RAVNOTEŽA FAZA:

POTPUNO MEŠLJIVE, DELIMIČNO MEŠLJIVE I NEMEŠLJIVE TEČNOSTI

Dvokomponentni sistemi

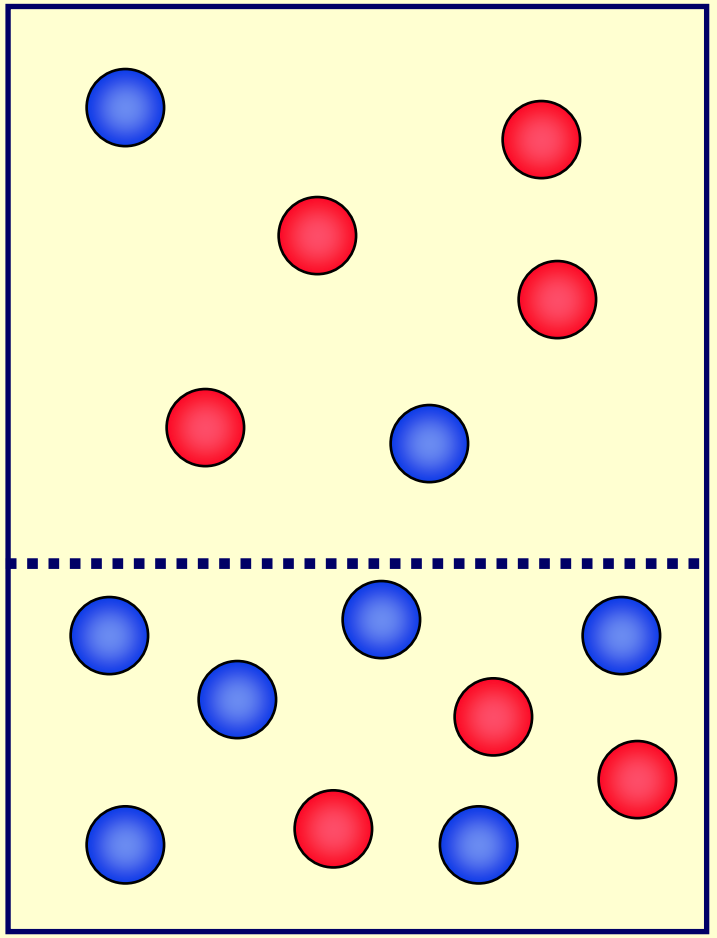
- potpuno mešljive tečnosti
- delimično mešljive tečnosti
- nemešljive tečnosti

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

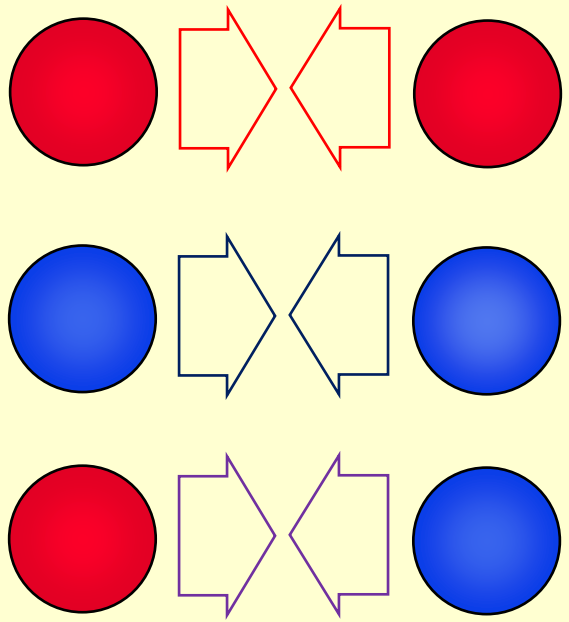
$$F = C - P + 2 = 2 - 2 + 2; \qquad F = 2$$

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

$$\boxed{p_i = x_i p_i^0}$$

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



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

Idealni rastvori (entalpija)

$$P = const \qquad x = const$$

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

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

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

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

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

Idealni rastvori (zapremina)

$$T = const \qquad x = const$$

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

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

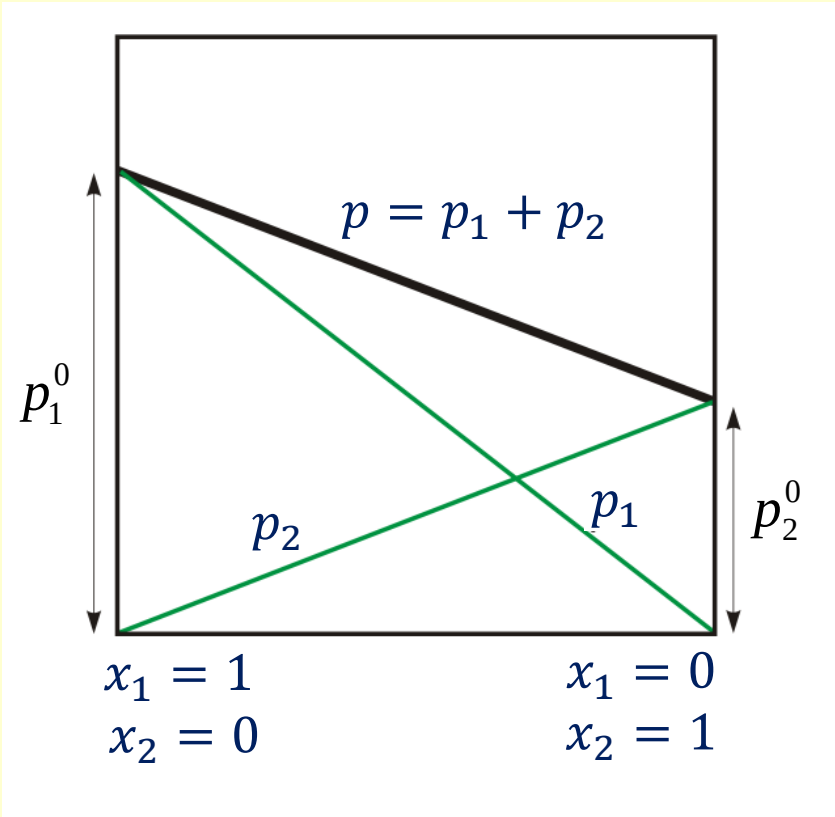
$$\bar{V}_i^t dP = \bar{V}_i^g dp_i \approx \frac{RT}{p_i} dp_i$$

$$RTd\ln p_i = \bar{V}_i^t dP \qquad RTd\ln p_i^0 = V_i^t dP$$

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

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

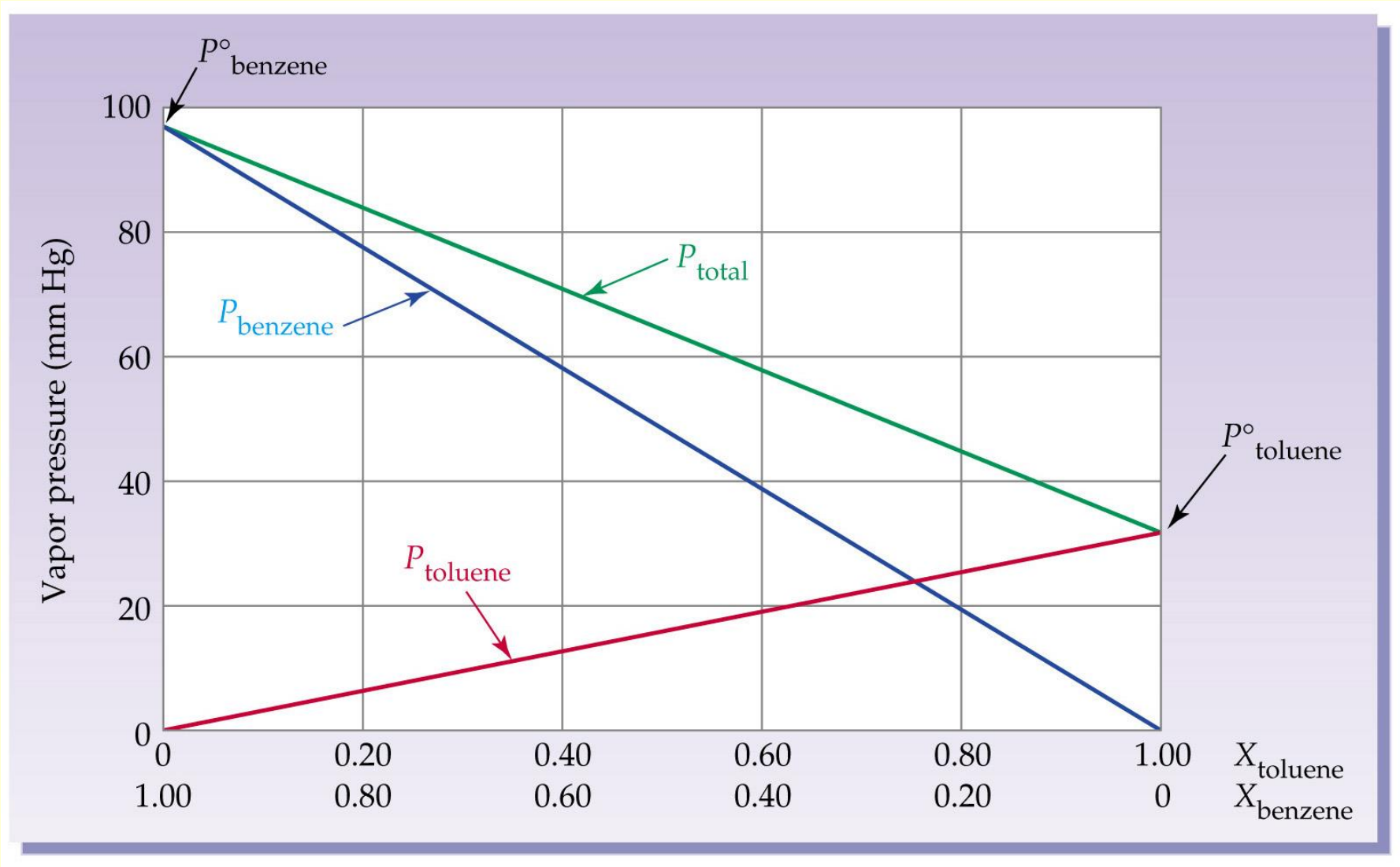
Zavisnost napona pare od sastava tečnosti



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

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

Benzen i toluen



Sastavi tečnosti i pare se razlikuju

$p_b^0 = 12{,}3\ kPa$ $\qquad$ $p_t^0 = 5{,}1\ kPa$

$x_b = x_t = 0{,}5$

para iznad tečnosti koja ključa

$x_b' = 0{,}71$ $\qquad$ $x_t' = 0{,}29$

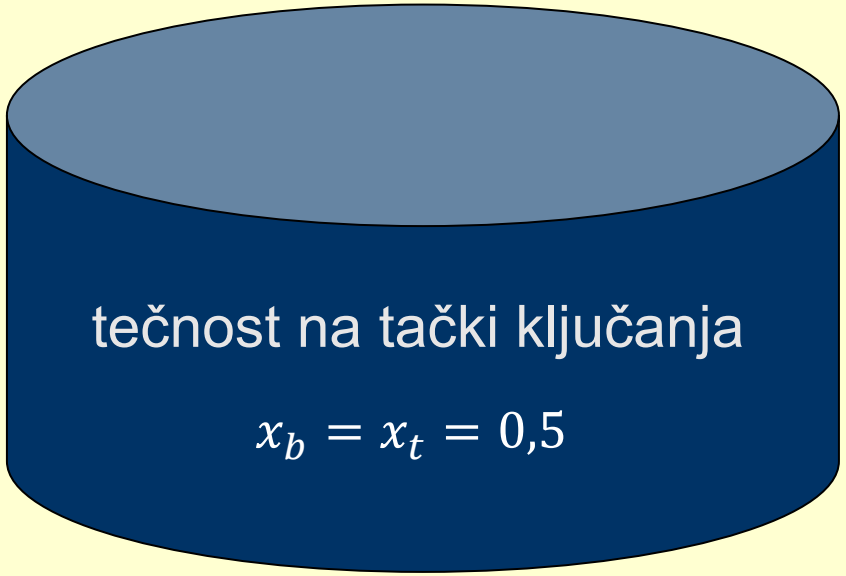
$p_b = x_b \cdot p_b^0 = 0{,}5 \cdot 12{,}3kPa = 6{,}15kPa$

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

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

$$x_b' = \frac{6{,}15kPa}{8{,}7kPa} = 0{,}71$$

$$x_t' = 1 - 0{,}71 = 0{,}29$$



Zavisnost napona pare od sastava pare

Pretpostavka: para se može posmatrati kao smeša idealnih gasova.

$$x_1' = \frac{n_1'}{n_1' + n_2'}$$

$$p_1 V = n_1' RT \quad \rightarrow \quad n_1' = \frac{p_1 V}{RT}$$

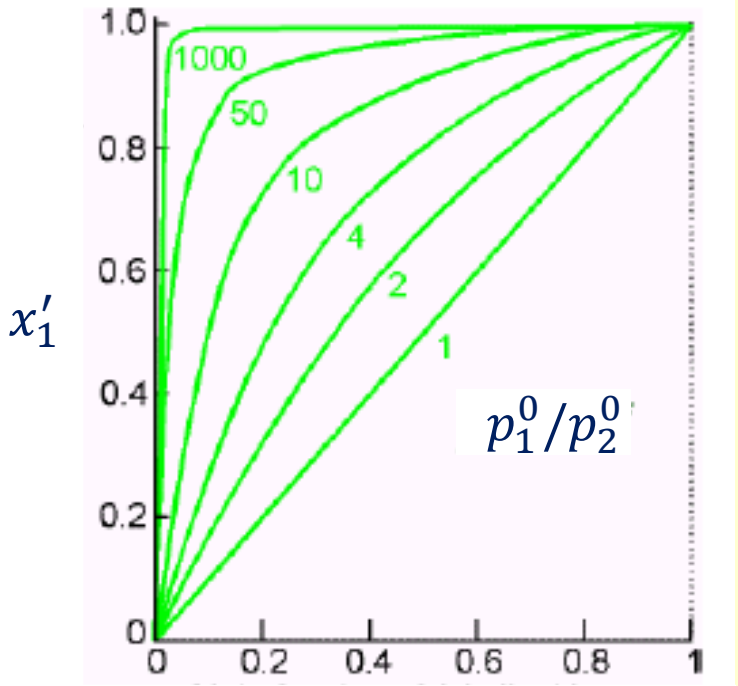
$$x_1' = \frac{p_1}{p_1 + p_2} = \frac{x_1 p_1^0}{x_1 p_1^0 + x_2 p_2^0}$$

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

Zavisnost napona pare od sastava pare

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

$$x_2' = 1 - x_1'$$

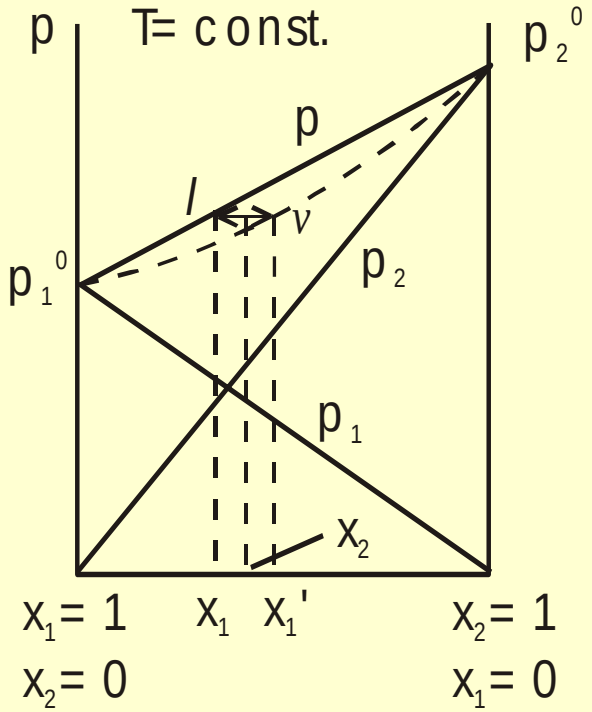


Za $p_1^0 \geq p_2^0$ je $x_1' \geq x_1$ (para je bogatija isparljivijom komponentom).

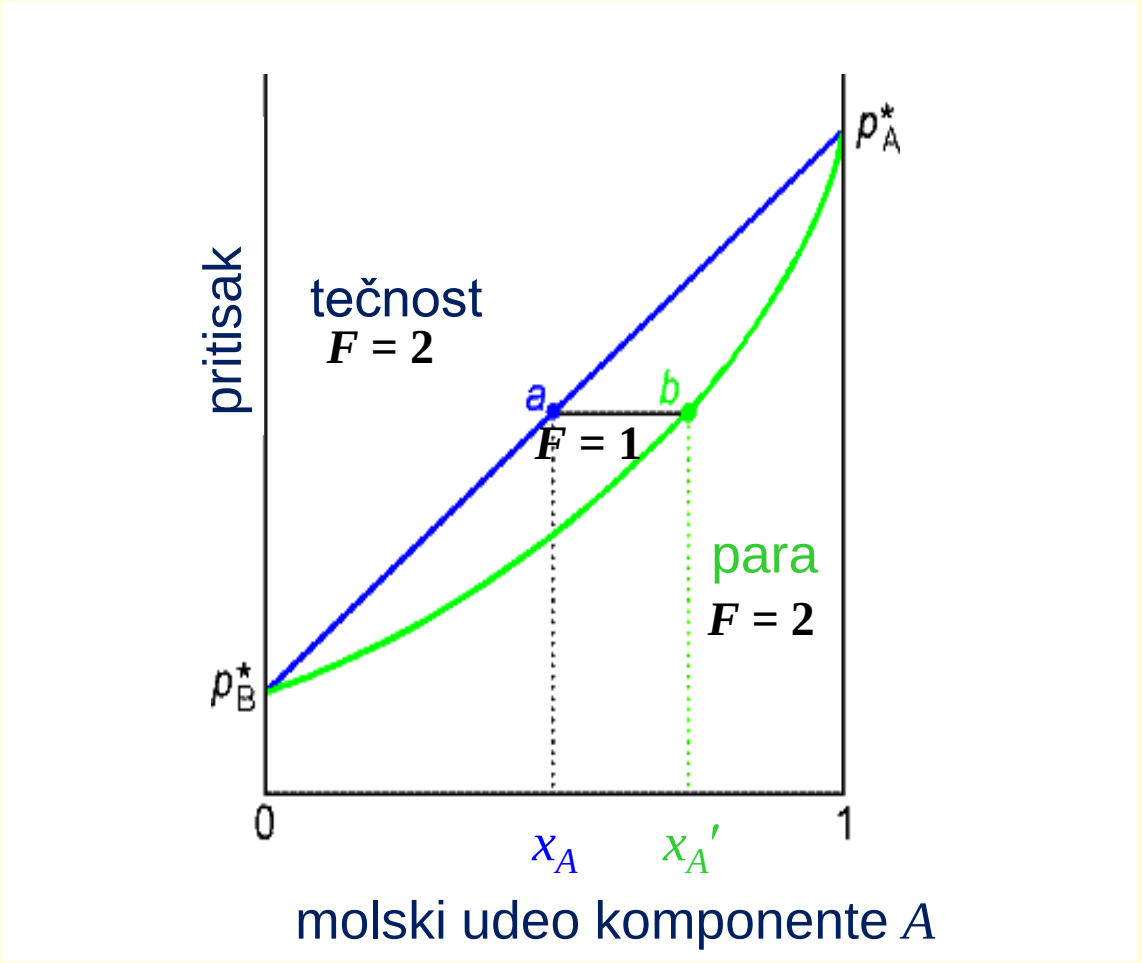
Što se komponente više razlikuju u isparljivosti, to će se više razlikovati sastav tečne od sastava parne faze.

Zavisnost napona pare od sastava pare

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

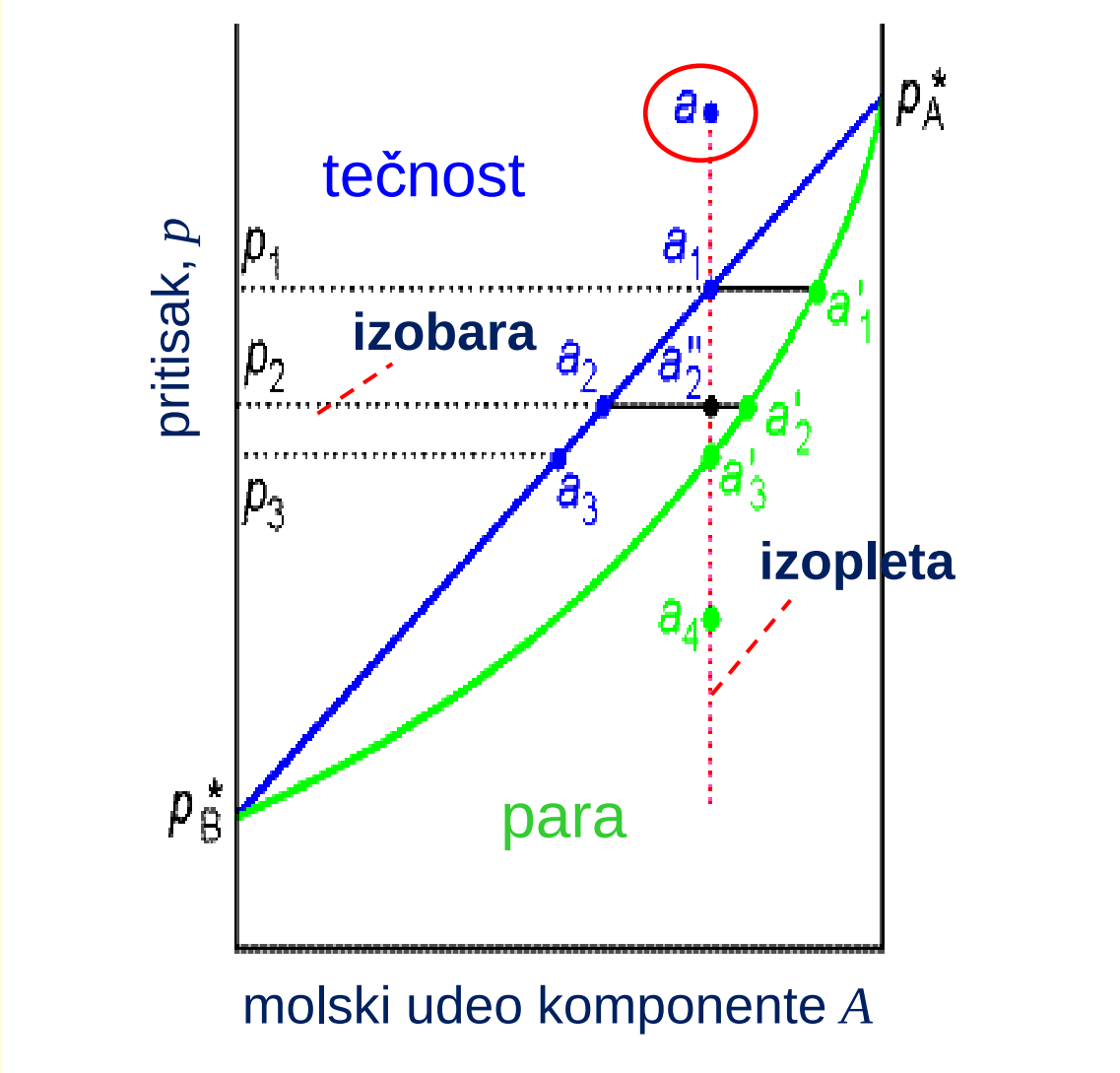


Fazni dijagram idealnog rastvora

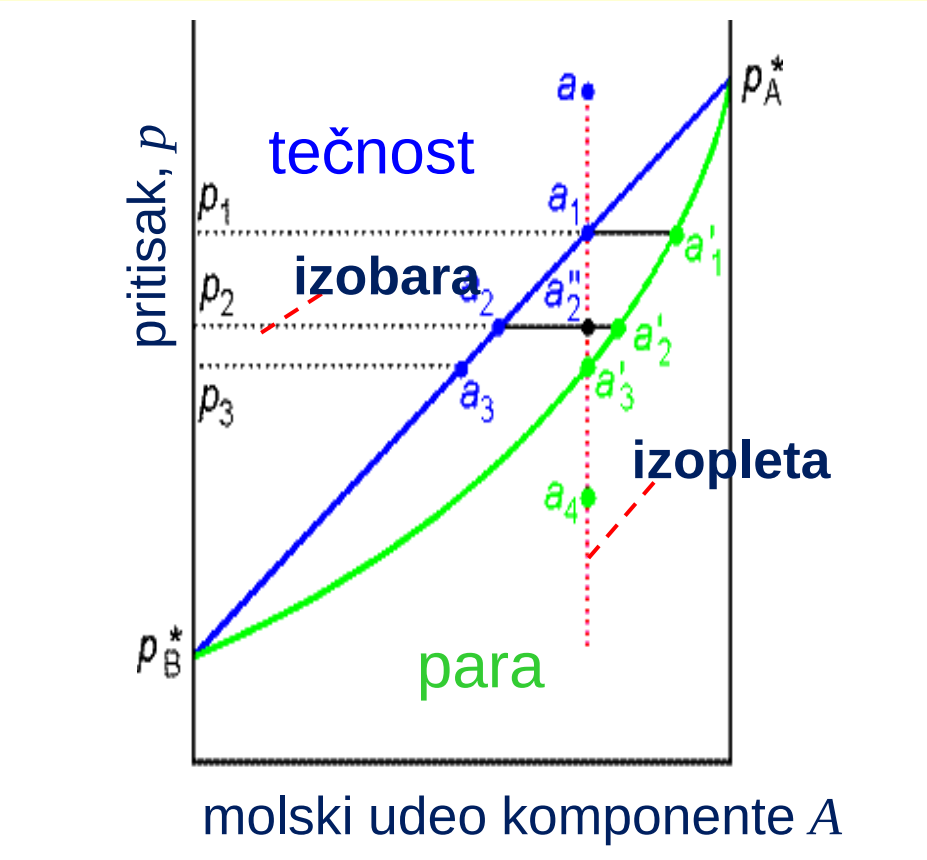


Promene duž izoplete

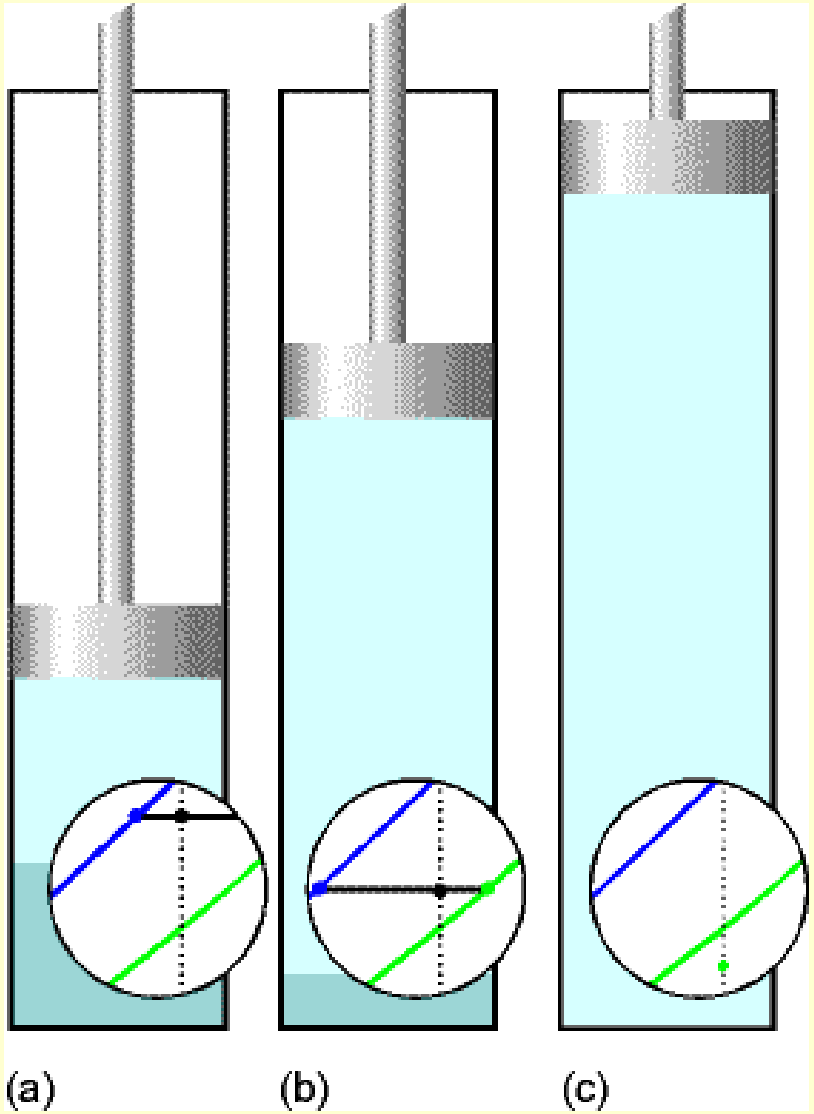
Izopleta – linija konstantnog sastava



Fizička slika procesa

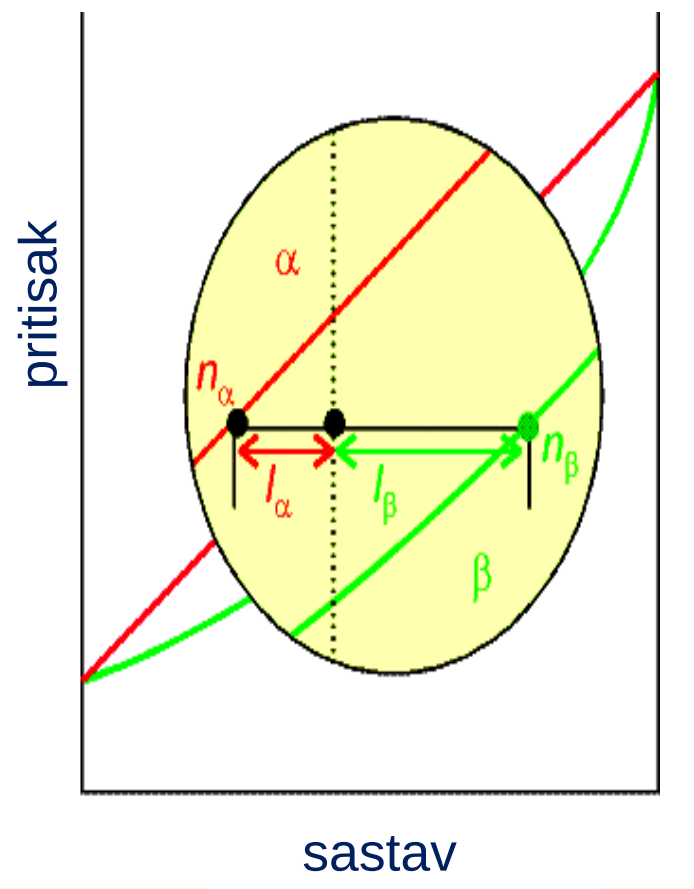


(a) – Nešto pare se pojavilo.
(b) – Samo malo tečnosti je ostalo.
(c) – Samo je para prisutna.



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

$$n = n_\alpha + n_\beta$$

$$x^A = \frac{n^A}{n} \rightarrow n^A = nx^A$$

$$x_\alpha^A = \frac{n_\alpha^A}{n_\alpha} \rightarrow n_\alpha^A = n_\alpha x_\alpha^A$$

$$x_\beta^A = \frac{n_\beta^A}{n_\beta} \rightarrow n_\beta^A = n_\beta x_\beta^A$$

$$n^A = n_\alpha^A + n_\beta^A$$

$$nx^A = n_\alpha x_\alpha^A + n_\beta x_\beta^A$$

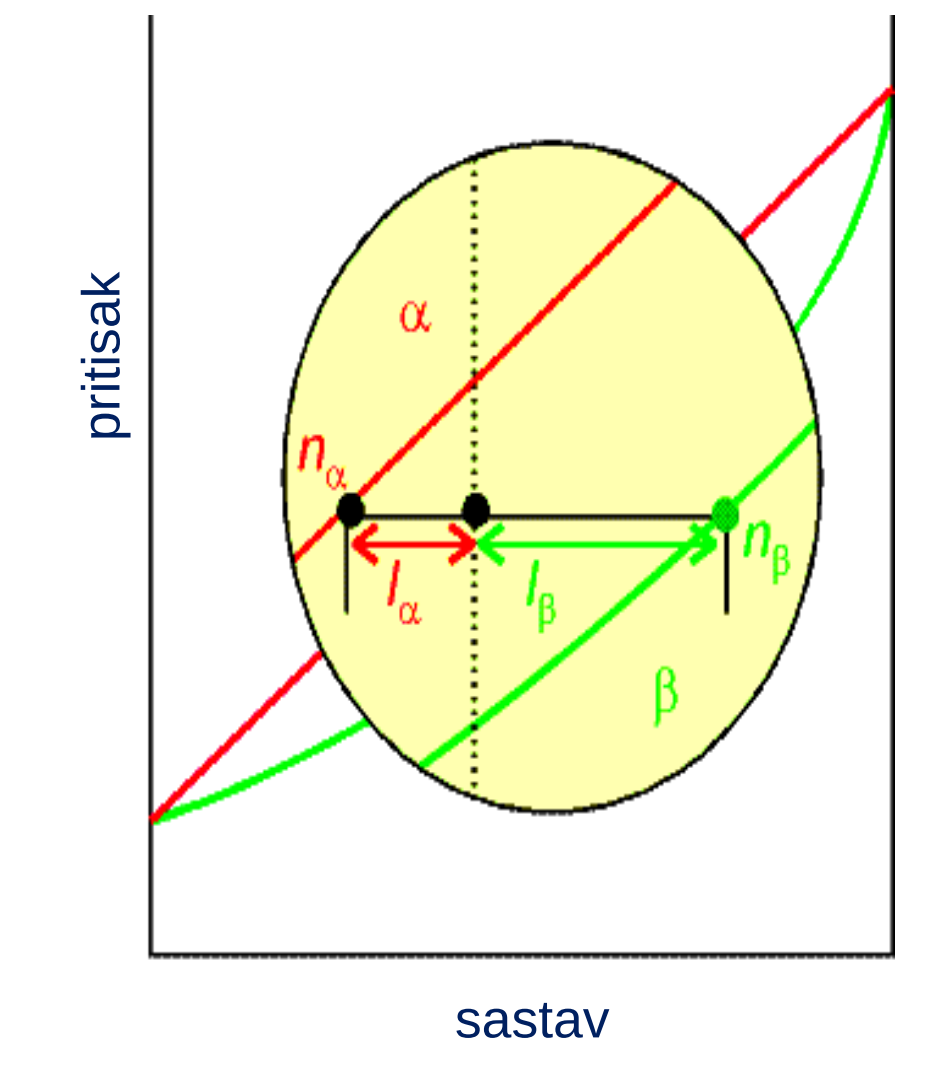
$$nx^A = n_\alpha x^A + n_\beta x^A$$

$$n_\alpha x_\alpha^A + n_\beta x_\beta^A = n_\alpha x^A + n_\beta x^A$$

$$n_\alpha (x^A - x_\alpha^A) = n_\beta (x_\beta^A - x^A)$$

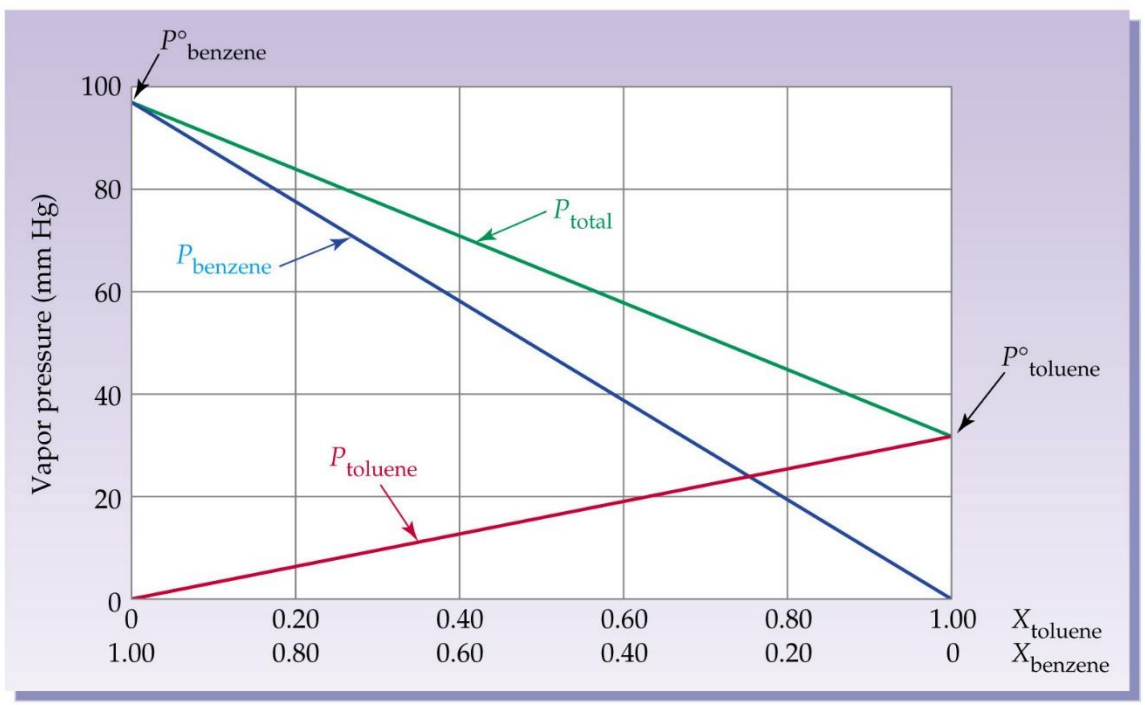
$$\boxed{\frac{n_\alpha}{n_\beta} = \frac{x_\beta^A - x^A}{x^A - x_\alpha^A}}$$

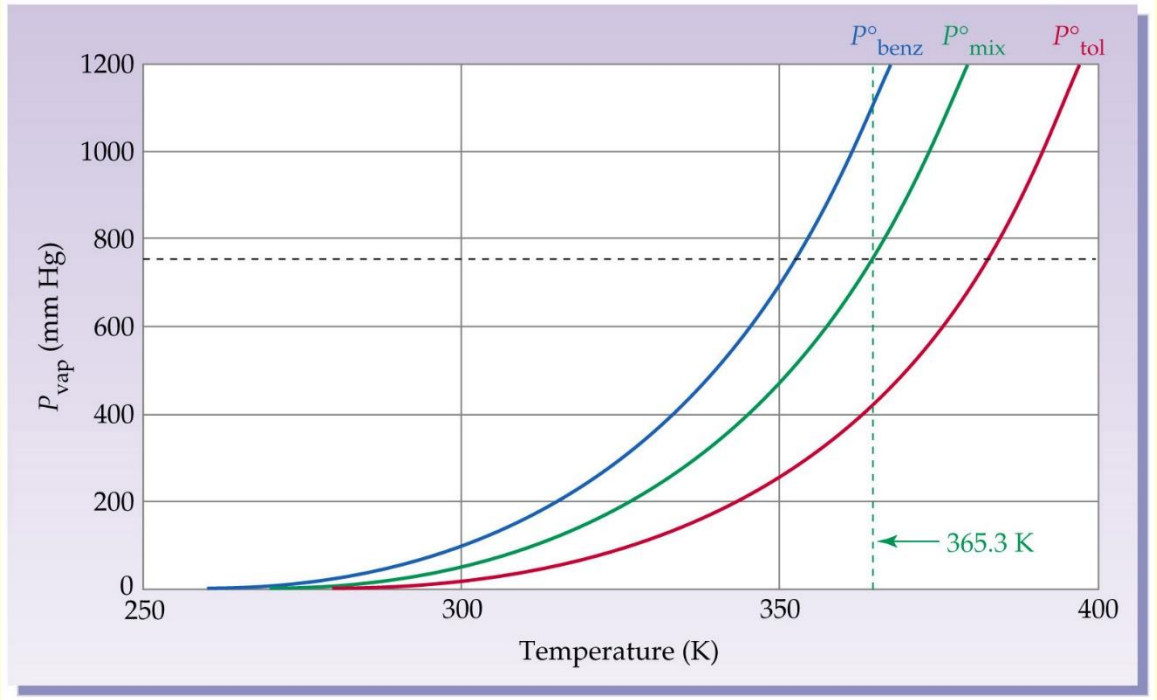
Spojna linija i pravilo poluge



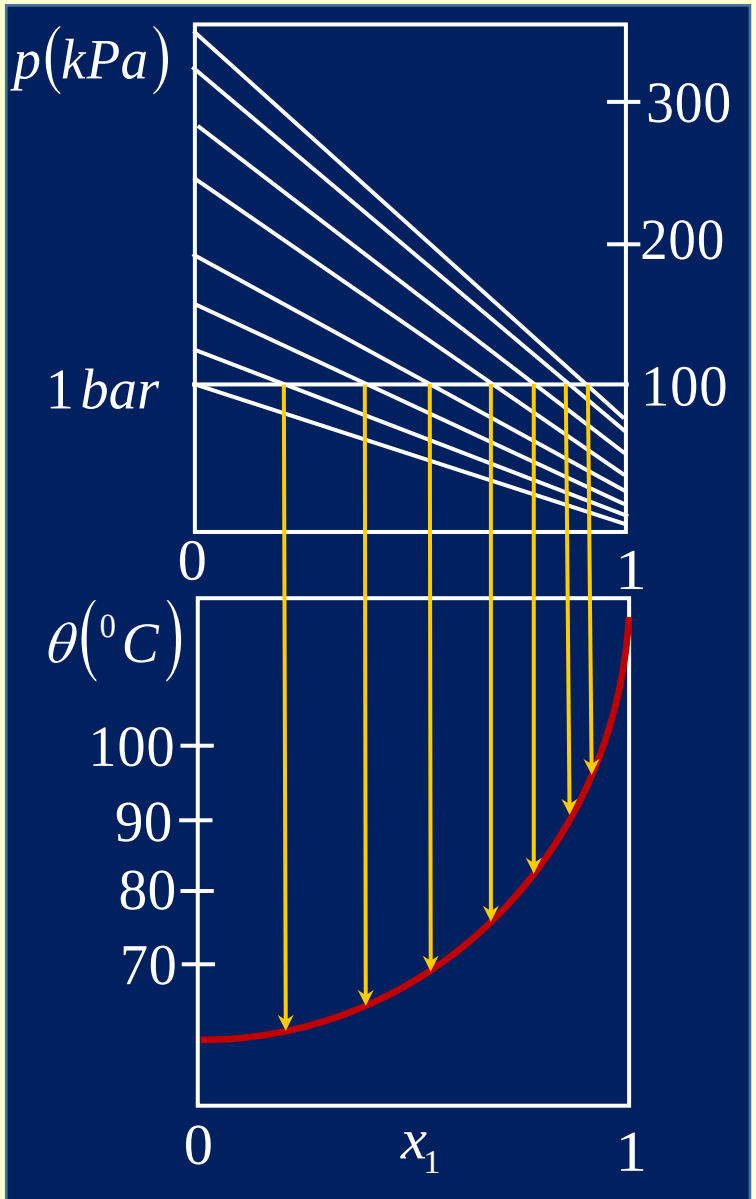
$$\frac{n_\alpha}{n_\beta} = \frac{x_\beta^A - x^A}{x^A - x_\alpha^A} = \frac{l_\beta}{l_\alpha}$$

Benzen i toluen



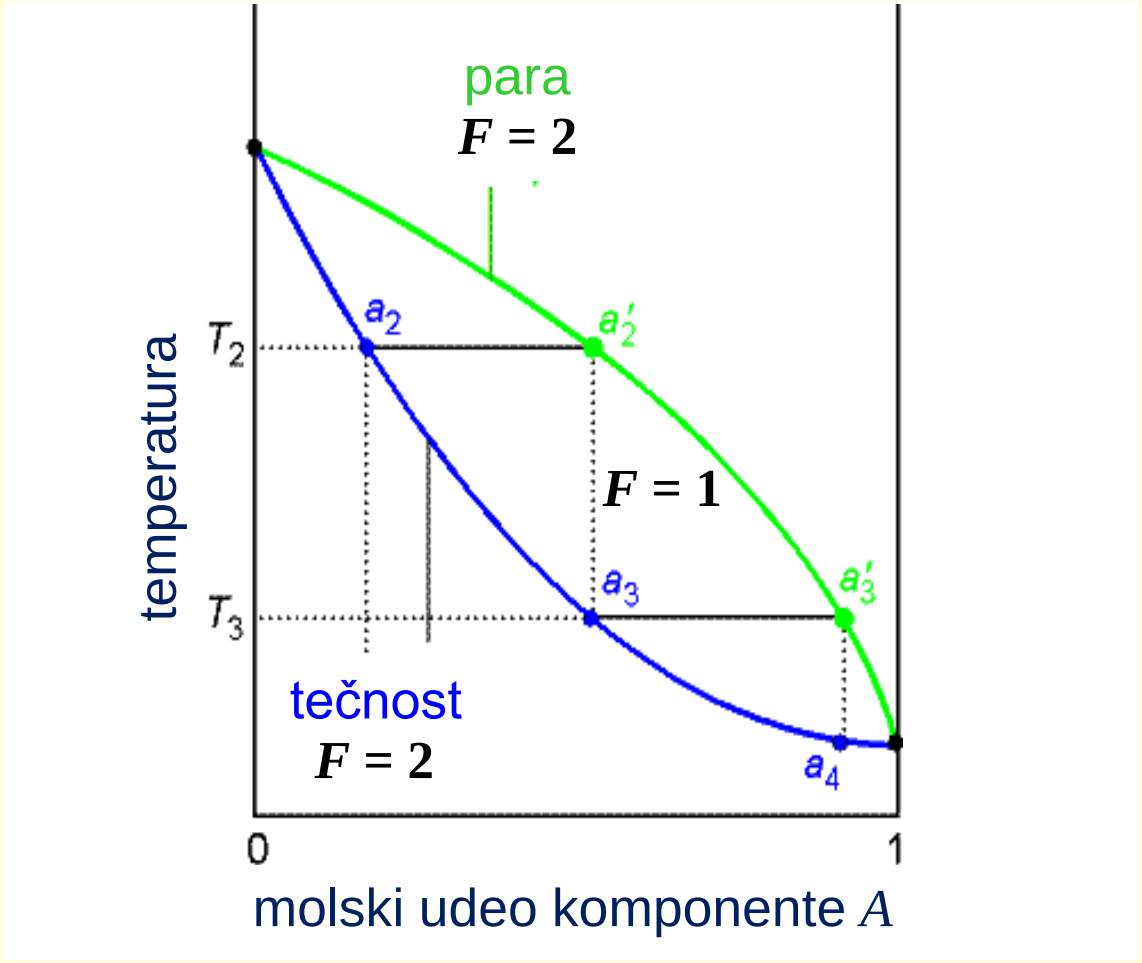


Tačka ključanja idealnih rastvora

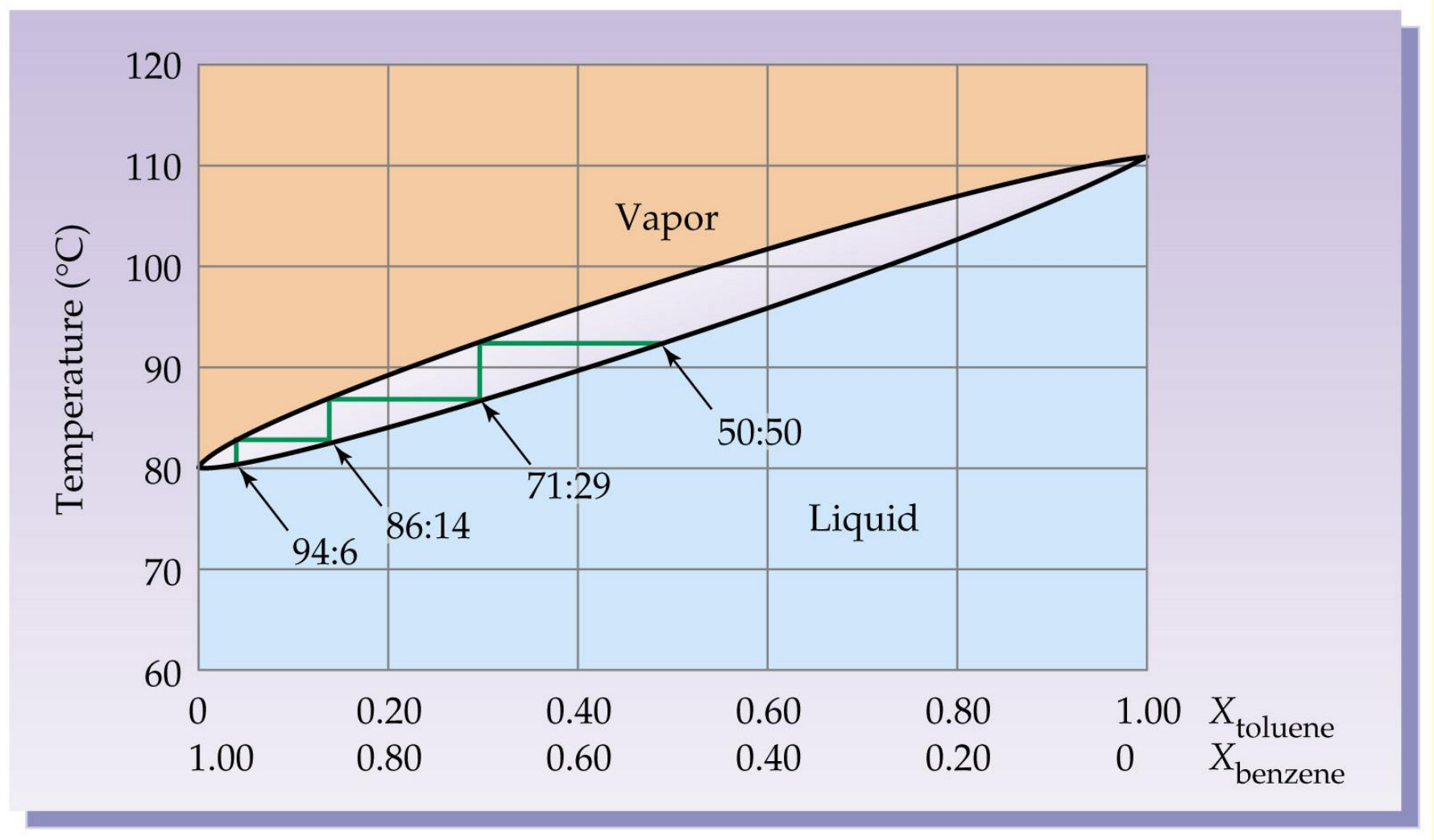


Zavisnost tačke ključanja od sastava

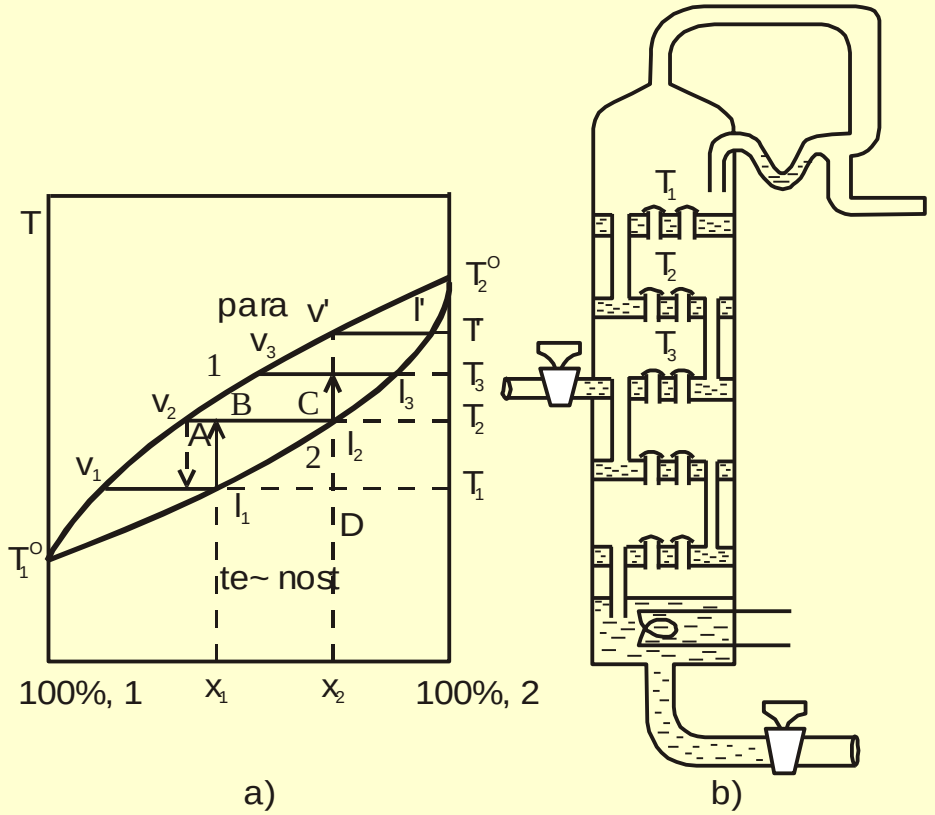
$$p = const$$



Rastvor benzena i toluena

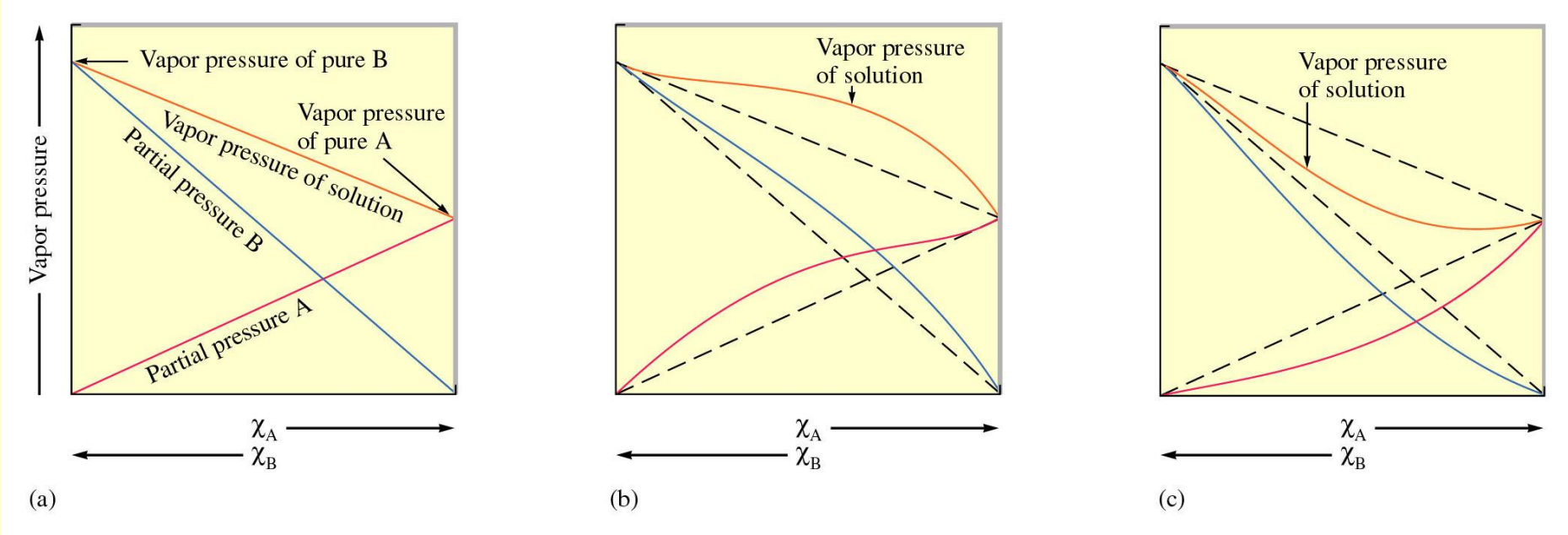


Frakciona destilacija



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

Idealini i neidealni rastvori

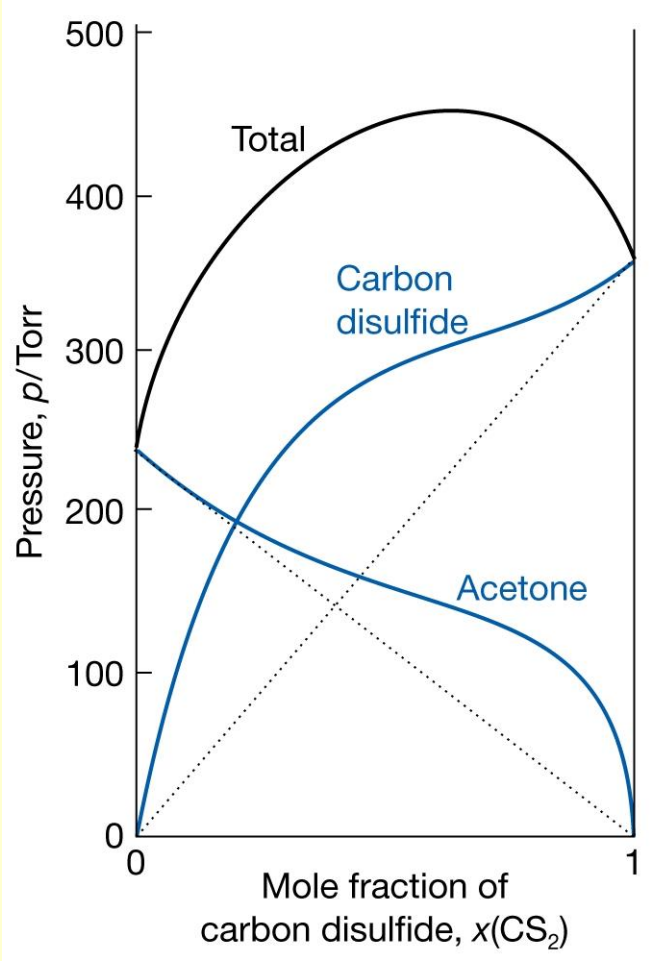


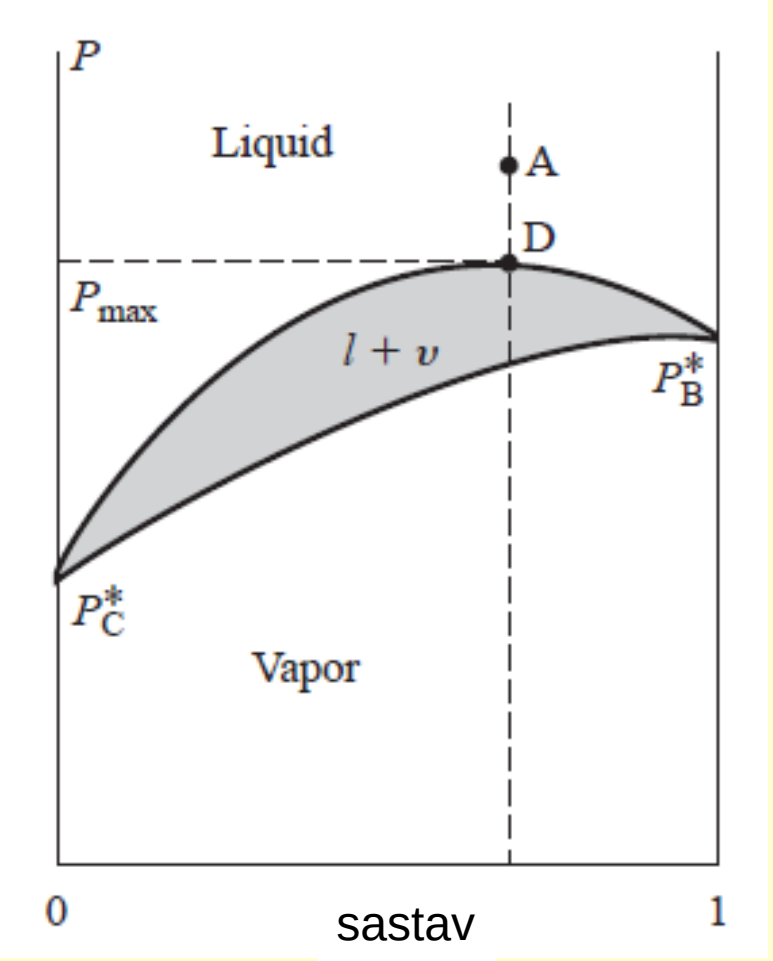
idealni rastvor

pozitivna odstupanja

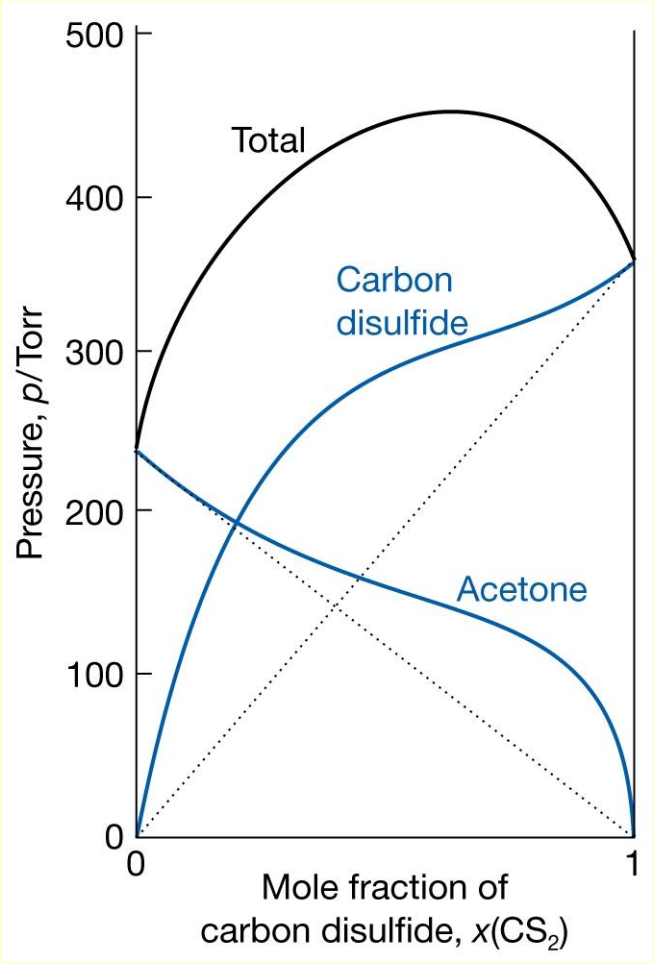
negativna odstupanja

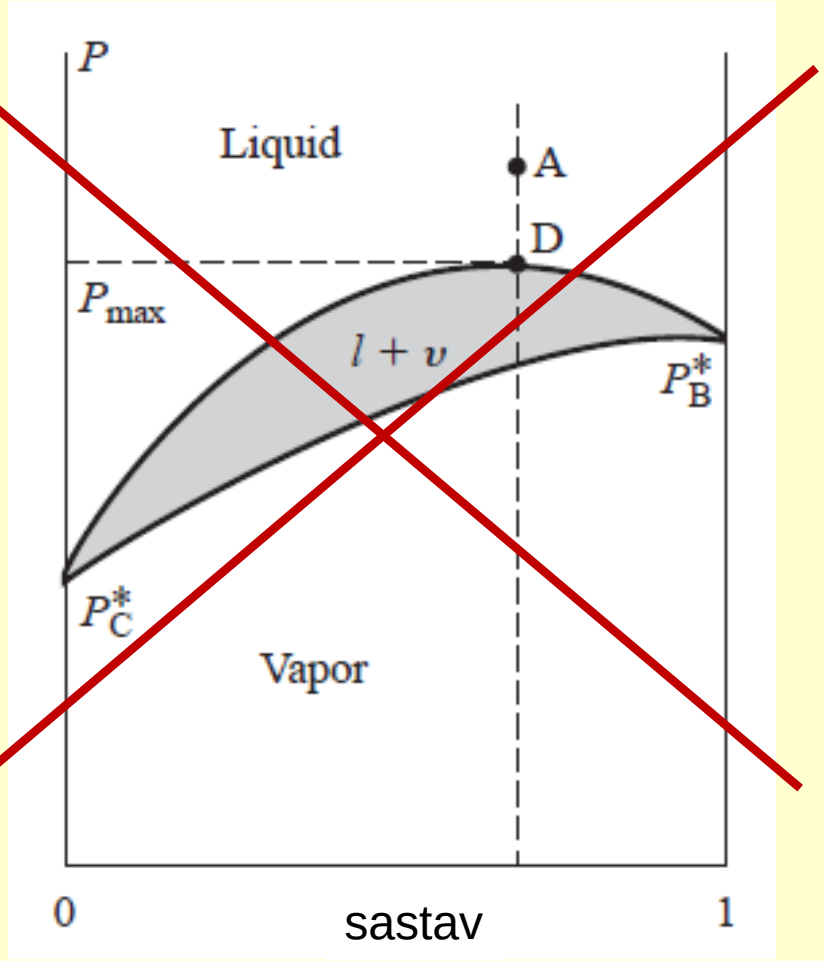
Neidealni rastvor: pozitivna odstupanja



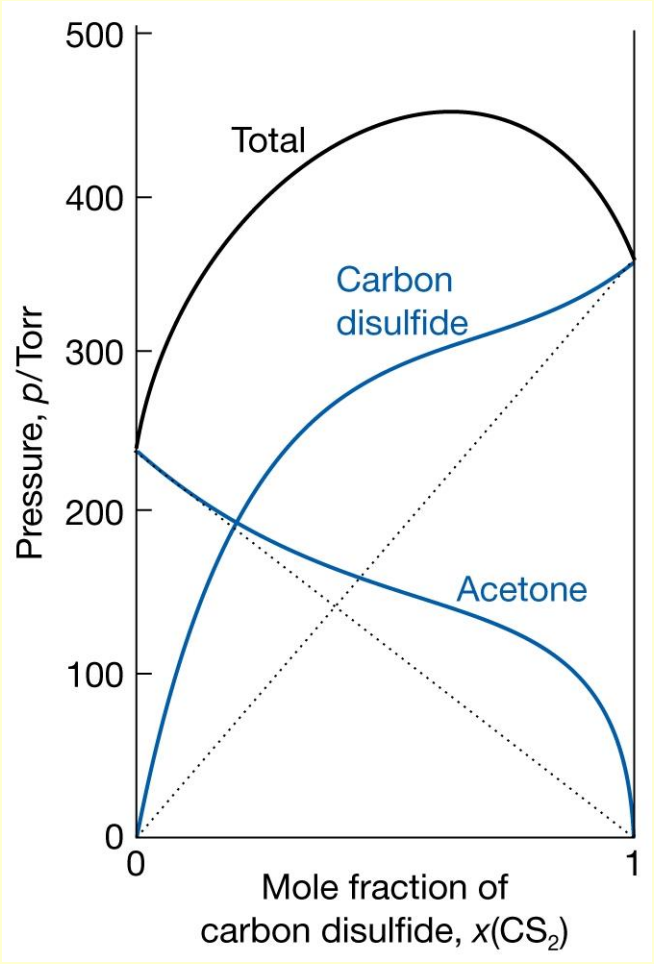


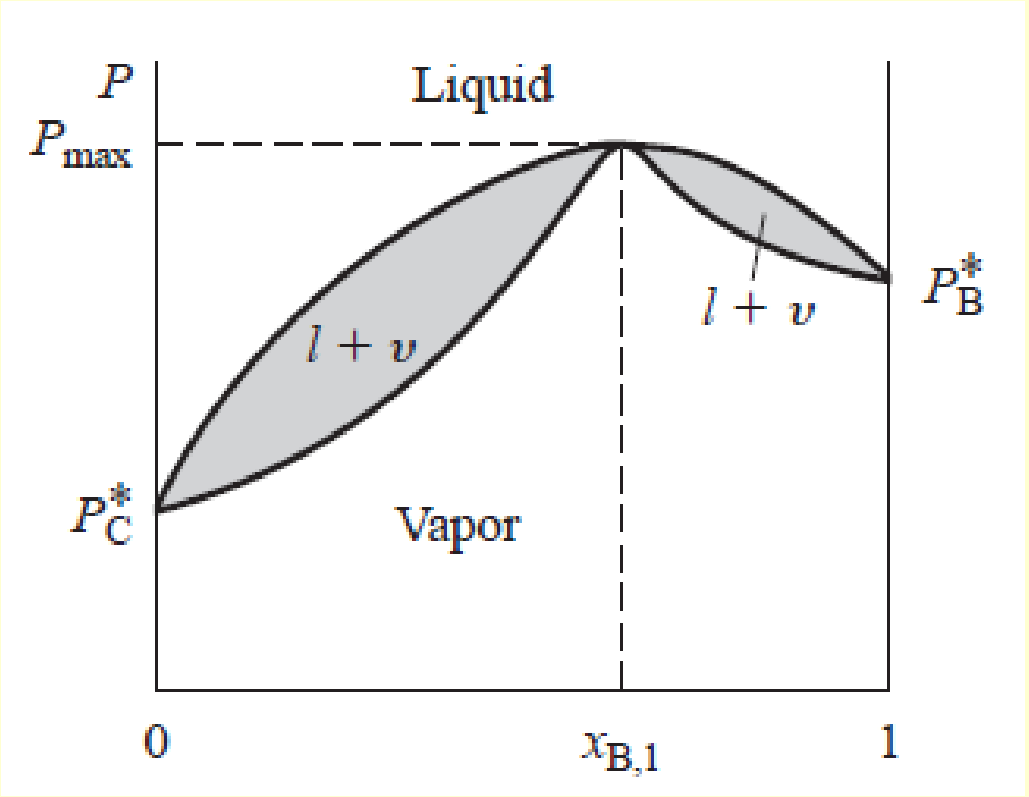
Neidealni rastvor: pozitivna odstupanja



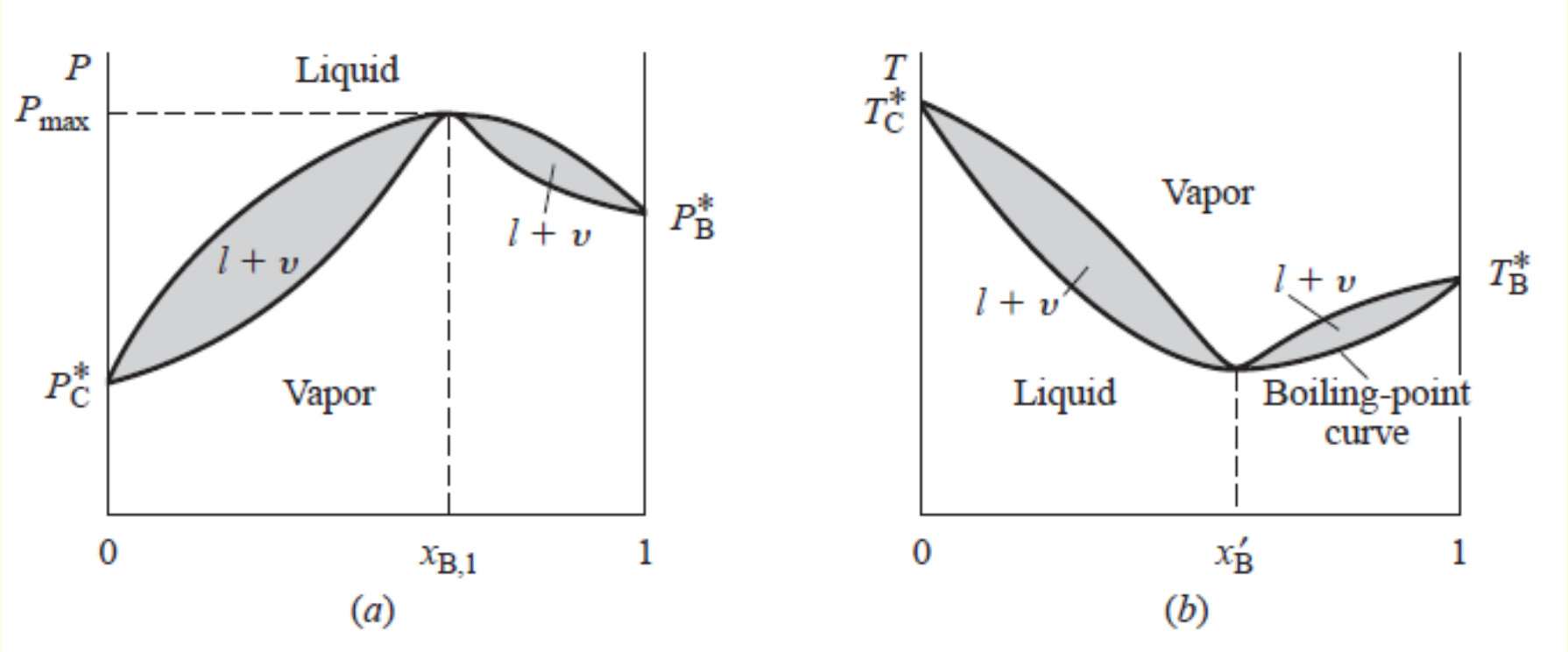


Neidealni rastvor: pozitivna odstupanja

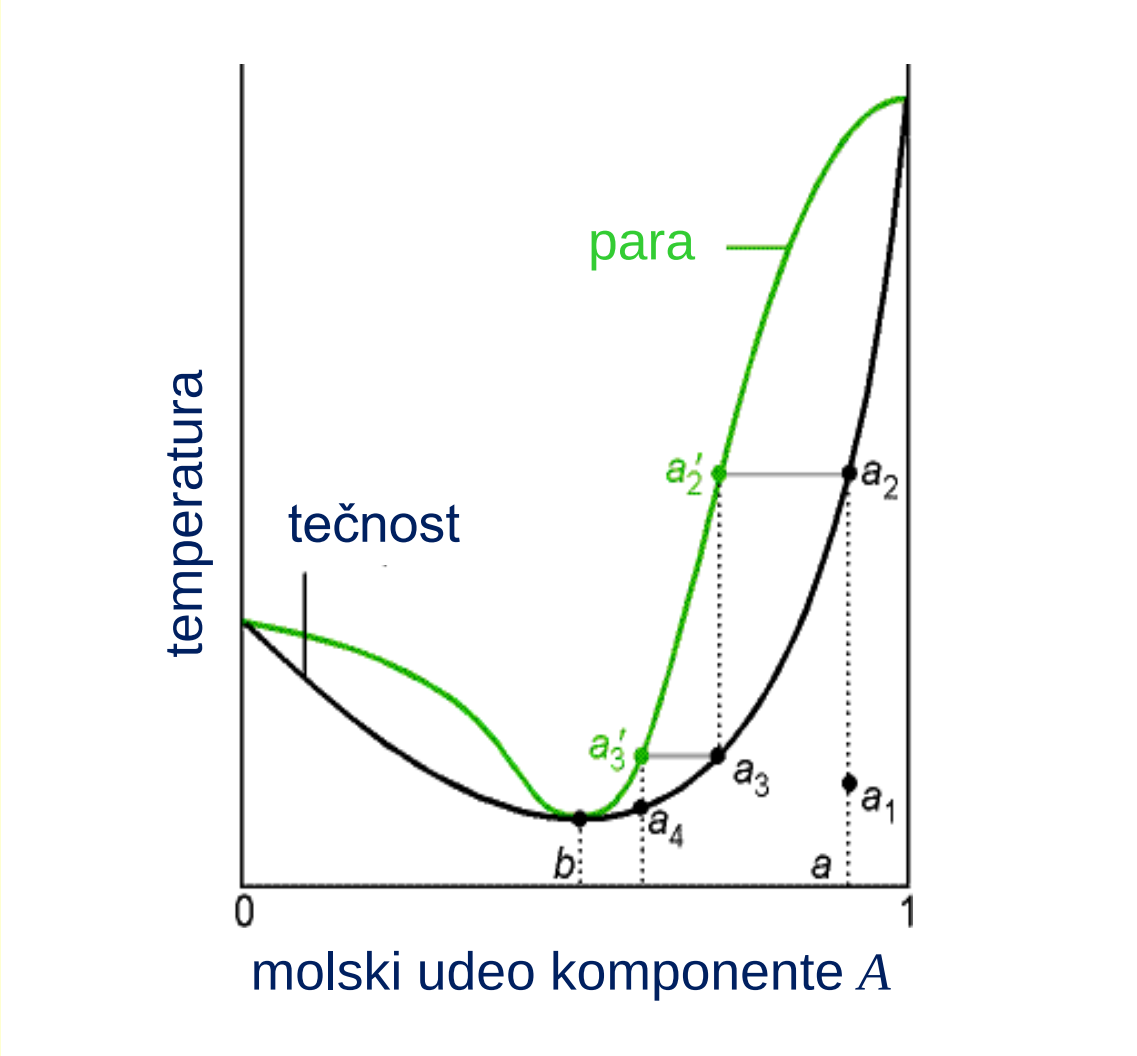




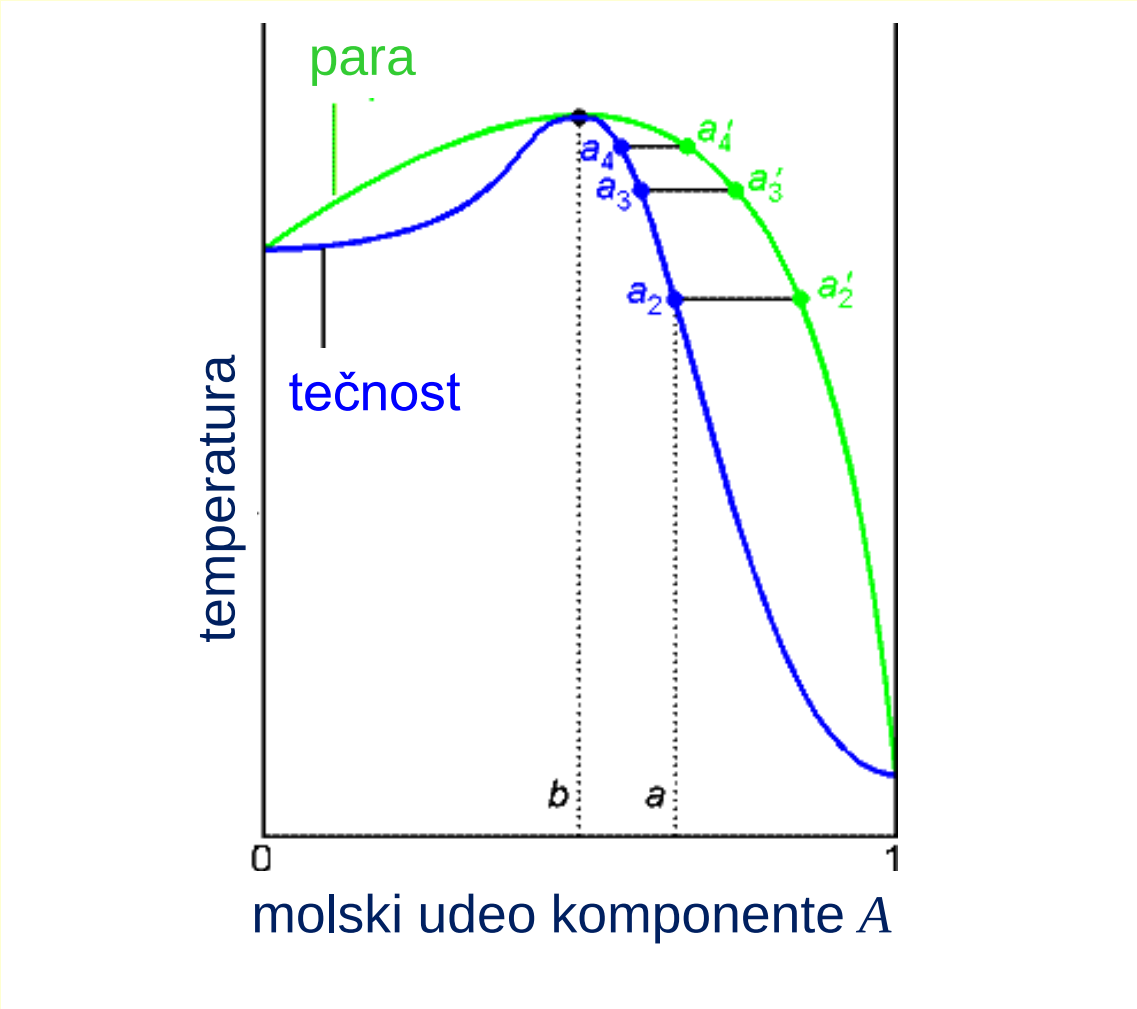
Neidealni rastvor: pozitivna odstupanja



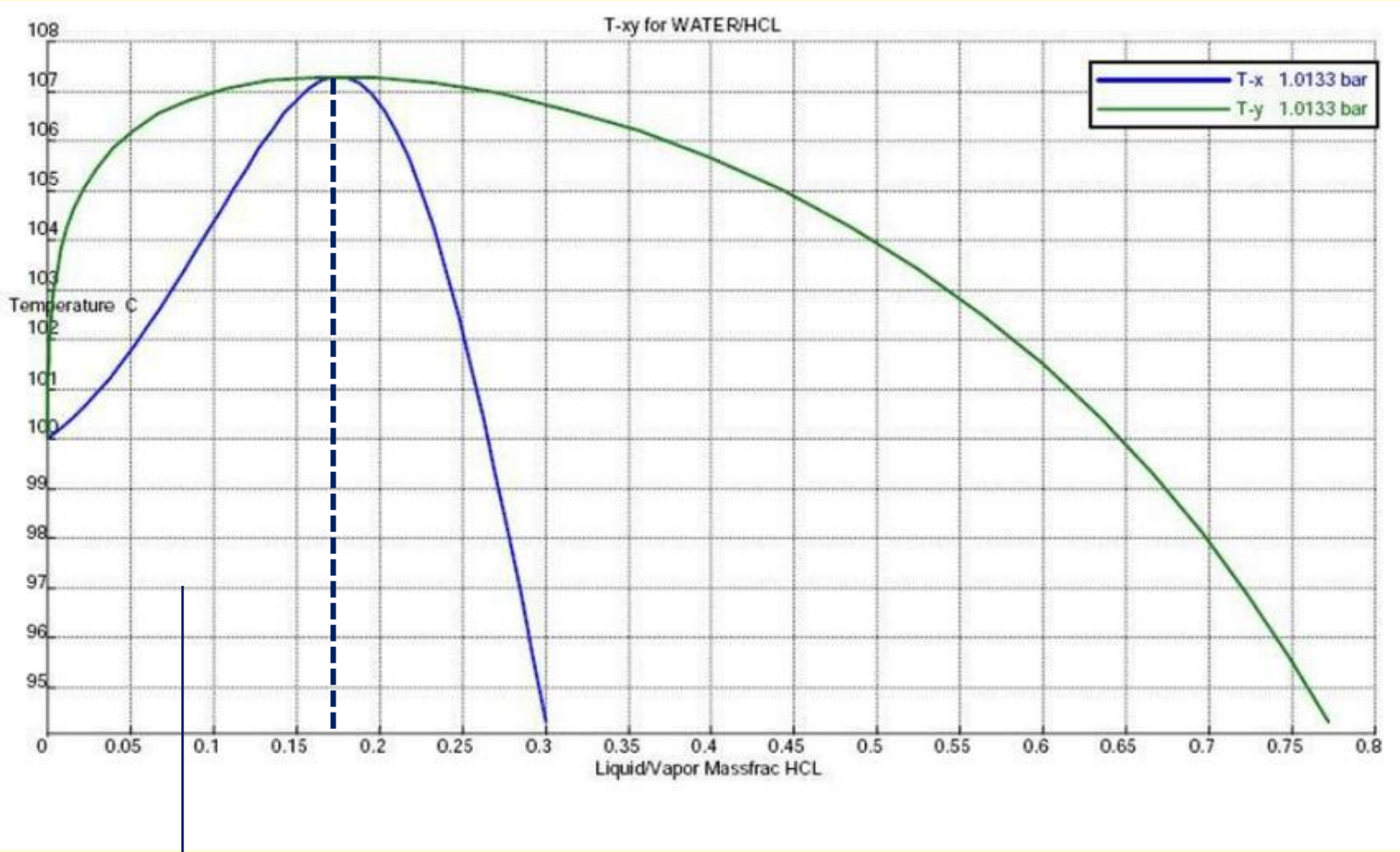
Neidealni rastvor: pozitivna odstupanja



Neidealni rastvor: negativna odstupanja



Primer: H_2O-HCl

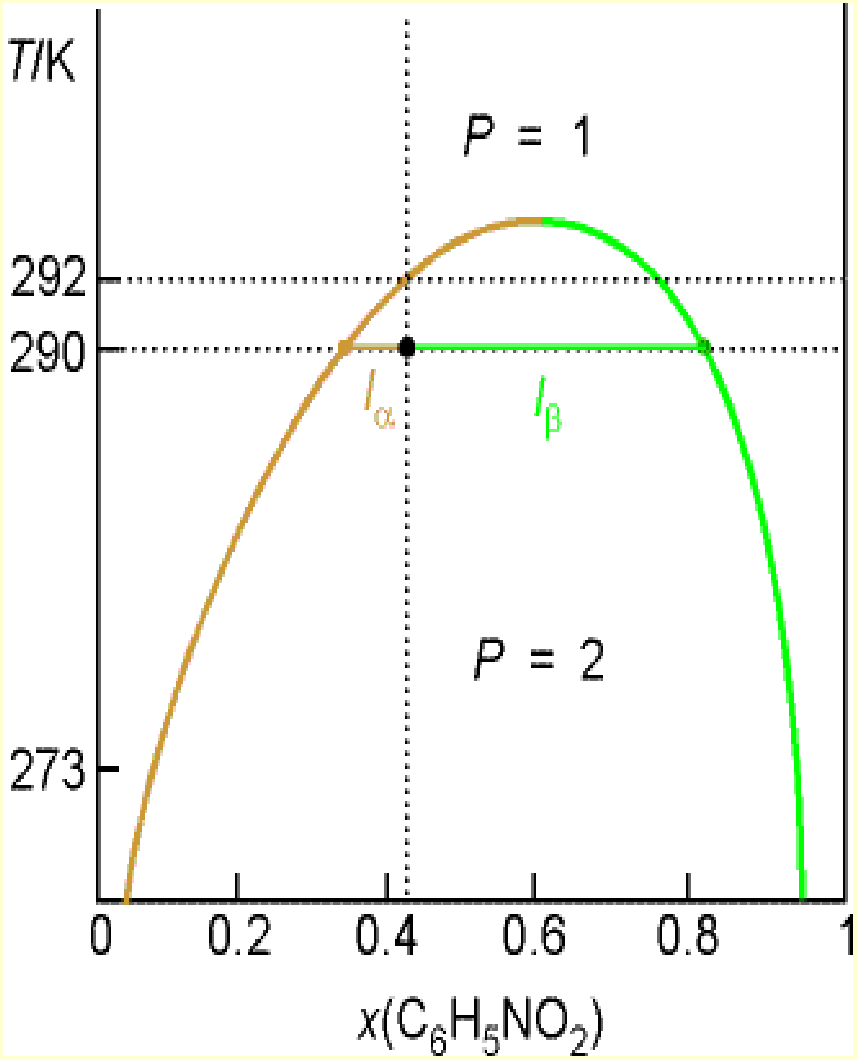


povećanje temperature dovodi do povećanja rastvorljivosti HCl u H_2O

Dvokomponentni sistemi

- potpuno mešljive tečnosti
- delimično mešljive tečnosti
- nemešljive tečnosti

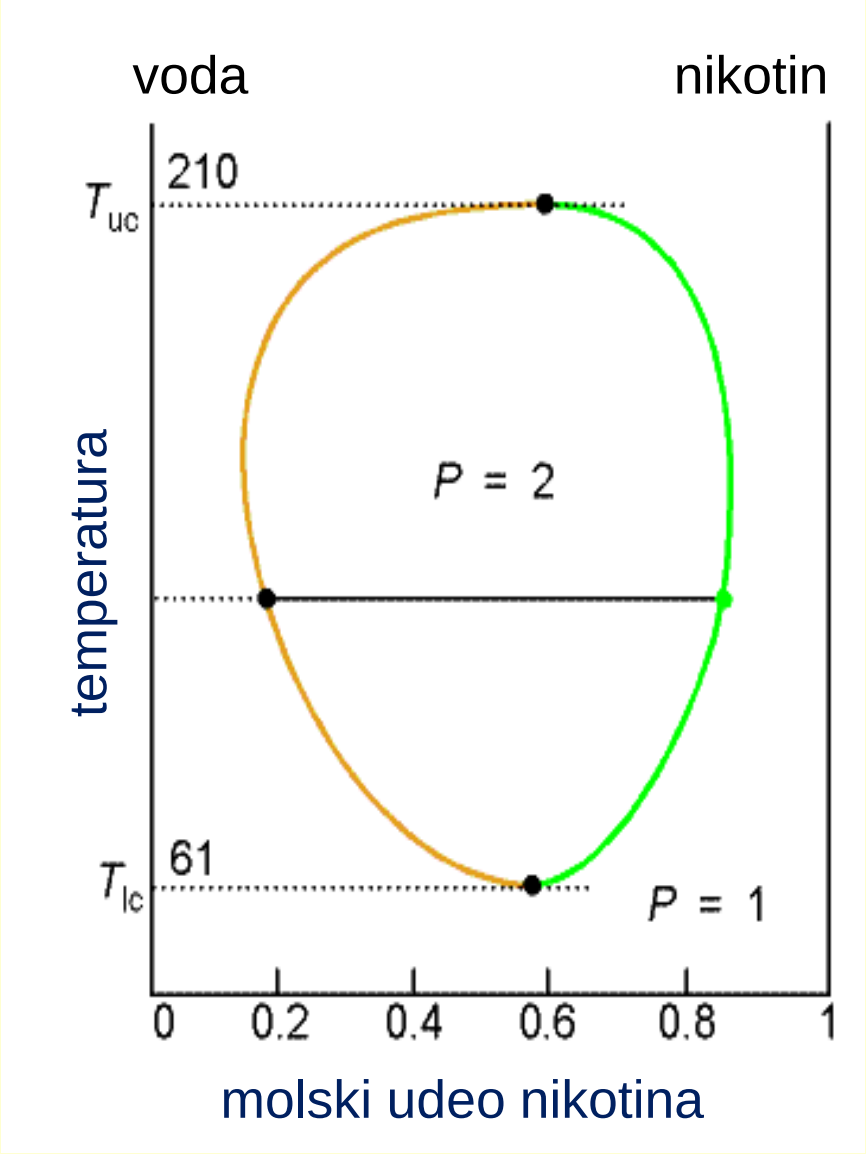
Delimično mešljive tečnosti



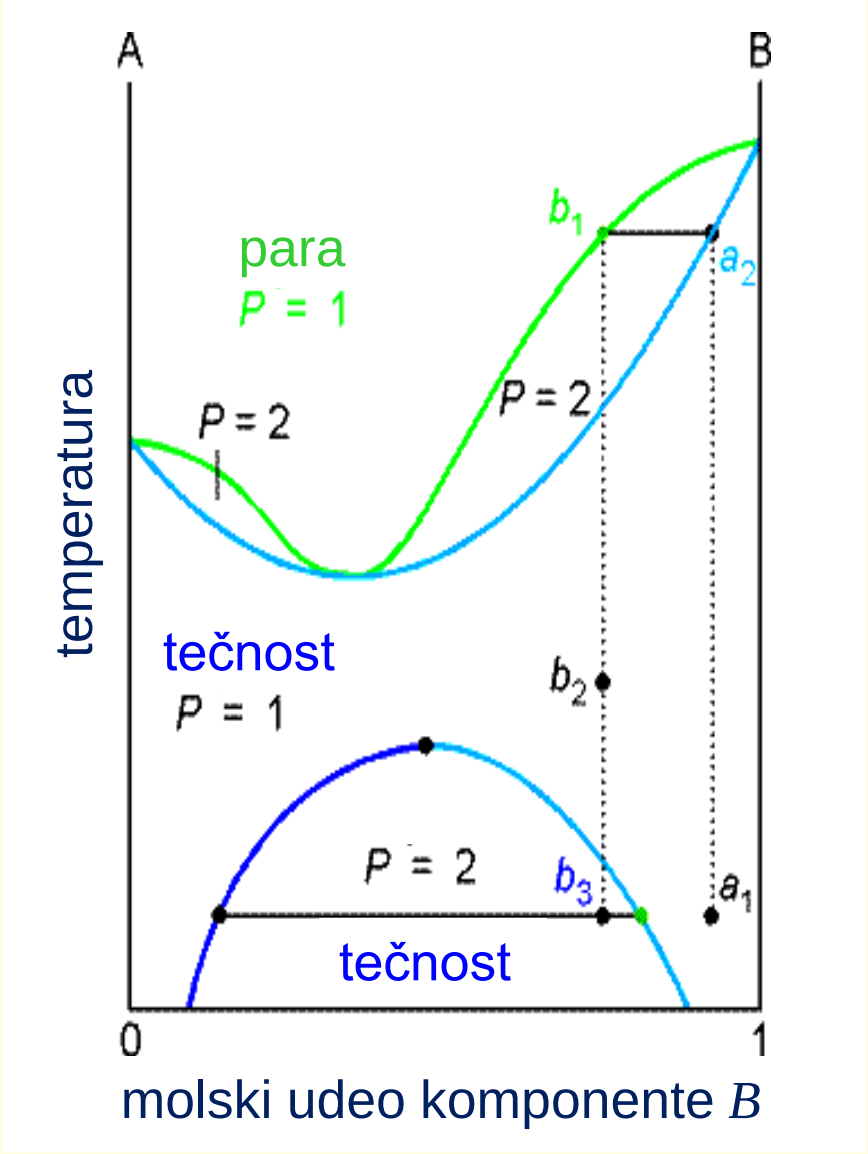
heksan i nitrobenzen

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

Kritične temperature rastvora

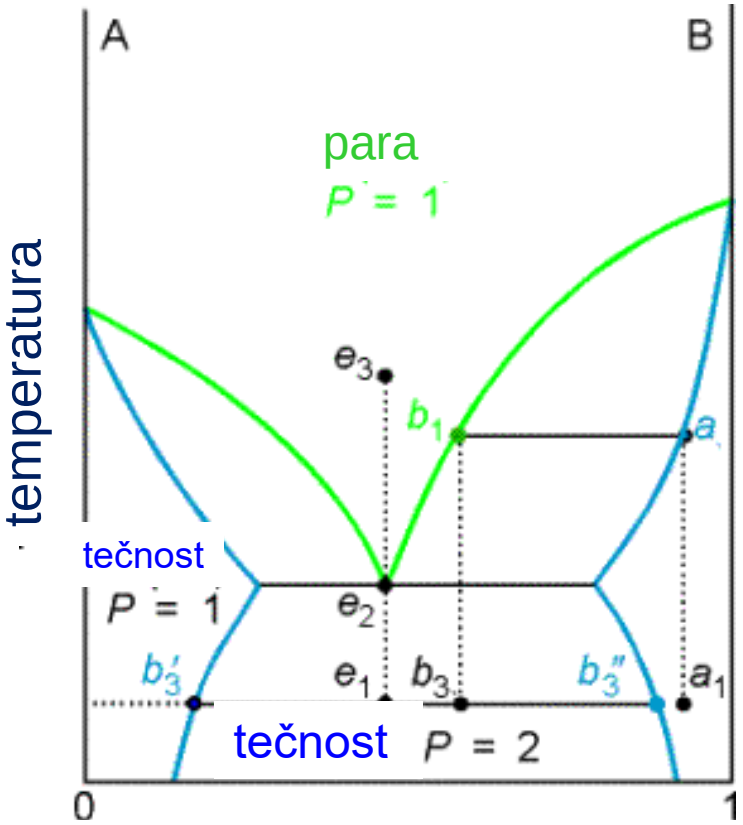


Delimično mešljive tečnosti



Delimično mešljive tečnosti

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



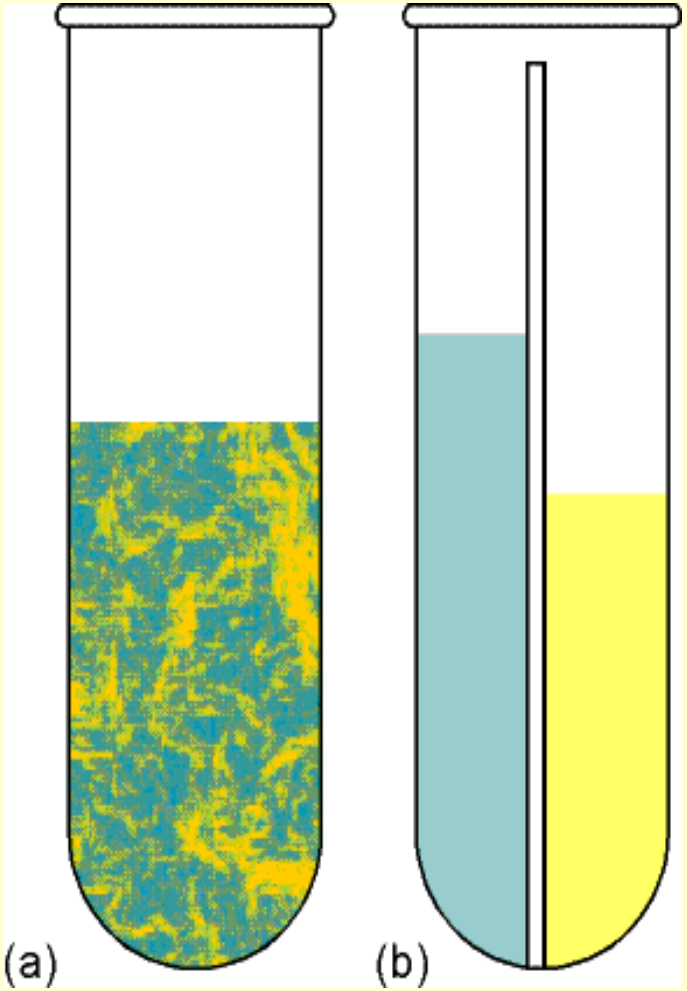
Dvokomponentni sistemi

- 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 = atmosferski pritisak.



Zakon raspodele

$$\mu_1 = \mu_1^0 + RT \ln a_1$$

$$\mu_2 = \mu_2^0 + RT \ln a_2$$

$$\ln \frac{a_1}{a_2} = \frac{\mu_2^0 - \mu_1^0}{RT}$$

$$\boxed{\frac{a_1}{a_2} = K}$$

Razblaženi rastvor

$$\frac{c_1}{c_2} = K$$

Disocijacija

$$\frac{(1-\alpha_1)c_1}{(1-\alpha_2)c_2} = K$$

Ekstrakcija

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

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

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

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