

3. ZADATAK

Procijeniti molarni volumen etana u području zasićenja pri temperaturi od 298 K i tlaku od 41,3 atm. Pretpostaviti da se plin pri tim uvjetima vlada prema Redlich-Kwongovu modelu.

Redlich-Kwongovu jednadžbu iskazati u polinomnom obliku, $f(z)=0$, i rješavati je Newton-Gossetovim postupkom.

Podaci:

$$T_K=305,5 \text{ K}; \quad p_K=48,2 \text{ atm}; \quad \omega=0.098$$

REDLICH KWONG (1949)

Prva moderna enačba stanja tretjega stopnja

Jednadžba

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

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

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

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

Parametri

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

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

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

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

Zadatak:

$T=298\text{ K}$ ($T_K=305,5\text{ K}$)

Temperatura je ispod kritične, plin se (načelno) može ukapljiti

Zadatak:

$41,3\text{ atm}$ ($p_K=48,2\text{ atm}$)

Razmjerno visok tlak

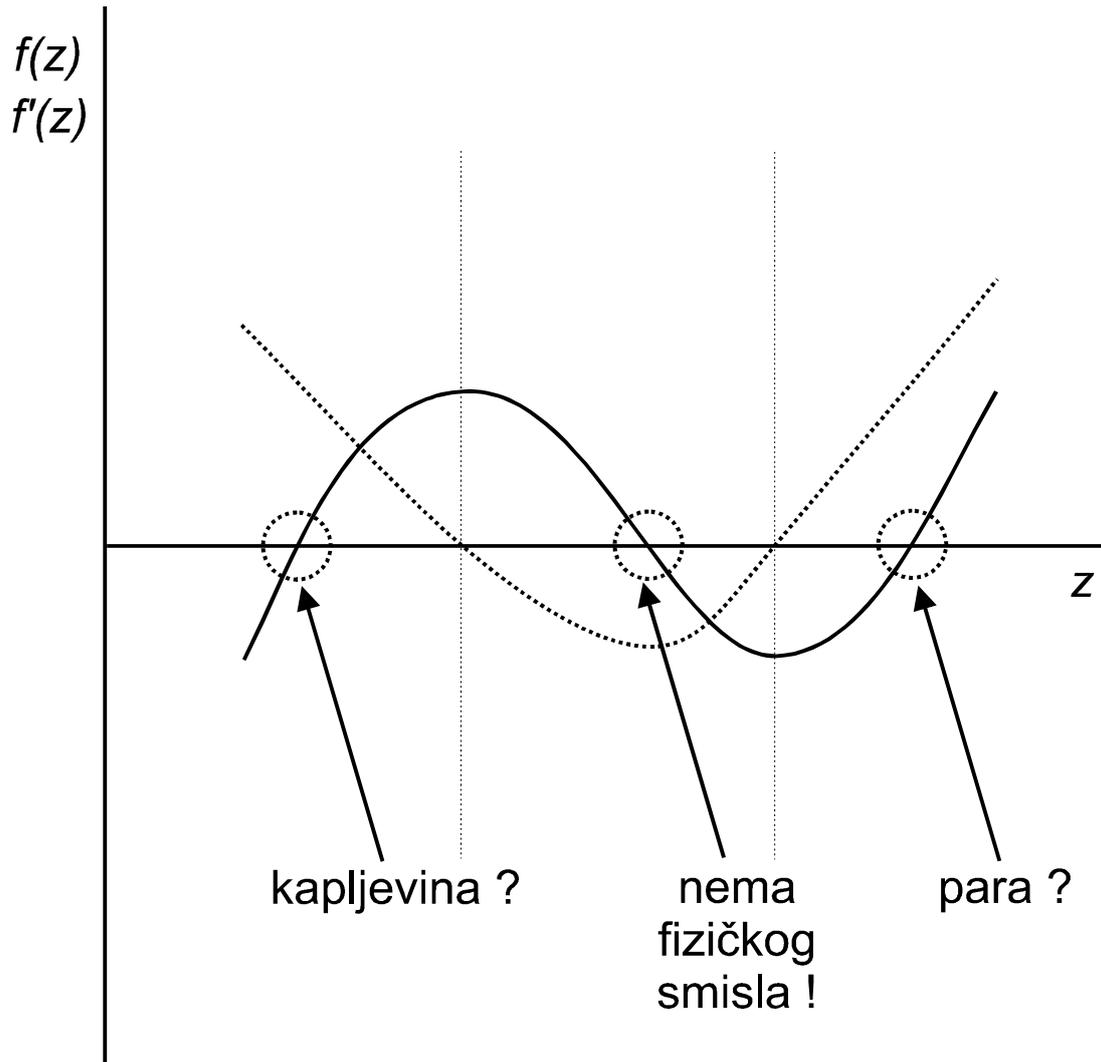
$$f(z) = 0$$

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

GOSSET NEWTON METODA (1986)

Jednadžbe stanja trećeg stupnja po z
(Redlich Kwong)

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



GOSSET NEWTON METODA (1986)

Realizacija

1. Inicijacija

kapljevina $z := B$
para $z := pv / RT = 1$

2. Izračunavanje funkcije $f(z)$

$f(z) := ?$ $f(z) := 0 \rightarrow$ kraj proračuna

3. Izračunavanje derivacije $f'(z)$

$f'(z) := ?$

$f'(z) > 0 \rightarrow z = z - \frac{f(z)}{f'(z)}$ povratak na
točku 2

$f'(z) < 0 \rightarrow$ para: $z = 2z$ povratak na
točku 2

kapljevina: $z = 0,3z$ povratak na
točku 2

Zadatak:

$$p = 41,3 \text{ atm} = 4,18472 \cdot 10^6 \text{ Pa}$$

$$T = 298 \text{ K}$$

Jednadžba stanja trećeg stupnja

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

Parametri:

$$a = \frac{\Omega_a R^2 T_K^{5/2}}{p_K} = \frac{0,427480 \cdot 8,314^2 \cdot 305,5^{2,5}}{48,2 \cdot 101325} = 9,870$$

$$b = \frac{\Omega_b R T_K}{p_K} = \frac{0,086640 \cdot 8,314 \cdot 305,5}{48,2 \cdot 101325} = 4,506 \cdot 10^{-5}$$

$$A = \frac{ap}{R^2 T^{5/2}} = \frac{9,870 \cdot 41,3 \cdot 101325}{8,314^2 \cdot 298^{2,5}} = 0,3898$$

$$B = \frac{bp}{RT} = \frac{4,506 \cdot 10^{-5} \cdot 41,3 \cdot 101325}{8,314 \cdot 298} = 0,0761$$

Proračun parne faze:

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

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

$$f(z) = 0$$

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

Prva aproksimacija – idealni plin:

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

$$f(z^{(0)}) = 1^3 - 1^2 + (0,3898 - 0,0761^2 - 0,0761)1 - 0,3898 \cdot 0,0761 = 0,2782$$

$$f'(z^{(0)}) = 3 \cdot 1^2 - 2 \cdot 1 + (0,3898 - 0,0761^2 - 0,0761) = 1,3079$$

$$z^{(1)} = z^{(0)} - \frac{f(z^{(0)})}{f'(z^{(0)})} = 1 - \frac{0,2782}{1,3079} = 0,7873$$

$$f(z^{(1)}) = 0,7873^3 - 0,7873^2 + (0,3079)0,7873 - 0,02966 = 0,0809$$

$$f'(z^{(1)}) = 3 \cdot 0,7873^2 - 2 \cdot 0,7873 + (0,3079) = 0,5928$$

$$z^{(2)} = z^{(1)} - \frac{f(z^{(1)})}{f'(z^{(1)})} = 0,7873 - \frac{0,0809}{0,5928} = 0,6508$$

$z^{(3)} = 0,5685$	$z^{(5)} = 0,5129$
$z^{(4)} = 0,5265$	$z^{(6)} = 0,5114$

$$v^V = \frac{z^V RT}{p} = \frac{0,5114 \cdot 8,314 \cdot 298}{41,3 \cdot 101325} = 3,028 \cdot 10^{-4} \text{ m}^3 \text{ mol}^{-1}$$

Proračun kapljevite faze:

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

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

$$f(z) = 0$$

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

Prva aproksimacija – reducirani volumen čestica:

$$z^{(0)} = B = \frac{b}{v^{\text{id}}} = \frac{bp}{RT}$$

$$f(z^{(0)}) = 0,0761^3 - 0,0761^2 + (0,3079)0,0761 - 0,02966 = -0,0116$$

$$f'(z^{(0)}) = 3 \cdot 0,0761^2 - 2 \cdot 0,0761 + (0,3079) = 0,1731$$

$$z^{(1)} = z^{(0)} - \frac{f(z^{(0)})}{f'(z^{(0)})} = 0,0761 - \frac{-0,0116}{1,3079} = 0,1431$$

$z^{(2)} = 0,2019$	$z^{(4)} = 0,2034$
$z^{(3)} = 0,2021$	

$$v^{\text{L}} = \frac{z^{\text{L}} RT}{p} = \frac{0,2034 \cdot 8,314 \cdot 298}{41,3 \cdot 101325} = 1,2042 \cdot 10^{-4} \text{ m}^3 \text{ mol}^{-1}$$

Izbor stabilne faze:

Izraz za koeficijent fugaciteta:

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

Para:

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

$$\begin{aligned} \ln \varphi^V &= \ln \frac{3,028 \cdot 10^{-4}}{3,028 \cdot 10^{-4} - 4,506 \cdot 10^{-5}} + \\ &+ \frac{9,870}{4,506 \cdot 10^{-5} \cdot 8,314 \cdot 298^{3/2}} \ln \frac{3,028 \cdot 10^{-4}}{3,028 \cdot 10^{-4} + 4,506 \cdot 10^{-5}} + \\ &+ (0,5114 - 1) - \ln 0,5114 \end{aligned}$$

$$\ln \varphi^V = -0,36736$$

$$\varphi^V = 0,692561$$

Kapljevina:

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

$$\begin{aligned} \ln \varphi^L &= \ln \frac{1,2042 \cdot 10^{-4}}{1,2042 \cdot 10^{-4} - 4,506 \cdot 10^{-5}} + \\ &+ \frac{9,870}{4,506 \cdot 10^{-5} \cdot 8,314 \cdot 298^{3/2}} \ln \frac{1,2042 \cdot 10^{-4}}{1,2042 \cdot 10^{-4} + 4,506 \cdot 10^{-5}} + \\ &+ (0,2034 - 1) - \ln 0,2034 \end{aligned}$$

$$\ln \varphi^L = -0,363233$$

$$\varphi^L = 0,695424$$

Manji koeficijent fugaciteta →

Manji fugacitet →

Manja Gibbsova energija →

Stabilna faza →

Para

