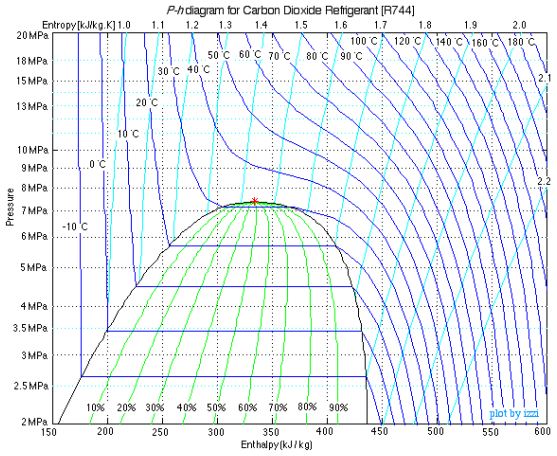
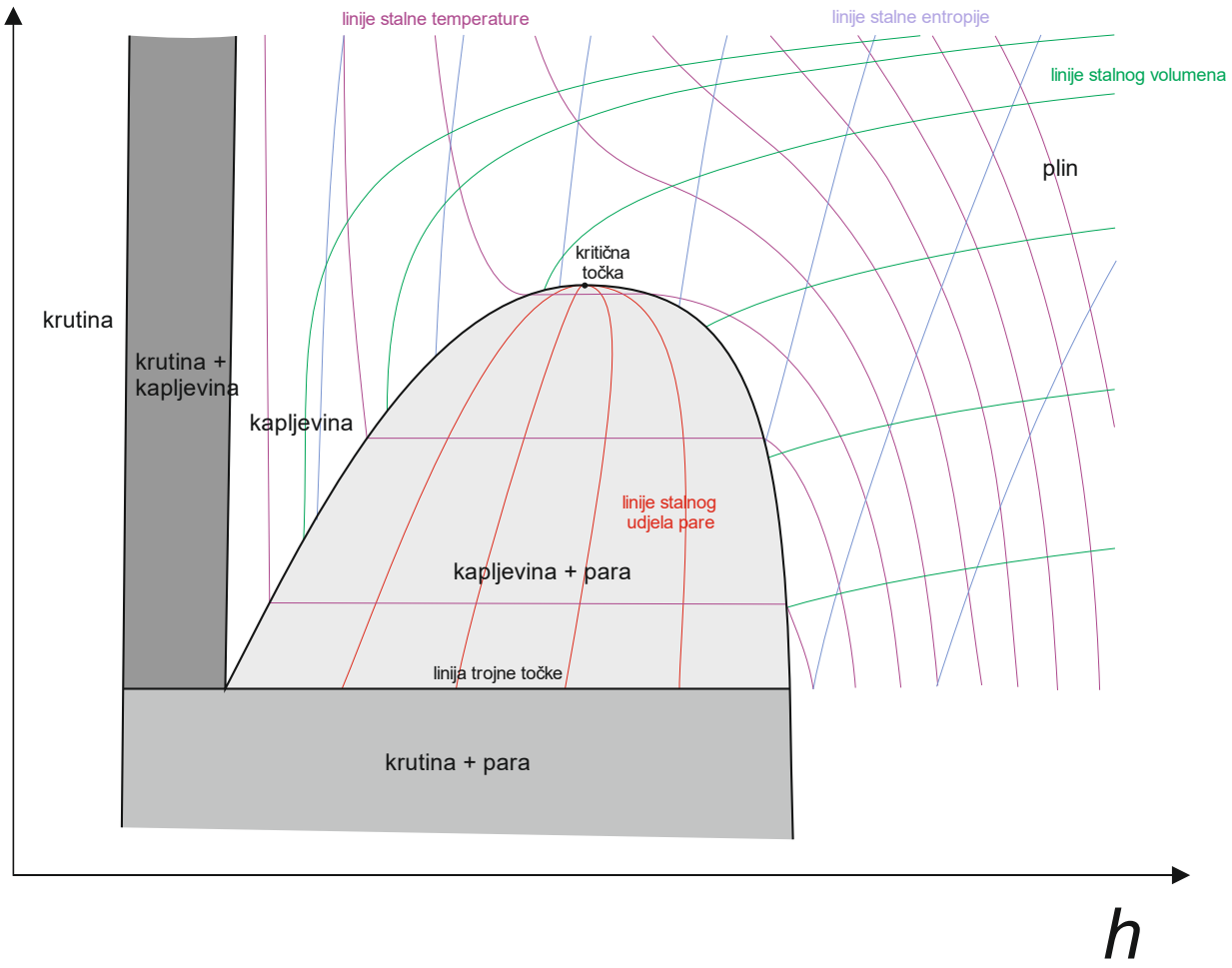
Termodinamička svojstva realnih fluida

Toplinske tablice i dijagrami

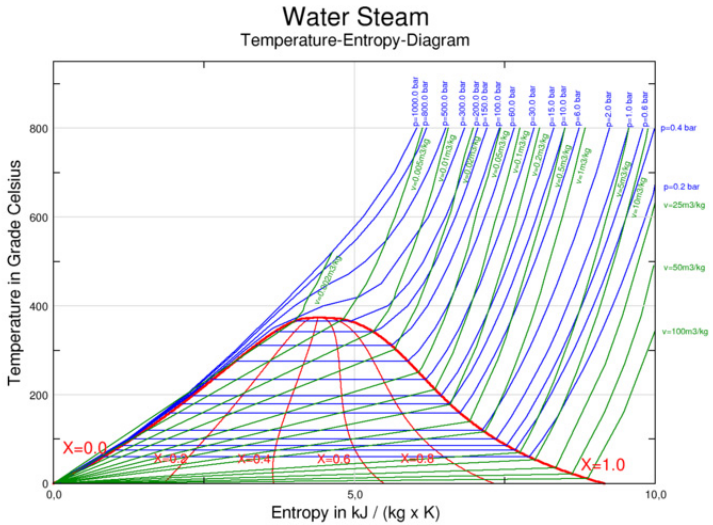
ph-dijagram
Rashladni
uređaji

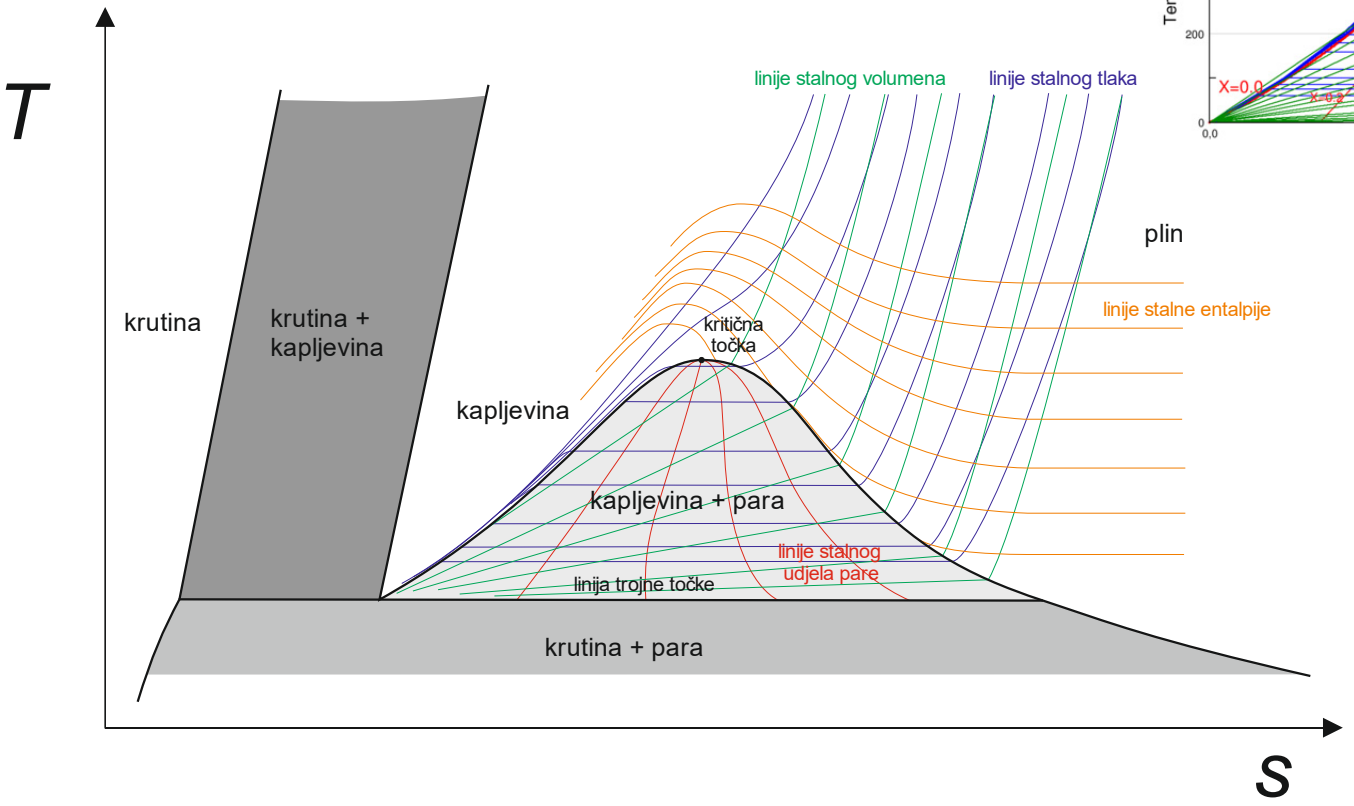




Toplinske tablice i dijagrami

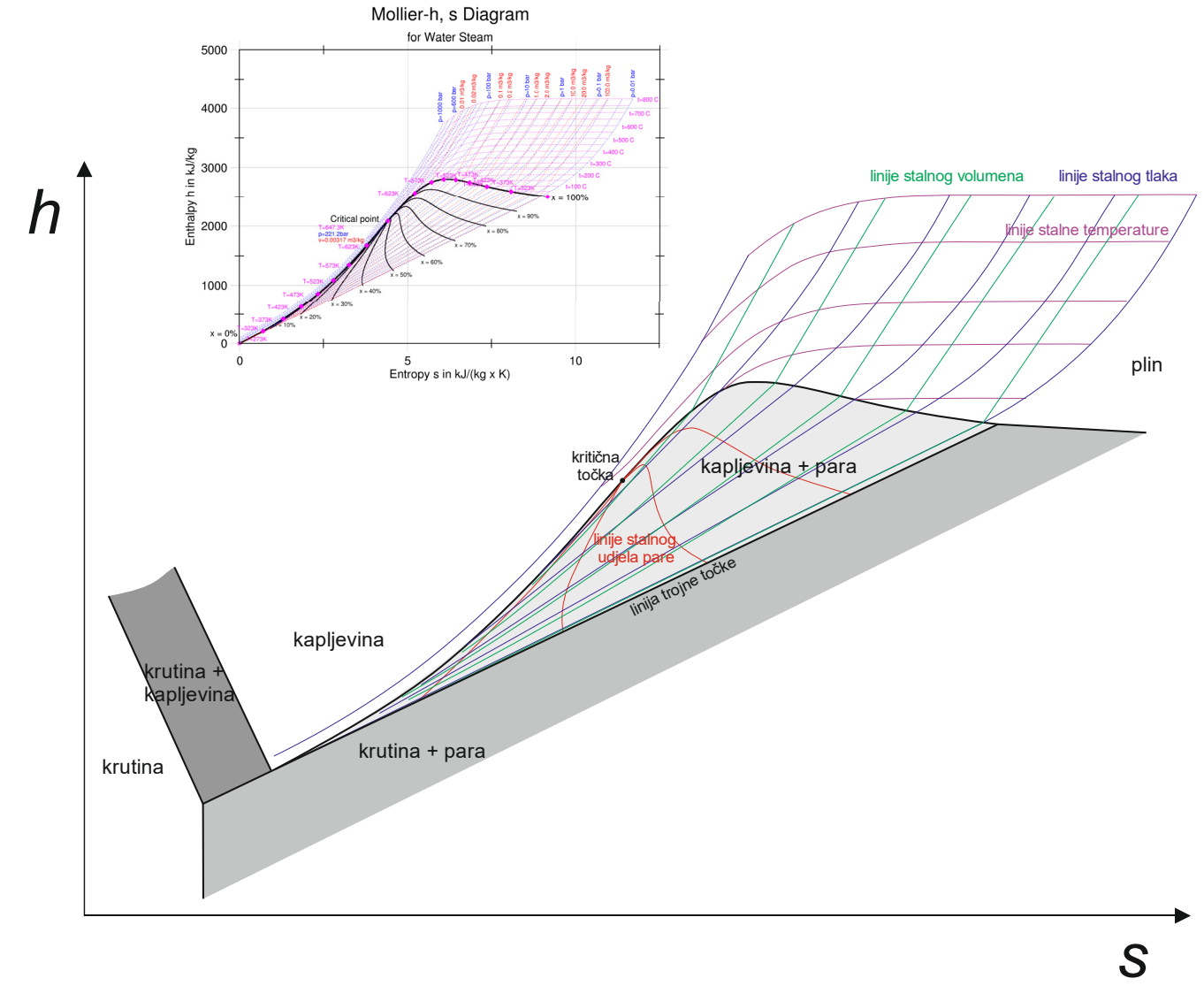
Ts-dijagram
Pretvorba
Energije





Toplinske tablice i dijagrami

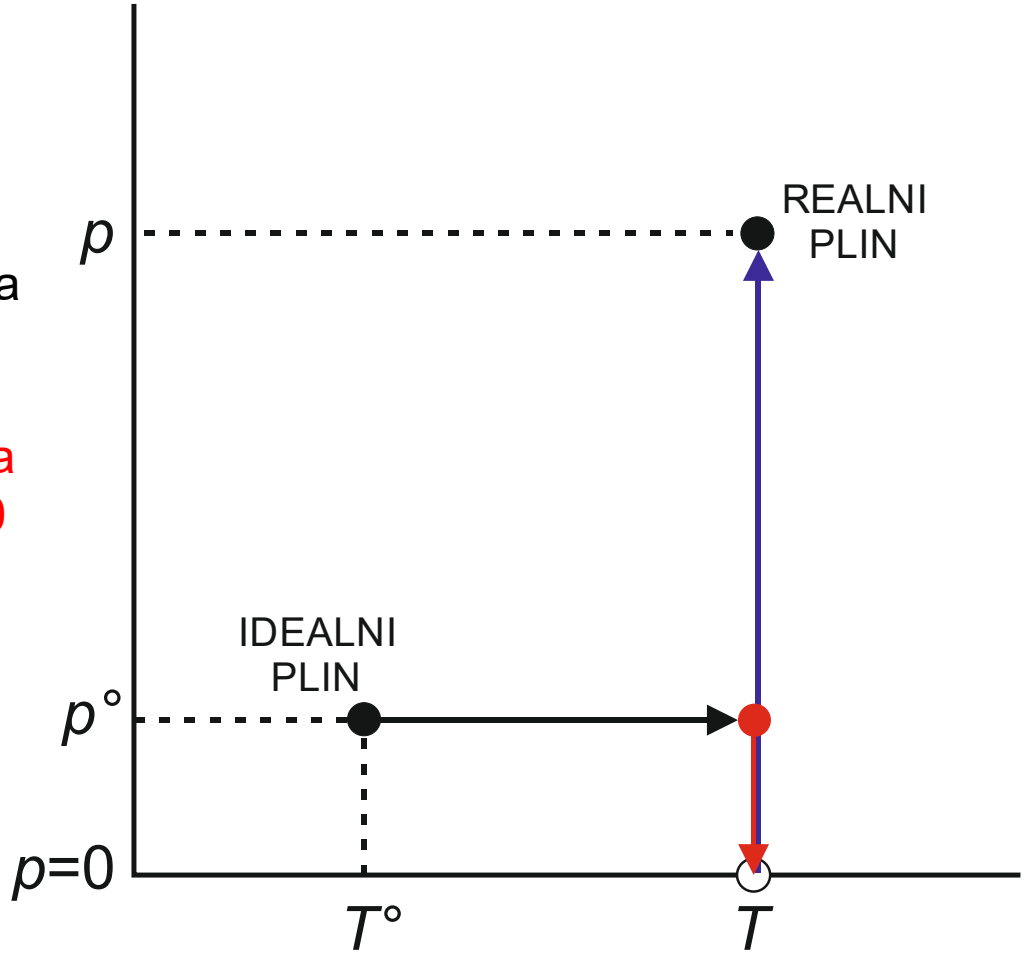
hs-dijagram
Mlaznice
Difuzori
Turbine
Kompresori



Konstrukcija toplinskih dijagrama

Shema izračunavanja

- **izobarno zagrijavanje** idealnog plina od $T°$ do T pri referentnom tlaku $p°$
- **izotermna ekspanzija** idealnog plina pri T od referentnoga tlaka $p°$ do $p=0$
- realni plin jednak idealnom pri $p=0$
- **izotermna kompresija** realnog plina od $p=0$ do p pri T



Konstrukcija toplinskih dijagrama

Entalpijska promjena

Temperatura

$$\left(\frac{\partial h}{\partial T}\right)_p = c_p^{\mathrm{id}} \qquad \Delta_1 h = \int_{T^\circ}^{T} c_p^{\mathrm{id}}\, dT$$

$$c_p^{\mathrm{id}} = a + bT + cT^2 + dT^3 + \cdots$$

Tlak

$$\left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p$$

$$h - h^\circ = \int_{p^\circ}^{0}\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]dp + \int_{0}^{p}\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]dp$$

$$h - h^\circ = \int_{p^\circ}^{0}\left[\frac{RT}{p} - T\frac{R}{p}\right]dp + \int_{0}^{p}\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]dp$$

Funkcija odstupanja
Deviation ili
Departure Function

$$h - h^\circ = 0 + \int_{0}^{p}\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]dp$$

Konstrukcija toplinskih dijagrama

Entalpijska promjena

Za jednadžbe stanja eksplicitne po

Funkcija odstupanja *Deviation ili Departure Function*

$$h - h^\circ = \int_0^p \left[v - T\left(\frac{\partial v}{\partial T}\right)_p \right] dp$$ volumenu

$$h - h^\circ = RT(z-1) + \int_\infty^v \left[T\left(\frac{\partial p}{\partial T}\right)_v - p \right] dv$$ tlaku

Konačna entalpija:

$$h = h_{\text{ref}} + \int_{T^\circ}^{T} c_p^{\text{id}} dT + RT(z-1) + \int_\infty^v \left[T\left(\frac{\partial p}{\partial T}\right)_v - p \right] dv$$

Konstrukcija toplinskih dijagrama

Entropijska promjena

$$\left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p^{\mathrm{id}}}{T} \qquad \Delta_1 s = \int_{T^\circ}^{T} \frac{c_p^{\mathrm{id}}}{T} dT$$

Temperatura

$$c_p^{\mathrm{id}} = a + bT + cT^2 + dT^3 + \cdots$$

Tlak

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \qquad s - s^\circ = \int_{p^\circ}^{0} \left[-\left(\frac{\partial v}{\partial T}\right)_p\right] dp + \int_{0}^{p} \left[-\left(\frac{\partial v}{\partial T}\right)_p\right] dp$$

$$s - s^\circ = \int_{p^\circ}^{0} \left[-\frac{R}{p}\right] dp - \int_{0}^{p} \left[\frac{R}{p}\right] dp + \int_{0}^{p} \left[-\left(\frac{\partial v}{\partial T}\right)_p\right] dp$$

Funkcija odstupanja
Deviation ili
Departure Function

$$s - s^\circ - R \ln \frac{p}{p^\circ} + \int_0^p \left[\frac{R}{p} - \left(\frac{\partial v}{\partial T}\right)_p\right] dp$$

Konstrukcija toplinskih dijagrama

Entropijska promjena

Za jednadžbe stanja eksplicitne po

Funkcija odstupanja *Deviation ili Departure Function*

$$s - s^\circ = -R \ln \frac{p}{p^\circ} + \int_0^p \left[\frac{R}{p} - \left(\frac{\partial v}{\partial T} \right)_p \right] dp$$ volumenu

$$s - s^\circ = R \ln \frac{v}{v^\circ} + \int_\infty^v \left[\left(\frac{\partial p}{\partial T} \right)_v - \frac{R}{v} \right] dv$$ tlaku

Konačna entropija

$$s = s_{\text{ref}} + \int_{T^\circ}^{T} \frac{c_p^{\text{id}}}{T} dT + R \ln \frac{v}{v^\circ} + \int_\infty^v \left[\left(\frac{\partial p}{\partial T} \right)_v - \frac{R}{v} \right] dv$$

Funkcije odstupanja

$$h - h^\circ = RT(z-1) + \int_\infty^v \left[T\left(\frac{\partial p}{\partial T}\right)_v - p \right] dv$$

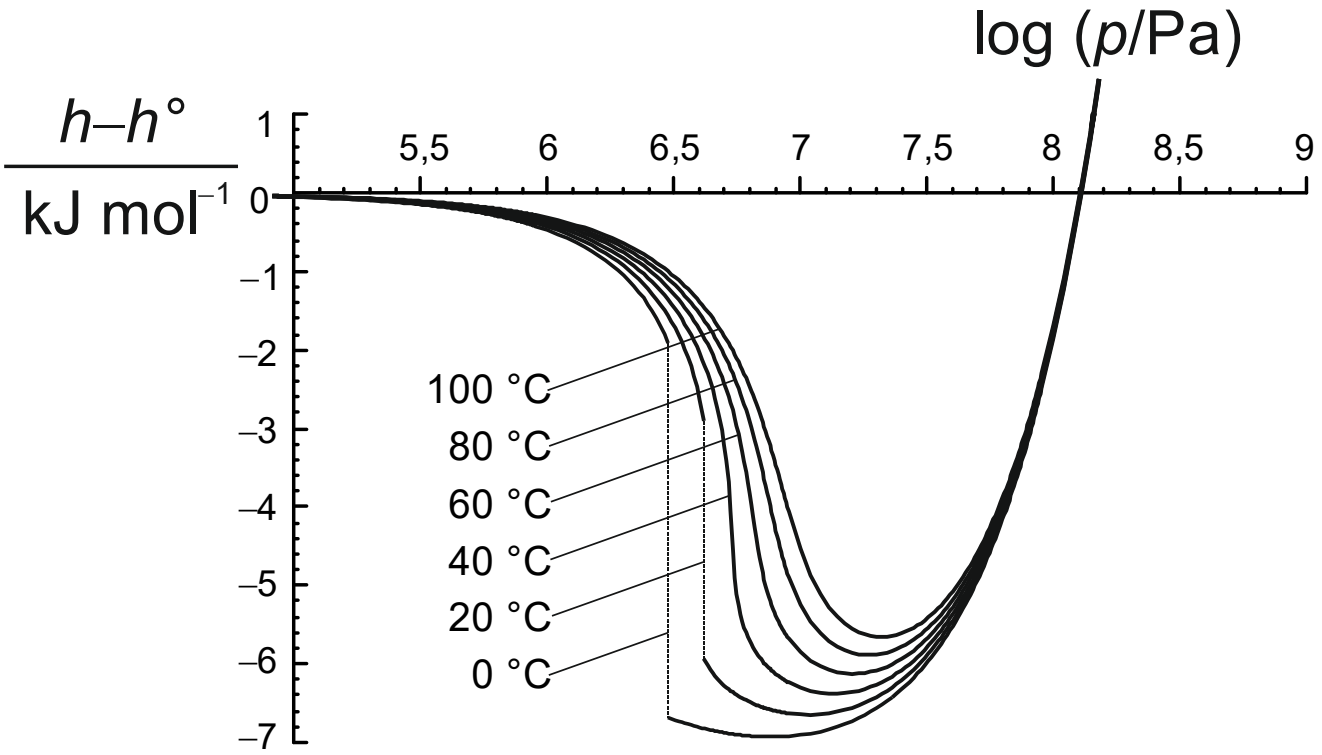
$$h - h^\circ = RT(z-1) - \frac{a}{v}$$

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b}$$

vdW

etan



Funkcije odstupanja

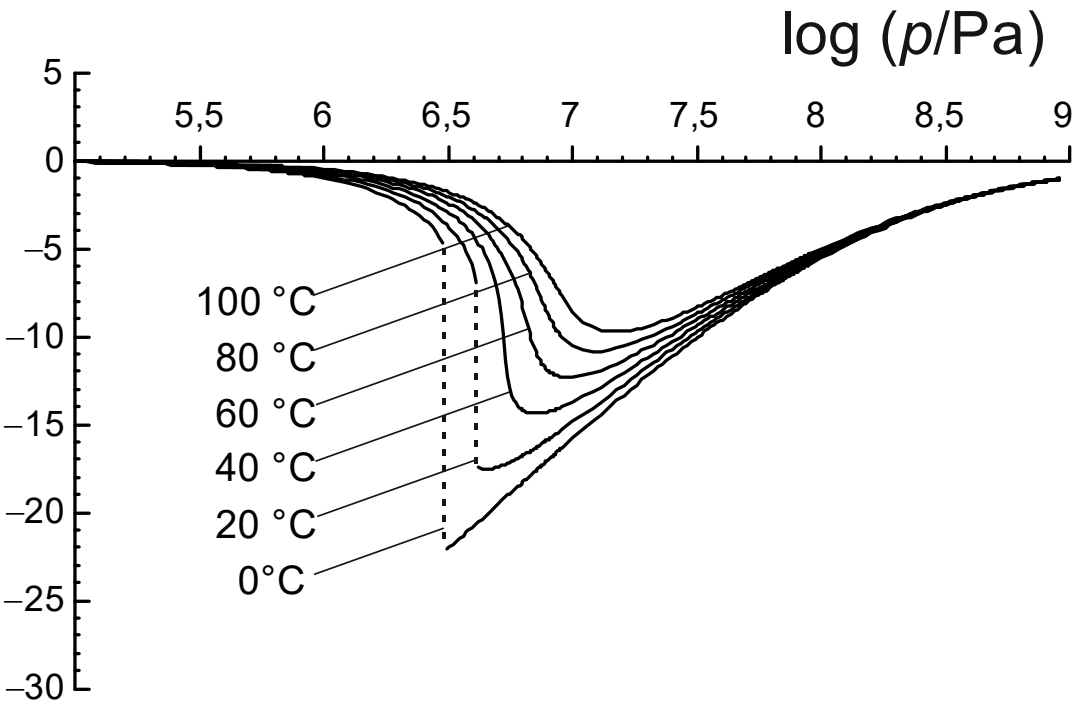
$$s - s^\circ - R\ln\frac{p^\circ}{p} = R\ln z + \int_\infty^v \left[\left(\frac{\partial p}{\partial T}\right)_v - \frac{R}{v}\right] dv$$

$$s - s^\circ - R\ln\frac{p^\circ}{p} = R\ln z + R\ln\frac{v-b}{v}$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b}$$

vdW

etan



Funkcije odstupanja

Peng-Robinsonova jednadžba

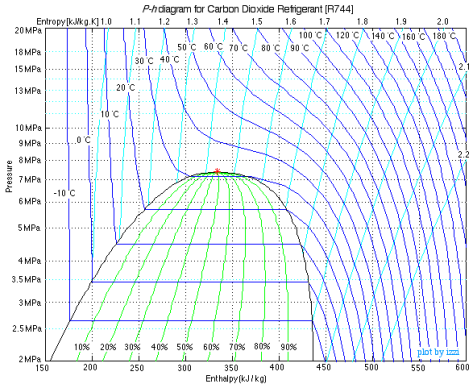
$$s - s^{\circ} = -R \ln \frac{v^{\circ}}{v - b} + \frac{a}{b\, 2\sqrt{2}} \ln \frac{v + b\left(1 + \sqrt{2}\right)}{v + b\left(1 - \sqrt{2}\right)} \left(\frac{\partial \alpha}{\partial T} \right)_v$$

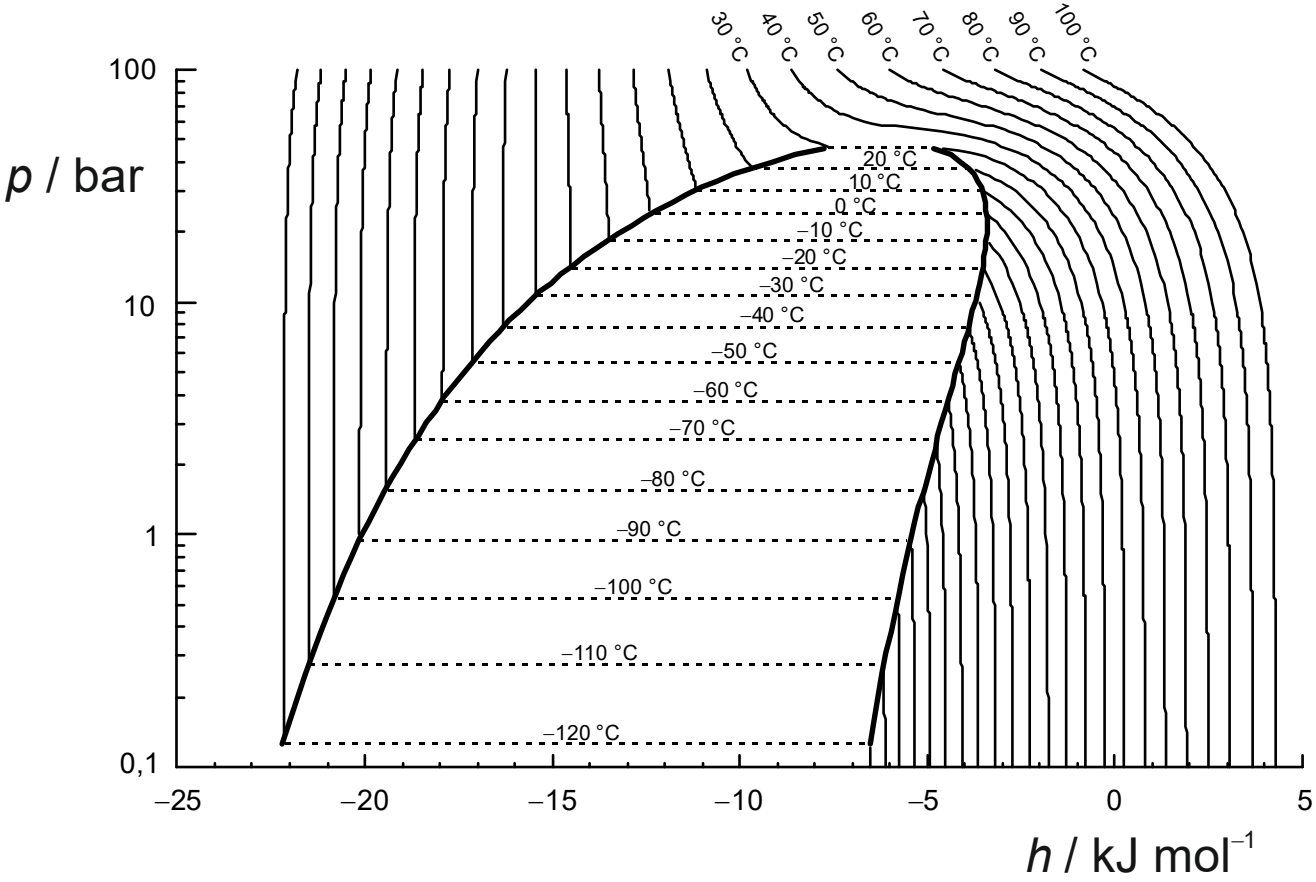
$$h - h^{\circ} = \frac{a}{b\, 2\sqrt{2}} \ln \frac{v + b\left(1 + \sqrt{2}\right)}{v + b\left(1 - \sqrt{2}\right)} \left[T \left(\frac{\partial \alpha}{\partial T} \right)_v - \alpha \right] + RT\left(z - 1\right)$$

Konstrukcija toplinskih dijagrama

Etan T_K=305,32 K, p_K=48,72 bar, ω=0,099

$$\frac{c_p^{id}}{R} = 4{,}178 - 4{,}427\cdot10^{-3}\frac{T}{K} + 5{,}660\cdot10^{-5}\left(\frac{T}{K}\right)^2 - 6{,}651\cdot10^{-8}\left(\frac{T}{K}\right)^3 + 2{,}487\cdot10^{-11}\left(\frac{T}{K}\right)^4$$

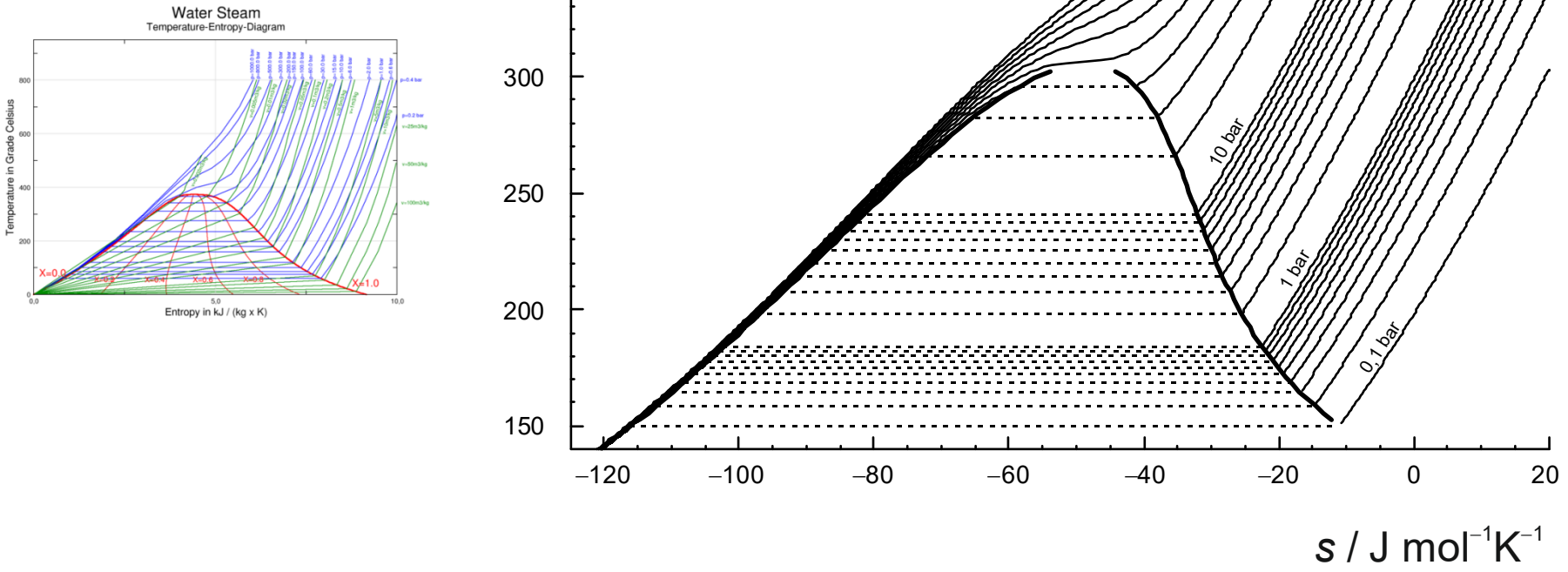




Konstrukcija toplinskih dijagrama

Etan T_K=305,32 K, p_K=48,72 bar, ω=0,099

$$\frac{c_p^{id}}{R} = 4{,}178 - 4{,}427\cdot10^{-3}\frac{T}{\mathrm{K}} + 5{,}660\cdot10^{-5}\left(\frac{T}{\mathrm{K}}\right)^2 - 6{,}651\cdot10^{-8}\left(\frac{T}{\mathrm{K}}\right)^3 + 2{,}487\cdot10^{-11}\left(\frac{T}{\mathrm{K}}\right)^4$$



Načelo korespondentnih stanja

$$h - h^\circ = \int_0^p \left[v - T\left(\frac{\partial v}{\partial T}\right)_p \right] dp$$

$$s - s^\circ = \int_0^p \left[\frac{R}{p} - \left(\frac{\partial v}{\partial T}\right)_p \right] dp$$

$$\frac{h - h^\circ}{T_\mathrm{K}} = -RT_\mathrm{r}^2 \int_0^{p_\mathrm{r}} \left[\frac{1}{p_\mathrm{r}} \left(\frac{\partial z}{\partial T_\mathrm{r}}\right)_{p_\mathrm{r}} \right] dp_\mathrm{r}$$

$$s - s^\circ = R \int_0^{p_\mathrm{r}} \left[\frac{1 - z}{p_\mathrm{r}} - \frac{T_\mathrm{r}}{p_\mathrm{r}} \left(\frac{\partial z}{\partial T_\mathrm{r}}\right)_{p_\mathrm{r}} \right] dp_\mathrm{r}$$

Načelo korespondentnih stanja

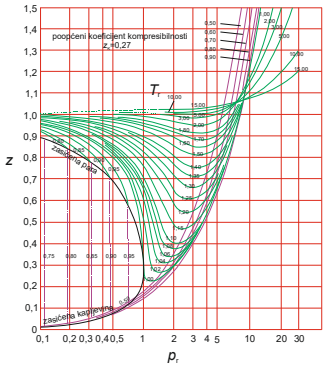
$$h - h^\circ = \int_0^p \left[v - T\left(\frac{\partial v}{\partial T}\right)_p \right] dp \qquad s - s^\circ = \int_0^p \left[\frac{R}{p} - \left(\frac{\partial v}{\partial T}\right)_p \right] dp$$

$$\frac{h - h^\circ}{R T_\mathrm{K}} = -T_\mathrm{r}^2 \int_0^{p_\mathrm{r}} \left[\frac{1}{p_\mathrm{r}} \left(\frac{\partial z}{\partial T_\mathrm{r}}\right)_{p_\mathrm{r}} \right] dp_\mathrm{r} \qquad s - s^\circ = R \int_0^{p_\mathrm{r}} \left[\frac{1 - z}{p_\mathrm{r}} - \frac{T_\mathrm{r}}{p_\mathrm{r}} \left(\frac{\partial z}{\partial T_\mathrm{r}}\right)_{p_\mathrm{r}} \right] dp_\mathrm{r}$$

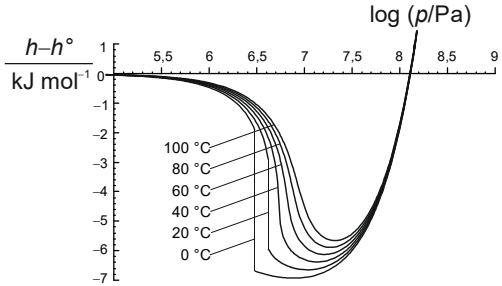
$$\frac{h - h^\circ}{T_\mathrm{K}} = \mathrm{f}\left(p_\mathrm{r}, T_\mathrm{r}\right) \qquad s - s^\circ = \mathrm{f}\left(p_\mathrm{r}, T_\mathrm{r}\right)$$

Načelo termodinamičke sličnosti

$$z = \mathrm{f}\left(p_\mathrm{r}, T_\mathrm{r}, z_\mathrm{K}\right)$$

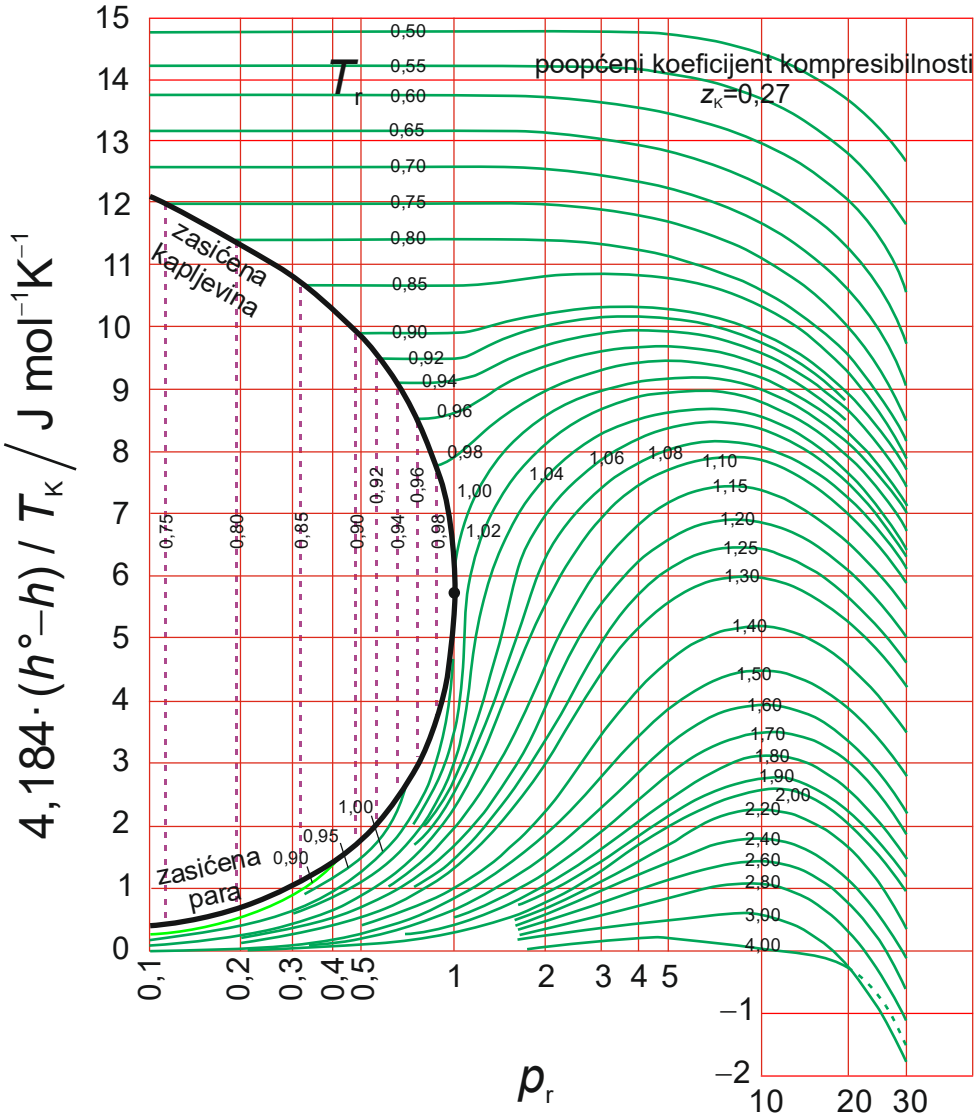


Jednadžbe stanja



$$\frac{h - h^\circ}{T_\mathrm{K}} = \mathrm{f}\left(p_\mathrm{r}, T_\mathrm{r}, z_\mathrm{K}\right)$$

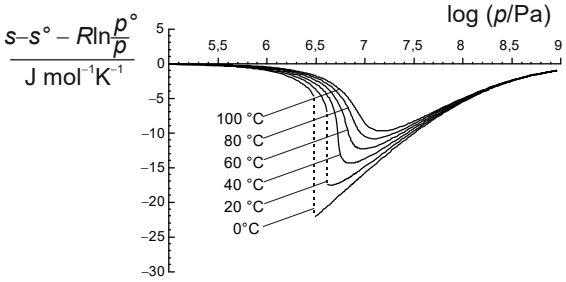
$$s - s^\circ = \mathrm{f}\left(p_\mathrm{r}, T_\mathrm{r}, z_\mathrm{K}\right)$$

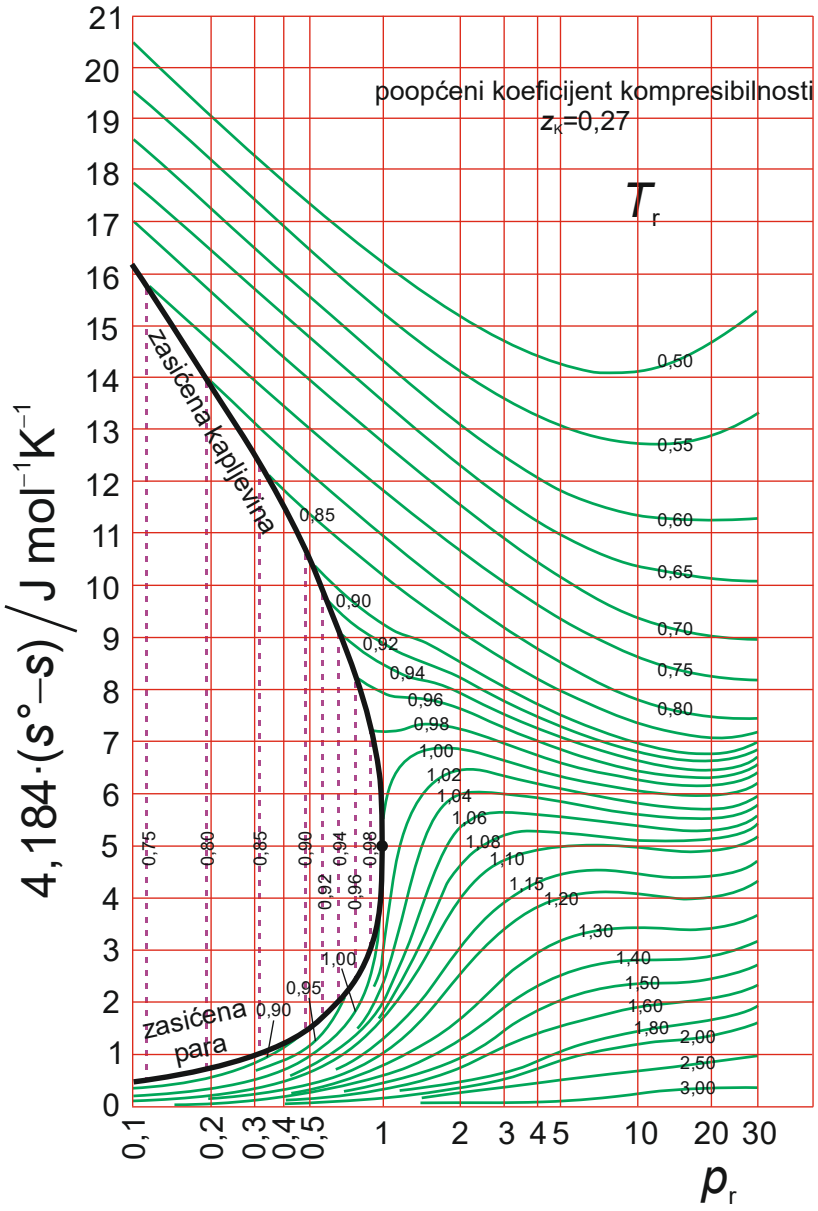


Načelo termodinamičke sličnosti

$$s - s^\circ = \mathrm{f}\left(p_\mathrm{r}, T_\mathrm{r}, z_\mathrm{K}\right)$$

Jednadžbe stanja



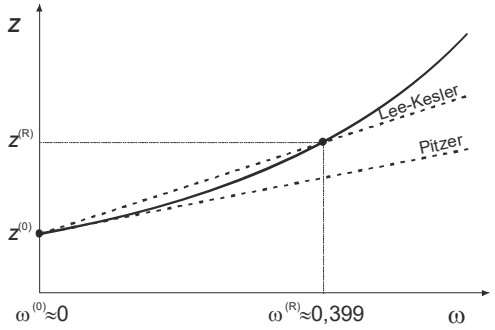


Načelo termodinamičke sličnosti

Lee-Keslerova korelacija (1975)

$$z = \mathrm{f}\left(p_\mathrm{r}, T_\mathrm{r}, \omega\right)$$

$$z = z^{(0)}\left(T_\mathrm{r}, p_\mathrm{r}\right) + \omega z^{(1)}\left(T_\mathrm{r}, p_\mathrm{r}\right)$$



$$\left(\frac{h^\circ - h}{RT_\mathrm{K}}\right) = \left(\frac{h^\circ - h}{RT_\mathrm{K}}\right)^{(0)} + \omega\left(\frac{h^\circ - h}{RT_\mathrm{K}}\right)^{(1)}$$

$$\left(\frac{s^\circ - s}{R}\right) = \left(\frac{s^\circ - s}{R}\right)^{(0)} + \omega\left(\frac{s^\circ - s}{R}\right)^{(1)} - \ln\frac{p^\circ}{p}$$

Fugacitet

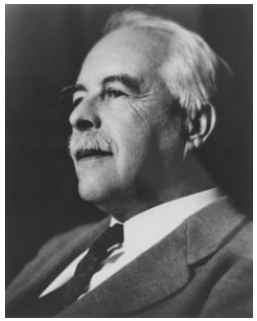
Zatvoreni sustavi, p,T=konst

$$g = h - Ts = u + pv - Ts$$

$$dg = vdp - sdT$$

$$(dg)_T = vdp$$

$$(dg)_T^{\mathrm{id}} = \frac{RT}{p}dp = RTd\ln p$$



G. N. Lewis (1901)

$$(dg)_T = vdp = RTd\ln f$$

Fugacitet je tlak koji bi realni plin imao kada bi se vladao kao idealan ???

„Convenience functions" Sandler
„Zgodne, prikladne funkcije"



Logaritamsko računalo (šiber)

Koeficijent fugaciteta

Razlika realnog i idealnog plina

$$(dg)_T - (dg)_T^{\mathrm{id}} = RTd\ln f - RTd\ln p$$

$$d\left(g - g^{\mathrm{id}}\right) = RTd\ln\frac{f}{p}$$

$$\int_{g-g^{\mathrm{id}}(p=0)}^{g-g^{\mathrm{id}}(p)} d\left(g - g^{\mathrm{id}}\right) = RT\int_{\ln(f/p)(p=0)}^{\ln(f/p)(p)} d\ln\frac{f}{p}$$

$$g - g^{\mathrm{id}} = \ln\frac{f}{p}$$

$$\lim_{p\to 0}\frac{f}{p} = 1$$

G. N. Lewis (1901)

Koeficijent fugaciteta

$$\varphi = \frac{f}{p}$$

„Convenience functions” Sandler
„Zgodne, prikladne funkcije”

Izračunavanje fugaciteta iz jednadžbi stanja

Definicijski izraz – volumetrijska svojstva

$$\left(dg\right)_T = vdp = RTd\ln f$$

$$RT\left(\frac{\partial \ln f}{\partial p}\right)_T = v$$

Jednadžbe stanja eksplicitne po

volumenu

$$f = p\exp\left[\frac{1}{RT}\int_0^p\left(v-\frac{RT}{p}\right)dp\right]$$

$$\ln\varphi = \int_0^p\left(z-1\right)d\ln p$$

tlaku

$$f = p\exp\left[\left(z-1\right)-\ln z+\frac{1}{RT}\int_\infty^v\left(\frac{RT}{v}-p\right)dv\right]$$

$$\ln\varphi = \frac{1}{RT}\int_\infty^v\left(\frac{RT}{v}-p\right)dv+\left(z-1\right)-\ln z$$

Izračunavanje koeficijenta fugaciteta iz jednadžbi stanja

$$\ln\varphi = \ln\frac{v}{v-b} + \frac{a}{bRT^{3/2}}\ln\frac{v}{v+b} + (z-1) - \ln z$$ RK

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

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

Izračunavanje Gibbsove energije iz fugaciteta

Iznos Gibbsove energije ovisi o izboru referentnog stanja
Preko funkcija odstupanja (u odnosu na idealni plin pri 1 bar i 25 °C)

$$g = h - Ts$$

$$h = h_{\text{ref}} + \int_{T^\circ}^{T} c_p^{\text{id}}\, dT + RT(z-1) + \int_{\infty}^{v}\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] dv$$

$$s = s_{\text{ref}} + \int_{T^\circ}^{T} \frac{c_p^{\text{id}}}{T}\, dT + R\ln\frac{v}{v^\circ} + \int_{\infty}^{v}\left[\left(\frac{\partial p}{\partial T}\right)_v - \frac{R}{v}\right] dv$$

Preko fugaciteta (u odnosu na realni plin pri 1 bar i temperaturi sustava)
Standardno stanje plina – stanje realnog plina pri 1 bar i temperaturi sustava

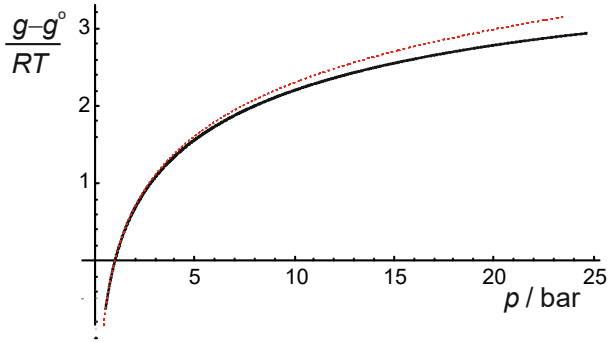
$$f^\circ = p^\circ = 1 \text{ bar (nekad jedna atmosfera)}$$

Izračunavanje Gibbsove energije iz fugaciteta

Idealni plin

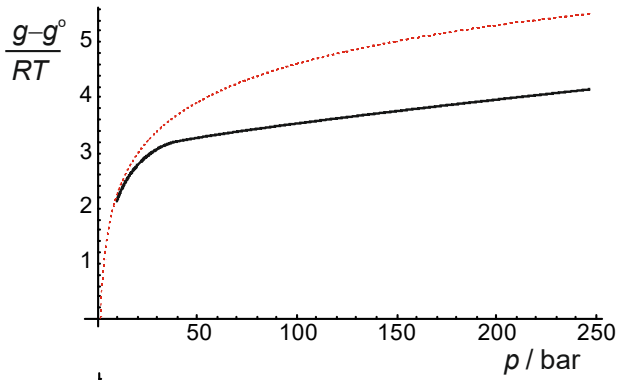
$$g = g^\circ + RT \ln \frac{p}{p^\circ}$$

$$\frac{\left(g - g^\circ\right)^{\mathrm{id}}}{RT} = \ln \frac{p}{p^\circ}$$

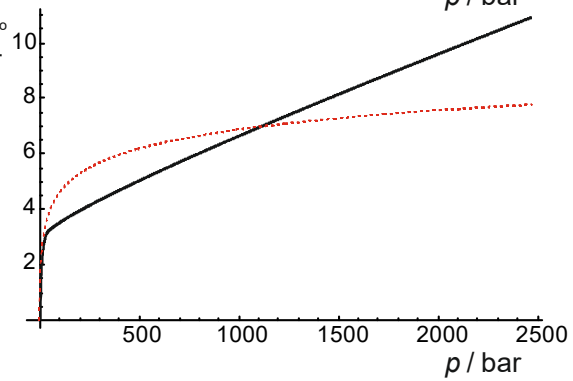


SRK, dušik

$$\frac{g - g^\circ}{RT} = \ln \frac{f}{f^\circ}$$

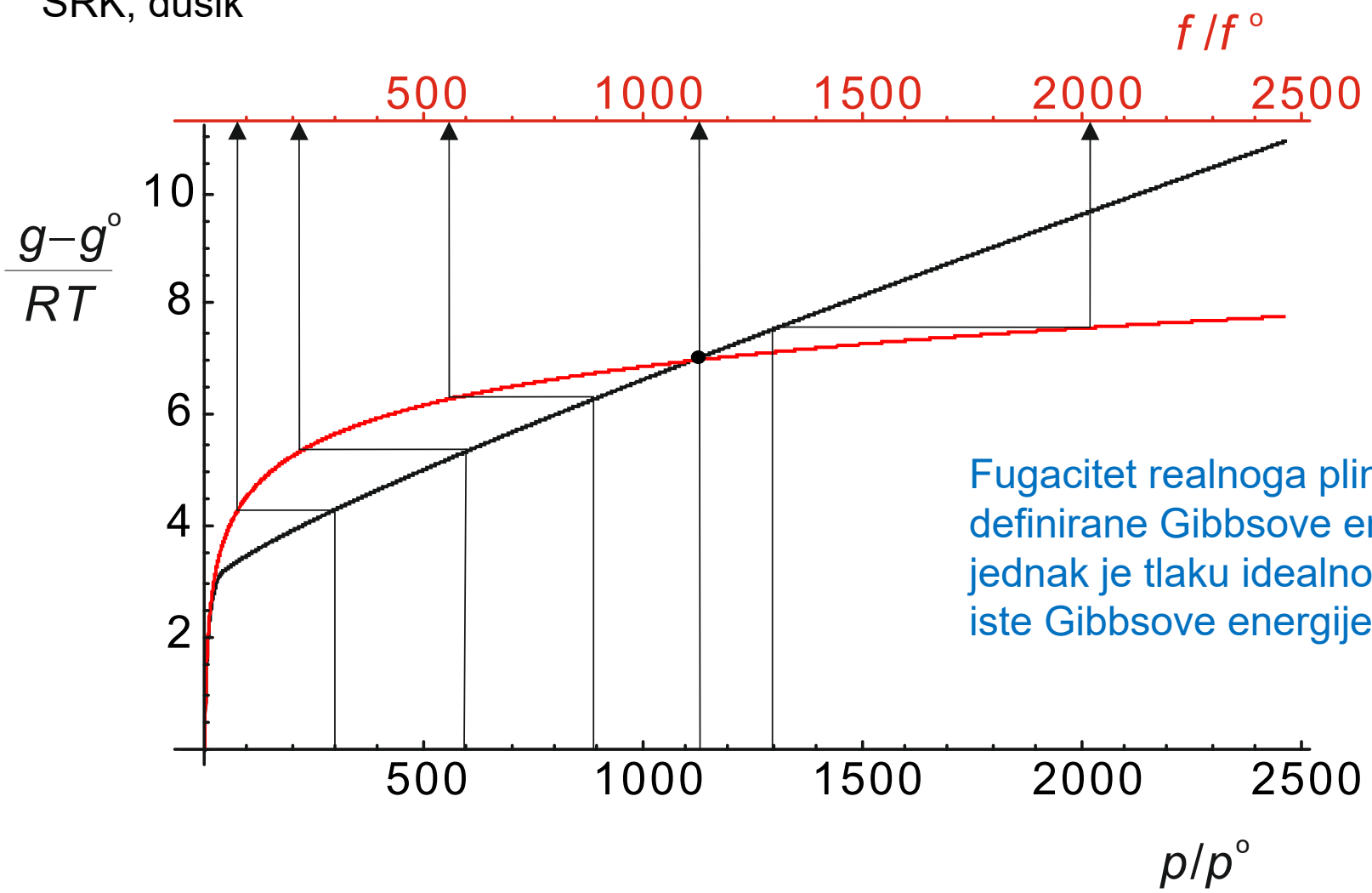


$$\frac{g - g^\circ}{RT} = \ln \frac{v^\circ}{v - b} + \frac{a\alpha}{bRT} \ln \frac{v}{v + b} + (z - 1)$$



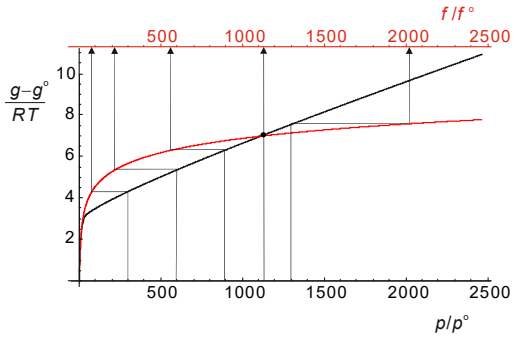
Izračunavanje Gibbsove energije iz fugaciteta

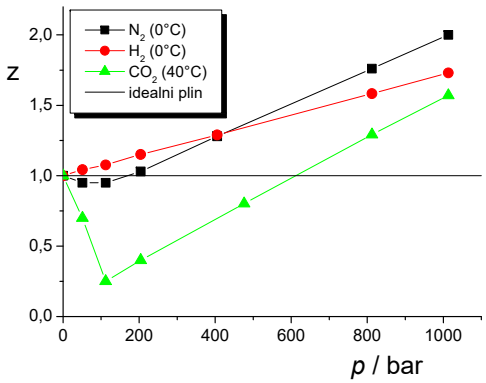
SRK, dušik

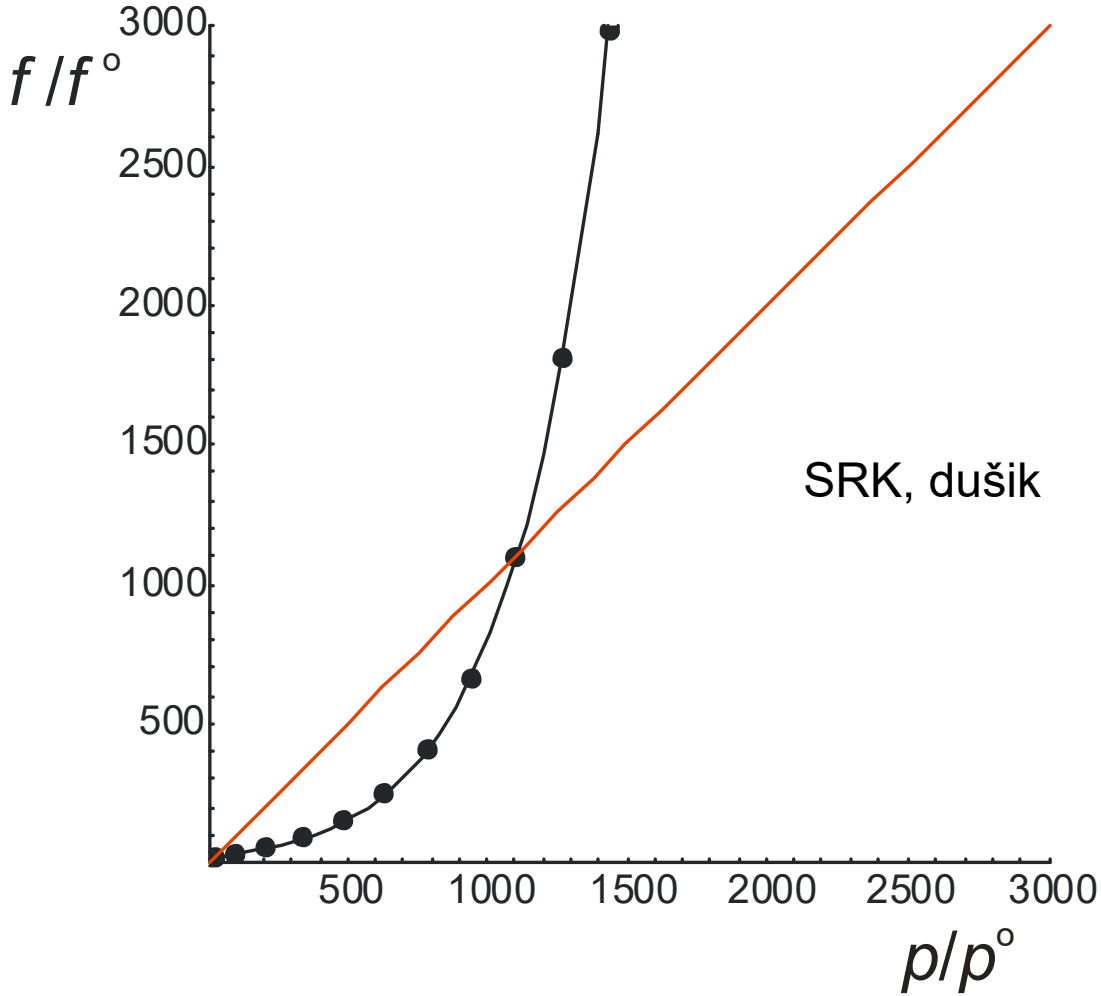


Fugacitet realnoga plina definirane Gibbsove energije jednak je tlaku idealnoga plina iste Gibbsove energije.

Izračunavanje Gibbsove energije iz fugaciteta







Načelo usporedivih stanja

$$\ln\varphi = \int_0^p \frac{(z-1)}{p} dp$$

$$\ln\varphi = \int_0^p \frac{(z-1)}{p_r} dp_r$$

Dijagrami i tablice

$$\ln\varphi = \mathrm{f}\left(p_r, T_r\right)$$

Načelo termodinamičke sličnosti

Lee-Kesler $\ln\varphi = \mathrm{f}\left(p_\mathrm{r}, T_\mathrm{r}, \omega\right)$

$$\ln\varphi = \ln\varphi^{(0)} + \frac{\omega}{\omega^{(\mathrm{R})}}\left(\ln\varphi^{(\mathrm{R})} - \ln\varphi^{(0)}\right)$$

$$z = \frac{v}{v_\mathrm{id}}$$

$$\ln\varphi = \ln\varphi^{(0)} + \omega\ln\varphi^{(1)}$$

$$z = z^{(0)}\left(T_\mathrm{r}, p_\mathrm{r}\right) + \omega z^{(1)}\left(T_\mathrm{r}, p_\mathrm{r}\right)$$

$$\varphi = \frac{f}{p}$$

$$\left(\frac{h^\circ - h}{RT_\mathrm{K}}\right) = \left(\frac{h^\circ - h}{RT_\mathrm{K}}\right)^{(0)} + \omega\left(\frac{h^\circ - h}{RT_\mathrm{K}}\right)^{(1)}$$

$$\left(\frac{s^\circ - s}{R}\right) = \left(\frac{s^\circ - s}{R}\right)^{(0)} + \omega\left(\frac{s^\circ - s}{R}\right)^{(1)} - \ln\frac{p^\circ}{p}$$