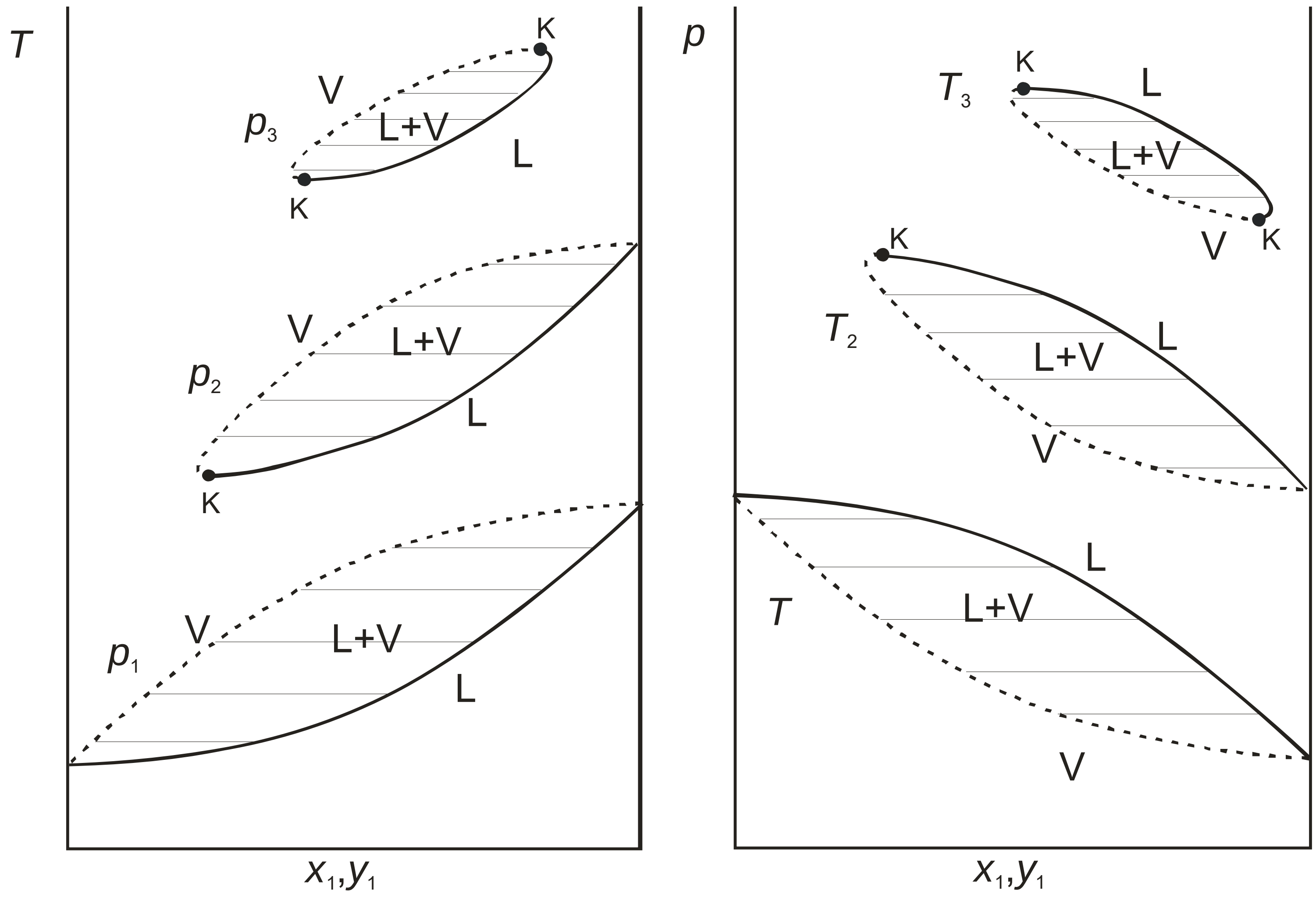
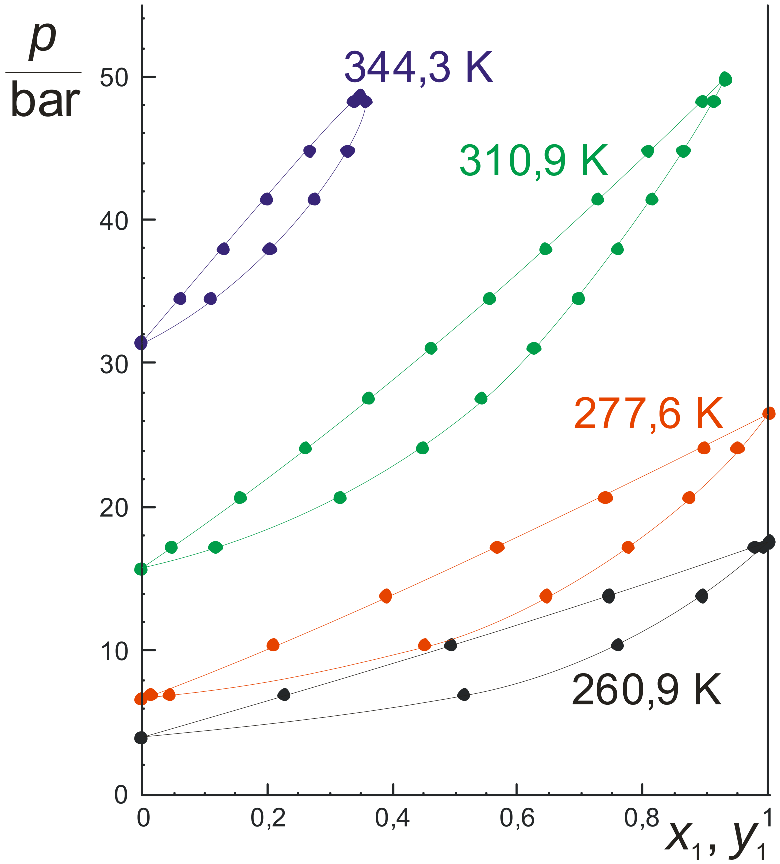
Ravnoteža para-kapljevina 2

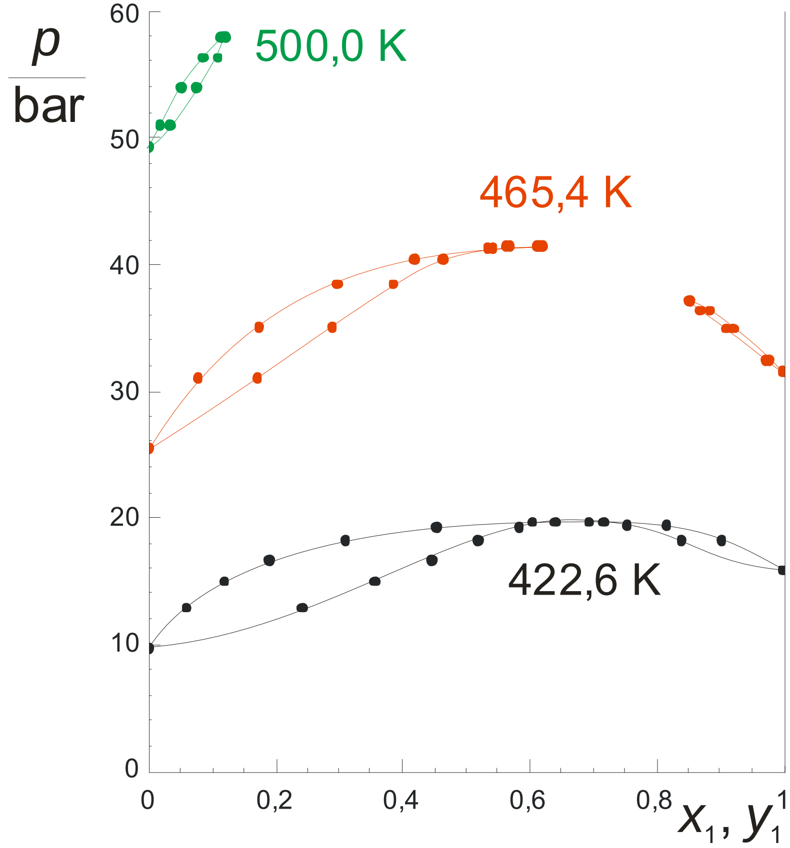
Fazni dijagrami u kritičnom području



Fazni dijagrami u kritičnom području

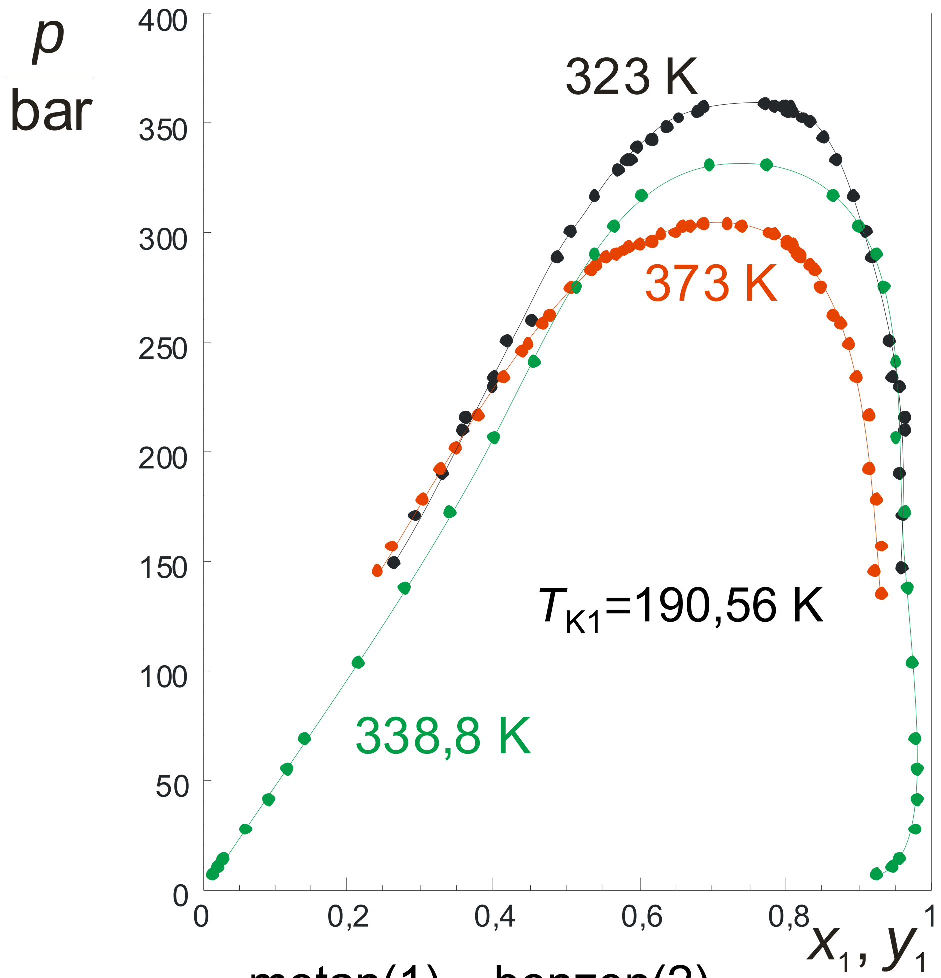


etan(1) – propen(2)
McKay i suradnici



n-pentan(1) – etanol(2)
Seol i suradnici

Retrogradna kondenzacija

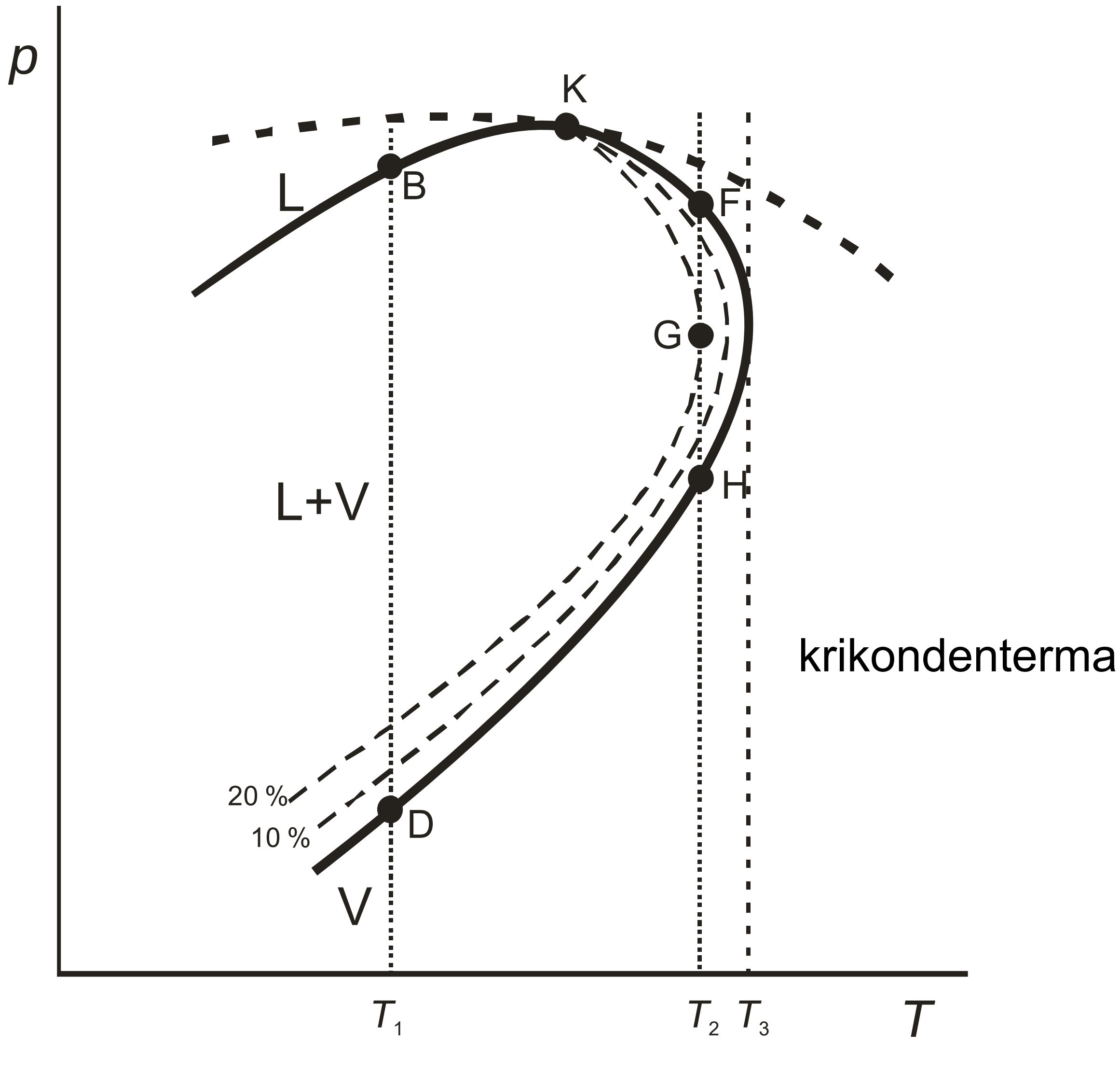


metan(1) – benzen(2)
Marteau; Elbishlaur

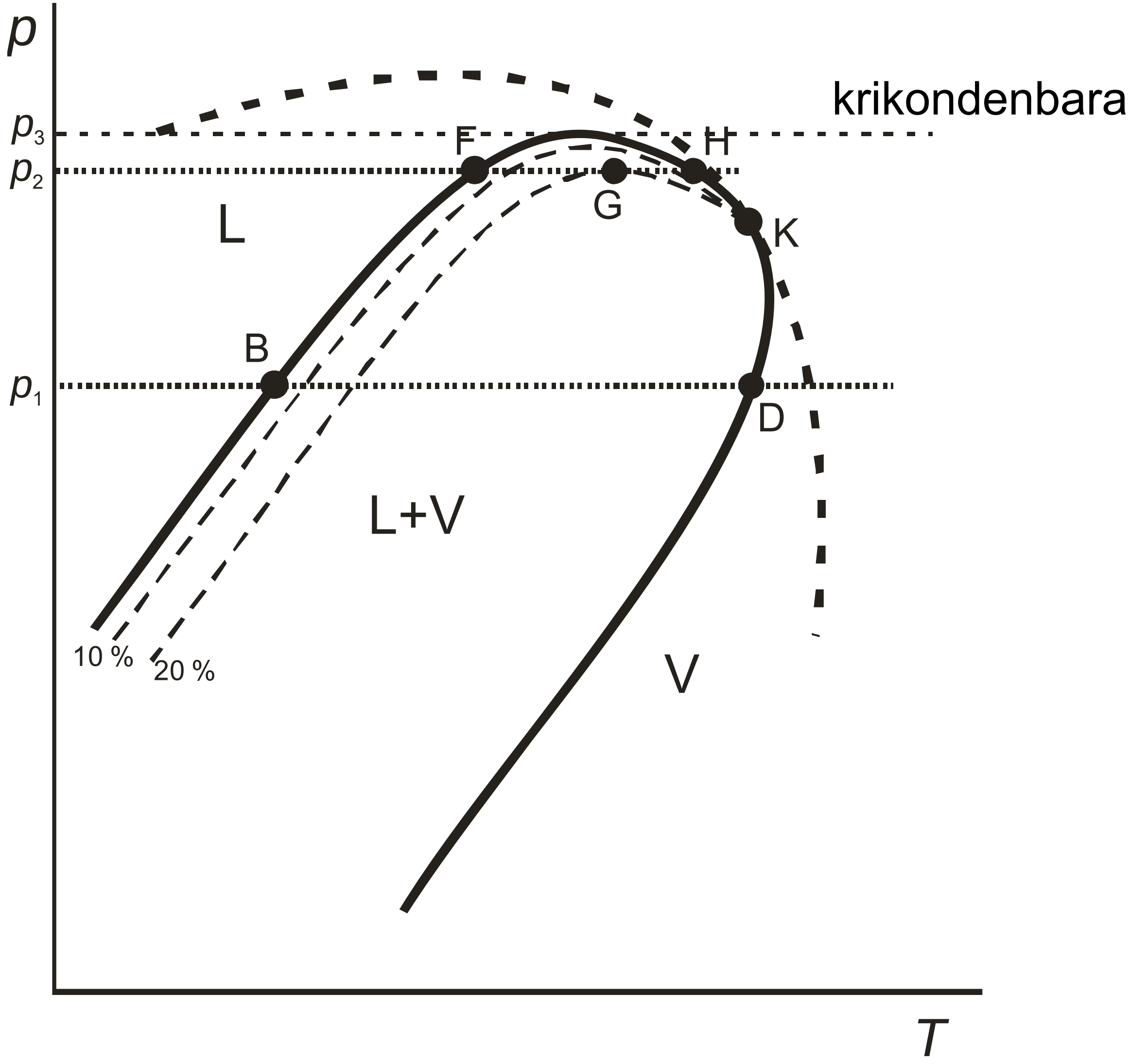
Kritične točke su na maksimumima krivulja

Za y_1=0,95, s povećanjem tlaka dolazi do ukapljivanja, a zatim do isparavanja (zelena krivulja).

Retrogradna kondenzacija



Retrogradna kondenzacija



Proračun vrelišta

Formulacija $T, x_i \rightarrow p, y_i$

$$-1 + \sum_{i=1}^{nk} y_i = 0$$ Bilanca za parnu fazu

$$K_i = \frac{y_i}{x_i} = f\left(p, T, x_i, y_i\right)$$ Ravnotežne jednadžbe

$$-1 + \sum_{i=1}^{nk} K_i x_i = 0$$ Kombinacija

$$K_i = \frac{\hat{\varphi}_i^{\mathrm{L}}}{\hat{\varphi}_i^{\mathrm{V}}}$$ Koeficijent raspodjele

Proračun jednokratnog isparavanja

Formulacija $p, T, z_i \rightarrow x_i, y_i, \Psi$

Bilančne jednadžbe za komponente

$$z_i = (1-\Psi)x_i + \Psi y_i$$

$$\sum_{i=1}^{nk} y_i - \sum_{i=1}^{nk} x_i = 0$$ Rachford-Riceov bilančni uvjet

$$K_i = \frac{y_i}{x_i} = f\left(p, T, x_i, y_i\right)$$ Ravnotežne jednadžbe

$$f(\Psi) = \sum_{i=1}^{nk} \frac{z_i\left(K_i - 1\right)}{1 + \Psi\left(K_i - 1\right)} = 0$$ Kombinacija

$$K_i = \frac{\hat{\varphi}_i^{\mathrm{L}}}{\hat{\varphi}_i^{\mathrm{V}}}$$ Koeficijent raspodjele

Topljivost plinova u kapljevinama

Apsorpcija

Slučaj 1: Smjese jednostavna ponašanja u kapljevitoj fazi

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

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

npr. topljivost metana u heksanu

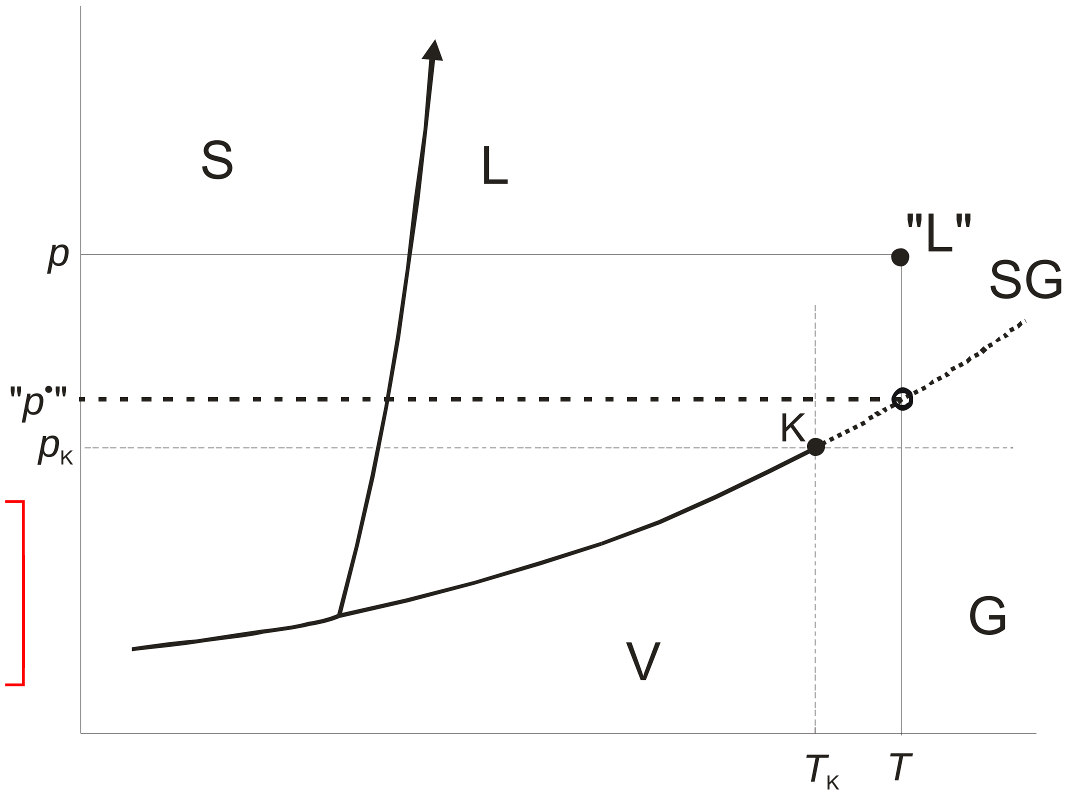
Topljivost plinova u kapljevinama

Slučaj 2: Ekstrapolacijski postupak

$$y_1 p \hat{\varphi}_1^{\mathrm{V}} = x_1 \gamma_1^{\mathrm{L}} f_1^{\mathrm{L}\circ}$$

$$f_1^{\mathrm{L}\circ} = p_1^{\bullet} \varphi_1^{\bullet} \exp\left[\int_{p_1^{\bullet}}^{p} \frac{v_1^{\mathrm{L}}}{RT} dp \right]$$

$$K_1 = \frac{y_1}{x_1} = \frac{\gamma_1^{\mathrm{L}} p_1^{\bullet} \varphi_1^{\bullet}}{p \hat{\varphi}_1^{\mathrm{V}}} \exp\left[\int_{p_1^{\bullet}}^{p} \frac{v_1^{\mathrm{L}}}{RT} dp \right]$$

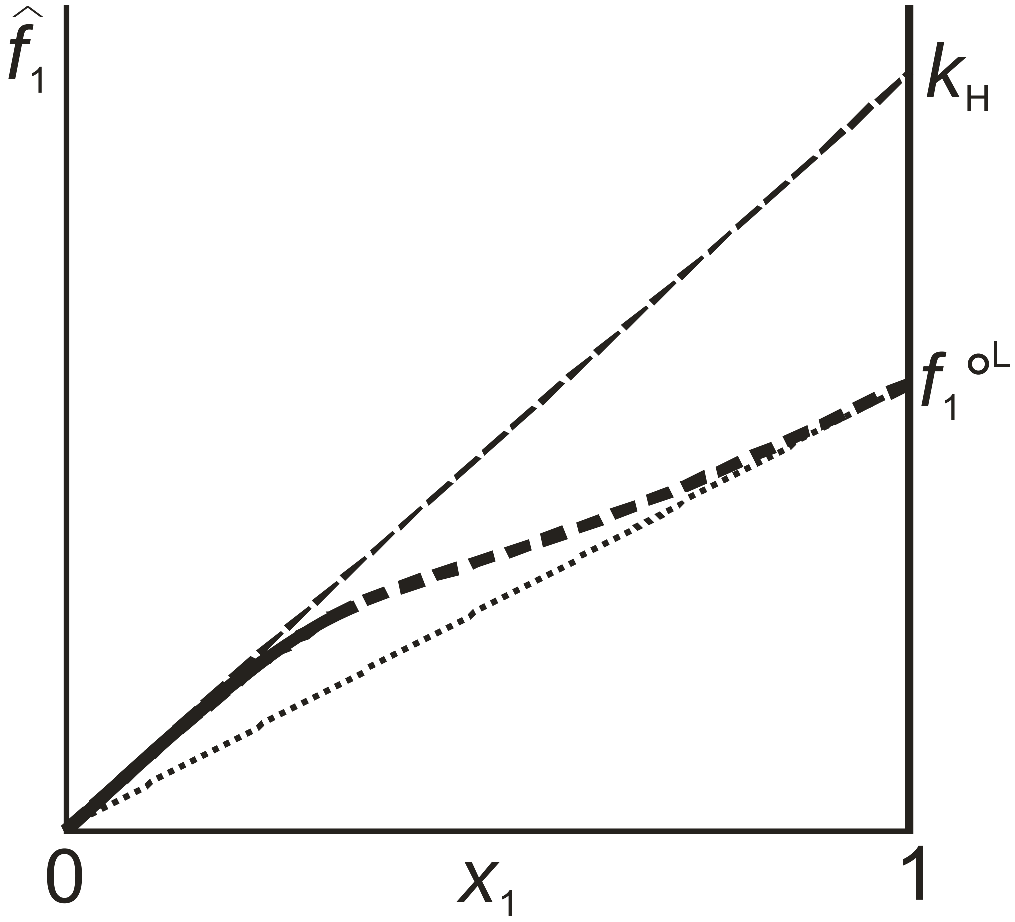


Topljivost plinova u kapljevinama

Slučaj 3: Asimetrična definicija standardnog stanja

$$y_1 p \hat{\varphi}_1^{\mathrm{V}} = x_1 \gamma_{\mathrm{H}1} k_{\mathrm{H}}$$

$$K_1 = \frac{y_1}{x_1} = \frac{\gamma_{\mathrm{H}1} k_{\mathrm{H}}}{p \hat{\varphi}_1^{\mathrm{V}}}$$



Topljivost plinova u kapljevinama

Slučaj 4: Grafička korelacija Prausnitza i Shaira

$$y_1 p \hat{\varphi}_1^{\mathrm{V}} = x_1 \gamma_1^{\mathrm{L}} f_1^{\mathrm{L}\circ}$$

$$K_1 = \frac{y_1}{x_1} = \frac{\gamma_1^{\mathrm{L}}}{p\hat{\varphi}_1^{\mathrm{V}}} f_1^{\mathrm{L}}\left(T,\ p_0 = 1\ \mathrm{atm}\right)\exp\left[\frac{v_1^{\mathrm{L}}\left(p - p_0\right)}{RT}\right]$$

$$f_1^{\mathrm{L}\circ}\left(T, p\right) = f_1^{\mathrm{L}}\left(T,\ p_0 = 1\ \mathrm{atm}\right)\exp\left[\int_{p_0}^{p} \frac{v_1^{\mathrm{L}}}{RT} dp\right] \approx$$

$$\approx f_1^{\mathrm{L}}\left(T,\ p_0 = 1\ \mathrm{atm}\right)\exp\left[\frac{v_1^{\mathrm{L}}\left(p - p_0\right)}{RT}\right]$$

Hipotetska standardna fugacitivnost ukapljenog plina

Hipotetski molarni volumen ukapljenog plina

Topljivost plinova u kapljevinama

Slučaj 4: Grafička korelacija Prausnitza i Shaira

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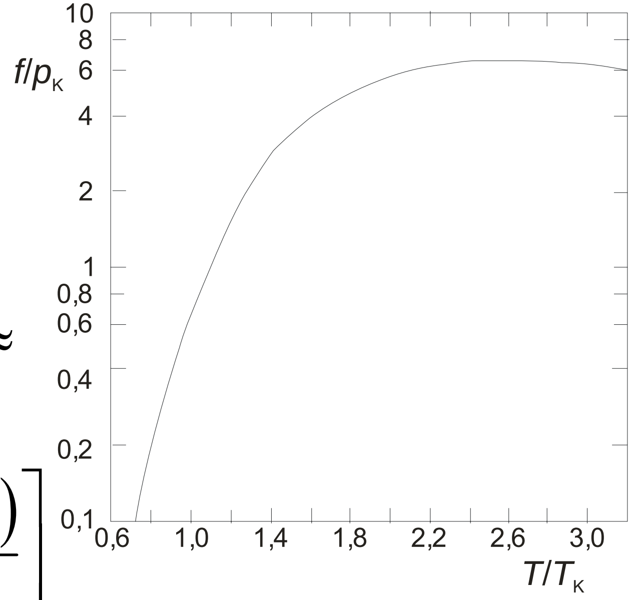
$$\approx f_1^{\mathrm{L}}(T,\ p_0 = 1\ \mathrm{atm}) \exp\left[\frac{v_1^{\mathrm{L}}(p - p_0)}{RT}\right]$$



Hipotetska standardna fugacitivnost ukapljenog plina

Hipotetski molarni volumen ukapljenog plina

Model koeficijenta aktivnosti

$$\ln \gamma_1 = \frac{v_1^{\mathrm{L}} \phi_2^2}{RT} (\delta_1 - \delta_2)^2 \qquad \ln \gamma_1 = \frac{v_1^{\mathrm{L}}}{RT} (\delta_1 - \bar{\delta})^2$$

plin	$v^{\mathrm{L}}/(\mathrm{cm^3 mol^{-1}})$	$\delta/\mathrm{MPa}^{1/2}$
N_2	32,4	5,28
CO	32,1	6,40
O_2	33,0	8,18
Ar	57,1	10,9
CH_4	52	11,6