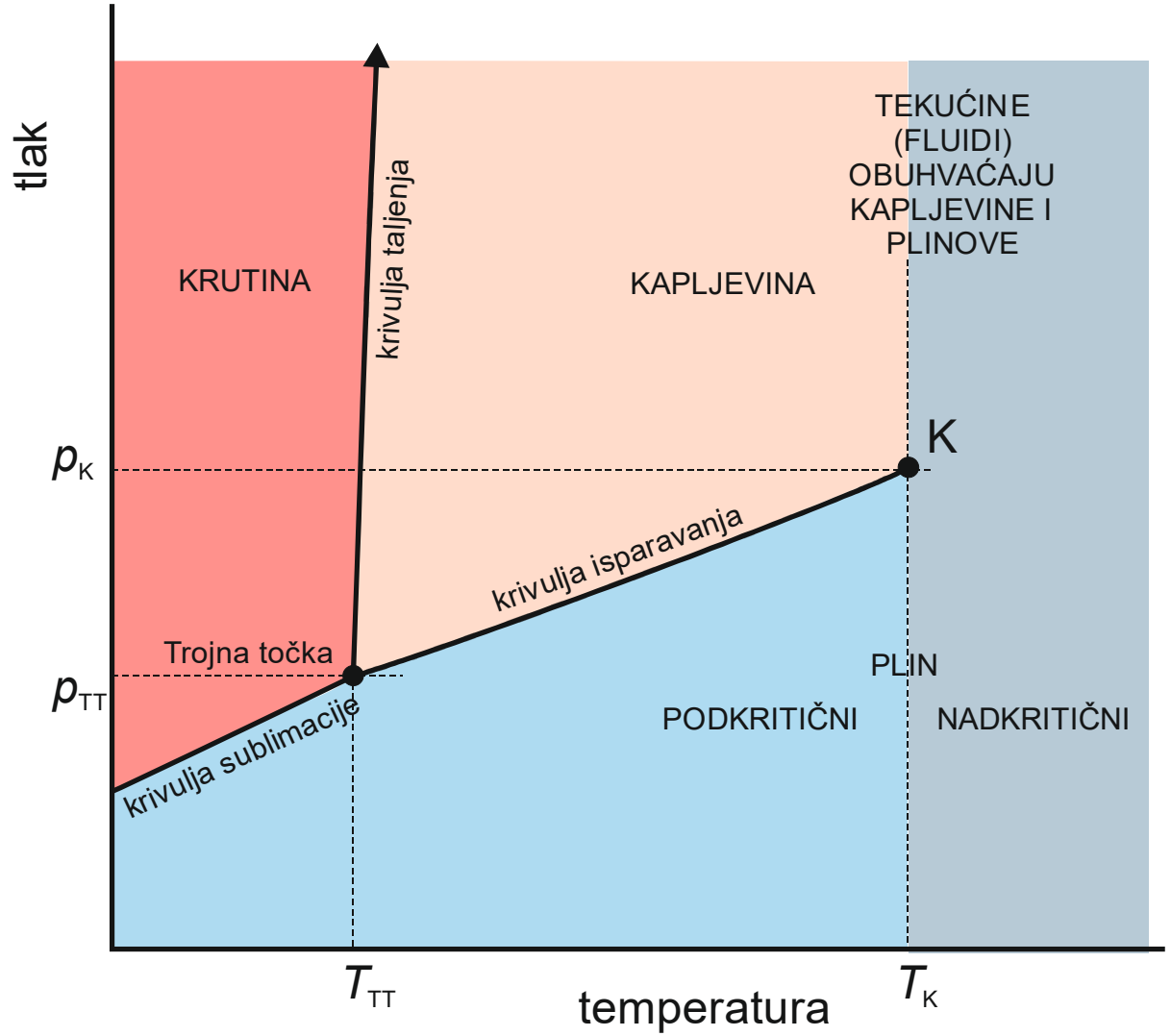
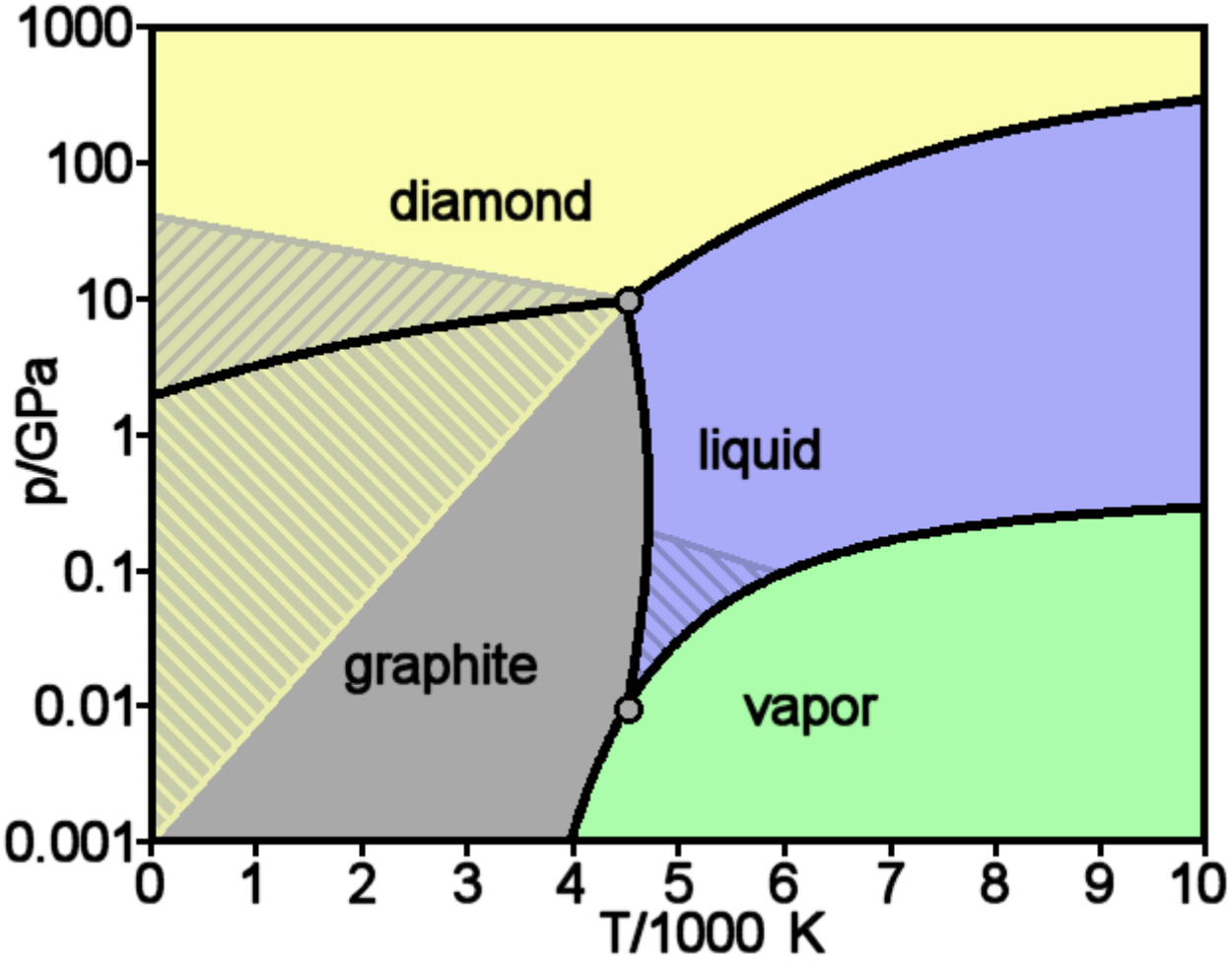
Volumetrijska svojstva realnih fluida

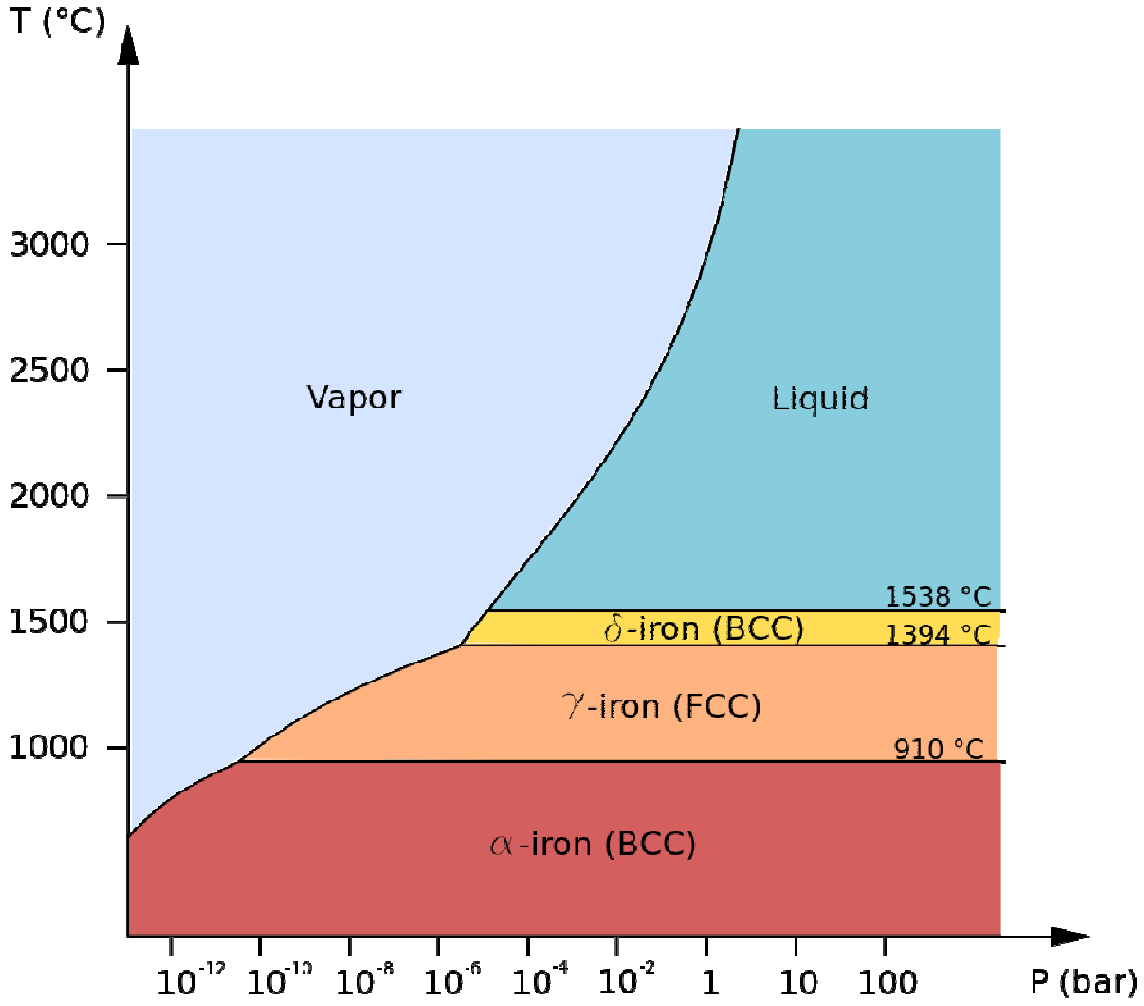
p-*T* dijagram za čistu tvar

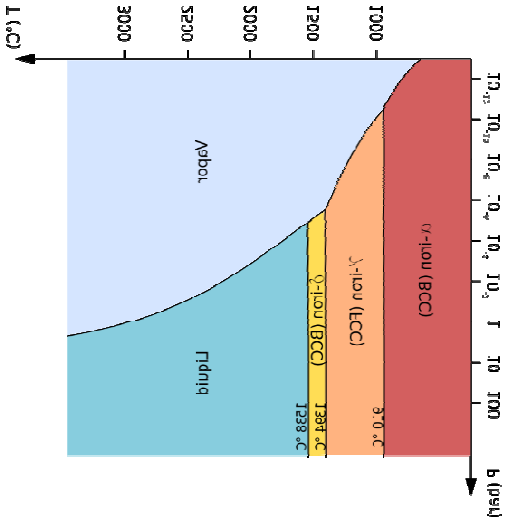


p-*T* dijagram za čistu tvar

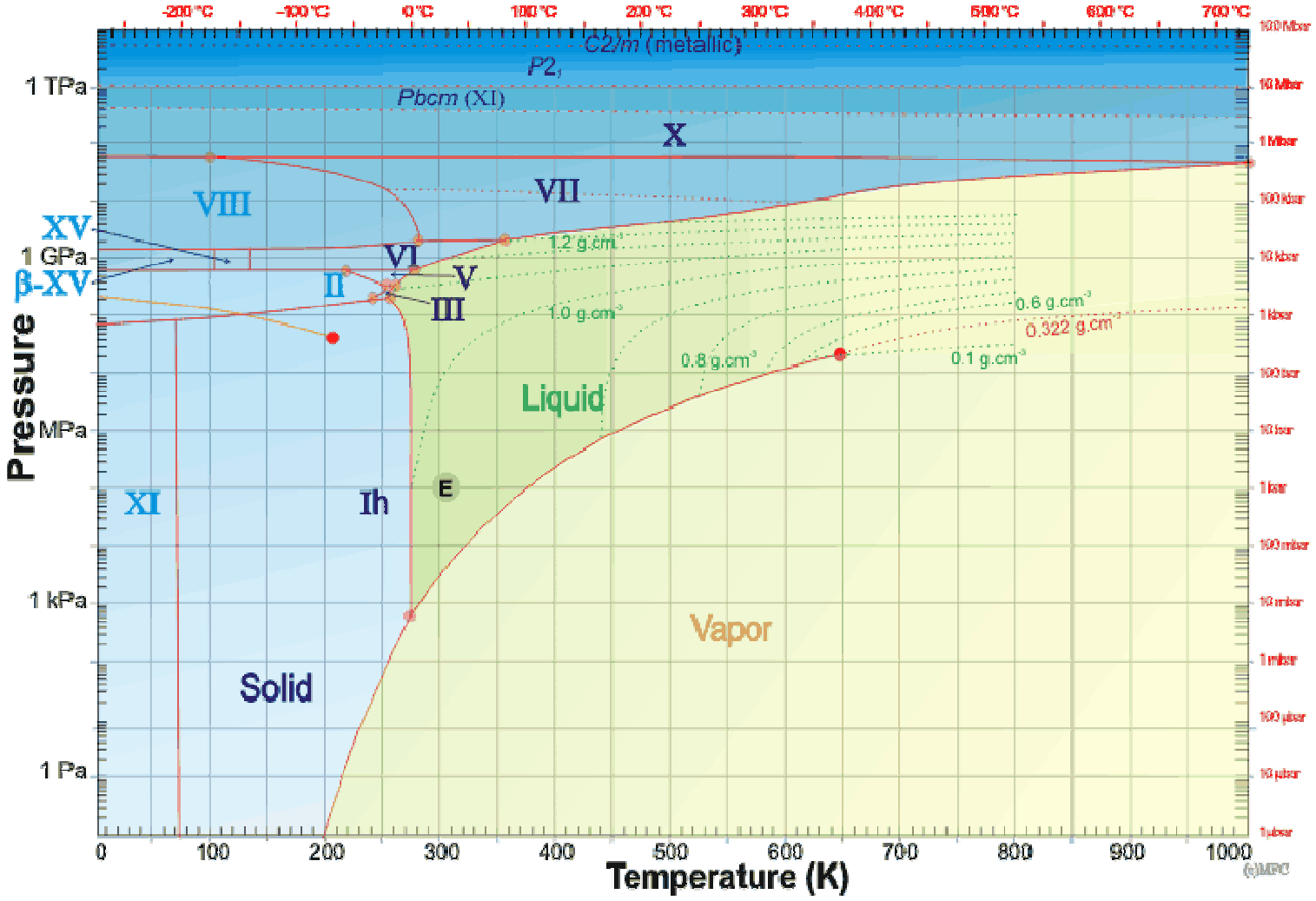


p-*T* (*T*-*p*)dijagram za čistu tvar





p-*T* dijagram za čistu tvar



Jednadžbe stanja

Gibbsovo pravilo faza $f = N_{\mathrm{K}} - N_{\mathrm{F}} + 2$

Jednofazni, jednokomponentni sustavi $f = 2$

Termodinamička svojstva $p, T, s, v, h, u, g, \ldots$

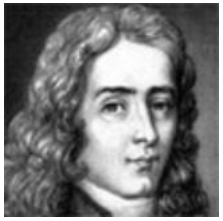
Jednadžbe stanja u širem smislu: $p = \mathrm{f}(T, s)$ $T = \mathrm{f}(s, v)$

$g = \mathrm{f}(u, v)$ $h = \mathrm{f}(p, T)$

Jednadžbe stanja u užem smislu: $p = \mathrm{f}(v, T)$

$\mathrm{f}(p, T, v) = 0$ $v = \mathrm{f}(p, T)$

Opća plinska jednadžba

Robert Boyle i Edme Mariotte

$$(pV)_T = \text{konst}$$




Jacques Charles, Joseph Louis Gay-Lussac

$$\left(\frac{V}{T}\right)_p = \text{konst}$$

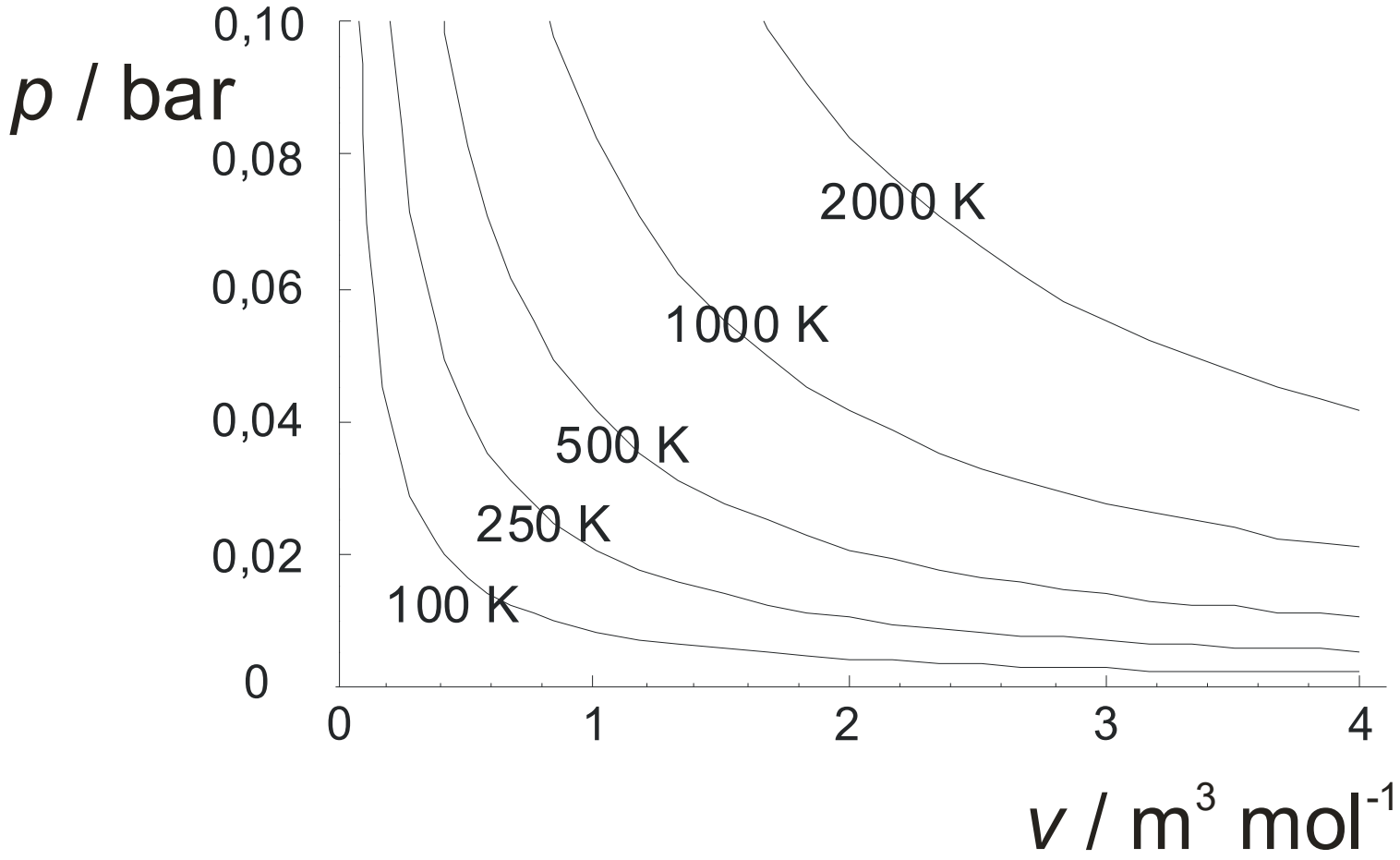


Avogadro:
Jednaki volumeni plina sadrže jednak broj čestica

$$pV = nRT$$

$$pv = RT$$

Opća plinska jednadžba



Opća plinska jednadžba

Izvod: metodama statističke termodinamike iz modela idealnog plina:

Pretpostavke:
zanemariv volumen čestica
zanemariva međudjelovanja
(elastični srazovi)

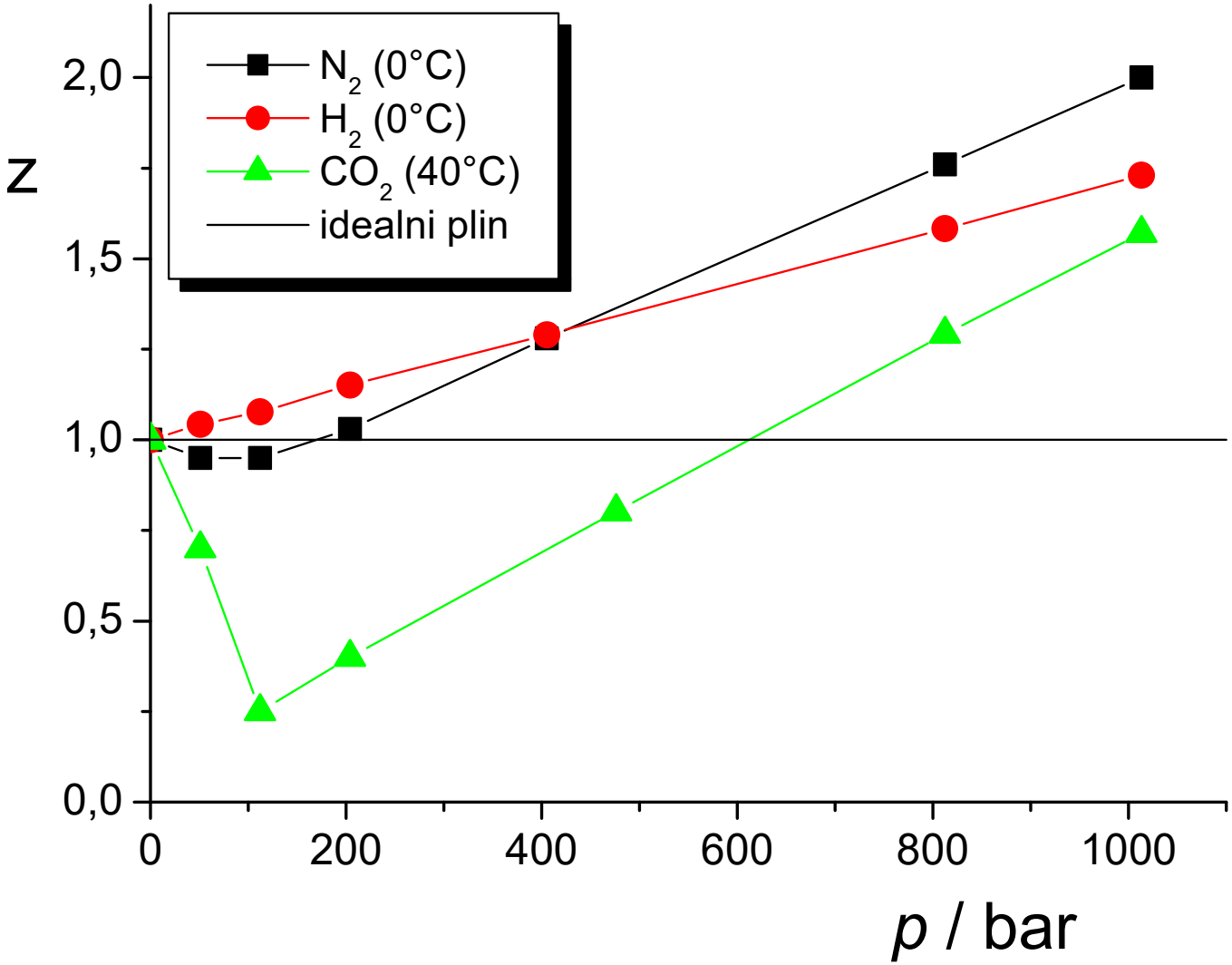
Uvjeti:
visoke temperature
niski tlakovi

Odstupanja od idealnosti

Volumetrijski podaci

$$\lim_{p\to 0}(pV) = RT$$

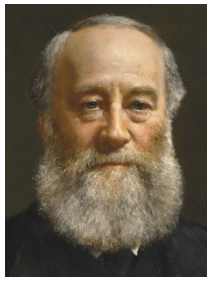
$$z = \frac{pv}{RT} = \frac{v}{v_{\mathrm{id}}}$$

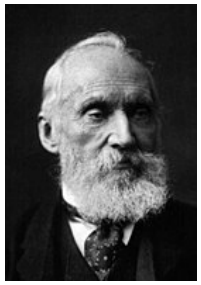


Odstupanja od idealnosti

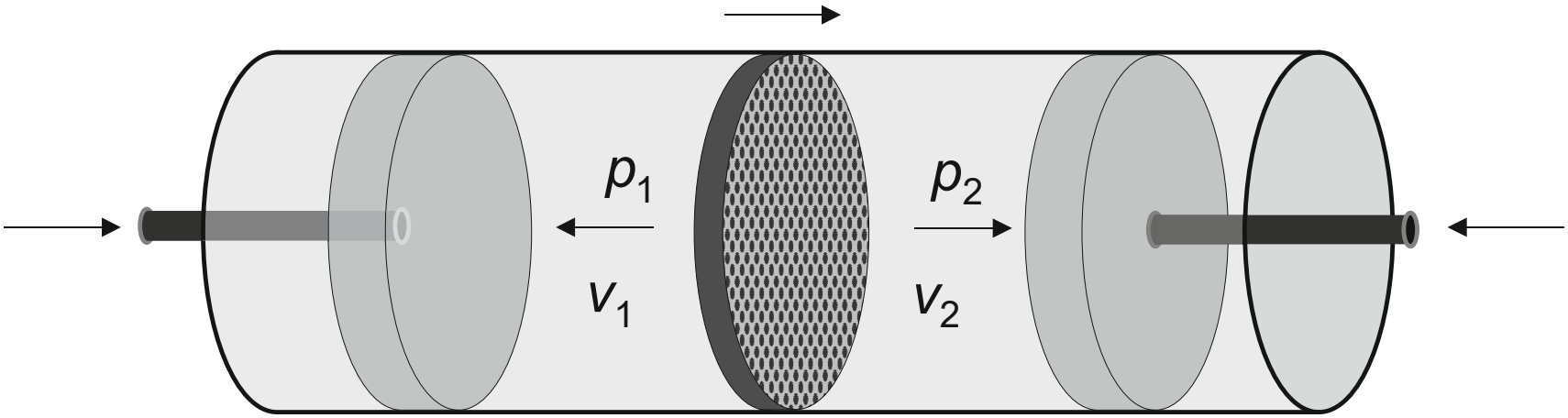
Prigušivanje
realnog
plina

Joule, Thomson (Kelvin)





Uvjet stalne entalpije
(nema izmjene topline s okolinom)



Odstupanja od idealnosti

Prigušivanje realnog plina

Totalni diferencijal:

$$dh = \left(\frac{\partial h}{\partial p}\right)_T dp + \left(\frac{\partial h}{\partial T}\right)_p dT$$

dh=0

$$\left(\frac{\partial h}{\partial T}\right)_p = c_p$$

Joule -Thomsonov koeficijent:

$$\mu = \left(\frac{\partial T}{\partial p}\right)_h = -\frac{1}{c_p}\left(\frac{\partial h}{\partial p}\right)_T$$

Ovisnost entalpije plina o tlaku:

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

Ovisnost entalpije idealnog plina o tlaku:

$v=RT/p$, $(\partial v/\partial T)p=R/p$

$$\left(\frac{\partial h}{\partial p}\right)_T = \frac{RT}{p} - T\frac{R}{p} = 0$$

Odstupanja od idealnosti

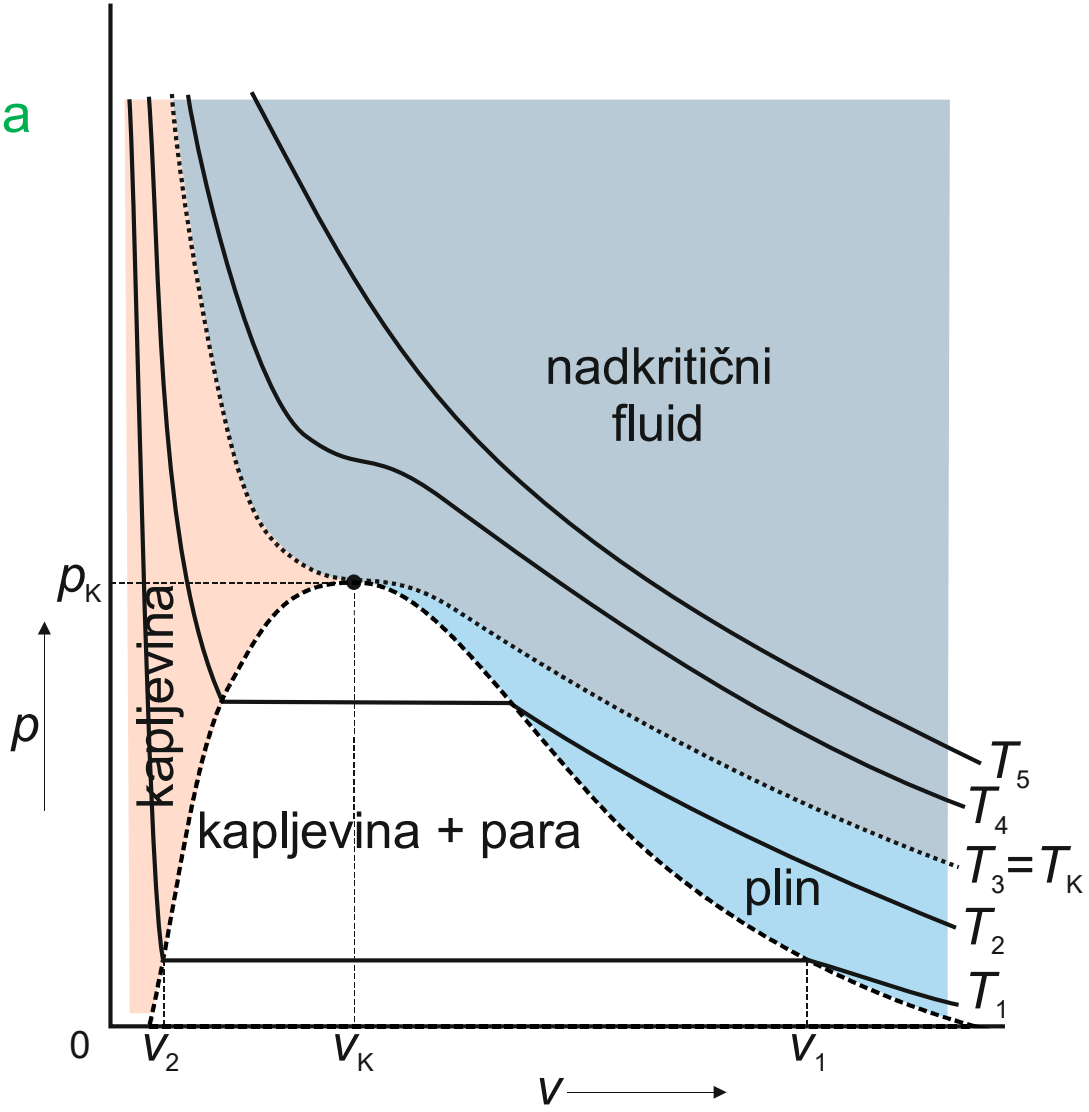
Ukapljivanje realnog plina

Kritična temperatura
najviša temperatura na
kojoj se plin još može ukapljiti

Kritični tlak
tlak potreban za
ukapljivanje plina
pri kritičnoj temperaturi

Kritični molarni volumen
volumen 1 mola
plina pri kritičnoj
temperaturi i
kritičnom tlaku

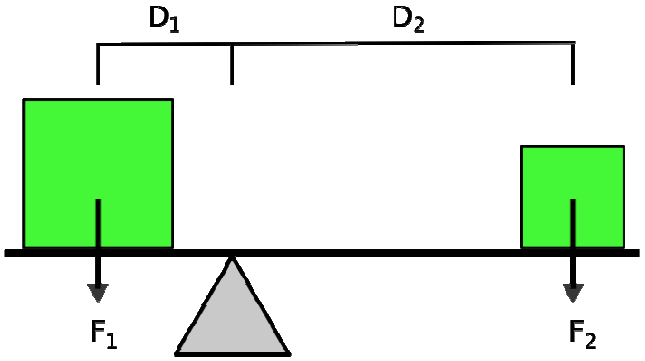
Kritična gustoća
gustoća plina pri
kritičnom tlaku i
kritičnoj temperaturi

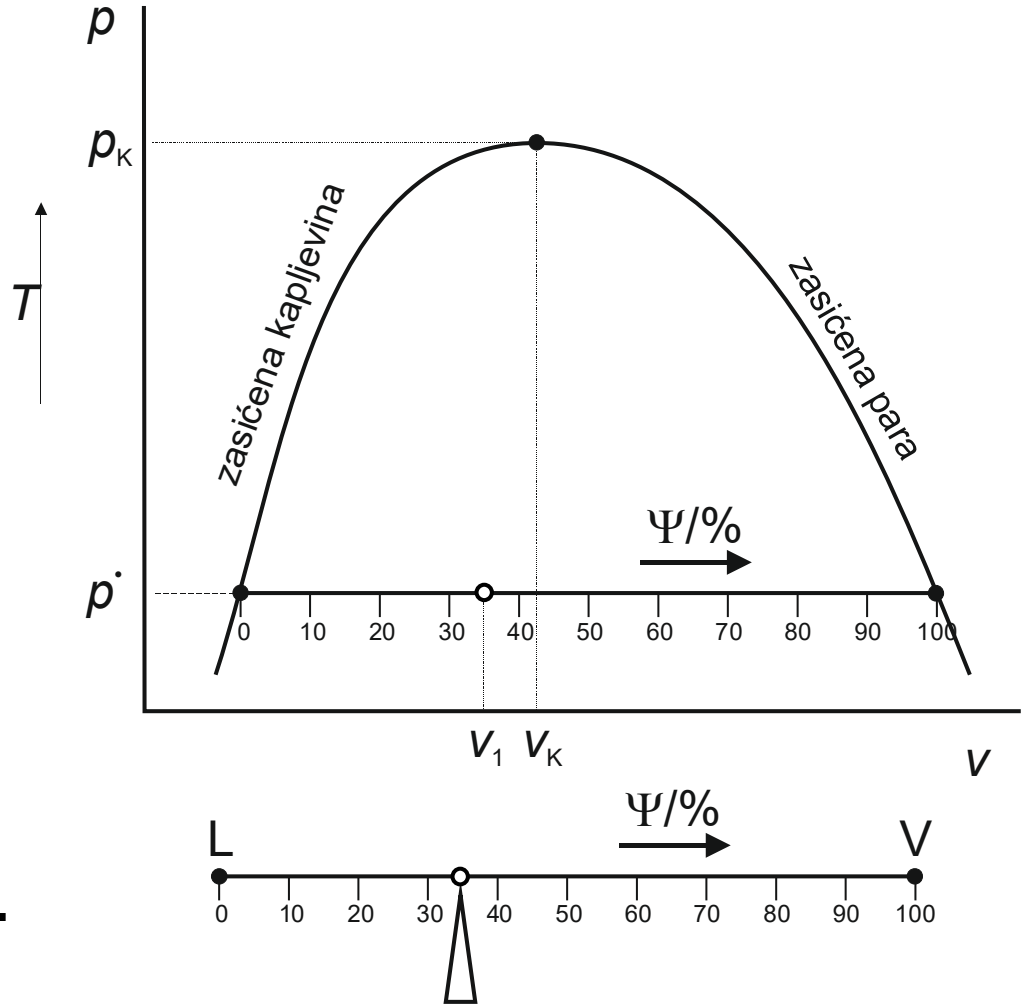


Odstupanja od idealnosti

Pravilo poluge







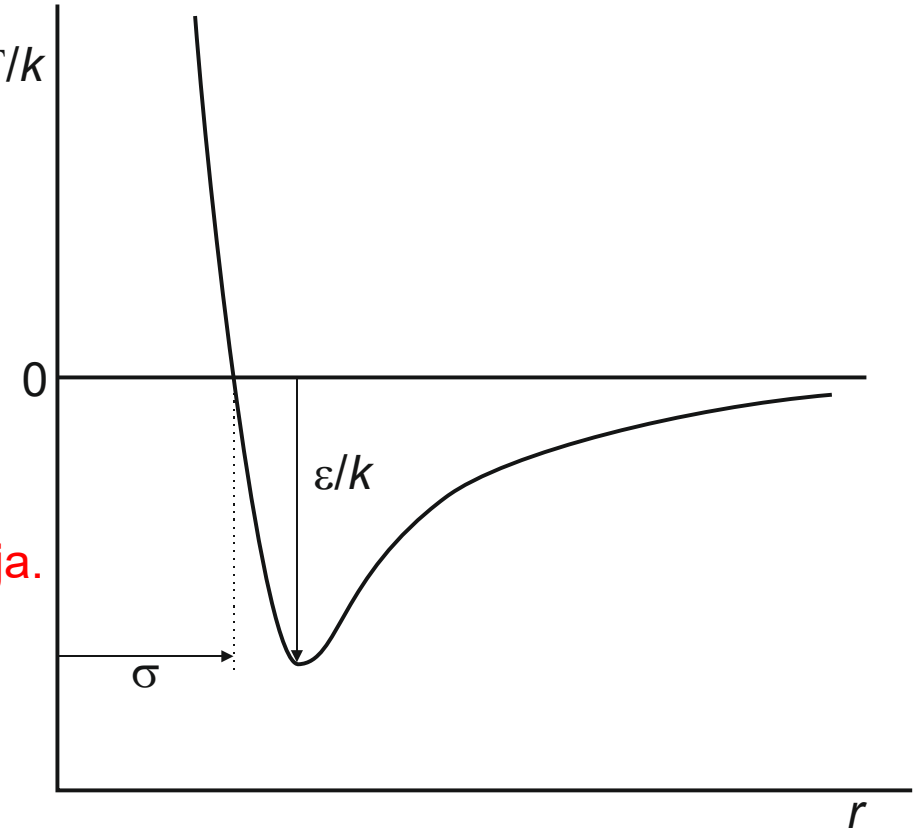
Virijalna jednadžba stanja

Opis međudjelovanja

$$\Gamma = \Gamma_{\text{odb}} + \Gamma_{\text{priv}} = \frac{A}{r^n} - \frac{B}{r^m}$$

van der Waalsove sile:
inducirani dipol – inducirani dipol (London)
dipol – inducirani dipol (Debye)
dipol – dipol (Keesom)

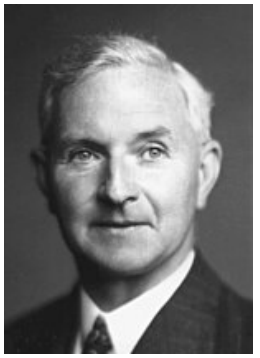
Coulombova elektrostatska međudjelovanja.



Virijalna jednadžba stanja

Lennard-Jones 6 – 12 potencijal

$$\Gamma = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



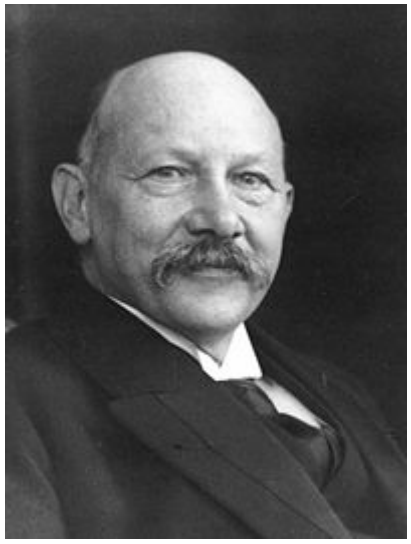
Clausiusov (virijalni poučak)

$$z = \frac{pv}{RT} = 1$$

$$z = \frac{pv}{RT} = 1 + \frac{B(T)}{v}$$

Virijalna jednadžba stanja

Heike
Kamerlingh Onnes
(Nobel 1913.)



Proširena, empirijska virijalna jednadžba stanja

$$z = \frac{pv}{RT} = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \ldots$$

$$z = \frac{pv}{RT} = 1 + B(T)\frac{p}{RT} + \left(C(T) - B(T)^2\right)\left(\frac{p}{RT}\right)^2 + \ldots$$

Virijalna jednadžba stanja

Pojednostavljenja

$$\frac{pv}{RT} = 1 + \frac{B(T)}{RT} p \qquad p\left[v - B(T)\right] = RT$$

$$v > 2v_{\mathrm{K}}$$

$$\frac{pv}{RT} = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} \qquad v^3 - \frac{RT}{p} v^2 - \frac{B(T)RT}{p} v - \frac{C(T)RT}{p} = 0$$

do 50 bar, POLINOM TREĆEG STUPNJA PO VOLUMENU

Virijalna jednadžba stanja

Empirijska proširenja

Benedict, Webb i Rubin (BWR), 1940

$$z = \frac{pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{a\alpha}{RTv^5} + \frac{\beta}{RT^3 v}\left(1 + \frac{\gamma}{v^2}\right)\exp\left(-\frac{\gamma}{v^2}\right)$$

$$B = \left(b_1 - \frac{b_2}{RT} - \frac{b_3}{RT^3}\right) \qquad C = \left(c_1 - \frac{c_2}{RT}\right)$$

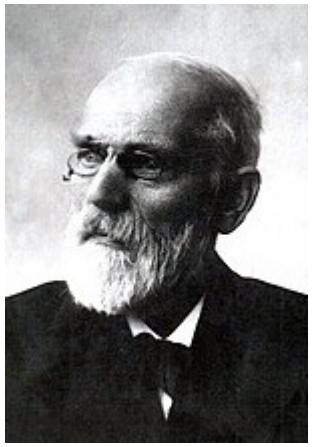
Starling BWR (SBWR), 1973 REDUCIRANI OBLIK

$$z = \frac{pv}{RT} = 1 + \frac{B}{v_\mathrm{r}} + \frac{C}{v_\mathrm{r}^2} + \frac{D}{v_\mathrm{r}^5} + \frac{c_4}{T_\mathrm{r}^3 v_\mathrm{r}^2} + \left[\beta + \frac{\gamma}{v_\mathrm{r}^2}\right]\exp\left[-\frac{\gamma}{v_\mathrm{r}^2}\right]$$

$$B = b_1 - \frac{b_2}{T_\mathrm{r}} - \frac{b_3}{T_\mathrm{r}^2} - \frac{b_4}{T_\mathrm{r}^3} \qquad C = c_1 - \frac{c_2}{T_\mathrm{r}} - \frac{c_3}{T_\mathrm{r}^2} \qquad D = d_1 - \frac{d_2}{T_\mathrm{r}}$$

vdW jednadžba stanja

Johannes Diderik van der Waals 1873
(Nobel 1910.)



$$p = \frac{RT}{v-b} - \frac{a}{v^2} \qquad v^3 - v^2\left(b + \frac{RT}{p}\right) + v\left(\frac{a}{p}\right) - \frac{ab}{p} = 0$$

Usporedba s virijalnom jednadžbom

$$v^3 - \frac{RT}{p}v^2 - \frac{B(T)RT}{p}v - \frac{C(T)RT}{p} = 0$$

POLINOM TREĆEG STUPNJA PO VOLUMENU

Usporedba s općom plinskom jednadžbom

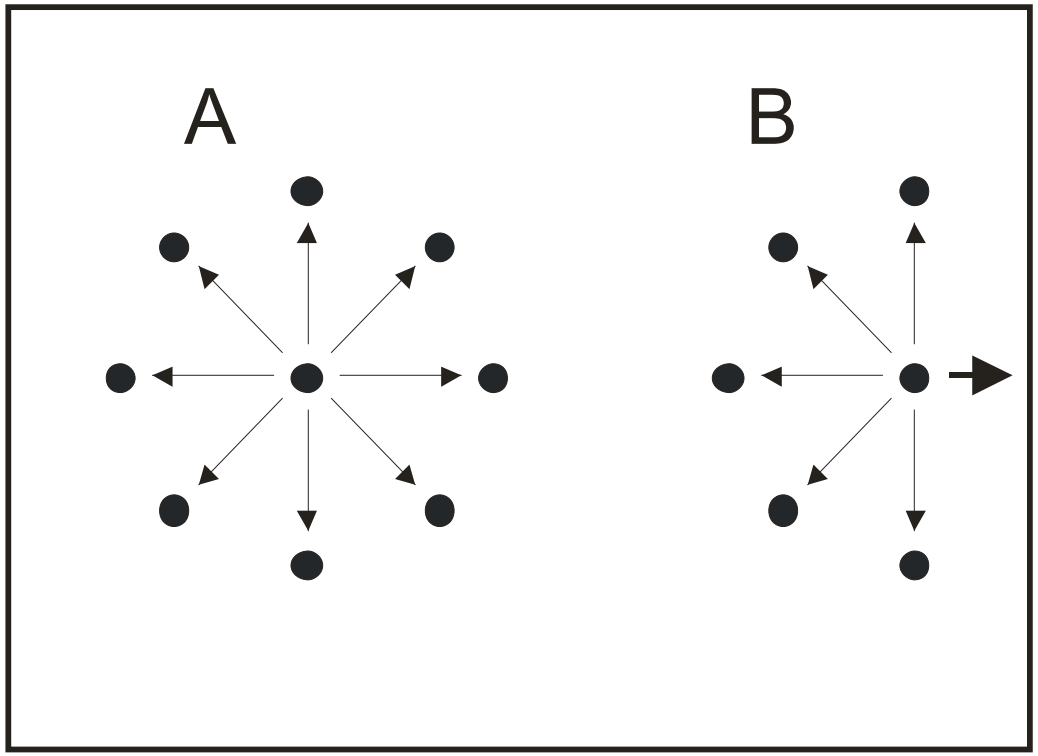
$$\left(p + \frac{a}{v^2}\right)(v-b) = RT$$

vdW jednadžba stanja

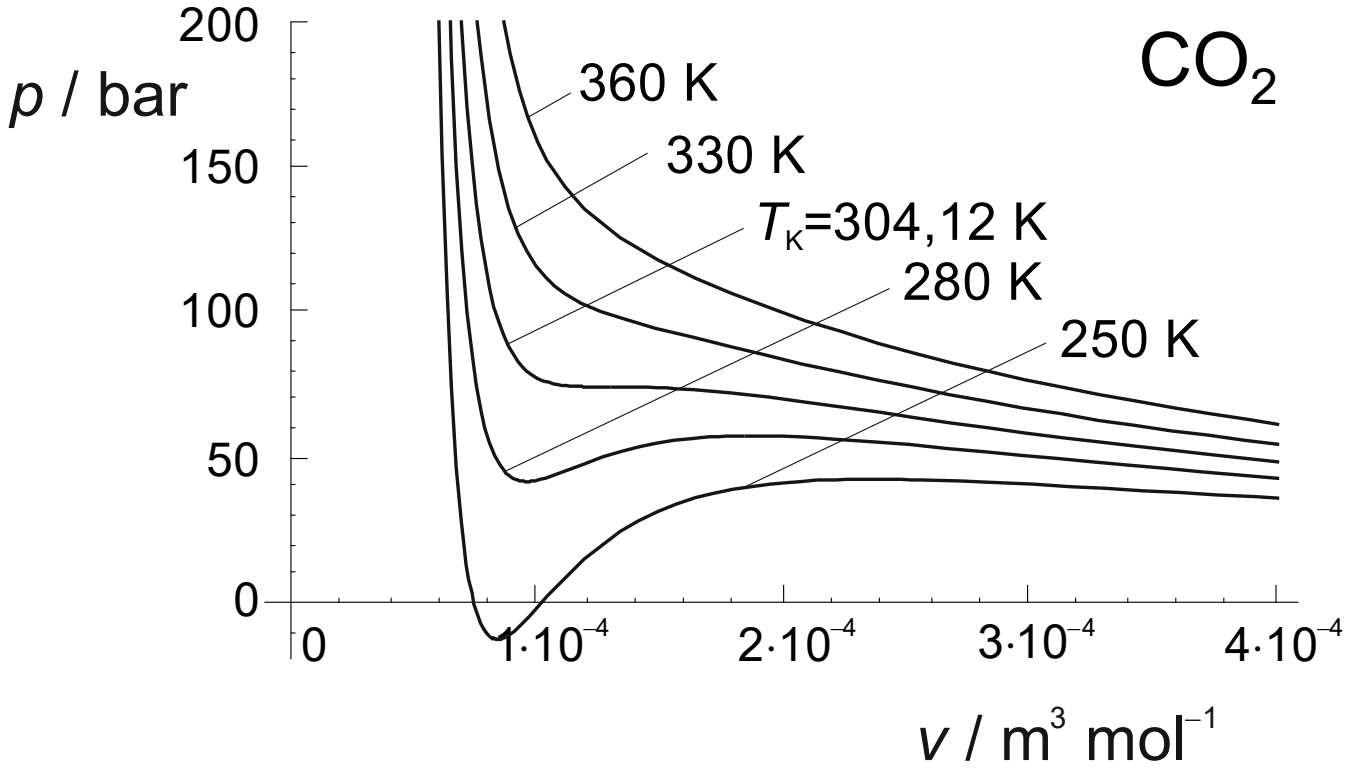
Korekcija volumena $(v-b)$

Korekcija tlaka $\left(p+\frac{a}{v^2}\right)$



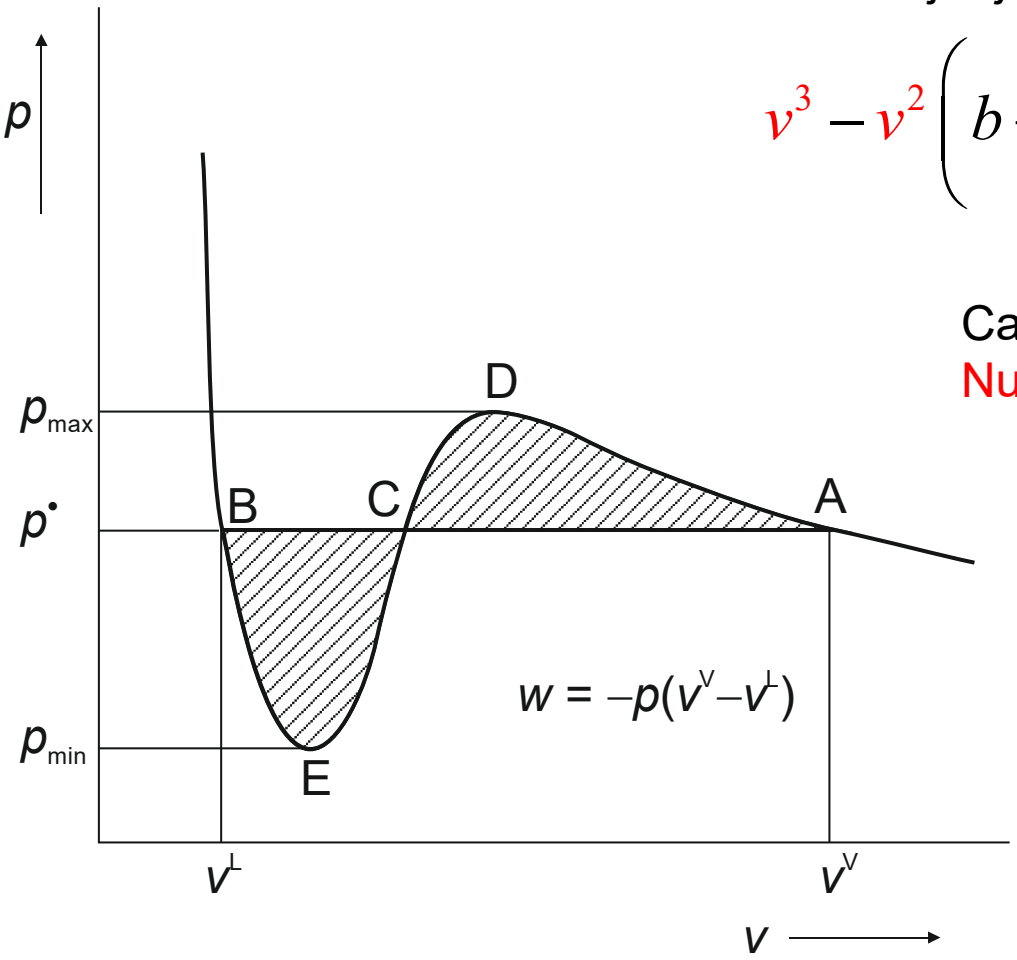


vdW jednadžba stanja



vdW jednadžba stanja

Izbor stabilne faze



Izračunavanje rješenja polinoma trećega stupnja ?

$$v^3 - v^2\left(b + \frac{RT}{p}\right) + v\left(\frac{a}{p}\right) - \frac{ab}{p} = 0$$

Cardanove formule ?

Numerički postupci ?



vdW jednadžba stanja

Izbor stabilne faze

$$w_{\text{real}} = -\int_{v^{\text{L}}}^{v^{\text{V}}} p\,dv = -p\left(v^{\text{V}} - v^{\text{L}}\right)$$

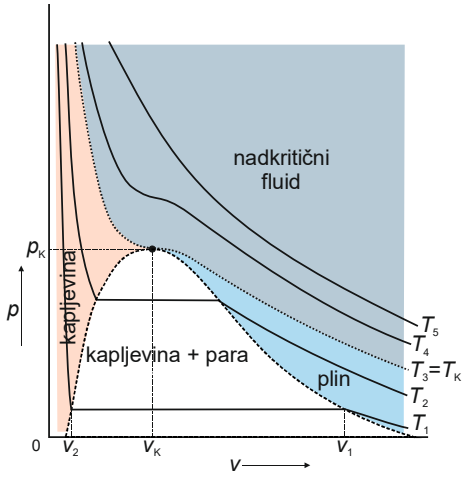
$$w_{\text{vdW}} = -\int_{v^{\text{L}}}^{v^{\text{V}}} p(v)\,dv = -\int_{v^{\text{L}}}^{v^{\text{V}}} \left(\frac{RT}{v-b} - \frac{a}{v^2}\right) dv = -\left(RT \ln \frac{v^{\text{V}} - b}{v^{\text{L}} - b} - \frac{v^{\text{V}} - v^{\text{L}}}{v^{\text{V}} v^{\text{L}}} a\right)$$

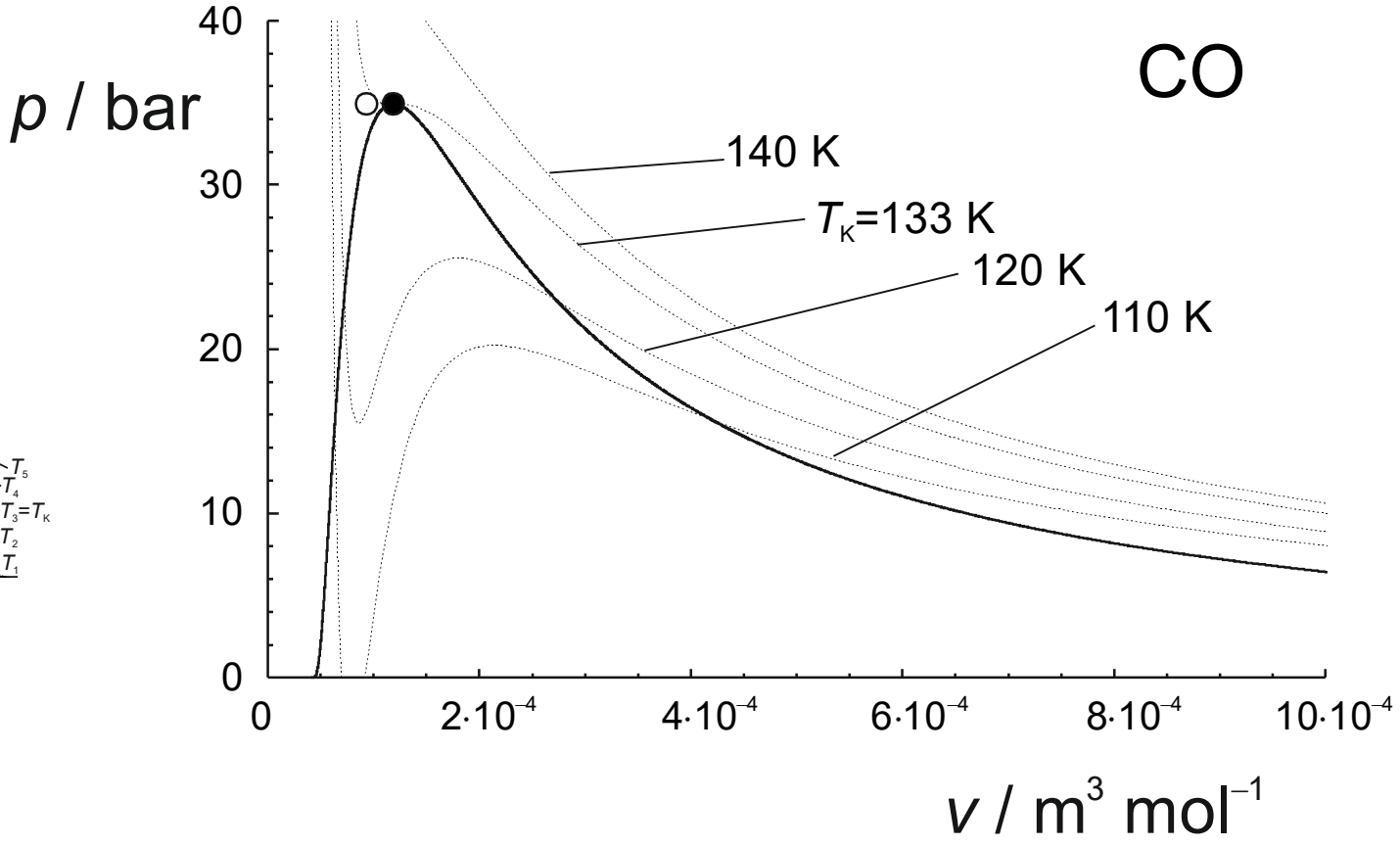
$$p\left(v^{\text{V}} - v^{\text{L}}\right) = RT \ln \frac{v^{\text{V}} - b}{v^{\text{L}} - b} - \frac{v^{\text{V}} - v^{\text{L}}}{v^{\text{V}} v^{\text{L}}} a$$

vdW jednadžba stanja

Izračunavanje ravnotežnog tlaka, $p^{\bullet}$

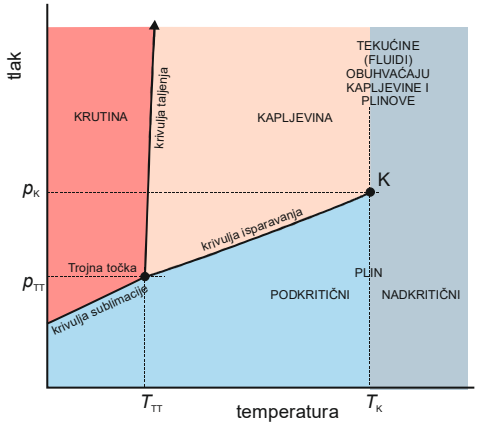
$$p = \frac{RT}{v^{\mathrm{V}} - v^{\mathrm{L}}} \ln \frac{v^{\mathrm{V}} - b}{v^{\mathrm{L}} - b} - \frac{a}{v^{\mathrm{V}} v^{\mathrm{L}}}$$

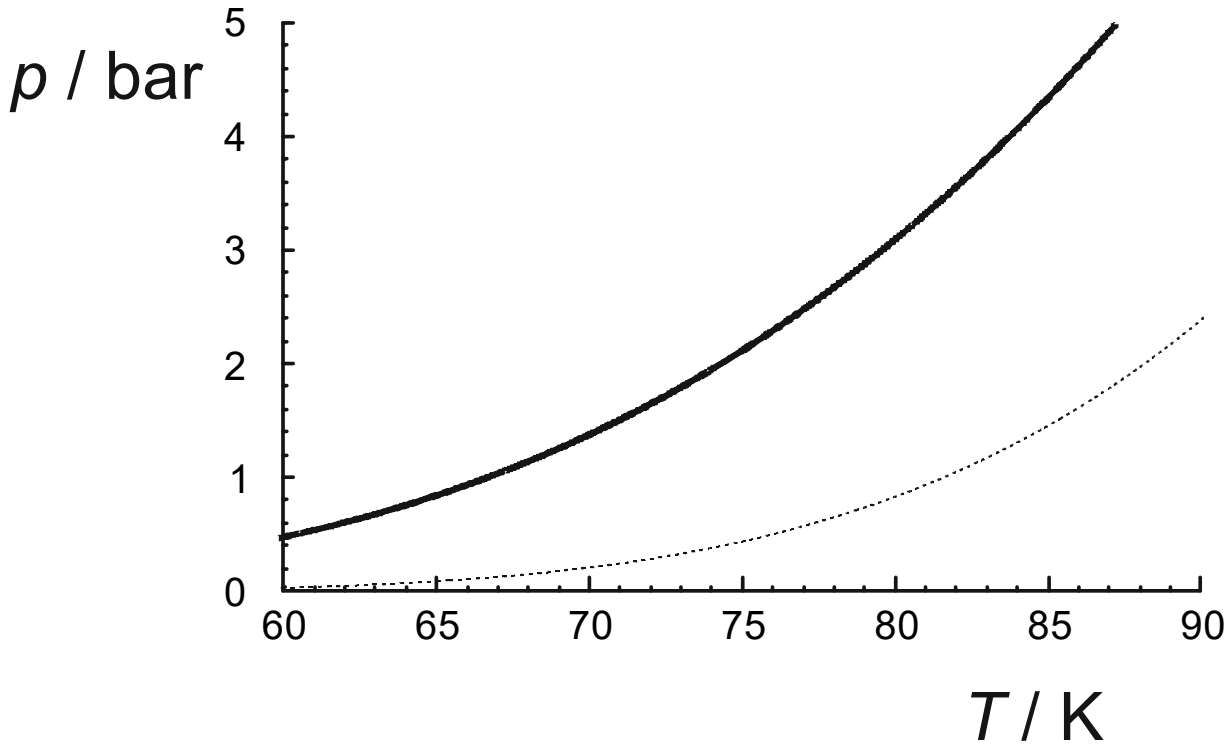




vdW jednadžba stanja

Izračunavanje ravnotežnog tlaka





vdW parametri

Troparametarska

$$b = \frac{v_K}{3}$$

$$a = 3 p_K v_K^2$$

$$R = \frac{8 p_K v_K}{3 T_K}$$

	T_K / K	p_K / bar	v_K / cm^3 mol^{-1}	R / J mol^{-1} K^{-1}
Ar	150,86	48,98	74,57	6,456
H_2	32,98	12,93	64,20	6,712
O_2	154,58	50,43	73,37	6,383
H_2O	647,14	220,64	55,95	5,087
NH_3	405,40	113,53	72,47	5,412
CO_2	304,12	73,74	94,07	6,082
CH_4	190,56	45,99	98,60	6,346
C_2H_6	305,32	48,72	145,50	6,191
CO	132,85	34,94	93,10	6,530

Dvoparametarska

$$a = \frac{27 R^2 T_K^2}{64 p_K} \qquad b = \frac{R T_K}{8 p_K}$$

Načelo usporedivih stanja

Reducirane veličine

$$p_\mathrm{r} = \frac{p}{p_\mathrm{K}}$$

$$T_\mathrm{r} = \frac{T}{T_\mathrm{K}}$$

$$v_\mathrm{r} = \frac{v}{v_\mathrm{K}}$$

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

Reducirana vdW jednadžba

$$\left(p_\mathrm{r} + \frac{3}{v_\mathrm{r}^2}\right)\left(3v_\mathrm{r} - 1\right) = 8T_\mathrm{r}$$

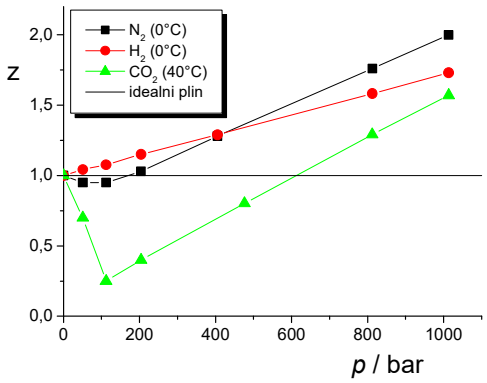
z-oblik

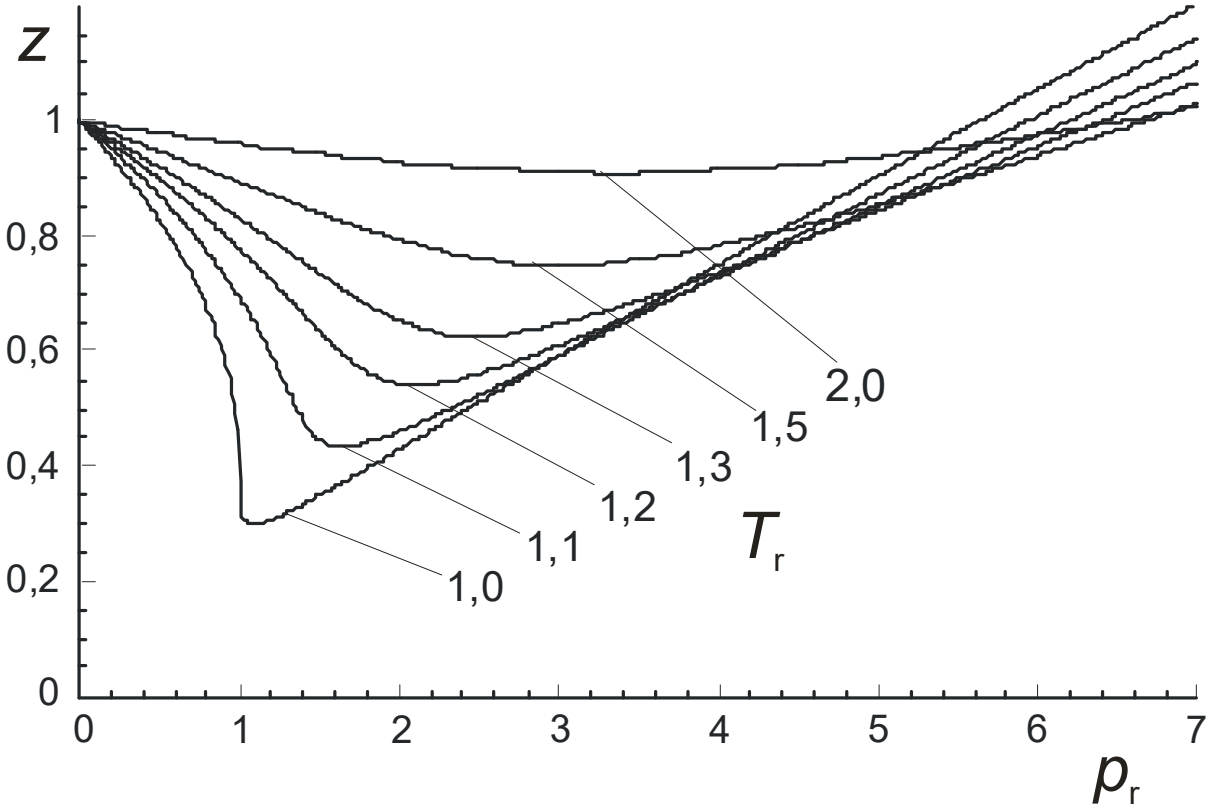
$$z^3 - z^2\left(\frac{bp}{RT} + 1\right) + z\frac{ap}{R^2T^2} - \frac{abp^2}{R^3T^3} = 0$$

$$z^3 - z^2\left(\frac{p_\mathrm{r}}{8T_\mathrm{r}} + 1\right) + z\frac{27\,p_\mathrm{r}}{64T_\mathrm{r}^2} - \frac{27}{512}\frac{p_\mathrm{r}^2}{T_\mathrm{r}^3} = 0$$

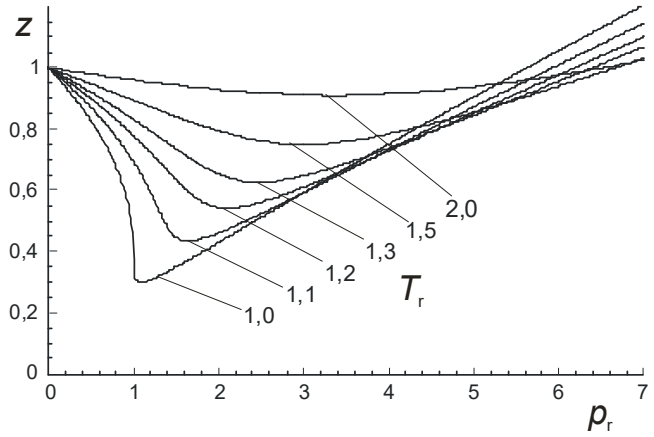
Načelo usporedivih stanja

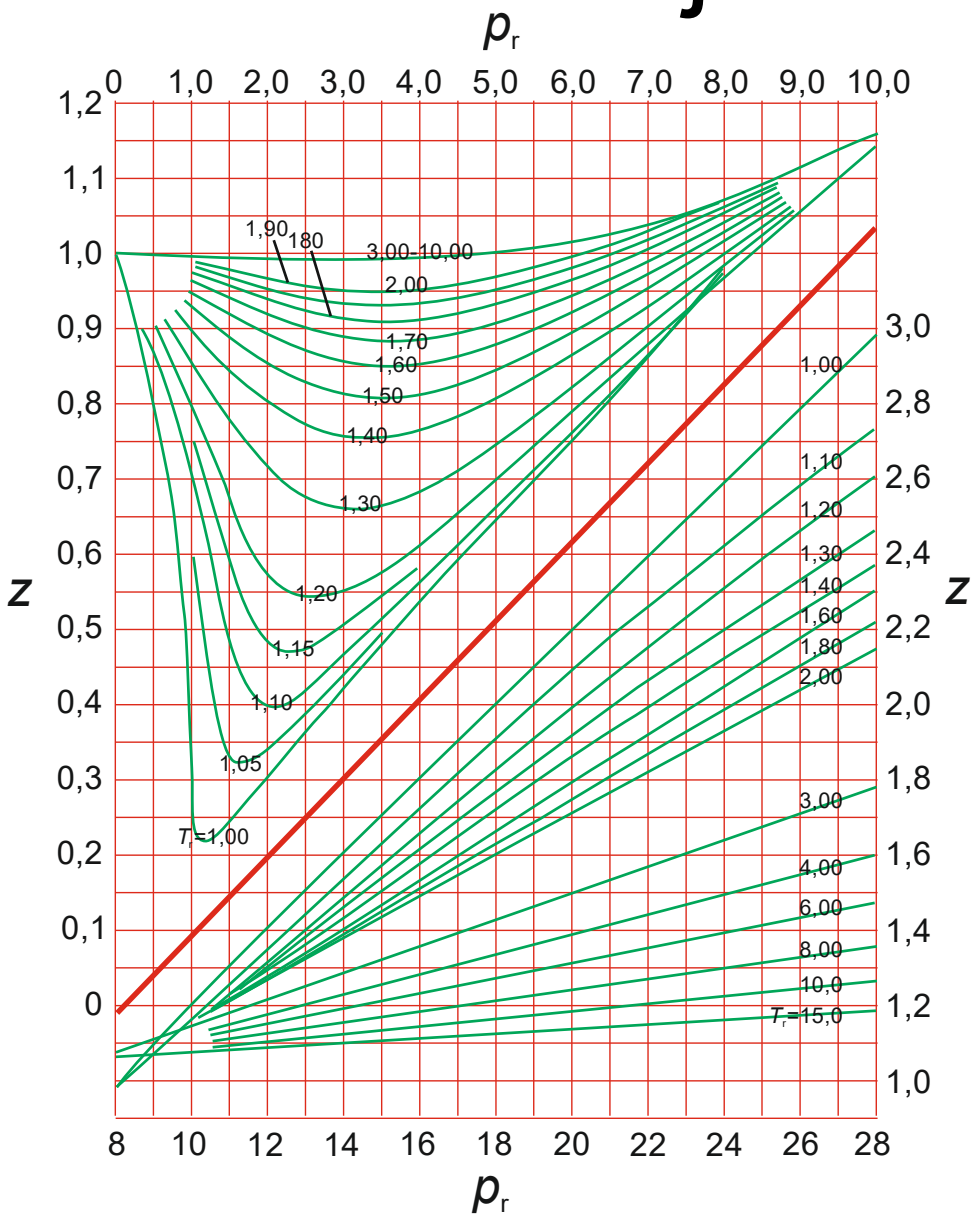
$$z = \frac{v}{v_{\mathrm{id}}} = \frac{pv}{RT} = \mathrm{f}\left(p_{\mathrm{r}}, T_{\mathrm{r}}\right)$$



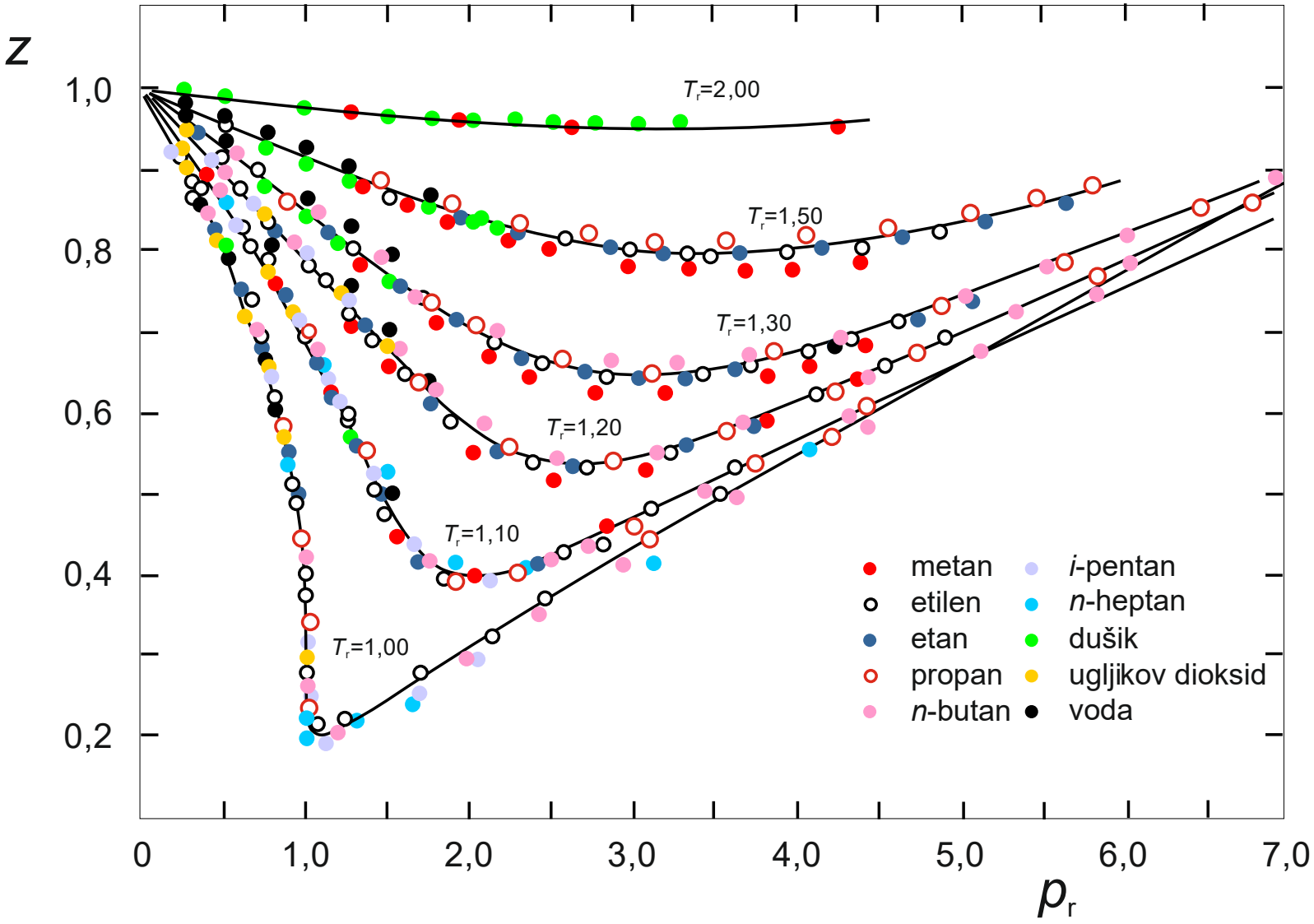


Načelo usporedivih stanja





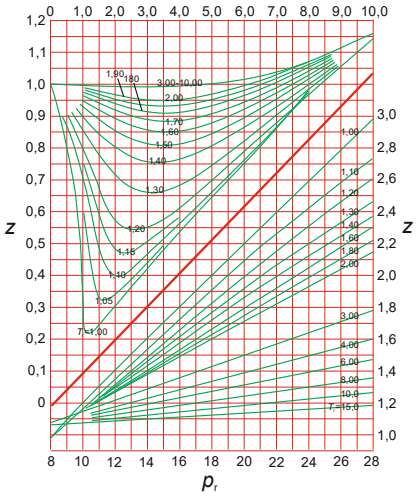
Načelo termodin. sličnosti



Načelo termodin. sličnosti

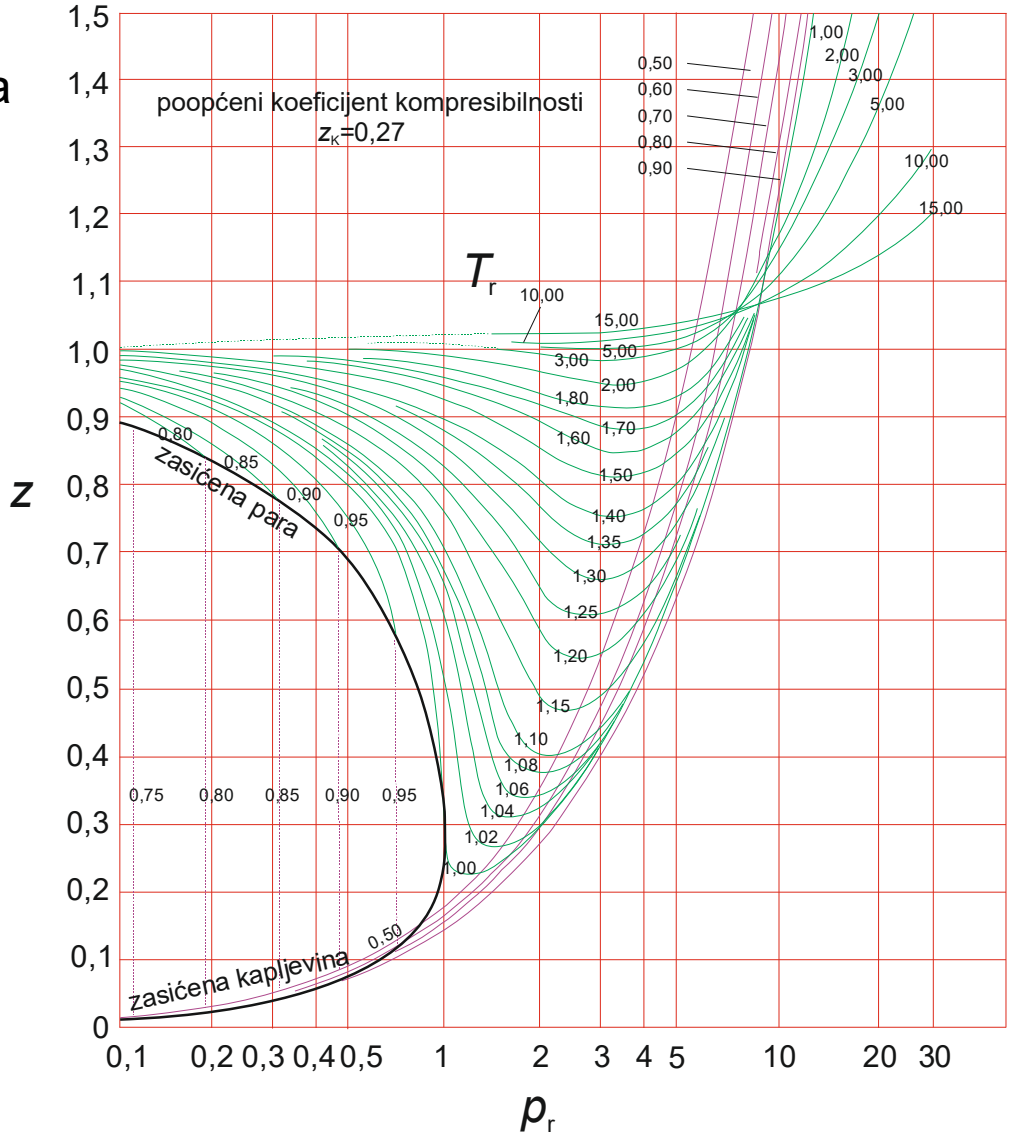
Dvoparametarska grafička korelacija

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



Troparametarska grafička korelacija

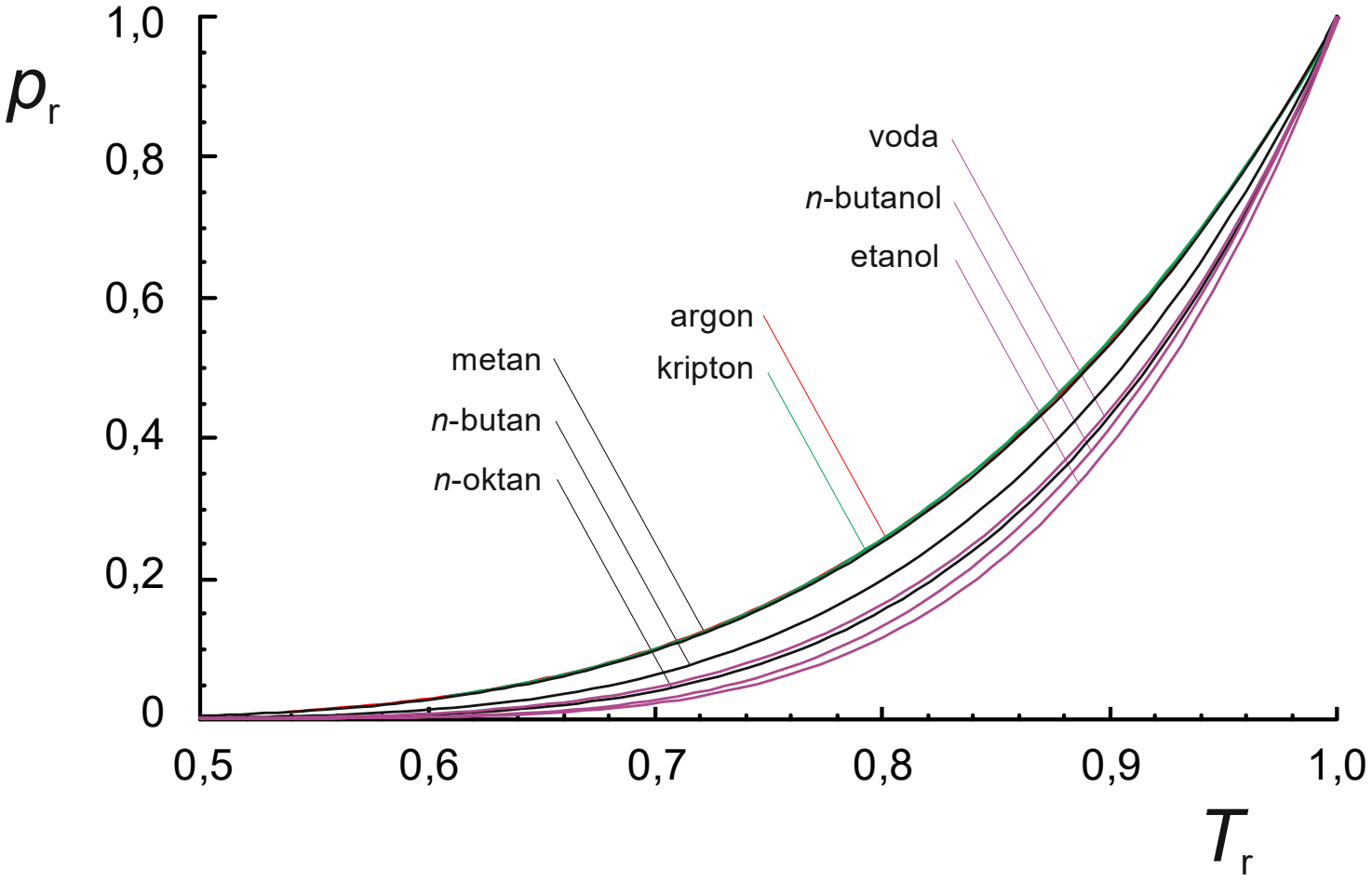
$$z = \mathrm{f}(p_\mathrm{r}, T_\mathrm{r}, z_\mathrm{K})$$



Načelo termodin. sličnosti

Pitzerova korelacija (1955)





Načelo termodin. sličnosti

Pitzerova korelacija (1955)

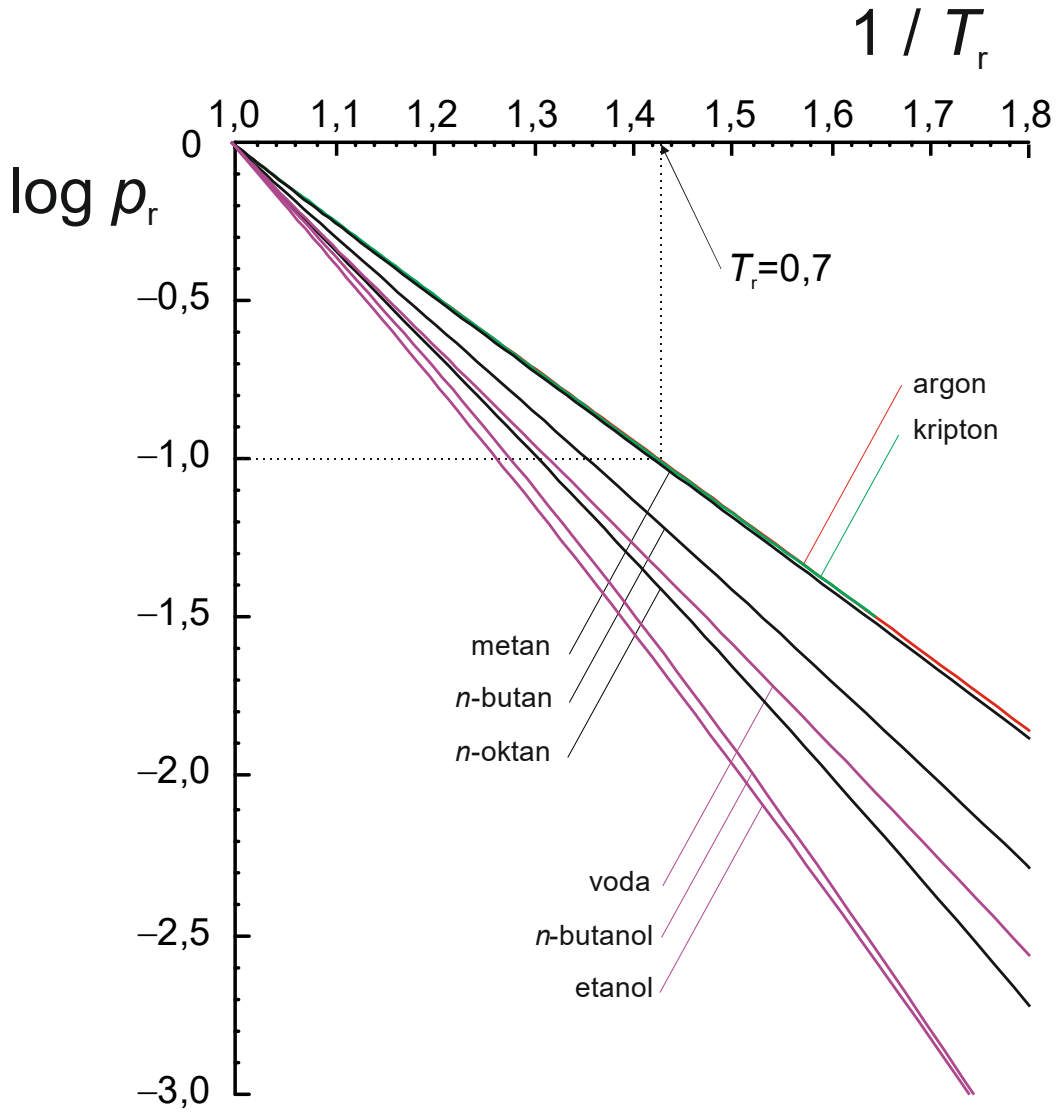
$$\omega = -\log\left(p_{\mathrm{r}}^{\bullet}\right)_{T_{\mathrm{r}}=0,7} - 1$$

Dvoparametarska korelacija

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

Troparametarska korelacija

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



Načelo termodin. sličnosti

Pitzerova korelacija (1955)

Taylorov red



$$z = z_{\omega=0} + \omega\left(\frac{\partial z}{\partial \omega}\right)_{\omega=0} + \frac{\omega^2}{2}\left(\frac{\partial^2 z}{\partial \omega^2}\right)_{\omega=0} + \ldots$$

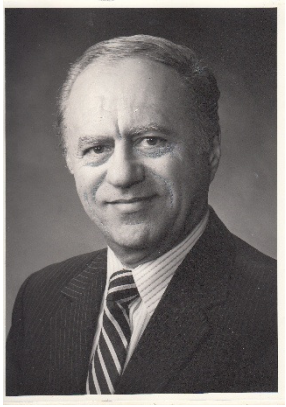
$$z = z^{(0)} + \omega z^{(1)} + \ldots$$

Linearizacija

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

$z^{(0)}$ – odsječak, $z^{(1)}$ – nagib

Načelo termodin. sličnosti

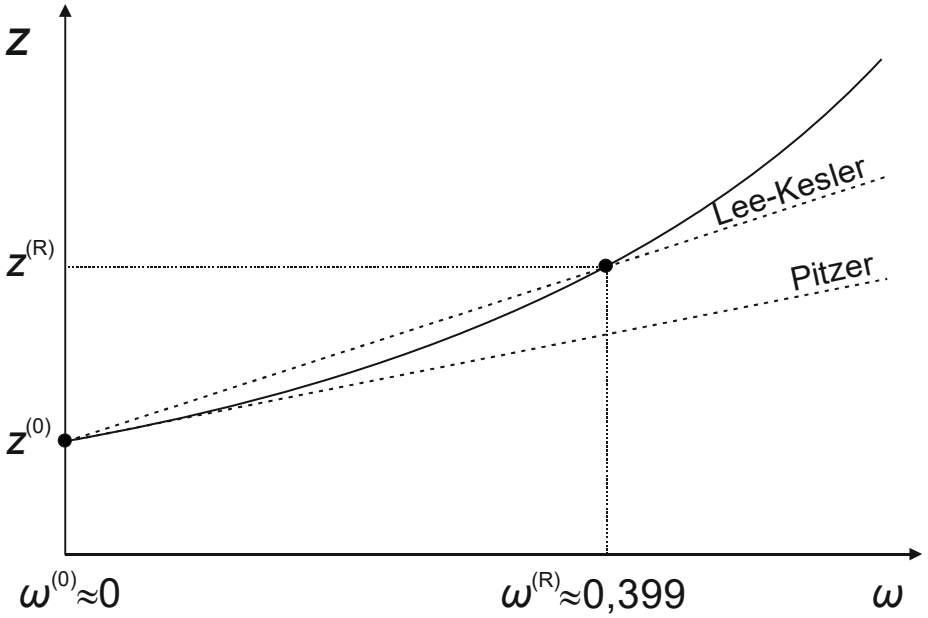


Lee-Keslerova korelacija (1975)

Dvije kapljevine
argon (sferična), ω=0
n-oktan (izdužena), ω=0,399

$$\frac{z - z^{(0)}}{\omega - \omega^{(0)}} = \frac{z^{(R)} - z^{(0)}}{\omega^{(R)} - \omega^{(0)}}$$

$z^{(0)}$ – odsječak (argon)
$z^{(R)}$ – (*n*-oktan)



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

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

$z^{(0)}$ – odsječak, $z^{(1)}$ – nagib

Načelo termodin. sličnosti

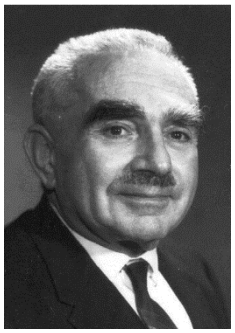
	argon	*n*-oktan		argon	*n*-oktan
b_1	0,118193	0,2026579	c_3	0	0,016901
b_2	0,265728	0,331511	c_4	0,042724	0,041577
b_3	0,154790	0,027655	d_1	0,155488	0,48736
b_4	0,030323	0,203488	d_2	0,623689	0,0740336
c_1	0,236744	0,0313385	β	0,65392	1,226
c_2	0,0186984	0,0503618	γ	0,60167	0,03754

Starling BWR (SBWR), 1973 $$z = \frac{pv}{RT} = 1 + \frac{B}{v_r} + \frac{C}{v_r^2} + \frac{D}{v_r^5} + \frac{c_4}{T_r^3 v_r^2} + \left[\beta + \frac{\gamma}{v_r^2}\right] \exp\left[-\frac{\gamma}{v_r^2}\right]$$

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3} \qquad C = c_1 - \frac{c_2}{T_r} - \frac{c_3}{T_r^2} \qquad D = d_1 - \frac{d_2}{T_r}$$

Jed. stanja trećeg stupnja

Redlich-Kwong
(1949)





$$p = \frac{RT}{v-b} - \frac{a}{\sqrt{T}v(v+b)}$$

$$v^3 - \frac{RT}{p}v^2 - \left(b^2 + \frac{RTb}{p} - \frac{a}{p\sqrt{T}}\right)v - \frac{ab}{p\sqrt{T}} = 0$$

$$z^3 - z^2 - \left(\frac{b^2p^2}{R^2T^2} + \frac{pb}{RT} - \frac{ap}{R^2T^2\sqrt{T}}\right)z - \frac{abp^2}{R^3T^3\sqrt{T}} = 0$$

$$z^3 - z^2 + \left(A - B^2 - B\right)z - AB = 0$$

Jed. stanja trećeg stupnja

Redlich-Kwong (1949)

dvoparametarska

$$a = \frac{\Omega_a R^2 T_{\mathrm{K}}^{5/2}}{p_{\mathrm{K}}} \qquad b = \frac{\Omega_b R T_{\mathrm{K}}}{p_{\mathrm{K}}}$$

Mikroskopski parametri

Makroskopski parametri

$$A = \frac{ap}{R^2 T^{5/2}} \qquad B = \frac{bp}{RT}$$

Jed. stanja trećeg stupnja

Redlich-Kwong (1949)

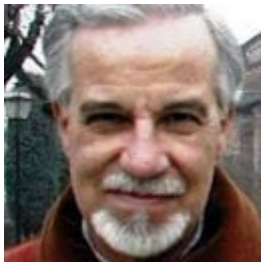
Načelo korespondentnih stanja $\left[p_r + \frac{1}{\sqrt{T_r} v_r \Omega \left(v_r + \Omega \right)} \right] \left(v_r - \Omega \right) = 3 T_r$

$$z^3 - z^2 - \left(\frac{\Omega^2 p_r^2}{9 T_r^2} + \frac{\Omega p_r}{3 T_r} - \frac{1}{9\Omega} \frac{p_r}{T_r^{5/2}} \right) z - \frac{p_r^2}{27 T_r^{7/2}} = 0$$

z_K(RK)=1/3 z_K(vdW)=3/8 z_K(exp)=0,23-0,31

Jed. stanja trećeg stupnja

Soave-Redlich-Kwong (1972)



$$p = \frac{RT}{v-b} - \frac{a\alpha}{v\left(v+b\right)}$$

$$v^3 - \frac{RT}{p}v^2 - \left(b^2 + \frac{RTb}{p} - \frac{a\alpha}{p}\right)v - \frac{a\alpha b}{p} = 0$$

$$z^3 - z^2 - \left(\frac{b^2p^2}{R^2T^2} + \frac{bp}{RT} - \frac{a\alpha p}{R^2T^2}\right)z - \frac{a\alpha bp^2}{R^3T^3} = 0$$

$$z^3 - z^2 + \left(A - B^2 - B\right)z - AB = 0$$

Jed. stanja trećeg stupnja

Soave-Redlich-Kwong (1972)

$$a = \frac{\Omega_a R^2 T_{\mathrm{K}}^2}{p_{\mathrm{K}}} \qquad b = \frac{\Omega_b R T_{\mathrm{K}}}{p_{\mathrm{K}}}$$

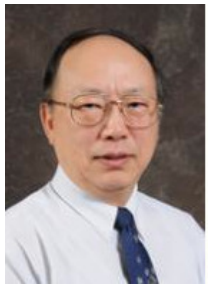
$$\alpha = \left[1 + \kappa\left(1 - \sqrt{T_{\mathrm{r}}}\right)\right]^2$$

$$\kappa = 0,48508 + 1,55171\omega - 0,15613\omega^2$$

$$A = \frac{a\alpha p}{R^2 T^2} \qquad B = \frac{bp}{RT}$$

Jed. stanja trećeg stupnja

Peng-Robinson (1976)





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

$$v^3 - \left(\frac{RT}{p} - b\right)v^2 - \left(3b^2 + \frac{2RTb}{p} - \frac{a\alpha}{p}\right)v - \left(\frac{a\alpha b}{p} - \frac{RTb^2}{p} - b^3\right) = 0$$

$$z^3 - \left(1 - \frac{bp}{RT}\right)z^2 - \left(\frac{3b^2p^2}{R^2T^2} + \frac{2bp}{RT} - \frac{a\alpha p}{R^2T^2}\right)z - \left(\frac{a\alpha bp^2}{R^3T^3} - \frac{b^2p^2}{R^2T^2} - \frac{b^3p^3}{R^3T^3}\right) = 0$$

$$z^3 - (1-B)z^2 + \left(A - 3B^2 - 2B\right)z - \left(AB - B^2 - B^3\right) = 0$$

Jed. stanja trećeg stupnja

Peng-Robinson (1976)

$$a = \frac{\Omega_a R^2 T_{\mathrm{K}}^2}{p_{\mathrm{K}}} \qquad b = \frac{\Omega_b R T_{\mathrm{K}}}{p_{\mathrm{K}}}$$

$$\alpha = \left[1 + \kappa\left(1 - \sqrt{T_{\mathrm{r}}}\right)\right]^2$$

$$\kappa = 0,37464 + 1,54226\omega - 0,26992\omega^2$$

$$A = \frac{a\alpha p}{R^2 T^2}$$

$$B = \frac{bp}{RT}$$

z_{K}(PR)=0,3074

Jed. stanja trećeg stupnja

Clausius

$$p = \frac{RT}{v-b} - \frac{a}{T(v+c)^2}$$

Berthelot

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

Patel-Teja

$$p = \frac{RT}{v-b} - \frac{a\alpha}{v(v+b)+c(v-b)}$$

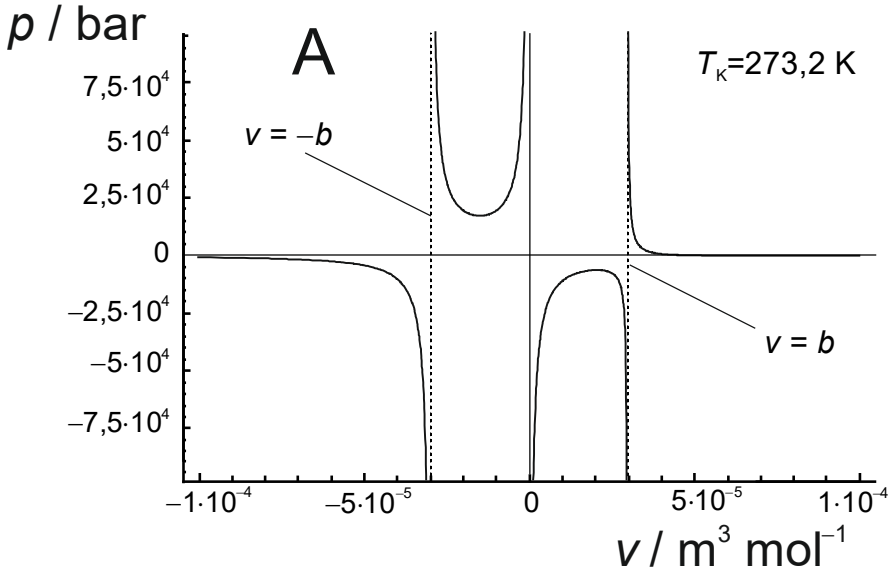
Peng-Robinson-Stryjek-Vera

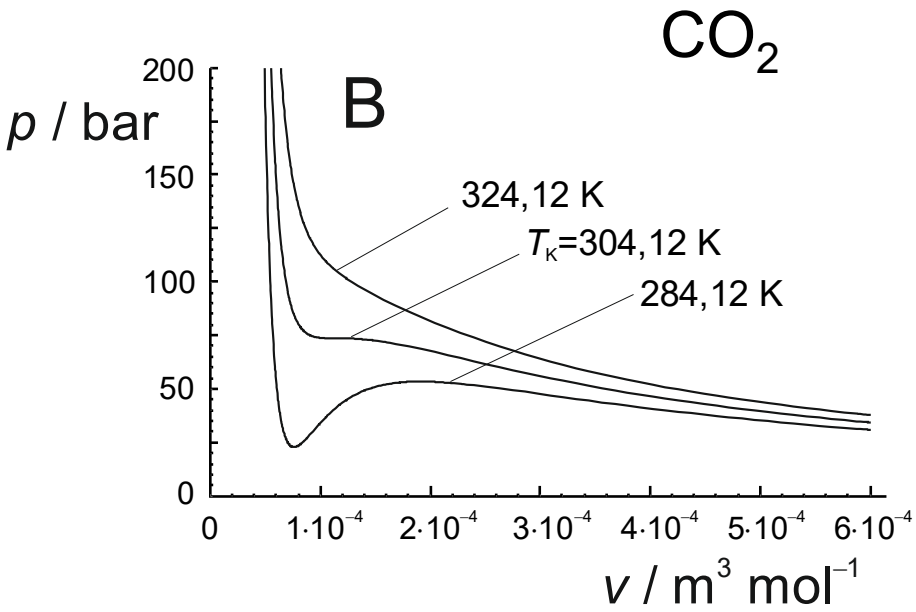
Treble-Bishnoi

$$p = \frac{RT}{v-b} - \frac{a\alpha}{v^2+(b+c)v-bc+d^2}$$

Jed. stanja trećeg stupnja

Izračunavanje volumetrijskih svojstava

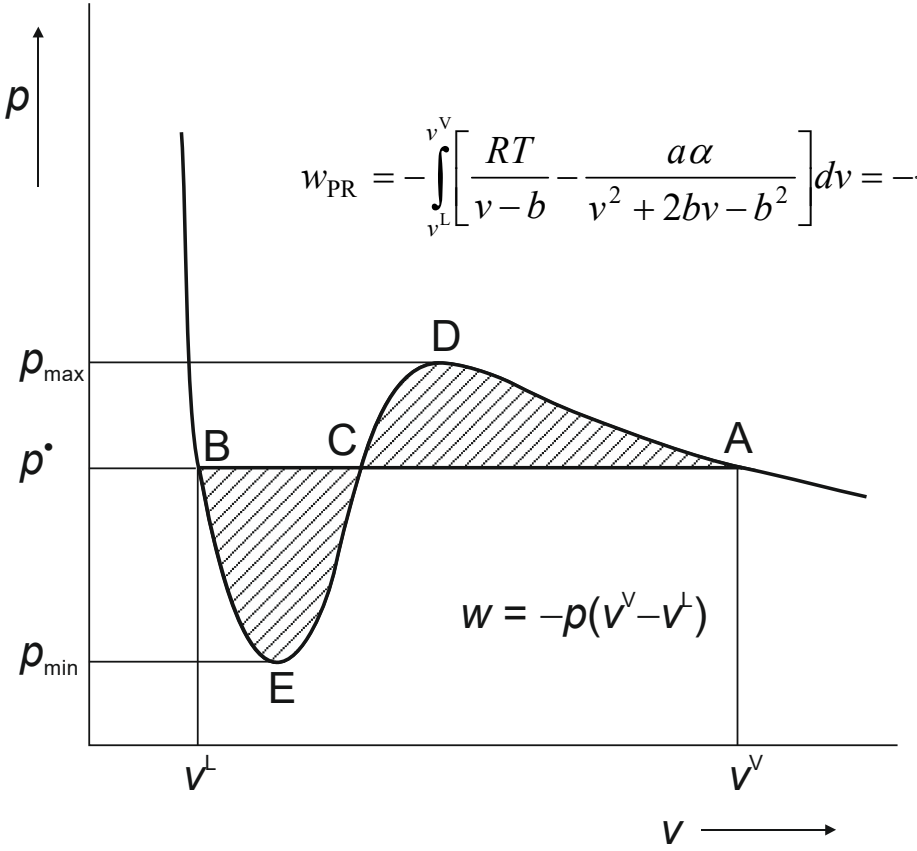




Jed. stanja trećeg stupnja

Izračunavanje volumetrijskih svojstava

Izbor stabilne faze



$$w_{\mathrm{PR}} = -\int_{v^{\mathrm{L}}}^{v^{\mathrm{V}}}\left[\frac{RT}{v-b} - \frac{a\alpha}{v^2+2bv-b^2}\right]dv = -\left\{RT\ln\frac{v^{\mathrm{V}}-b}{v^{\mathrm{L}}-b} + \frac{a\alpha}{2\sqrt{2}b}\ln\left[\frac{v^{\mathrm{V}}+b\left(1+\sqrt{2}\right)}{v^{\mathrm{V}}+b\left(1-\sqrt{2}\right)}\right]\left[\frac{v^{\mathrm{L}}+b\left(1-\sqrt{2}\right)}{v^{\mathrm{L}}+b\left(1+\sqrt{2}\right)}\right]\right\}$$

Peng-Robinson

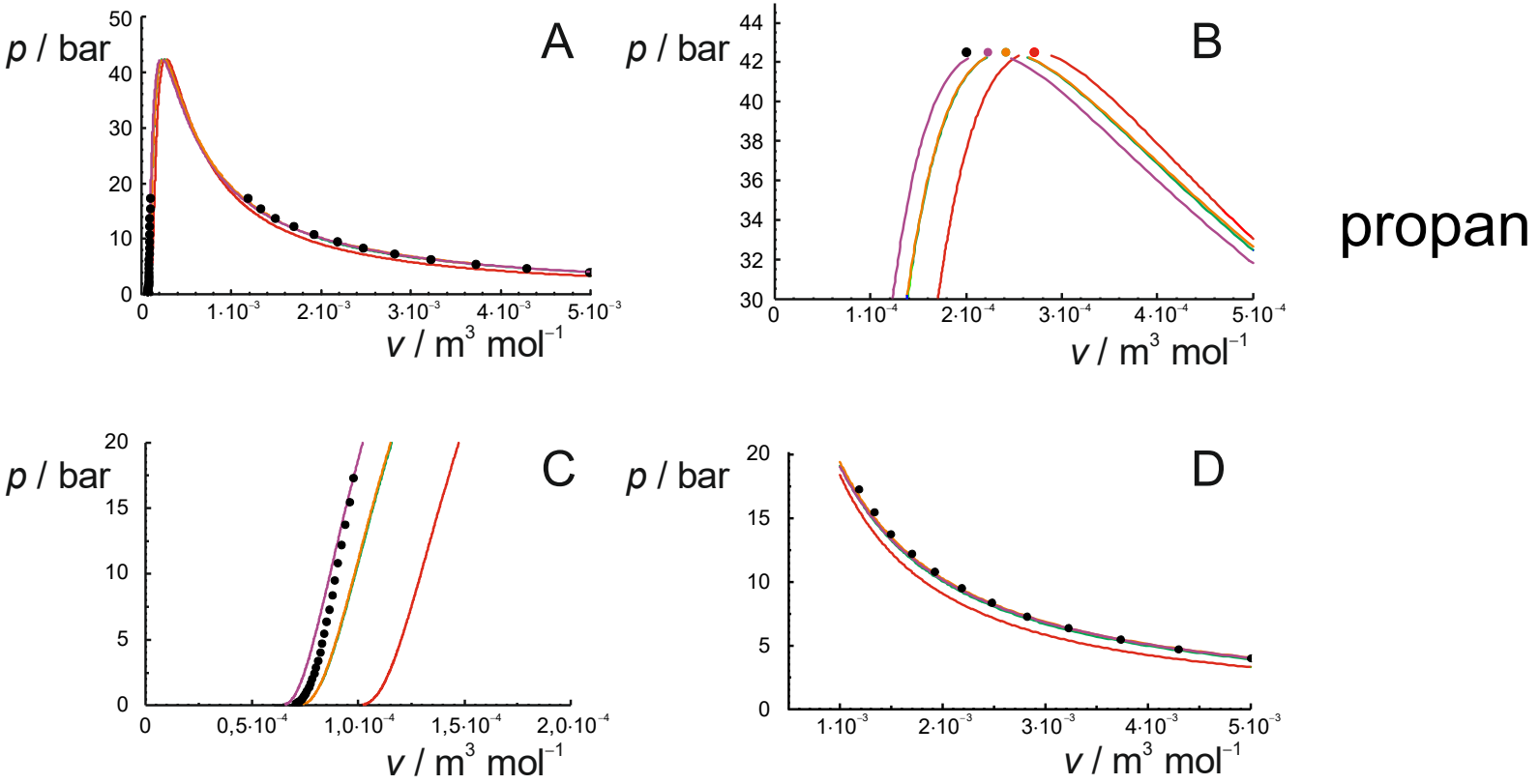
Usporedba jednadžbi stanja

NAZIV	FORMALNI PRIKAZ	PARAMETRI
Opća plinska jednadžba	$pv = RT$	-
van der Waals	$\left[p + \frac{a}{v^2}\right](v - b) = RT$	$T_\mathrm{K}, p_\mathrm{K}$
Virijalna jednadžba stanja, dvočlana	$p[v - B(T)] = RT$	$T_\mathrm{K}, p_\mathrm{K}(v_\mathrm{K}), \omega, \mu, a_3,$ ...
Virijalna jednadžba stanja, tročlana	$\left[p - \frac{RTvB(T) + RTC(T)}{v^3}\right]v = RT$	$T_\mathrm{K}, p_\mathrm{K}(v_\mathrm{K}), \omega, \mu, a_3,$ ...
Clausius	$\left[p + \frac{a}{T(v+c)^2}\right](v - b) = RT$	$T_\mathrm{K}, p_\mathrm{K}, v_\mathrm{K}$
Berthelot	$\left(p + \frac{a}{Tv^2}\right)(v - b) = RT$	a, b
Redlich-Kwong	$\left[p + \frac{a}{\sqrt{T}v(v+b)}\right](v - b) = RT$	$T_\mathrm{K}, p_\mathrm{K}$

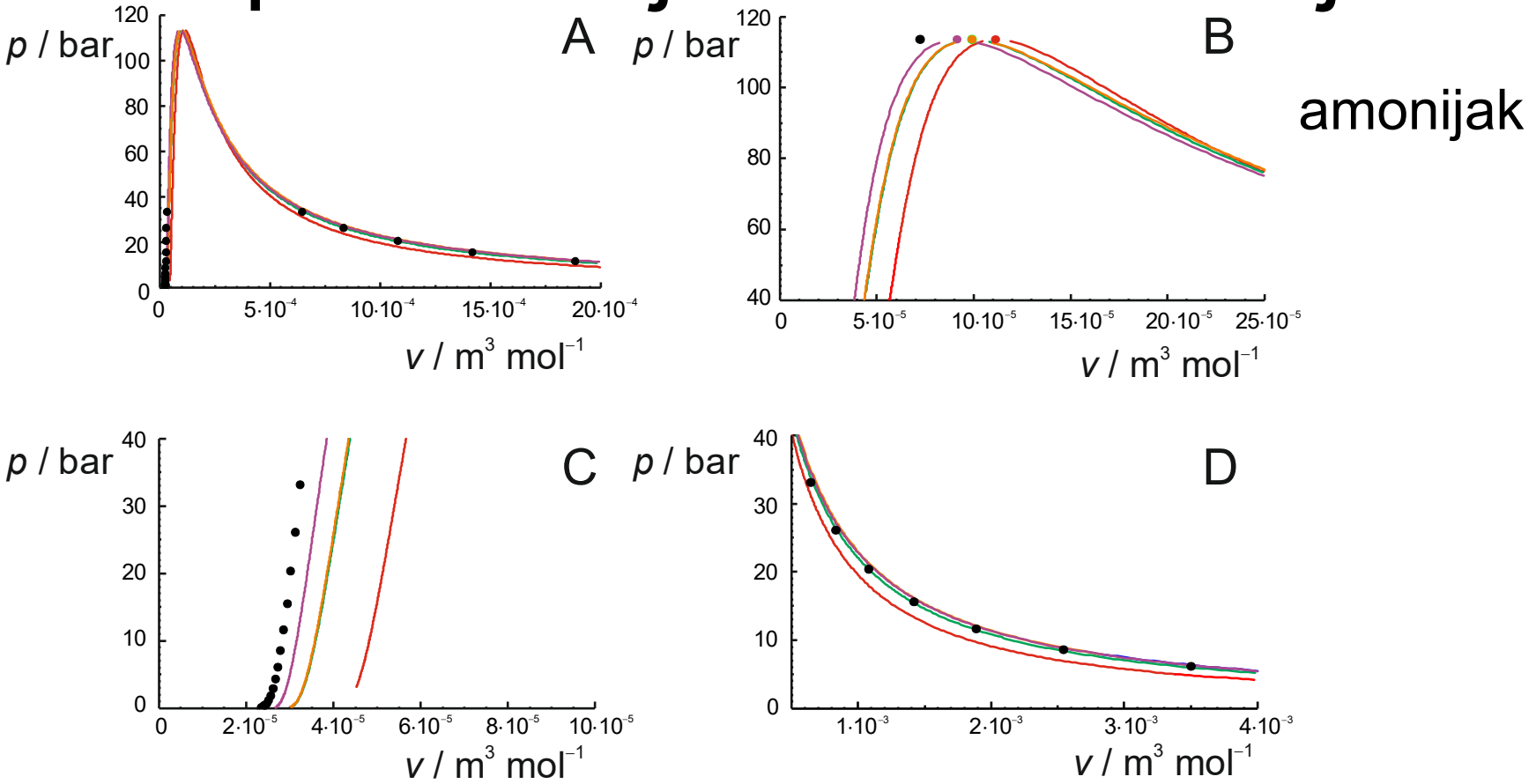
Usporedba jednadžbi stanja

NAZIV	FORMALNI PRIKAZ	PARAMETRI
Soave-Redlich-Kwong	$\left[p+\frac{a\alpha(T)}{v(v+b)}\right](v-b)=RT$	T_K, p_K, ω
Peng-Robinson	$\left[p+\frac{a\alpha(T)}{v(v+b)+b(v-b)}\right](v-b)=RT$	T_K, p_K, ω
Patel-Teja	$\left[p+\frac{a\alpha(T)}{v(v+b)+c(v-b)}\right](v-b)=RT$	T_K, p_K, ω
Stryjek-Vera-Peng-Robinson	$\left[p+\frac{a\alpha(T)}{v(v+b)+b(v-b)}\right](v-b)=RT$	T_K, p_K, ω, κ_1
Treble-Bishnoi	$\left\{p+\frac{a\alpha(T)}{v^2+[b(T)+c]v-b(T)c+d^2}\right\}[v-b(T)]=RT$	T_K, p_K, z_K, (v_K), ω

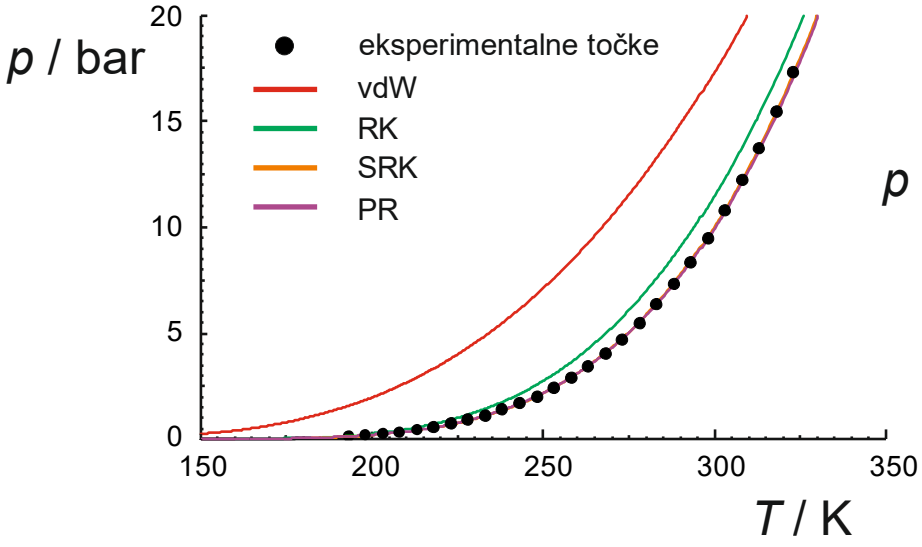
Usporedba jednadžbi stanja



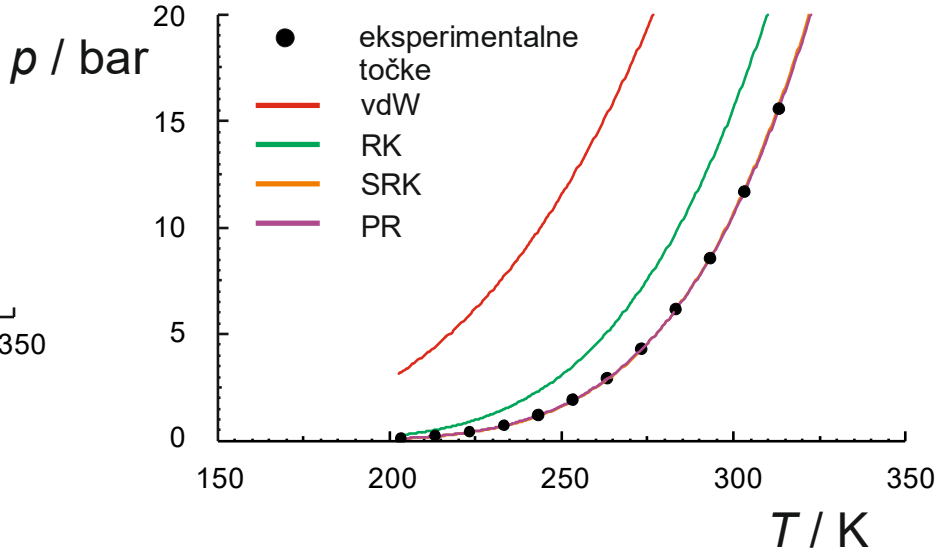
Usporedba jednadžbi stanja



Usporedba jednadžbi stanja

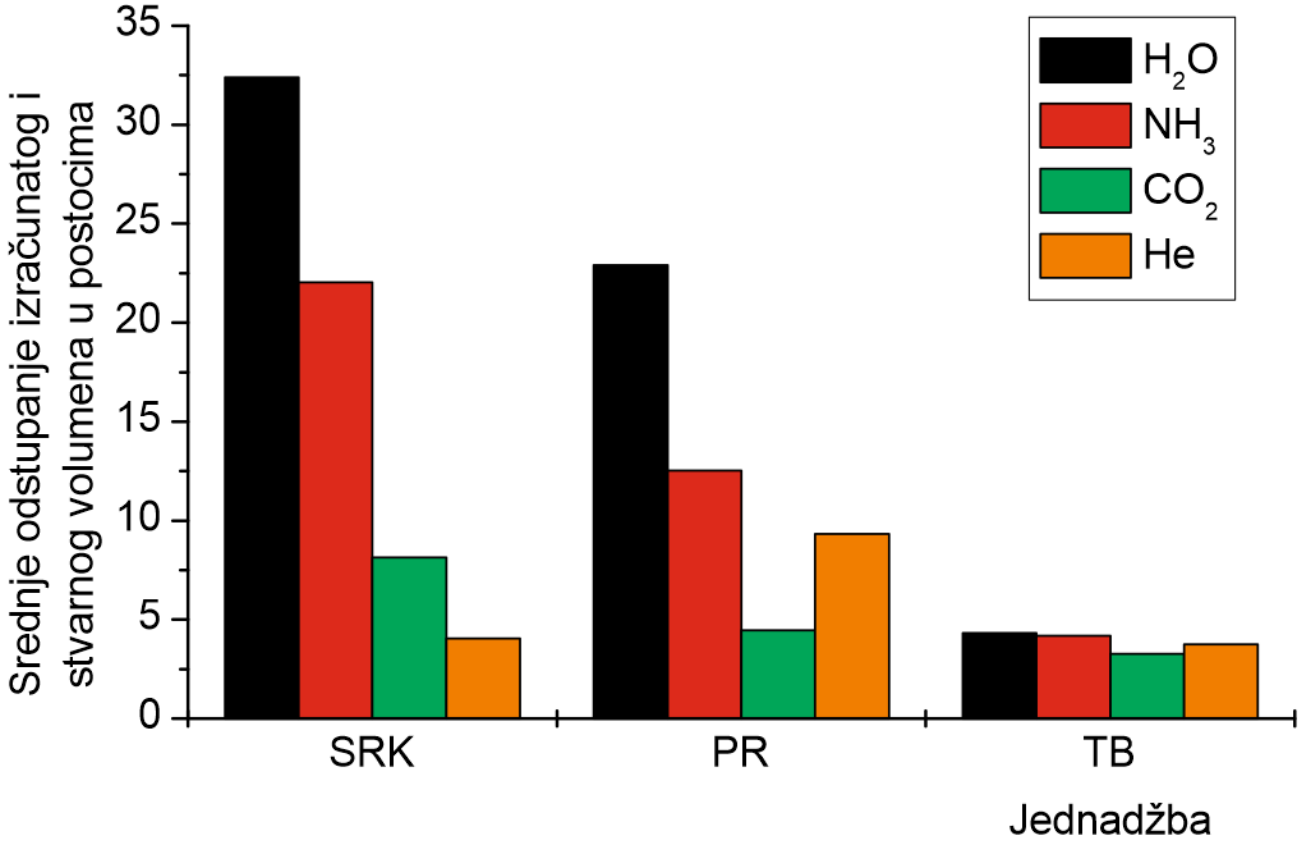


propan



amonijak

Usporedba jednadžbi stanja



Plinske smjese

Jednadžba stanja Redlich-Kwong za smjesu:

$$p = \frac{RT}{v - b_{\mathrm{M}}} - \frac{a_{\mathrm{M}}}{\sqrt{T}\, v\left(v + b_{\mathrm{M}}\right)}$$

PRAVILA MIJEŠANJA

Parametri jednadžbe stanja za smjesu:

$$a_{\mathrm{M}} = f\left(a_i\right)$$
$$b_{\mathrm{M}} = f\left(b_i\right)$$

Parametri jednadžbe stanja za smjesu:

$$a_{\mathrm{M}} = \frac{\Omega_a R^2 T_{\mathrm{PK}}^{5/2}}{p_{\mathrm{PK}}}$$
$$b_{\mathrm{M}} = \frac{\Omega_b R T_{\mathrm{PK}}}{p_{\mathrm{PK}}}$$

Parametri jednadžbe stanja za komponente:

$$a_i = \frac{\Omega_a R^2 T_{\mathrm{K}i}^{5/2}}{p_{\mathrm{K}i}}$$
$$b_i = \frac{\Omega_b R T_{\mathrm{K}i}}{p_{\mathrm{K}i}}$$

Pseudokritični parametri za smjesu:

$$T_{\mathrm{PK}} = f\left(T_{\mathrm{K}i}\right)$$
$$p_{\mathrm{PK}} = f\left(p_{\mathrm{K}i}\right)$$

PSEUDOKRITIČNI PARAMETRI

Eksperimentalni podaci: kritični parametri komponenata

$$p_{\mathrm{K}i}, T_{\mathrm{K}i}$$

Plinske smjese

Pseudokritični parametri

Van der Waals

$$v_{PK} = \sum y_i v_{Ki}$$

$$\frac{T_{PK}}{\sqrt{p_{PK}}} = \sum \frac{y_i T_{Ki}}{\sqrt{p_{Ki}}}$$

$$\frac{T_{PK}}{p_{PK}} = \sum \frac{y_i T_{Ki}}{p_{Ki}}$$

Kay (1930)

$$v_{PK} = \sum y_i v_{Ki}$$

$$T_{PK} = \sum y_i T_{Ki}$$

$$p_{PK} = \sum y_i p_{Ki}$$

Prausnitz-Gunn (1958)

$$v_{PK} = \sum y_i v_{Ki}$$

$$z_{PK} = \sum y_i z_{Ki}$$

$$T_{PK} = \sum y_i T_{Ki}$$

$$p_{PK} = \frac{z_{PK} R T_{PK}}{v_{PK}}$$

Plinske smjese

Pravila miješanja

RK, SRK, PR

$$b_M = \sum y_i b_i$$

$$B_M = \sum y_i B_i$$

$$b_M = y_1 b_1 + y_2 b_2$$

$$(a\alpha)_M = \sum\sum y_i y_j (a\alpha)_{ij}$$

$$A_M = \sum\sum y_i y_j A_{ij}$$

$$a_M = \sum\sum y_i y_j a_{ij} \quad \text{RK}$$

$$a_M = y_1^2 a_1 + 2 y_1 y_2 a_{12} + y_2^2 a_2$$

$$a_{ij} = \sqrt{a_i a_j} \quad \text{RK}$$

$$a_{ij} = (1 - k_{ij})\sqrt{a_i a_j} \quad \text{SRK, PR}$$