1. ZADATAK

Izračunati volumen 100 kg CO_2 pri tlaku od 5,0 MPa i temperaturi od 100 °C. Pretpostaviti da se plin pri tim uvjetima vlada prema:

A) Redlich-Kwongovoj jednadžbi stanja

1) postupkom direktne iteracije

2) Newtonovim postupkom tangente

B) Korigiranoj općoj plinskoj jednadžbi stanja. Koeficijent kompresibilnosti računati kao troparametarsku veličinu

Podaci:

T_K=304,1 K; p_K=7,387 MPa; M=44 g mol^{-1};

ω=0,239; Ω_a=0,427480; Ω_b=0,086640

REDLICH KWONG (1949)

Prva moderna jednadžba stanja trećeg stupnja

Jednadžba

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

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

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

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

Parametri

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

$$\Omega_a = \frac{1}{9\left(2^{1/3} - 1\right)} = 0{,}427480$$

$$\Omega_b = \frac{\left(2^{1/3} - 1\right)}{3} = 0{,}086640$$

$$A = \frac{ap}{R^2T^{5/2}} = \frac{\Omega_a p_{\mathrm{r}}}{T_{\mathrm{r}}^{5/2}} \qquad B = \frac{bp}{RT} = \frac{\Omega_b p_{\mathrm{r}}}{T_{\mathrm{r}}}$$

Idealni plin

$$pv = RT$$

Bezdimenzijske čestice – niski tlakovi
Nema međudjelovanja – niski tlakovi, visoke temperature

Zadatak:
T=100 °C (T_K=304,1 K)
Je li to visoka temperatura?

Zadatak:
p=5 MPa (p_K=7,387 MPa)
Je li to niski tlak?

Redlich-Kwong

$$\left[p + \frac{a}{\sqrt{T}\, v\left(v+b\right)} \right]\left(v-b\right) = RT$$

Fizički smisao parametara *a* i *b*?
Ovisnost interakcijske korekcije o temperaturi?

- Empirijska jednadžba stanja
- Parametri se računaju iz kritičnih svojstava
- Primjena kod visokih tlakova
- Ne primjenjivati kod previsokih temperatura
- Primjenjivati kod nepolarnih i slabo polarnih fluida i njihovih smjesa

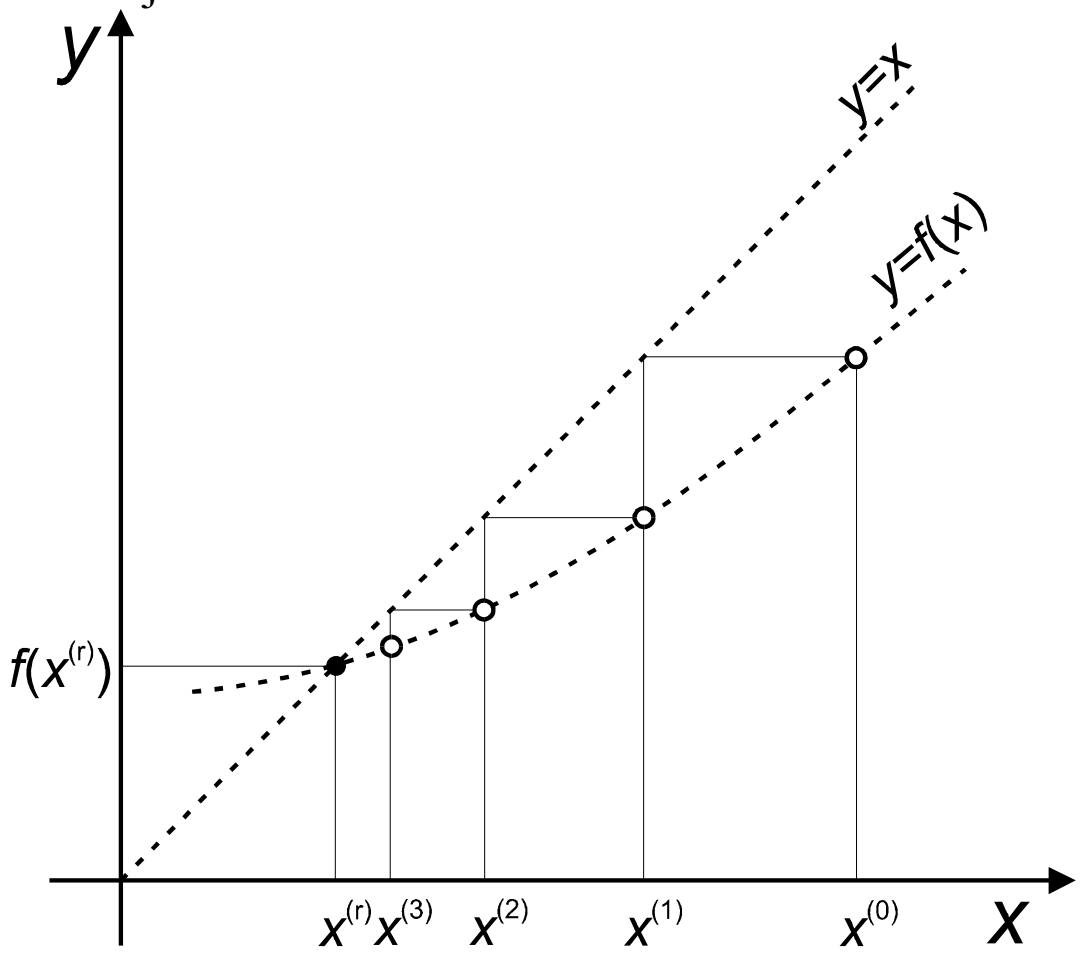
IZRAVNA (DIREKTNA) ITERACIJA

Numerička shema

$$g(x) = 0 \quad \Rightarrow \quad x = f(x)$$

$$x^{(i+1)} = f\left(x^{(i)}\right)$$

Ilustracija



Zadatak:

$$m\left(\mathrm{CO_2}\right) = 100\ \mathrm{kg}$$

$$p = 5,0\ \mathrm{MPa} = 5 \cdot 10^6\ \mathrm{Pa}$$

$$T = 100\ ^\circ\mathrm{C} = 373,15\ \mathrm{K}$$

$$n = \frac{m}{M} = \frac{100}{44 \cdot 10^{-3}} = 2272,73\ \mathrm{mol}$$

Jednadžba stanja trećeg stupnja

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

Parametri:

$$a = \frac{\Omega_a R^2 T_\mathrm{K}^{5/2}}{p_\mathrm{K}} = \frac{0,427480 \cdot 8,314^2 \cdot 304,1^{2,5}}{7,387 \cdot 10^6} = 6,451$$

$$b = \frac{\Omega_b R T_\mathrm{K}}{p_\mathrm{K}} = \frac{0,086640 \cdot 8,314 \cdot 304,1}{7,387 \cdot 10^6} = 2,965 \cdot 10^{-5}$$

Nije eksplicitna po volumenu!

$$v = f(v)$$

$$v^{(i+1)} = f\left(v^{(i)}\right)$$

$$v^{(i+1)} = \frac{RT}{p + \frac{a}{\sqrt{T}v^{(i)}\left(v^{(i)} + b\right)}} + b$$

Prva aproksimacija – idealni plin:

$$pv = RT$$

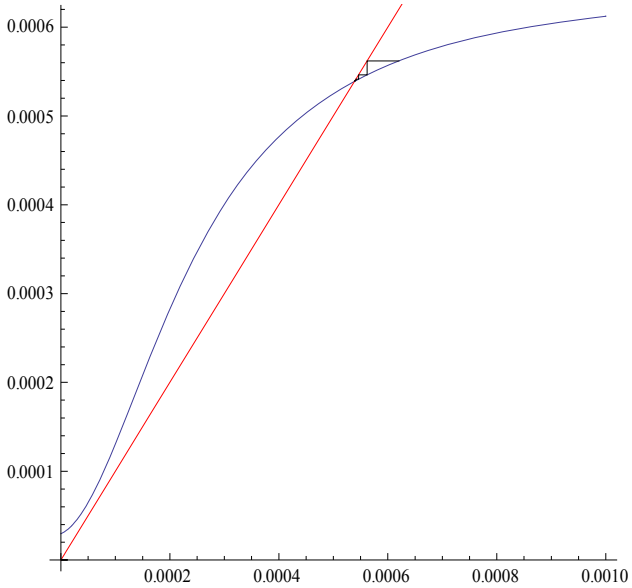
$$v^{(0)} = \frac{RT}{p} = \frac{8,314 \cdot 373,15}{5 \cdot 10^6} = 6,205 \cdot 10^{-4}\ \mathrm{m^3 mol^{-1}}$$

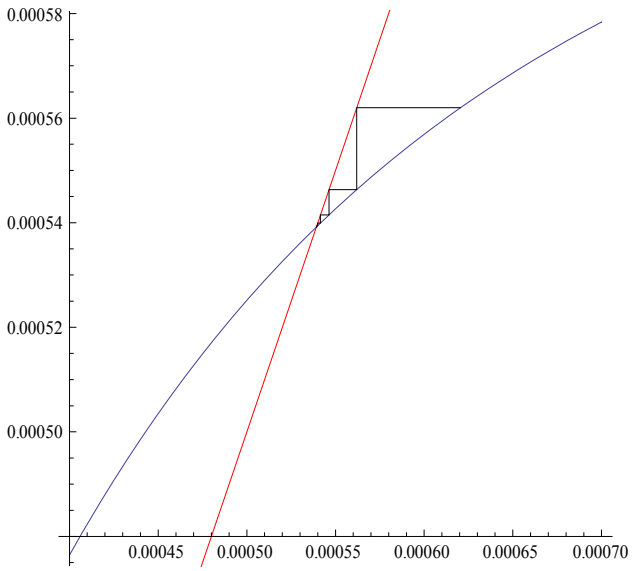
$$v^{(1)} = \frac{RT}{p + \frac{a}{\sqrt{T}v^{(0)}\left(v^{(0)} + b\right)}} + b$$

$$v^{(1)} = \frac{8,314 \cdot 373,15}{5 \cdot 10^6 + \frac{6,451}{\sqrt{373,15} \cdot 6,205 \cdot 10^{-4}\left(6,205 \cdot 10^{-4} + 2,965 \cdot 10^{-5}\right)}} + 2,965 \cdot 10^{-5}$$

$$v^{(1)} = \frac{3102,369}{5 \cdot 10^6 + \frac{0,33395}{6,205 \cdot 10^{-4}\left(6,205 \cdot 10^{-4} + 2,965 \cdot 10^{-5}\right)}} + 2,965 \cdot 10^{-5}$$

$v^{(1)} = 5,61983 \cdot 10^{-4}\ \mathrm{m^3 mol^{-1}}$	$v^{(6)} = 5,39242 \cdot 10^{-4}\ \mathrm{m^3 mol^{-1}}$
$v^{(2)} = 5,46332 \cdot 10^{-4}\ \mathrm{m^3 mol^{-1}}$	$v^{(7)} = 5,39187 \cdot 10^{-4}\ \mathrm{m^3 mol^{-1}}$
$v^{(3)} = 5,41486 \cdot 10^{-4}\ \mathrm{m^3 mol^{-1}}$	$v^{(8)} = 5,39168 \cdot 10^{-4}\ \mathrm{m^3 mol^{-1}}$
$v^{(4)} = 5,39922 \cdot 10^{-4}\ \mathrm{m^3 mol^{-1}}$	$v^{(9)} = 5,39162 \cdot 10^{-4}\ \mathrm{m^3 mol^{-1}}$
$v^{(5)} = 5,39410 \cdot 10^{-4}\ \mathrm{m^3 mol^{-1}}$	$v^{(10)} = 5,39160 \cdot 10^{-4}\ \mathrm{m^3 mol^{-1}}$





$$V = nv = 2272,73 \cdot 5,39160 \cdot 10^{-4} = 1,22537\ \mathrm{m^3}$$

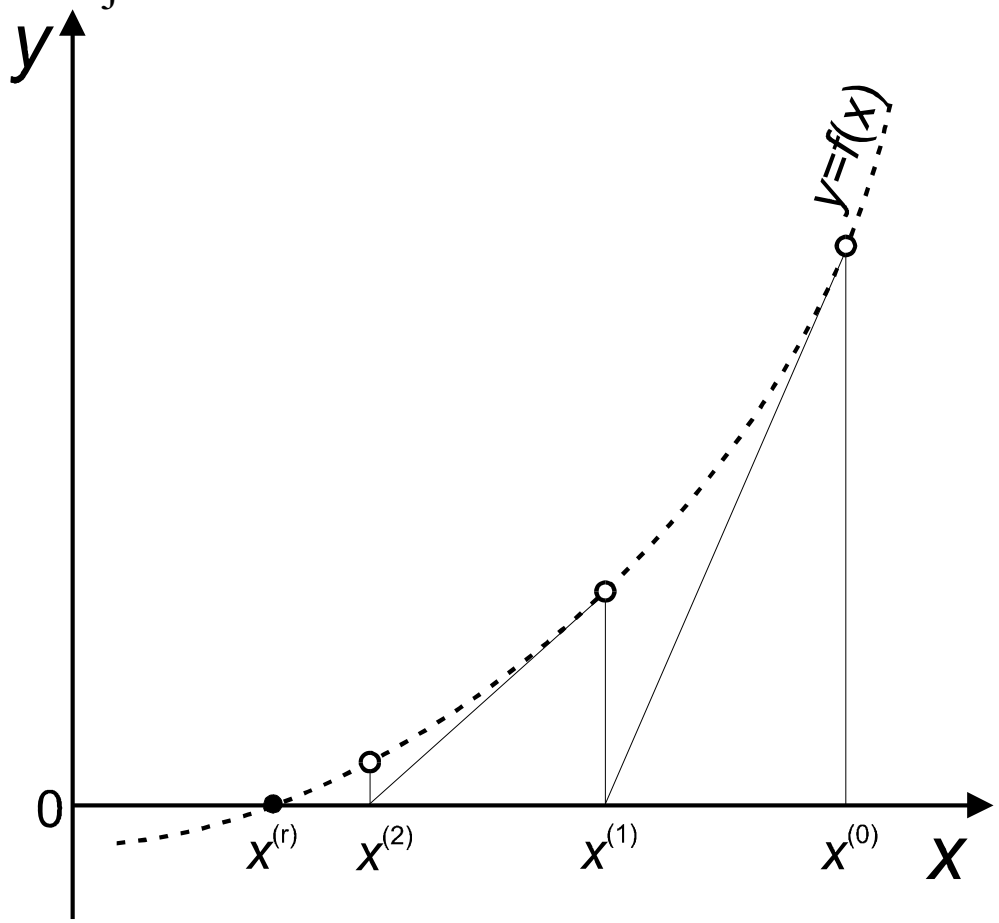
NEWTONOVA METODA TANGENTE

Numerička shema

$$f(x) = 0$$

$$x^{(i+1)} = x^{(\mathrm{i})} - \frac{f\left(x^{(\mathrm{i})}\right)}{f'\left(x^{(\mathrm{i})}\right)}$$

Ilustracija



Zadatak:

$$m\left(\mathrm{CO_2}\right) = 100\ \mathrm{kg}$$

$$p = 5{,}0\ \mathrm{MPa} = 5 \cdot 10^6\ \mathrm{Pa}$$

$$T = 100\ ^\circ\mathrm{C} = 373{,}15\ \mathrm{K}$$

$$n = \frac{m}{M} = \frac{100}{44 \cdot 10^{-3}} = 2272{,}73\ \mathrm{mol}$$

Jednadžba stanja trećeg stupnja

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

Parametri:

$$a = \frac{\Omega_a R^2 T_\mathrm{K}^{5/2}}{p_\mathrm{K}} = \frac{0{,}427480 \cdot 8{,}314^2 \cdot 304{,}1^{2{,}5}}{7{,}387 \cdot 10^6} = 6{,}451$$

$$b = \frac{\Omega_b R T_\mathrm{K}}{p_\mathrm{K}} = \frac{0{,}086640 \cdot 8{,}314 \cdot 304{,}1}{7{,}387 \cdot 10^6} = 2{,}965 \cdot 10^{-5}$$

$$A = \frac{ap}{R^2 T^{5/2}} = \frac{6{,}451 \cdot 5 \cdot 10^6}{8{,}314^2 \cdot 373{,}15^{2{,}5}} = 0{,}1735$$

$$B = \frac{bp}{RT} = \frac{2{,}965 \cdot 10^{-5} \cdot 5 \cdot 10^6}{8{,}314 \cdot 373{,}15} = 0{,}0478$$

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

$$f'(z) = 3z^2 - 2z + \left(A - B^2 - B\right)$$

$$f(z) = 0$$

$$z^{(i+1)} = z^{(i)} - \frac{f\left(z^{(i)}\right)}{f'\left(z^{(i)}\right)}$$

Temperatura iznad kritične, očekuje se samo jedno realno rješenje polinoma:

Prva aproksimacija – idealni plin:

$$z^{(0)} = \frac{pv}{RT} = 1$$

$$f\left(z^{(0)}\right) = 1^3 - 1^2 + \left(0{,}1735 - 0{,}0478^2 - 0{,}0478\right)1 - 0{,}1735 \cdot 0{,}0478 = 0{,}1151$$

$$f'\left(z^{(0)}\right) = 3 \cdot 1^2 - 2 \cdot 1 + \left(0{,}1735 - 0{,}0478^2 - 0{,}0478\right) = 1{,}1234$$

$$z^{(1)} = z^{(0)} - \frac{f\left(z^{(0)}\right)}{f'\left(z^{(0)}\right)} = 1 - \frac{0{,}1151}{1{,}1234} = 0{,}8975$$

$$f\left(z^{(1)}\right) = 0{,}8975^3 - 0{,}8975^2 + \left(0{,}1234\right)0{,}8975 - 0{,}1735 \cdot 0{,}0478 = 0{,}01989$$

$$f'\left(z^{(1)}\right) = 3 \cdot 0{,}8975^2 - 2 \cdot 0{,}8975 + \left(0{,}1234\right) = 0{,}7449$$

$$z^{(2)} = z^{(1)} - \frac{f\left(z^{(1)}\right)}{f'\left(z^{(1)}\right)} = 0{,}8975 - \frac{0{,}01989}{0{,}7449} = 0{,}8708$$

$$f\left(z^{(2)}\right) = 0,8708^3 - 0,8708^2 + (0,1234)0,8708 - 0,1735 \cdot 0,0478 = 0,0011920$$

$$f'\left(z^{(2)}\right) = 3 \cdot 0,8708^2 - 2 \cdot 0,8708 + (0,1234) = 0,6567$$

$$z^{(3)} = z^{(2)} - \frac{f\left(z^{(2)}\right)}{f'\left(z^{(2)}\right)} = 0,8708 - \frac{0,0011920}{0,6567} = 0,8690$$

$$f\left(z^{(3)}\right) = 0,8690^3 - 0,8690^2 + (0,1234)0,8690 - 0,1735 \cdot 0,0478 = 1,5209 \cdot 10^{-5}$$

$$f'\left(z^{(3)}\right) = 3 \cdot 0,8690^2 - 2 \cdot 0,8690 + (0,1234) = 0,6509$$

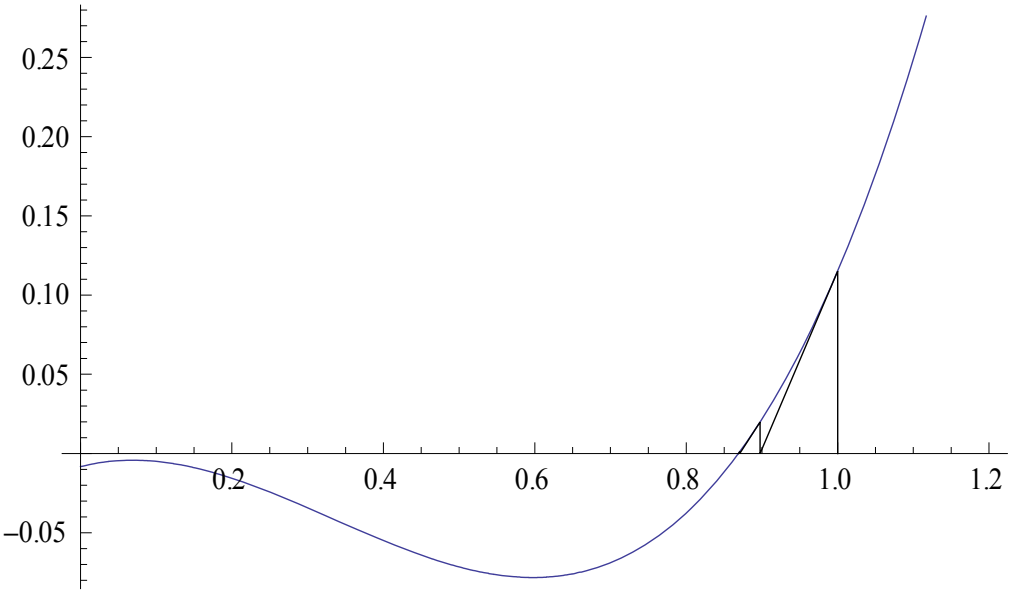
$$z^{(4)} = z^{(3)} - \frac{f\left(z^{(3)}\right)}{f'\left(z^{(3)}\right)} = 0,8690 - \frac{1,5209 \cdot 10^{-5}}{0,6509} = 0,8690$$

$$pv = zRT$$

$$pV = znRT$$

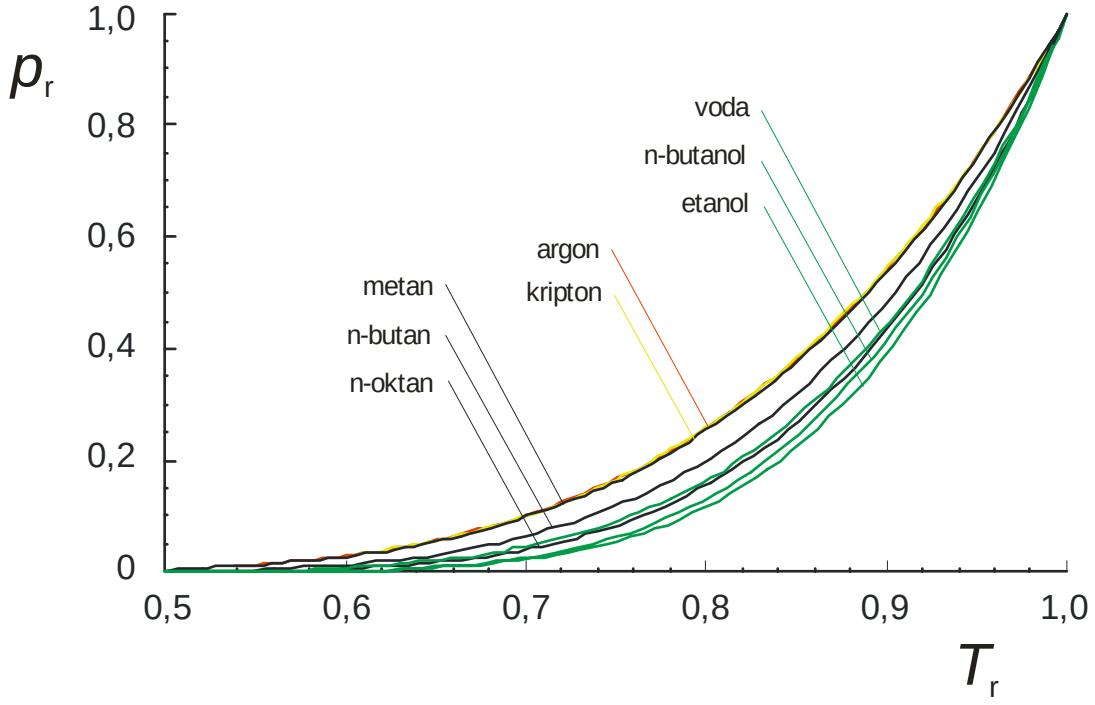
$$V = \frac{znRT}{p}$$

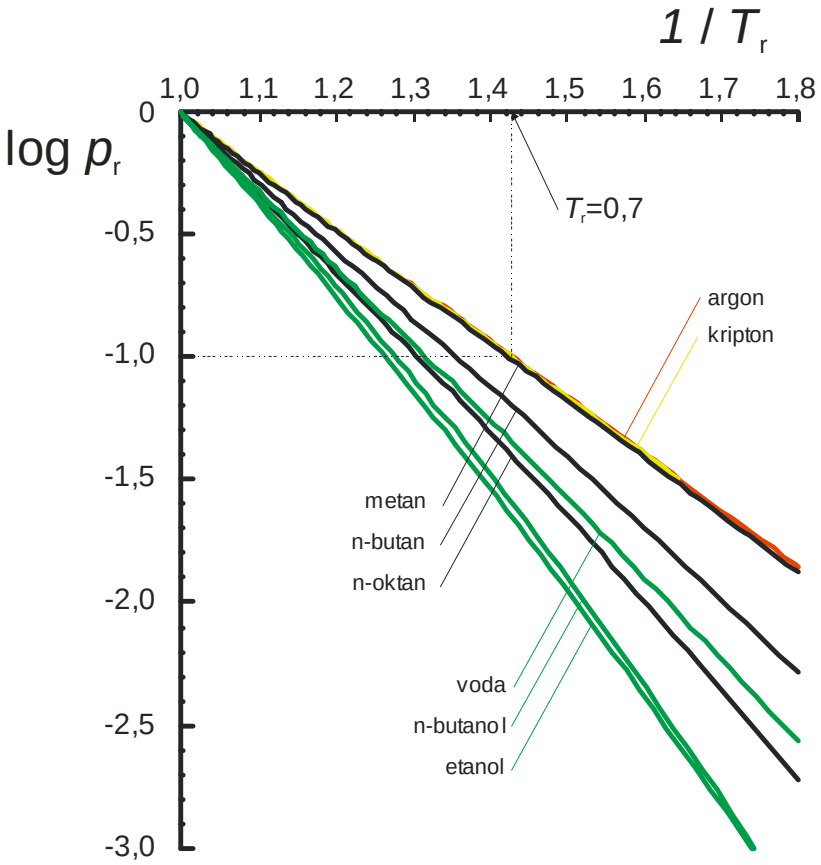
$$V = \frac{0,8690 \cdot 2272,73 \cdot 8,314 \cdot 373,15}{5 \cdot 10^6} = 1,225 \text{ m}^3$$

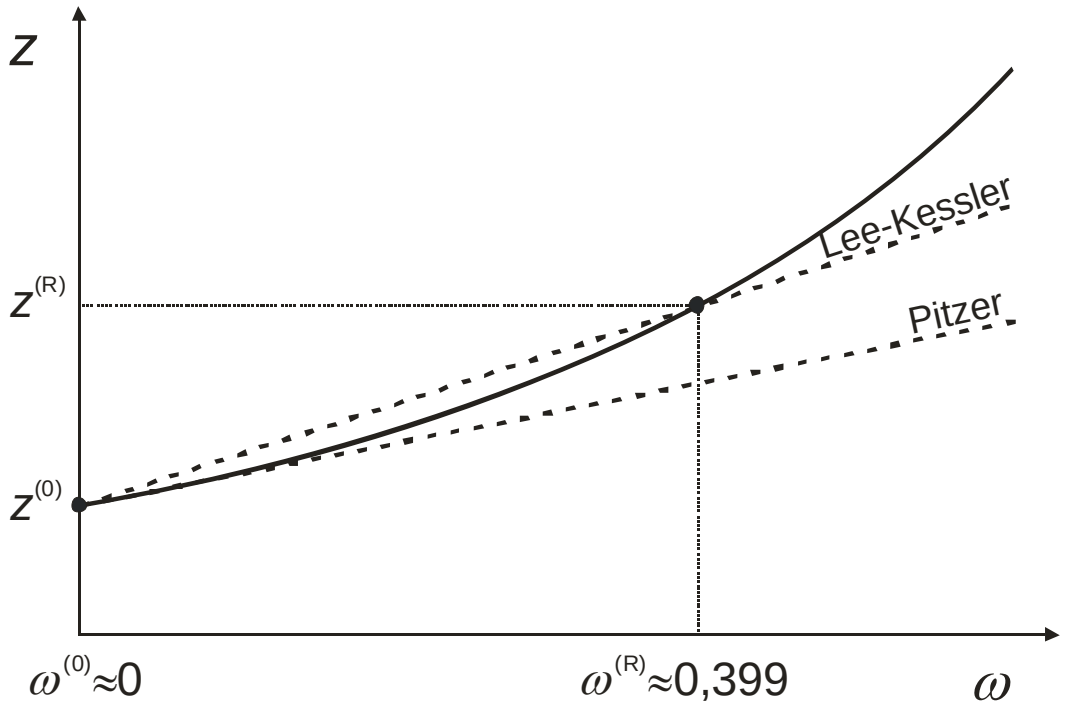


NAČELO TERMODINAMIČKE SLIČNOSTI

Pitzerov koeficijent acentričnosti







Parametri Starlingove modifikacije Benedict-Webb-Rubinove jednadžbe stanja za argon i *n*-oktan.

	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

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

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

Zadatak:

$$m\left(\mathrm{CO_2}\right) = 100\ \mathrm{kg}$$

$$p = 5{,}0\ \mathrm{MPa} = 5 \cdot 10^6\ \mathrm{Pa}$$

$$T = 100\ ^\circ\mathrm{C} = 373{,}15\ \mathrm{K}$$

$$n = \frac{m}{M} = \frac{100}{44 \cdot 10^{-3}} = 2272{,}73\ \mathrm{mol}$$

$$T_\mathrm{r} = \frac{T}{T_\mathrm{K}} = \frac{373{,}15}{304{,}1} = 1{,}2271\Big|_{1{,}20}^{1{,}30}$$

$$p_\mathrm{r} = \frac{p}{p_\mathrm{K}} = \frac{5 \cdot 10^6}{7{,}387 \cdot 10^6} = 0{,}6769\Big|_{0{,}60}^{0{,}80}$$

$$y = y_1 + \frac{y_2 - y_1}{x_2 - x_1}\left(x - x_1\right)$$ Linearna interpolacija

$$z^{(0)}\left(1{,}20\right) = 0{,}8779 + \frac{0{,}8330 - 0{,}8779}{0{,}800 - 0{,}600}\left(0{,}6769 - 0{,}600\right)$$

$$z^{(0)}\left(1{,}20\right) = 0{,}8606$$

$$z^{(0)}\left(1{,}30\right) = 0{,}9083 + \frac{0{,}8764 - 0{,}9083}{0{,}800 - 0{,}600}\left(0{,}6769 - 0{,}600\right)$$

$$z^{(0)}\left(1{,}30\right) = 0{,}8960$$

$$z^{(0)}\left(1{,}2271\right) = 0{,}8606 + \frac{0{,}8960 - 0{,}8606}{1{,}30 - 1{,}20}\left(1{,}2271 - 1{,}20\right)$$

$$z^{(0)}\left(1{,}2271\right) = 0{,}8702$$

$$z^{(1)}\left(1,20\right)=0,0326+\frac{0,0499-0,0326}{0,800-0,600}\left(0,6769-0,600\right)$$

$$z^{(1)}\left(1,20\right)=0,0392$$

$$z^{(1)}\left(1,30\right)=0,0429+\frac{0,0612-0,0429}{0,800-0,600}\left(0,6769-0,600\right)$$

$$z^{(1)}\left(1,30\right)=0,0499$$

$$z^{(1)}\left(1,2271\right)=0,0392+\frac{0,0499-0,0392}{1,30-1,20}\left(1,2271-1,20\right)$$

$$z^{(1)}\left(1,2271\right)=0,0421$$

$$\begin{aligned}z&=z^{(0)}\left(T_{\mathrm{r}},p_{\mathrm{r}}\right)+\omega z^{(1)}\left(T_{\mathrm{r}},p_{\mathrm{r}}\right)=\\&=0,8702+0,239\cdot 0,0421=\\&=0,8803\end{aligned}$$

$$pv=zRT$$

$$pV=znRT$$

$$V=\frac{znRT}{p}$$

$$V=\frac{0,8803\cdot 2272,73\cdot 8,314\cdot 373,15}{5\cdot 10^{6}}=1,241\ \mathrm{m}^{3}$$

ITERACIJA ZA SOAVE REDLICH KWONG

$$v^{(i+1)} = \frac{RT}{p + \dfrac{a\alpha}{v^{(i)}\left(v^{(i)} + b\right)}} + b$$