

# 1. ZADATAK

Izračunati volumen 100 kg CO<sub>2</sub> 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.

Faktor kompresibilnosti računati kao  
troparametarsku veličinu

Podaci:

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

$\omega=0,239$ ;  $\Omega_a=0,427480$ ;  $\Omega_b=0,086640$

# REDLICH KWONG (1949)

Prva moderna jednačba stanja trećeg stupnja

Jednačba

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

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

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

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

Parametri

$$a = \frac{\Omega_a R^2 T_K^{5/2}}{p_K} \qquad b = \frac{\Omega_b R T_K}{p_K}$$

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

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

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

## Idealni plin

$$pv = RT$$

Bezdimenzijske čestice – niski tlakovi

Nema međudjelovanja – niski tlakovi, visoke temperature

Zadatak:

$$T=100\text{ }^{\circ}\text{C} \text{ } (T_K=304,1\text{ K})$$

Je li to visoka temperatura?

Zadatak:

$$p=5\text{ MPa} \text{ } (p_K=7,387\text{ MPa})$$

Je li to niski tlak?

## Redlich-Kwong

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

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

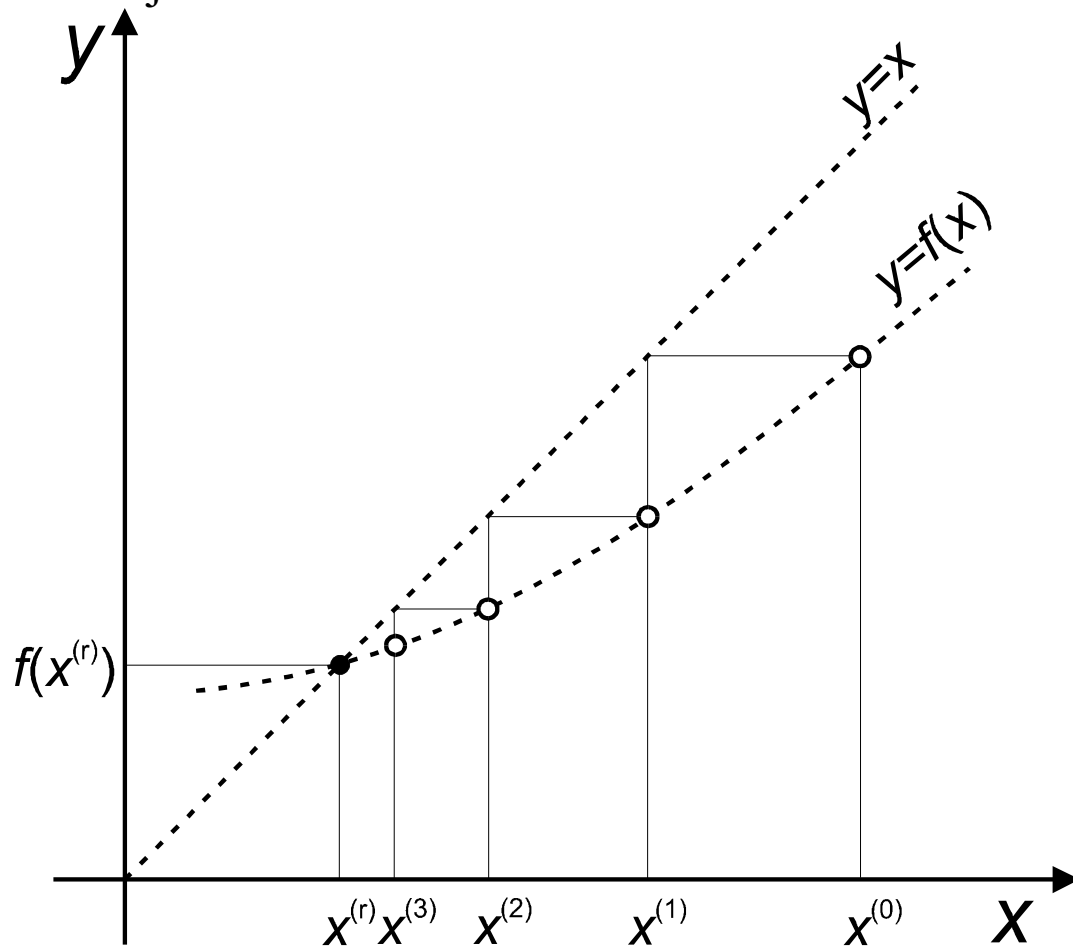
## IZRAVNA (DIREKTNA) ITERACIJA

Numerička shema

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

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

Ilustracija



Zadatak:

$$m(\text{CO}_2) = 100 \text{ kg}$$

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

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

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

Jednadžba stanja trećeg stupnja

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

Parametri:

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

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

Nije eksplicitna po volumenu!

$$v = f(v)$$

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

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

Prva aproksimacija – idealni plin:

$$pv = RT$$

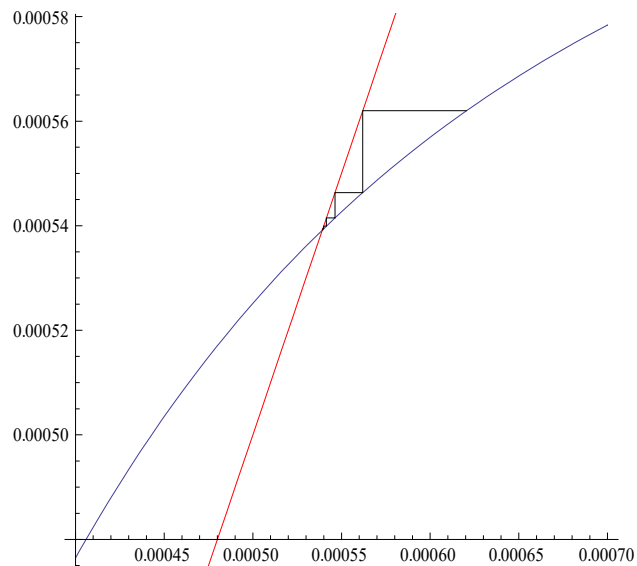
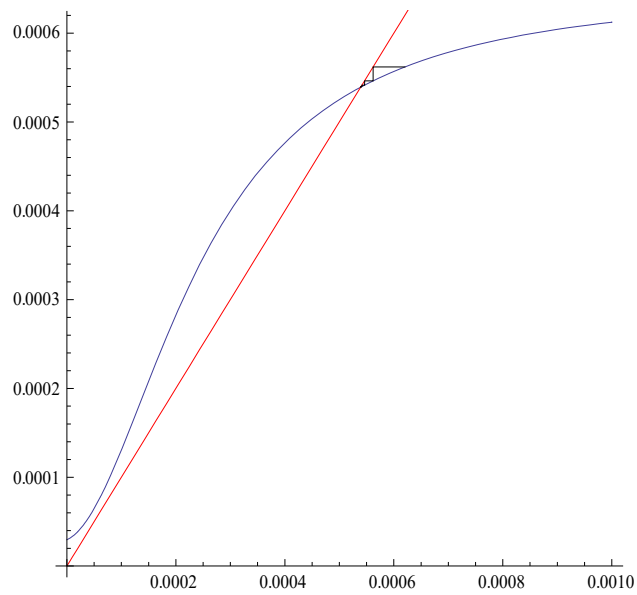
$$v^{(0)} = \frac{RT}{p} = \frac{8,314 \cdot 373,15}{5 \cdot 10^6} = 6,205 \cdot 10^{-4} \text{ m}^3 \text{ mol}^{-1}$$

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

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

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

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



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

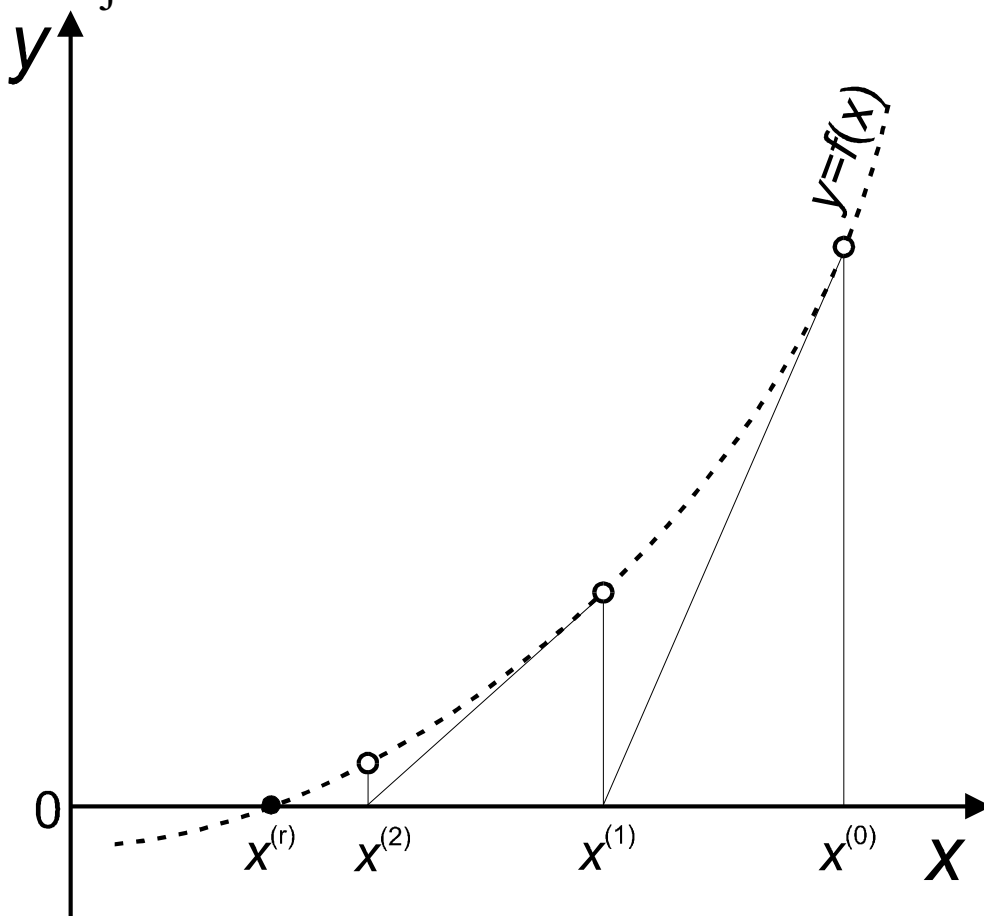
# NEWTONOVA METODA TANGENTE

Numerička shema

$$f(x) = 0$$

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

Ilustracija





Zadatak:

$$m(\text{CO}_2) = 100 \text{ kg}$$

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

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

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

Jednadžba stanja trećeg stupnja

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

Parametri:

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

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

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

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

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

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

$$f(z) = 0$$

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

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

Prva aproksimacija – idealni plin:

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

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

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

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

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

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

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

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

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

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

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

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

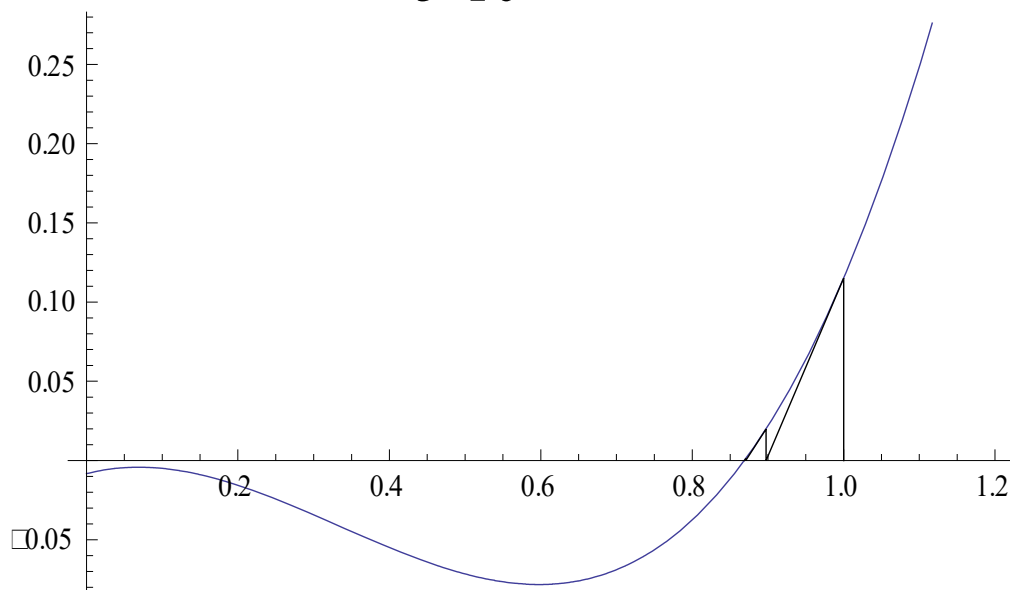
$$z^{(4)}=z^{(3)}-\frac{f\left(z^{(3)}\right)}{f'\left(z^{(3)}\right)}=0,8690-\frac{1,5209\cdot 10^{-5}}{0,6509}=0,8690$$

$$pv = zRT$$

$$pV = znRT$$

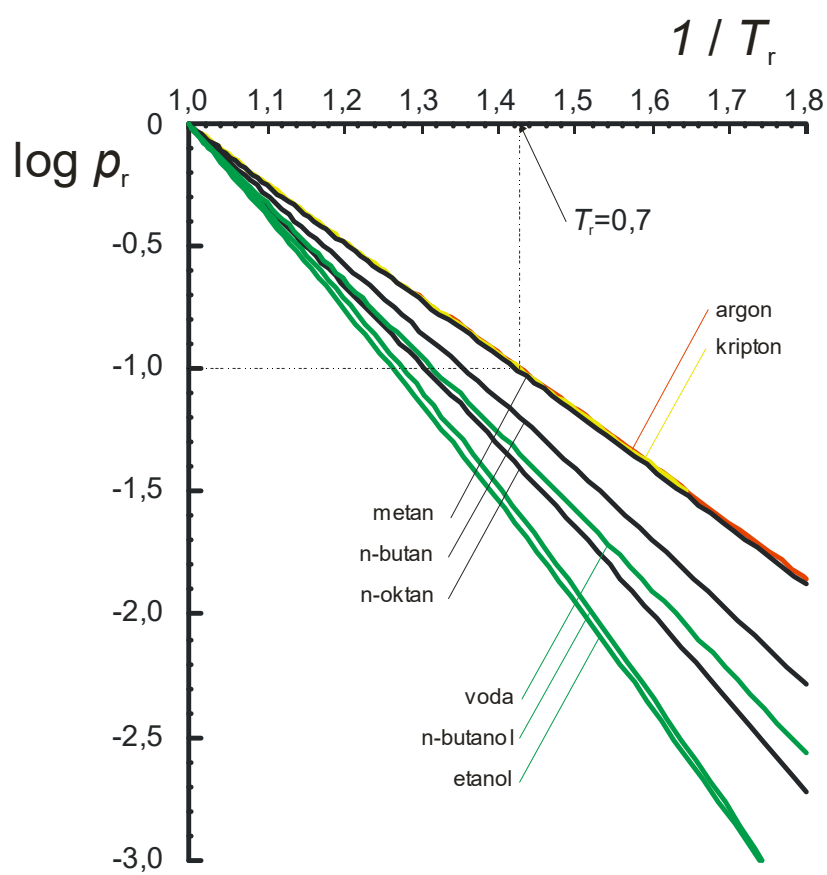
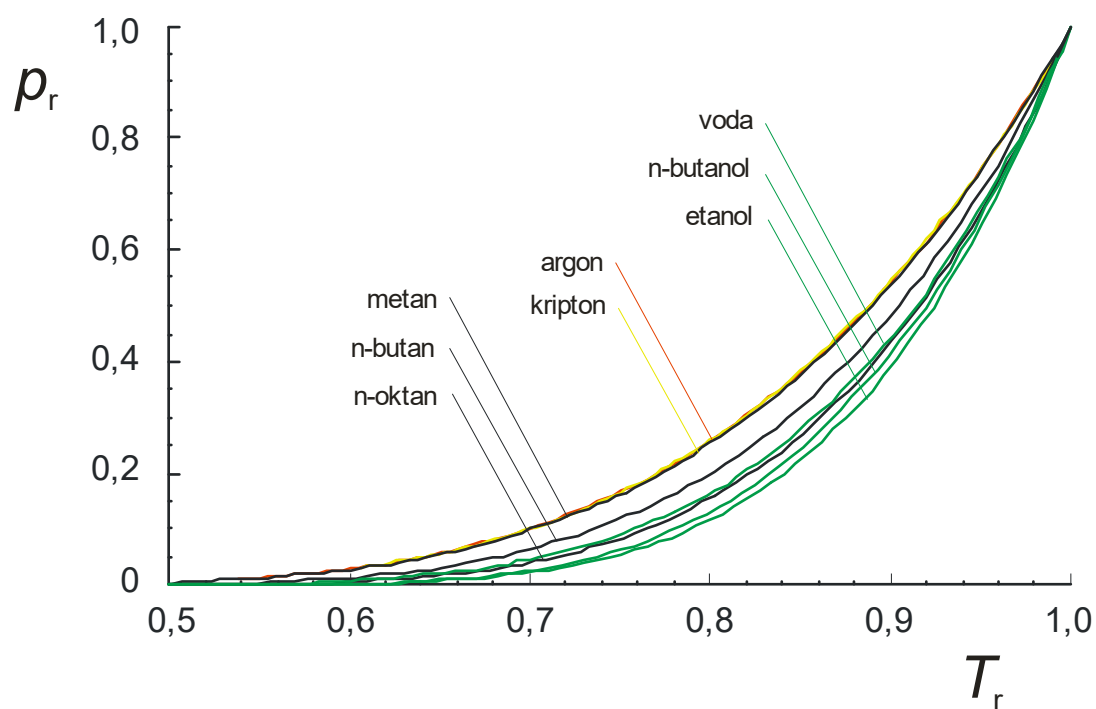
$$V = \frac{znRT}{p}$$

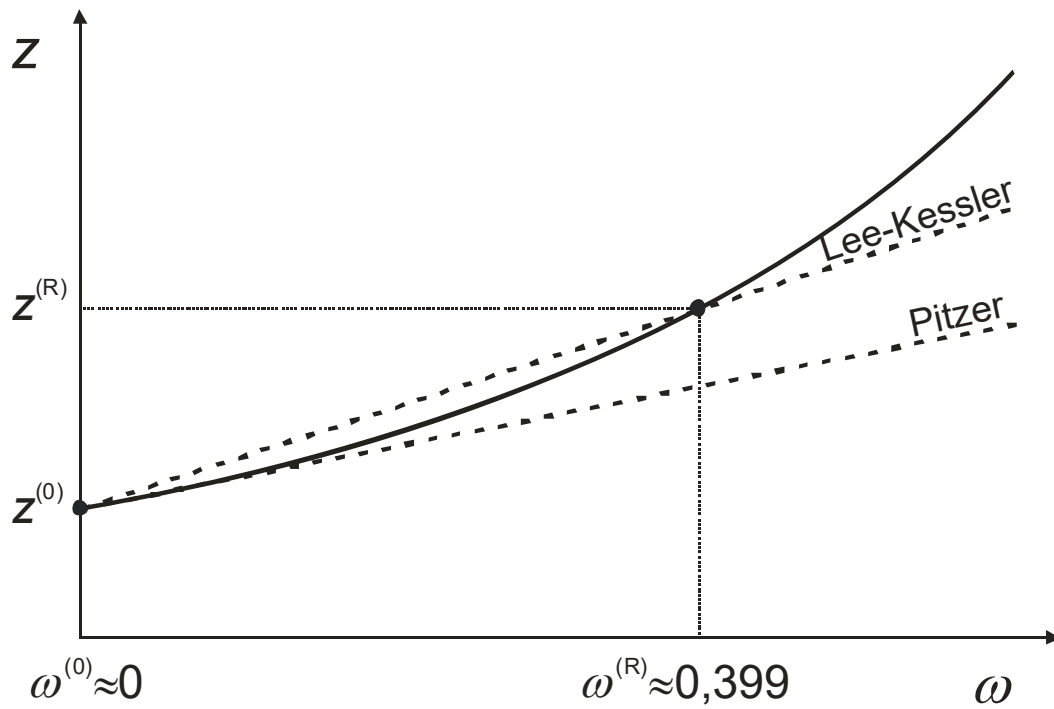
$$V = \frac{0,8690\cdot 2272,73\cdot 8,314\cdot 373,15}{5\cdot 10^6}=1,225\text{ m}^3$$



# NAČELO TERMODINAMIČKE SLIČNOSTI

## Pitzerov faktor 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	$\beta$	0,65392	1,226
$c_2$	0,0186984	0,0503618	$\gamma$	0,60167	0,03754

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

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

Zadatak:

$$m(\text{CO}_2) = 100 \text{ kg}$$

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

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

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

$$T_r = \frac{T}{T_K} = \frac{373,15}{304,1} = 1,2271 \Big|_{1,20}^{1,30}$$

$$p_r = \frac{p}{p_K} = \frac{5 \cdot 10^6}{7,387 \cdot 10^6} = 0,6769 \Big|_{0,60}^{0,80}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\begin{aligned} z &= z^{(0)}(T_r, p_r) + \omega z^{(1)}(T_r, p_r) = \\ &= 0,8702 + 0,239 \cdot 0,0421 = \\ &= 0,8803 \end{aligned}$$

$$pv = zRT$$

$$pV = znRT$$

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

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

## ITERACIJA ZA SOAVE REDLICH KWONG

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