

RAVNOTEŽA FAZA:

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

Dvokomponentni sistemi

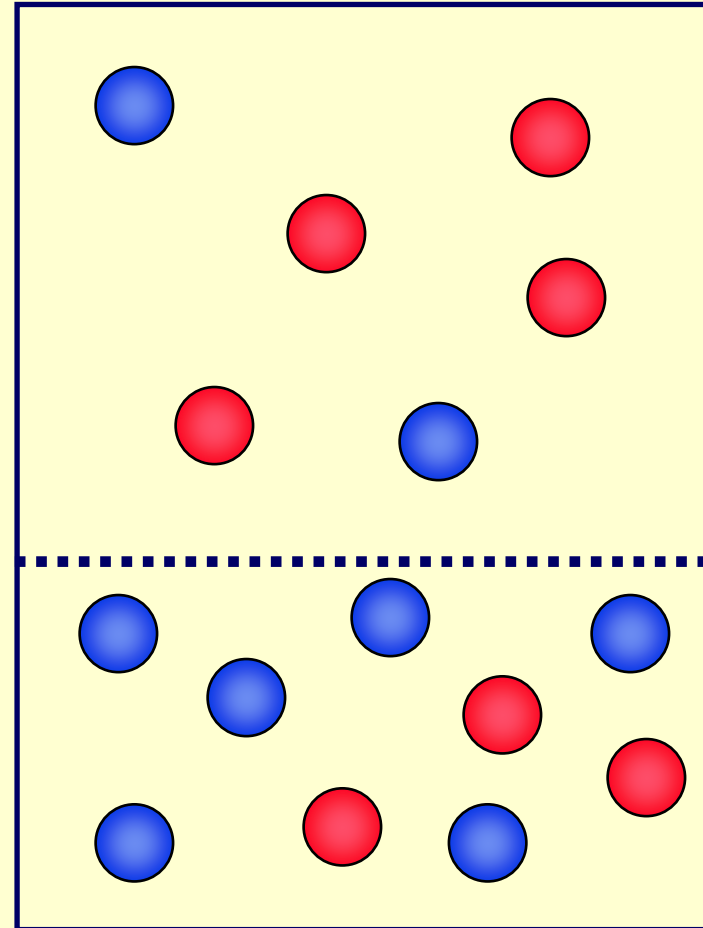
- **potpuno mešljive tečnosti**
- delimično mešljive tečnosti
- nemešljive tečnosti

Ravnoteža tečnost – para

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

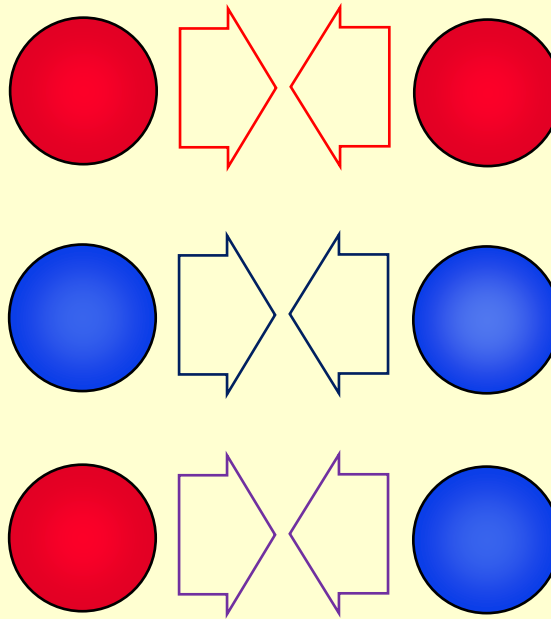
$$F = C - P + 2 = 2 - 2 + 2; \quad F = 2$$

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



$\Delta H_{\text{mešanja}} = 0$ 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)

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

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

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

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

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

Idealni rastvori (zapremina)

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

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

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

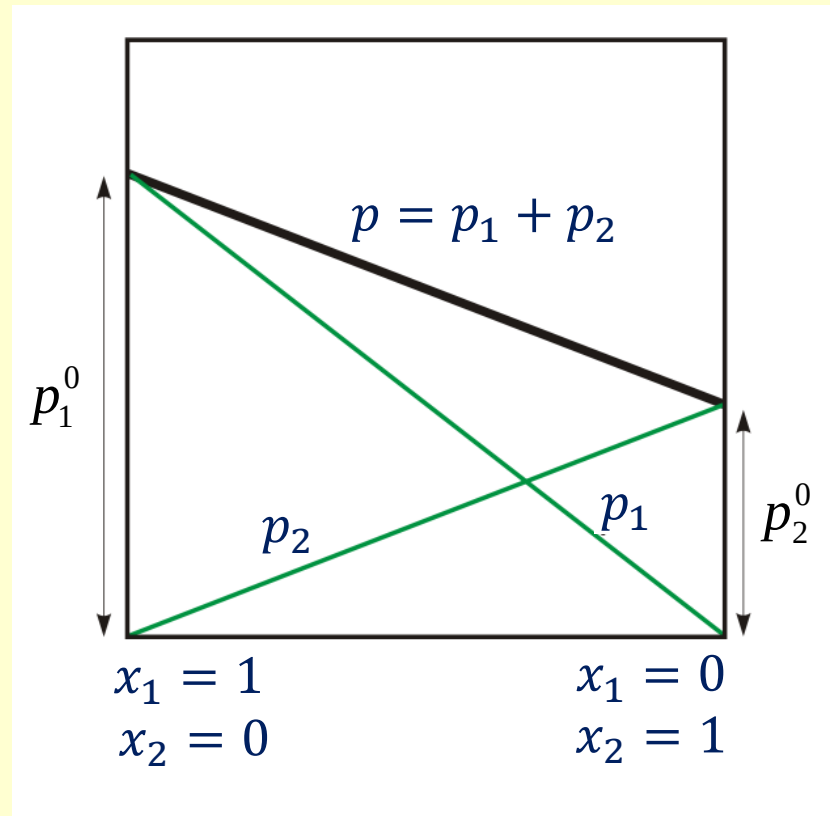
$$\bar{V}_i^t dP = \bar{V}_i^g dp_i \approx \frac{RT}{p_i} dp_i$$

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

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

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

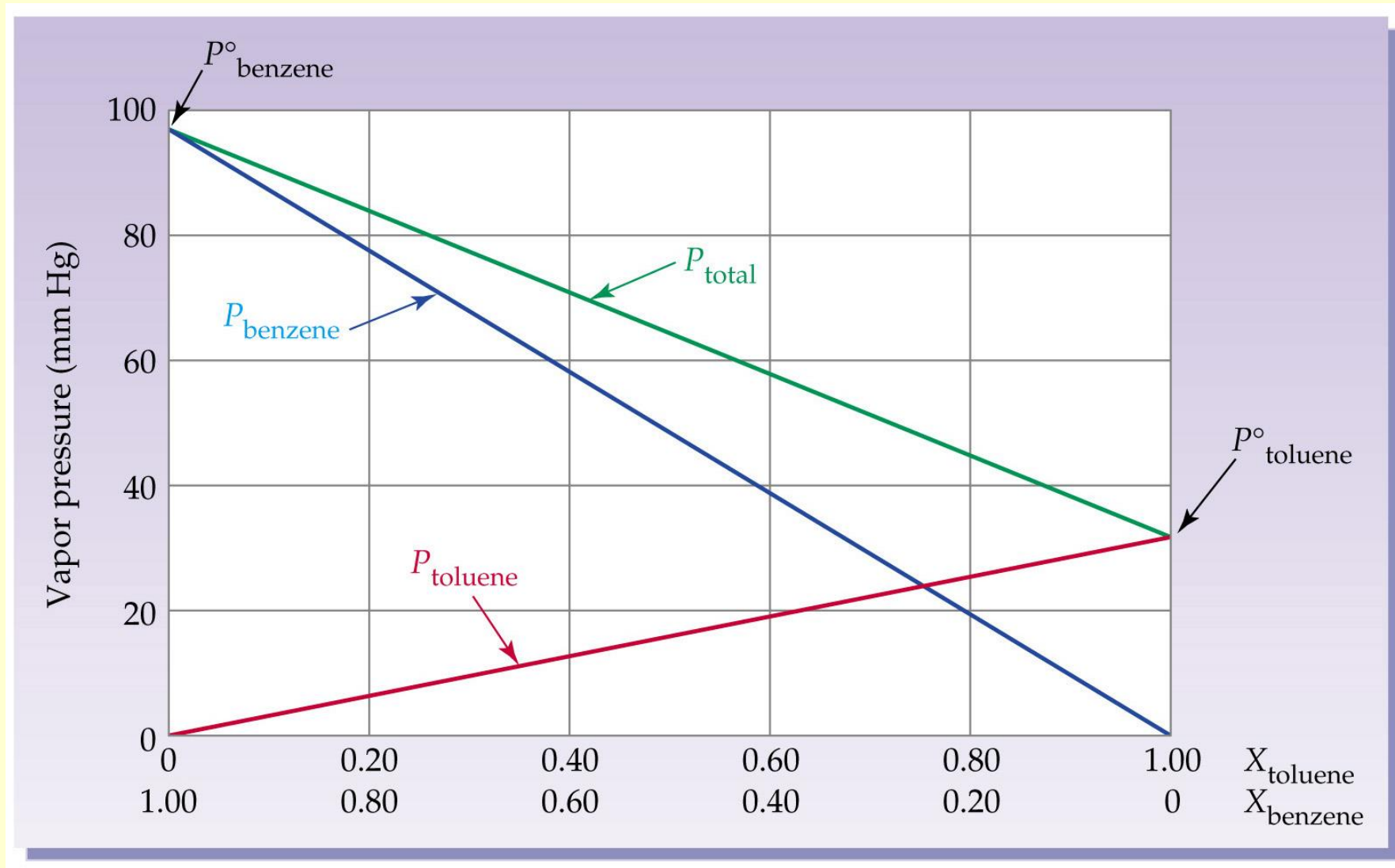
Zavisnost napona pare od sastava tečnosti



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

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

Benzen i toluen



Sastavi tečnosti i pare se razlikuju

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

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

$$x_b = x_t = 0,5$$

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

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

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

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

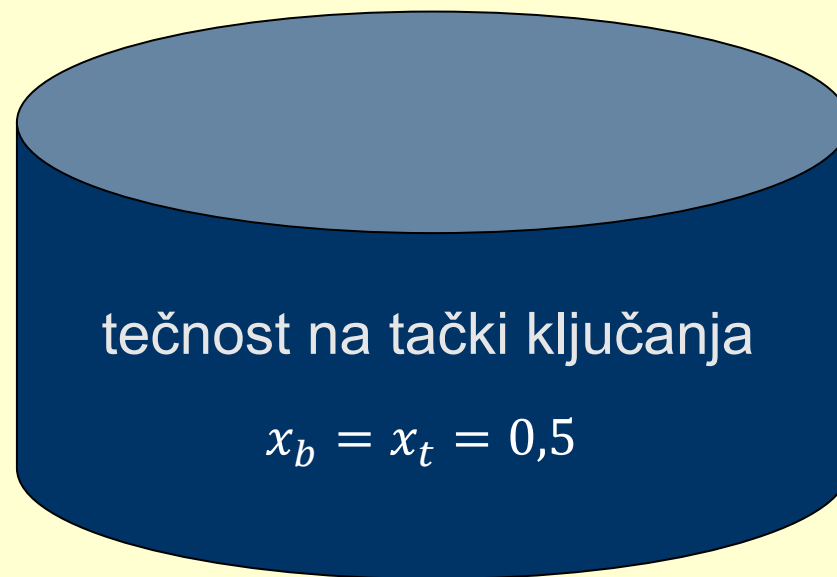
$$x'_t = 1 - 0,71 = 0,29$$

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

Pretpostavka: para se može posmatrati kao smeša idealnih gasova.

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

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

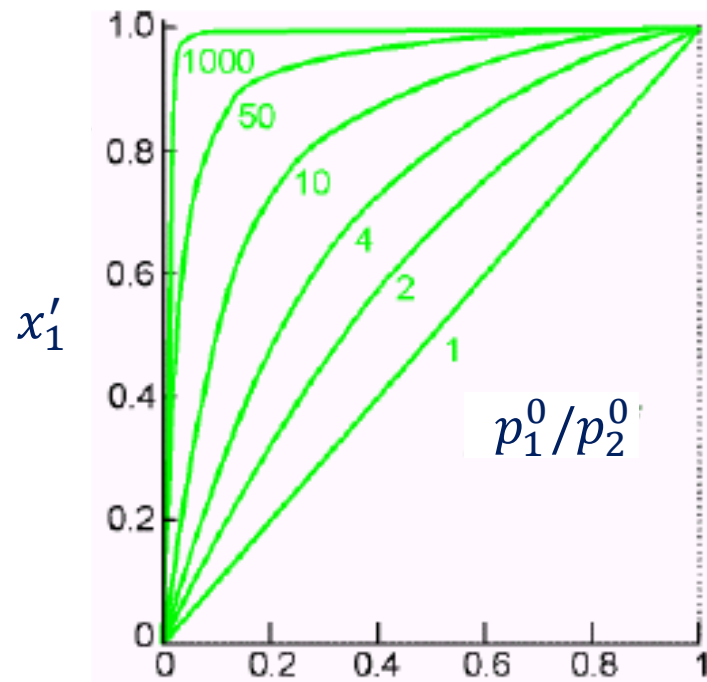
$$x'_1 = \frac{p_1}{p_1 + p_2} = \frac{x_1 p_1^0}{x_1 p_1^0 + x_2 p_2^0}$$

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

Zavisnost napona pare od sastava pare

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

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

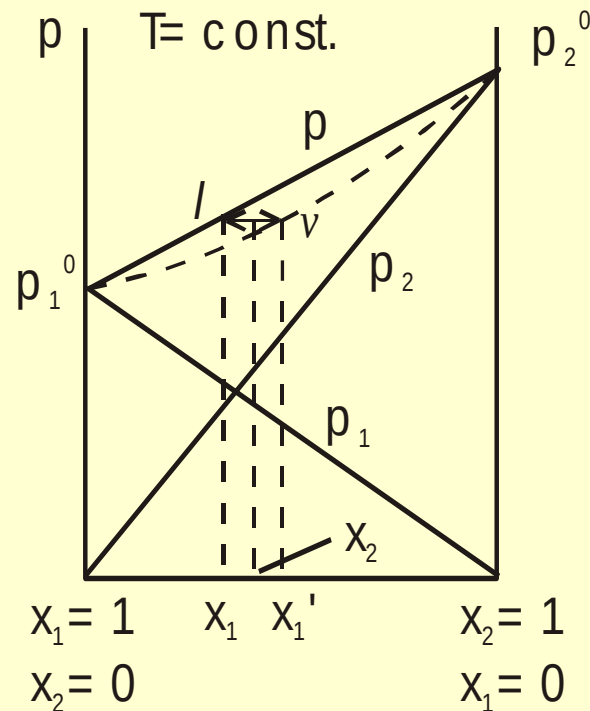


Što se komponente više razlikuju u isparljivosti, to će se više razlikovati sastav tečne od sastava parne faze.

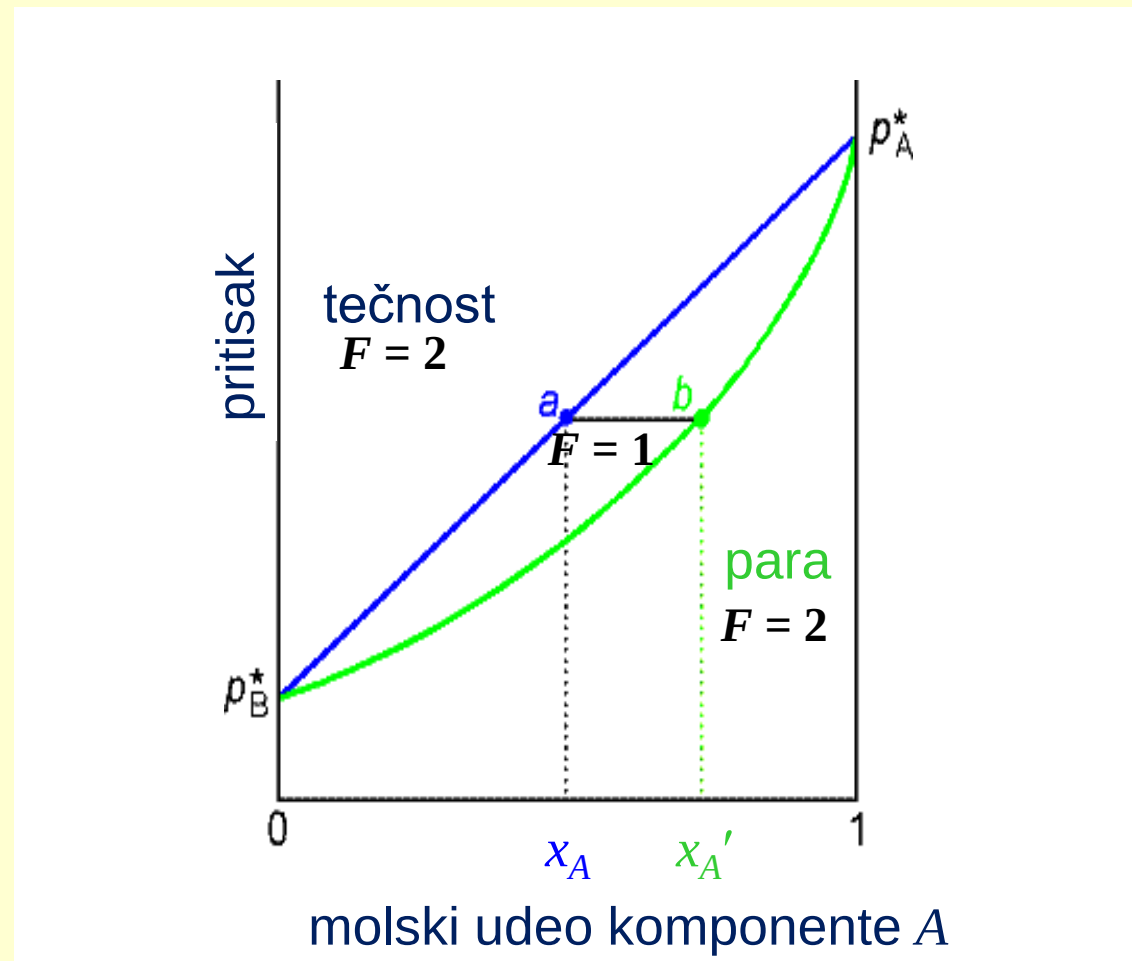
Za $p_1^0 \geq p_2^0$ je $x'_1 \geq x_1$ (para je bogatija isparljivijom komponentom).

Zavisnost napona pare od sastava pare

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

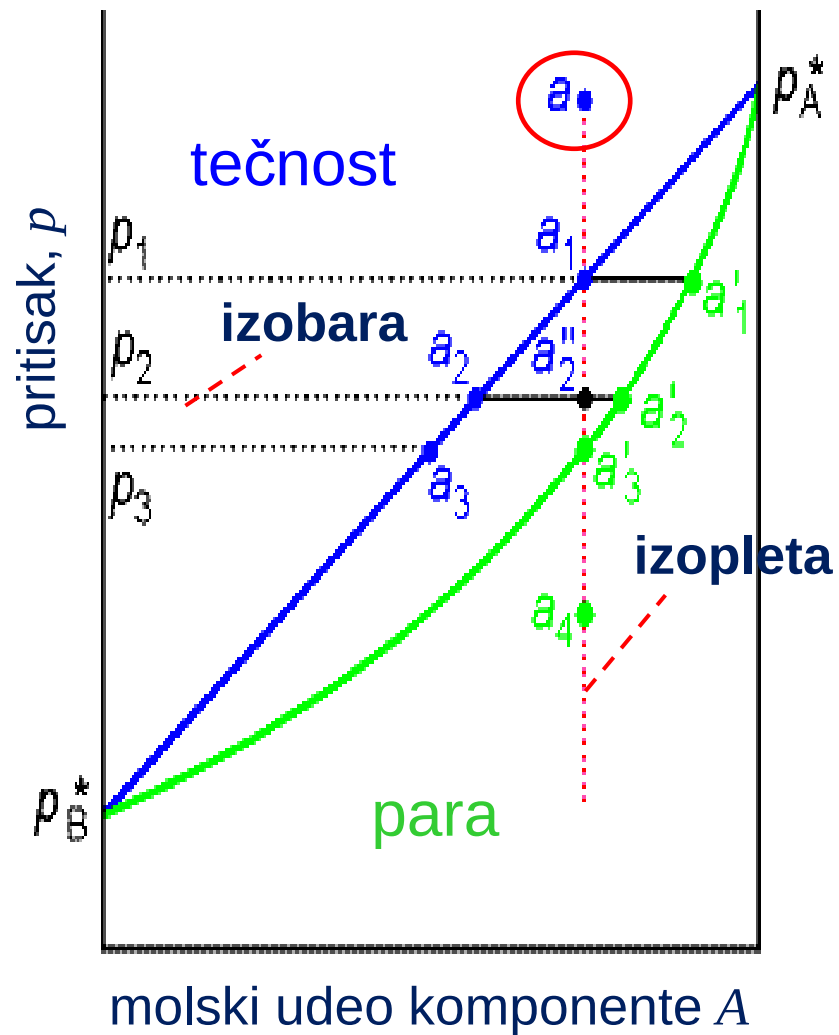


Fazni dijagram idealnog rastvora

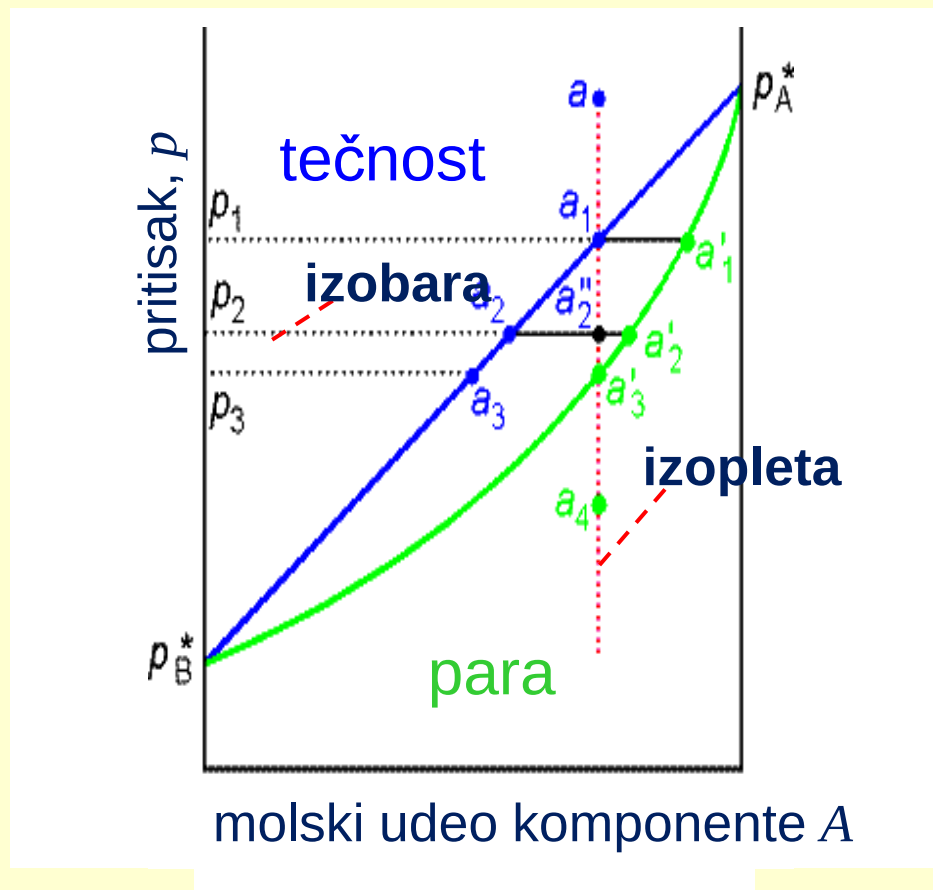


Promene duž izoplete

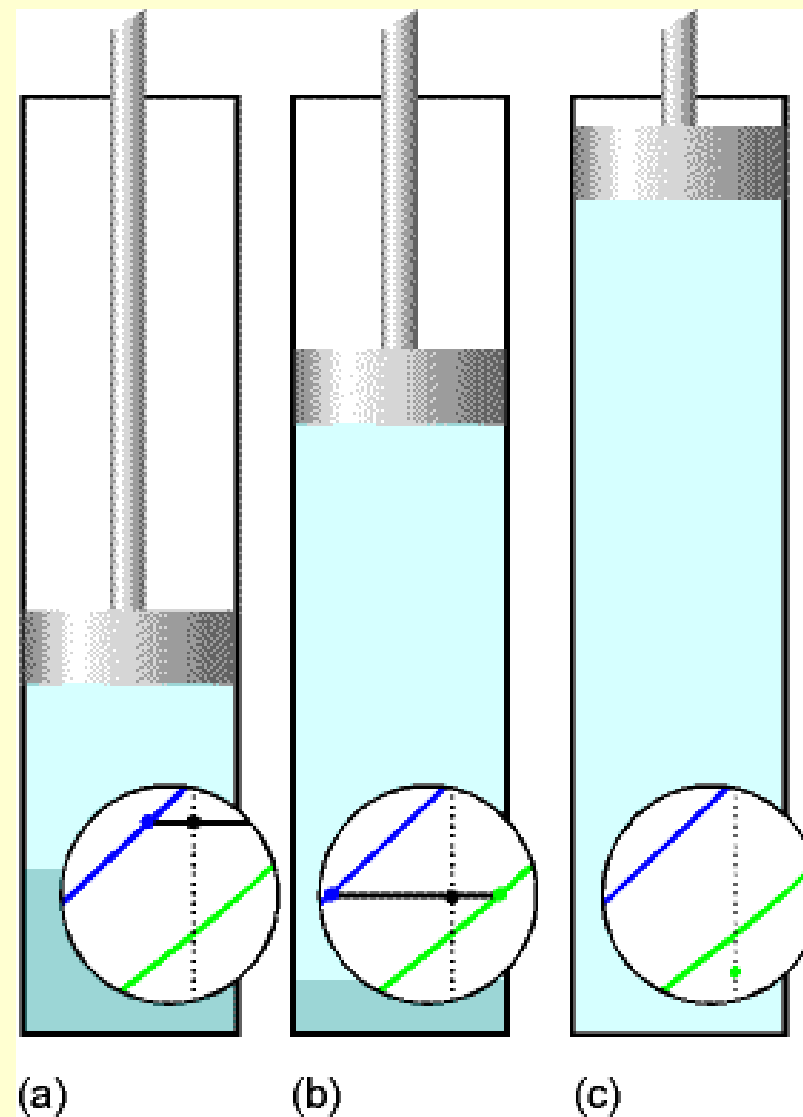
Izopleta – linija konstantnog sastava



Fizička slika procesa

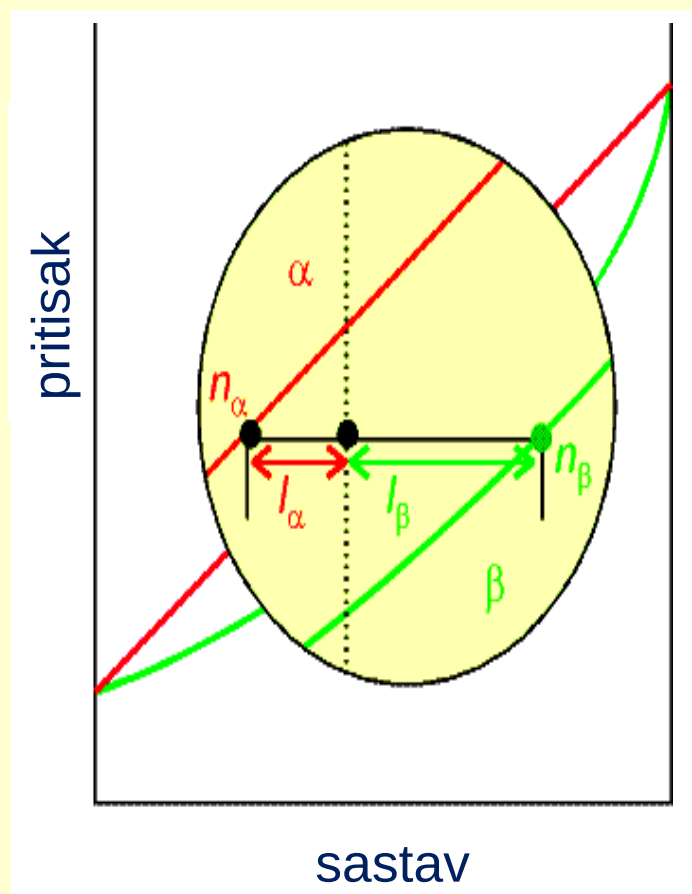


- (a) – Nešto pare se pojavilo.
- (b) – Samo malo tečnosti je ostalo.
- (c) – Samo je para prisutna.



Spojna linija i pravilo poluge

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



Pravilo poluge

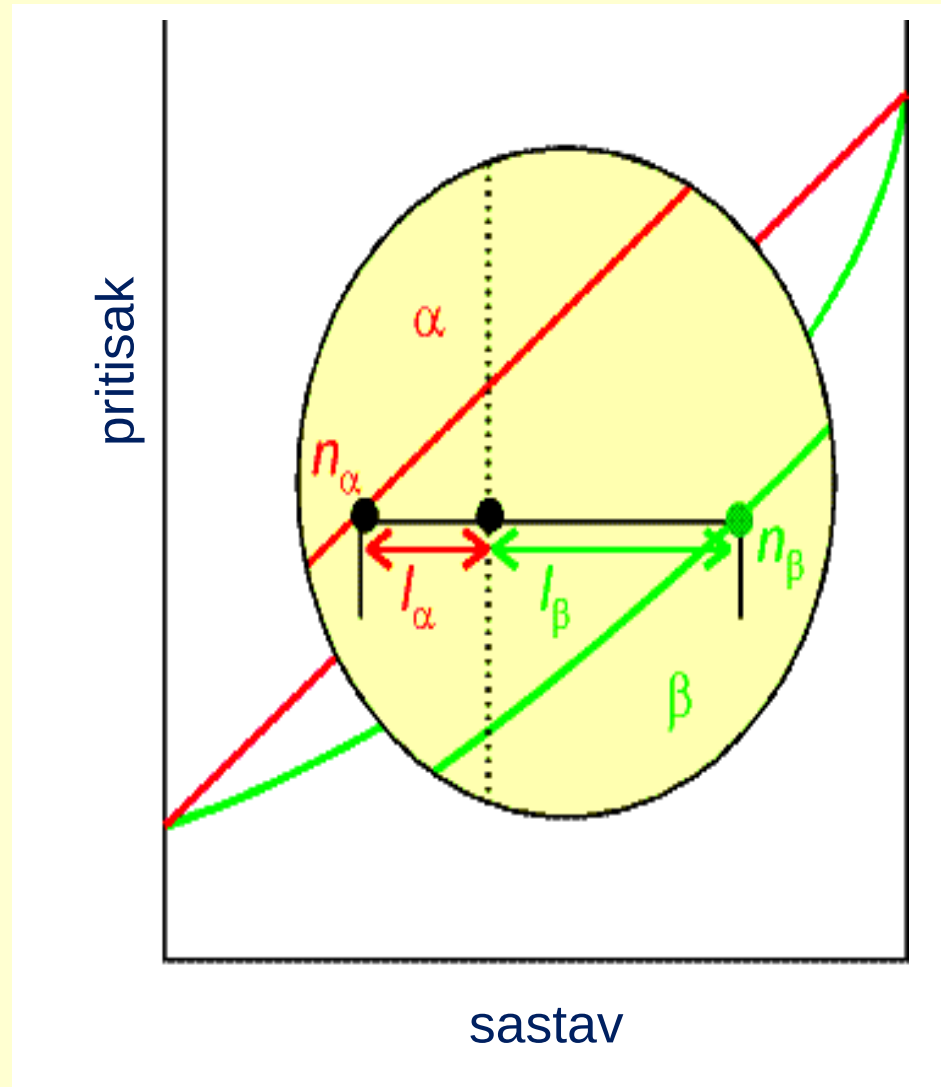
komponente A i B, faze α i β

n – ukupni broj molova u sistemu

n^α/n^β – ukupni broj molova u fazi α/β

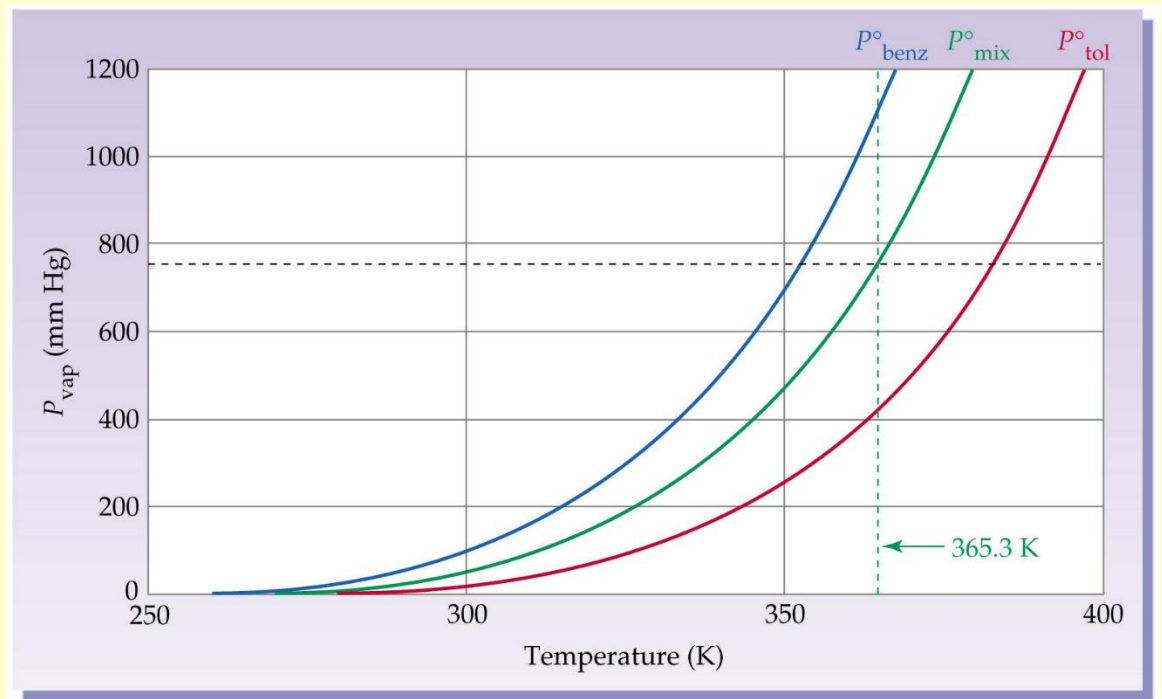
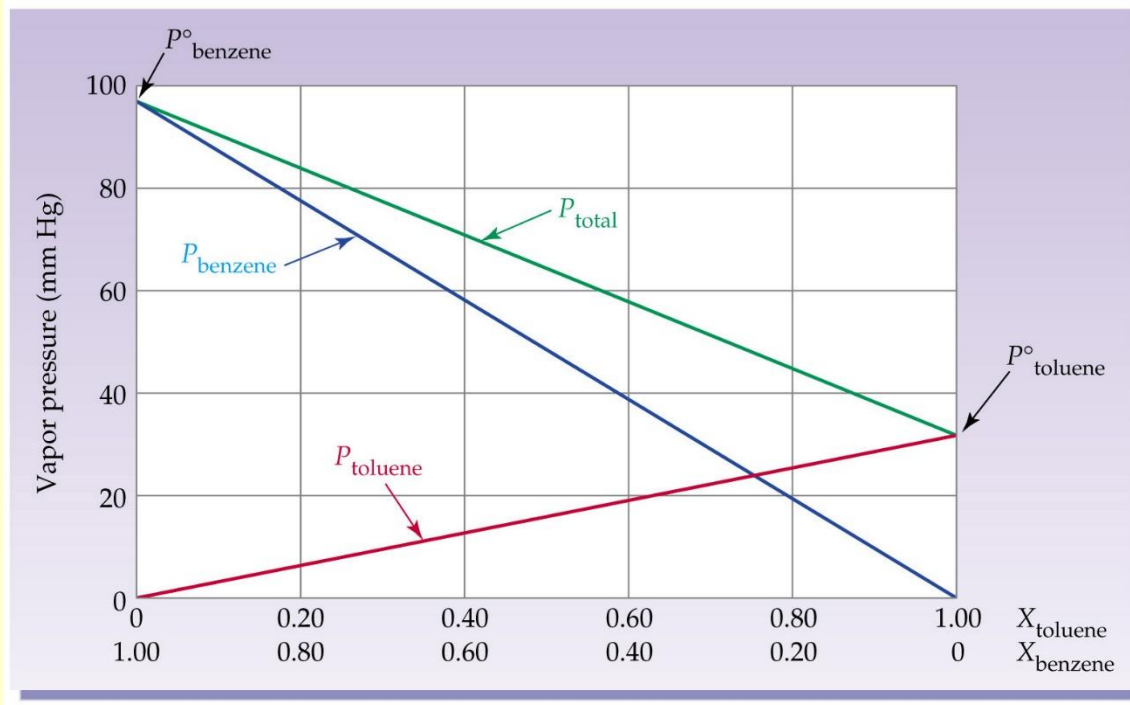
$$\begin{array}{l} n = n_\alpha + n_\beta \\ \left. \begin{array}{l} x^A = \frac{n^A}{n} \rightarrow n^A = nx^A \\ x_\alpha^A = \frac{n_\alpha^A}{n_\alpha} \rightarrow n_\alpha^A = n_\alpha x_\alpha^A \\ x_\beta^A = \frac{n_\beta^A}{n_\beta} \rightarrow n_\beta^A = n_\beta x_\beta^A \end{array} \right\}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

Spojna linija i pravilo poluge

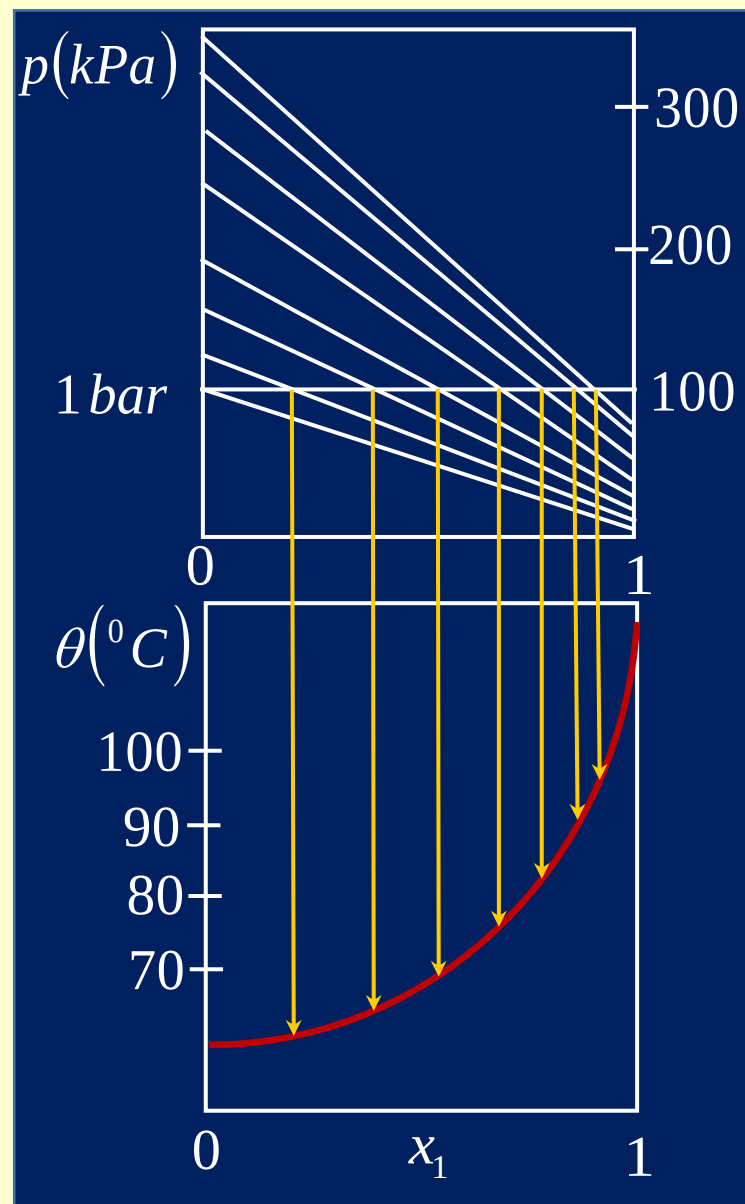


$$\frac{n_\alpha}{n_\beta} = \frac{x_\beta^A - x^A}{x^A - x_\alpha^A} = \frac{l_\beta}{l_\alpha}$$

Benzen i toluen

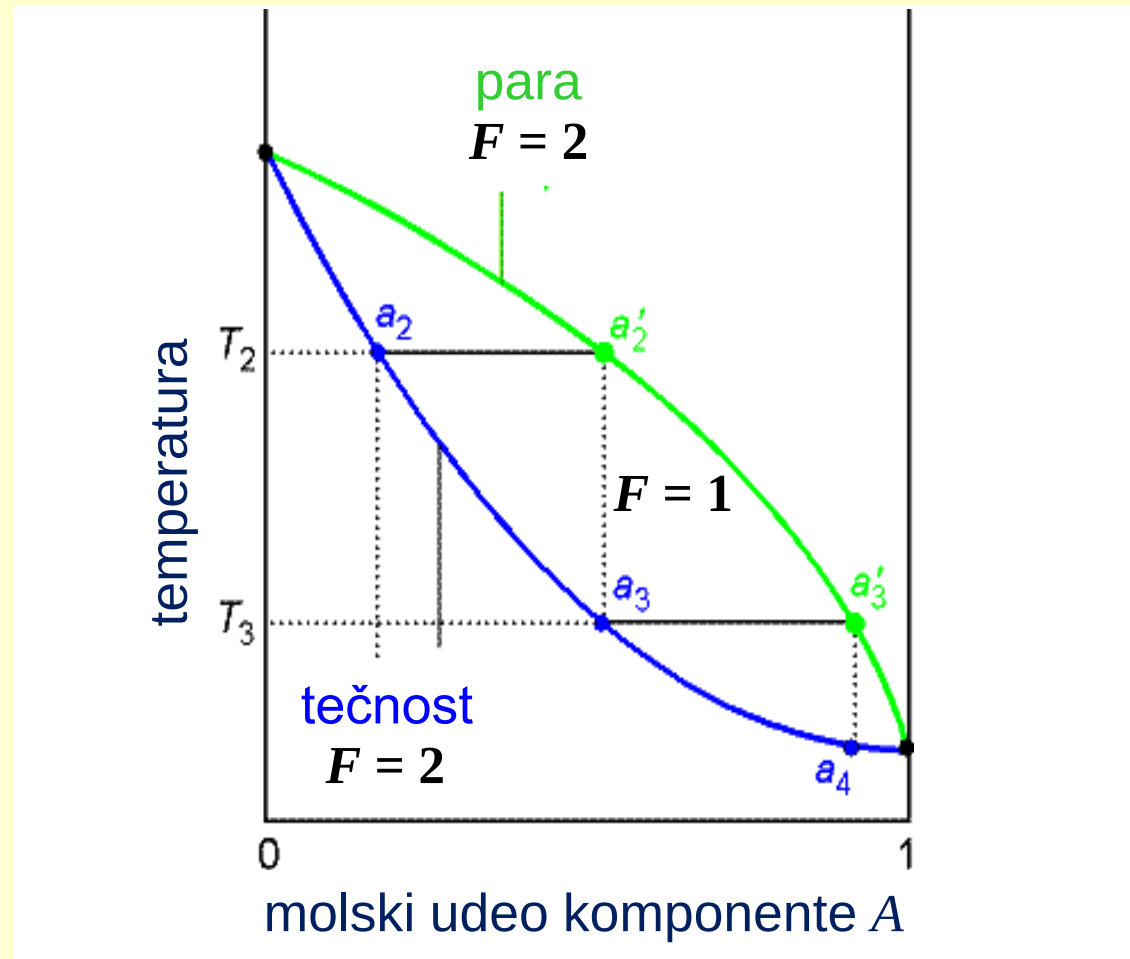


Tačka ključanja idealnih rastvora

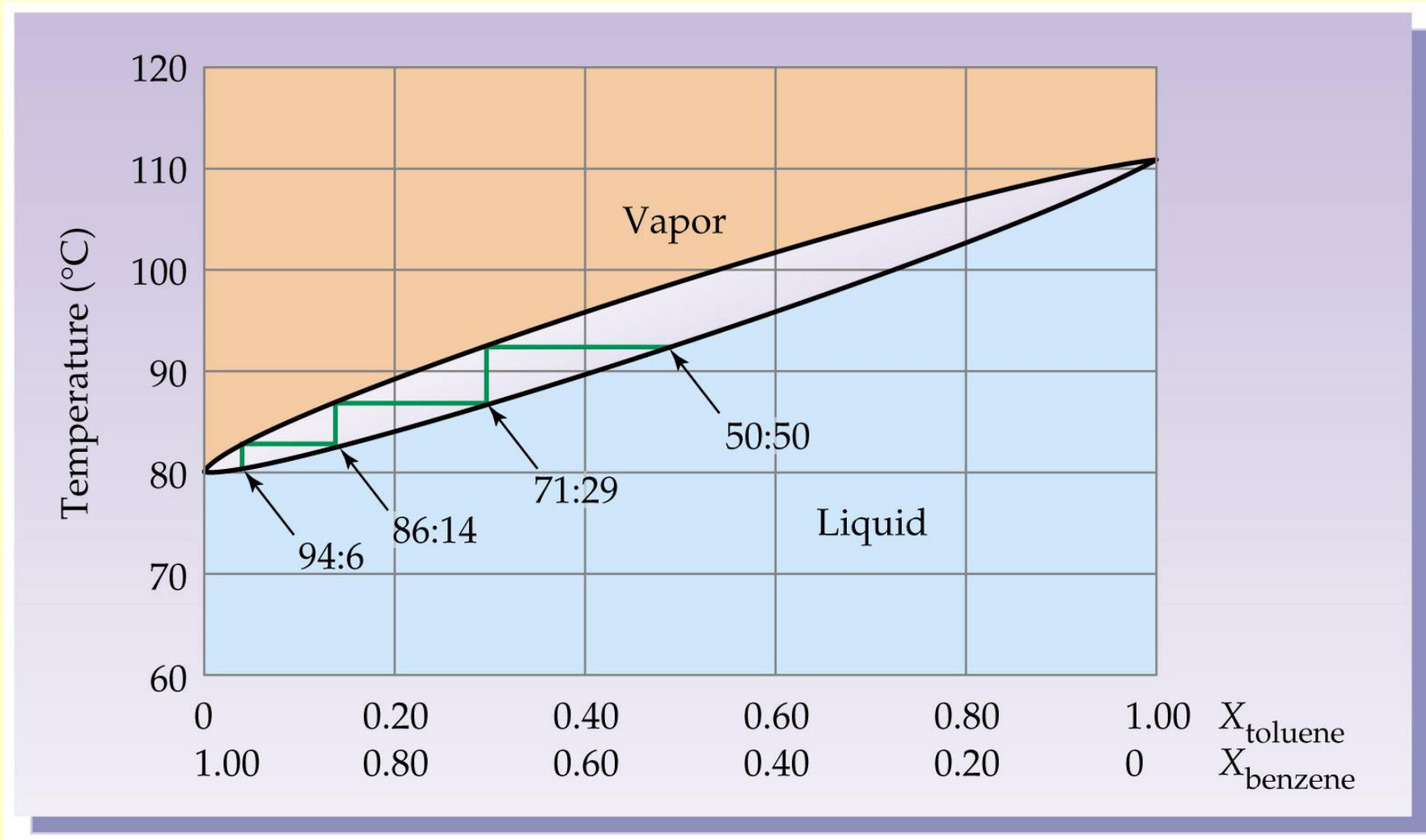


Zavisnost tačke ključanja od sastava

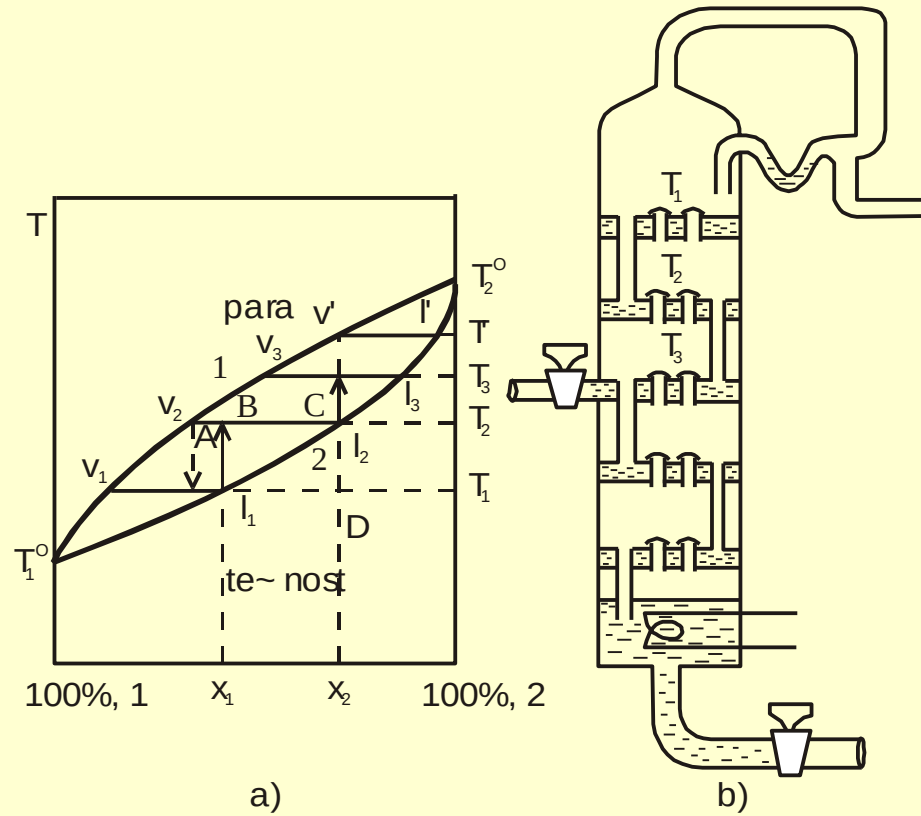
$$p = \text{const}$$



Rastvor benzena i toluena

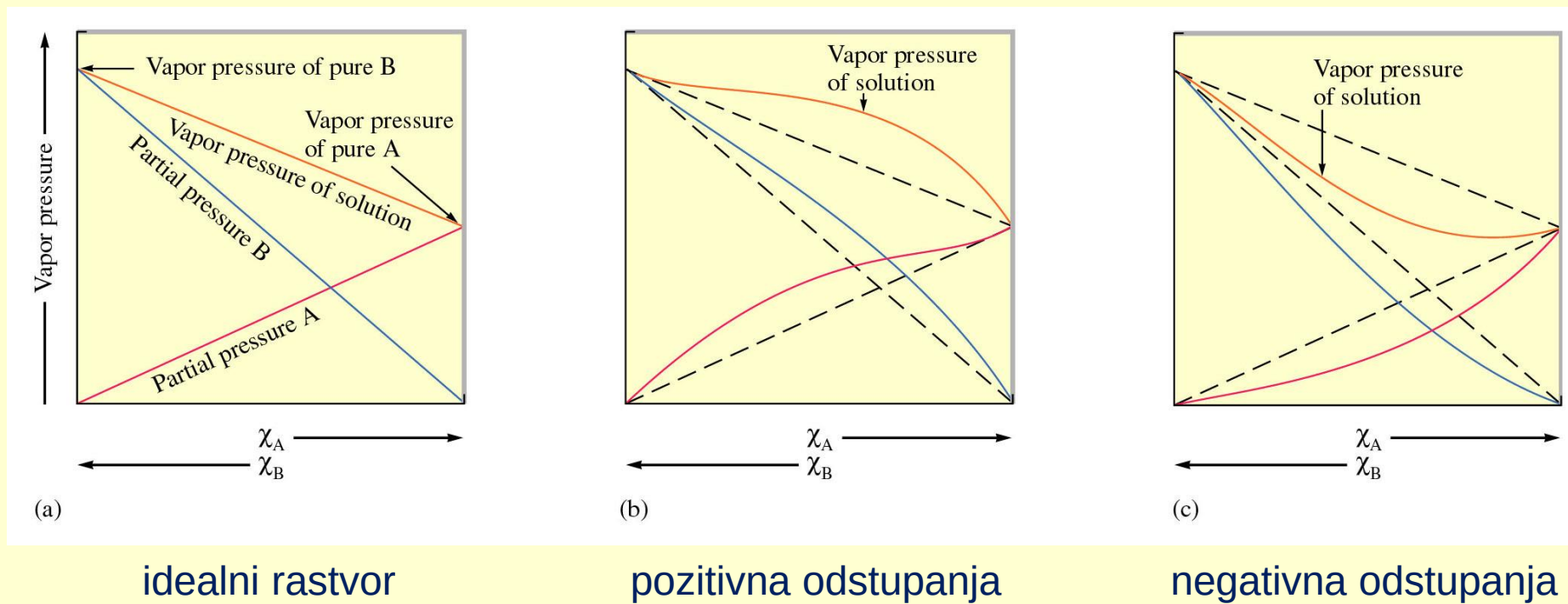


Frakciona destilacija

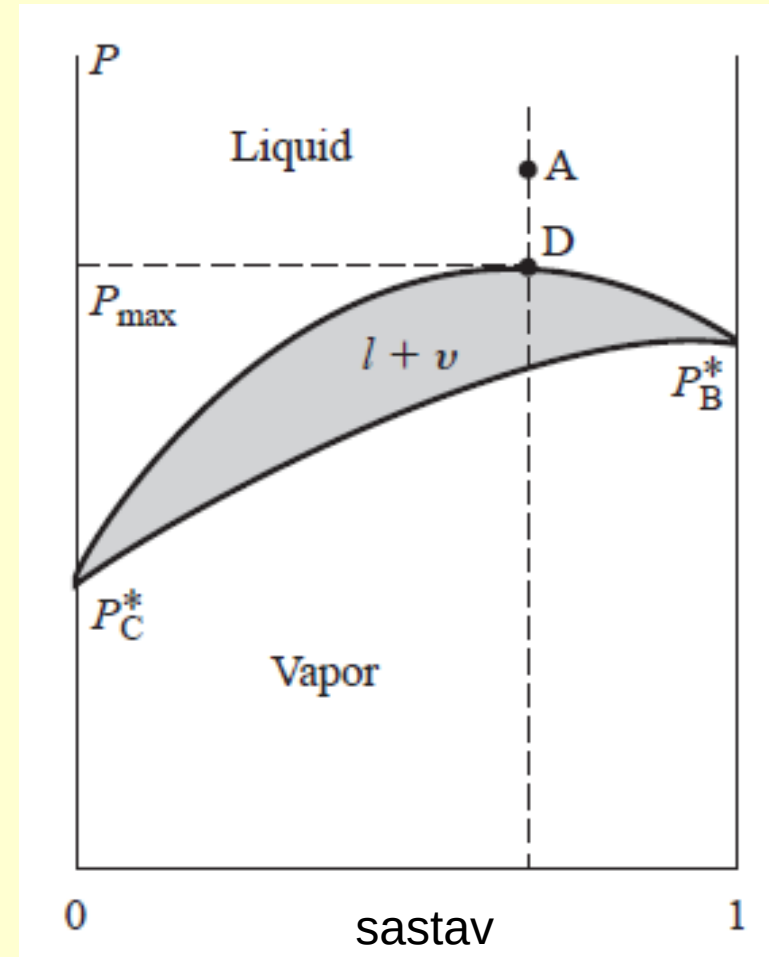
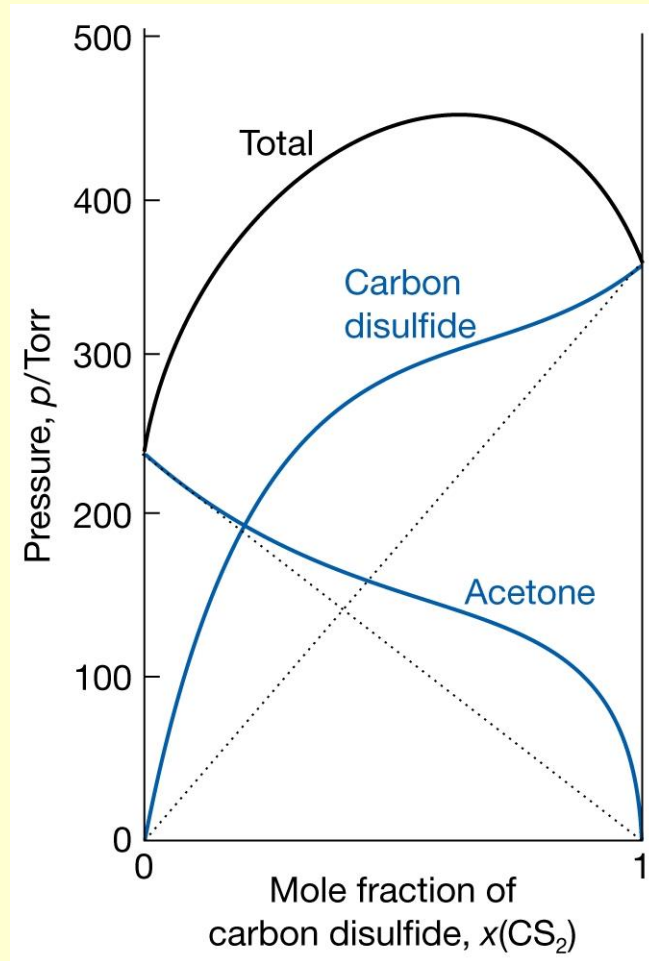


Metodom frakcione destilacije moguće je izvršiti razdvajanje čistih komponenata iz rastvora.

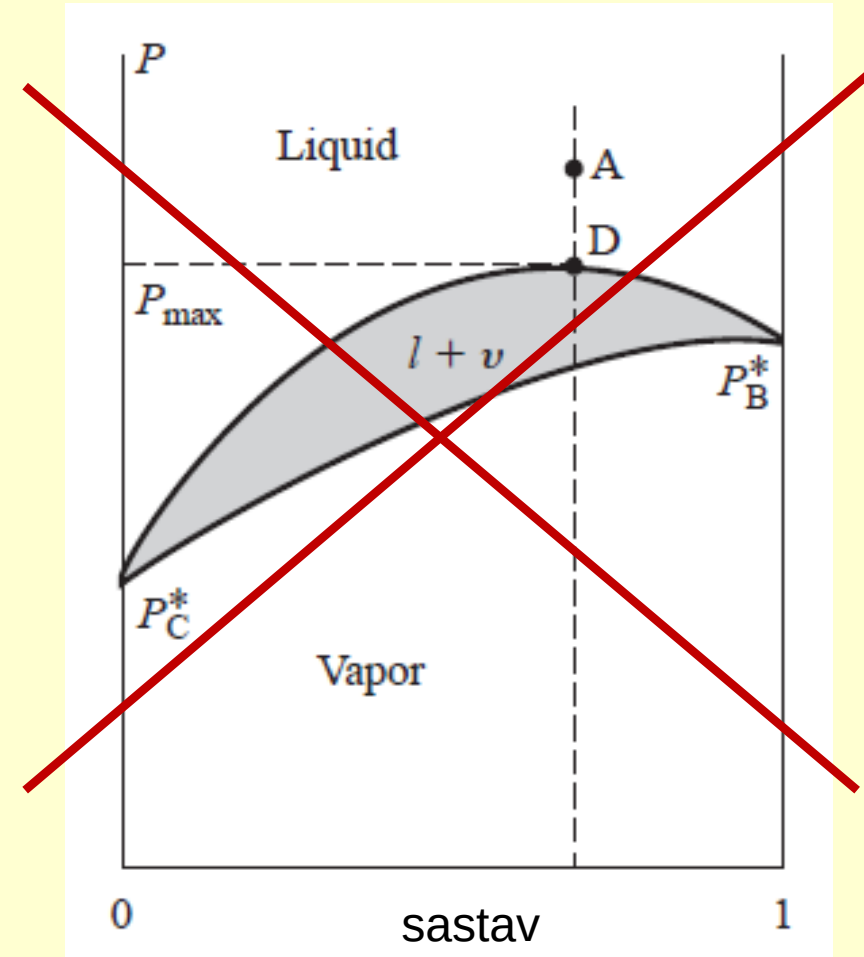
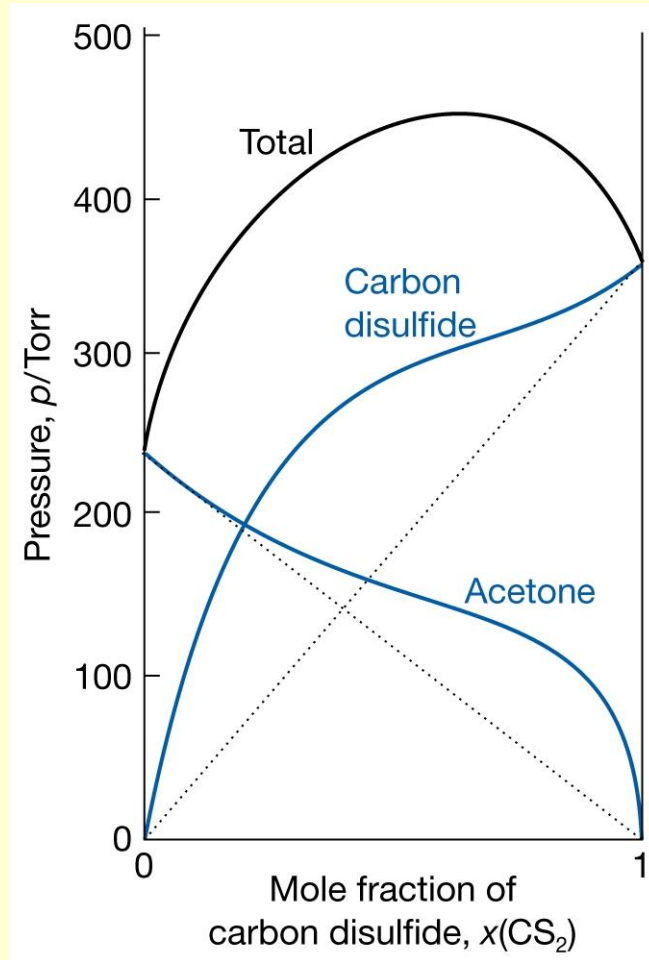
Idealni i neidealni rastvori



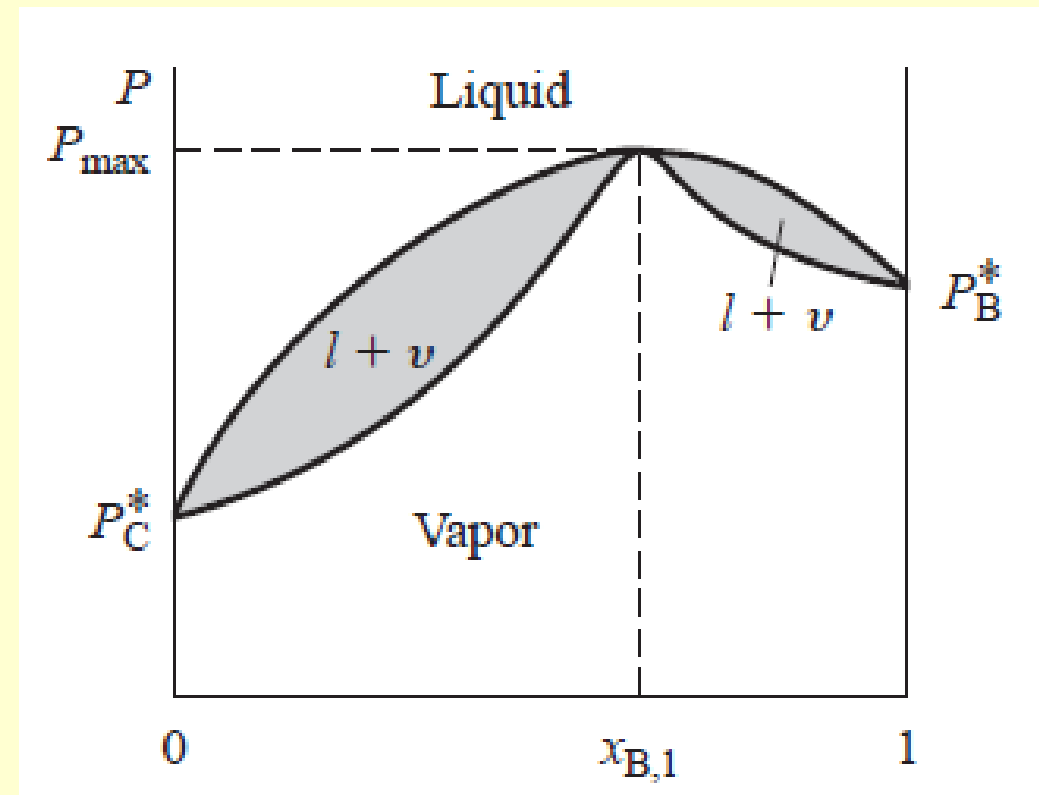
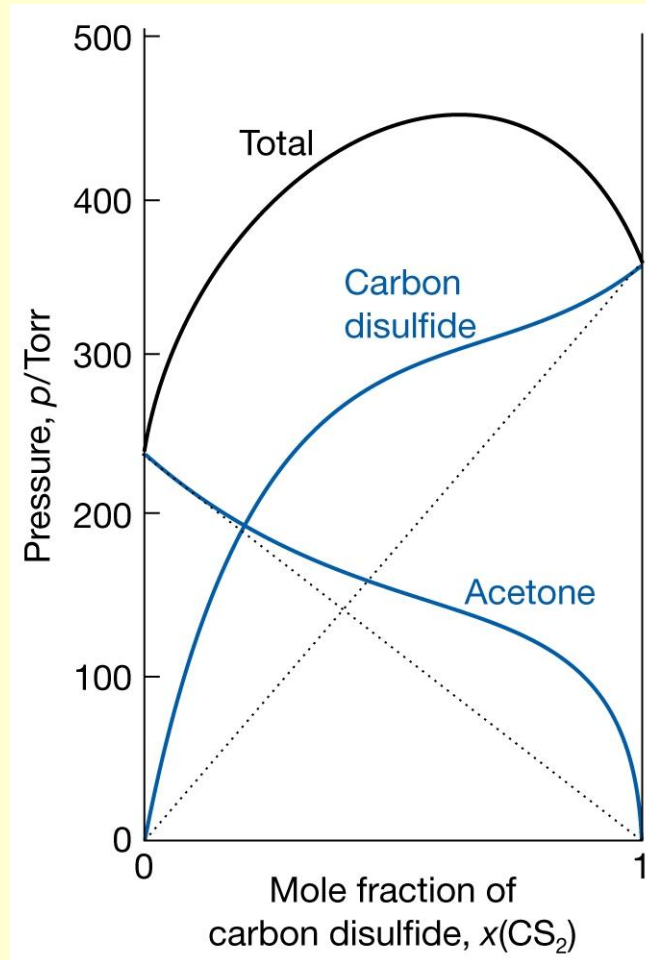
Neidealni rastvor: pozitivna odstupanja



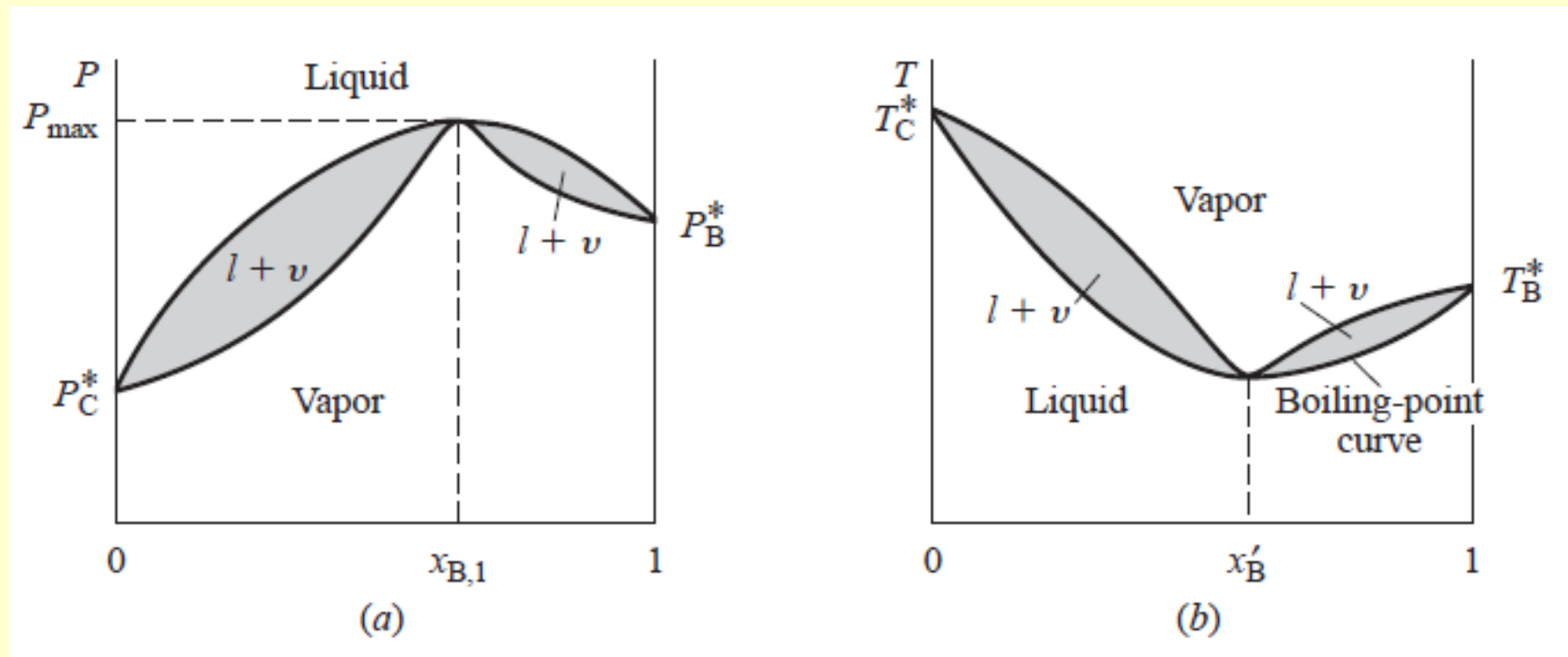
Neidealni rastvor: pozitivna odstupanja



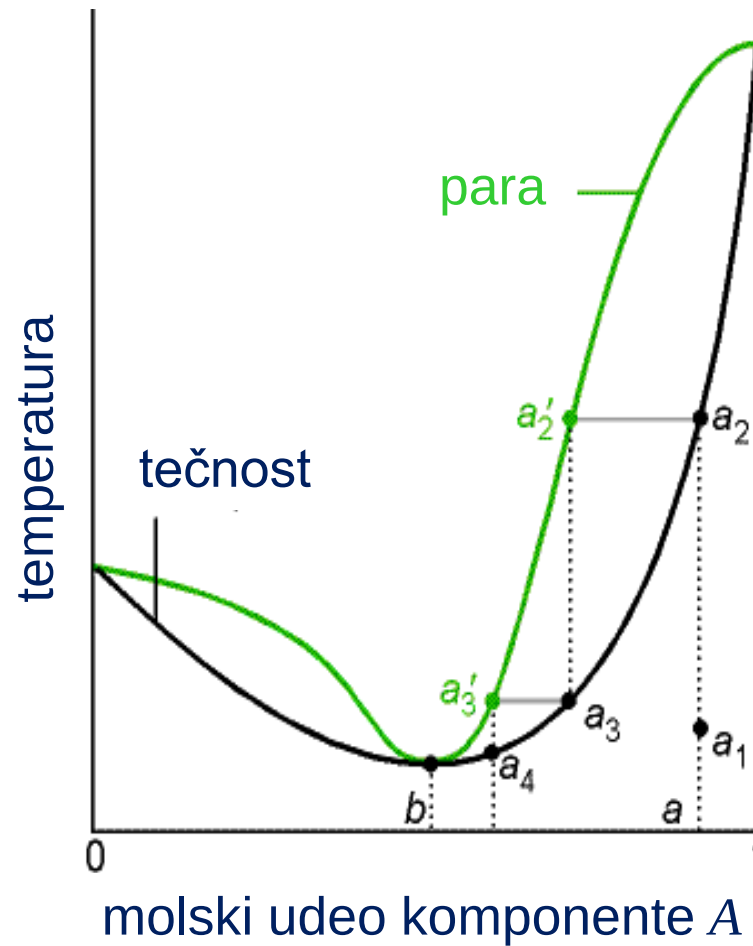
Neidealni rastvor: pozitivna odstupanja



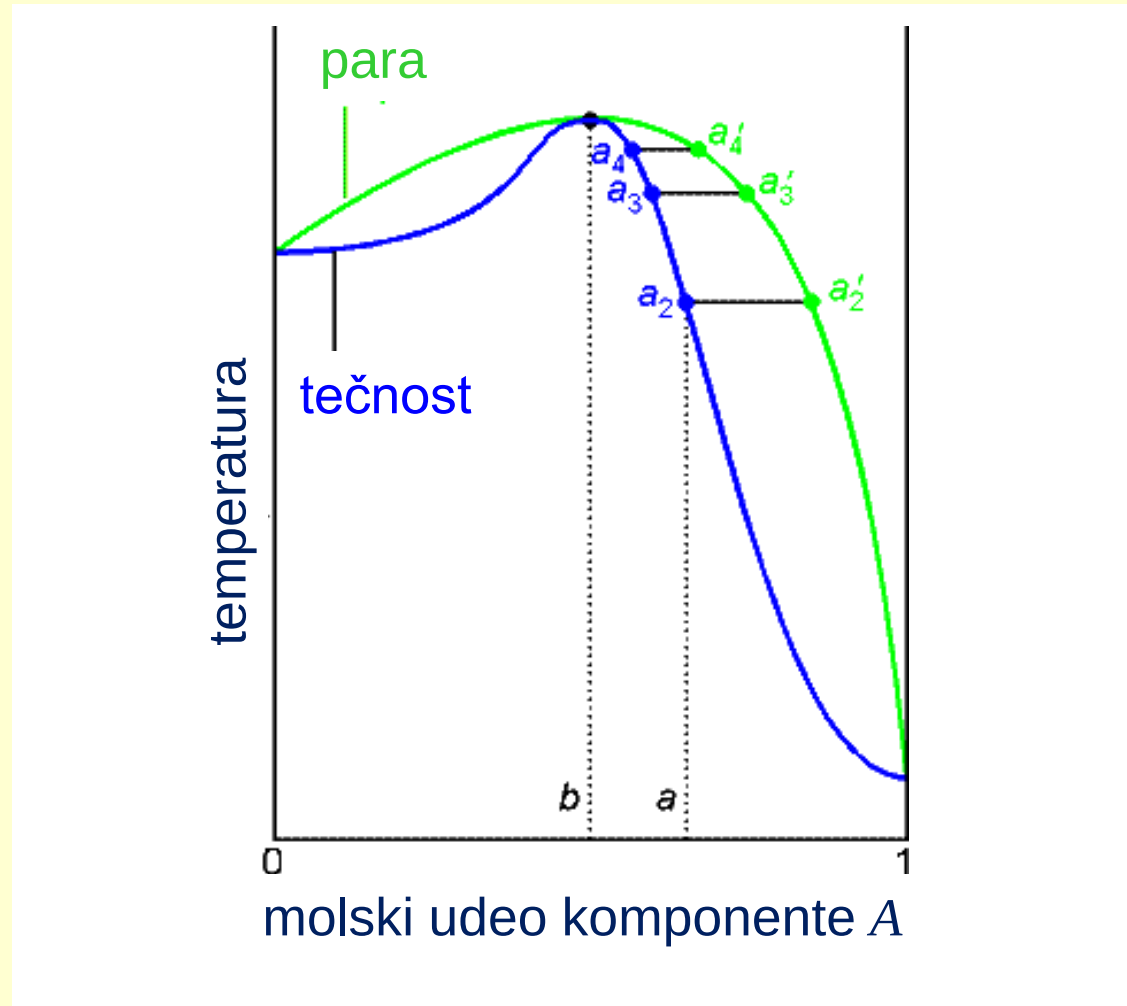
Neidealni rastvor: pozitivna odstupanja



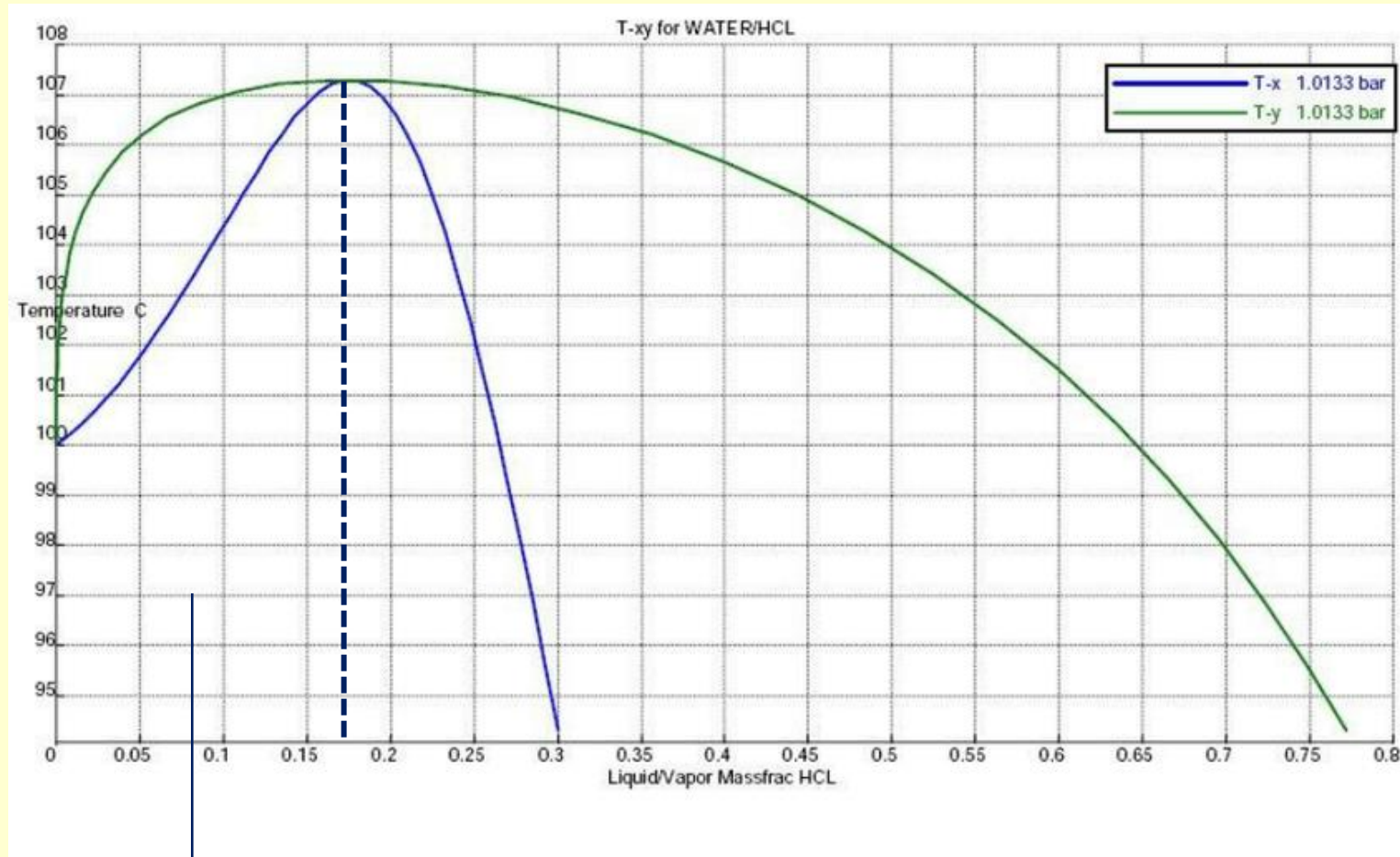
Neidealni rastvor: pozitivna odstupanja



Neidealni rastvor: negativna odstupanja



Primer: H₂O-HCl

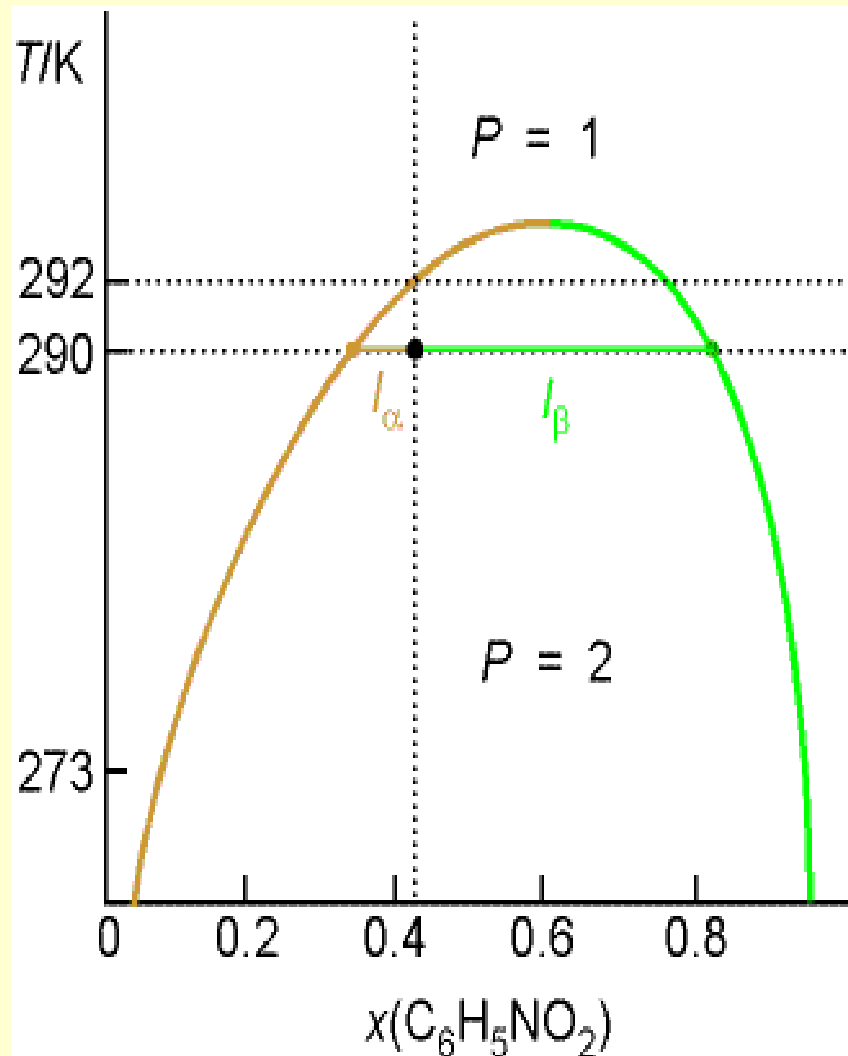


povećanje temperature dovodi do povećanja rastvorljivosti HCl u H₂O

Dvokomponentni sistemi

- potpuno mešljive tečnosti
- delimično mešljive tečnosti
- nemešljive tečnosti

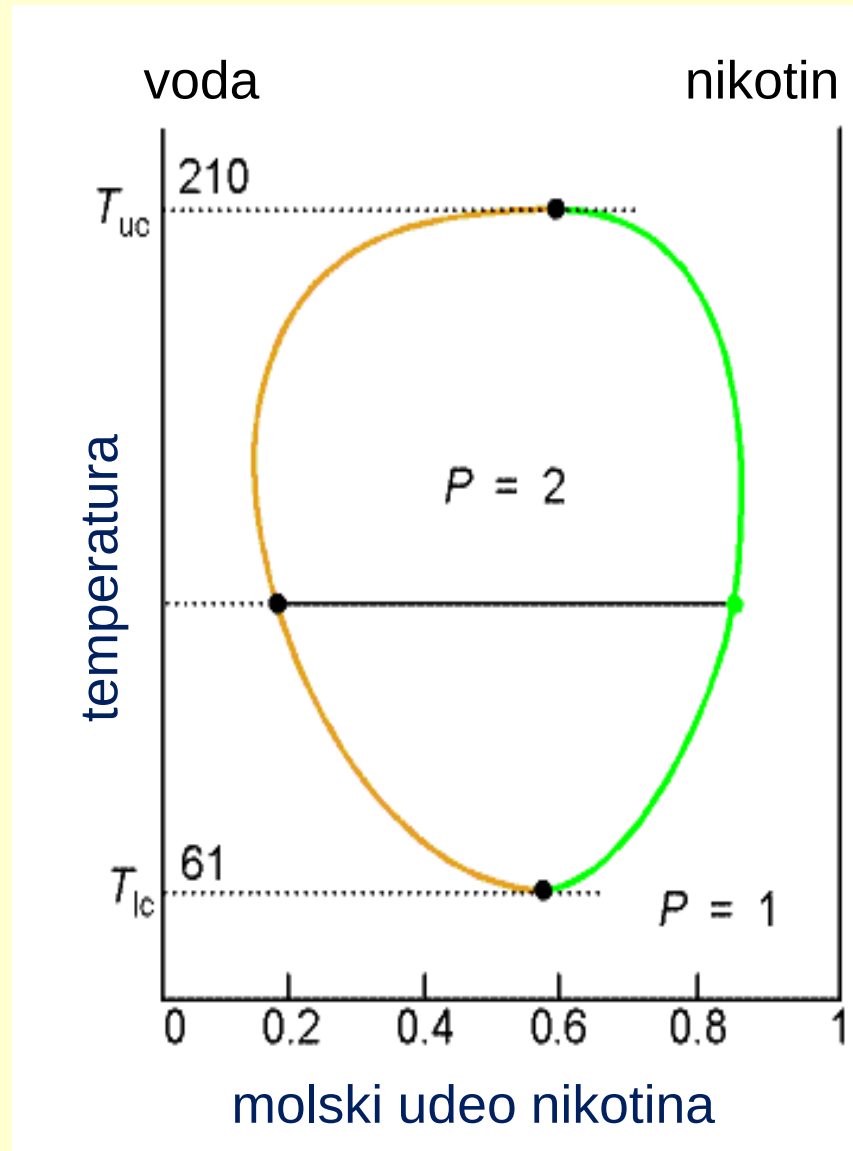
Delimično mešljive tečnosti



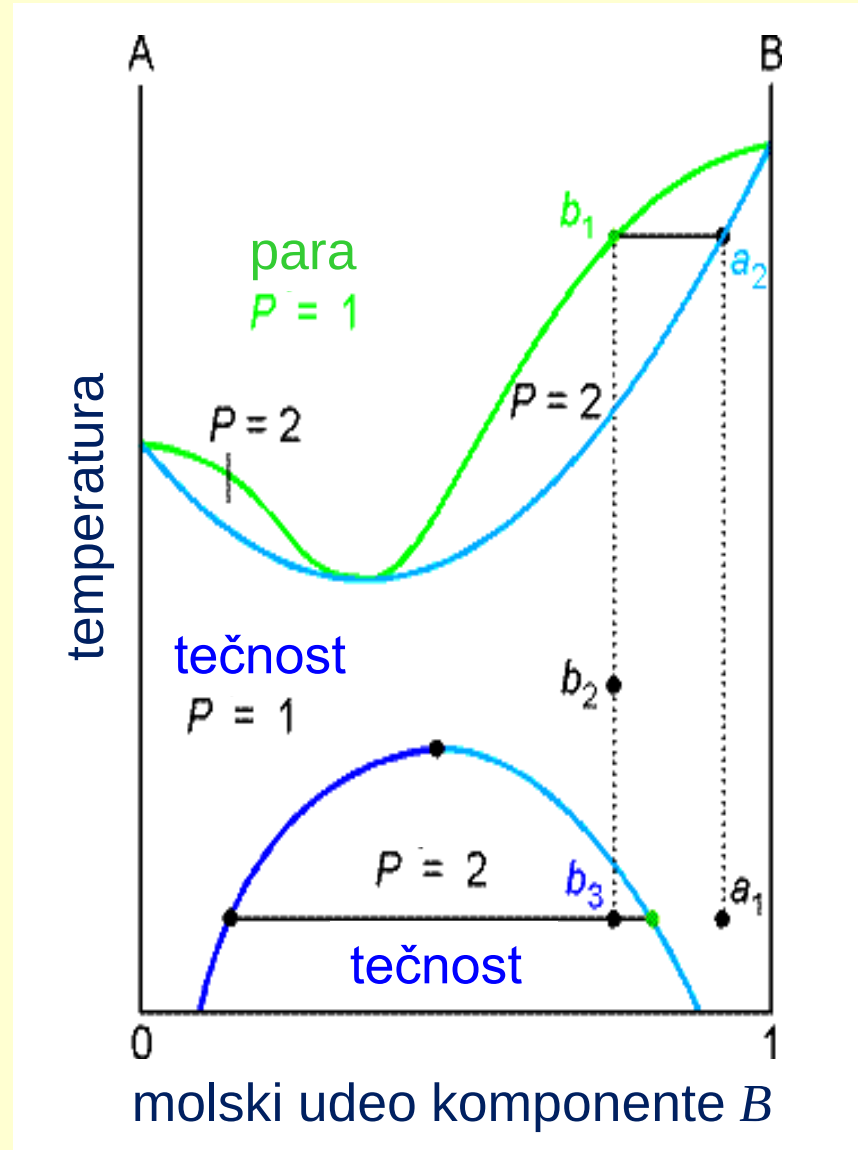
$$\frac{n_\alpha}{n_\beta} = \frac{x_\beta^A - x^A}{x^A - x_\alpha^A} = \frac{l_\beta}{l_\alpha}$$

heksan i nitrobenzen

Kritične temperature rastvora

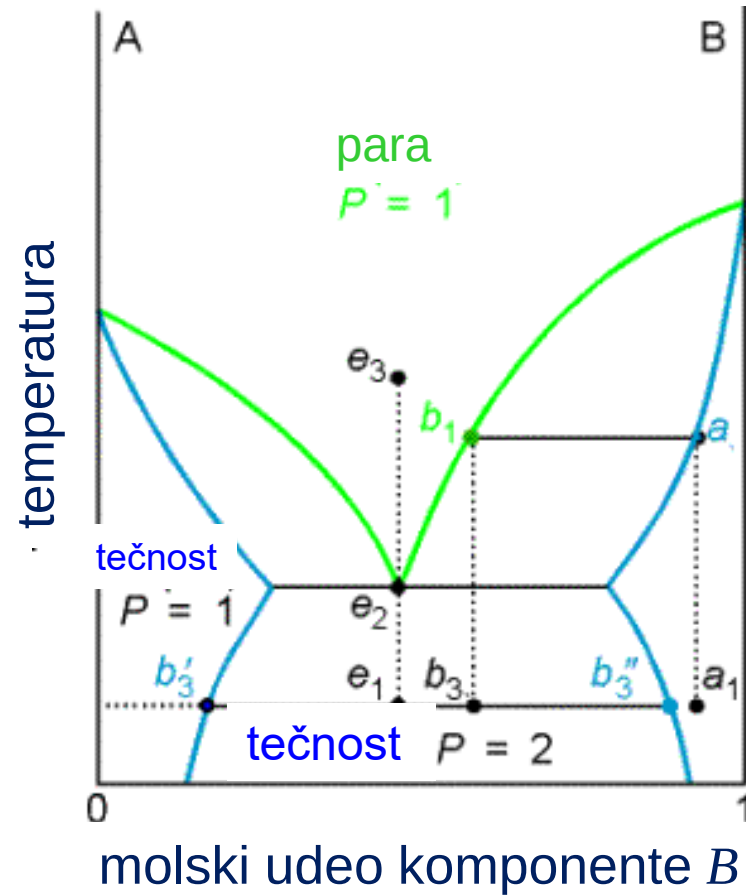


Delimično mešljive tečnosti



Delimično mešljive tečnosti

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



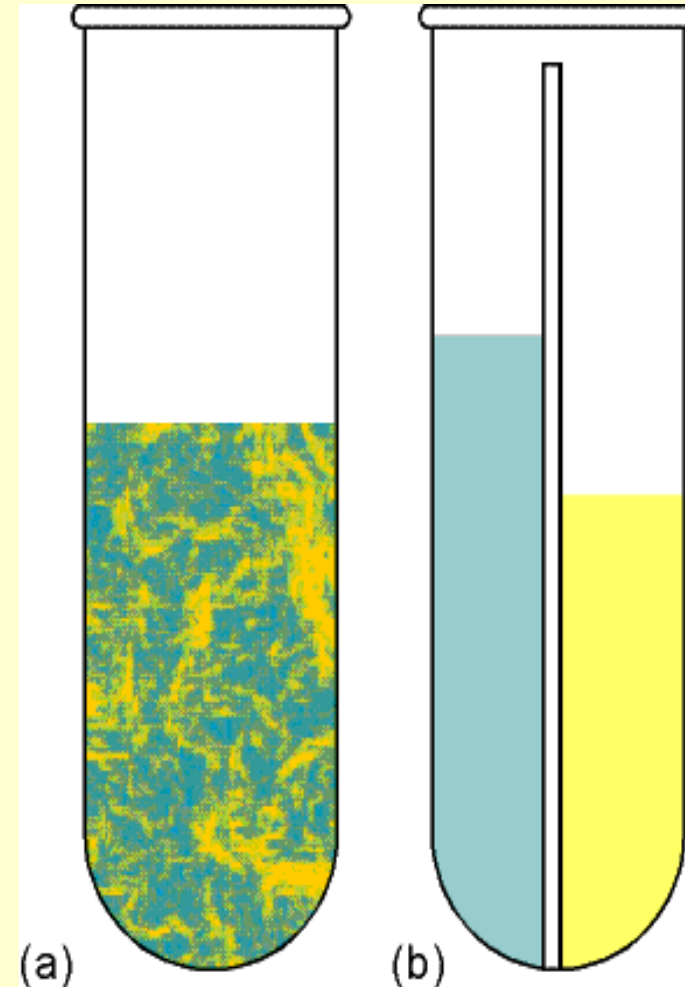
Dvokomponentni sistemi

- potpuno mešljive tečnosti
- delimično mešljive tečnosti
- nemešljive tečnosti

Nemešljive tečnosti

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

Obe tečnosti će ključati kada je ukupni
pritisak $p = \text{atmosferski pritisak}$.



Zakon raspodele

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

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

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

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

Razblaženi rastvor

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

Disocijacija

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

Ekstrakcija

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

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

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

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