

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

$$H^F = H^L + H^V \quad \text{Bilanca energije}$$

Izolirani sustavi

$$H^F = H^L + H^V + Q \quad \text{Bilanca energije}$$

Zatvoreni sustavi

I. zakon termodinamike

$$\sum_{i=1}^{nk} n_i^F = \sum_{i=1}^{nk} n_i^L + \sum_{i=1}^{nk} n_i^V \quad \text{Ukupna bilanca tvari}$$

$$n^F z_i^F = n^L x_i^L + n^V y_i^V \quad \text{Bilanca po komponentama}$$

$$\sum_{i=1}^{nk} y_i^V = 1 \quad \sum_{i=1}^{nk} x_i^L = 1 \quad \text{Bilanca po fazama}$$

Uvjeti fazne ravnoteže

II. zakon termodinamike

$$S = \max. \quad dS = 0 \quad \text{Izolirani sustavi}$$

$$T^L = T^V \quad \begin{array}{l} \text{Izolirani jednokomponentni sustavi} \\ \text{Ekvivalentan skup uvjeta} \end{array}$$

$$p^L = p^V$$

$$g^L = g^V$$

$$\mu_i^L = \mu_i^V \quad \text{Višekomponentni sustavi}$$

Jednadžba fazne ravnoteže

Neidealnost preko koeficijenta fugacitivnosti

$$\mu_i = RTd \ln \hat{f}_i \quad \text{Definicija parc. fugacitivnosti}$$

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

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

$$\hat{\phi}_i^V = \frac{\hat{f}_i^V}{p_i^V} \quad \text{Definicija parc. koef. fugacitivnosti}$$

$$\hat{\phi}_i^V p_i^V = \hat{\phi}_i^L p_i^L$$

Definicija parc. tlaka

$$p_i^V = y_i p \quad p_i^L = x_i p$$

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

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

Koeficijent raspodjele
K-vrijednost

$$K_i = \frac{y_i}{x_i} \quad K_i = \frac{\hat{\phi}_i^L}{\hat{\phi}_i^V}$$

Jednadžba fazne ravnoteže

Primjena jednadžbi stanja za opis neidealnosti pare i kapljevine

Redlich-Kwong

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

Peng-Robinson

$$\ln \hat{\phi}_i = \frac{b_i}{b_M} (z-1) - \ln \left[z \left(1 - \frac{b_M}{v} \right) \right] + \frac{(a\alpha)_M}{RT 2\sqrt{2}b_M} \left(\frac{b_i}{b_M} - \frac{2}{(a\alpha)_M} \sum_j y_j (a\alpha)_{ij} \right) \ln \frac{v + b_M (1 + \sqrt{2})}{v + b_M (1 - \sqrt{2})}$$

Jednadžba fazne ravnoteže

Mješoviti oblik jednadžbe ravnoteže

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

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

$$\hat{f}_i^V = \hat{\phi}_i^V y_i p \quad \hat{f}_i^L = x_i \gamma_i^L f_i^{L^\circ}$$

Parna faza

Kapljevita faza

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

$$f_i^\bullet = \phi_i^\bullet p_i^\bullet \quad \text{Ravnotežno stanje za čistu tvar}$$

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

Jednadžba fazne ravnoteže

Mješoviti oblik jednadžbe ravnoteže

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

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

Potrebno: v_i^L ili ρ_i^L

Jednadžba stanja za ϕ_i^\bullet $\hat{\phi}_i^V$ T_K, p_K, ω Pravila miješanja

Model koeficijenta aktivnosti za γ_i^L

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

Jednadžba fazne ravnoteže

Model za krivulje isparavanja čistih komponenata

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

Clausius-Clapeyron

$$\ln p^\bullet = \left(\ln p_0^\bullet + \frac{\Delta h^{\text{isp}}}{RT_0} \right) - \frac{\Delta h^{\text{isp}}}{RT}$$

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

Antoine

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

Wagner, empirijski polinom

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

Jednadžba fazne ravnoteže

Pojednostavljenja

$$p \approx p_i \quad v_i^L (p - p_i^\bullet) \ll RT \quad \text{Mali raspon vrelišta} \quad PF_i = \exp \left[\frac{v_i^L (p - p_i^\bullet)}{RT} \right] \rightarrow 1$$

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

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

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

Lewis-Randallovo pravilo

Neidealne komponente se idealno miješaju u parnoj fazi

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

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

Jednadžba fazne ravnoteže

Pri niskim tlakovima

$$\mu_i^L = \mu_i^V$$

$$\mu_i^{V^\circ} + RT \ln(\gamma_i^V y_i) = \mu_i^{L^\circ} + RT \ln(\gamma_i^L x_i) \quad \text{Model koeficijenta aktivnosti za obje faze}$$

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

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

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

Jednadžba fazne ravnoteže

Pri niskim tlakovima

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

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

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

Jednadžba fazne ravnoteže

Pojednostavljenja

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

$p \approx p_i^\bullet$ $v_i^L (p - p_i^\bullet) \ll RT$ Mali raspon vrelišta $PF_i = \exp\left[\frac{v_i^L (p - p_i^\bullet)}{RT}\right] \rightarrow 1$

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

$\gamma_i^L = 1$ Idealne kapljevine

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

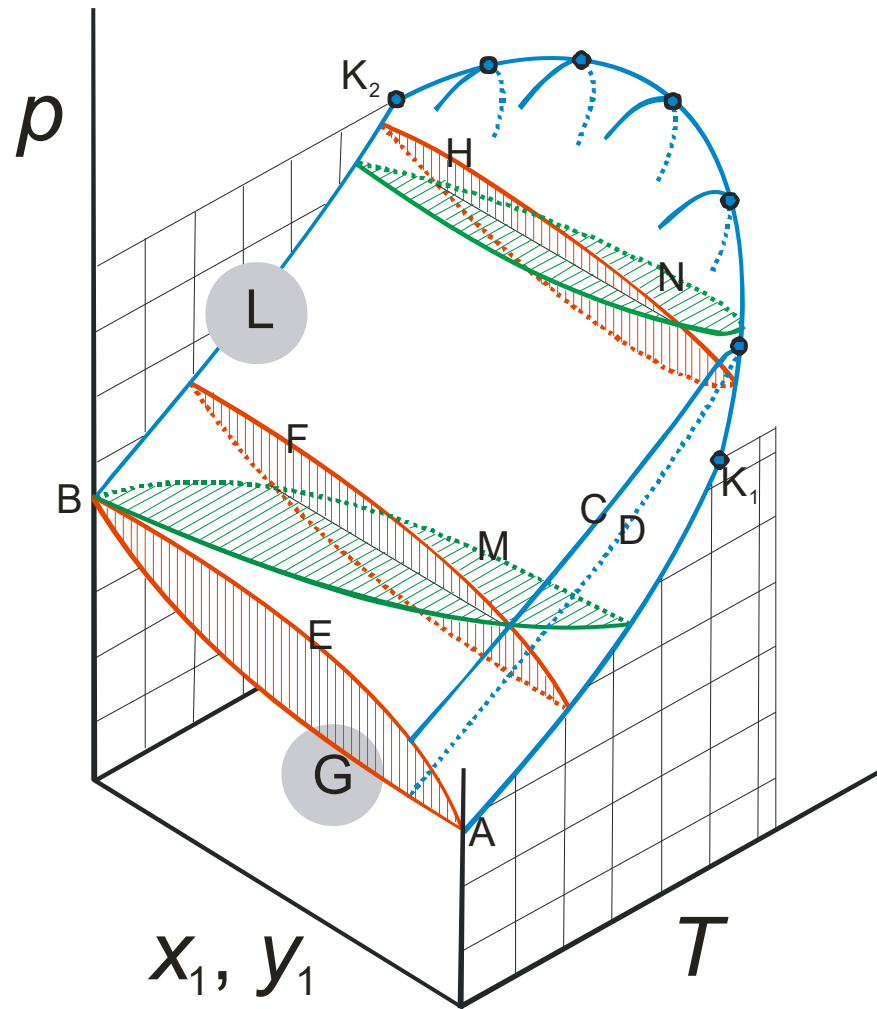
$$y_i p = x_i p_i^\bullet$$

$$p_i = x_i p_i^\bullet$$

Raoultov zakon

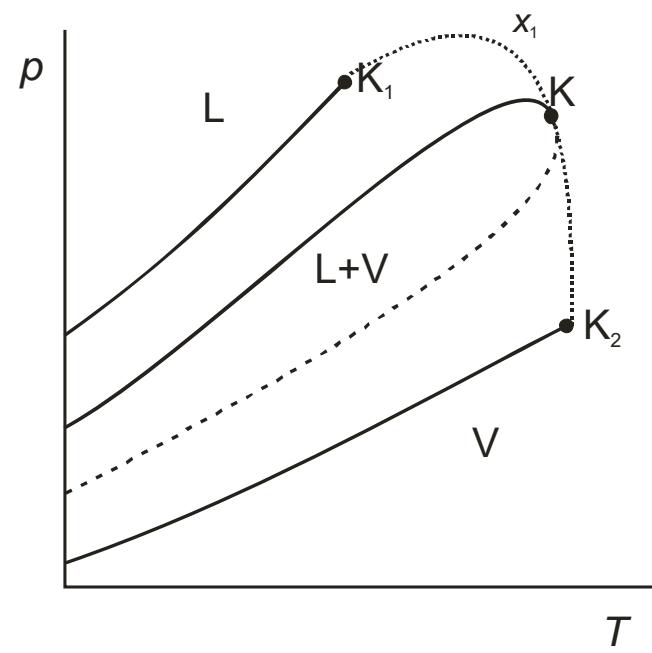
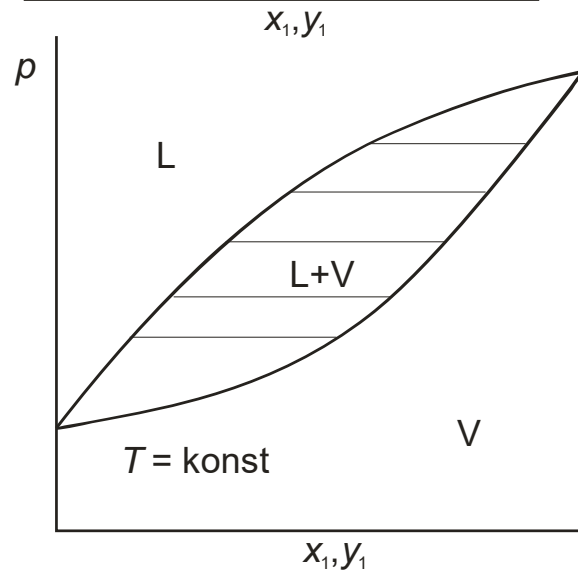
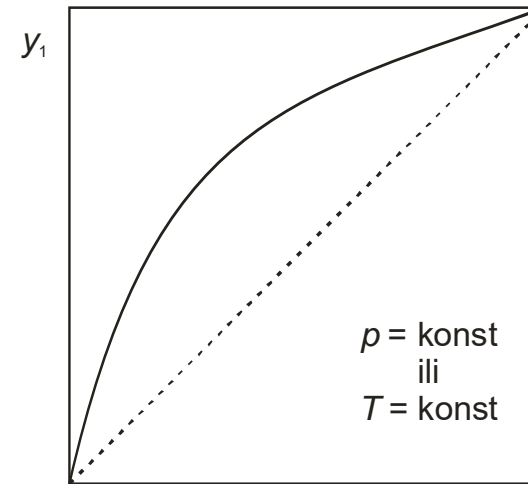
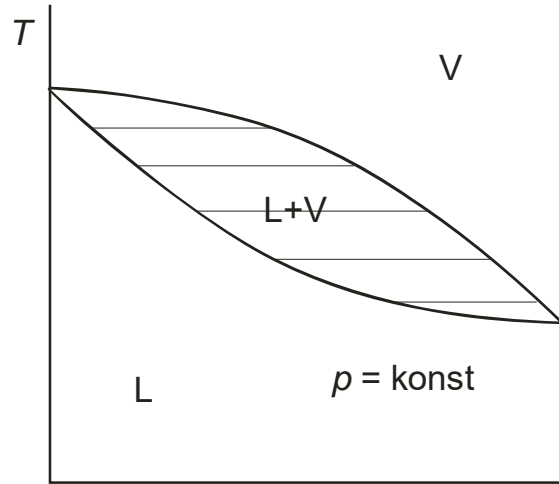
Zeotropne smjese

Fazni dijagrami



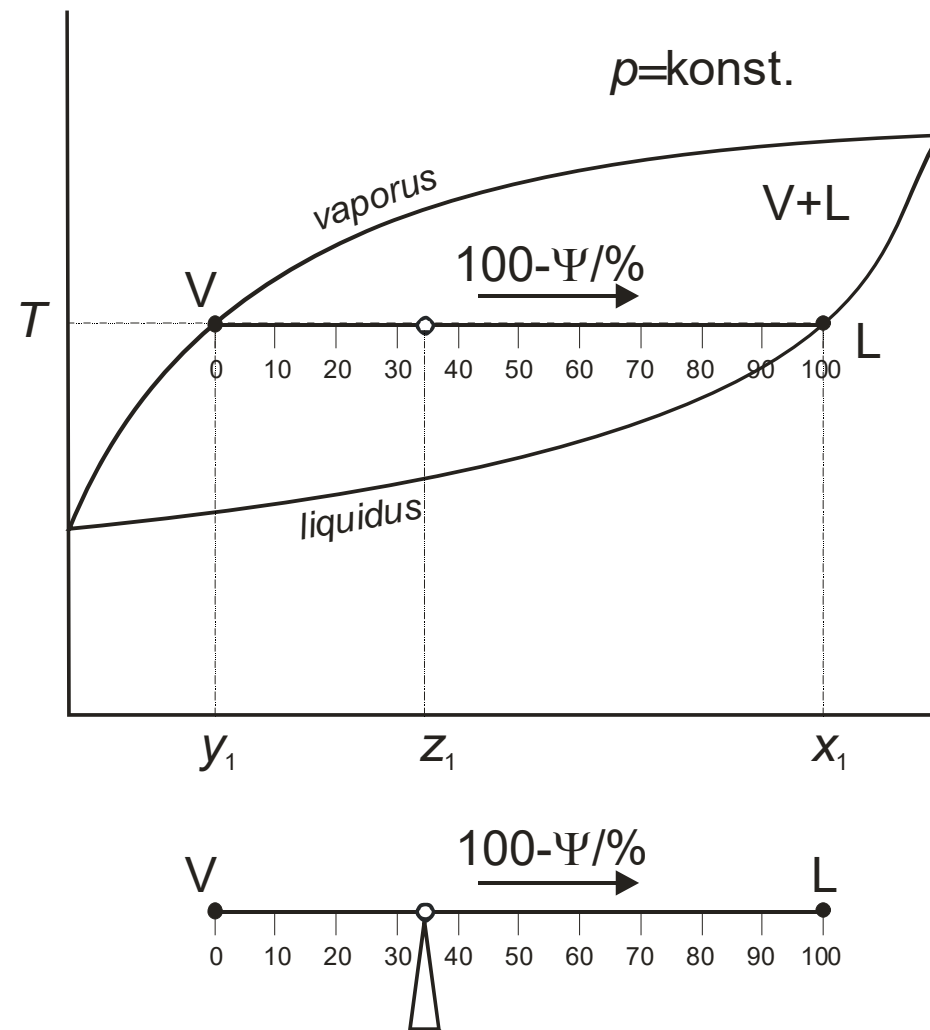
Fazni dijagrami

Zeotropne smjese



Fazni dijagrami

Pravilo poluge



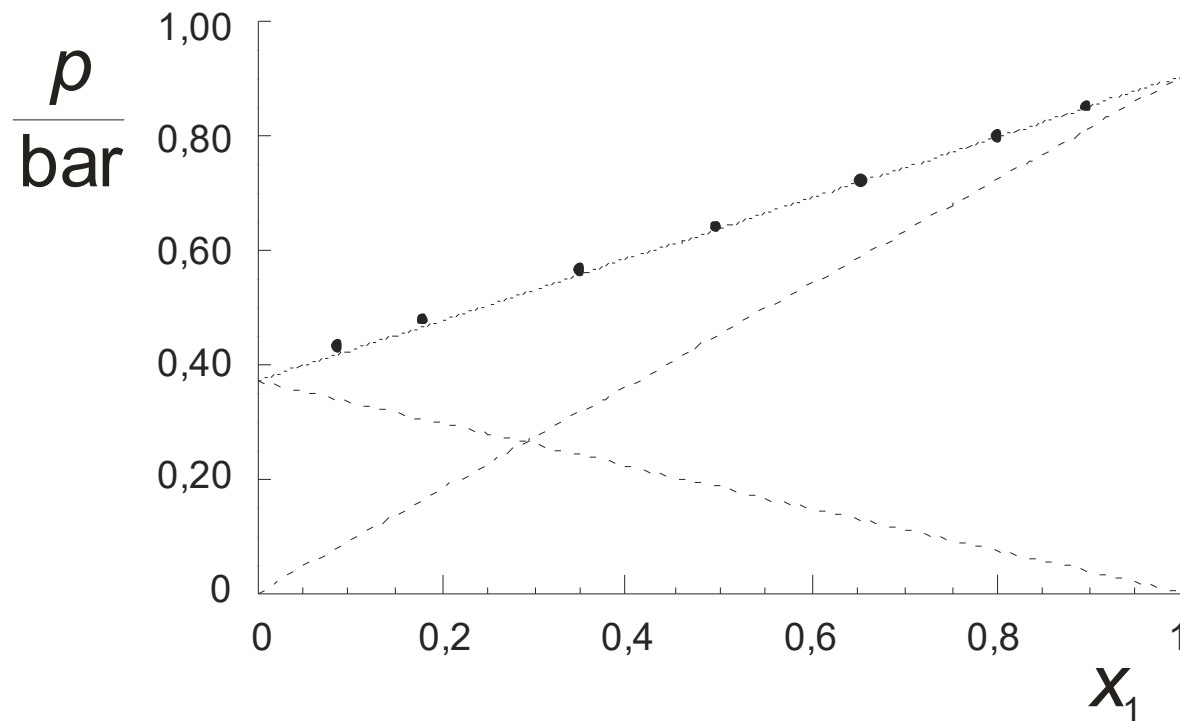
Fazni dijagrami

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 $\gamma_i > 1$

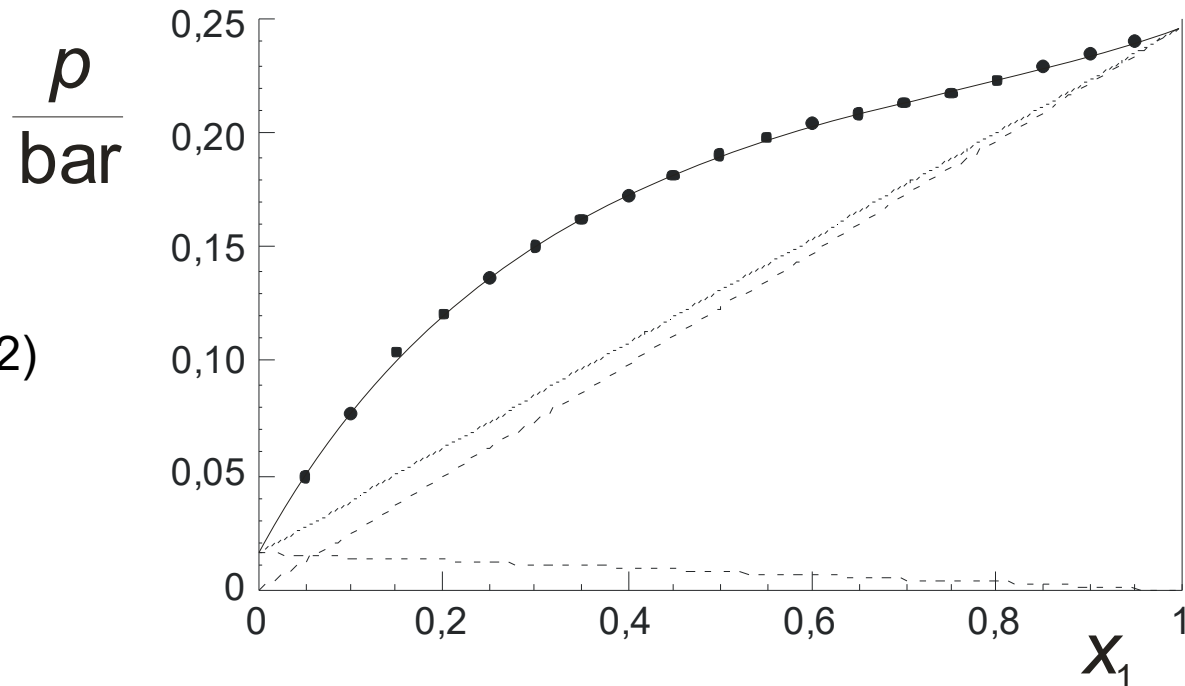
Neidealna kapljevina

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

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

Velika razlika u
Vrelištima
(tlakovima para)

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



Fazni dijagrami

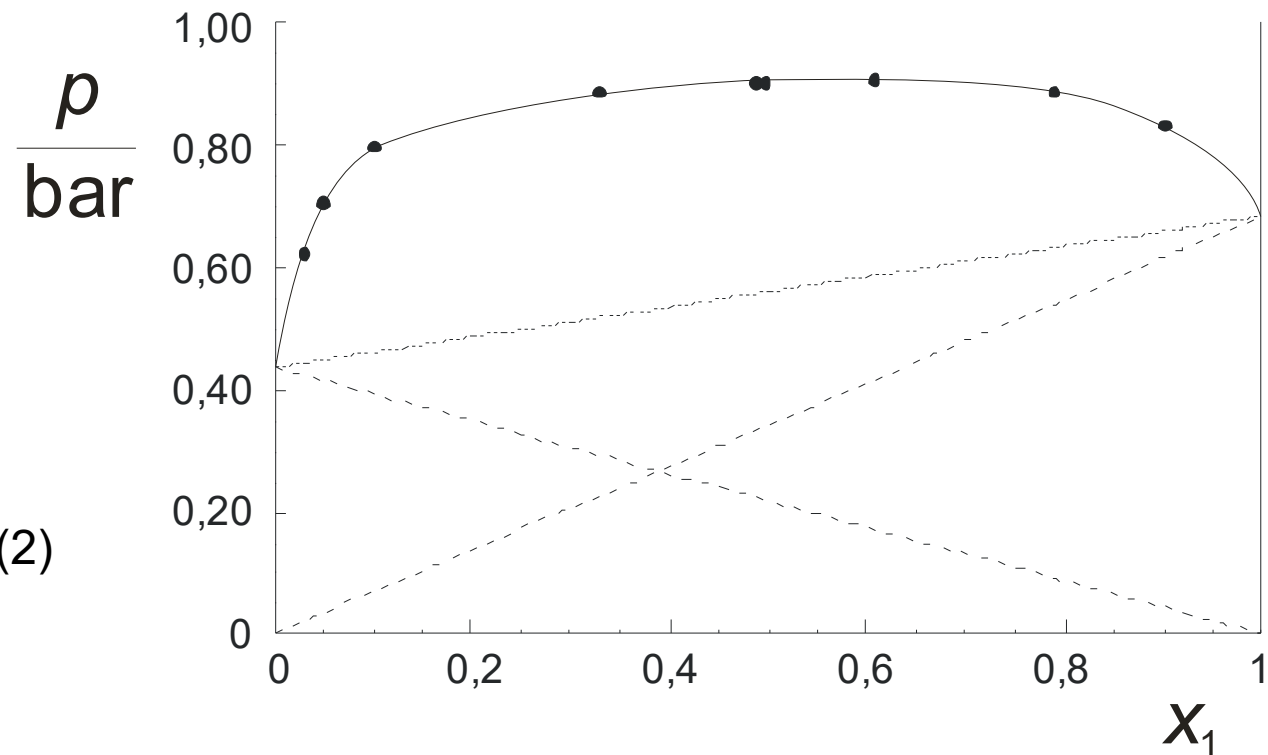
Nastanak azeotropa

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

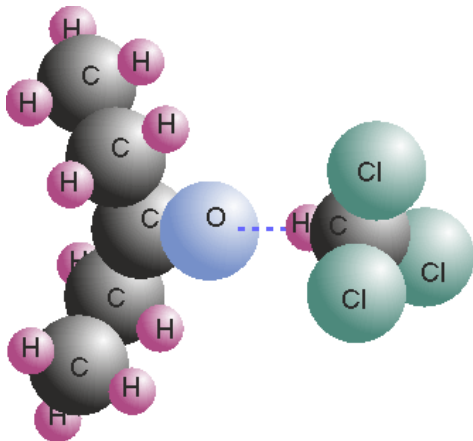
Nastanak azeotropa

Negativna odstupanja od Raoultova zakona $\gamma_i < 1$

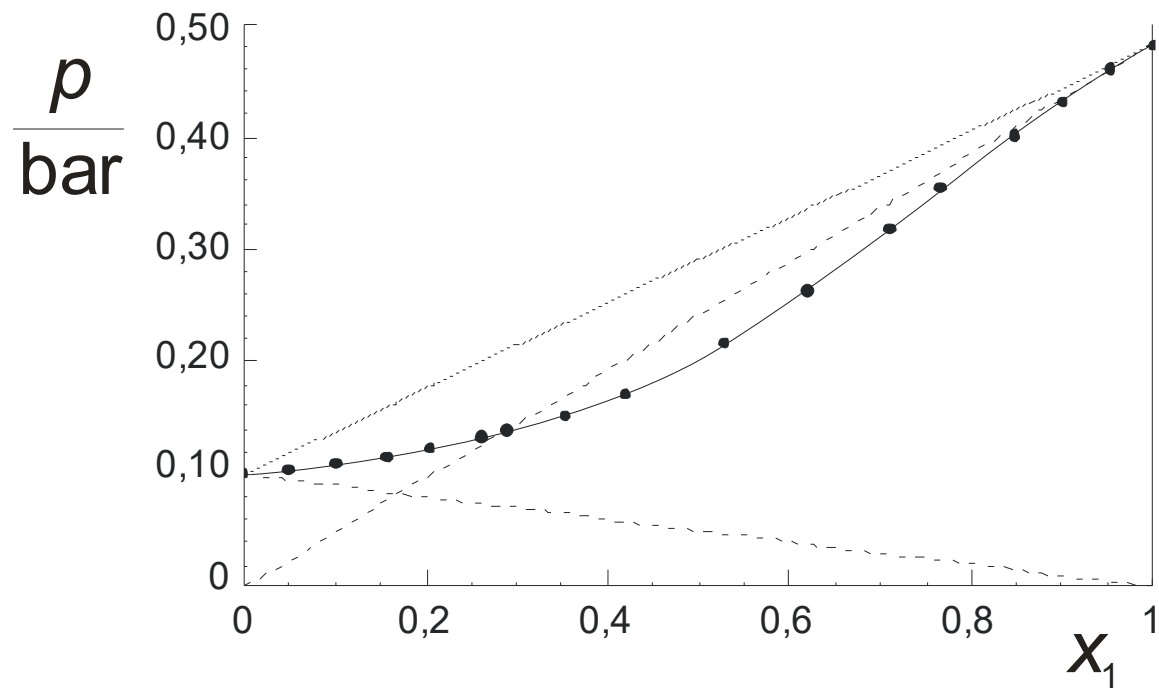
Neidealna kapljevin

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

Velika razlika u
vrelitima
(tlakovima para)



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



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

Fazni dijagrami

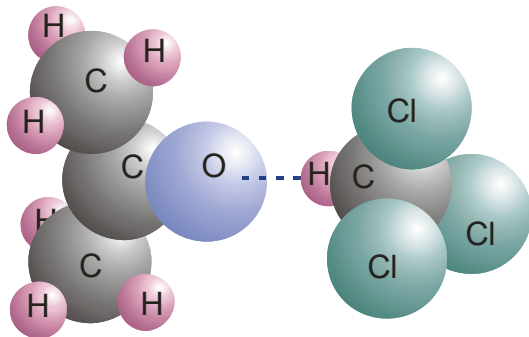
Nastanak azeotropa

Negativna odstupanja od Raoultova zakona $\gamma_i < 1$

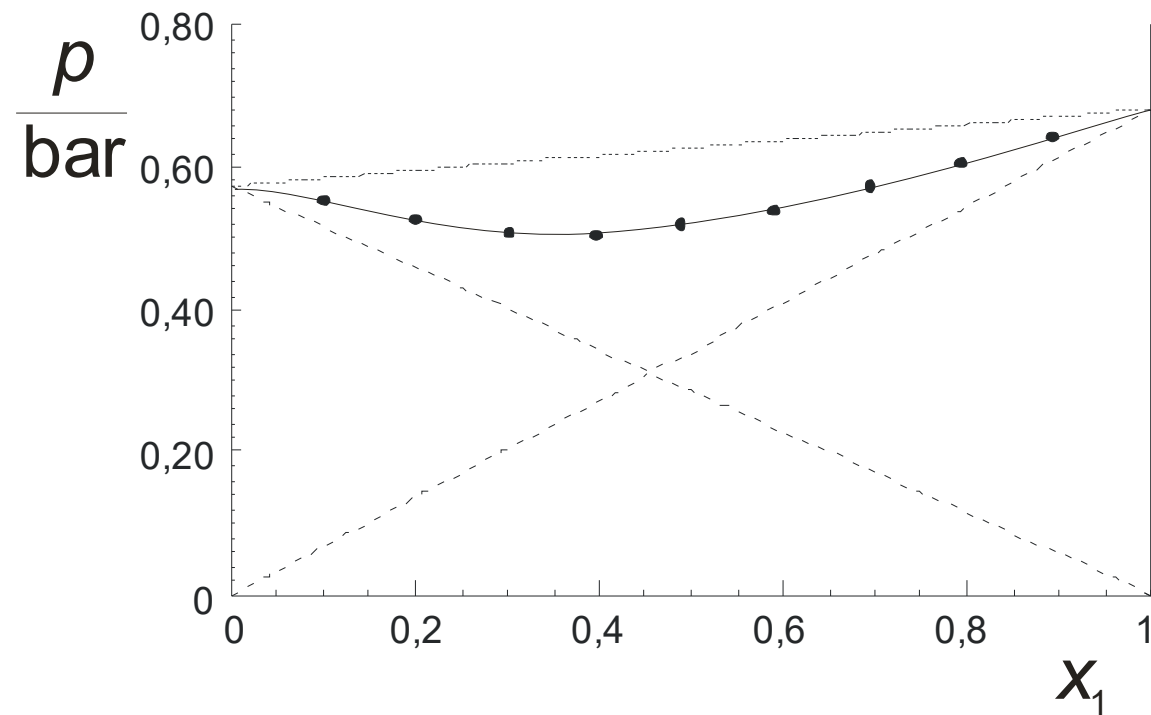
Neidealna kapljevina

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

Mala razlika u
vrelištima
(tlakovima para)



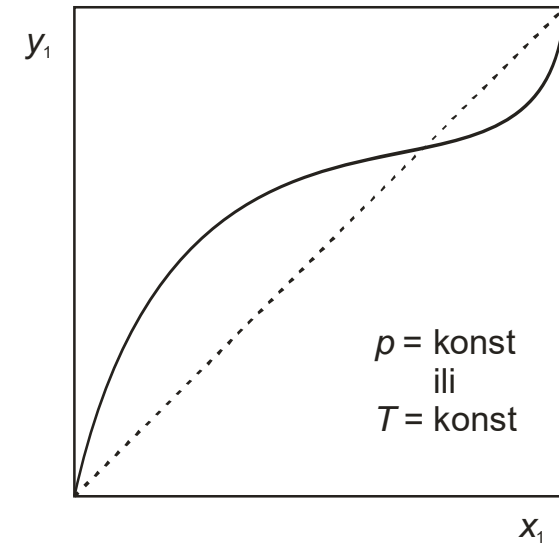
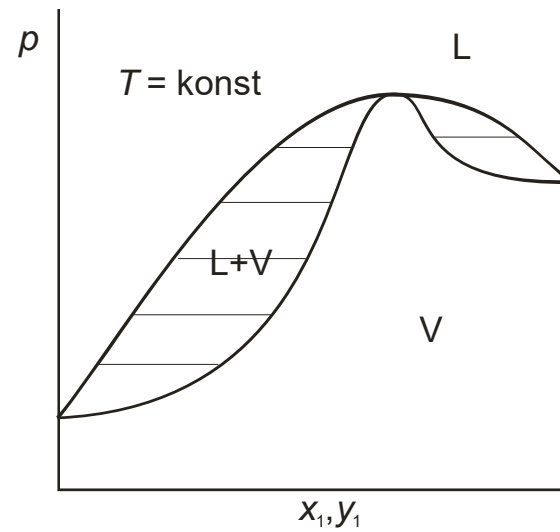
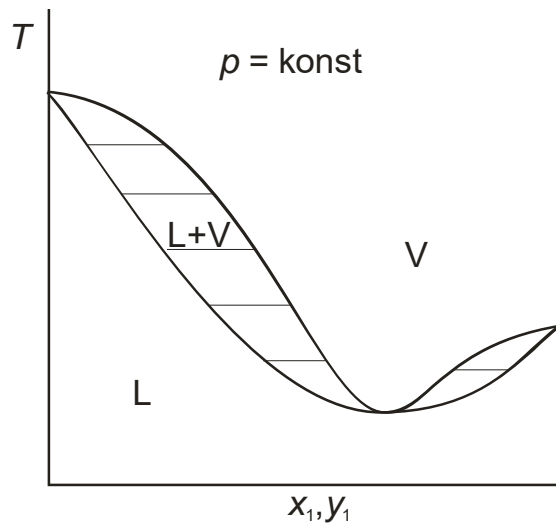
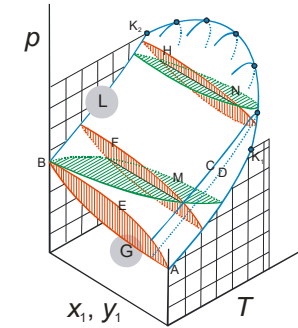
$$p = x_1 p_1^\bullet \gamma_1 + x_2 p_2^\bullet \gamma_2$$



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

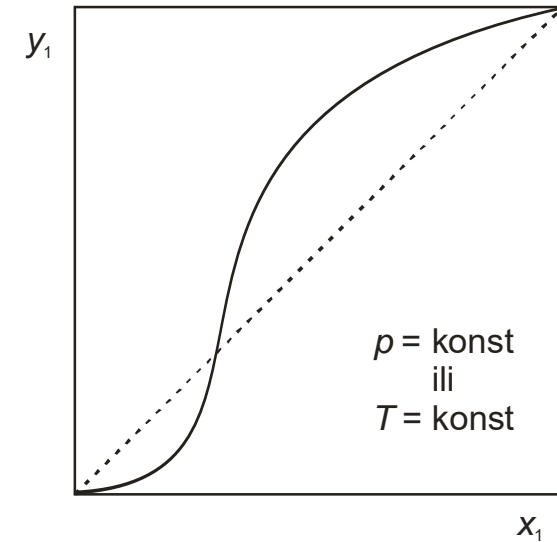
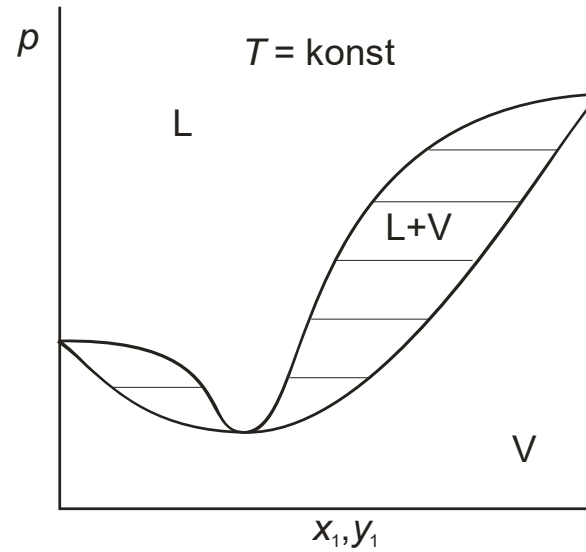
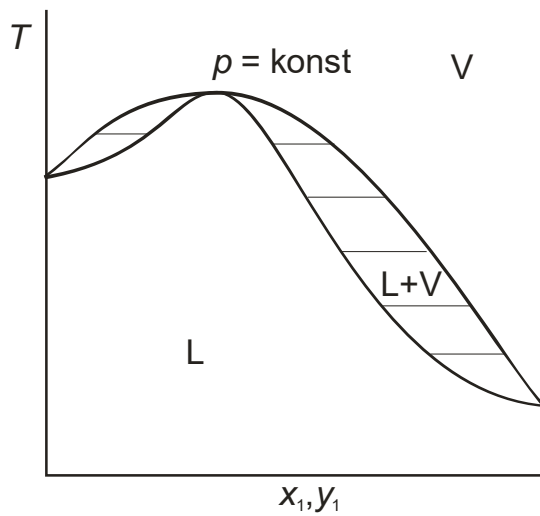
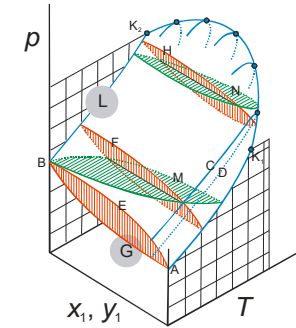
Fazni dijagrami

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**

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