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-Kwongovom modelu.

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

Podaci:

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

REDLICH KWONG (1949)

Prva moderna jednadžba stanja trećeg stupnja

Prva moderna jednadžba stanja trećeg stupnja

Jednadžba

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

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

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

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

Parametri

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

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

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

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

Zadatak:

T=298 K (T_K=305,5 K)

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

Zadatak:

41,3 atm (p_K=48,2 atm)

Razmjerno visok tlak

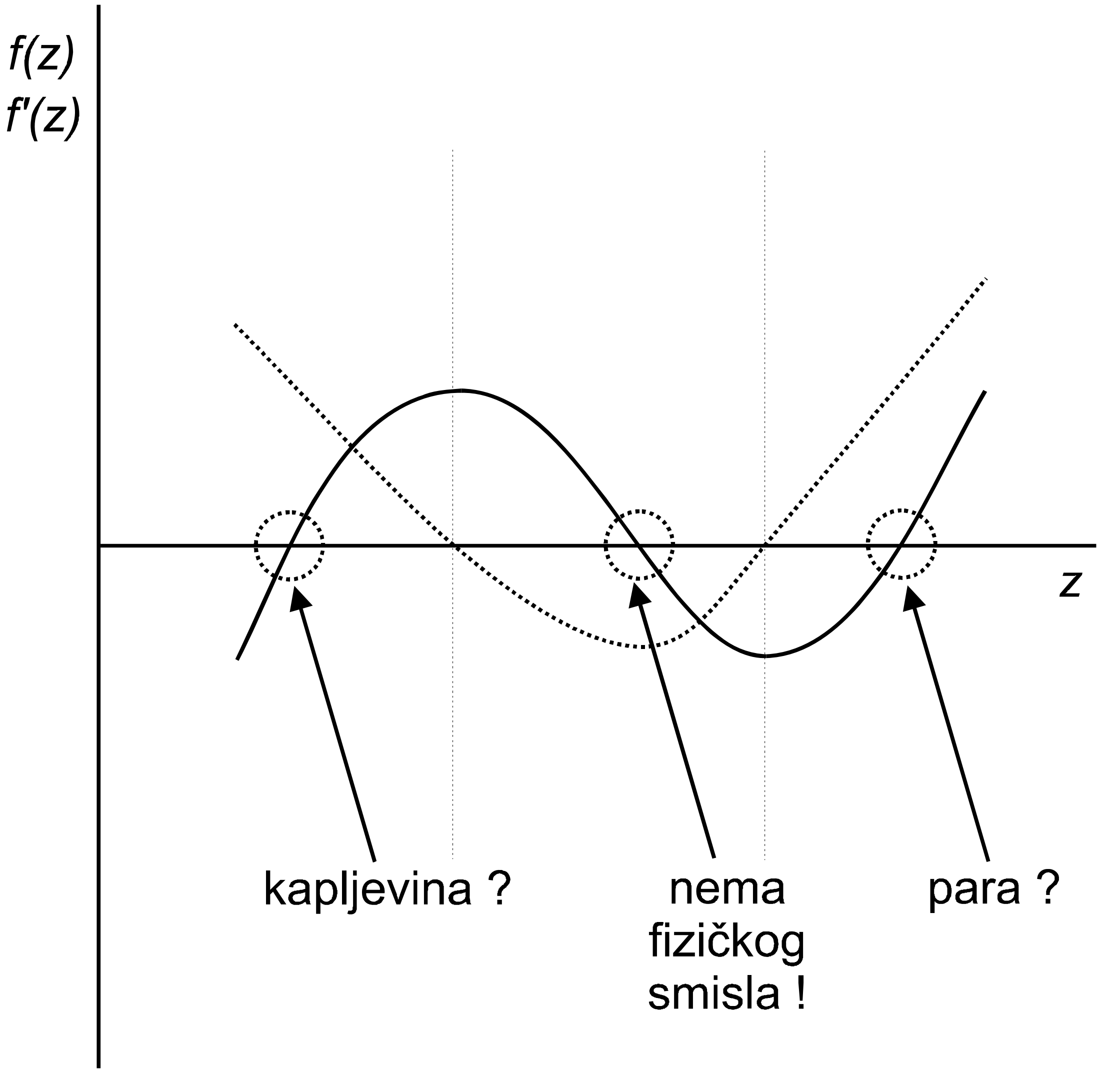
$$f\left(z\right)=0$$

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

GOSSET NEWTON METODA (1986)

Jednadžbe stanja trećeg stupnja po *z*
(Redlich Kwong)

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



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)

$f'(z) := ?$

$f'(z) :> 0 \rightarrow$ $z = z - \dfrac{f(z)}{f'(z)}$ 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

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

Parametri:

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

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

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

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

Proračun parne faze:

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

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

$$f(z) = 0$$

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

Prva aproksimacija – idealni plin:

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

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

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

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

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

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

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

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

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

Proračun kapljevite faze:

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

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

$$f\left(z\right)=0$$

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

Prva aproksimacija – reducirani volumen čestica:

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

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

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

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

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

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

Izbor stabilne faze:

Izraz za koeficijent fugacitivnosti:

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

Para:

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

$$\ln\varphi^{\mathrm{V}} = \ln\frac{3,028\cdot10^{-4}}{3,028\cdot10^{-4}-4,506\cdot10^{-5}} +$$

$$+\frac{9,870}{4,506\cdot10^{-5}\cdot8,314\cdot298^{3/2}}\ln\frac{3,028\cdot10^{-4}}{3,028\cdot10^{-4}+4,506\cdot10^{-5}} +$$

$$+(0,5114-1)-\ln 0,5114$$

$$\ln\varphi^{\mathrm{V}} = -0,36736$$

$$\varphi^{\mathrm{V}} = 0,692561$$

Kapljevina:

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

$$\ln\varphi^{\mathrm{L}} = \ln\frac{1,2042\cdot10^{-4}}{1,2042\cdot10^{-4}-4,506\cdot10^{-5}} +$$

$$+\frac{9,870}{4,506\cdot10^{-5}\cdot8,314\cdot298^{3/2}}\ln\frac{1,2042\cdot10^{-4}}{1,2042\cdot10^{-4}+4,506\cdot10^{-5}} +$$

$$+(0,2034-1)-\ln 0,2034$$

$$\ln\varphi^{\mathrm{L}} = -0,363233$$

$$\varphi^{\mathrm{V}} = 0,695424$$

Manji koeficijent fugacitivnosti→
Manja fugacitivnost→
Manja Gibbsova energija→
Stabilna faza→
Para