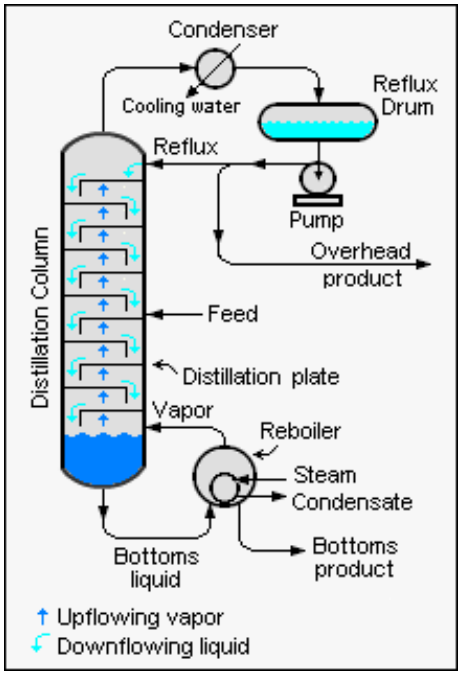
Ravnoteža para-kapljevina 1

Ravnoteža para-kapljevina



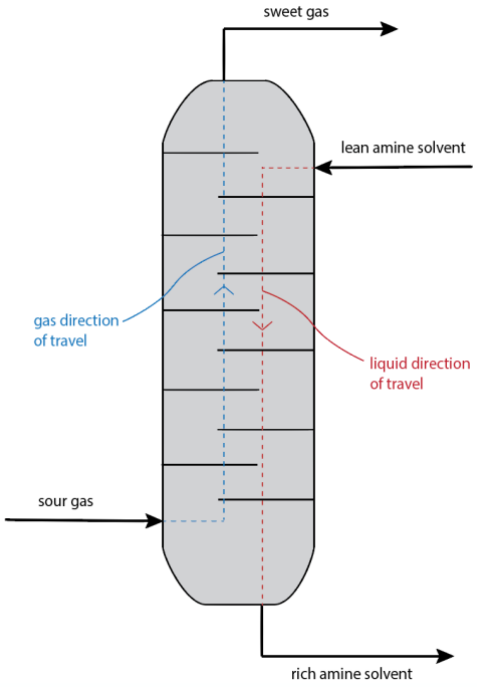
RAVNOTEŽA PARA - KAPLJEVINA

FAZNA RAVNOTEŽA
Nema kemijskih i elektrokemijskih procesa u sustavu

INDUSTRIJSKA PRAKSA
Razdvajanje smjesa u komponente

Jednokratno ili višekratno isparavanje = DESTILACIJA
Jednokratno ili višekratno ukapljivanje = DESTILACIJA

APSORPCIJA – razdvajanje plinova na osnovi razlike u topljivosti



Uvjeti fazne ravnoteže

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

Bilanca energije
Izolirani sustavi

$$H^{\mathrm{F}} = H^{\mathrm{L}} + H^{\mathrm{V}} + Q$$

Bilanca energije
Zatvoreni sustavi

I. zakon termodinamike

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

Ukupna bilanca tvari

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

Bilanca po komponentama

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

Bilanca po fazama

Uvjeti fazne ravnoteže

II. zakon termodinamike

$S = \max. \qquad dS = 0$ Izolirani sustavi

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

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

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

Izolirani jednokomponentni sustavi
Ekvivalentan skup uvjeta

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

Višekomponentni sustavi

Jednadžba fazne ravnoteže

Neidealnost preko koeficijenta fugacitivnosti

$$\mu_i = RTd \ln \hat{f}_i$$

Definicija parc. fugacitivnosti

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

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

Definicija parc. tlaka

$$p_i^{\mathrm{V}} = y_i p \qquad p_i^{\mathrm{L}} = x_i p$$

$$\hat{\varphi}_i^{\mathrm{V}} y_i p = \hat{\varphi}_i^{\mathrm{L}} x_i p$$

$$\hat{\varphi}_i^{\mathrm{V}} y_i = \hat{\varphi}_i^{\mathrm{L}} x_i$$

$$\hat{\varphi}_i^{\mathrm{V}} = \frac{\hat{f}_i^{\mathrm{V}}}{p_i^{\mathrm{V}}}$$

Definicija parc. koef. fugacitivnosti

$$\hat{\varphi}_i^{\mathrm{V}} p_i^{\mathrm{V}} = \hat{\varphi}_i^{\mathrm{L}} p_i^{\mathrm{L}}$$

Koeficijent raspodjele
K-vrijednost

$$K_i = \frac{y_i}{x_i} \qquad K_i = \frac{\hat{\varphi}_i^{\mathrm{L}}}{\hat{\varphi}_i^{\mathrm{V}}}$$

Jednadžba fazne ravnoteže

Primjena jednadžbi stanja za opis neidealnosti pare i kapljevine

Redlich-Kwong

$$\ln\hat{\varphi}_i = \frac{b_i}{b_\mathrm{M}}(z-1) - \ln\left[z\left(1-\frac{b_\mathrm{M}}{v}\right)\right] + \frac{1}{b_\mathrm{M}RT^{3/2}}\left(\frac{a_\mathrm{M}b_i}{b_\mathrm{M}} - 2\sum_j y_j a_{ij}\right)\ln\left(1+\frac{b_\mathrm{M}}{v}\right)$$

Peng-Robinson

$$\ln\hat{\varphi}_i = \frac{b_i}{b_\mathrm{M}}(z-1) - \ln\left[z\left(1-\frac{b_\mathrm{M}}{v}\right)\right] + \frac{(a\alpha)_\mathrm{M}}{RT2\sqrt{2}b_\mathrm{M}}\left(\frac{b_\mathrm{i}}{b_\mathrm{M}} - \frac{2}{(a\alpha)_\mathrm{M}}\sum_j y_j(a\alpha)_{ij}\right)\ln\frac{v+b_\mathrm{M}\left(1+\sqrt{2}\right)}{v+b_\mathrm{M}\left(1-\sqrt{2}\right)}$$

Jednadžba fazne ravnoteže

Mješoviti oblik jednadžbe ravnoteže

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

$$y_i p \hat{\varphi}_i^{\mathrm{V}} = x_i \gamma_i^{\mathrm{L}} f_i^{\mathrm{L}\circ}$$

$\hat{f}_i^{\mathrm{V}} = \hat{\varphi}_i^{\mathrm{V}} y_i p$ Parna faza

$\hat{f}_i^{\mathrm{L}} = x_i \gamma_i^{\mathrm{L}} f_i^{\mathrm{L}\circ}$ Kapljevita faza

$$f_i^{\mathrm{L}\circ} = f_i^{\bullet} \exp\left[\frac{1}{RT}\int_{p_i^{\bullet}}^{p} v_i^{\mathrm{L}} dp^{\circ}\right]$$

Poyntingov faktor

$f_i^{\bullet} = \varphi_i^{\bullet} p_i^{\bullet}$ Ravnotežno stanje za čistu tvar

$$y_i p \hat{\varphi}_i^{\mathrm{V}} = x_i \gamma_i^{\mathrm{L}} \varphi_i^{\bullet} p_i^{\bullet} \exp\left[\int_{p_i^{\bullet}}^{p} \frac{v_i^{\mathrm{L}}}{RT} dp\right]$$

Jednadžba fazne ravnoteže

Mješoviti oblik jednadžbe ravnoteže

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^{\mathrm{L}} \varphi_i^{\bullet} p_i^{\bullet}}{p \hat{\varphi}_i^{\mathrm{V}}} \exp\left[\int_{p_i^{\bullet}}^{p} \frac{v_i^{\mathrm{L}}}{RT} dp \right]$$

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^{\mathrm{L}} \varphi_i^{\bullet} p_i^{\bullet}}{p \hat{\varphi}_i^{\mathrm{V}}} \exp\left[\frac{v_i^{\mathrm{L}} \left(p - p_i^{\bullet} \right)}{RT} \right]$$

Potrebno: v_i^{L} ili ρ_i^{L}

Jednadžba stanja za $\varphi_i^{\bullet}$ $\hat{\varphi}_i^{\mathrm{V}}$ $T_{\mathrm{K}}, p_{\mathrm{K}}, \omega$ Pravila miješanja

Model koeficijenta aktivnosti za γ_i^{L}

Model za krivulje isparavanja čistih komponenata $p_i^{\bullet} = f\left(T\right)$

Jednadžba fazne ravnoteže

Model za krivulje isparavanja čistih komponenata

$$d \ln p^{\bullet} = -\frac{\Delta h^{\text{isp}}}{R} d\left(\frac{1}{T}\right)$$

$$\ln p^{\bullet} = \left(\ln p_0^{\bullet} + \frac{\Delta h^{\text{isp}}}{R T_0}\right) - \frac{\Delta h^{\text{isp}}}{R T}$$

Clausius-Clapeyron

$$\ln p^{\bullet} = A - \frac{B}{T}$$

Antoine

$$\ln p^{\bullet} = A - \frac{B}{C + T}$$

Wagner, empirijski polinom

$$\ln \frac{p^{\bullet}}{p_{\text{K}}} = \left(\frac{T_{\text{K}}}{T}\right)\left[a\left(1 - \frac{T}{T_{\text{K}}}\right) + b\left(1 - \frac{T}{T_{\text{K}}}\right)^{1{,}5} + c\left(1 - \frac{T}{T_{\text{K}}}\right)^{3} + d\left(1 - \frac{T}{T_{\text{K}}}\right)^{6}\right]$$

Jednadžba fazne ravnoteže

Pojednostavljenja

$p \approx p_i^{\bullet}$ $\quad v_i^{\mathrm{L}}\left(p - p_i^{\bullet}\right) \ll RT$ Mali raspon vrelišta $\quad PF_{\mathrm{i}} = \exp\left[\frac{v_{\mathrm{i}}^{\mathrm{L}}\left(p - p_{\mathrm{i}}^{\bullet}\right)}{RT}\right] \to 1$

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^{\mathrm{L}} \varphi_i^{\bullet} p_i^{\bullet}}{p \hat{\varphi}_i^{\mathrm{V}}}$$

$$\ln \hat{\varphi}_i = \frac{b_i}{b_{\mathrm{M}}}(z-1) - \ln\left[z\left(1 - \frac{b_{\mathrm{M}}}{v}\right)\right] + \frac{(a\alpha)_{\mathrm{M}}}{RT\,2\sqrt{2}\,b_{\mathrm{M}}}\left(\frac{b_{\mathrm{i}}}{b_{\mathrm{M}}} - \frac{2}{(a\alpha)_{\mathrm{M}}}\sum_j y_j (a\alpha)_{ij}\right) \ln \frac{v + b_{\mathrm{M}}\left(1+\sqrt{2}\right)}{v + b_{\mathrm{M}}\left(1-\sqrt{2}\right)}$$

$\hat{\varphi}_i = \varphi_i^{\circ}$

Lewis-Randallovo pravilo
Neidealne komponente se idealno miješaju u parnoj fazi

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^{\mathrm{L}} \varphi_i^{\bullet} p_i^{\bullet}}{p \varphi_i^{\circ}}$$

$$\ln \varphi = \ln \frac{v}{v-b} - \frac{a\alpha}{bRT\,2\sqrt{2}} \ln \frac{v + b\left(1+\sqrt{2}\right)}{v + b\left(1-\sqrt{2}\right)} + (z-1) - \ln z$$

Jednadžba fazne ravnoteže

Pri niskim tlakovima

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

$$\mu_{\mathrm{i}}^{\mathrm{V}\circ} + RT\ln\left(\gamma_{\mathrm{i}}^{\mathrm{V}} y_{\mathrm{i}}\right) = \mu_{\mathrm{i}}^{\mathrm{L}\circ} + RT\ln\left(\gamma_{\mathrm{i}}^{\mathrm{L}} x_{\mathrm{i}}\right)$$ Model koeficijenta aktivnosti za obje faze

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^{\mathrm{L}}}{\gamma_i^{\mathrm{V}}} \exp\left(\frac{\mu_i^{\mathrm{L}\circ} - \mu_i^{\mathrm{V}\circ}}{RT}\right)$$

$$\exp\left(\frac{\mu_i^{\mathrm{L}\circ} - \mu_i^{\mathrm{V}\circ}}{RT}\right) = \frac{p_i^{\bullet}}{p} \exp\left[\frac{v_i^{\mathrm{L}}\left(p - p_{\mathrm{i}}^{\bullet}\right)}{RT}\right] \exp\left[\frac{1}{RT}\int_{p_i^{\bullet}}^{p}\left(\frac{RT}{p} - v_i^{\mathrm{V}}\right)dp\right]$$ Dugački izvod

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^{\mathrm{L}} p_i^{\bullet}}{\gamma_i^{\mathrm{V}} p} \exp\left[\frac{v_i^{\mathrm{L}}\left(p - p_i^{\bullet}\right)}{RT}\right] \exp\left[\frac{1}{RT}\int_{p_i^{\bullet}}^{p}\left(\frac{RT}{p} - v_i^{\mathrm{V}}\right)dp\right]$$

Jednadžba fazne ravnoteže

Pri niskim tlakovima

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^{\mathrm{L}} p_i^{\bullet}}{\gamma_i^{\mathrm{V}} p} \exp\left[\frac{v_i^{\mathrm{L}}\left(p - p_i^{\bullet}\right)}{RT}\right] \exp\left[\frac{1}{RT}\int_{p_i^{\bullet}}^{p}\left(\frac{RT}{p} - v_i^{\mathrm{V}}\right)dp\right]$$

$\gamma_i^{\mathrm{V}} = 1$ Idealna parna faza $v_i^{\mathrm{V}} = \frac{RT}{p}$

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^{\mathrm{L}} p_i^{\bullet}}{p} \exp\left[\frac{v_i^{\mathrm{L}}\left(p - p_i^{\bullet}\right)}{RT}\right]$$

Jednadžba fazne ravnoteže

Pojednostavljenja

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^{\mathrm{L}} p_i^{\bullet}}{p} \exp\left[\frac{v_i^{\mathrm{L}}\left(p - p_i^{\bullet}\right)}{RT}\right]$$

$p \approx p_i^{\bullet}$ $\quad v_i^{\mathrm{L}}\left(p - p_i^{\bullet}\right) \ll RT$ Mali raspon vrelišta $\quad PF_{\mathrm{i}} = \exp\left[\frac{v_{\mathrm{i}}^{\mathrm{L}}\left(p - p_{\mathrm{i}}^{\bullet}\right)}{RT}\right] \to 1$

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^{\mathrm{L}} p_i^{\bullet}}{p}$$

$\gamma_i^{\mathrm{L}} = 1$ Idealne kapljevine

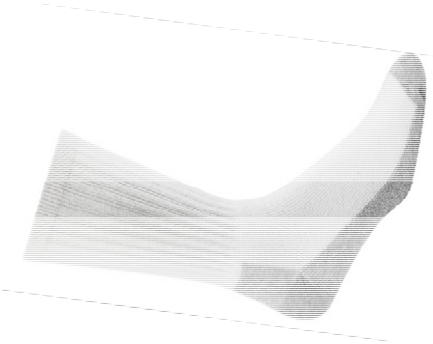
$$K_i = \frac{y_i}{x_i} = \frac{p_i^{\bullet}}{p} \qquad y_i p = x_i p_i^{\bullet}$$

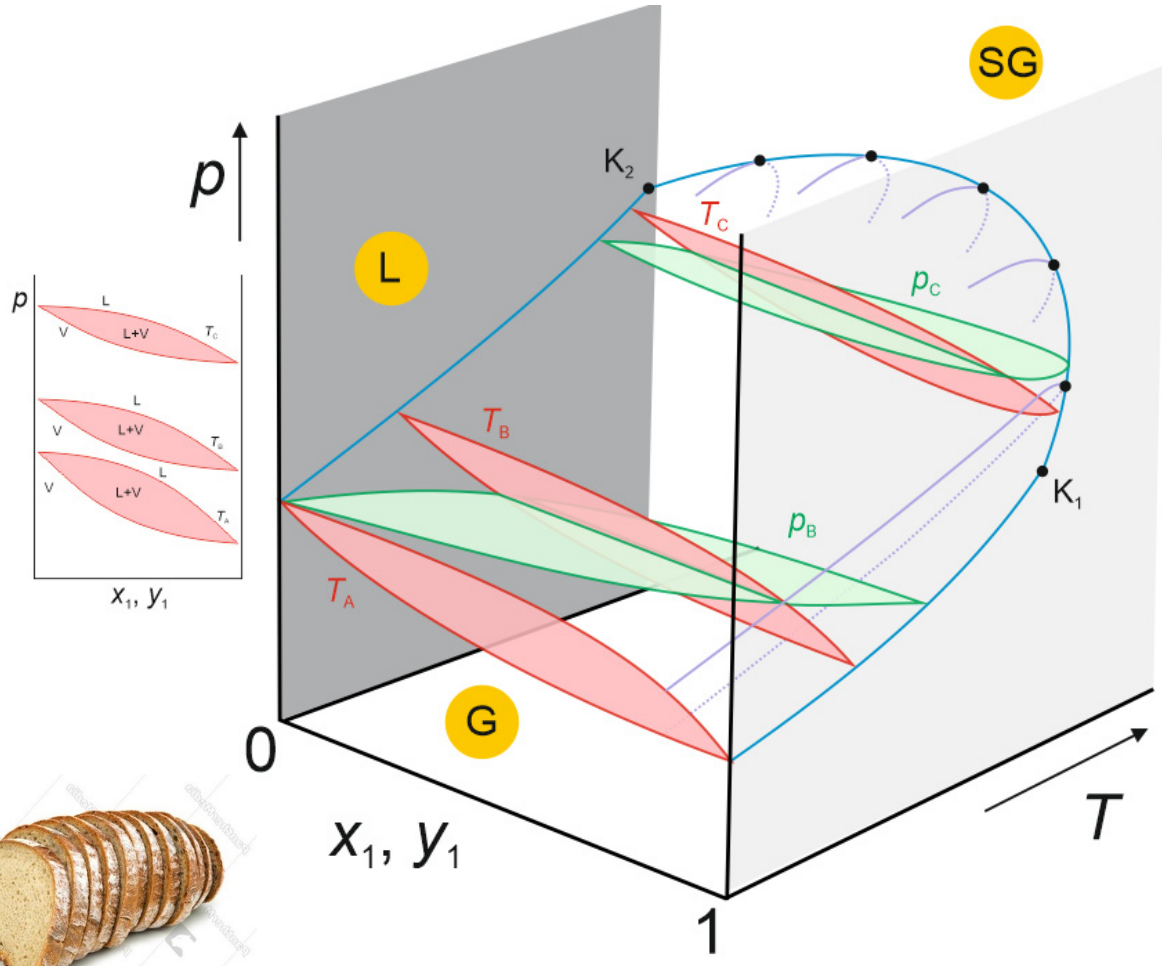
Raoultov zakon

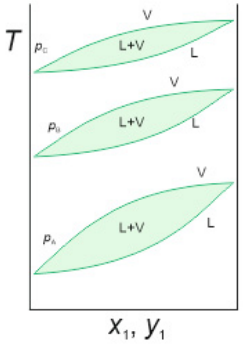
$$p_i = x_i p_i^{\bullet}$$

Zeotropne smjese

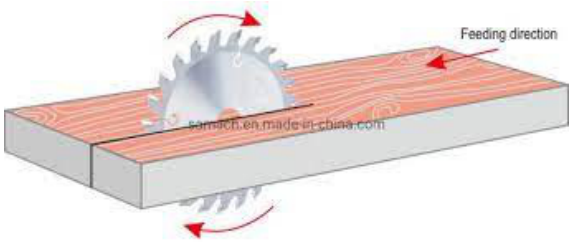
Fazni dijagrami





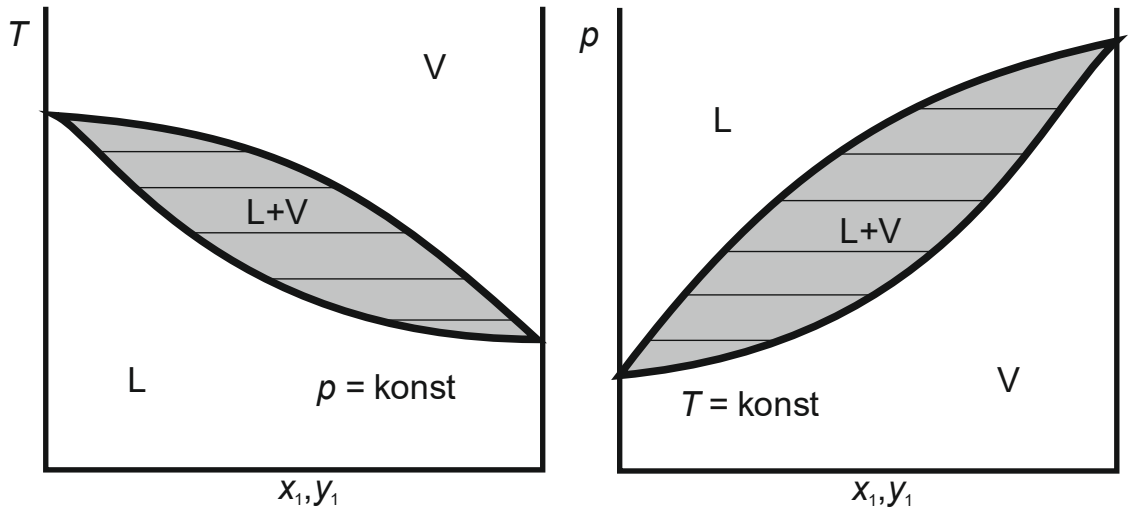


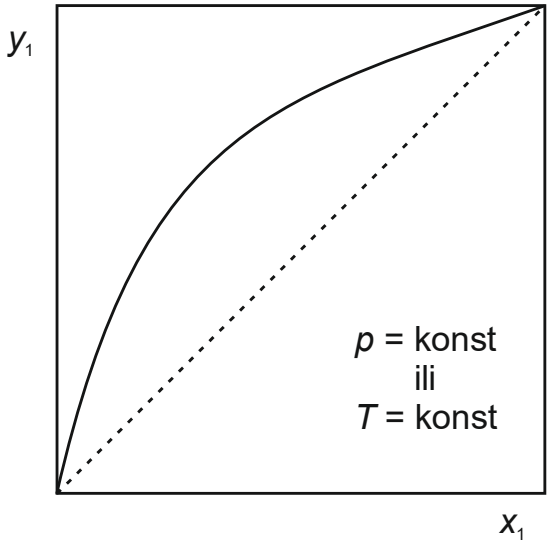


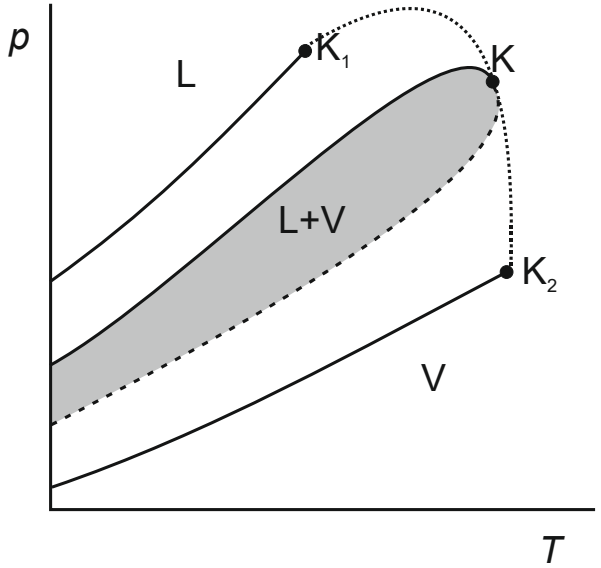


Fazni dijagrami

Zeotropne smjese

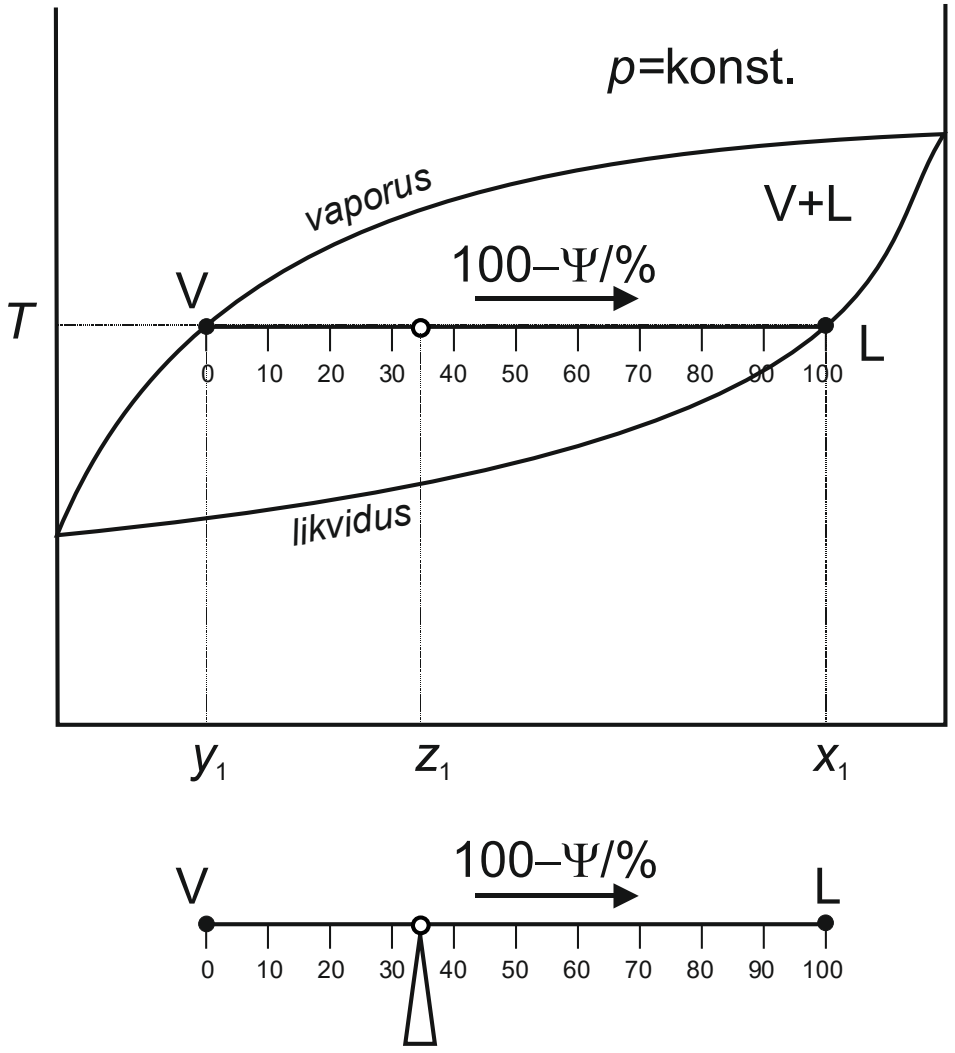






Fazni dijagrami

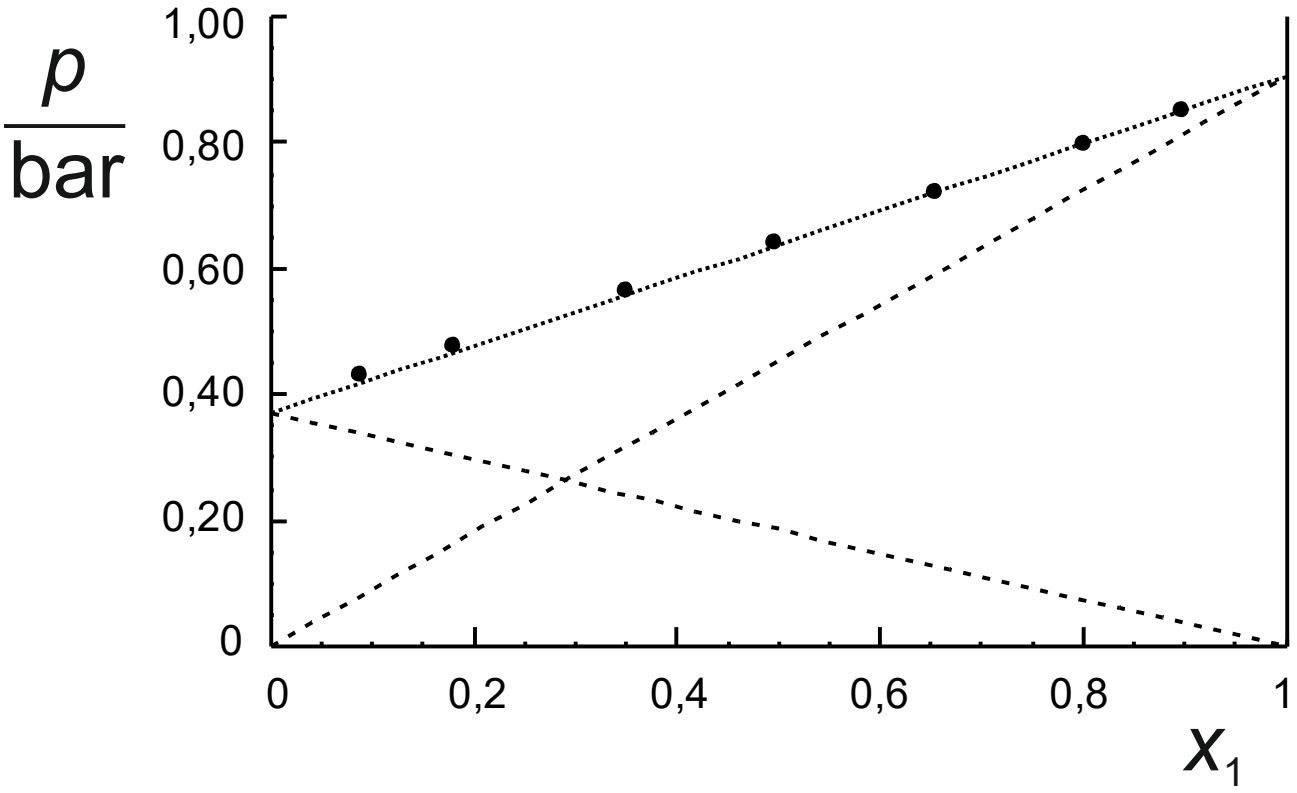
Pravilo poluge

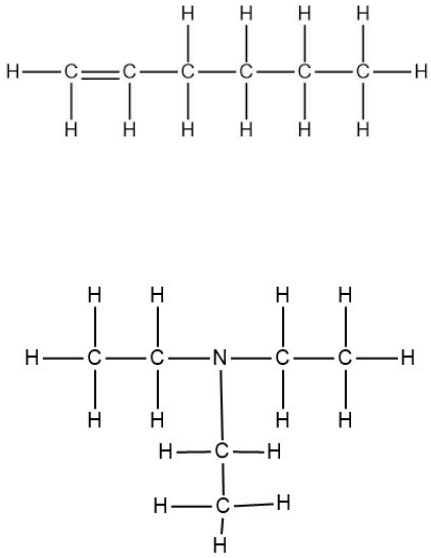


Fazni dijagrami

Zeotropne smjese

Idealna kapljevina $p = x_1 p_1^{\bullet} + x_2 p_2^{\bullet}$ Raoultov zakon





1-heksen(1) – trietilamin(2) 60 °C, Humphrey i Van Winkle

Fazni dijagrami

Nastanak azeotropa

Pozitivna odstupanja od Raoultova zakona $\gamma_i > 1$

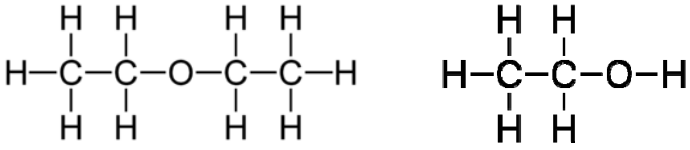
Neidealna kapljevina

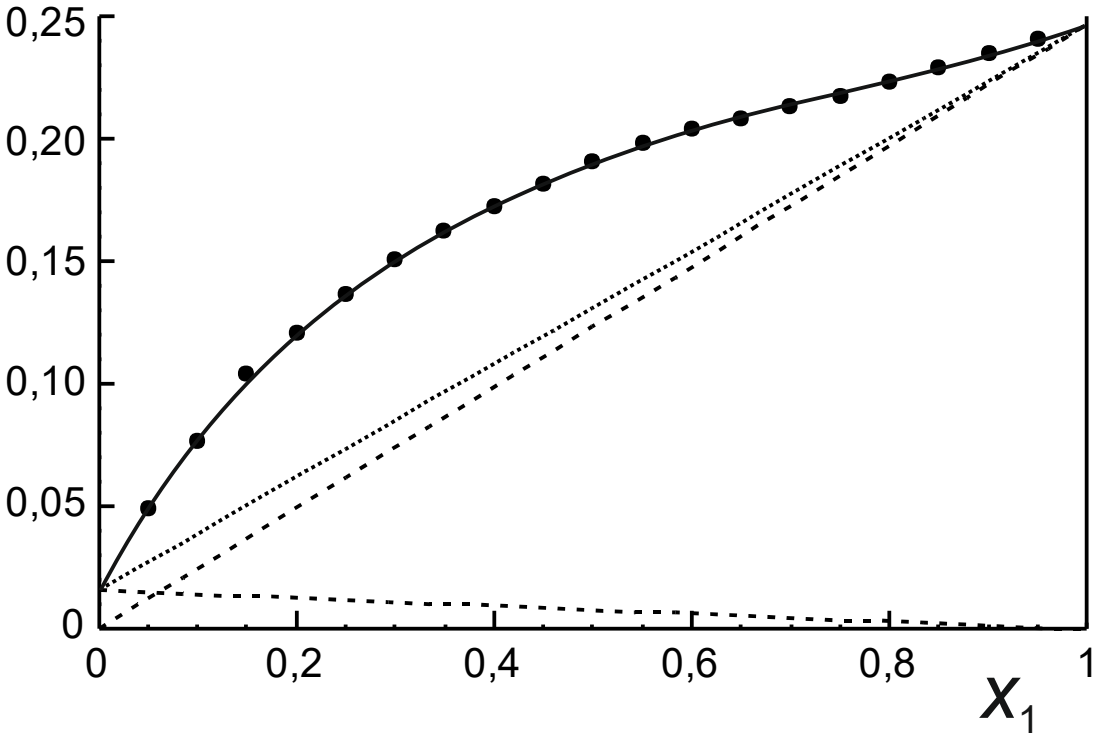
$$p_i = x_i p_i^{\bullet} \gamma_i$$

$$p = x_1 p_1^{\bullet} \gamma_1 + x_2 p_2^{\bullet} \gamma_2$$

Velika razlika u
Vrelištima
(tlakovima para)

dietileter(1) – etanol(2)
0°C
Nagai i Isii





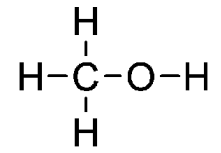
Fazni dijagrami

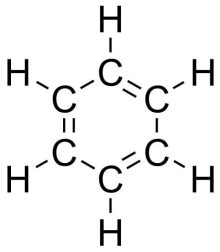
Nastanak azeotropa

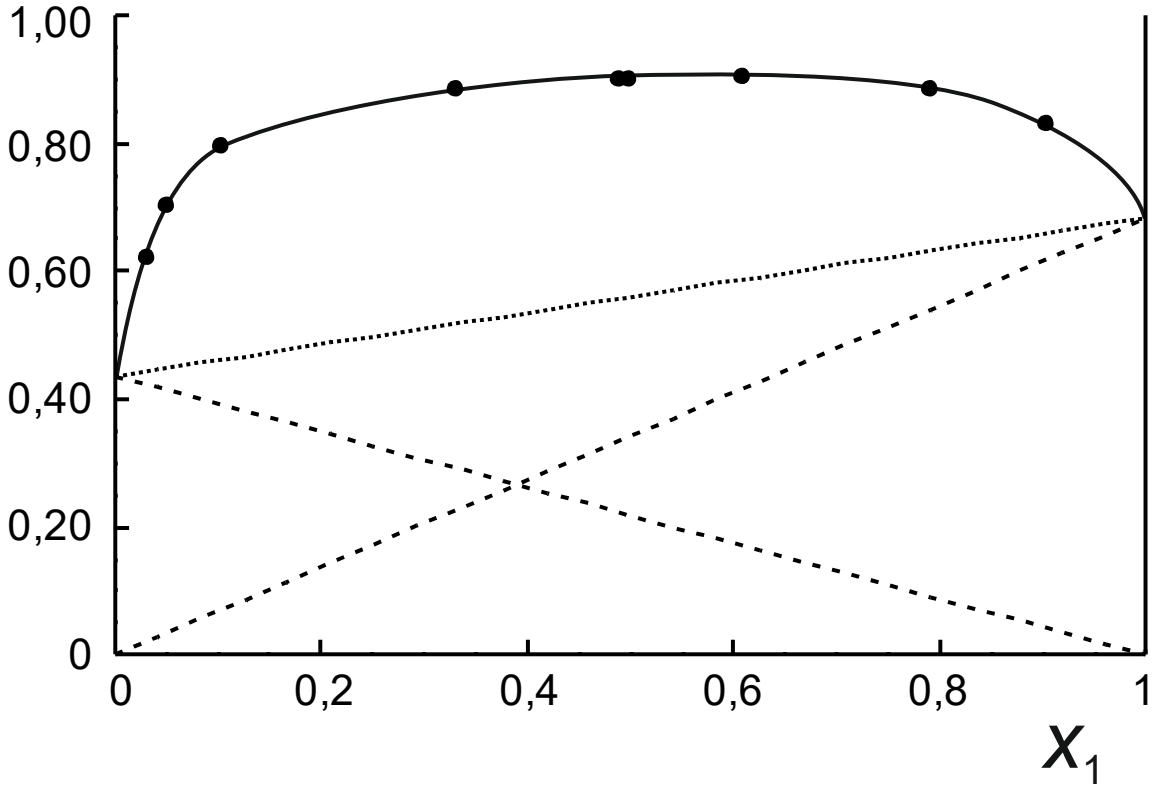
Pozitivna odstupanja od Raoultova zakona $\gamma_i > 1$

Mala razlika u vrelištima (tlakovima para)

$$p = x_1 p_1^{\bullet} \gamma_1 + x_2 p_2^{\bullet} \gamma_2$$







metanol(1) – benzen(2)
55°C
Scatchard i sur.

Fazni dijagrami

Nastanak azeotropa

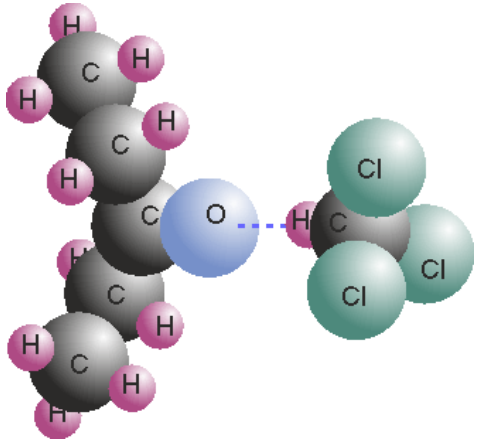
Negativna odstupanja od Raoultova zakona $\gamma_i < 1$

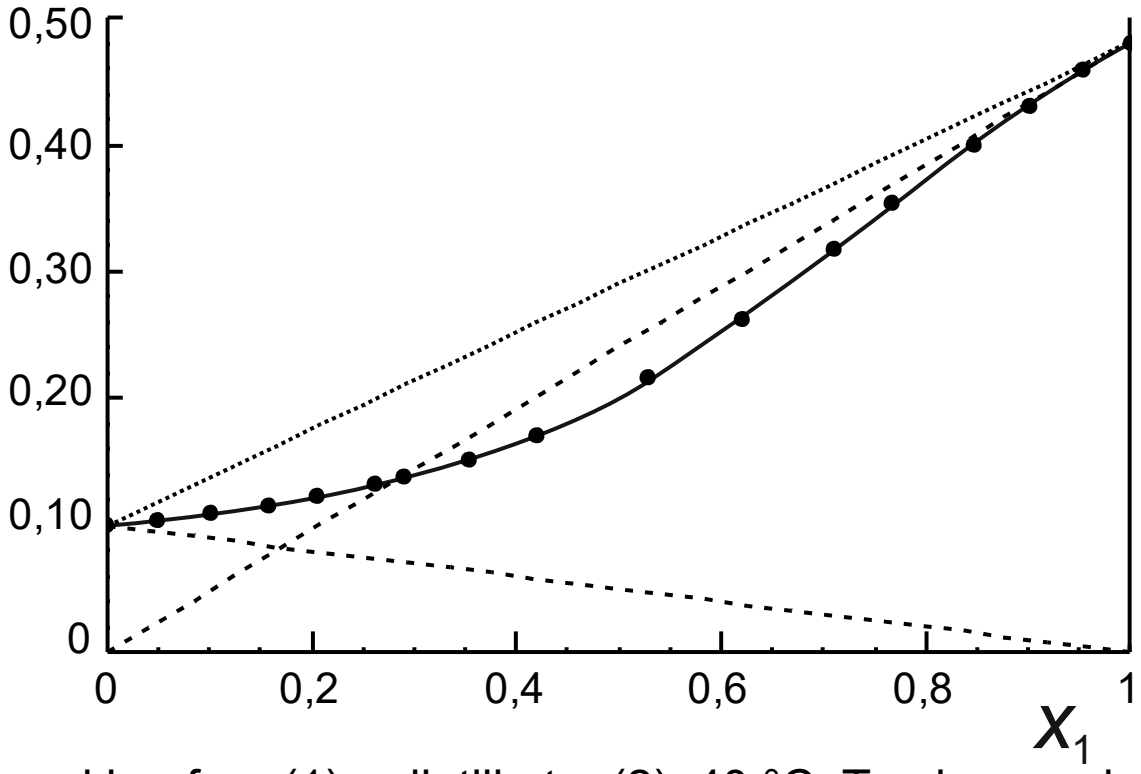
Neidealna kapljevina

$$p_i = x_i p_i^{\bullet} \gamma_i$$

$$p = x_1 p_1^{\bullet} \gamma_1 + x_2 p_2^{\bullet} \gamma_2$$

Velika razlika u vrelištima (tlakovima para)





kloroform(1) – dietilketon(2), 40 °C, Teodorescu i sur.

Fazni dijagrami

Nastanak azeotropa

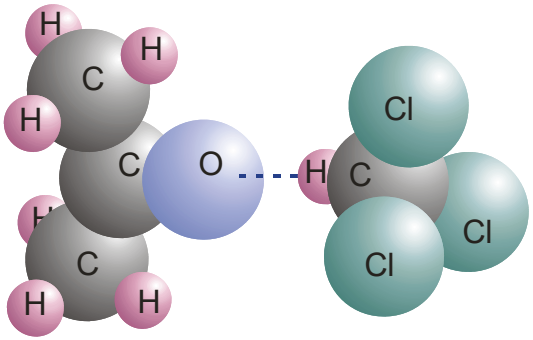
Negativna odstupanja od Raoultova zakona $\gamma_i < 1$

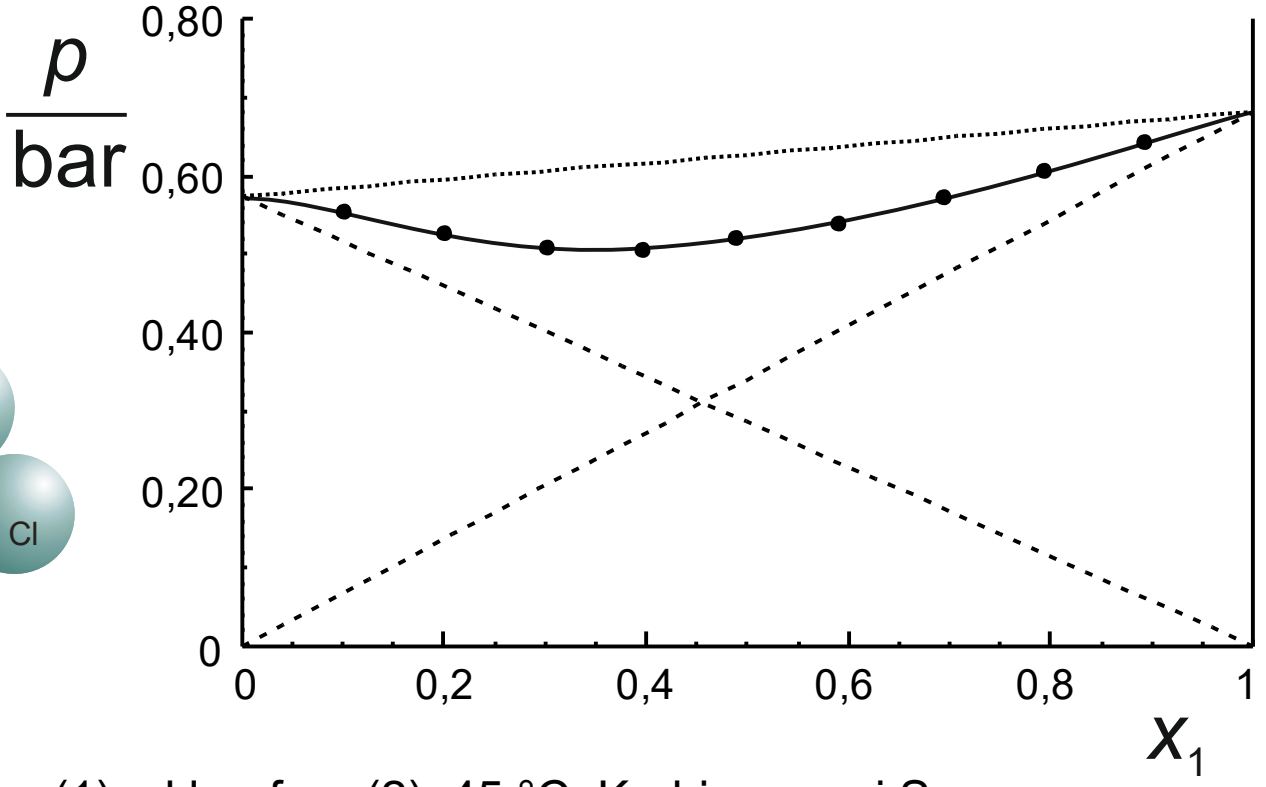
Neidealna kapljevina

$$p_i = x_i p_i^{\bullet} \gamma_i$$

$$p = x_1 p_1^{\bullet} \gamma_1 + x_2 p_2^{\bullet} \gamma_2$$

Mala razlika u vrelištima (tlakovima para)





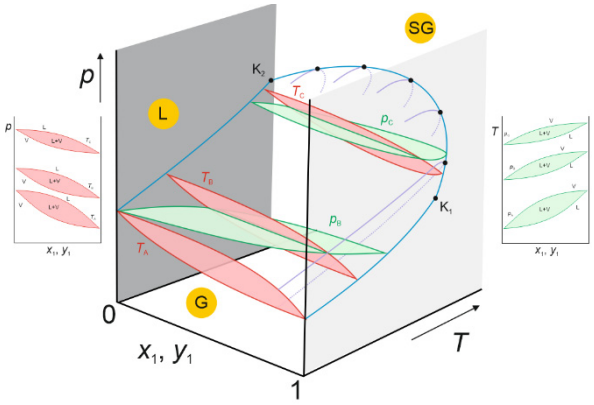
aceton(1) – kloroform(2), 45 °C, Kudrjavceva i Susarev

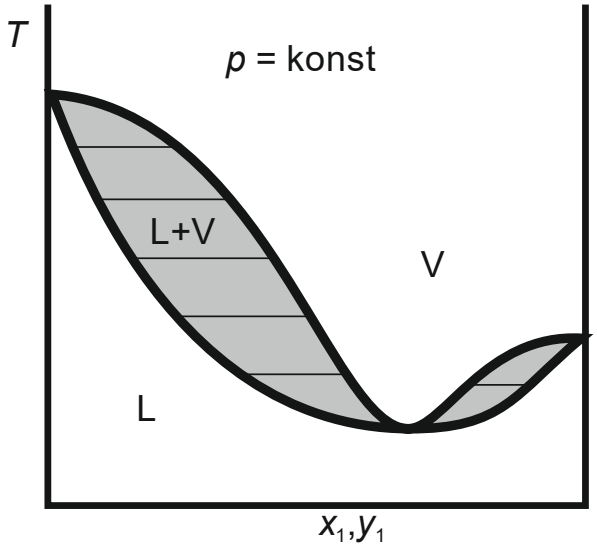
Fazni dijagrami

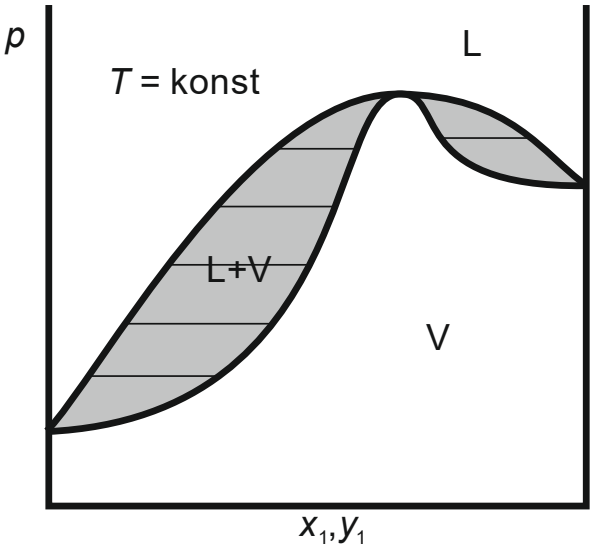
Nastanak azeotropa

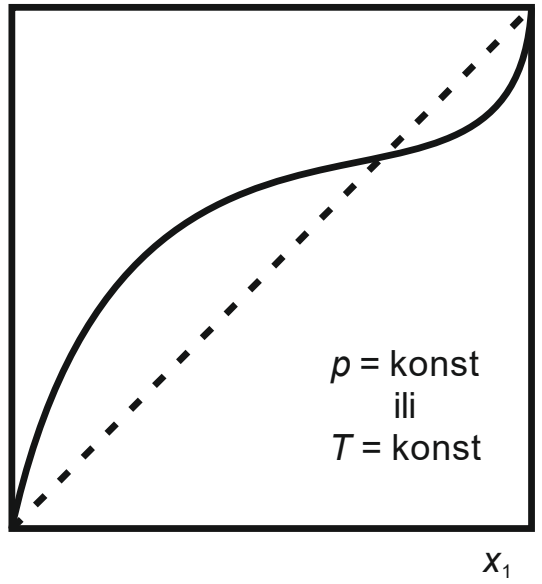










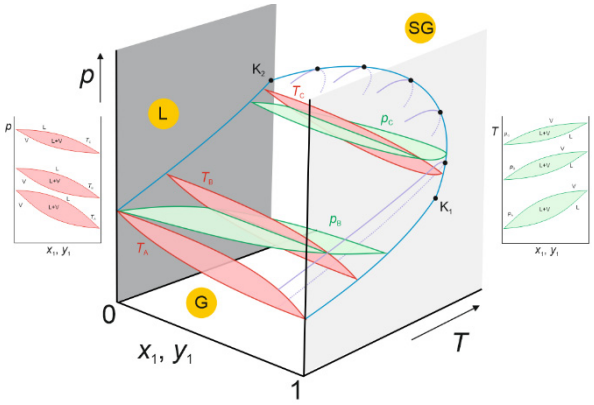


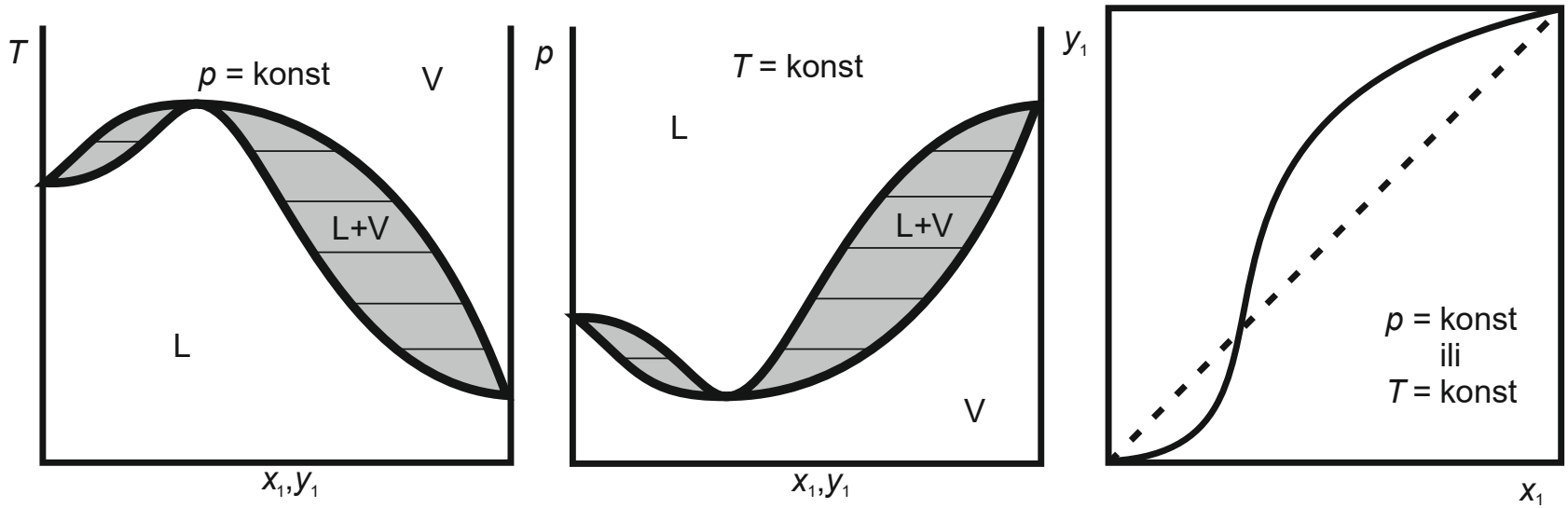
Azeotrop s minimumom vrelišta

Fazni dijagrami









Azeotrop s maksimumom vrelišta

Za kolokvij i za lab. vježbe

Određivanje parametara modela koeficijenta aktivnosti iz eksperimentalnih podataka

Predmet II. laboratorijske vježbe
Raspravljeno u nastavnom tekstu
Raspravljeno u uputama za II. laboratorijsku vježbu

Testovi konzistentnosti

Predmet II. laboratorijske vježbe
Raspravljeno u nastavnom tekstu
Raspravljeno u uputama za II. laboratorijsku vježbu

Provjeravaju zadovoljavaju li eksperimentalni podaci opće termodinamičke zakonitosti, poput poopćene Gibbs-Duhemove jednadžbe

$$\frac{h^{\mathrm{ex}}}{RT^2}dT - \frac{v^{\mathrm{ex}}}{RT}dp + x_1 d\ln\gamma_1 + x_2 d\ln\gamma_2 = 0$$