

**RAVNOTEŽA FAZA:**

**POTPUNO MEŠLJIVE,  
DELIMIČNO MEŠLJIVE  
I NEMEŠLJIVE TEČNOSTI**

# Dvokomponentni sistemi

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- **potpuno mešljive tečnosti**
- delimično mešljive tečnosti
- nemešljive tečnosti

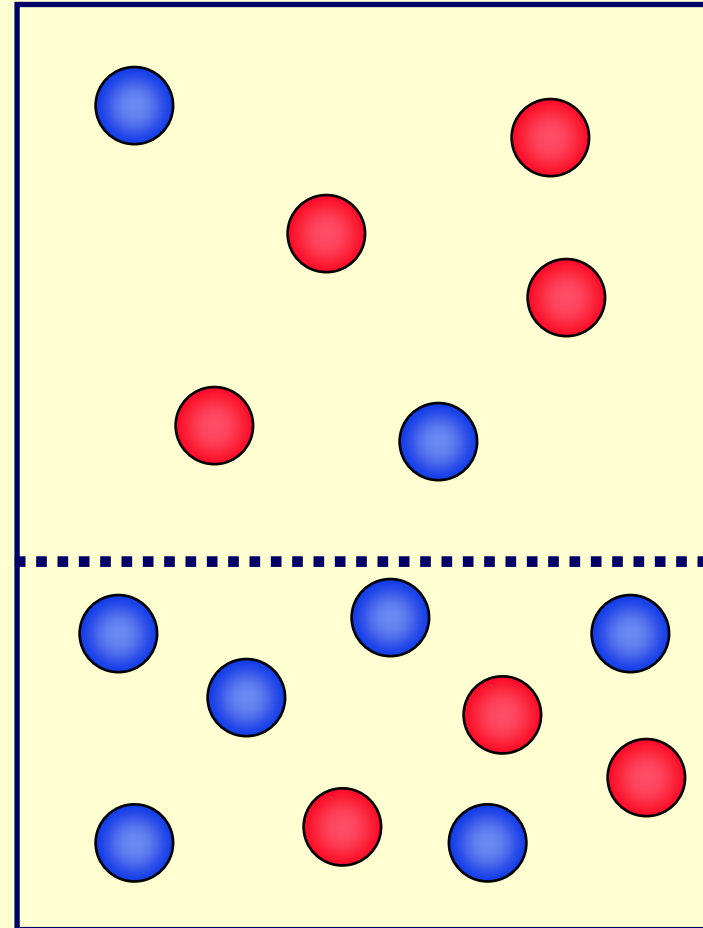
# Ravnoteža tečnost – para

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$x_1'$  i  $x_2'$  – molske frakcije u pari

$p_1$  i  $p_2$  – parcijalni pritisci

$x_1$  i  $x_2$  – molske frakcije u tečnosti



# Idealni rastvori

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$$F = c - p + 2 = 2 - 2 + 2; \quad F = 2$$

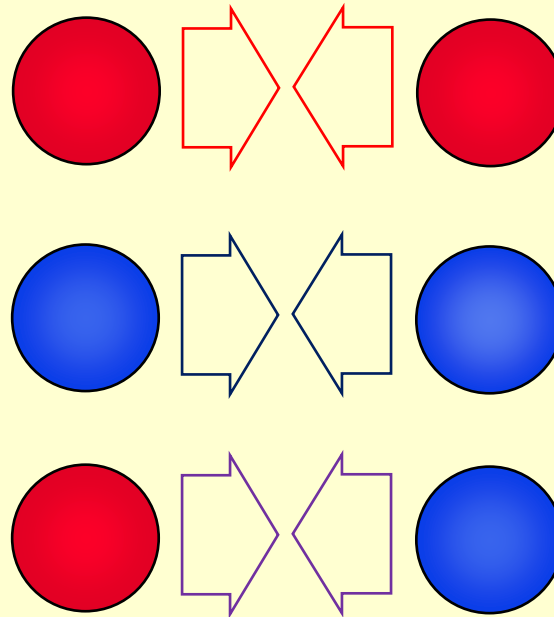
Nezavisno promenljive:  $T$  i  $x_i \rightarrow p = f(x_i)$  za svako  $T$ .

$$p_i = x_i p_i^0$$

Tečni rastvori koji se pokoravaju Raulovom zakonu u čitavom opsegu koncentracija (od čiste komponente 1 do čiste komponente 2) i pri svim temperaturama i pritiscima, nazivaju se **idealnim rastvorima**.

# Idealni rastvori

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$\Delta H_{\text{mešanja}} = 0$  i  $\Delta V_{\text{mešanja}} = 0$  znači da su sve interakcije iste jačine:  $F_{1-1} \approx F_{2-2} \approx F_{1-2}$

# Idealni rastvori (entalpija)

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$$P = \text{const} \quad x = \text{const}$$

$$\left(\frac{\partial \ln p_i^0}{\partial T}\right)_{P,x} = \frac{\Delta H_{m,isp}^0}{RT^2} = \frac{H_i^g - H_i^t}{RT^2} \quad \left(\frac{\partial \ln p_i}{\partial T}\right)_{P,x} = \frac{\Delta H_{m,isp}}{RT^2} = \frac{H_i^g - \bar{H}_i^t}{RT^2}$$

$$\left(\frac{\partial \ln \frac{p_i}{p_i^0}}{\partial T}\right)_{P,x} = \frac{H_i^t - \bar{H}_i^t}{RT^2}$$

$$\left(\frac{\partial \ln x_i}{\partial T}\right)_{P,x} = \frac{H_i^t - \bar{H}_i^t}{RT^2}$$

$$\boxed{H_i^t = \bar{H}_i^t}$$

# Idealni rastvori (zapremina)

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$$T = \text{const} \quad x = \text{const}$$

$$d\mu_i^t = d\mu_i^p$$

$$\bar{V}_i^t dP - \bar{S}_i^t dT = \bar{V}_i^g dp_i - \bar{S}_i^g dT$$

$$\bar{V}_i^t dP = \bar{V}_i^g dp_i \approx \frac{RT}{p_i} dp_i$$

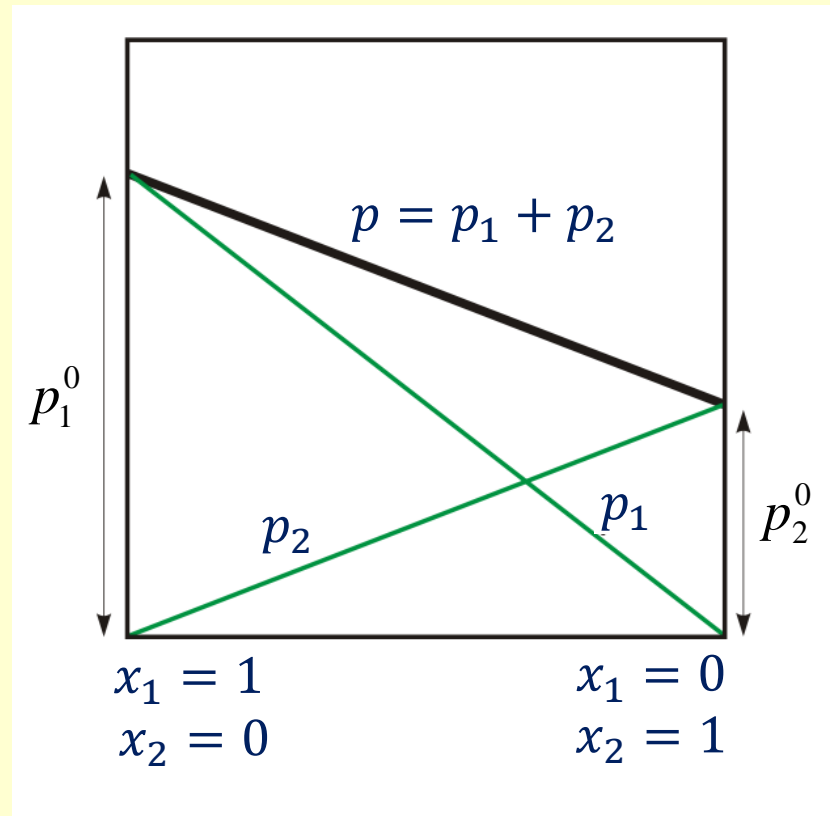
$$RT d \ln p_i = \bar{V}_i^t dP \quad RT d \ln p_i^0 = V_i^t dP$$

$$d \ln(p_i / p_i^0) = d \ln x_i = (\bar{V}_i^t - V_i^t) dP$$

$$\boxed{\bar{V}_i^t = V_i^t}$$

# Zavisnost napona pare od sastava tečnosti

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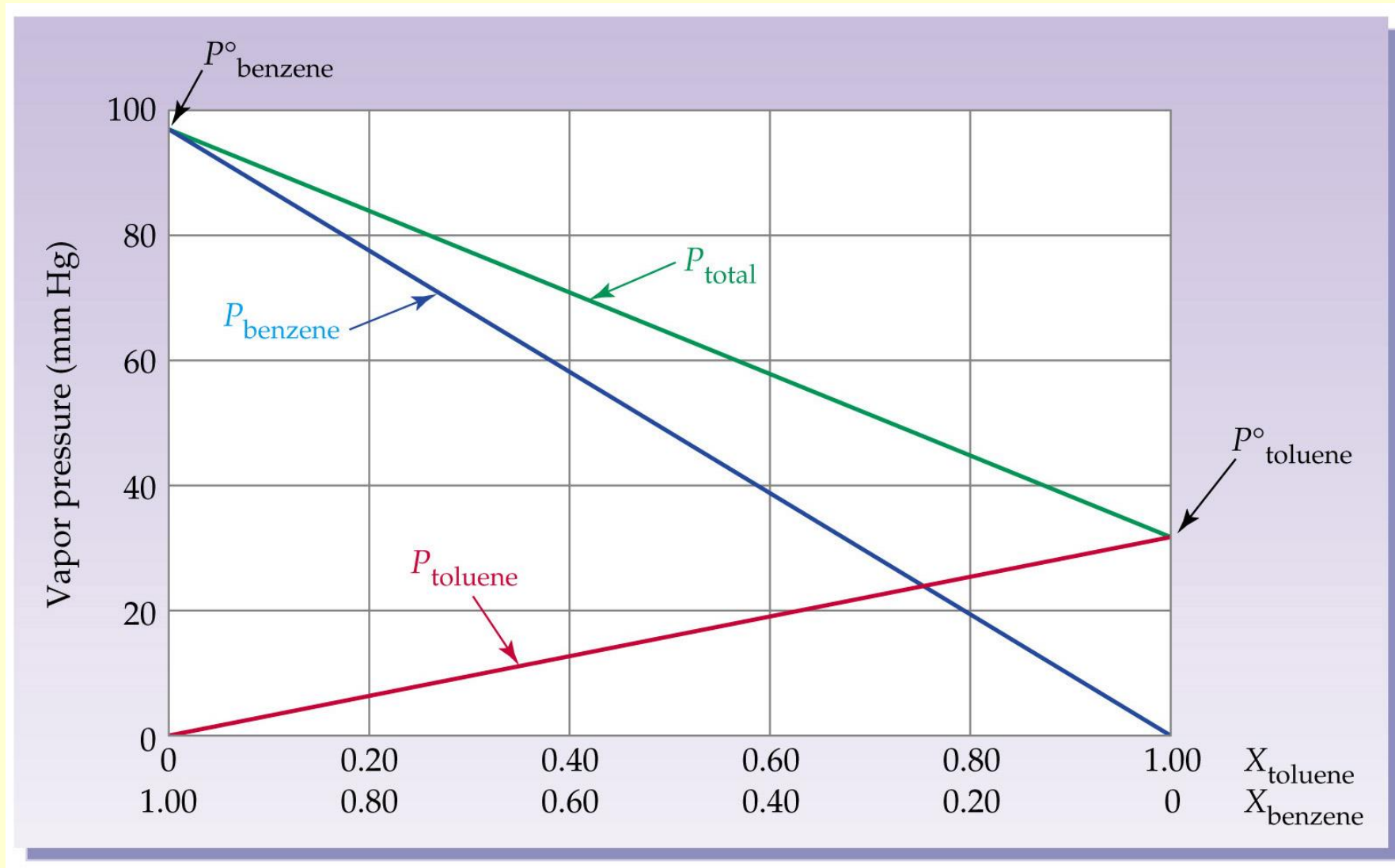


$$p = p_1 + p_2 = x_1 p_1^0 + x_2 p_2^0 = x_1 p_1^0 + (1 - x_1) p_2^0$$

$$p = x_1 (p_1^0 - p_2^0) + p_2^0$$



# Benzen i toluen



# Sastavi tečnosti i pare se razlikuju

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$$p_b^0 = 12,3 \text{ kPa}$$

$$p_t^0 = 5,1 \text{ kPa}$$

$$x_b = x_t = 0,5$$

$$p_b = x_b \cdot p_b^0 = 0,5 \cdot 12,3 \text{ kPa} = 6,15 \text{ kPa}$$

$$p_t = x_t \cdot p_t^0 = 0,5 \cdot 5,1 \text{ kPa} = 2,55 \text{ kPa}$$

$$p = p_b + p_t = 6,15 \text{ kPa} + 2,55 \text{ kPa} = 8,7 \text{ kPa}$$

$$x'_b = \frac{6,15 \text{ kPa}}{8,7 \text{ kPa}} = 0,71$$

$$x'_t = 1 - 0,71 = 0,29$$

para iznad tečnosti koja ključa

$$x'_b = 0,71 \quad x'_t = 0,29$$

tečnost na tački ključanja

$$x_b = x_t = 0,5$$

# Zavisnost napona pare od sastava pare

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Pretpostavka: para se može posmatrati kao smeša idealnih gasova.

$$x'_1 = \frac{n'_1}{n'_1 + n'_2}$$

$$p_1 V = n'_1 R T \quad \rightarrow \quad n'_1 = \frac{p_1 V}{R T}$$

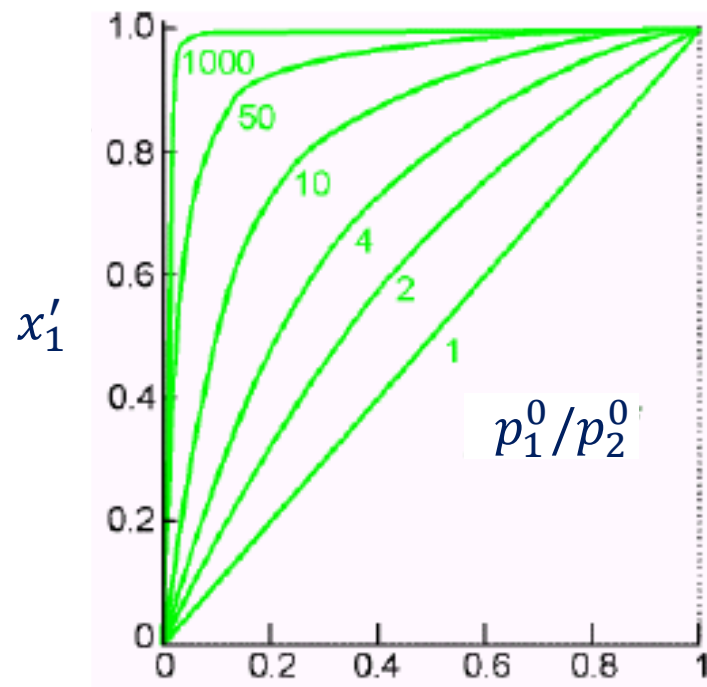
$$x'_1 = \frac{p_1}{p_1 + p_2} = \frac{x_1 p_1^0}{x_1 p_1^0 + x_2 p_2^0}$$

$$x'_1 = \frac{x_1 p_1^0}{x_1 (p_1^0 - p_2^0) + p_2^0} \qquad x_1 = \frac{x'_1 p_2^0}{x'_1 (p_2^0 - p_1^0) + p_1^0}$$

# Zavisnost napona pare od sastava pare

$$x'_1 = \frac{x_1 p_1^0}{x_1(p_1^0 - p_2^0) + p_2^0}$$

$$x'_2 = 1 - x'_1$$

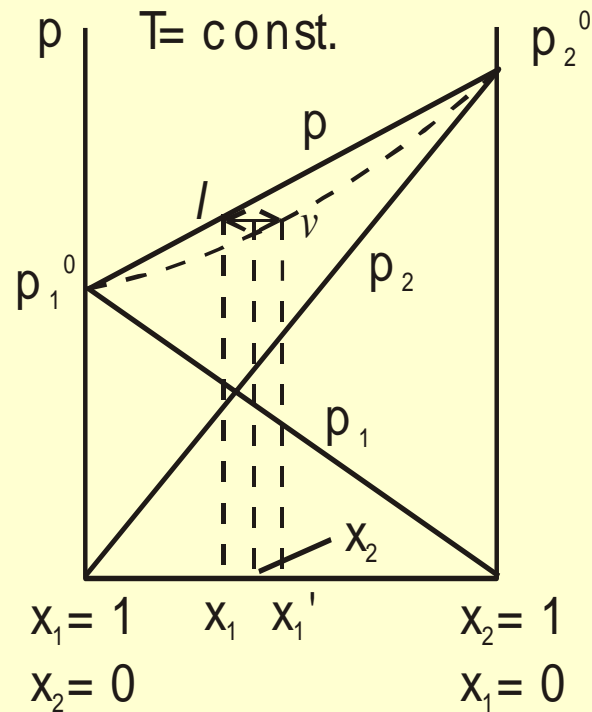


Što se komponente više razlikuju u isparljivosti, to će se više razlikovati sastav tečne od sastava parne faze.

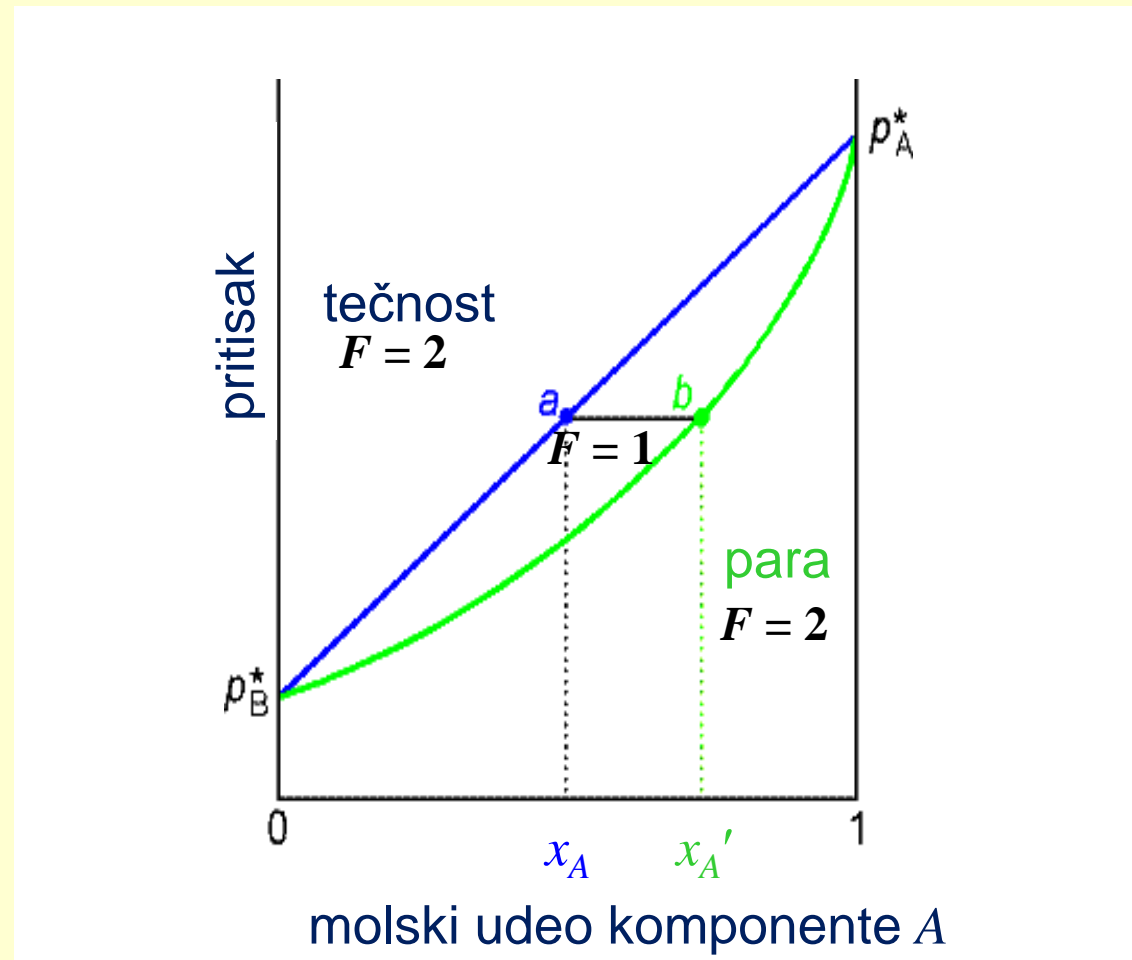
Za  $p_1^0 \geq p_2^0$  je  $x'_1 \geq x_1$  (para je bogatija isparljivijom komponentom).

# Zavisnost napona pare od sastava pare

$$p = \frac{p_1^0 p_2^0}{p_1^0 + (p_2^0 - p_1^0) x_1'}$$

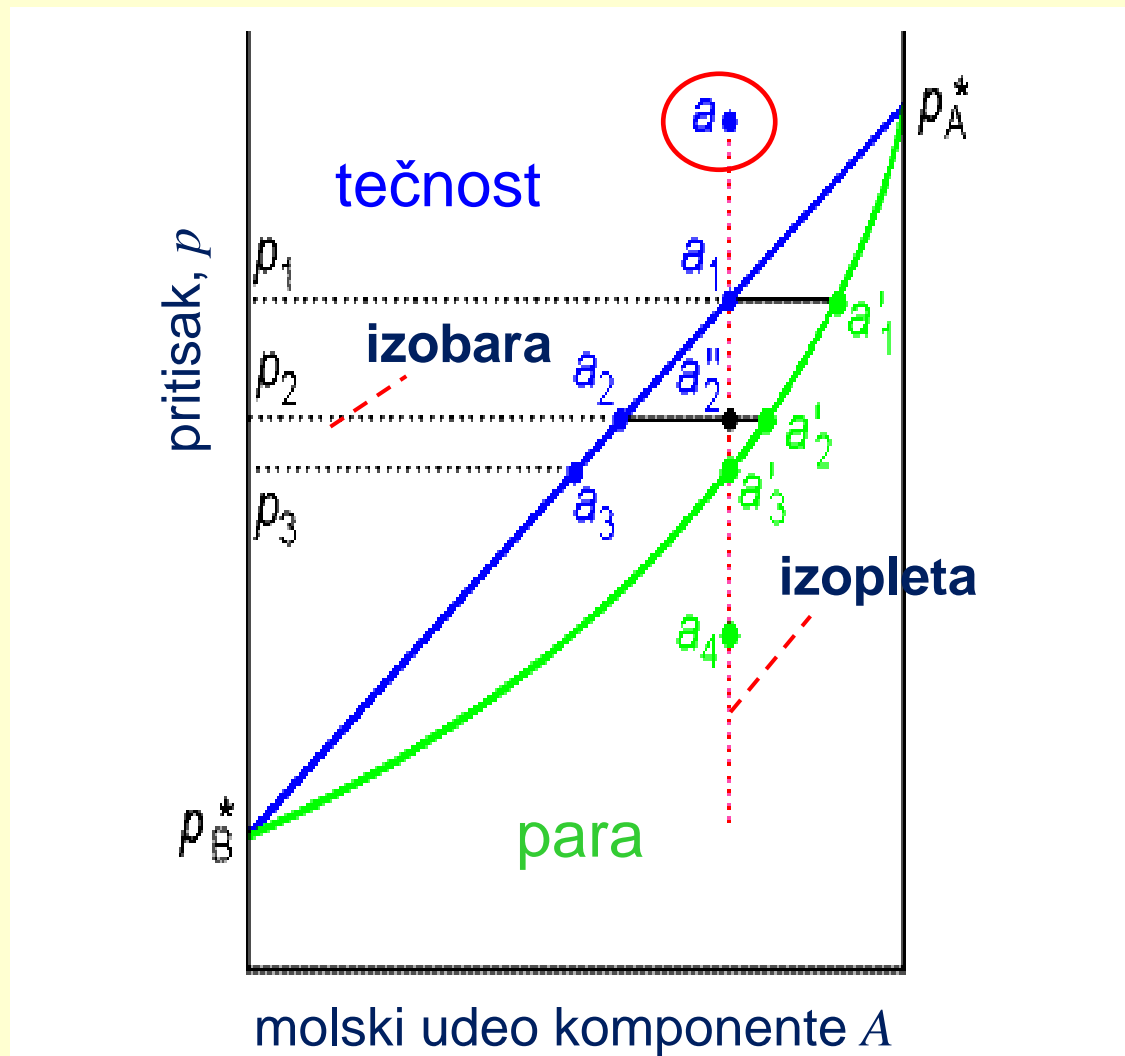


# Fazni dijagram idealnog rastvora

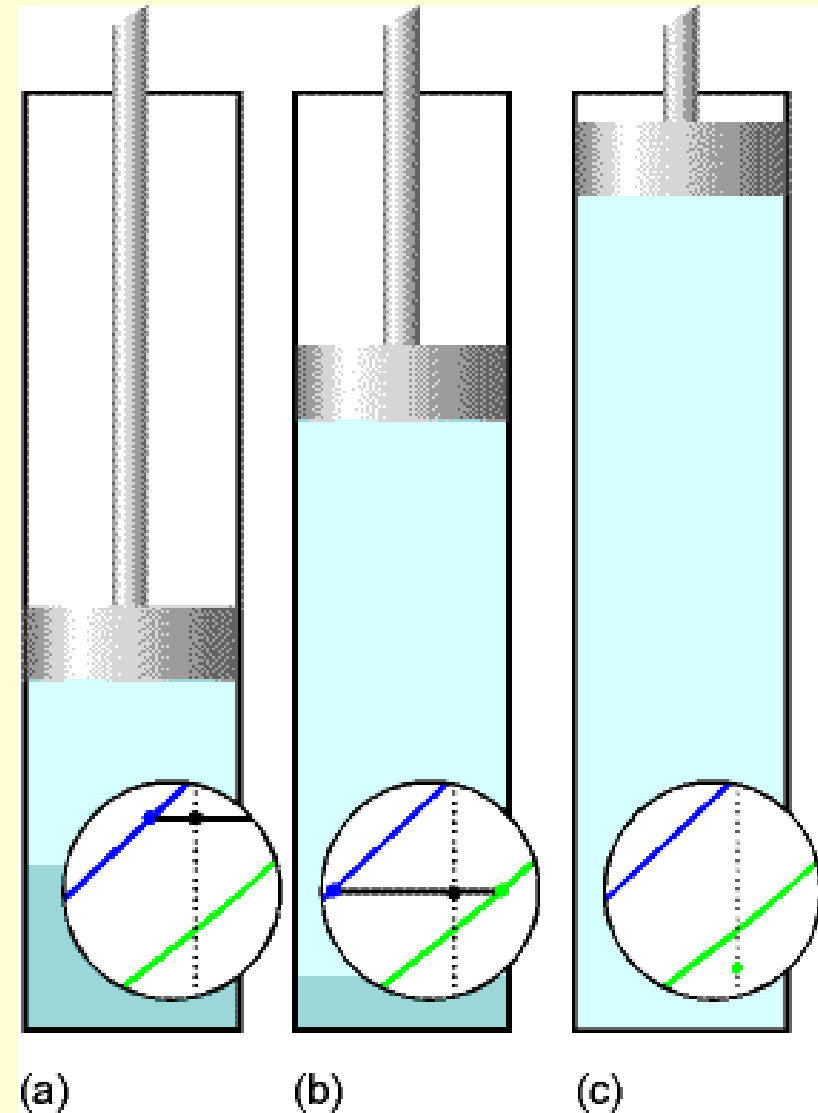
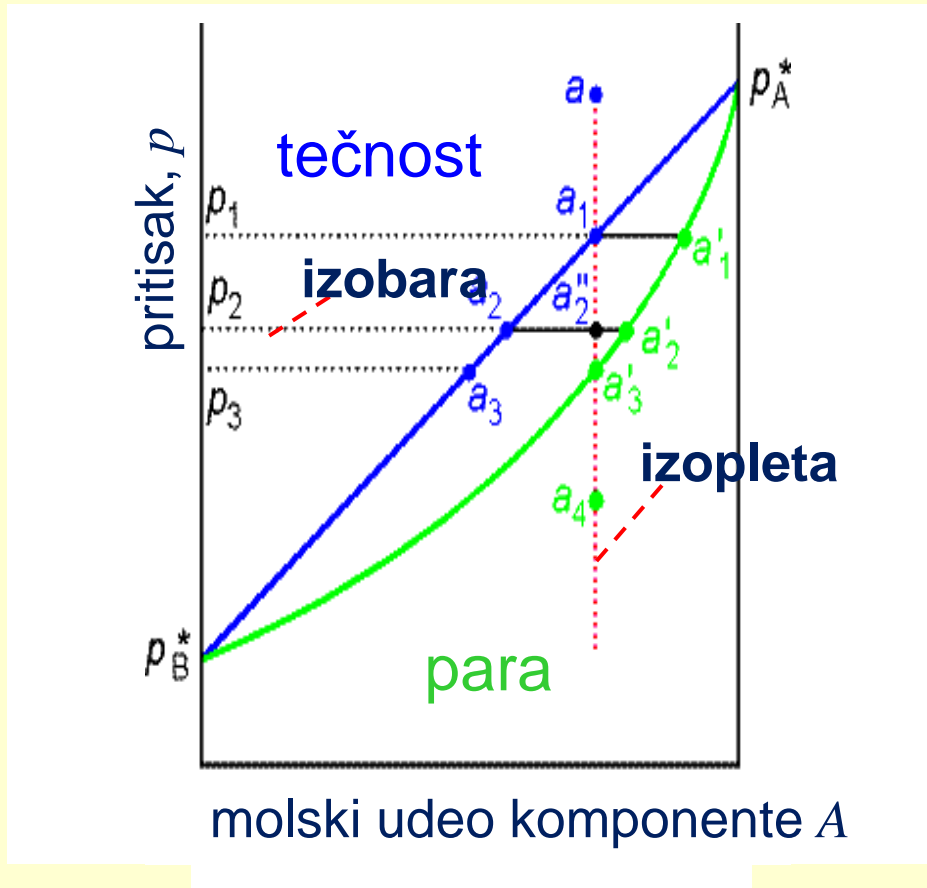


# Promene duž izoplete

Izopleta – linija konstantnog sastava



# Fizička slika procesa

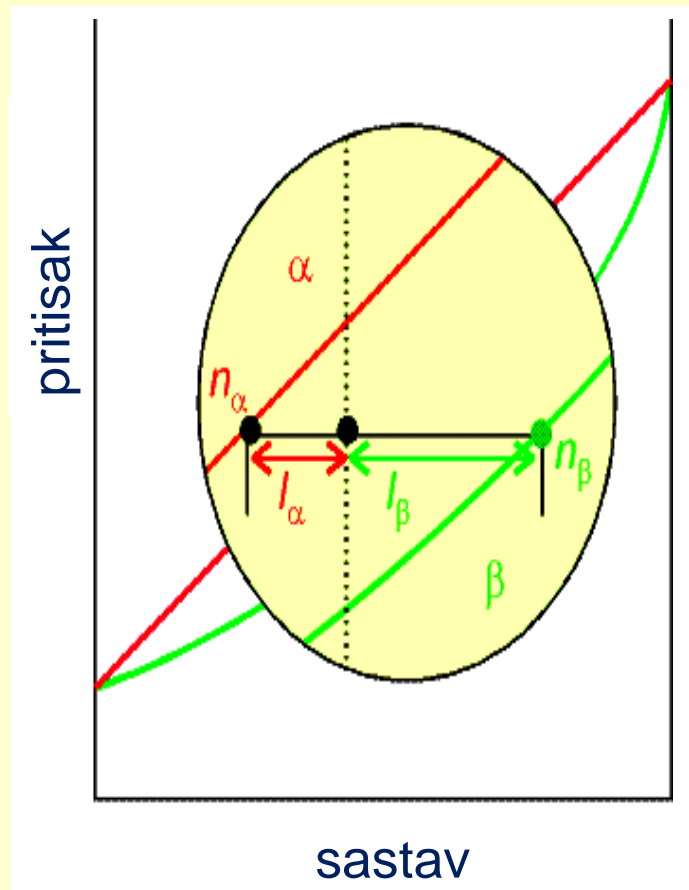


- (a) – Nešto pare se pojavilo.
- (b) – Samo malo tečnosti je ostalo.
- (c) – Samo je para prisutna.



# Spojna linija i pravilo poluge

$$n_{\alpha}l_{\alpha} = n_{\beta}l_{\beta}$$



# Pravilo poluge

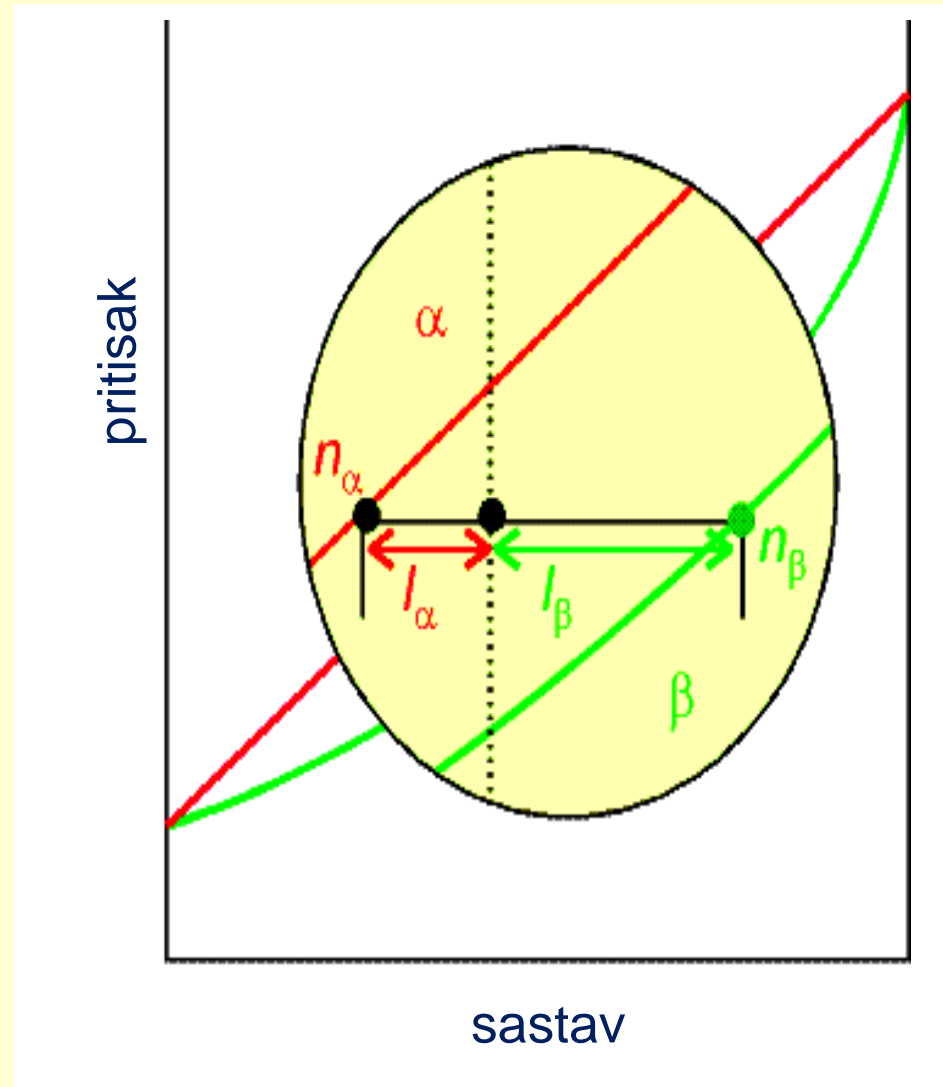
komponente  $A$  i  $B$ , faze  $\alpha$  i  $\beta$

$n$  – ukupni broj molova u sistemu

$n^\alpha/n^\beta$  – ukupni broj molova u fazi  $\alpha/\beta$

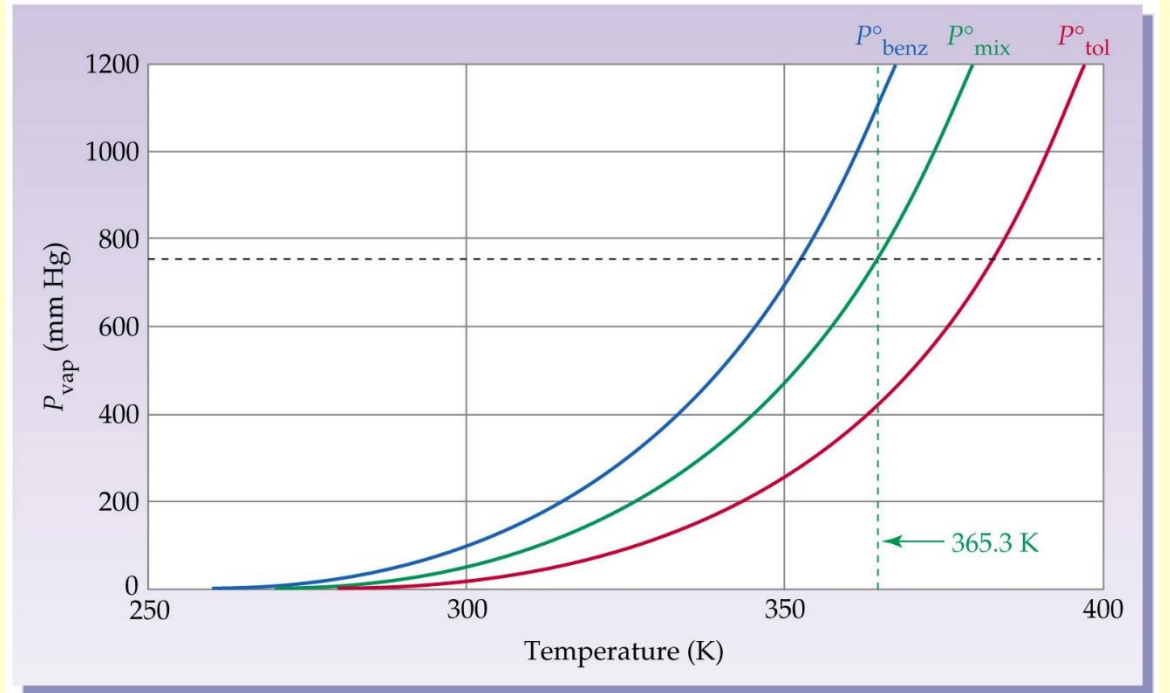
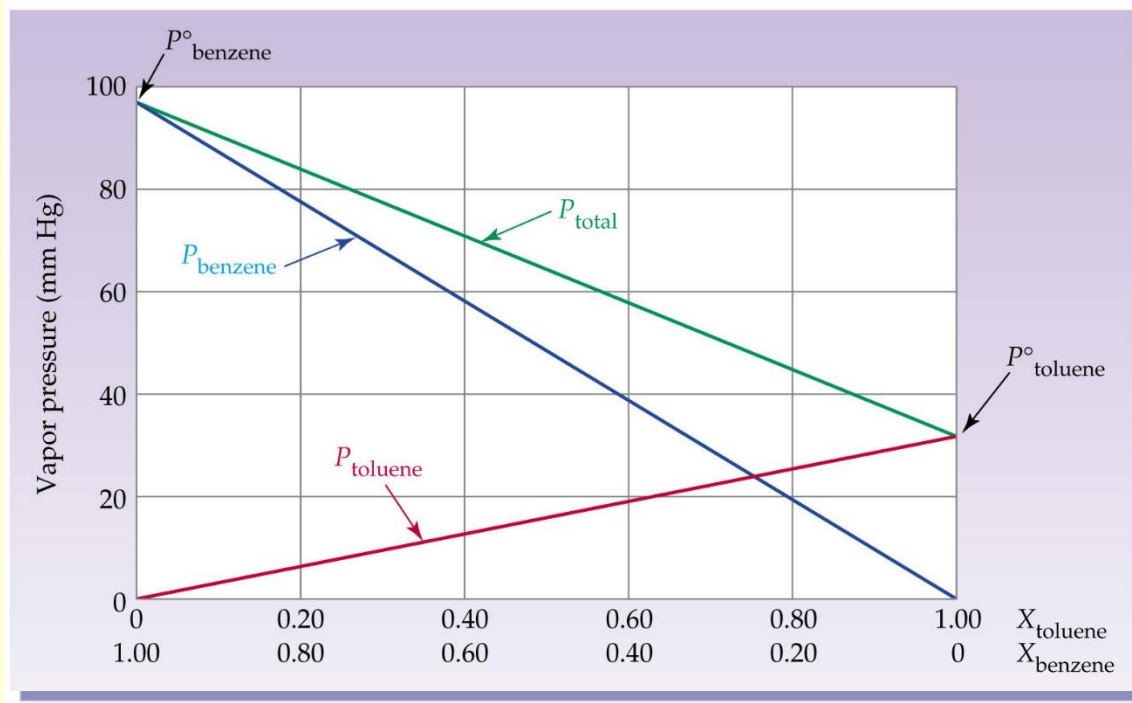
$$\begin{array}{l} n = n_\alpha + n_\beta \\ x^A = \frac{n^A}{n} \rightarrow n^A = nx^A \\ x_\alpha^A = \frac{n_\alpha^A}{n_\alpha} \rightarrow n_\alpha^A = n_\alpha x_\alpha^A \\ x_\beta^A = \frac{n_\beta^A}{n_\beta} \rightarrow n_\beta^A = n_\beta x_\beta^A \end{array} \left. \vphantom{\begin{array}{l} n = n_\alpha + n_\beta \\ x^A = \frac{n^A}{n} \rightarrow n^A = nx^A \\ x_\alpha^A = \frac{n_\alpha^A}{n_\alpha} \rightarrow n_\alpha^A = n_\alpha x_\alpha^A \\ x_\beta^A = \frac{n_\beta^A}{n_\beta} \rightarrow n_\beta^A = n_\beta x_\beta^A \end{array}} \right\} \begin{array}{l} n^A = n_\alpha^A + n_\beta^A \\ nx^A = n_\alpha x_\alpha^A + n_\beta x_\beta^A \end{array} \left. \vphantom{\begin{array}{l} n^A = n_\alpha^A + n_\beta^A \\ nx^A = n_\alpha x_\alpha^A + n_\beta x_\beta^A \end{array}} \right\} n_\alpha x_\alpha^A + n_\beta x_\beta^A = n_\alpha x^A + n_\beta x^A$$
$$\downarrow$$
$$n_\alpha(x^A - x_\alpha^A) = n_\beta(x_\beta^A - x^A)$$
$$\boxed{\frac{n_\alpha}{n_\beta} = \frac{x_\beta^A - x^A}{x^A - x_\alpha^A}}$$

# Spojna linija i pravilo poluge

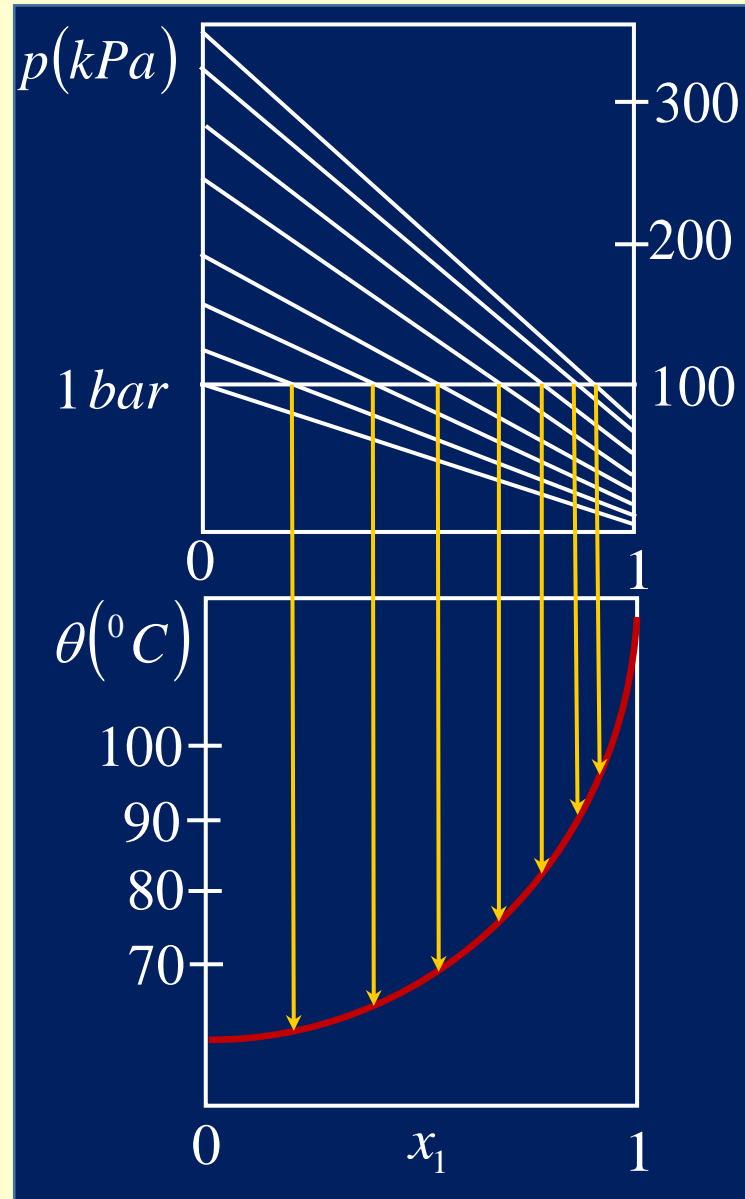


$$\frac{n_\alpha}{n_\beta} = \frac{x_\beta^A - x^A}{x^A - x_\alpha^A} = \frac{l_\beta}{l_\alpha}$$

# Benzen i toluen

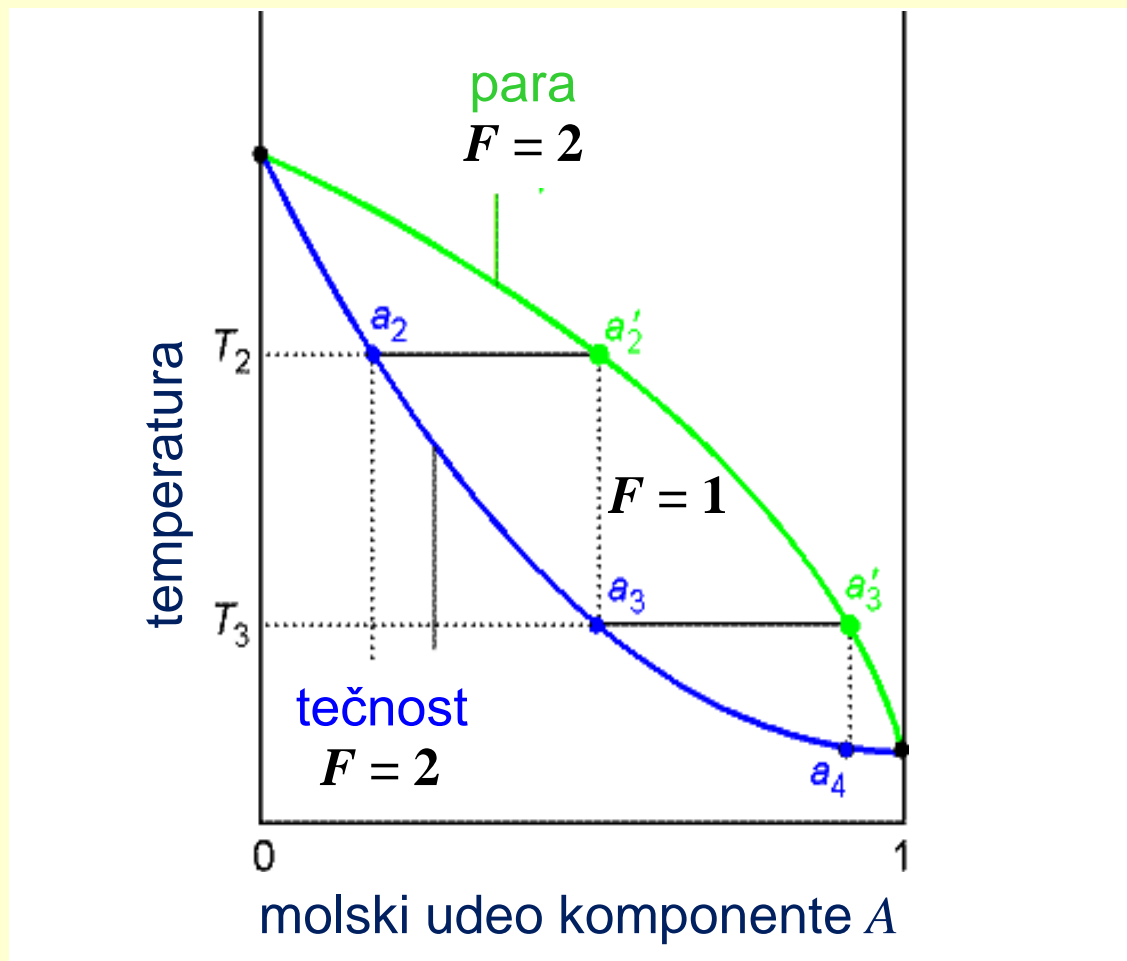


# Tačka ključanja idealnih rastvora

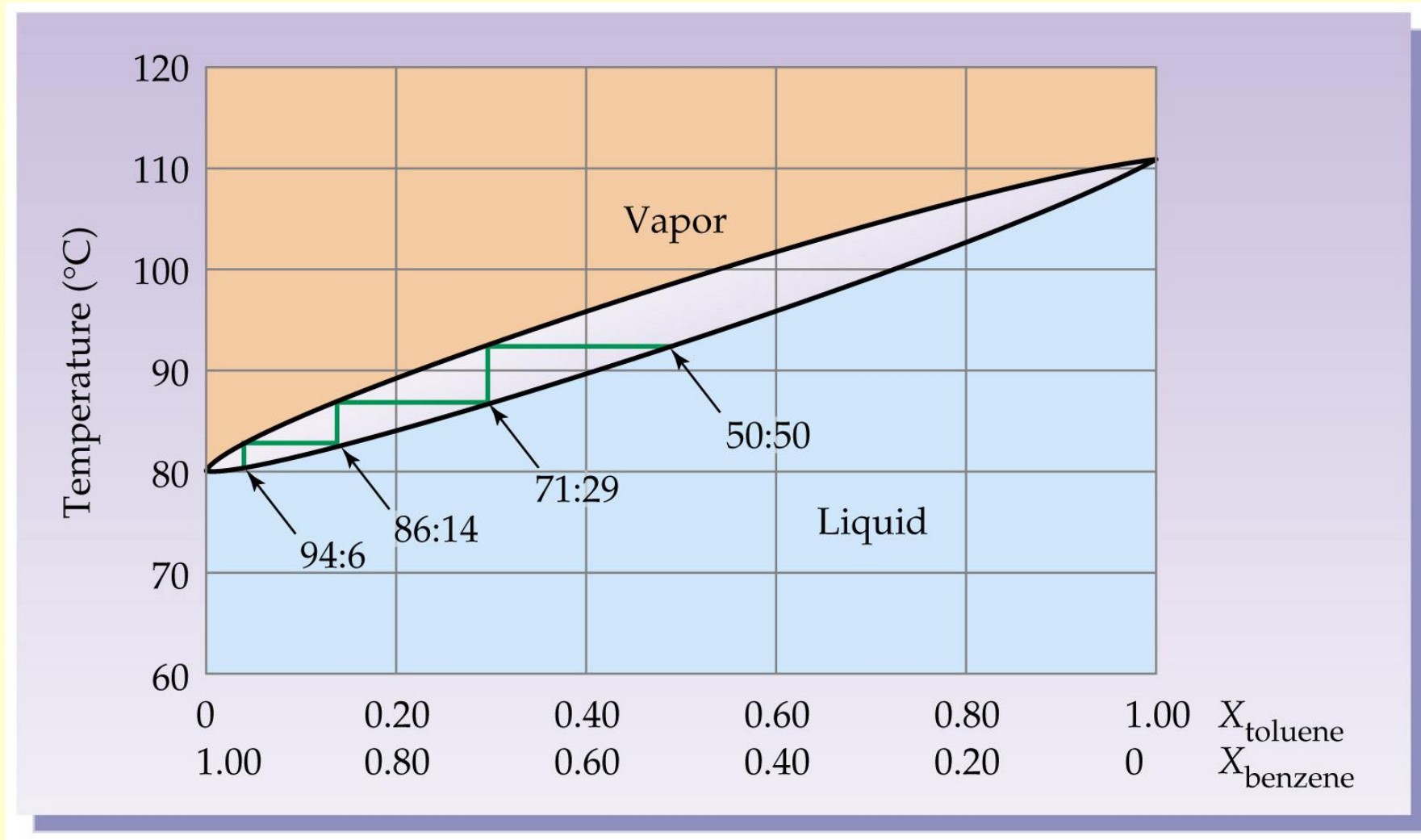


# Zavisnost tačke ključanja od sastava

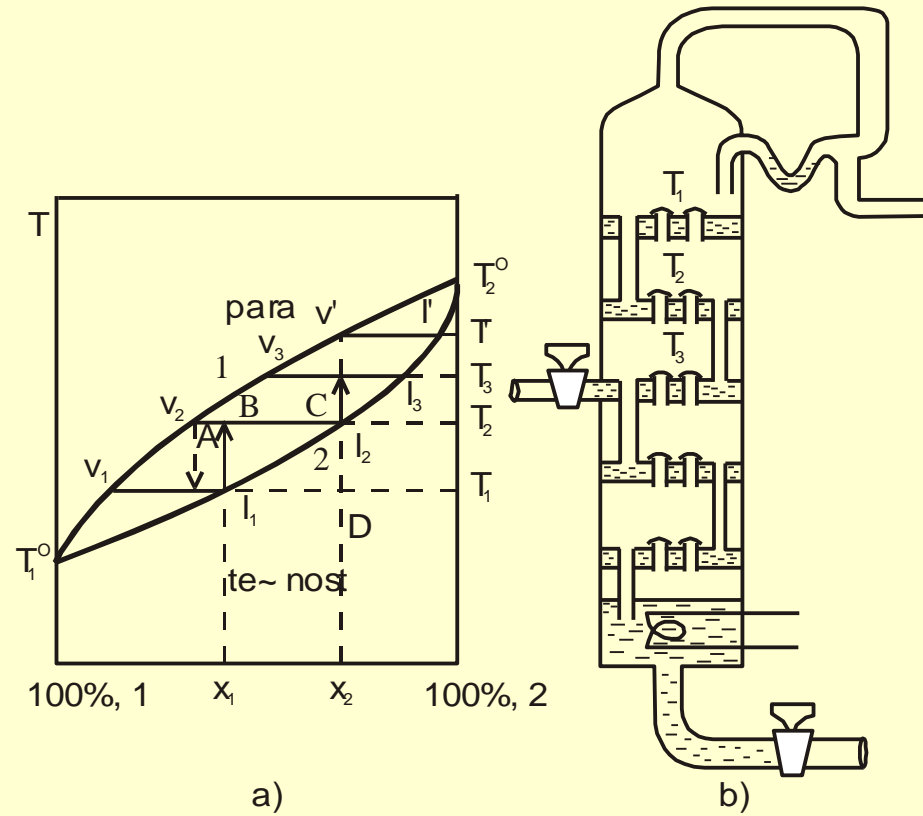
$$p = \text{const}$$



# Rastvor benzena i toluena



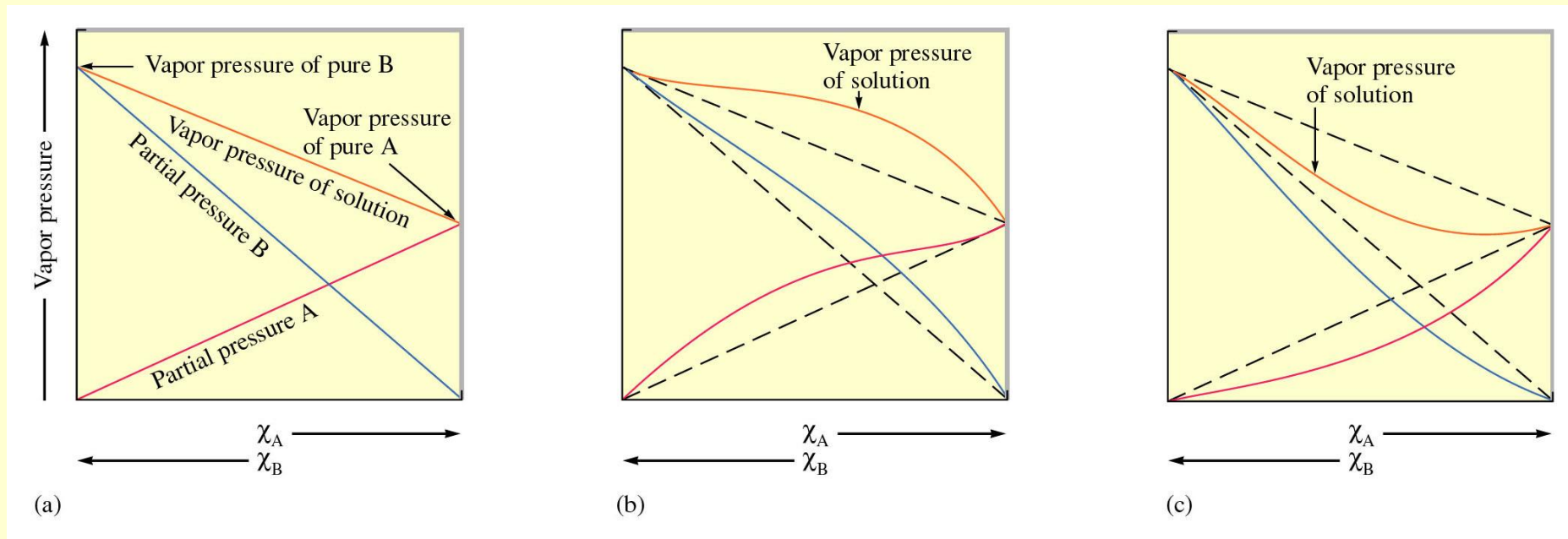
# Frakciona destilacija



Metodom frakcione destilacije moguće je izvršiti razdvajanje čistih komponenata iz rastvora.



# Idealni i neidealni rastvori

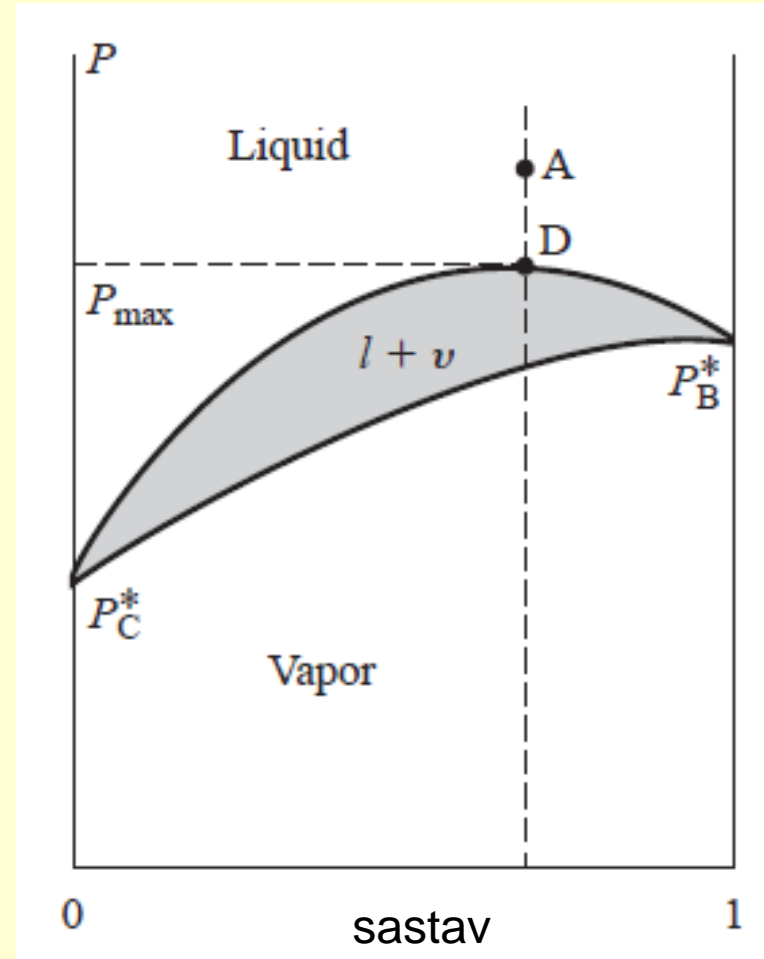
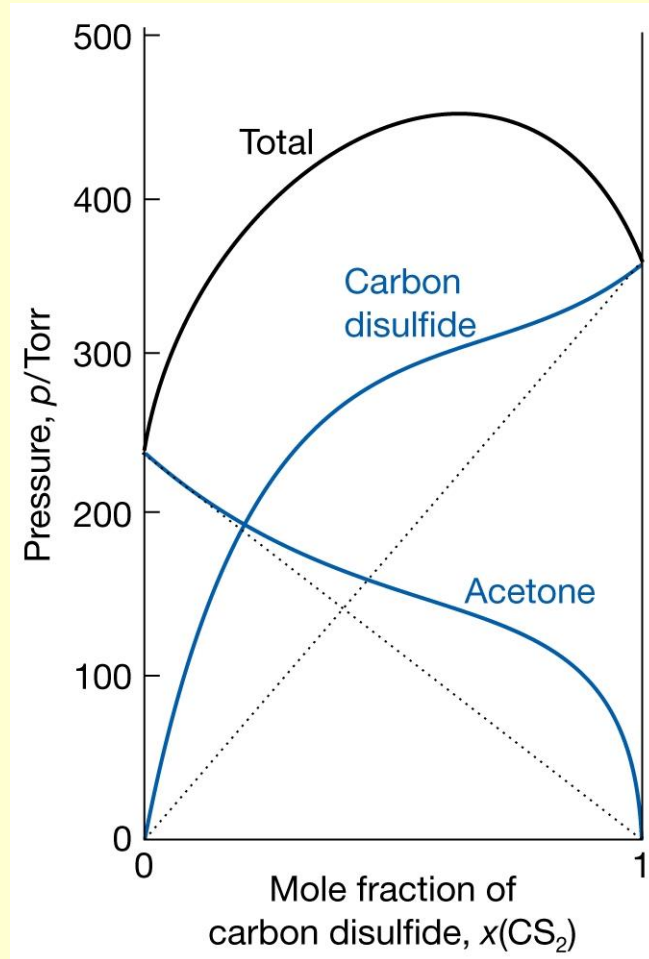


idealni rastvor

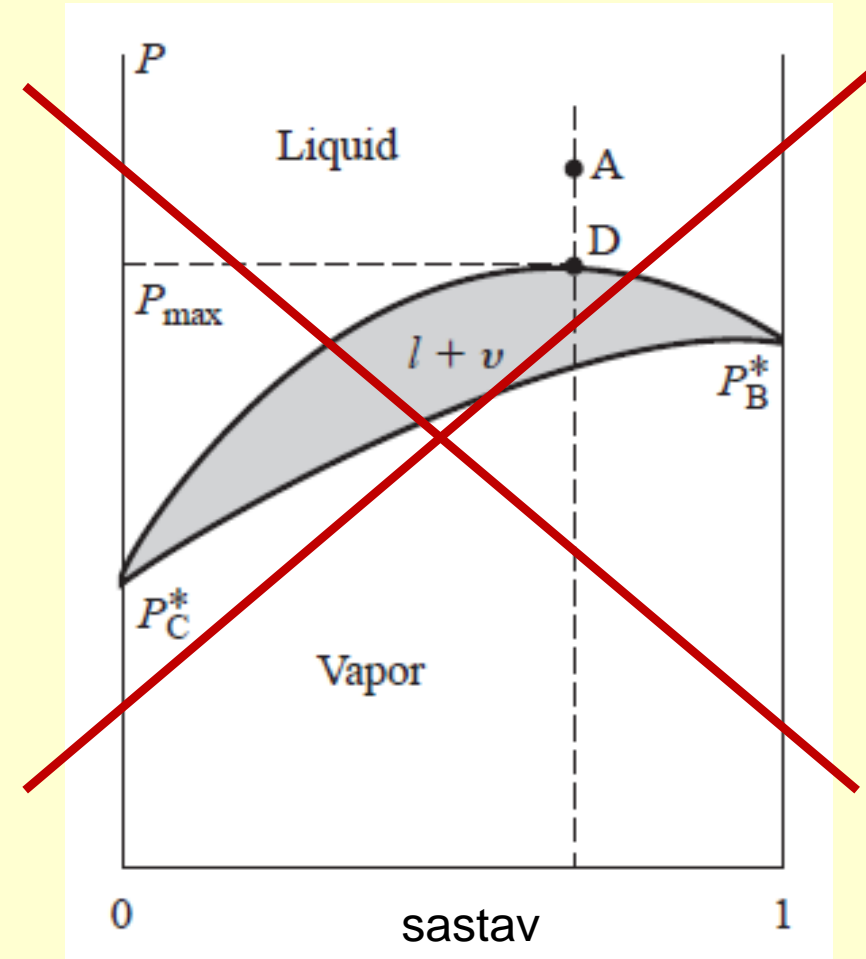
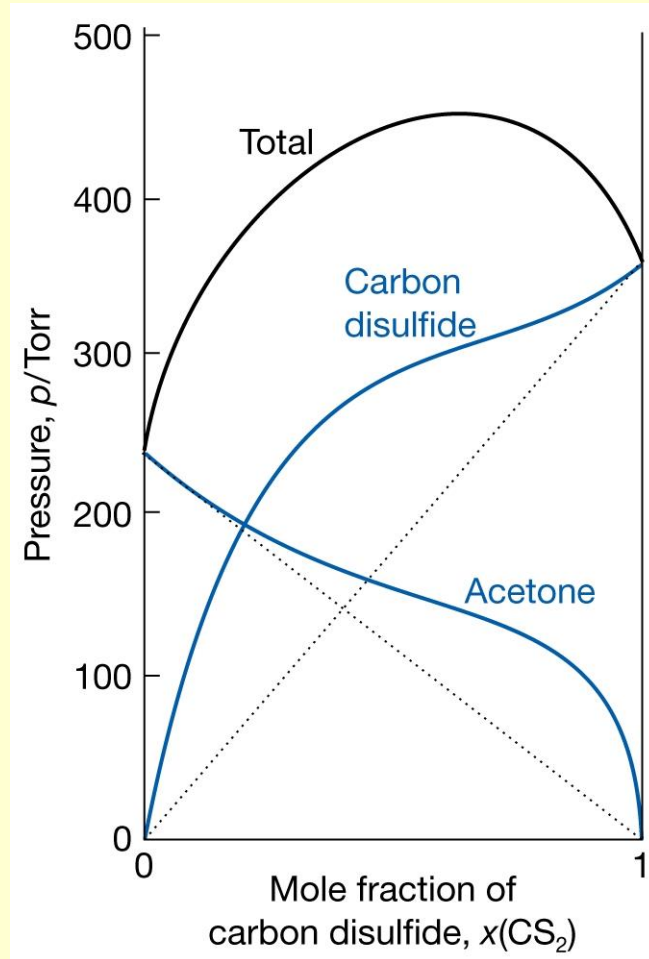
pozitivna odstupanja

negativna odstupanja

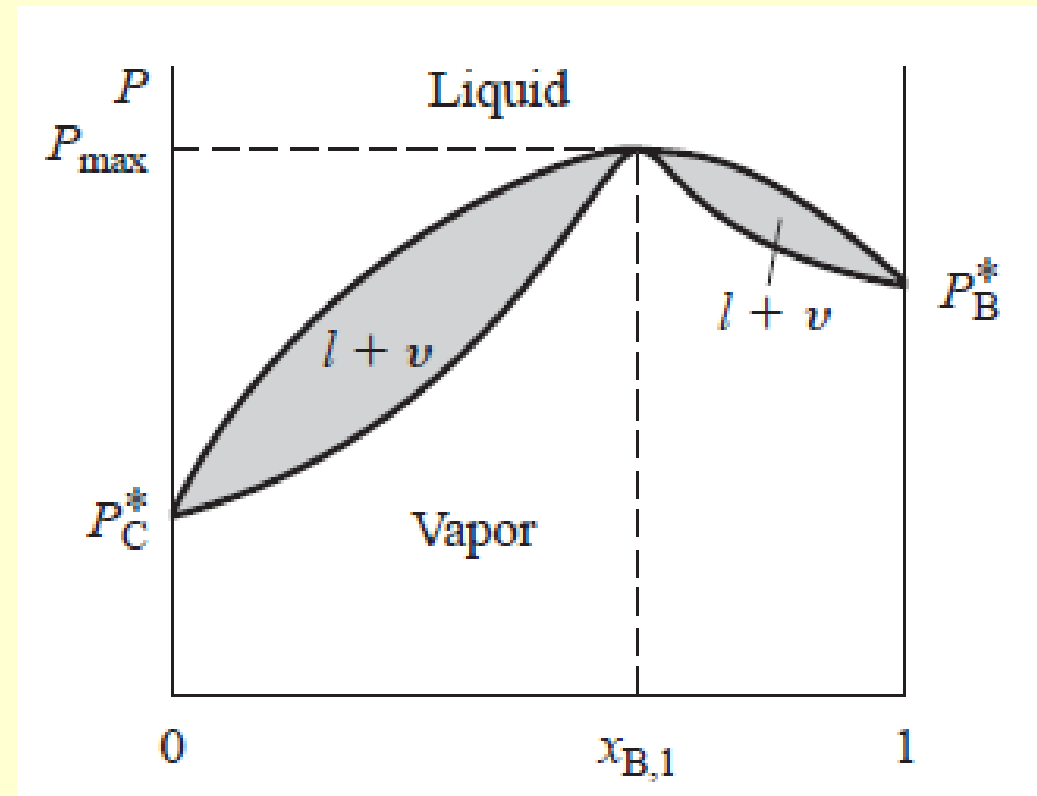
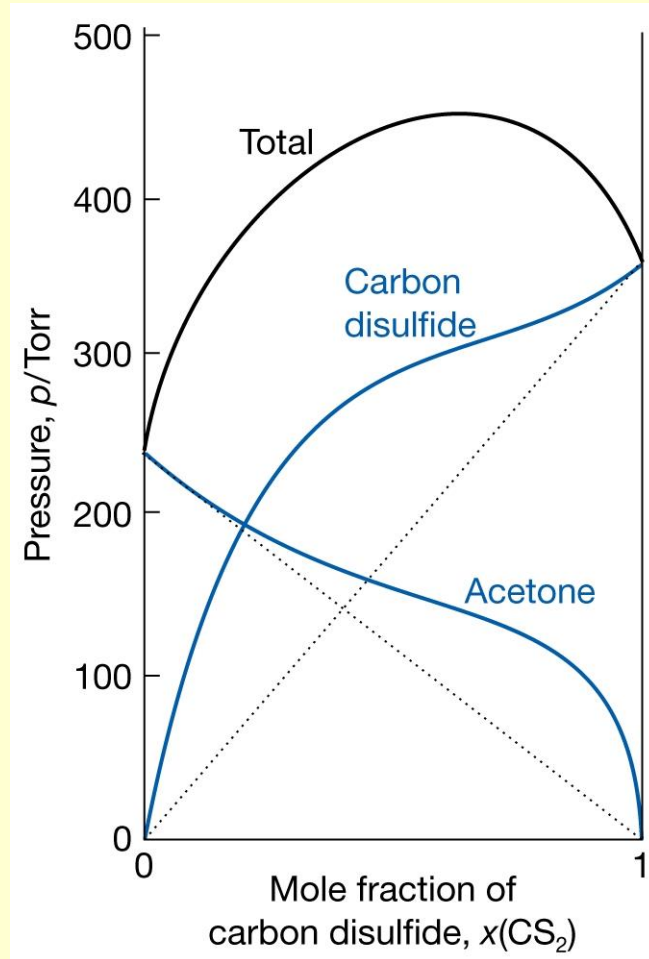
# Neidealni rastvor: pozitivna odstupanja



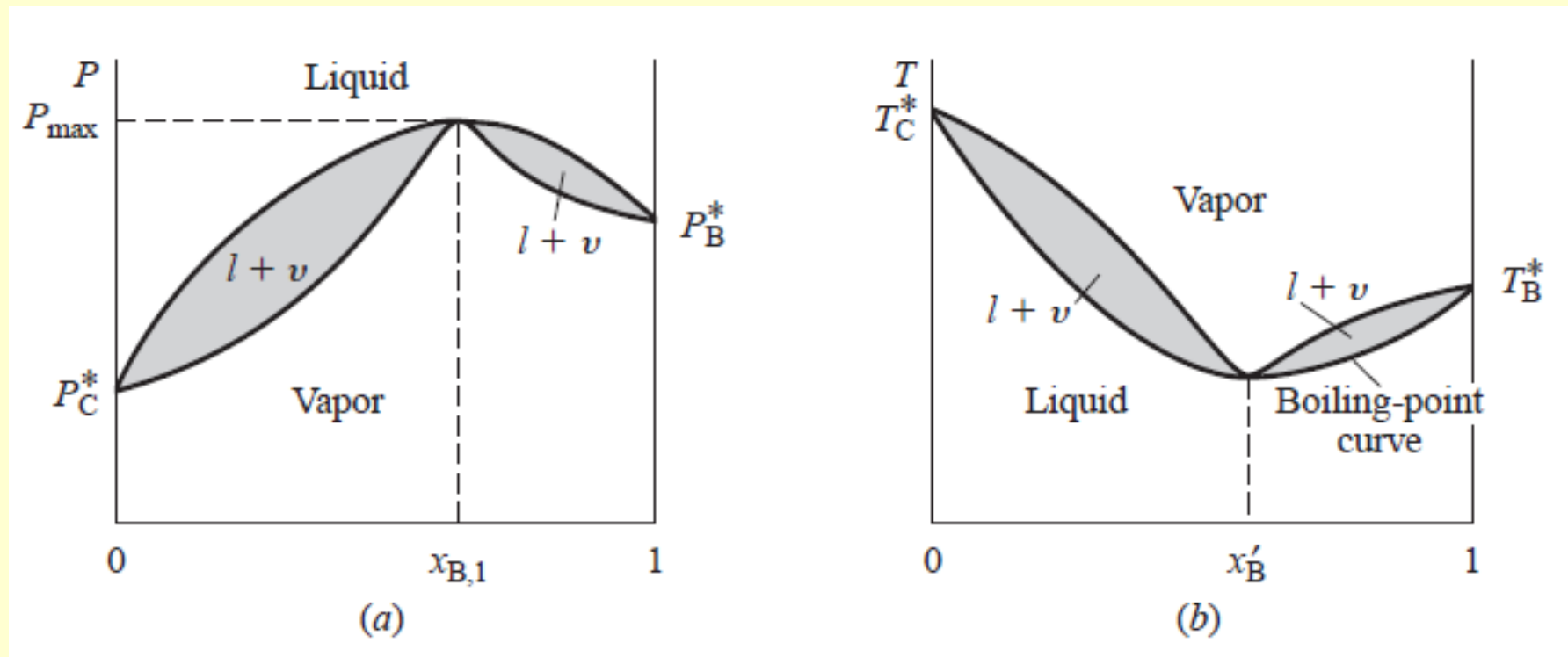
# Neidealni rastvor: pozitivna odstupanja



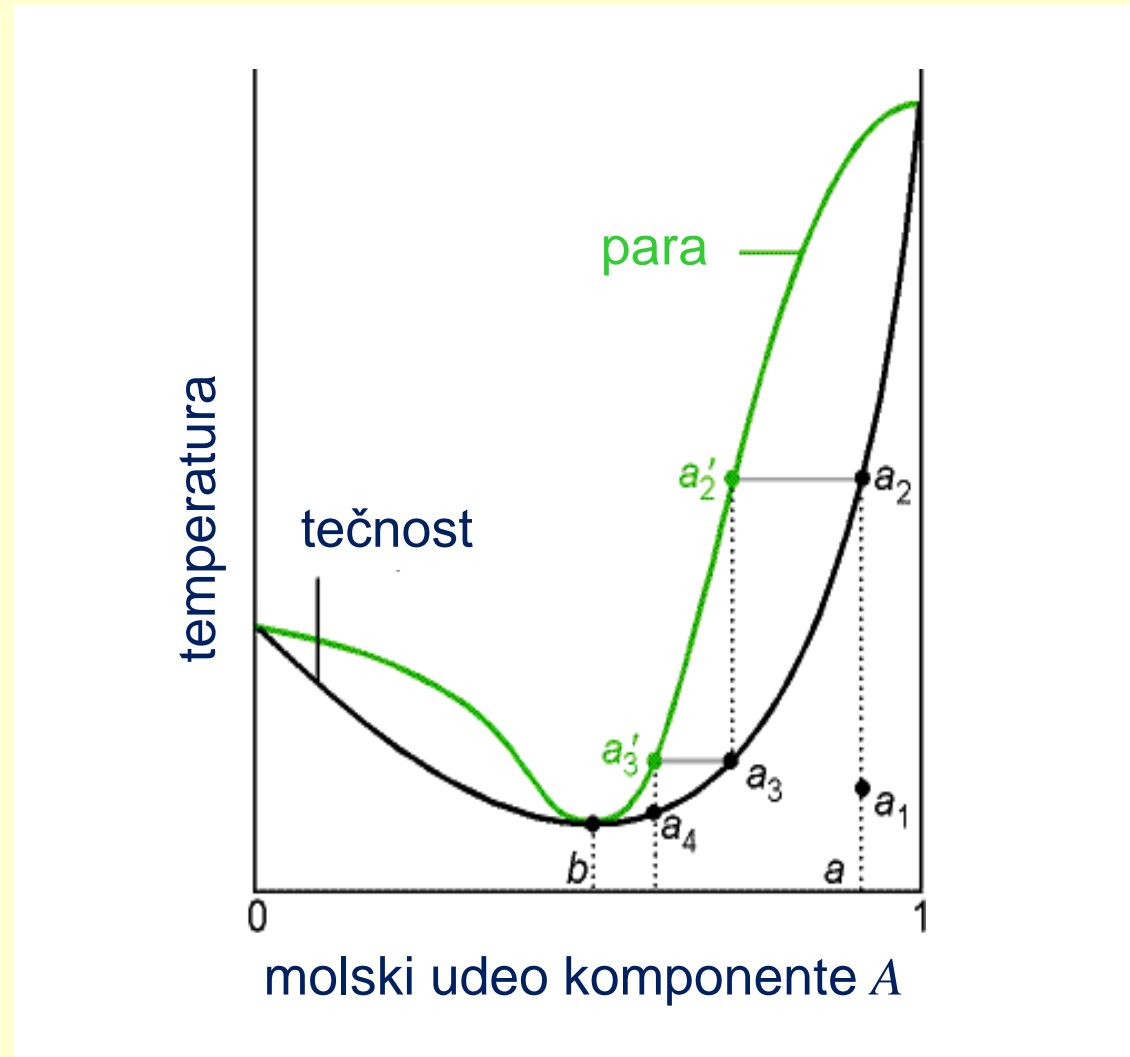
# Neidealni rastvor: pozitivna odstupanja



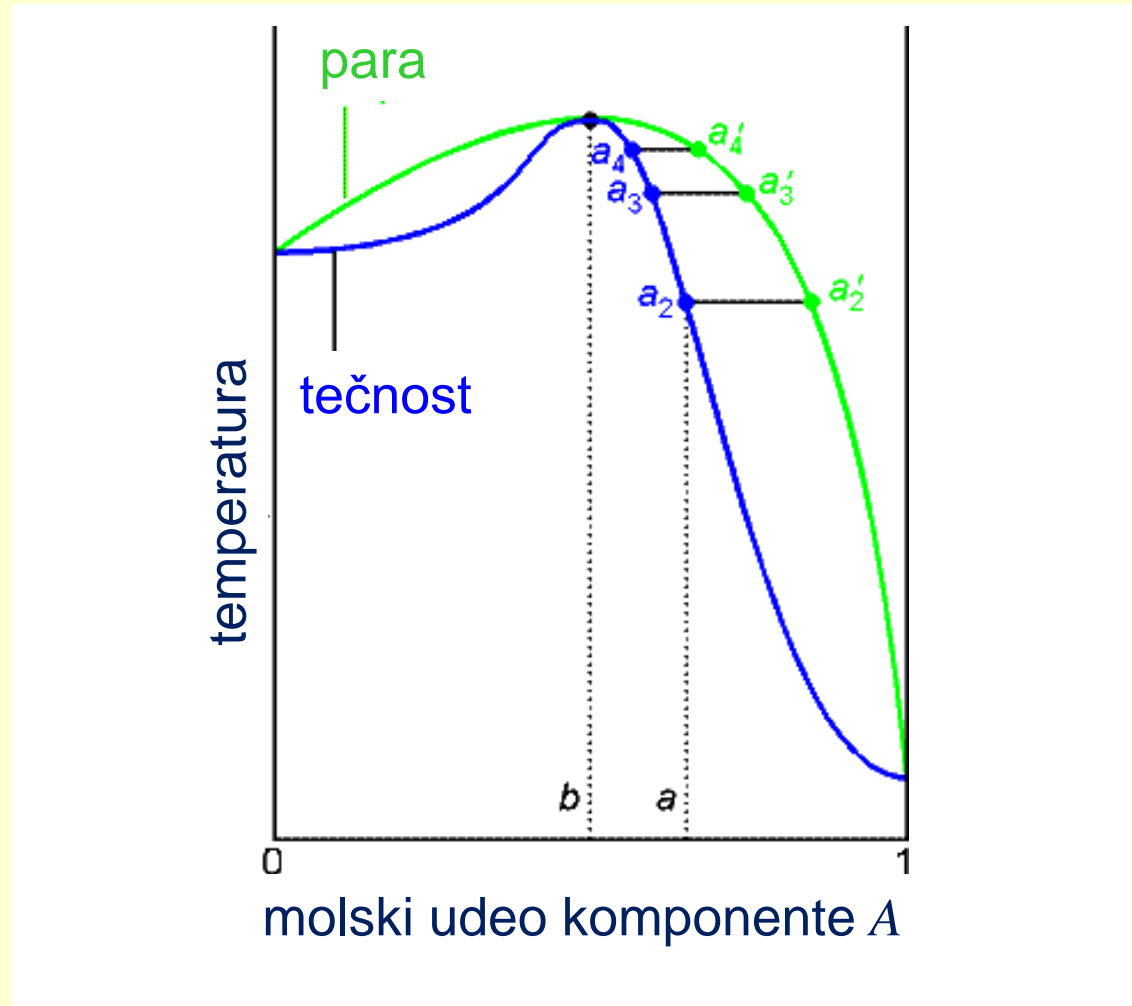
# Neidealni rastvor: pozitivna odstupanja



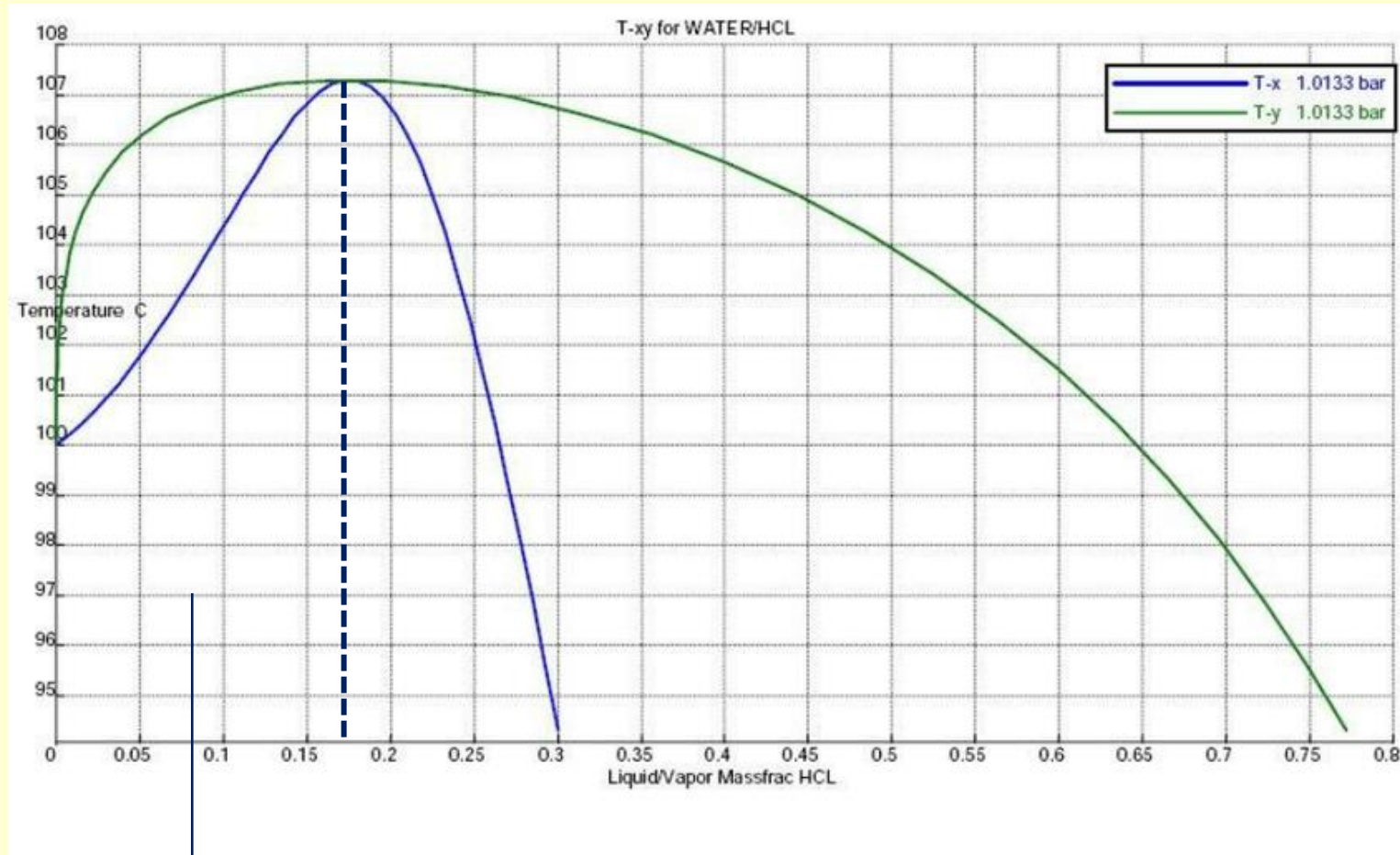
# Neidealni rastvor: pozitivna odstupanja



# Neidealni rastvor: negativna odstupanja



# Primer: H<sub>2</sub>O-HCl



povećanje temperature dovodi do povećanja rastvorljivosti HCl u H<sub>2</sub>O

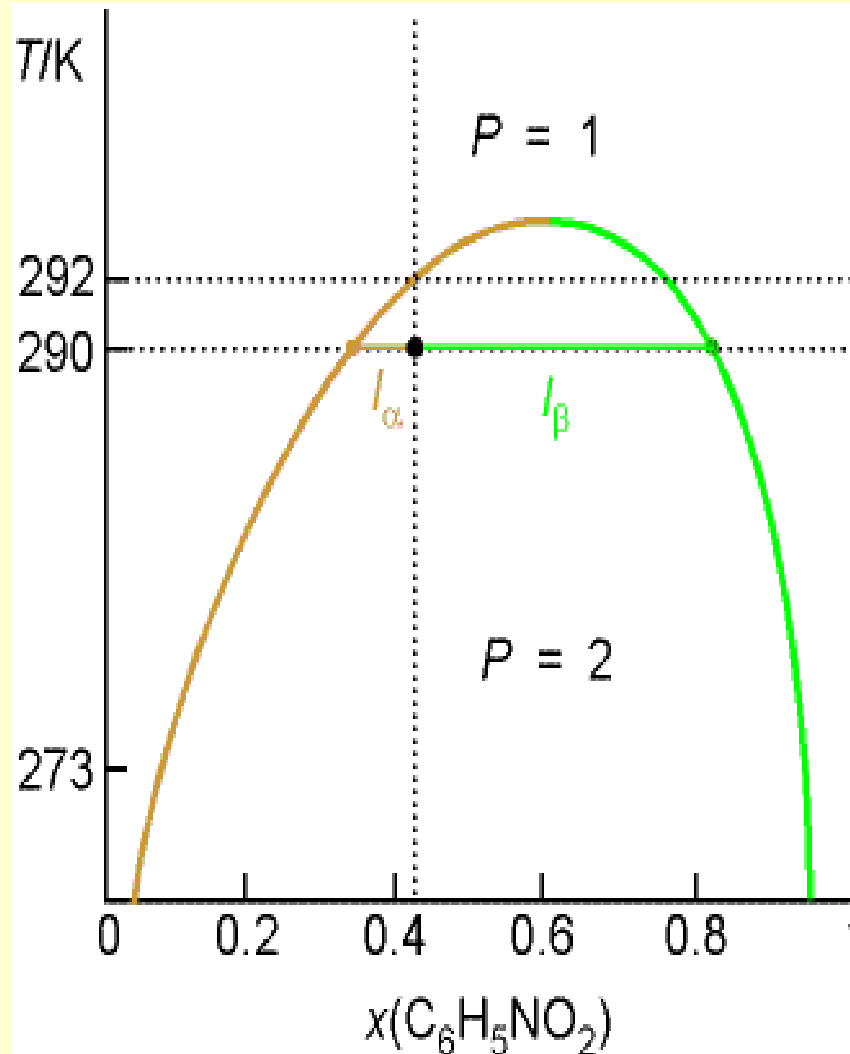


# Dvokomponentni sistemi

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- potpuno mešljive tečnosti
- delimično mešljive tečnosti
- nemešljive tečnosti

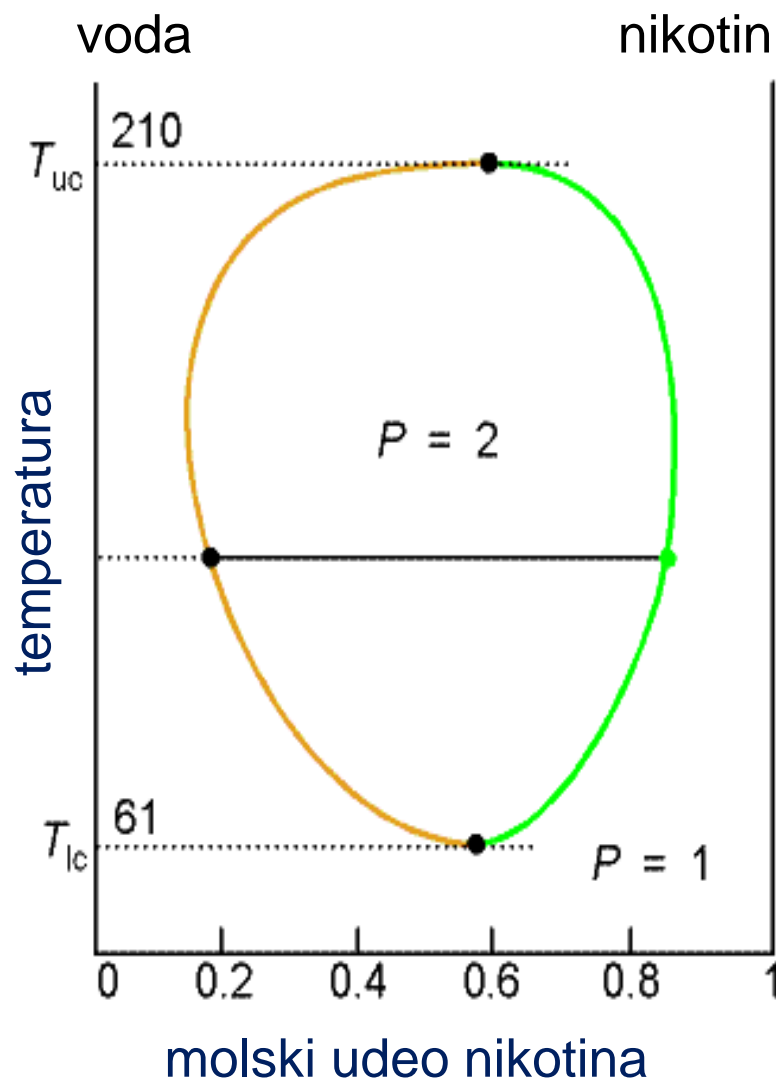
# Delimično mešljive tečnosti



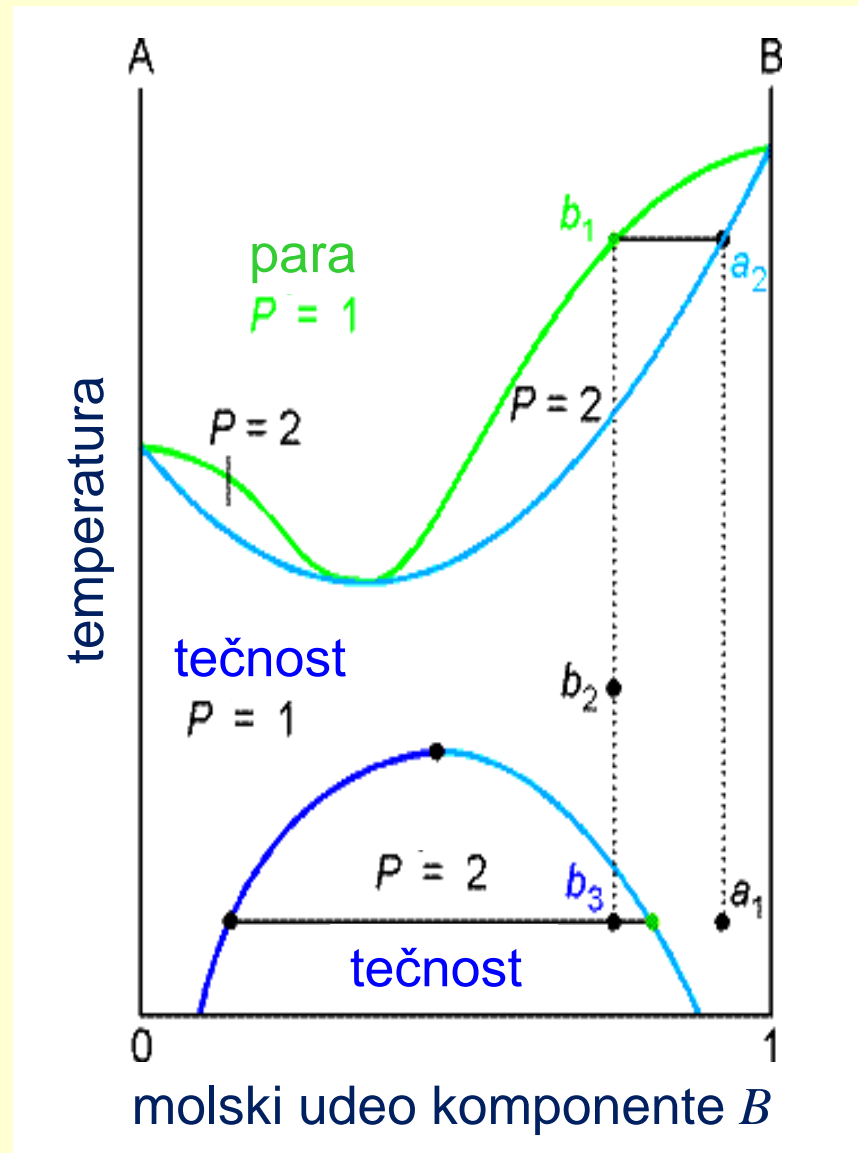
$$\frac{n_\alpha}{n_\beta} = \frac{x_\beta^A - x^A}{x^A - x_\alpha^A} = \frac{l_\beta}{l_\alpha}$$

heksan i nitrobenzen

# Kritične temperature rastvora

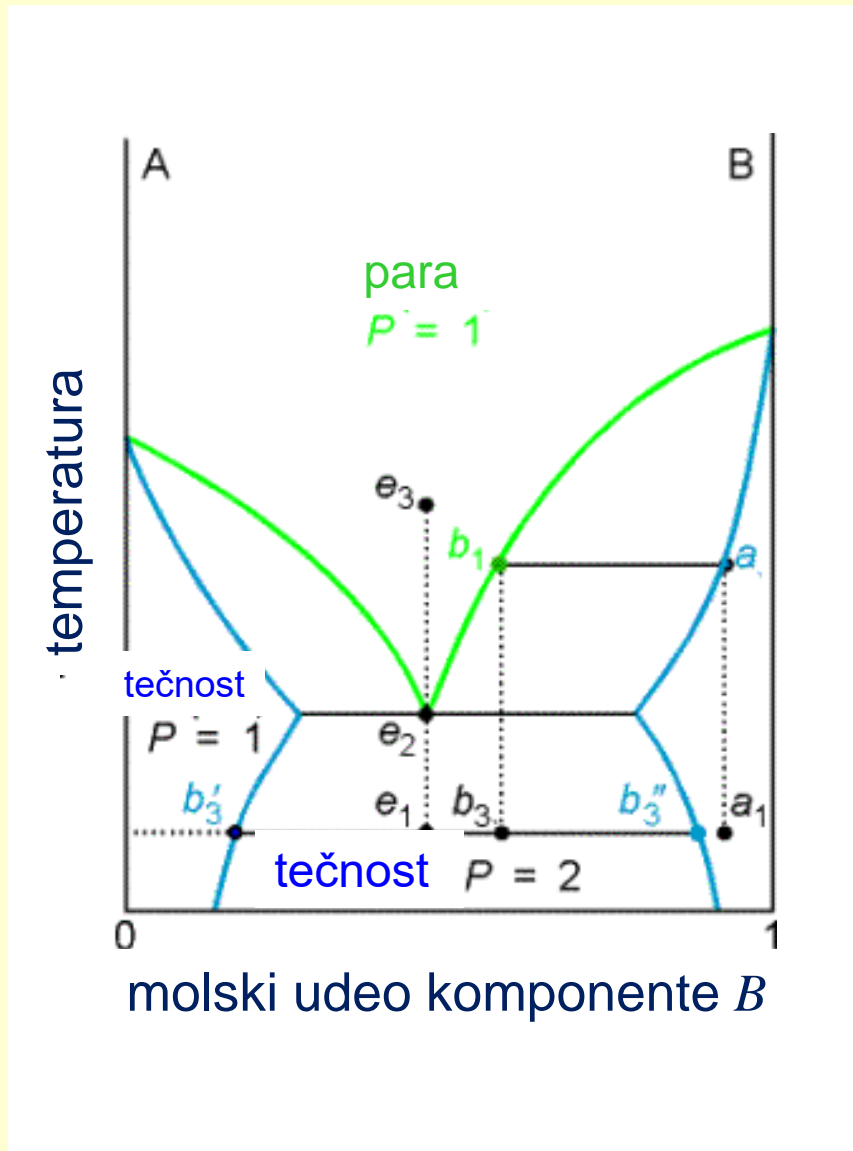


# Delimično mešljive tečnosti



# Delimično mešljive tečnosti

Ako do ključanja dolazi pre dostizanja gornja kritične temperature, dijagram faza će izgledati kao na slici.



# Dvokomponentni sistemi

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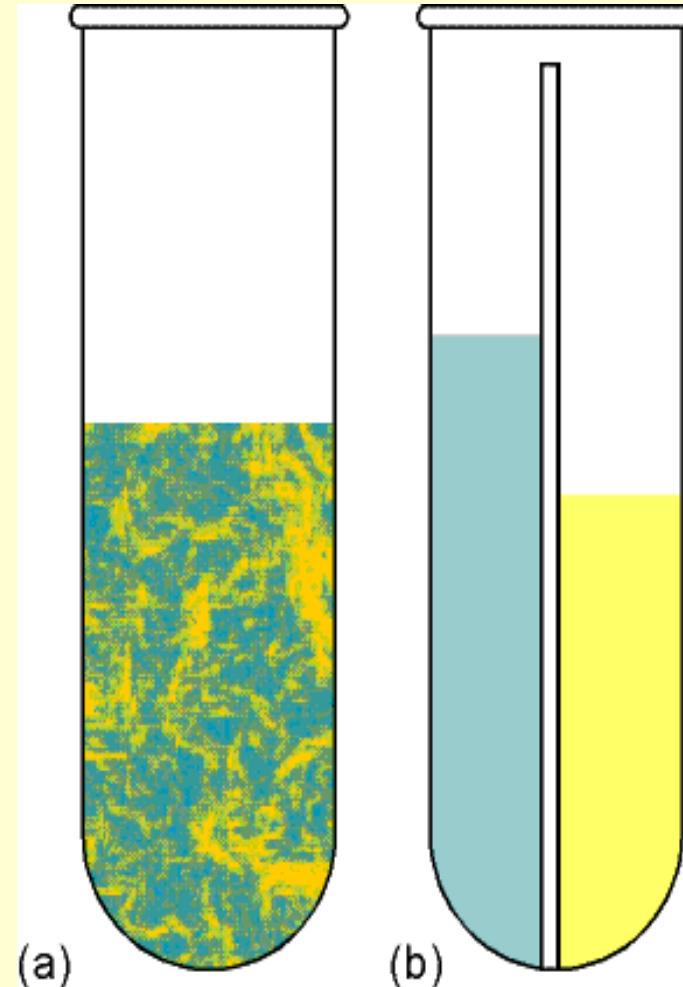
- potpuno mešljive tečnosti
- delimično mešljive tečnosti
- nemešljive tečnosti

# Nemešljive tečnosti

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Kada se dve nemešljive tečnosti  
mućkaju zajedno, ukupni napon pare  
je  $p = p_A + p_B$ .

Obe tečnosti će ključati kada je ukupni  
pritisak  $p =$  atmosferski pritisak.



# Zakon raspodele

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$$\mu_I = \mu_I^0 + RT \ln a_I$$

$$\mu_{II} = \mu_{II}^0 + RT \ln a_{II}$$

$$\ln \frac{a_I}{a_{II}} = \frac{\mu_{II}^0 - \mu_I^0}{RT}$$

$$\boxed{\frac{a_I}{a_{II}} = K}$$

Razblaženi rastvor

$$\frac{c_I}{c_{II}} = K$$

Disocijacija

$$\frac{(1 - \alpha_I)c_I}{(1 - \alpha_{II})c_{II}} = K$$



# Ekstrakcija

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Organske supstancije kao više rastvorljive u organskim rastvaračima nego u vodi mogu se ekstrahovati iz vodenih rastvora.

$$\frac{m_1/V}{(m - m_1)/l} = K \qquad m_1 = m \frac{KV}{KV + l}$$

$$m_2 = m_1 \frac{KV}{KV + l} = m \left( \frac{KV}{KV + l} \right)^2$$

$$m_n = m \left( \frac{KV}{KV + l} \right)^n$$