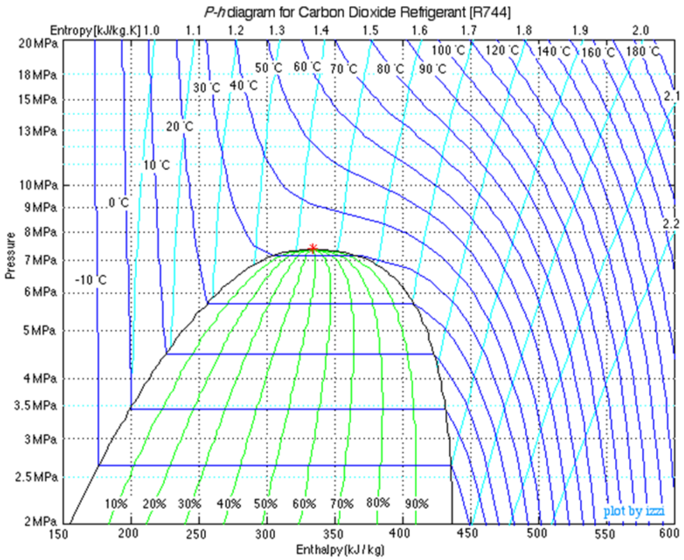
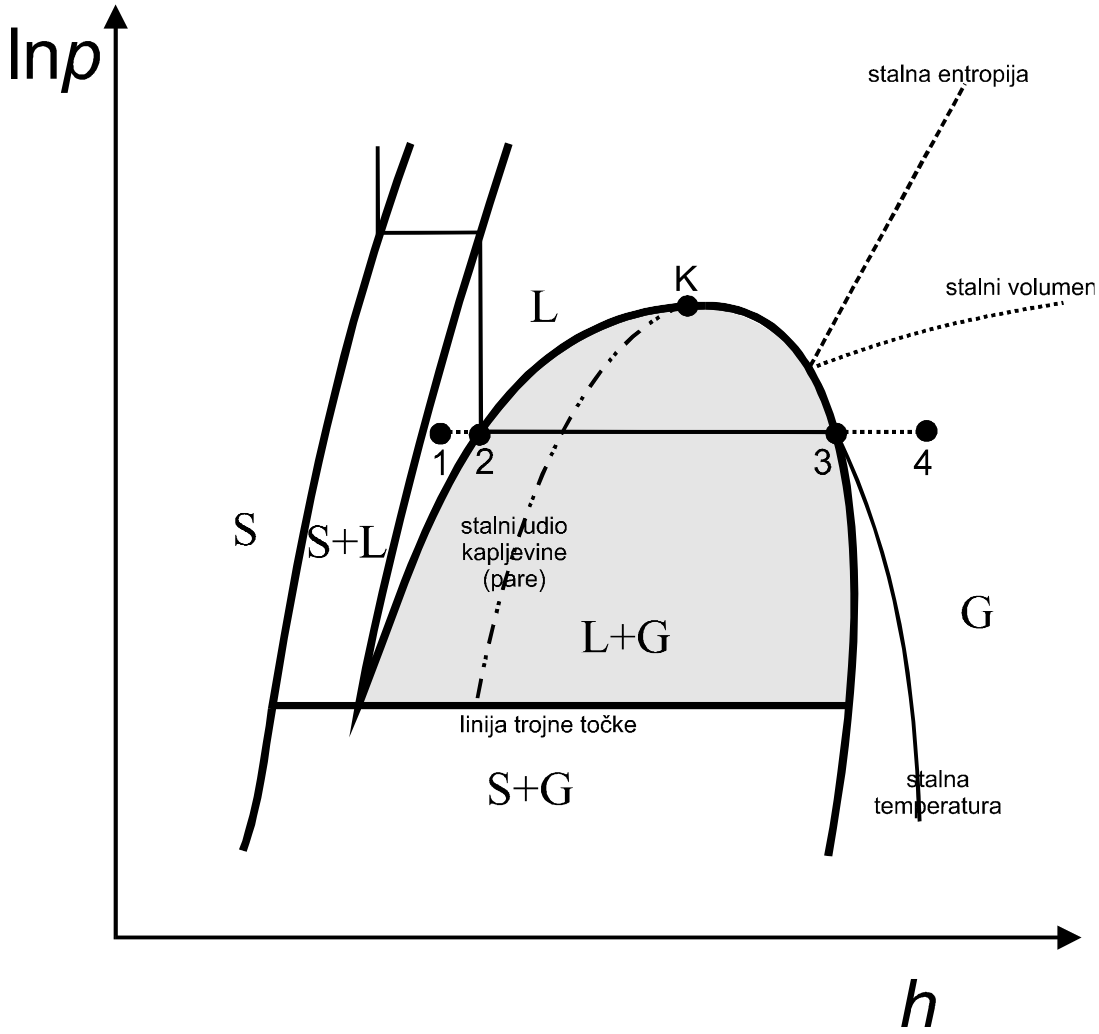
Termodinamička svojstva realnih fluida

Toplinske tablice i dijagrami

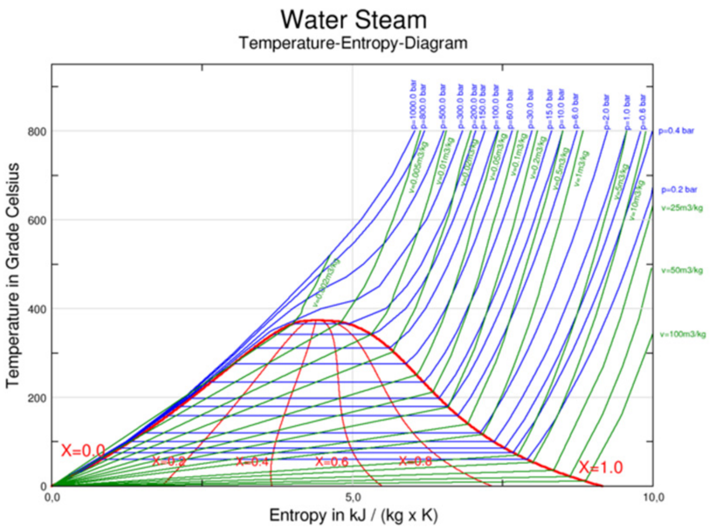
ph-dijagram
Rashladni
uređaji

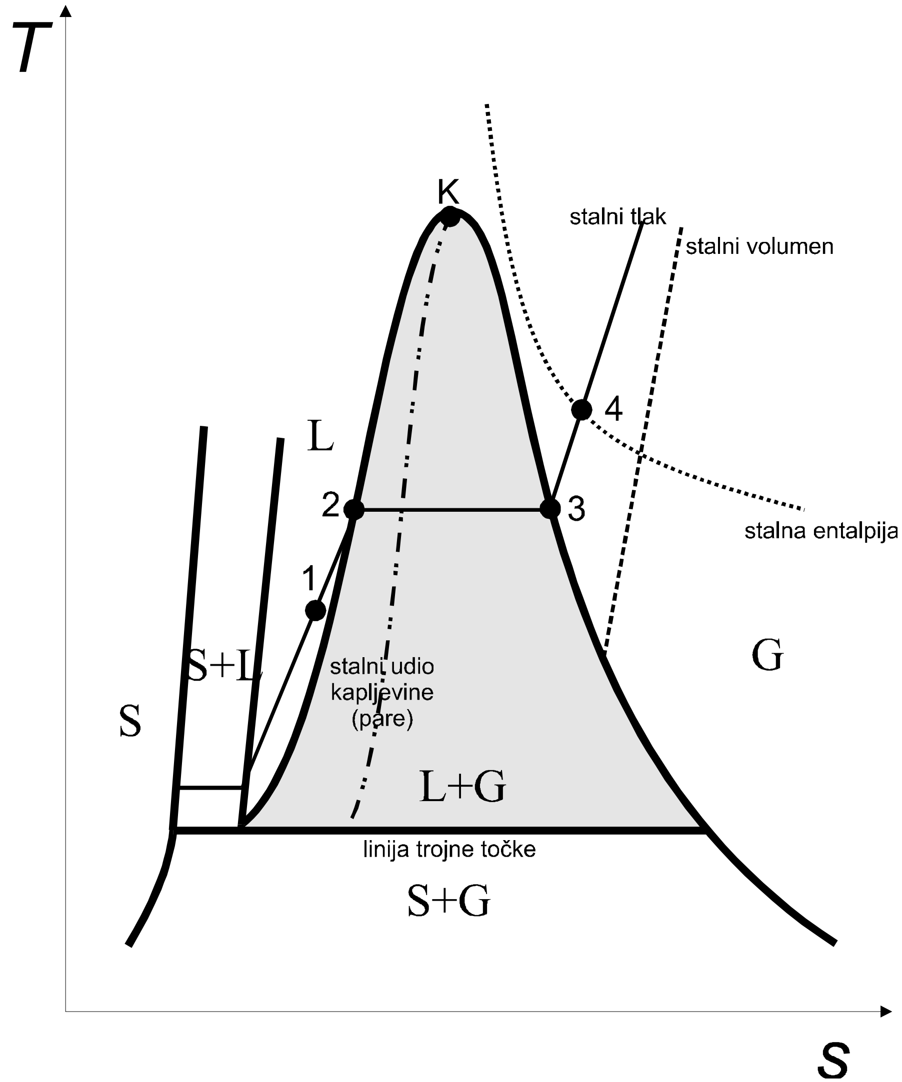




Toplinske tablice i dijagrami

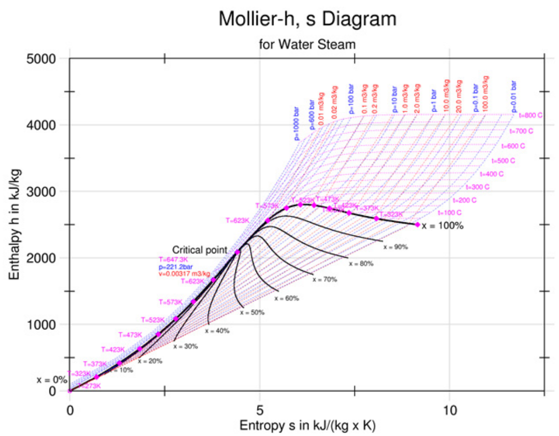
Ts-dijagram
Pretvorba
Energije

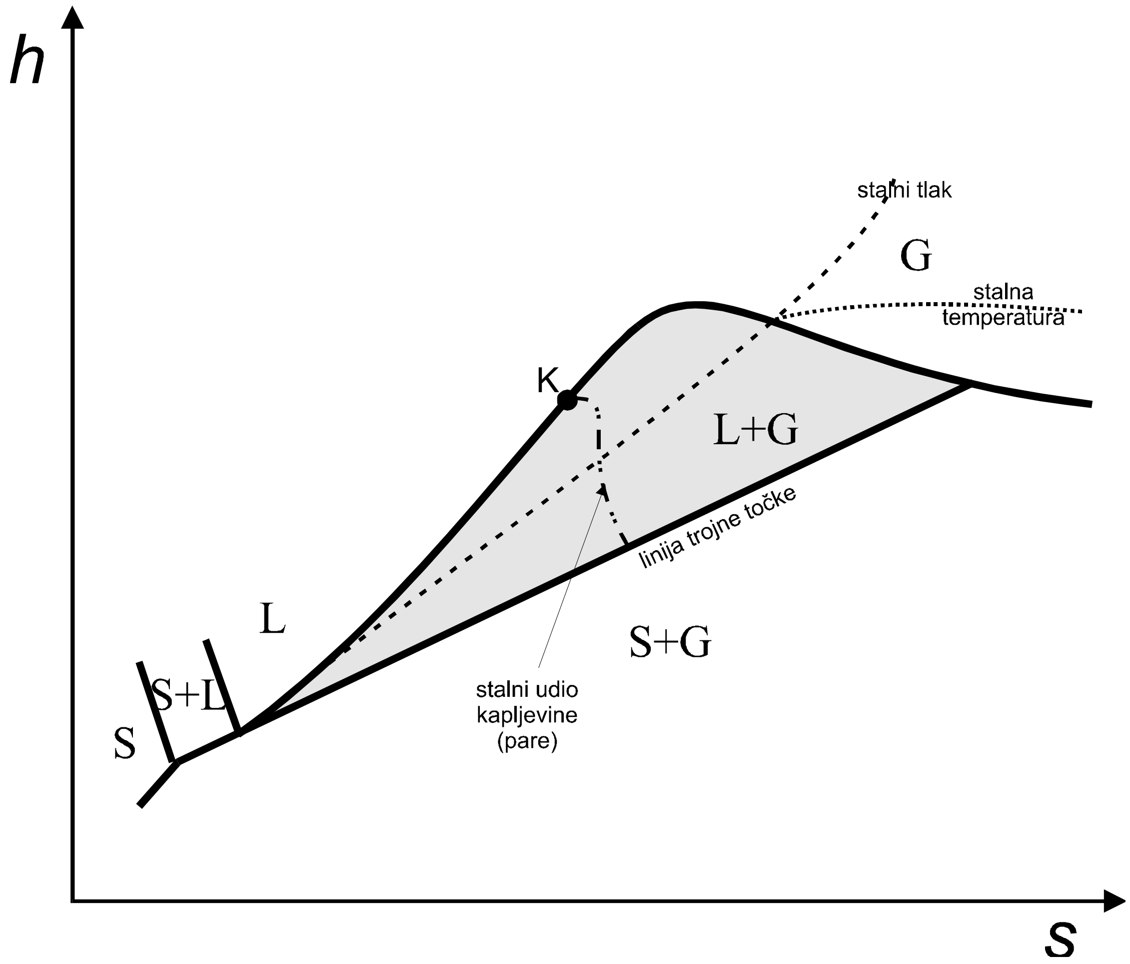




Toplinske tablice i dijagrami

hs-dijagram
Mlaznice
Difuzori
Turbine
Kompresori

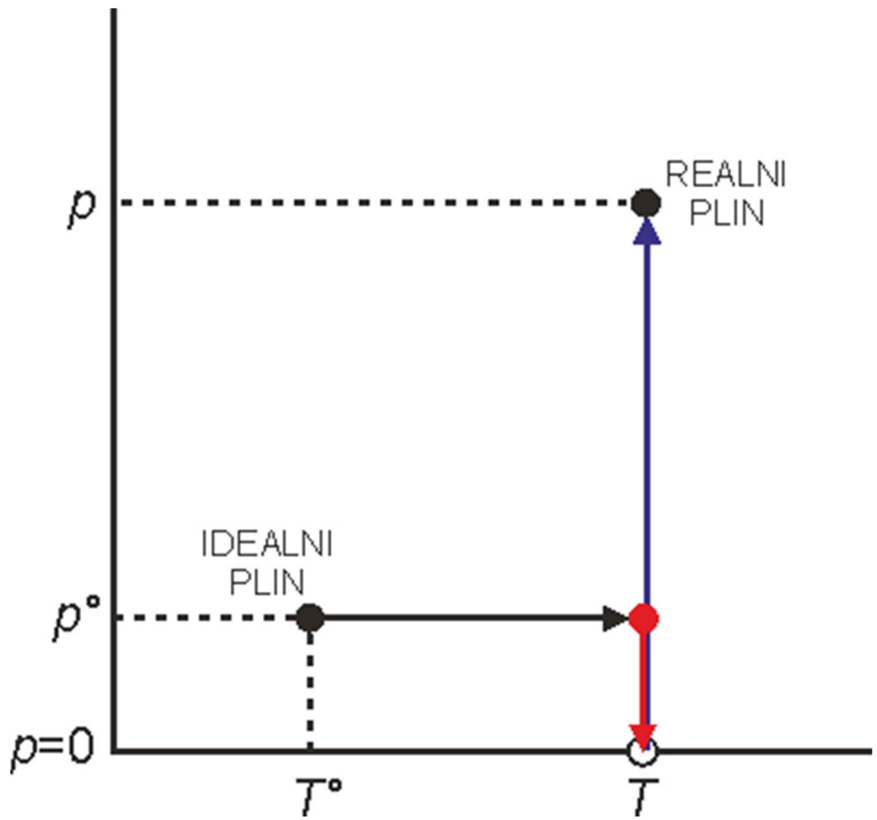




Konstrukcija toplinskih dijagrama

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

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

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

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:

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

Konstrukcija toplinskih dijagrama

Entropijska promjena

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

Temperatura

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

Tlak

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \qquad s - s^\circ = \int_{p^\circ}^{0} \left[-\left(\frac{\partial v}{\partial T}\right)_p \right] dp + \int_0^p \left[-\left(\frac{\partial v}{\partial T}\right)_p \right] dp$$

$$s - s^\circ = \int_{p^\circ}^{0} \left[-\frac{R}{p} \right] dp - \int_0^p \left[\frac{R}{p} \right] dp + \int_0^p \left[\frac{R}{p} \right] dp + \int_0^p \left[-\left(\frac{\partial v}{\partial T}\right)_p \right] dp$$

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

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

Funkcije odstupanja

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

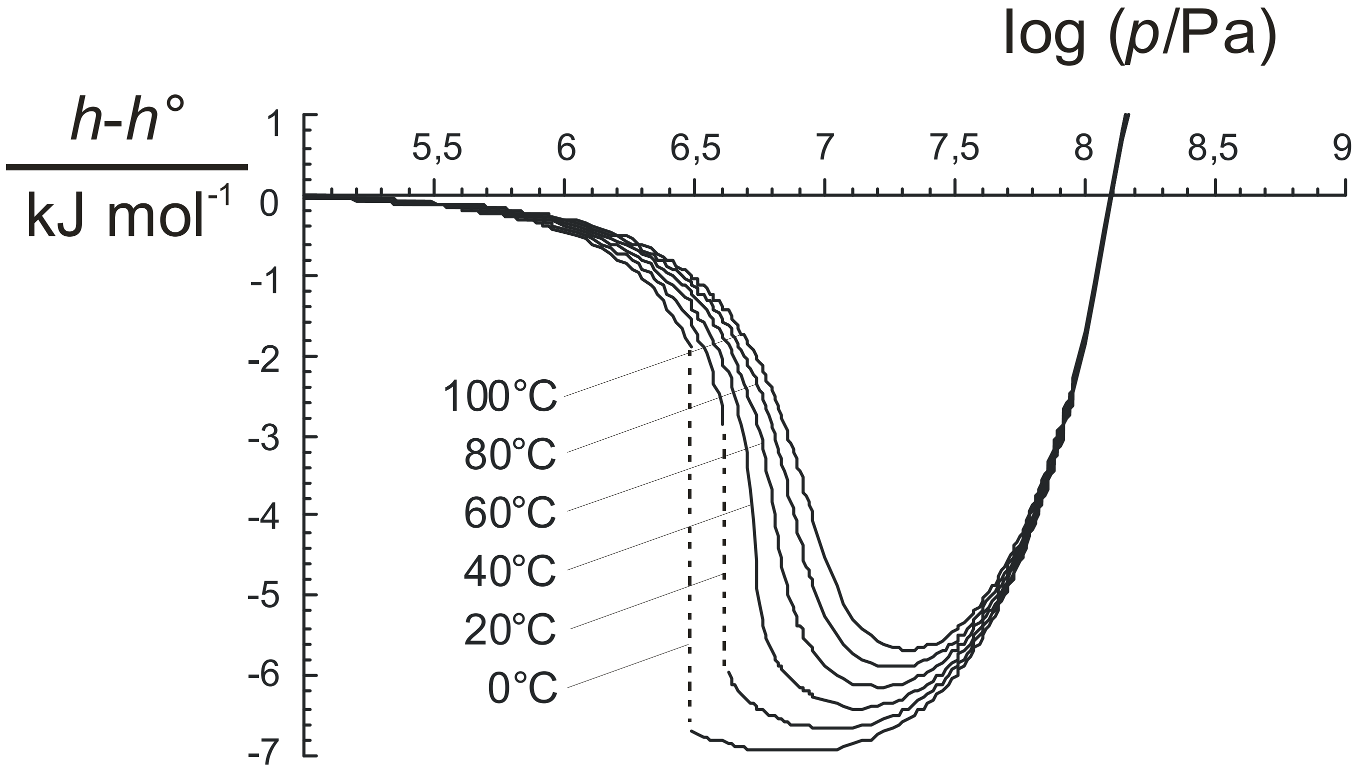
$$h - h^{\circ} = RT(z-1) - \frac{a}{v}$$

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

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

vdW

etan

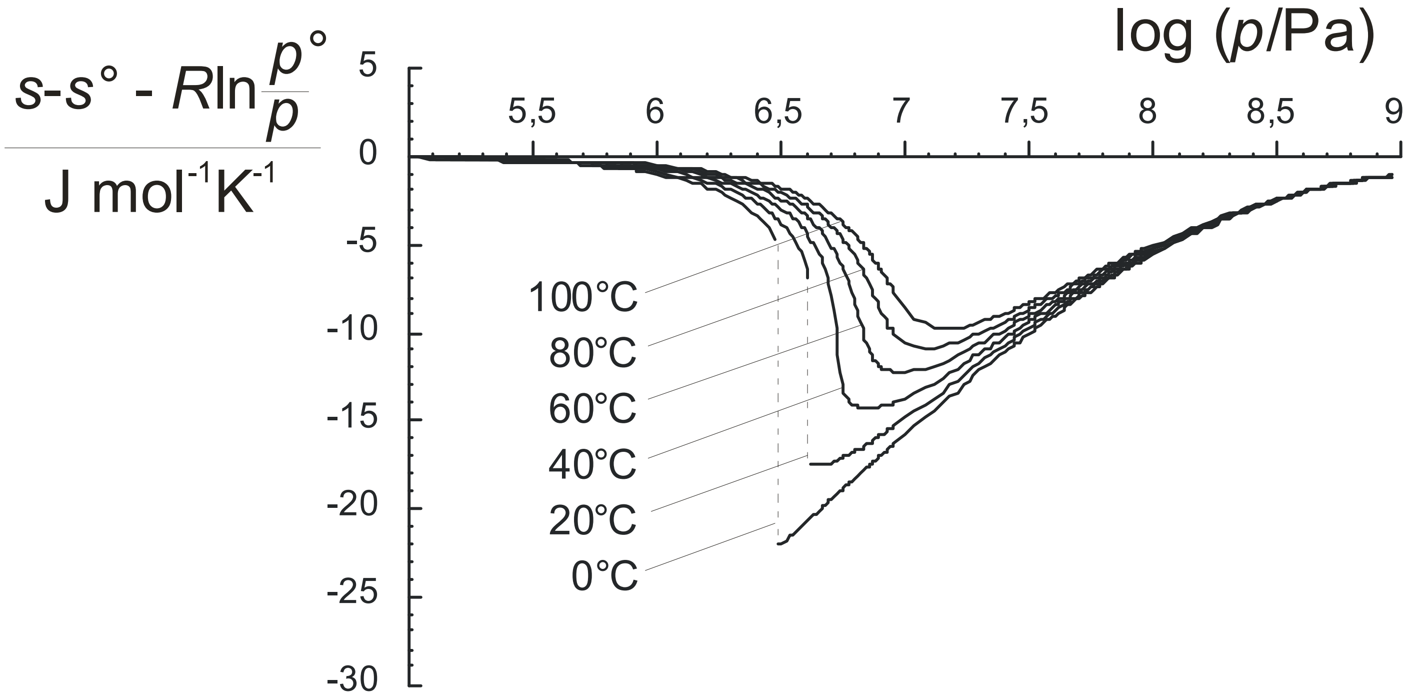


Funkcije odstupanja

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

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

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



vdW

etan

Funkcije odstupanja

Peng-Robinsonova jednadžba

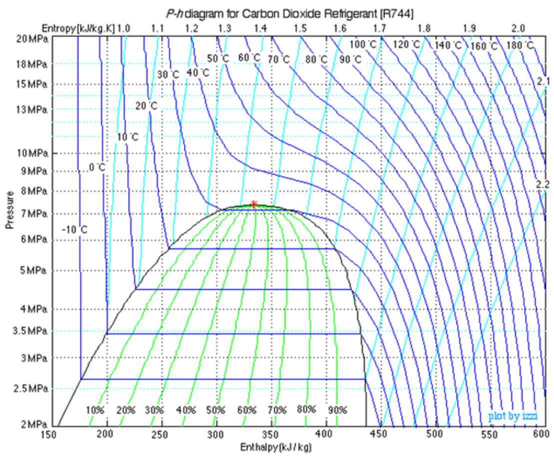
$$s - s^{\circ} = -R\ln\frac{v^{\circ}}{v-b} + \frac{a}{b\,2\sqrt{2}}\ln\frac{v+b\left(1+\sqrt{2}\right)}{v+b\left(1-\sqrt{2}\right)}\left(\frac{\partial\alpha}{\partial T}\right)_v$$

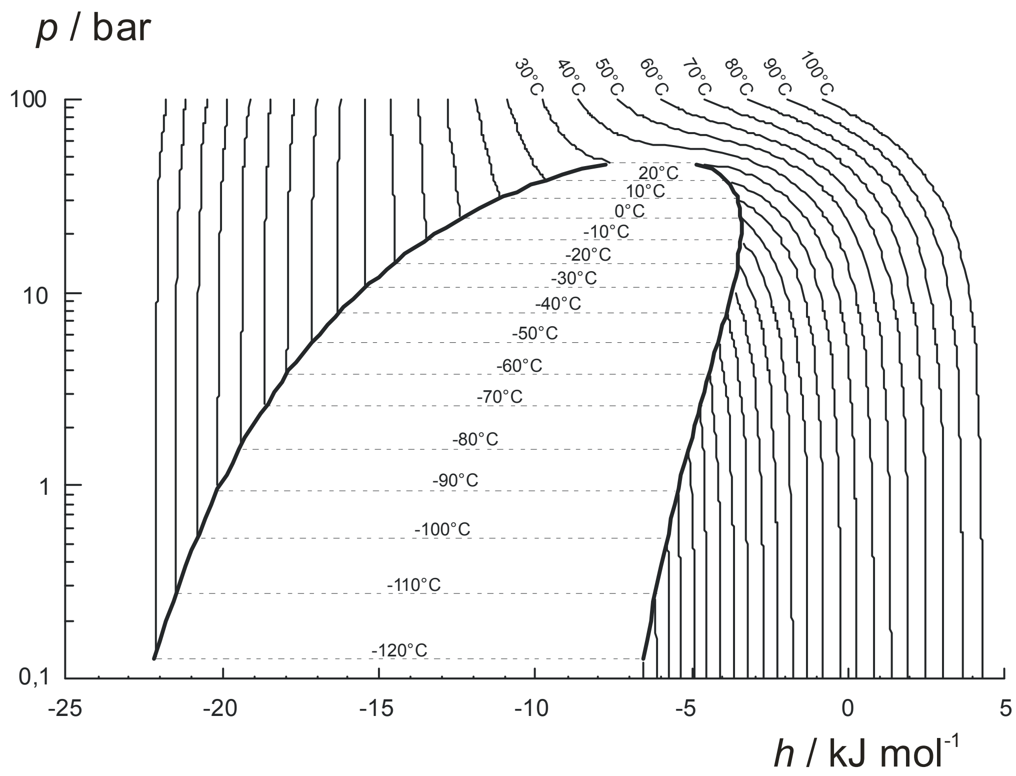
$$h - h^{\circ} = \frac{a}{b\,2\sqrt{2}}\ln\frac{v+b\left(1+\sqrt{2}\right)}{v+b\left(1-\sqrt{2}\right)}\left[T\left(\frac{\partial\alpha}{\partial T}\right)_v - \alpha\right] + RT\left(z-1\right)$$

Konstrukcija toplinskih dijagrama

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

$$\frac{c_p^{id}}{R} = 4{,}178 - 4{,}427\cdot 10^{-3}\frac{T}{\mathrm{K}} + 5{,}660\cdot 10^{-5}\left(\frac{T}{\mathrm{K}}\right)^2 - 6{,}651\cdot 10^{-8}\left(\frac{T}{\mathrm{K}}\right)^3 + 2{,}487\cdot 10^{-11}\left(\frac{T}{\mathrm{K}}\right)^4$$

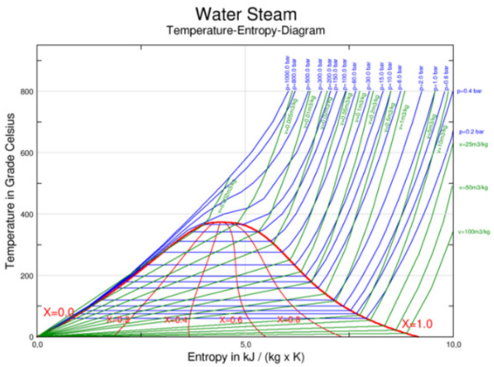


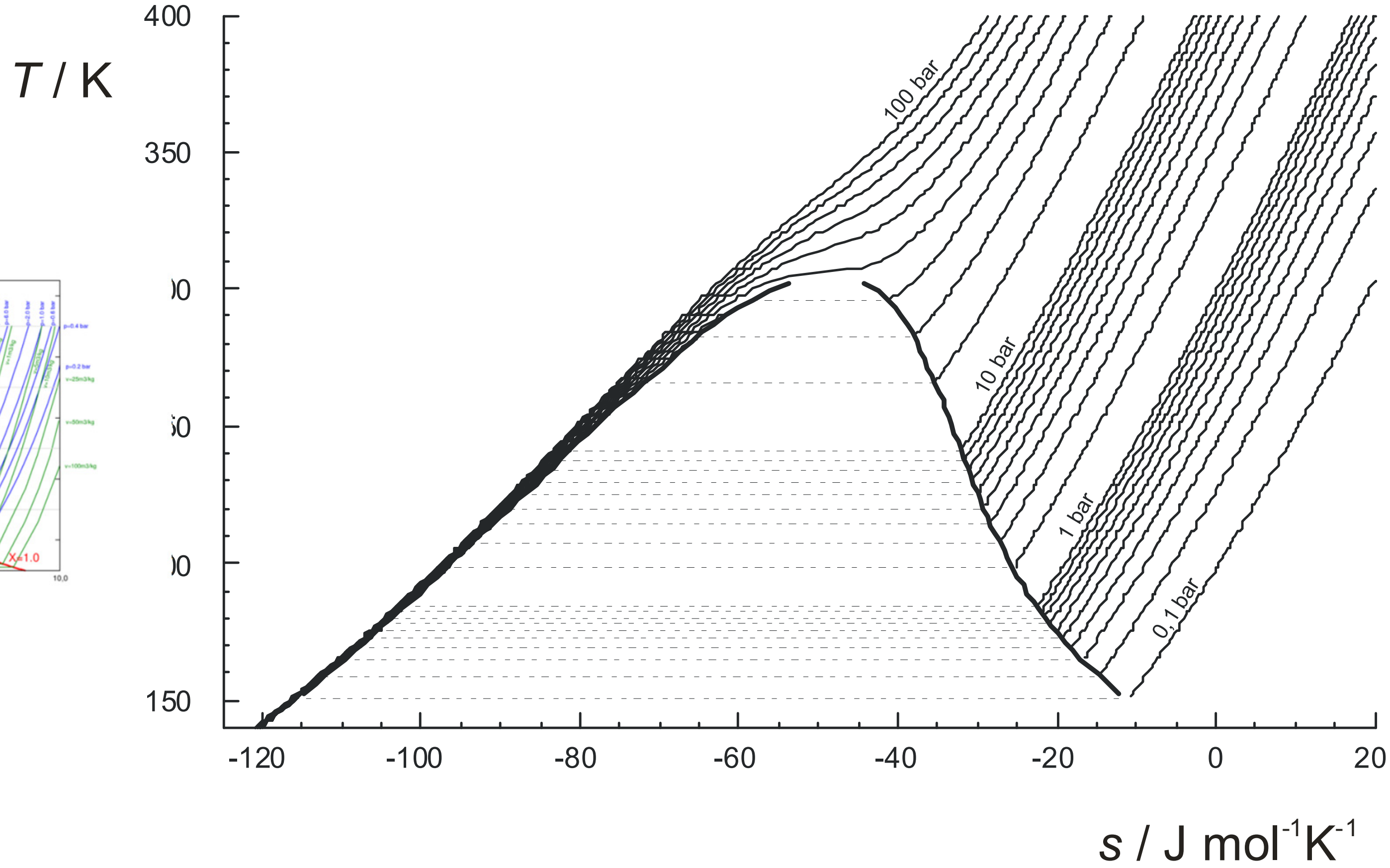


Konstrukcija toplinskih dijagrama

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

$$\frac{c_p^{\mathrm{id}}}{R} = 4,178 - 4,427\cdot 10^{-3}\,\frac{T}{\mathrm{K}} + 5,660\cdot 10^{-5}\left(\frac{T}{\mathrm{K}}\right)^2 - 6,651\cdot 10^{-8}\left(\frac{T}{\mathrm{K}}\right)^3 + 2,487\cdot 10^{-11}\left(\frac{T}{\mathrm{K}}\right)^4$$





Načelo korespondentnih stanja

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

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

Načelo korespondentnih stanja

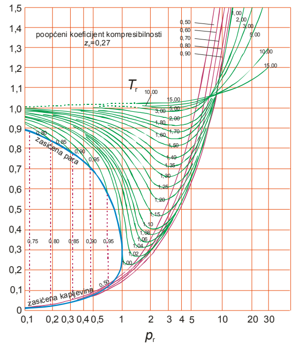
$$h - h^\circ = \int_0^p \left[v - T\left(\frac{\partial v}{\partial T}\right)_p \right] dp \qquad s - s^\circ = \int_0^p \left[\frac{R}{p} - \left(\frac{\partial v}{\partial T}\right)_p \right] dp$$

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

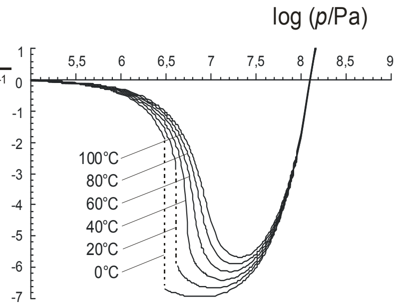
$$\frac{h - h^\circ}{T_\mathrm{K}} = \mathrm{f}\left(p_\mathrm{r}, T_\mathrm{r}\right) \qquad s - s^\circ = \mathrm{f}\left(p_\mathrm{r}, T_\mathrm{r}\right)$$

Načelo termodinamičke sličnosti

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

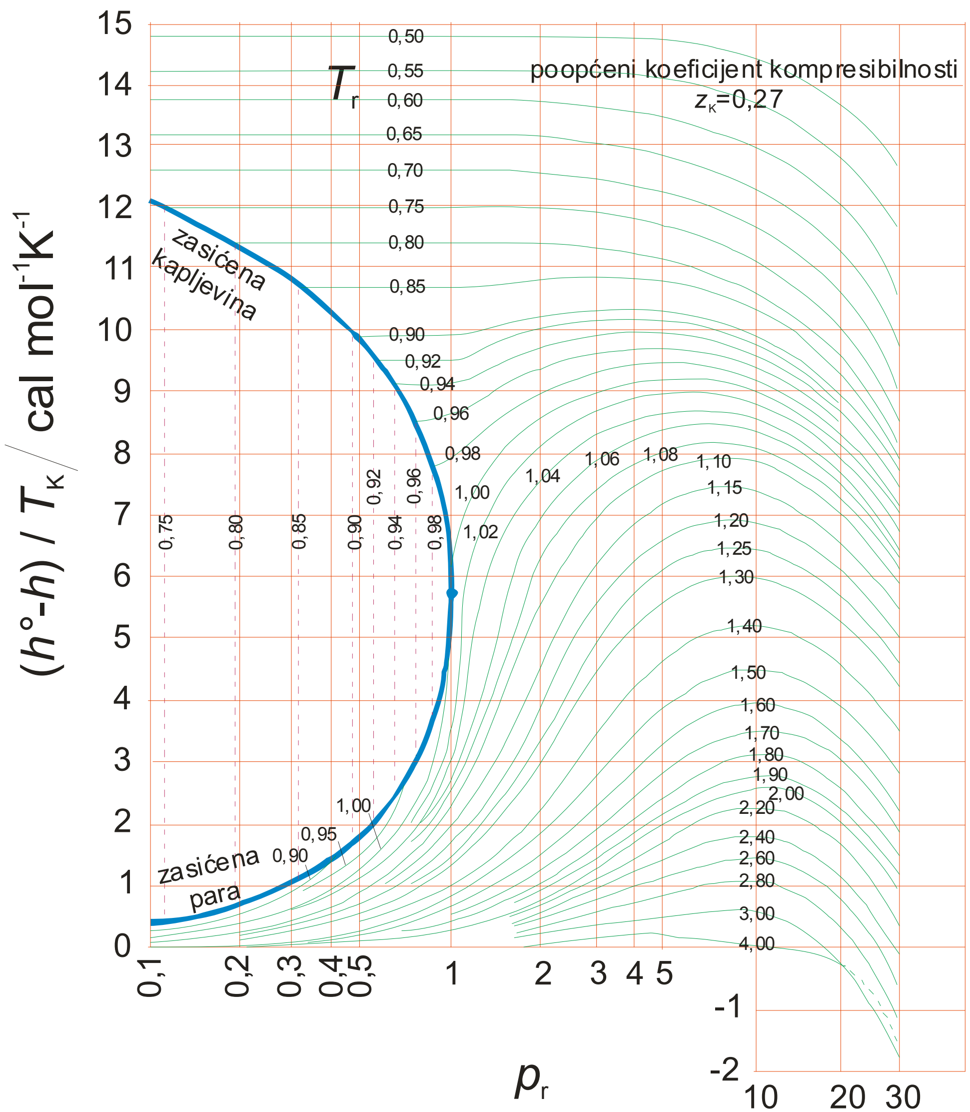


Jednadžbe stanja



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

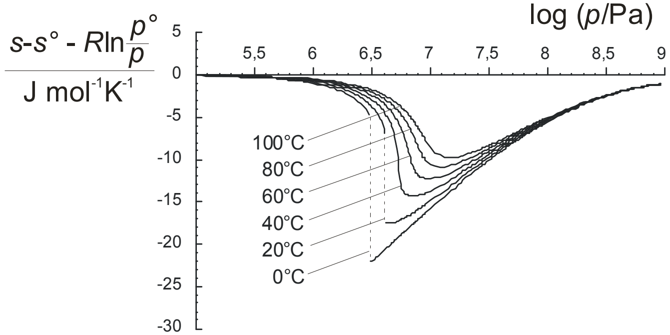
$$s - s^\circ = \mathrm{f}\left(p_\mathrm{r}, T_\mathrm{r}, z_\mathrm{K}\right)$$

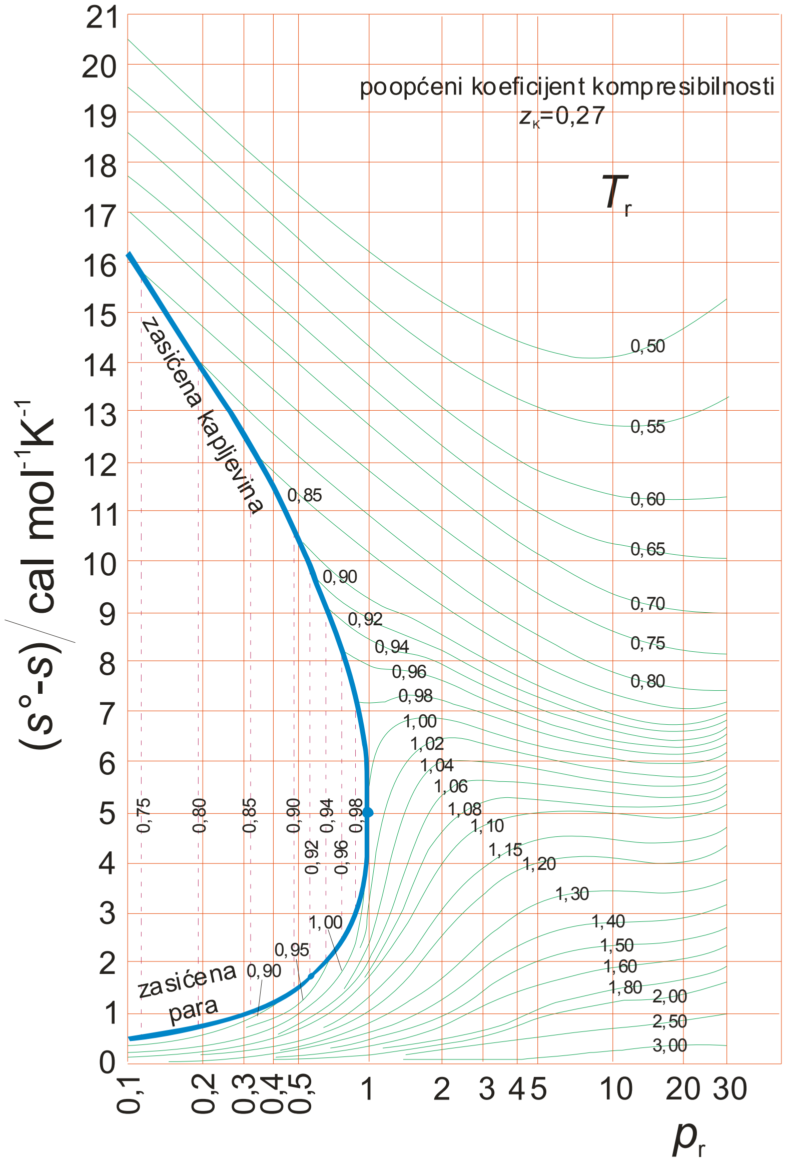


Načelo termodinamičke sličnosti

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

Jednadžbe stanja



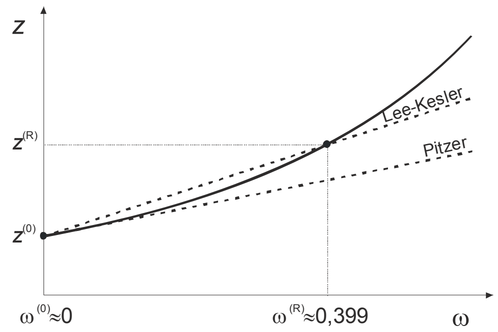


Načelo termodinamičke sličnosti

Lee-Keslerova korelacija (1975)

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

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



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

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

Fugacitivnost

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)

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

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

„Convenience functions” Sandler
„Zgodne, prikladne funkcije”

Logaritamsko računalo (šiber)

Koeficijent fugacitivnosti

Razlika realnog i idealnog plina

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

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

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

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

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

G. N. Lewis (1901)

Koeficijent fugacitivnosti

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

„Convenience functions” Sandler
„Zgodne, prikladne funkcije”

Izračunavanje fugacitivnosti iz jednadžbi stanja

Definicijski izraz – volumetrijska svojstva

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

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

Jednadžbe stanja eksplicitne po

volumenu

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

tlaku

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

Izračunavanje koeficijenta fugacitivnosti 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 fugacitivnosti

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 fugacitivnosti (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 fugacitivnosti

Idealni plin

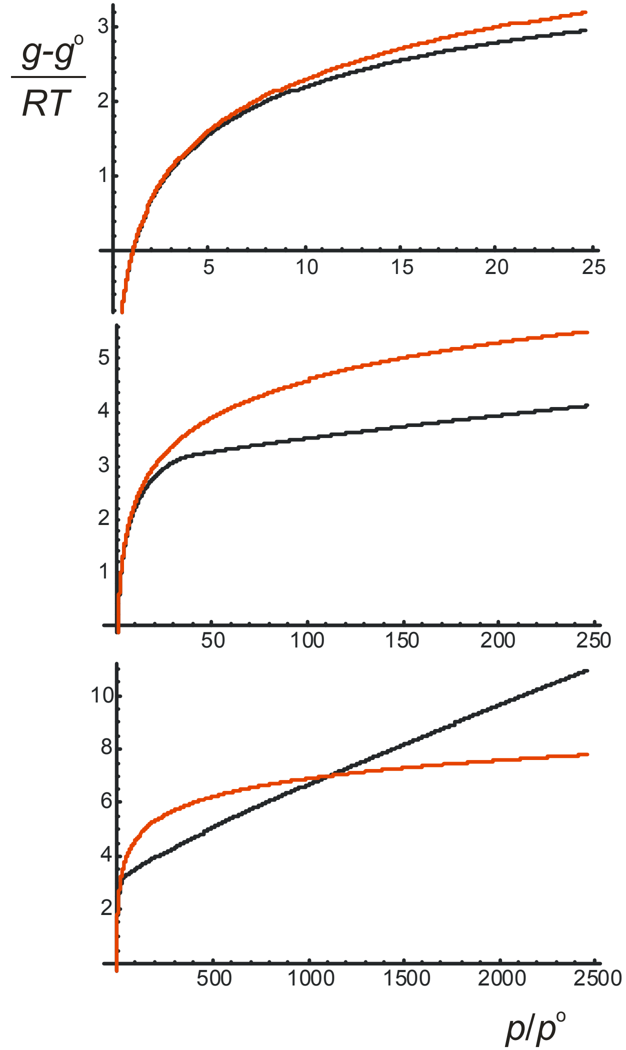
$$g = g^\circ + RT\ln\frac{p}{p^\circ}$$

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

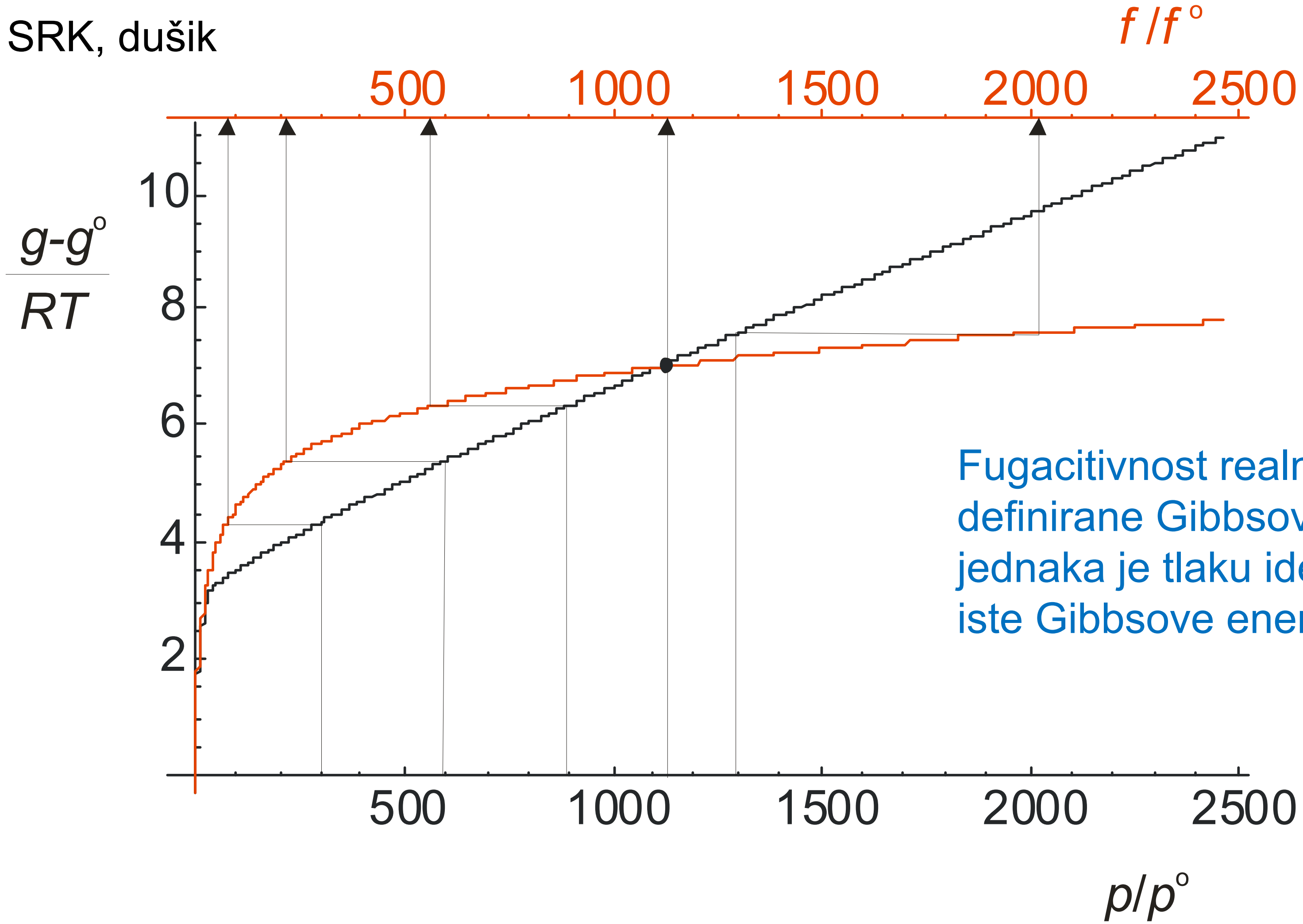
SRK, dušik

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

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

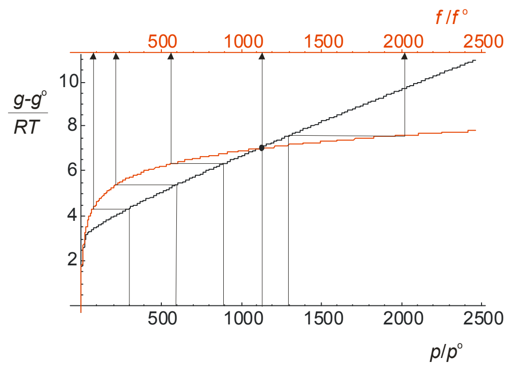


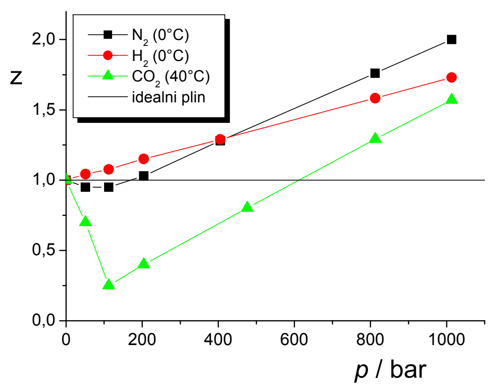
Izračunavanje Gibbsove energije iz fugacitivnosti

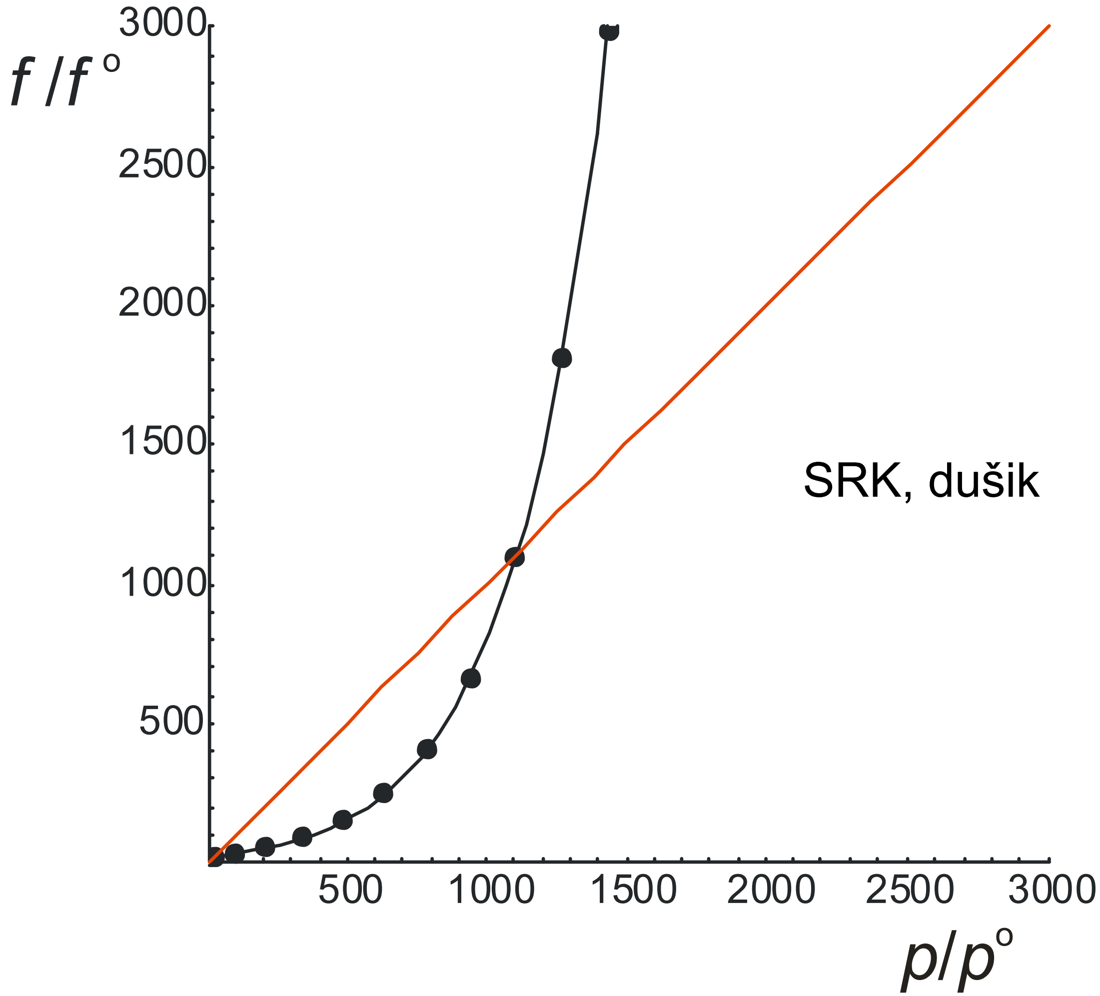


Fugacitivnost realnog plina definirane Gibbsove energije jednaka je tlaku idealnog plina iste Gibbsove energije.

Izračunavanje Gibbsove energije iz fugacitivnosti







Načelo usporedivih stanja

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

$$\ln\varphi = \int_0^p \frac{(z-1)}{p_\mathrm{r}}dp_\mathrm{r}$$

Dijagrami i tablice

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

Načelo termodin. sličnosti

Lee-Kesler $\ln\varphi = f(p_r, T_r, \omega)$

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

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

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

$$z = z^{(0)}(T_r, p_r) + \omega z^{(1)}(T_r, p_r)$$

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

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

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