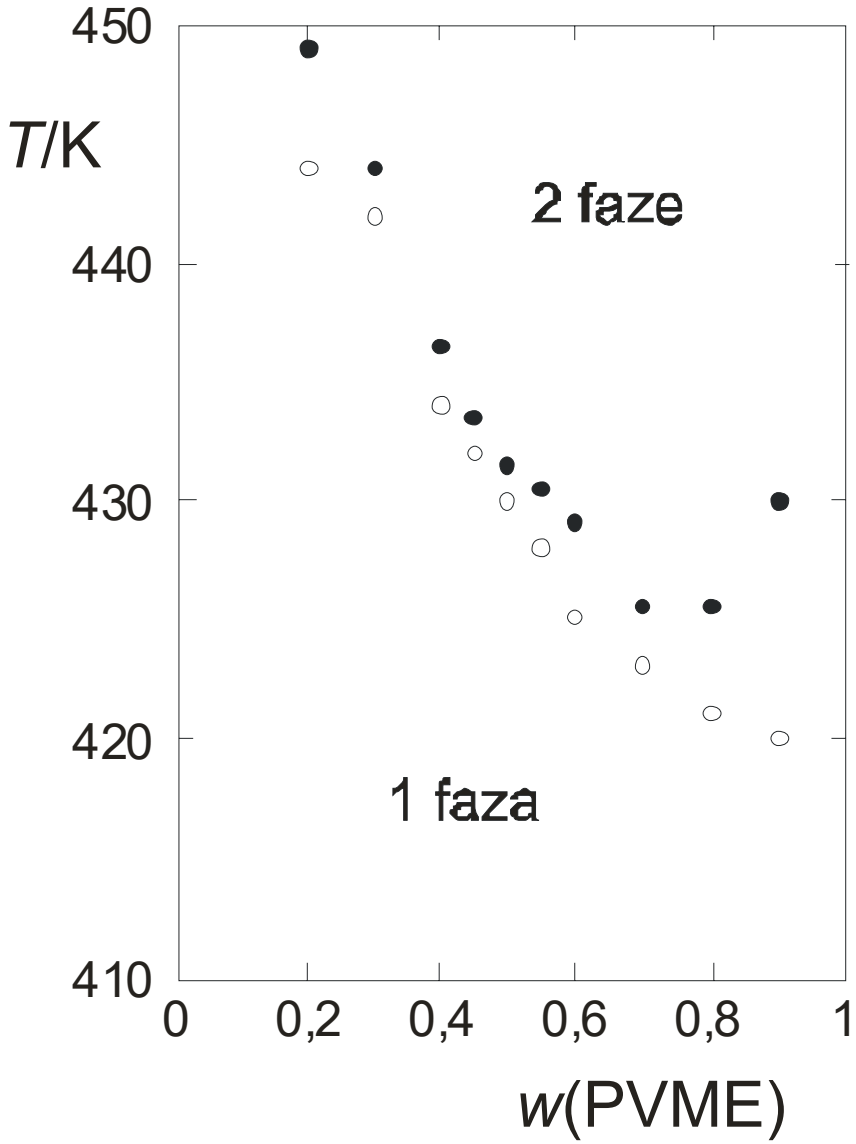
Fazni dijagrami

Ovisnost ravnotežnih sastava
o temperaturi



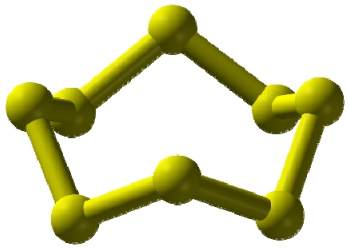


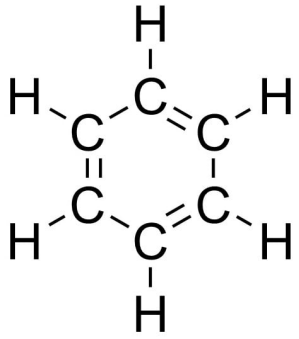
Polistiren – polivinilmetileter
Xie i suradnici

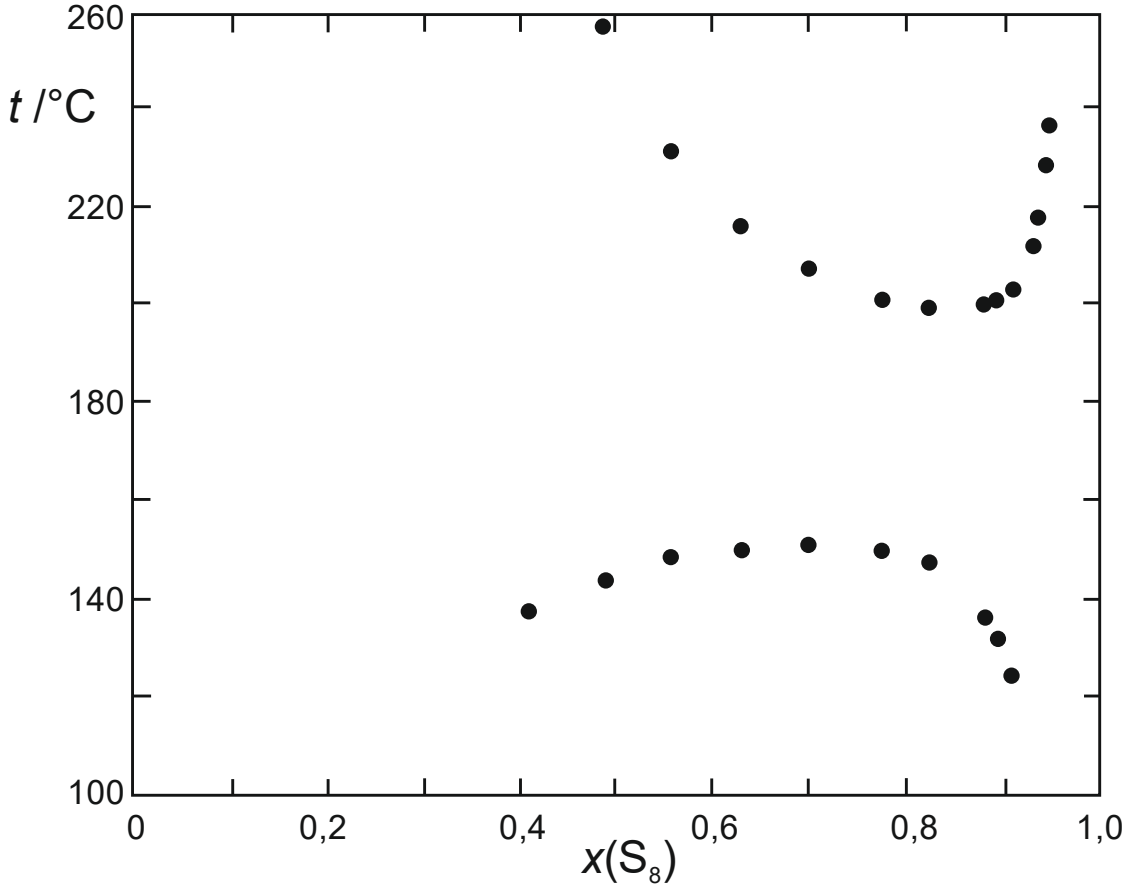


Fazni dijagrami

Ovisnost ravnotežnih sastava o temperaturi



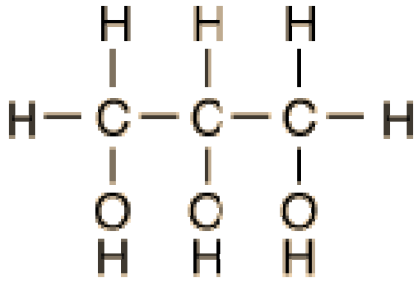


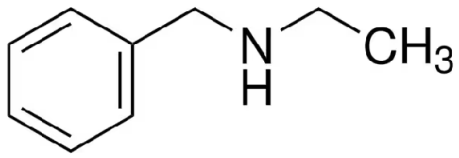


Sumpor - benzen

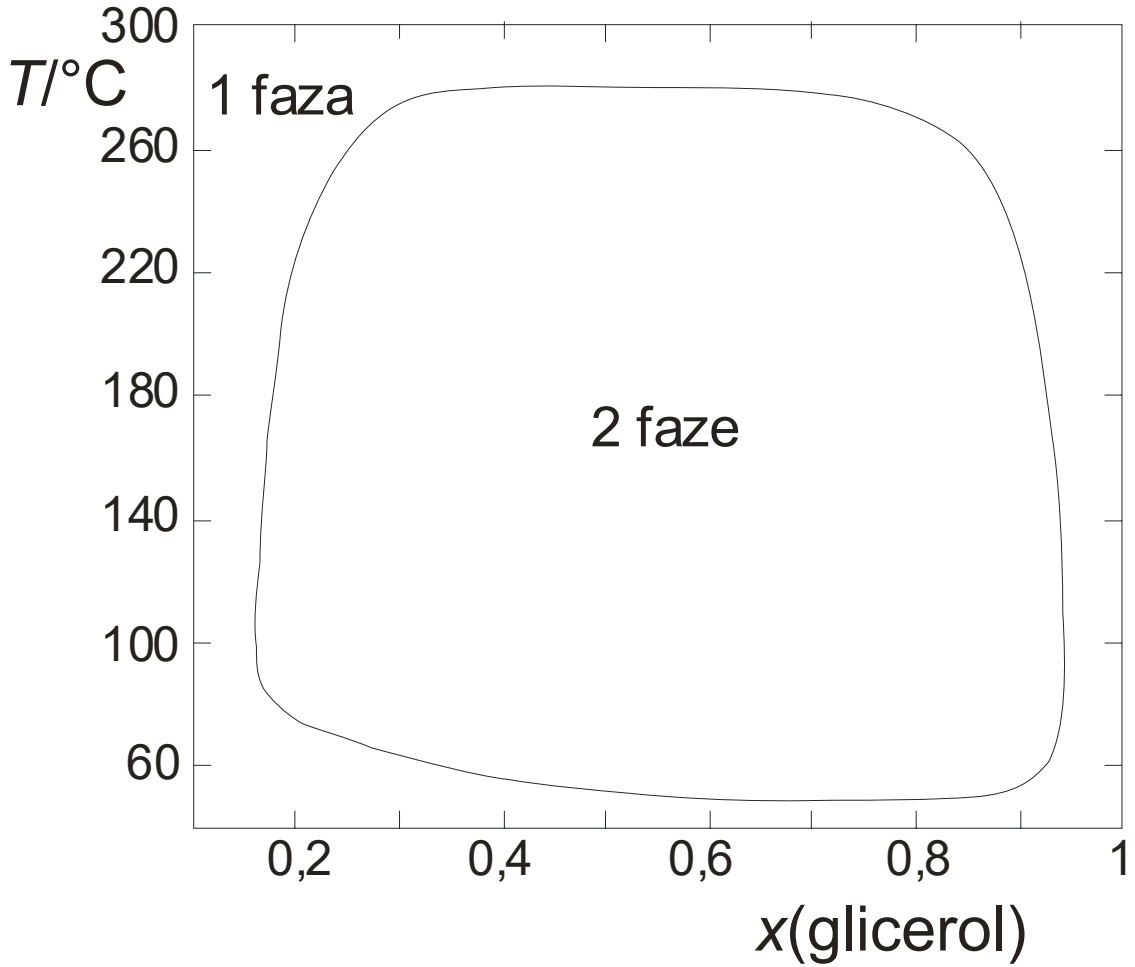
Fazni dijagrami

Ovisnost ravnotežnih sastava o temperaturi



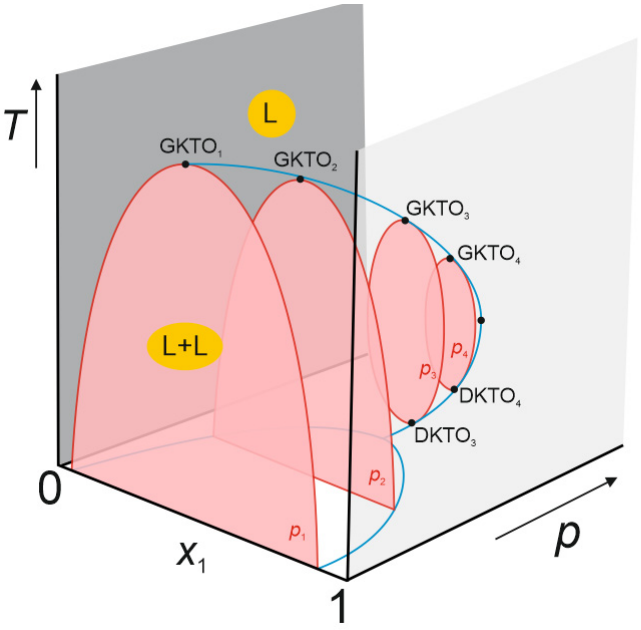


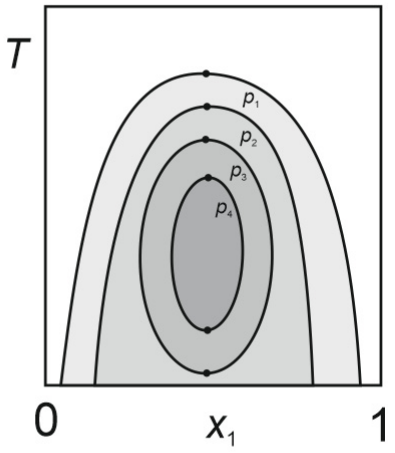
Glicerol – benziletilamin

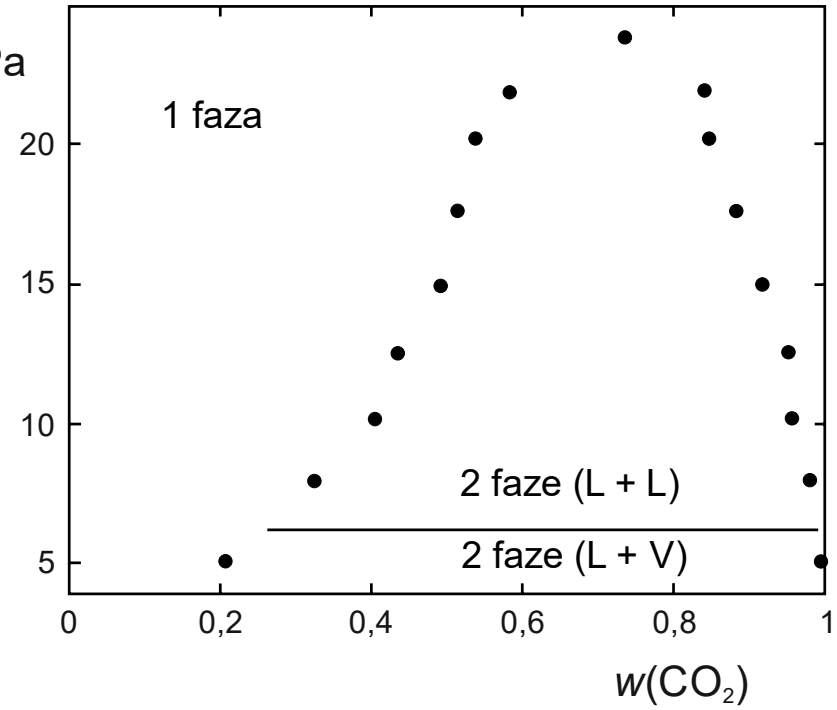


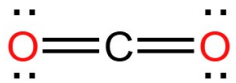
Fazni dijagrami

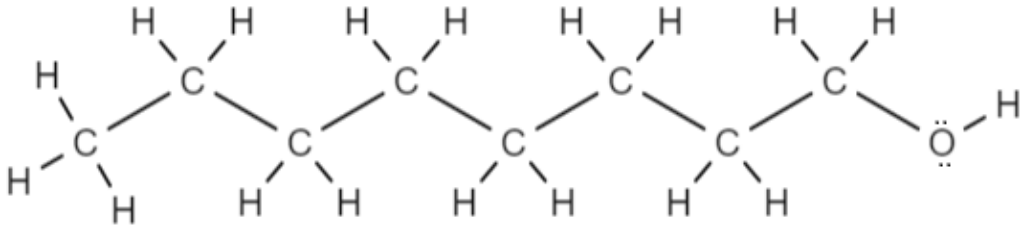
Ovisnost o tlaku – mala











CO_2 – *n*-oktanol
Gauter i suradnici
393 K

Uvjeti fazne ravnoteže

Prvi zakon termodinamike – bilančne jednadžbe

$$\sum_{i=1}^{nk} n_i^{\mathrm{F}} = \sum_{i=1}^{nk} n_i^{\mathrm{I}} + \sum_{i=1}^{nk} n_i^{\mathrm{II}}$$ Ukupna bilanca tvari

$$n^{\mathrm{F}} z_i^{\mathrm{F}} = n^{\mathrm{I}} x_i^{\mathrm{I}} + n^{\mathrm{II}} x_i^{\mathrm{II}}$$ Bilanca po komponentama

$$\sum_{i=1}^{nk} x_i^{\mathrm{I}} = 1 \qquad \sum_{i=1}^{nk} x_i^{\mathrm{II}} = 1$$ Bilanca po fazama

Bilanca energije za izolirani sustav

$$H^{\mathrm{F}} = H^{\mathrm{I}} + H^{\mathrm{II}}$$

Uvjeti fazne ravnoteže

Drugi zakon termodinamike

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

Ekvivalentni uvjeti za dvofazne, višekomponentne sustave

$$T^{\mathrm{I}} = T^{\mathrm{II}}$$

$$p^{\mathrm{I}} = p^{\mathrm{II}}$$

$$\mu_i^{\mathrm{I}} = \mu_i^{\mathrm{II}}$$

Jednadžba fazne ravnoteže

$$\mu_i^{\mathrm{I}} = \mu_i^{\mathrm{II}}$$ Jednakost kemijskih potencijala

$\mu_i = \mu_i^{\circ} + RT \ln a_i$ Uvođenje aktivnosti

$\mu_i^{\mathrm{I}\circ} + RT \ln a_i^{\mathrm{I}} = \mu_i^{\mathrm{II}\circ} + RT \ln a_i^{\mathrm{II}}$ Ravnotežna jednadžba

$\mu_i^{\mathrm{I}\circ} = \mu_i^{\mathrm{II}\circ}$ Simetrična definicija standardnog stanja
Čista kapljevina pri temperaturi i tlaku sustava

$$a_i^{\mathrm{I}} = a_i^{\mathrm{II}}$$ Jednakost aktivnosti

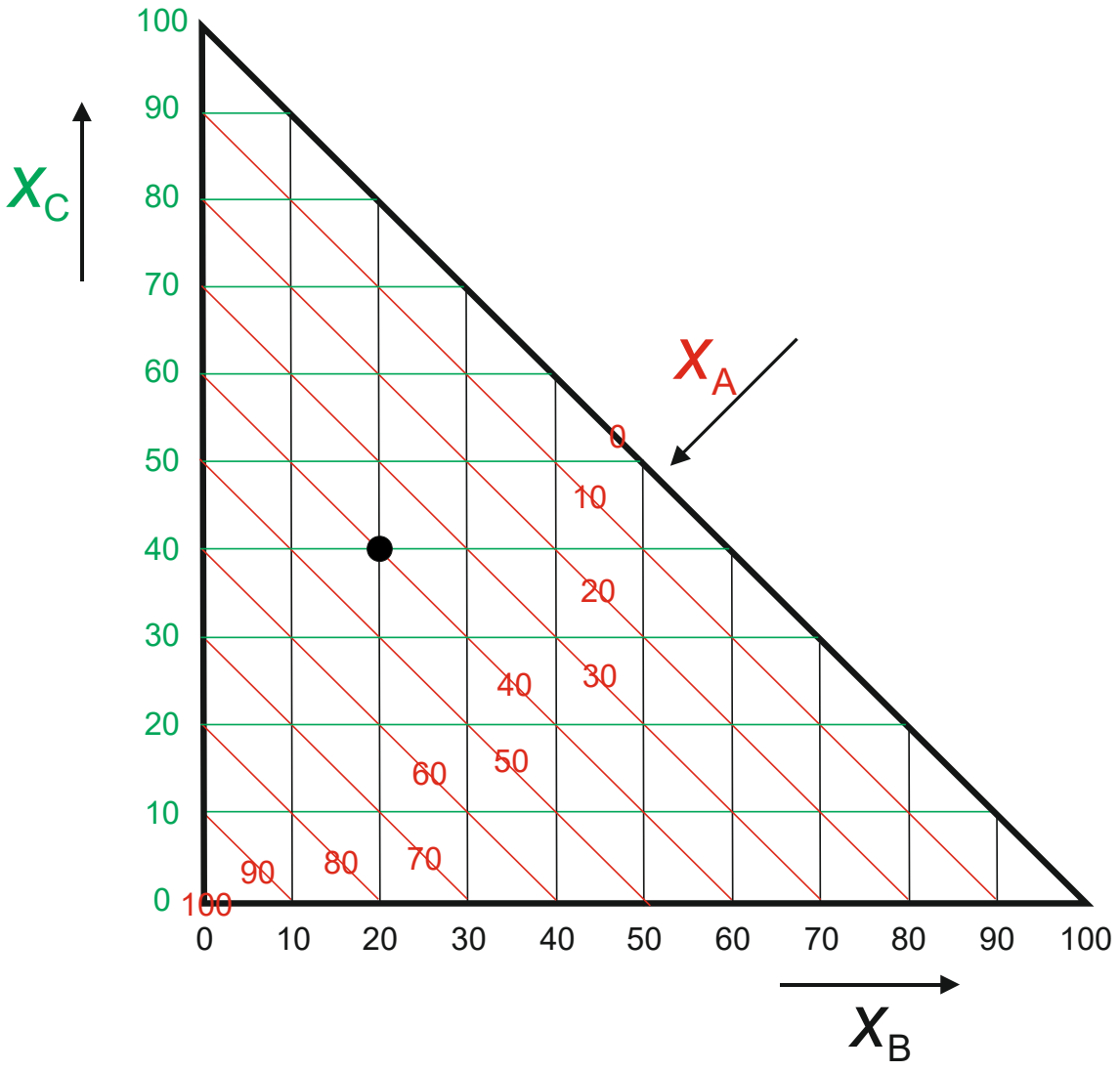
Koeficijent raspodjele
K-vrijednost

$a_i = x_i \gamma_i$ Uvođenje koeficijenta aktivnosti

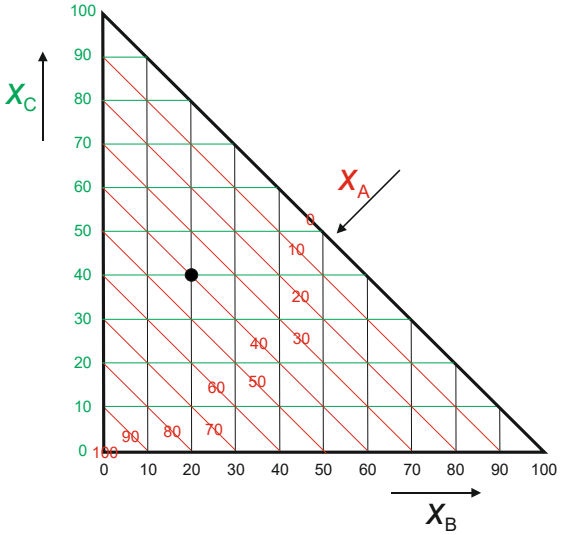
$$x_i^{\mathrm{I}} \gamma_i^{\mathrm{I}} = x_i^{\mathrm{II}} \gamma_i^{\mathrm{II}}$$ Ravnotežna jednadžba

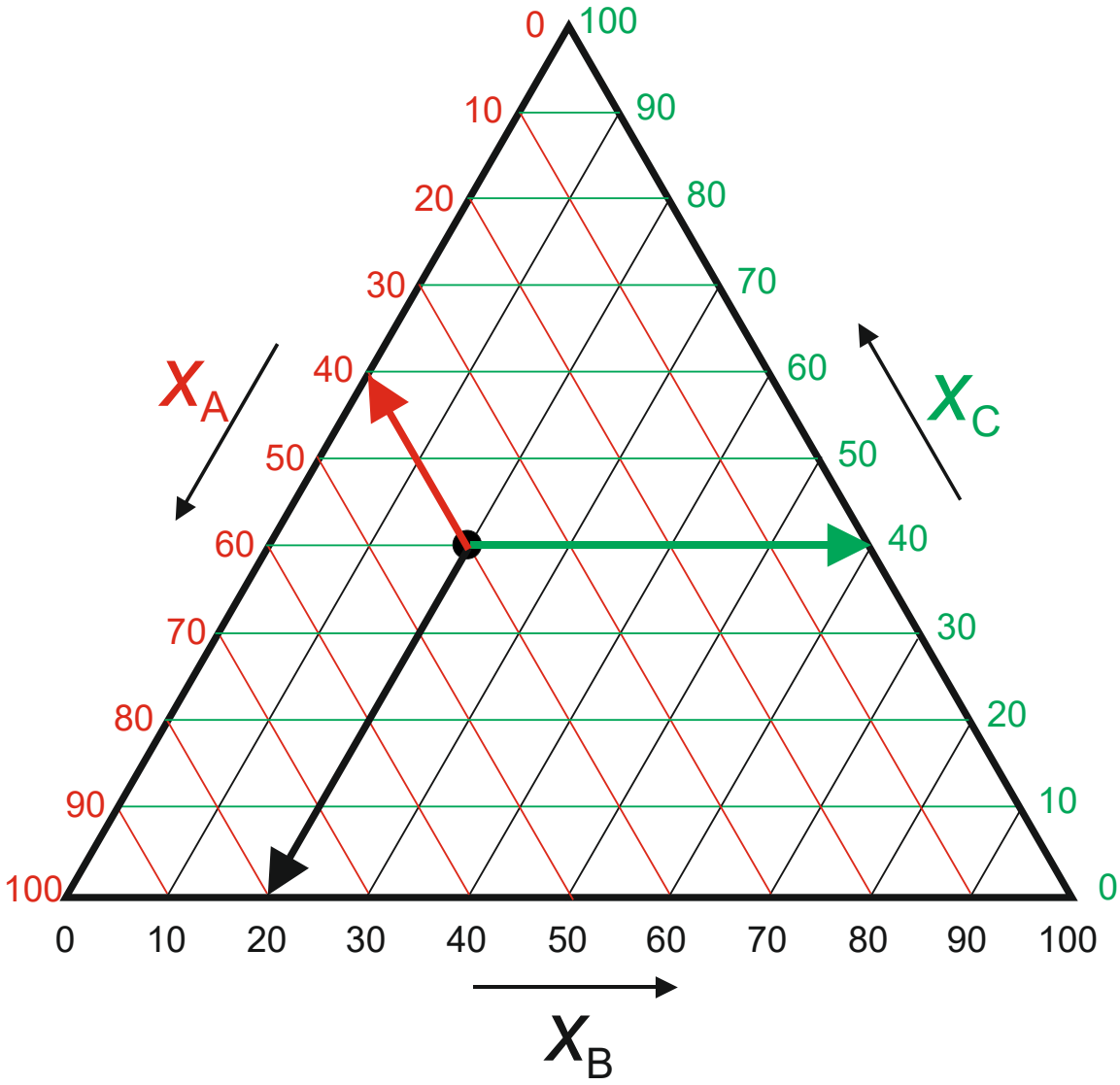
$$K_\gamma = \frac{x_i^{\mathrm{I}}}{x_i^{\mathrm{II}}} \quad K_\gamma = \frac{\gamma_i^{\mathrm{II}}}{\gamma_i^{\mathrm{I}}}$$

Trokutni dijagrami

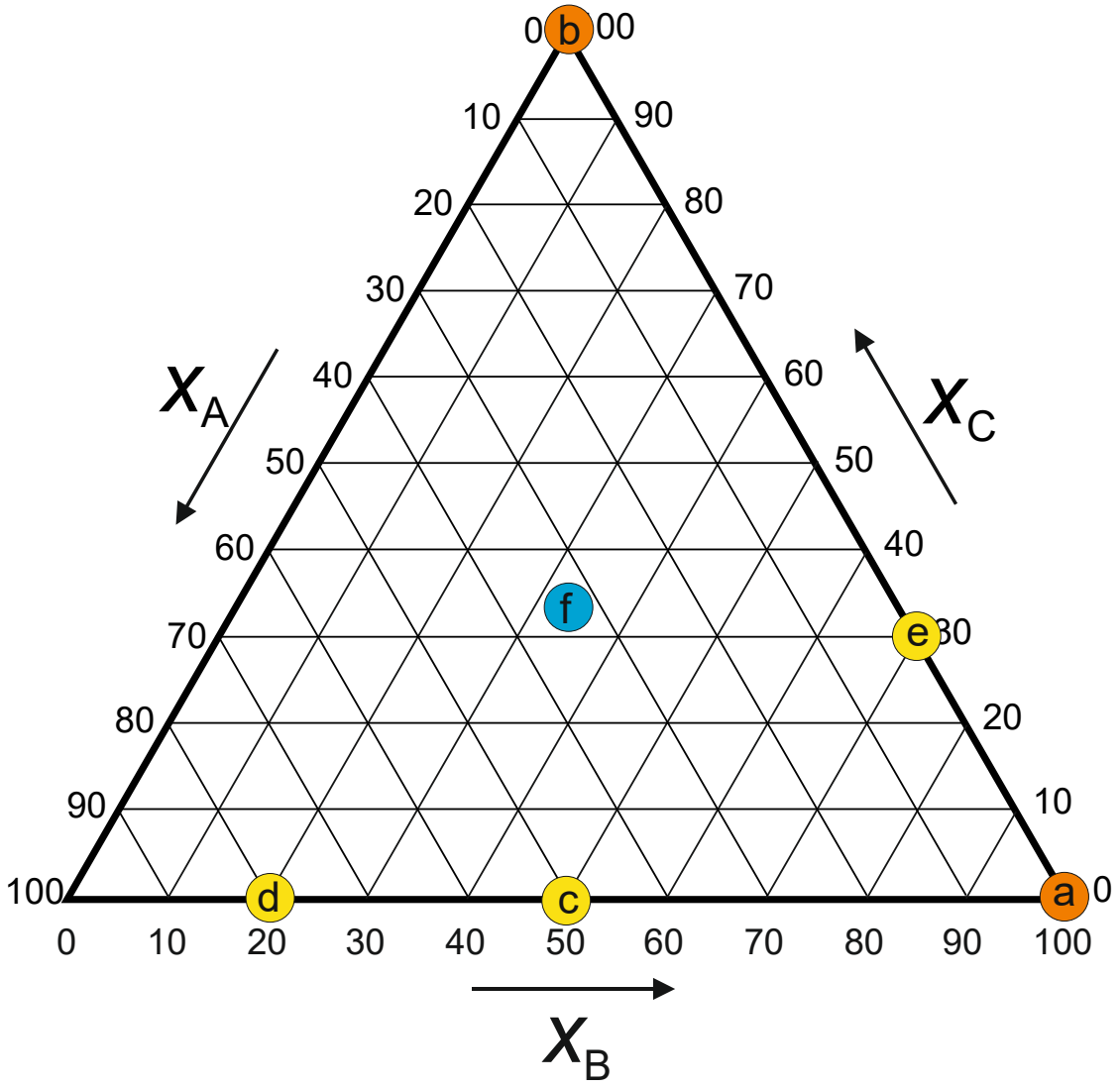


Trokutni dijagrami

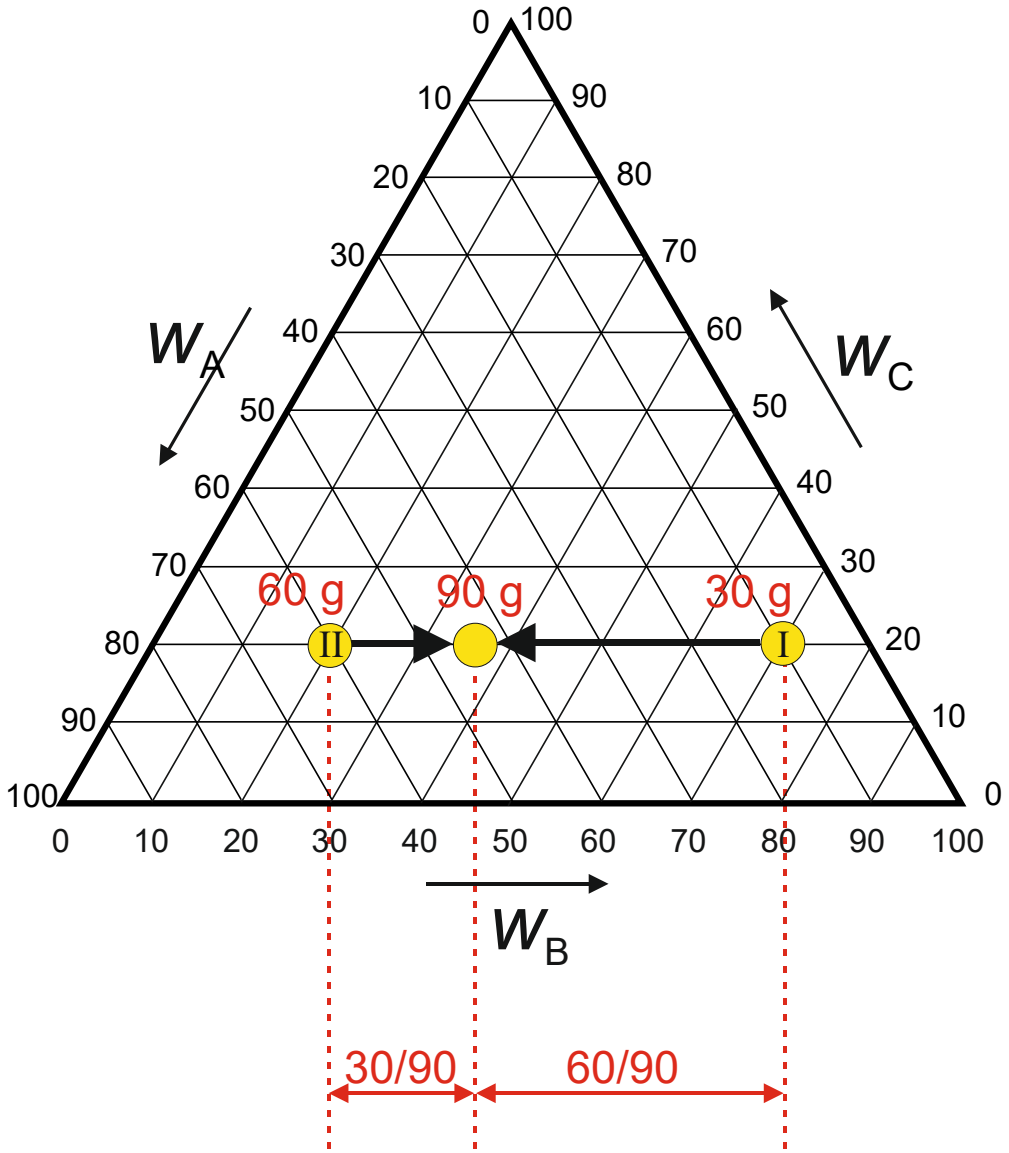




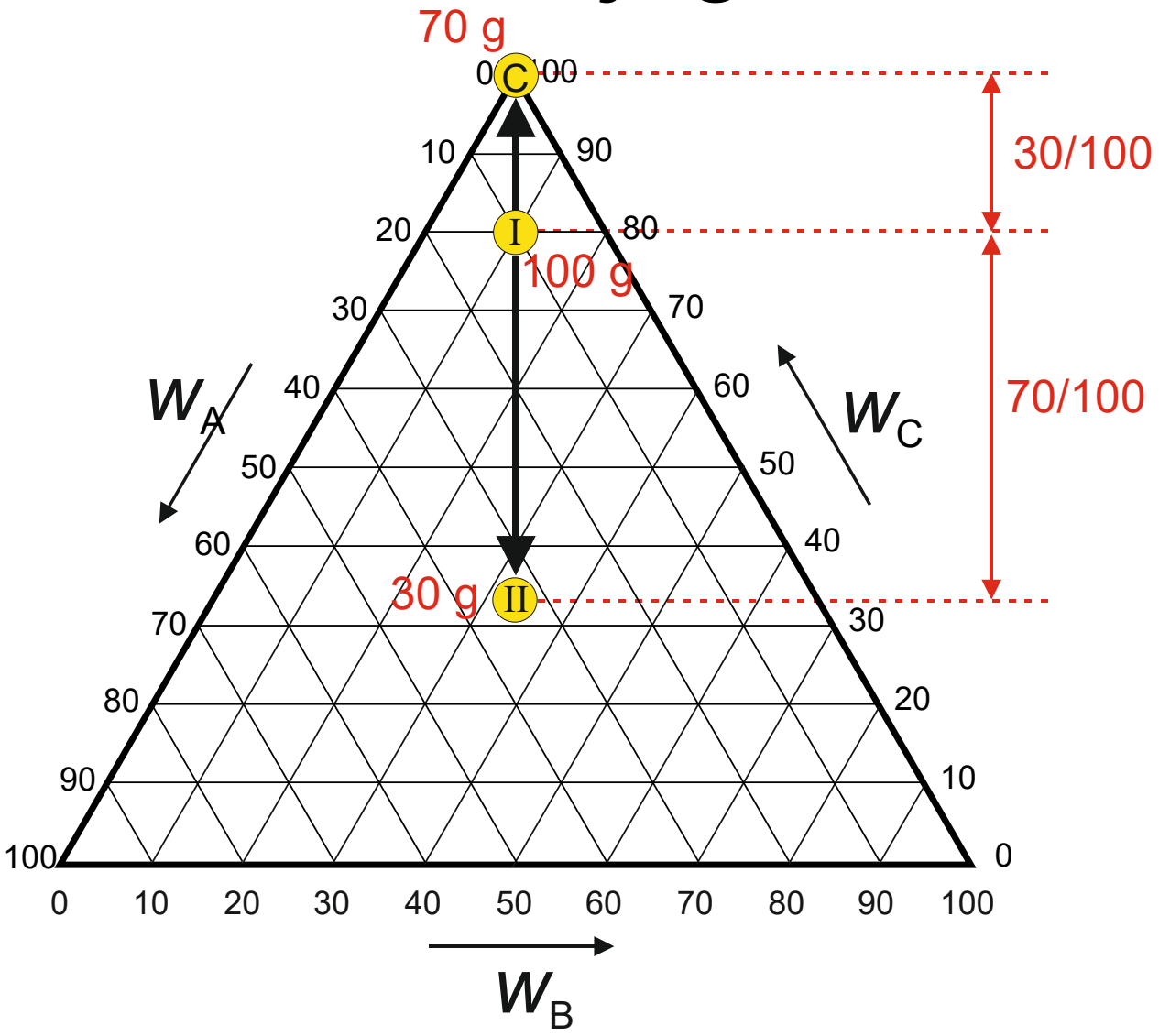
Trokutni dijagrami



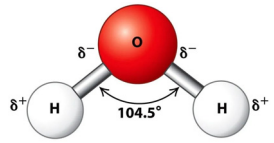
Trokutni dijagrami

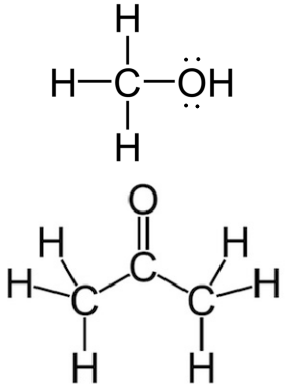


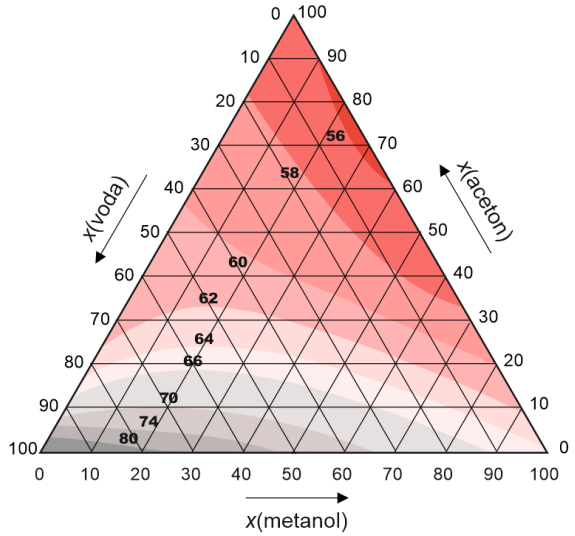
Trokutni dijagrami



Trokutni dijagrami

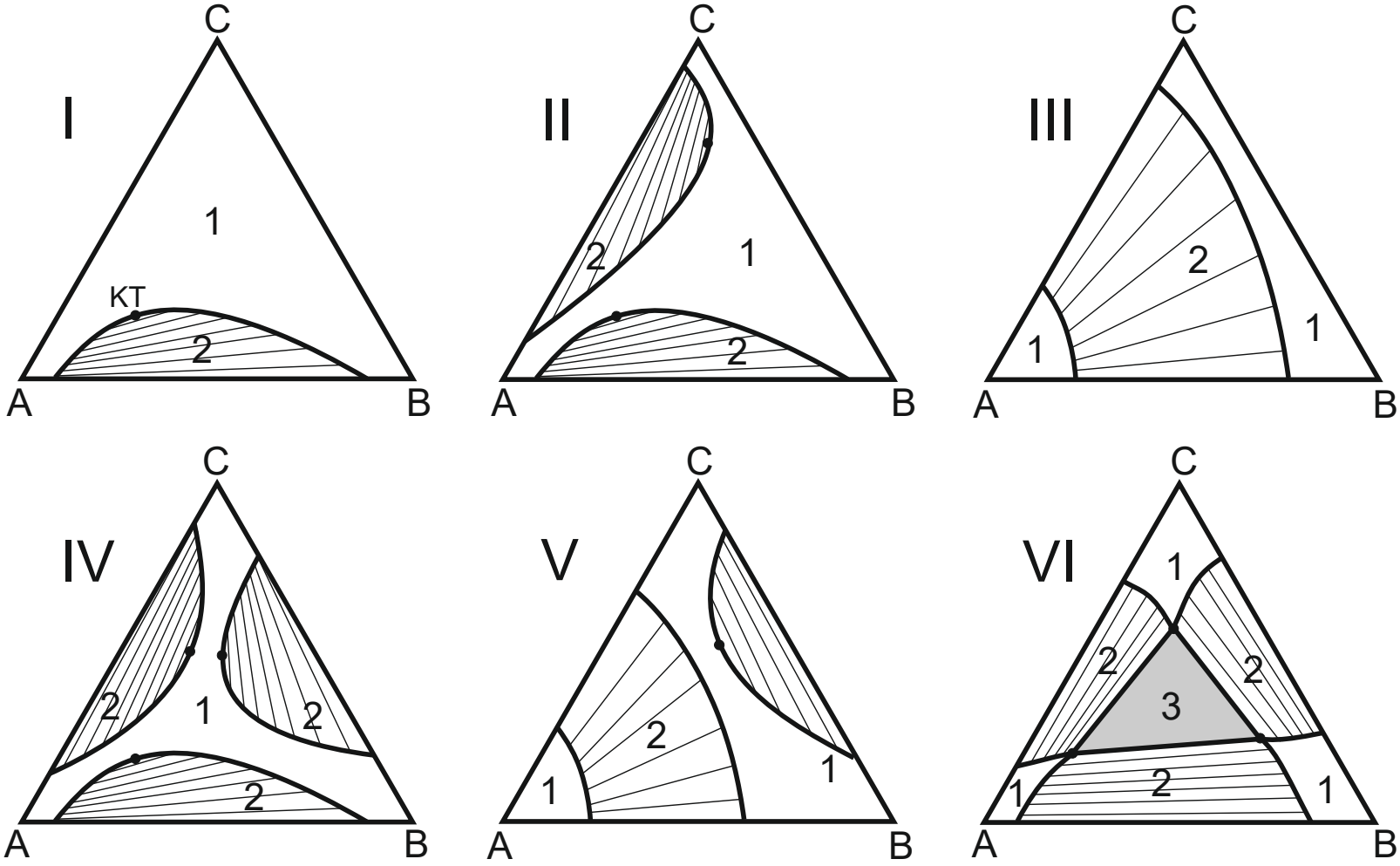






Griswold & Wong
100 °C
Ili
101325 Pa

Trokutni dijagrami



Binodalna krivulja

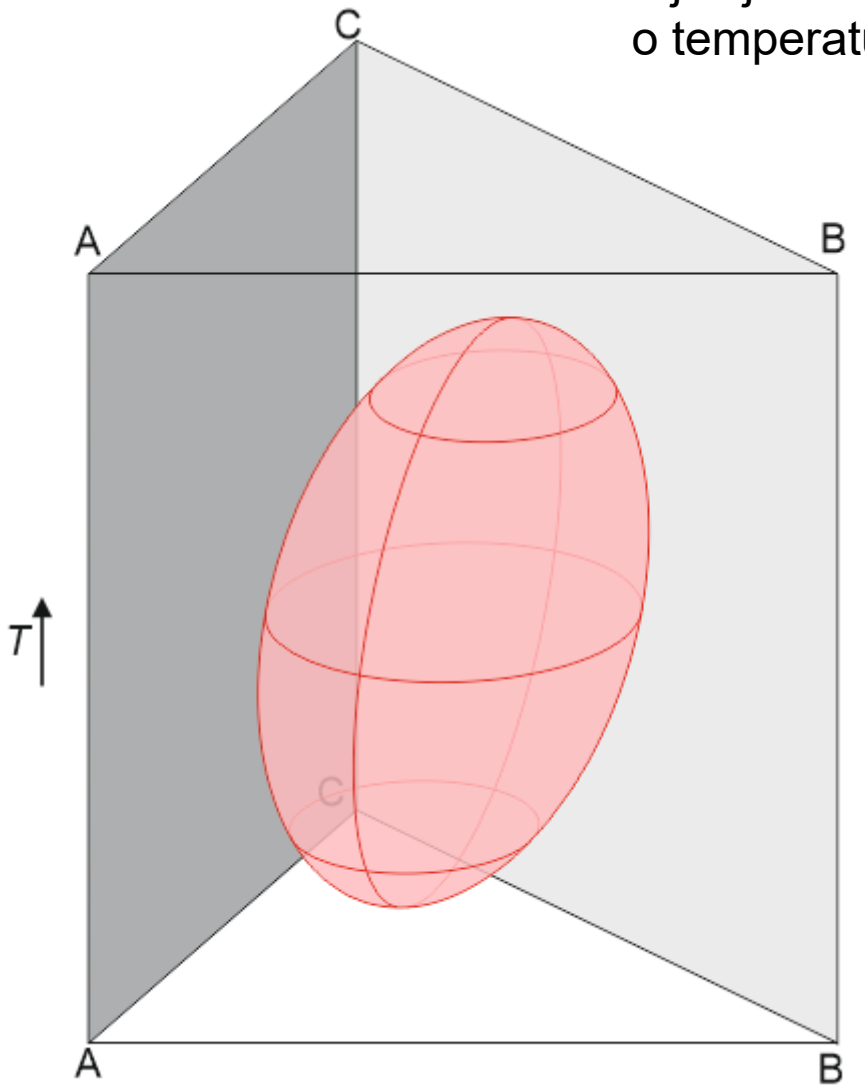
Vezna linija

Kritična točka

Trokutni dijagrami

Ovisnost
Mješljivost
o temperaturi

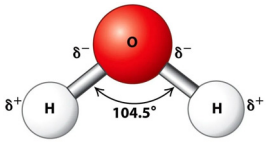


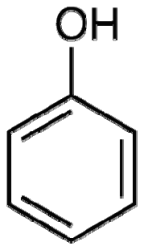


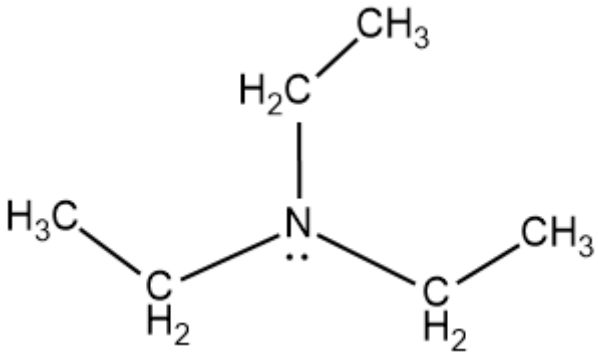
Trokutni dijagrami

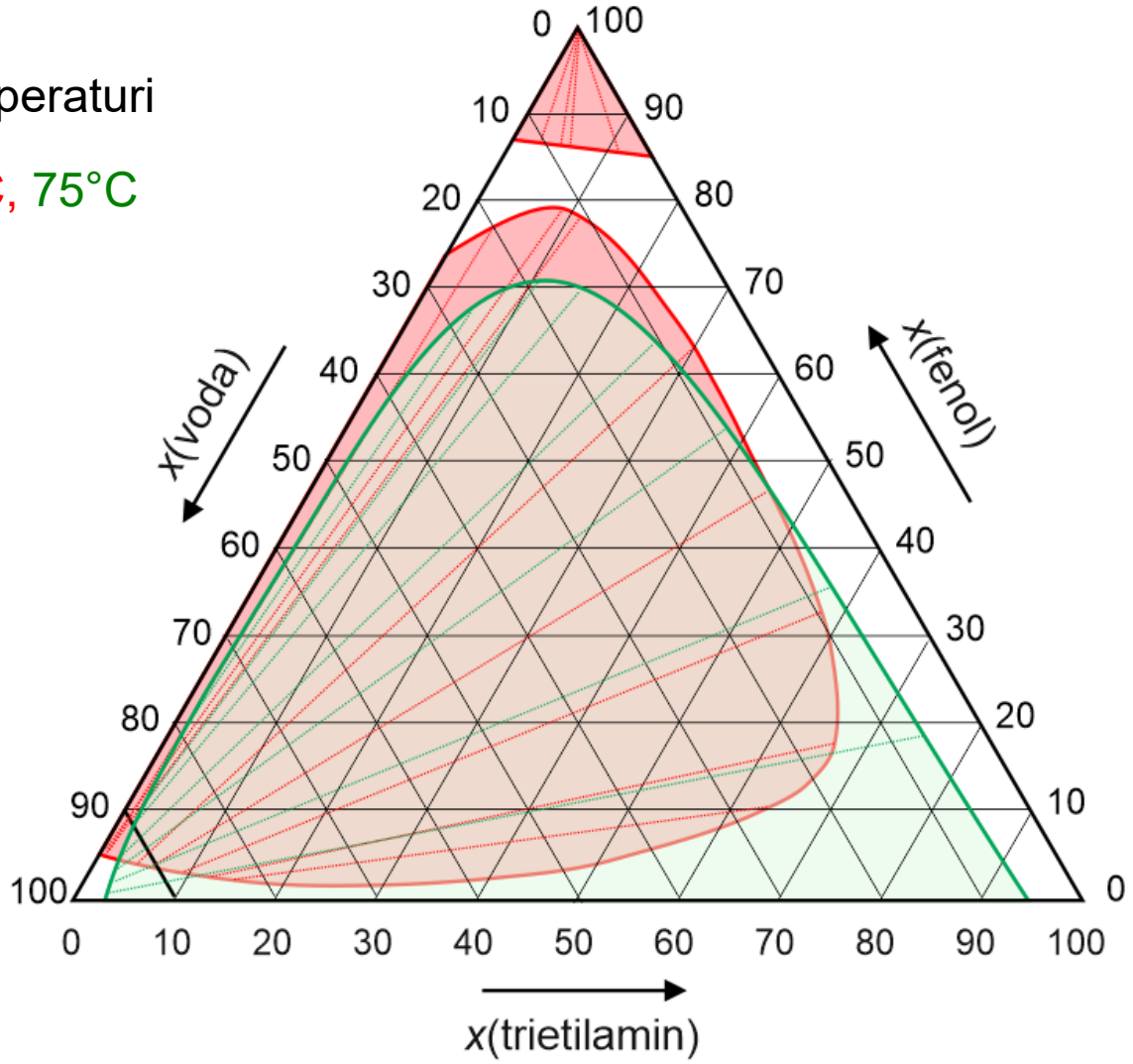
Ovisnost mješljivosti o temperaturi

Meerburg 10°C, 75°C









Trokomponentni dvofazni sustavi

Određivanje parametara modela iz eksperimenta

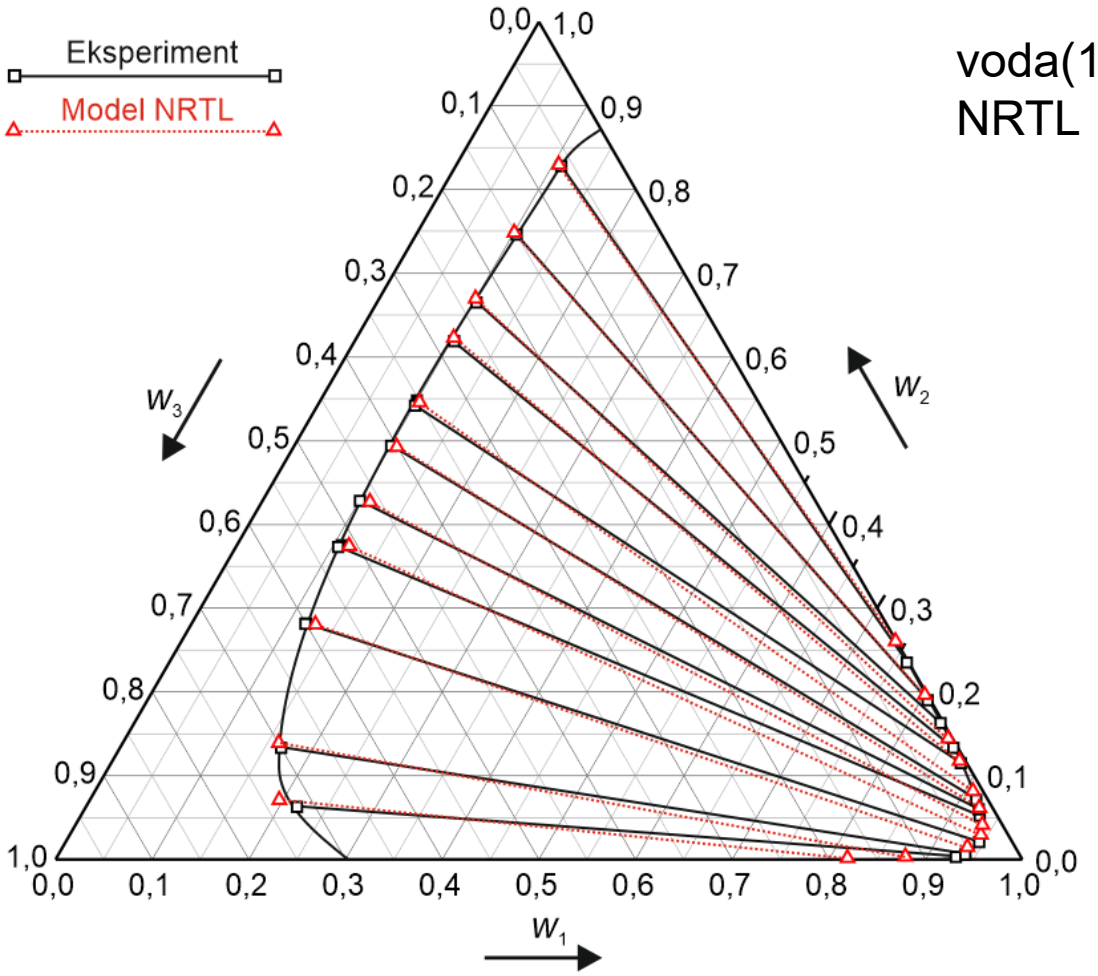
Sorensen-Arlt

$$OF_2 = \sum_{j=1}^{nd} \sum_{i=1}^{3} \left(\frac{x_i^{\mathrm{I}} \gamma_i^{\mathrm{I}} - x_i^{\mathrm{II}} \gamma_i^{\mathrm{II}}}{x_i^{\mathrm{I}} \gamma_i^{\mathrm{I}} + x_i^{\mathrm{II}} \gamma_i^{\mathrm{II}}} \right)_j^2$$

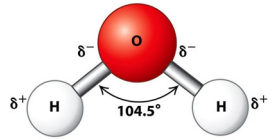
$$OF_3 = \sum_{j=1}^{nd} \sum_{i=1}^{3} \sum_{p=\mathrm{I,II}}^{2} \left[\left(x_i^p \right)_{\mathrm{exp}} - \left(x_i^p \right)_{\mathrm{mod}} \right]_j^2$$

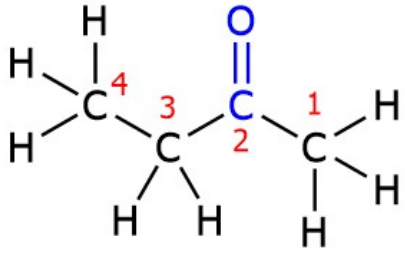
Trokomponentni dvofazni sustavi

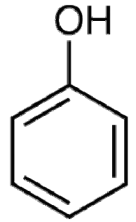
Određivanje parametara modela iz eksperimenta



voda(1) – 2-butanon(2) – fenol(3).
NRTL



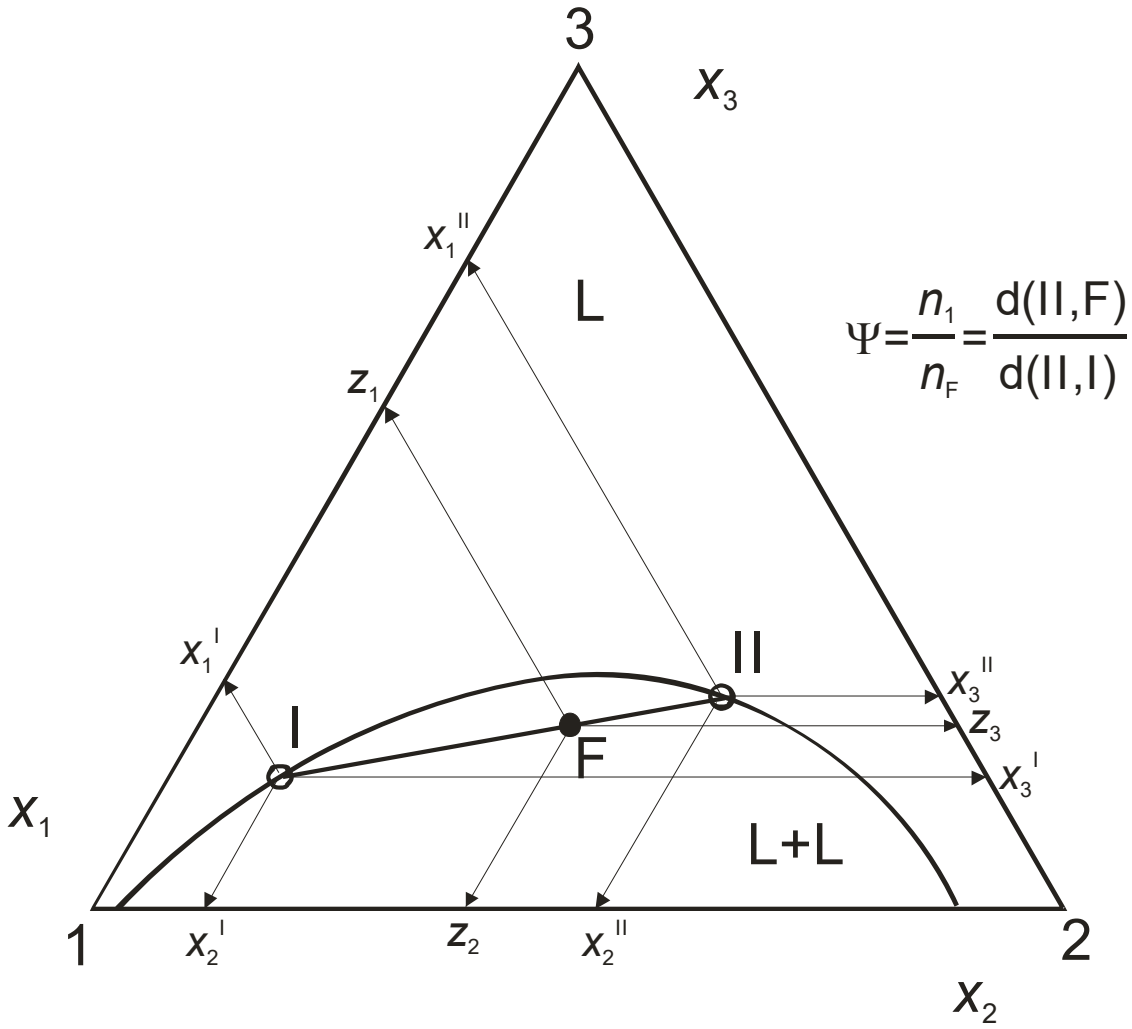




Trokomponentni dvofazni sustavi

Izračunavanje veznih linija – numeričke vježbe

Jednokratna ekstrakcija



$$\Psi = \frac{n_1}{n_F} = \frac{d(II,F)}{d(II,I)}$$

Trokomponentni dvofazni sustavi

Izračunavanje veznih linija – numeričke vježbe

Ekstrakcijski *flash*

Formulacija $p, T, z_i \rightarrow x_i^{\mathrm{I}}, x_i^{\mathrm{II}}, \Psi$

$$K_{\gamma i} = \frac{x_i^{\mathrm{I}}}{x_i^{\mathrm{II}}} = \frac{\gamma_i^{\mathrm{II}}\left(p, T, x_i^{\mathrm{II}}\right)}{\gamma_i^{\mathrm{I}}\left(p, T, x_i^{\mathrm{I}}\right)}$$

Ravnotežne jednadžbe

$$z_i = x_i^{\mathrm{I}}\Psi + x_i^{\mathrm{II}}\left(1-\Psi\right)$$

Bilanca za komponente

$$\sum_{i=1}^{nk} x_i^{\mathrm{I}} = 1 \quad \sum_{i=1}^{nk} x_i^{\mathrm{II}} = 1$$

Jedan od bilančnih faznih uvjeta

$$\sum_{i=1}^{nk} x_i^{\mathrm{I}} - \sum_{i=1}^{nk} x_i^{\mathrm{II}} = 0$$

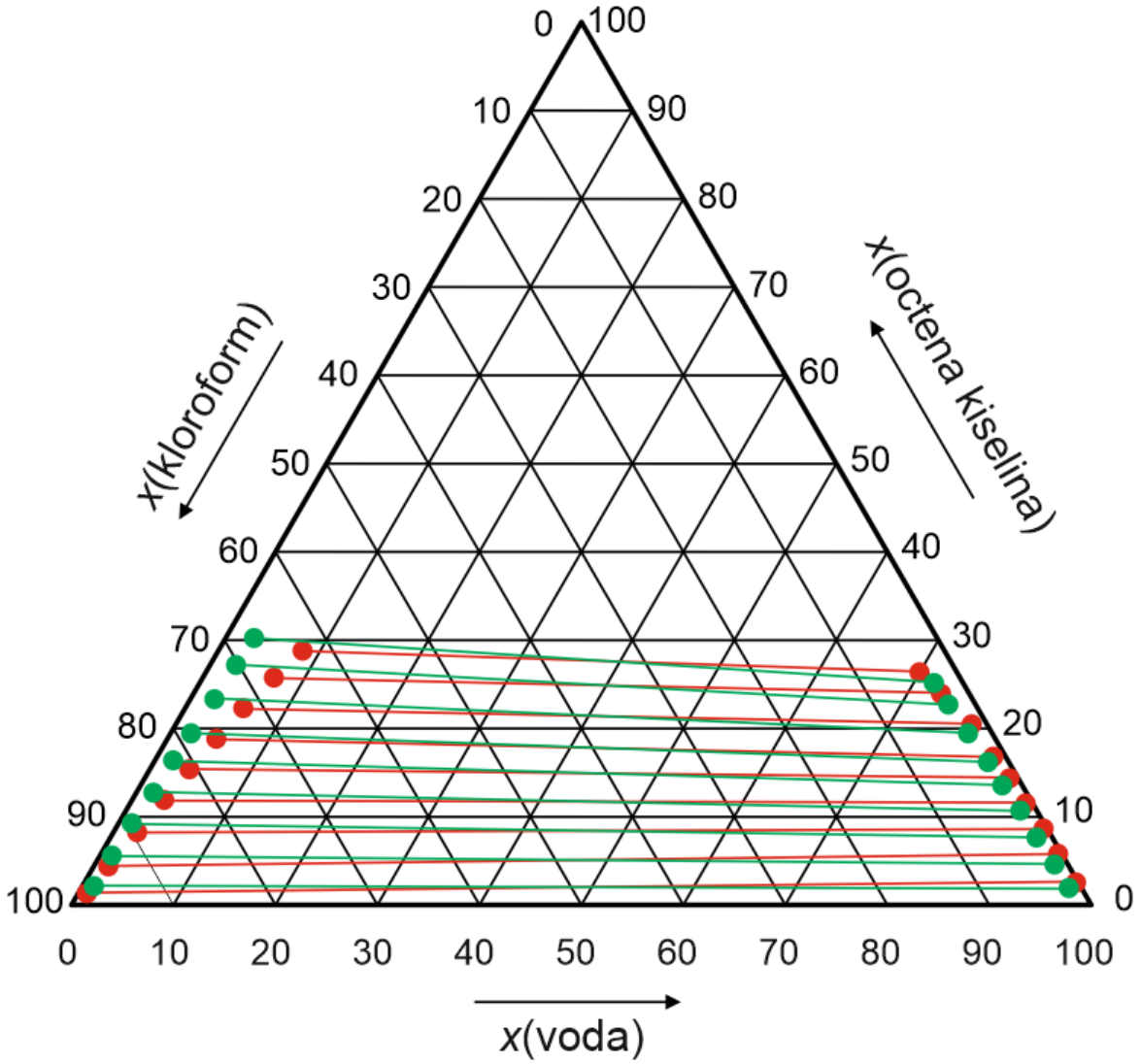
Rachford-Rice

$$f\left(\Psi\right) = -1 + \sum_{i=1}^{nk} \frac{z_i}{1+\Psi\left(K_{\gamma i}-1\right)} = 0$$

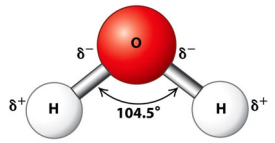
Kombinacija

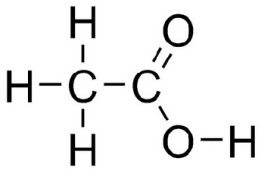
$$f\left(\Psi\right) = \sum_{i=1}^{nk} \frac{z_i\left(K_{\gamma i}-1\right)}{1+\Psi\left(K_{\gamma i}-1\right)} = 0$$

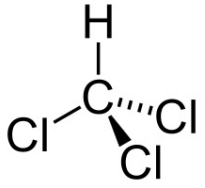
Trokomponentni dvofazni sustavi



Eksperiment
Proračun

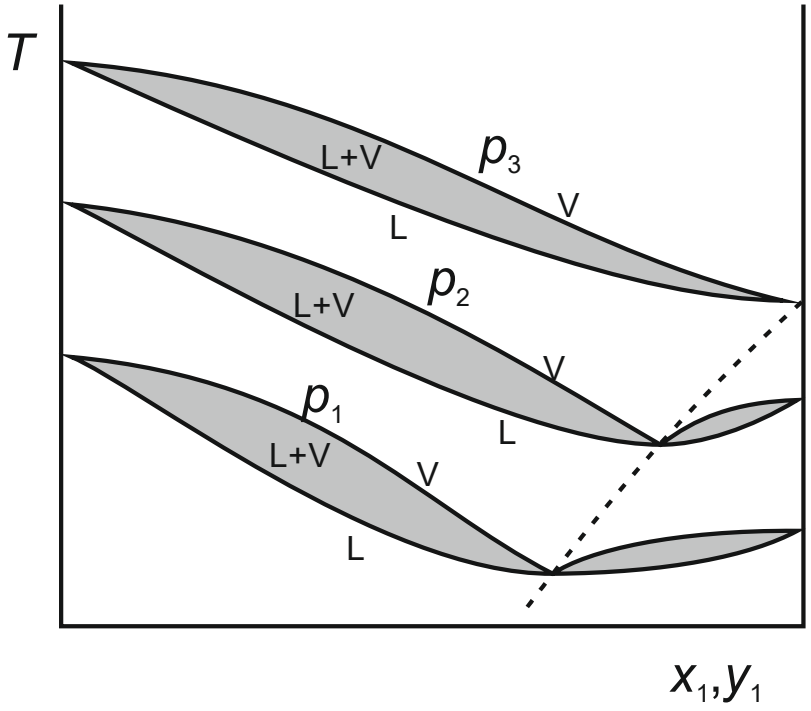


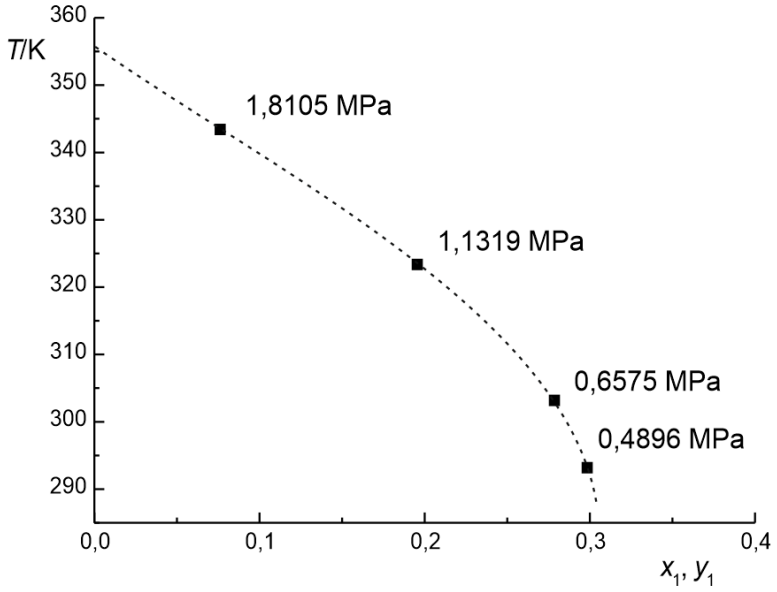




Razdvajanje azeotropa

Istiskivanje azeotropa mijenjanjem tlaka

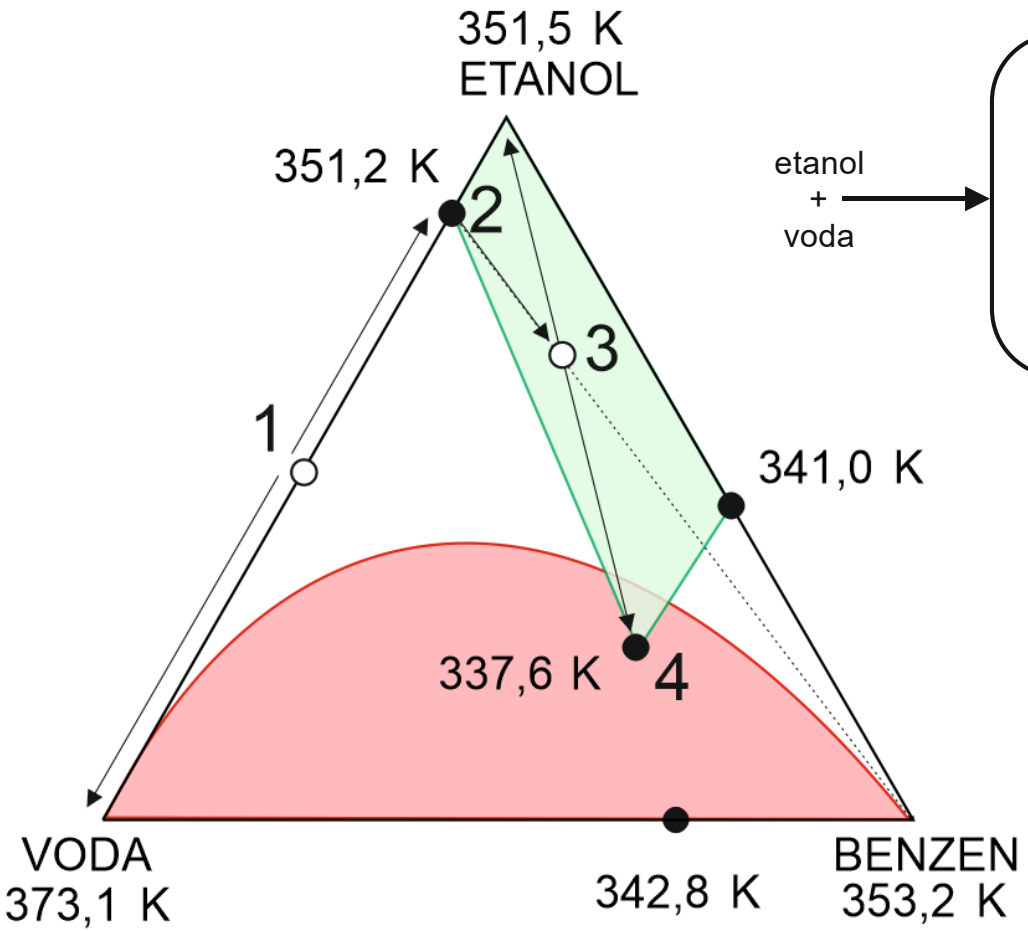


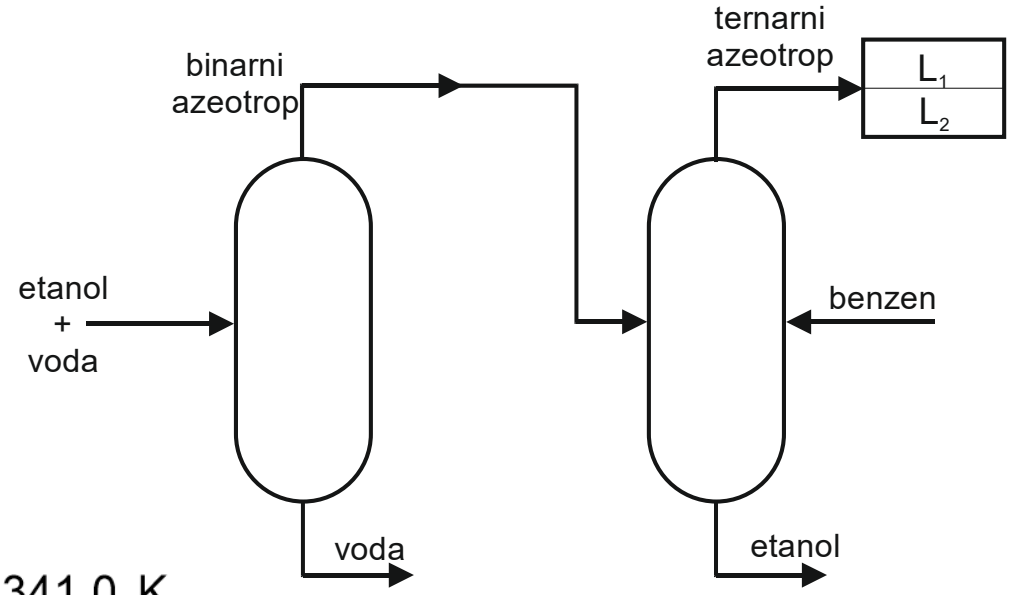


Valtz i suradnici
tetrafluoroetan (1) – dimetileter (2)

Razdvajanje azeotropa

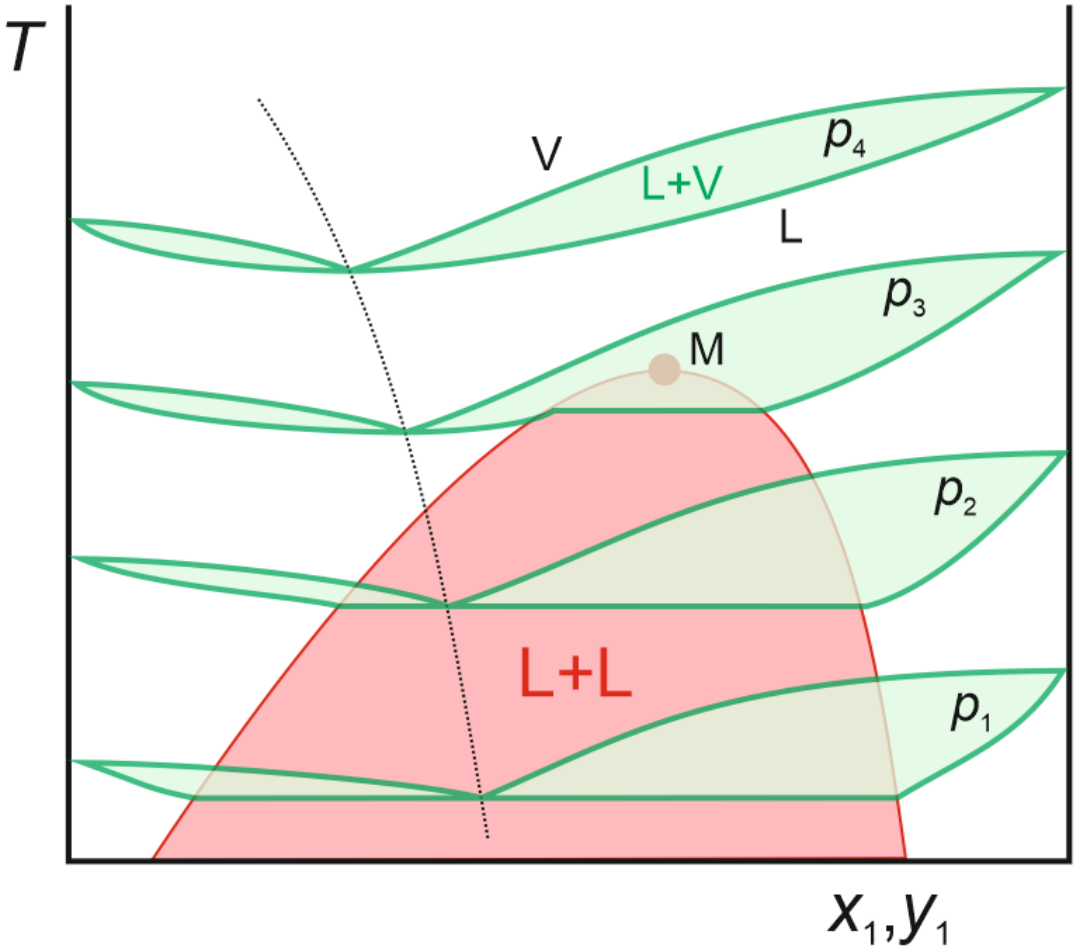
Uvođenje treće komponente





Para-kapljevina-kapljevina

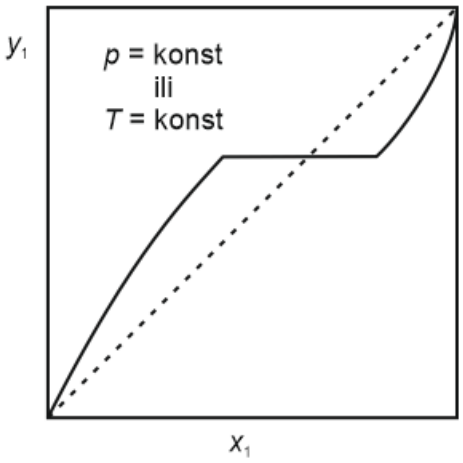
Fazni dijagrami

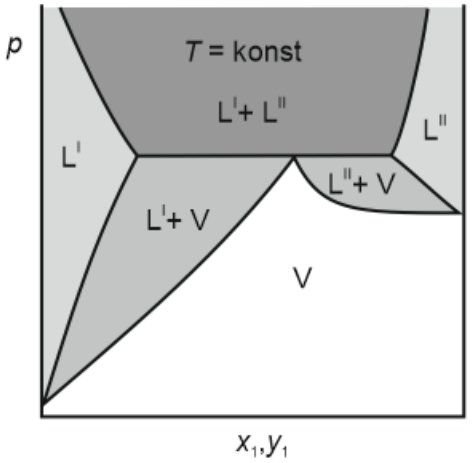


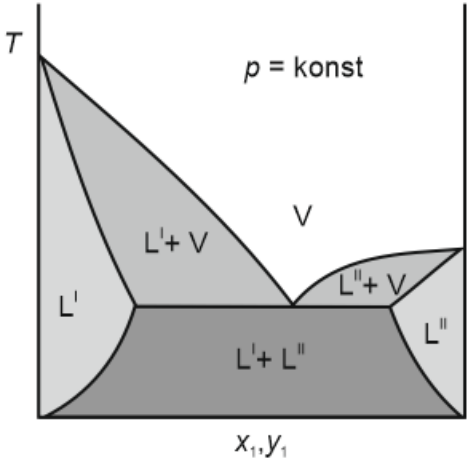


Para-kapljevina-kapljevina

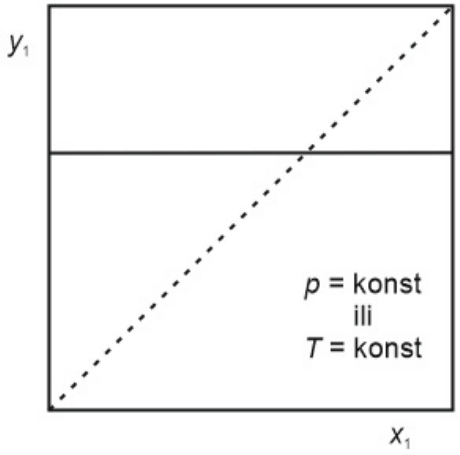
Heterogeni azeotrop s minimumom vrelišta

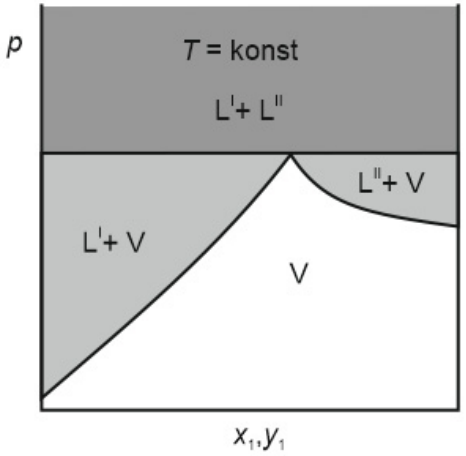


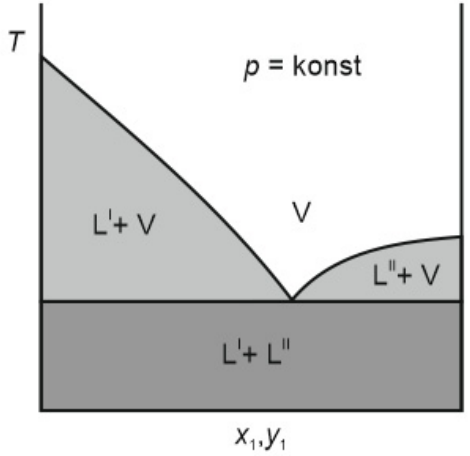




Heterogeni azeotrop s minimumom vrelišta – potpuna nemješljivost

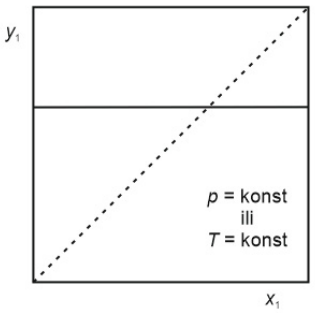


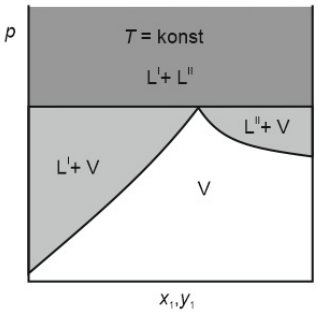


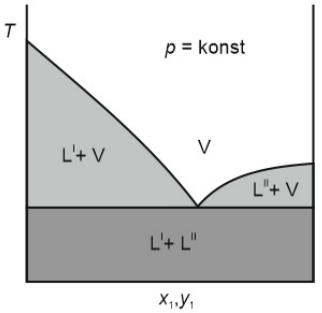


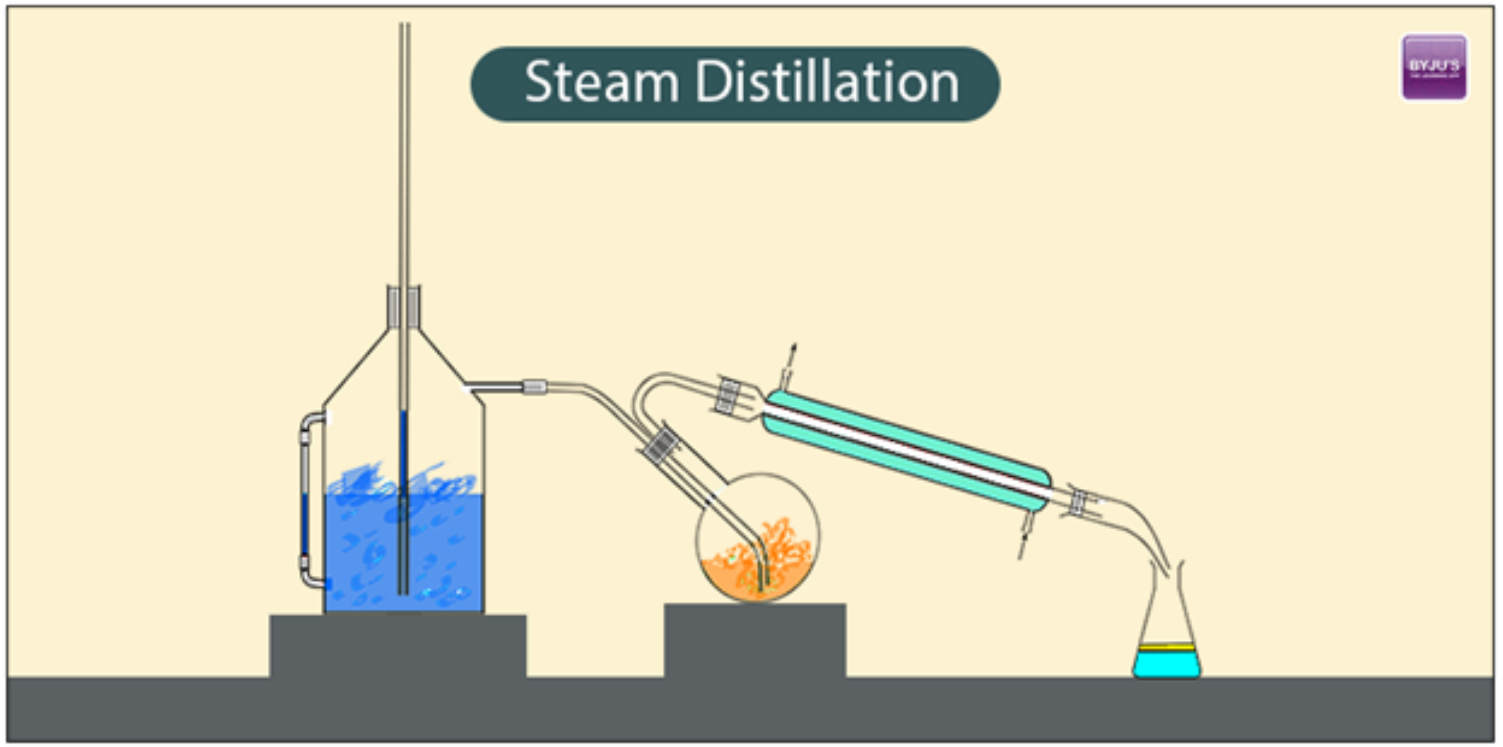
Para-kapljevina-kapljevina

Destilacija vodenom parom



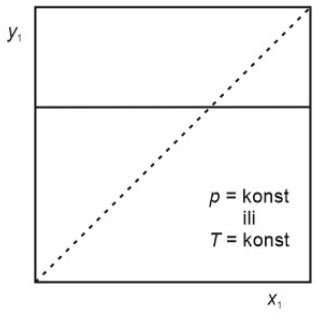


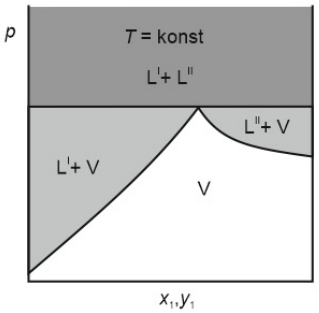


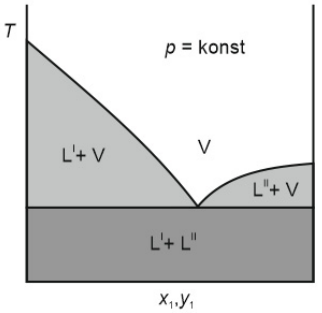


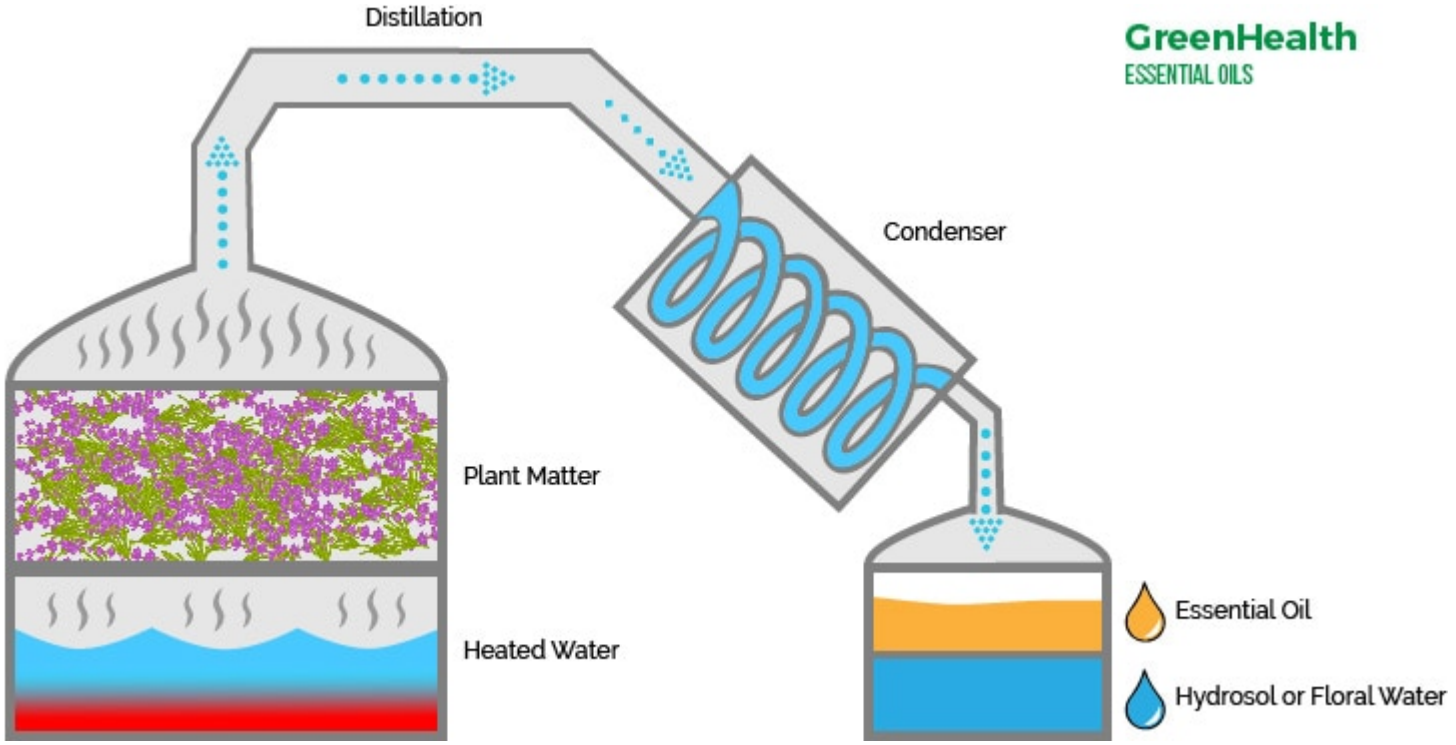
Para-kapljevina-kapljevina

Destilacija vodenom parom



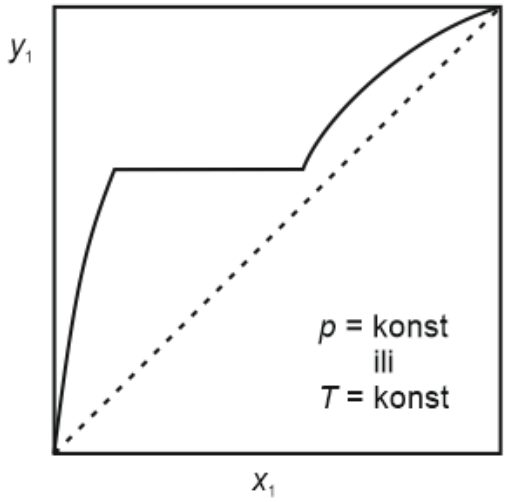


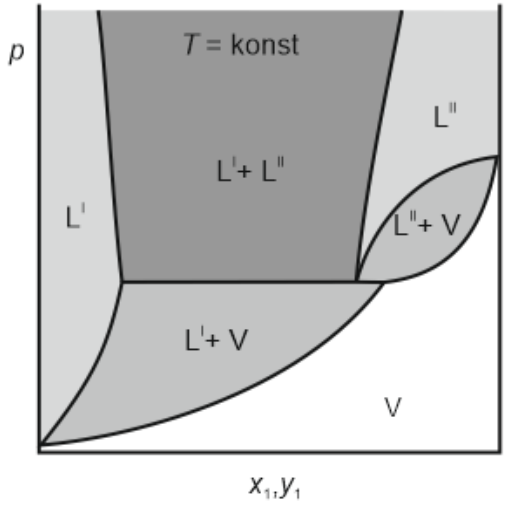


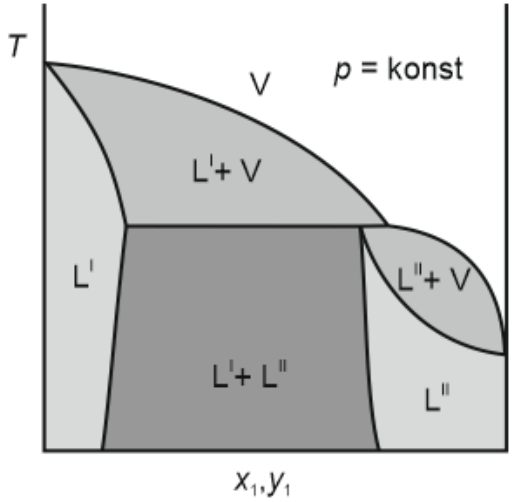


Para-kapljevina-kapljevina

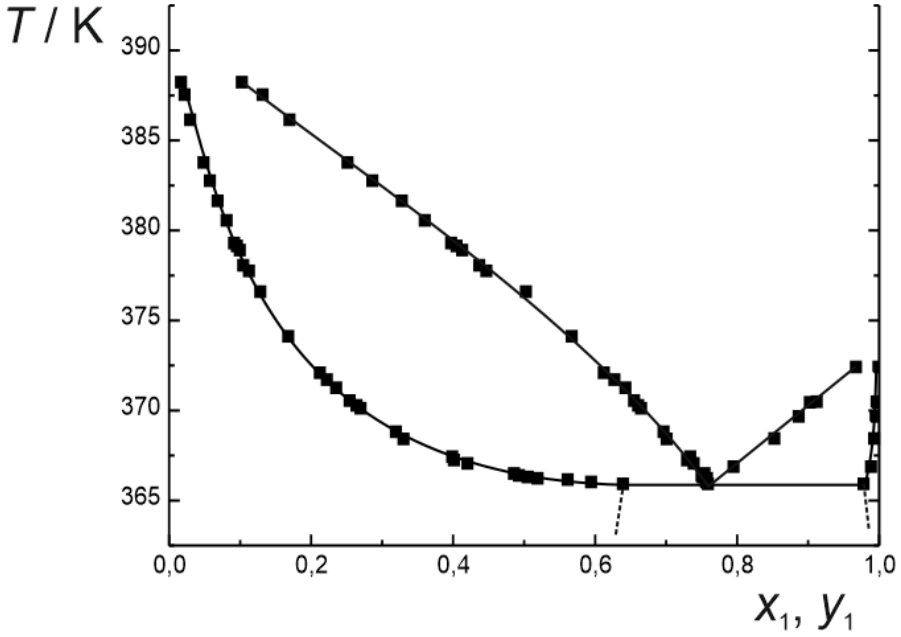
Djelimična mješljivost bez heterogenog azeotropa
Nemješljivost se pojavljuje između vrelišta čistih komponenata



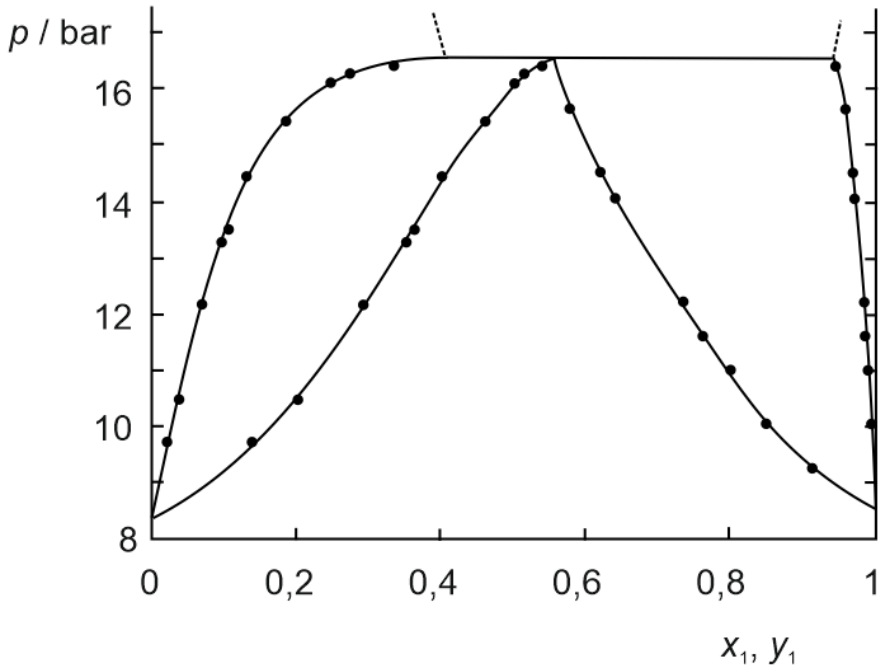




Para-kapljevina-kapljevina



Voda(1) – *n*-butanol(2)
101325 Pa
K. Iwakabe i H. Kosuge



amonijak (1) – voda (2)
293 K
Gmehling i Onken zbirka

Para-kapljevina-kapljevina

Proračuni

- proračun ravnoteže kapljevina-kapljevina
- proračun ravnoteže barem jedne od kapljevitih faza s parom.

$$L^{I} \leftrightarrow L^{II} \quad i \quad L^{I} \leftrightarrow V \quad \rightarrow \quad L^{II} \leftrightarrow V$$