

JEDNADŽBE STANJA

REDUCIRANE VELIČINE

$$p_r = \frac{p}{p_c}, \quad T_r = \frac{T}{T_c}, \quad v_r = \frac{v}{v_c} \quad (1)$$

KOEFICIJENT KOMPRESIBILNOSTI

$$z = \frac{v}{v_{id}} = \frac{pv}{RT} \quad (2)$$

PSEUDOKRITIČNA SVOJSTVA

Pseudokritična temperatura

$$T_{pc} = \sum_{i=1}^{nKo} y_i T_{ci} \quad (\text{KAYEVO PRAVILO}) \quad (3)$$

$$(0.5 < T_{c,i}/T_{c,j} < 2) \wedge (0.5 < p_{c,i}/p_{c,j} < 2)$$

$$T_{cm} = \left\{ \frac{\left[\sum_{i=1}^{nKo} y_i (T_{ci}^{5/2} / p_{ci})^{1/2} \right]^2}{\sum_{i=1}^{nKo} y_i (T_{ci} / p_{ci})} \right\}^{2/3} \quad (\text{REDLICH - KWONG}) \quad (4)$$

Pseudokritični tlak

$$p_{pc} = \frac{R \left(\sum_{i=1}^{nKo} y_i z_{c,i} \right) T_{pc}}{\sum_{i=1}^{nKo} y_i v_{c,i}} \quad (\text{PRAUSNITZ - GUNN}) \quad (5)$$

$$p_{cm} = \frac{T_{cm}}{\sum_{i=1}^{nKo} y_i (T_{c,i} / p_{c,i})} \quad (\text{REDLICH - KWONG}) \quad (6)$$

FAKTOR ACENTRIČNOSTI ZA SMJESU

$$\omega_m = \sum_{i=1}^{nKo} y_i \omega_i \quad (7)$$

VAN DER WAALSOVA JEDNADŽBA STANJA

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \quad (8a)$$

$$v^3 - v^2 \left(b + \frac{RT}{p} \right) + v \left(\frac{a}{p} \right) - \frac{ab}{p} = 0 \quad (8b)$$

$$z^3 - z^2 \left(\frac{bp}{RT} + 1 \right) + z \frac{ap}{R^2 T^2} - \frac{abp^2}{R^3 T^3} = 0 \quad (8c)$$

$$T = \frac{v-b}{R} \left(p + \frac{a}{v^2} \right) \quad (8d)$$

Parametri

$$a = \frac{27R^2 T_K^2}{64p_K} \quad (9)$$

$$b = \frac{RT_K}{8p_K} \quad (10)$$

Fugacitivnost

$$\ln f = \ln \frac{RT}{v-b} + \frac{b}{v-b} - \frac{2a}{RTv} \quad (11)$$

REDLICH-KWONGOVA JEDNADŽBA STANJA

$$p = \frac{RT}{v-b} - \frac{a}{T^{0.5}v(v+b)} \quad (12a)$$

$$v^3 - \frac{RT}{p}v^2 - \left(b^2 + \frac{RTb}{p} - \frac{a}{p\sqrt{T}} \right)v - \frac{ab}{p\sqrt{T}} = 0 \quad (12b)$$

$$z^3 - z^2 + (A - B^2 - B)z - AB = 0 \quad (12c)$$

$$v^{(i+1)} = \frac{RT}{p + \frac{a}{\sqrt{T}v^{(i)}(v^{(i)} + b)}} + b \quad (12d)$$

$$T^{(i+1)} = \frac{v-b}{R} \left[p + \frac{a}{\sqrt{T^{(i)}v(v+b)} \right] \quad (12e)$$

Parametri

$$a = \frac{\Omega_a R^2 T_c^{5/2}}{P_c} \quad (13)$$

$$b = \frac{\Omega_b RT_c}{P_c} \quad (14)$$

$$\Omega_a = \frac{1}{9(2^{1/3} - 1)} = 0.427480 \quad (15)$$

$$\Omega_b = \frac{(2^{1/3} - 1)}{3} = 0.086640 \quad (16)$$

$$A = \frac{ap}{R^2 T^{5/2}} \quad (17)$$

$$B = \frac{bp}{RT} \quad (18)$$

Unakrsni parametri

$$a_{ij} = \sqrt{a_i a_j} \quad (\text{REDLICH-KWONG}) \quad (19a)$$

$$(a\alpha)_{12} = (1 - k_{12}) \sqrt{(a\alpha)_1 (a\alpha)_2} \quad (\text{SOAVE-REDLICH-KWONG}) \quad (19b)$$

$$a_{ij} = (1 - c_{ij}) \sqrt{a_i a_j} \quad (\text{ZUDKEVICH-JOFFE}) \quad (19c)$$

$$a_{ij} = \frac{\Omega_a R (V_{ci}^{1/3} + V_{cj}^{1/3})^3 [(1 - k_{ij}) \sqrt{T_{ci} T_{cj}}]^{1.5}}{8[0.291 - 0.04(\omega_i + \omega_j)]} \quad (\text{PRAUSNITZ-CHUEH}) \quad (19d)$$

Pravila miješanja

$$a = \sum \sum y_i y_j a_{ij} \quad (20)$$

$$b = \sum y_i b_i \quad (21)$$

$$A = \sum \sum y_i y_j A_{ij} \quad (22)$$

$$B = \sum y_i B_i \quad (23)$$

Dvokomponentne smjese

$$a_M = y_1^2 a_1 + 2y_1 y_2 a_{12} + y_2^2 a_2 \quad (\text{vdW}) \quad (24)$$

$$\begin{aligned} a_M &= a_{11} y_1^2 + a_{12} y_1 y_2 + a_{21} y_2 y_1 + a_{22} y_2^2 = \\ &= a_1 y_1^2 + 2a_{12} y_1 y_2 + a_2 y_2^2 \end{aligned} \quad (\text{RK}) \quad (25)$$

$$a_{11} = a_1 \quad a_{22} = a_2 \quad a_{12} = a_{21}$$

$$\begin{aligned} (a\alpha)_M &= (a\alpha)_{11} y_1^2 + (a\alpha)_{12} y_1 y_2 + (a\alpha)_{21} y_2 y_1 + (a\alpha)_{22} y_2^2 = \\ &= (a\alpha)_1 y_1^2 + 2(a\alpha)_{12} y_1 y_2 + (a\alpha)_2 y_2^2 \end{aligned} \quad (\text{SRK}) \quad (26)$$

$$(a\alpha)_{11} = (a\alpha)_1 \quad (a\alpha)_{22} = (a\alpha)_2 \quad (a\alpha)_{12} = (a\alpha)_{21}$$

$$b_M = b_1 y_1 + b_2 y_2 \quad (27)$$

Koeficijent fugacitivnosti čiste tvari

$$\ln \phi = z - 1 - \ln(z - B) - \frac{A}{B} \ln\left(1 + \frac{B}{z}\right) \quad (28)$$

$$\ln \varphi = \ln \frac{v}{v-b} + \frac{a}{bRT^{3/2}} \ln \frac{v}{v+b} + (z-1) - \ln z \quad (29)$$

Koeficijent fugacitivnosti komponente u smjesi

$$\ln \hat{\phi}_i = \frac{B_i}{B} (z-1) - \ln(z-B) + \frac{A}{B} \left[\frac{B_i}{B} - 2\sqrt{\frac{A_i}{A}} \right] \ln\left(1 + \frac{B}{z}\right) \quad (30)$$

SOAVE-REDLICH-KWONGOVA JEDNADŽBA STANJA

$$p = \frac{RT}{v-b} - \frac{a\alpha}{v(v+b)} \quad (31a)$$

$$v^3 - \frac{RT}{p} v^2 - \left(b^2 + \frac{RTb}{p} - \frac{a\alpha}{p} \right) v - \frac{a\alpha b}{p} = 0 \quad (31b)$$

$$z^3 - z^2 + (A - B^2 - B)z - AB = 0 \quad (31c)$$

$$v^{(i+1)} = \frac{RT}{p + \frac{a\alpha}{v^{(i)}(v^{(i)} + b)}} + b \quad (31d)$$

$$T^{(i+1)} = \frac{v-b}{R} \left[p + \frac{a\alpha}{v(v+b)} \right] \quad (31e)$$

Parametri

$$a = \frac{\Omega_a R^2 T_c^2}{P_c} \quad (32)$$

$$b = \frac{\Omega_b R T_c}{P_c} \quad (33)$$

$$\Omega_a = \frac{1}{9(2^{1/3} - 1)} = 0.427480 \quad (34)$$

$$\Omega_b = \frac{(2^{1/3} - 1)}{3} = 0.086640 \quad (35)$$

$$\alpha = \left(1 + \kappa \left(1 - \sqrt{T_r} \right) \right)^2 \quad (36)$$

$$\kappa = 0.48508 + 1.55171\omega - 0.15613\omega^2 \quad (37)$$

za vodik: $\alpha = 1.202 \exp(-0.30288T_r)$ (GRABOSKI-DAUBERT) (38)

$$A = \frac{a\alpha p}{R^2 T^2} \quad (39)$$

$$B = \frac{bp}{RT} \quad (40)$$

Koeficijent fugacitivnosti čiste tvari

$$\ln \phi = z - 1 - \ln(z - B) - \frac{A}{B} \ln\left(1 + \frac{B}{z}\right) \quad (41)$$

$$\ln \varphi = \ln \frac{v}{v-b} + \frac{a\alpha(T)}{bRT} \ln \frac{v}{v+b} + (z-1) - \ln z \quad (42)$$

Koeficijent fugacitivnosti komponente u smjesi

$$\ln \hat{\varphi}_i = \frac{B_i}{B} (z-1) - \ln(z-B) + \frac{A}{B} \left[\frac{B_i}{B} - \frac{2}{a\alpha} \sum_{j=1}^{nK_o} y_j (a\alpha)_{ij} \right] \ln\left(1 + \frac{B}{z}\right) \quad (43)$$

PENG-ROBINSONOVA JEDNADŽBA STANJA

$$p = \frac{RT}{v-b} - \frac{a\alpha}{v^2 + 2bv - b^2} \quad (44a)$$

$$v^3 - \left(\frac{RT}{p} - b\right)v^2 - \left(3b^2 + \frac{2RTb}{p} - \frac{a\alpha}{p}\right)v - \left(\frac{a\alpha b}{p} - \frac{RTb^2}{p} - b^3\right) = 0 \quad (44b)$$

$$z^3 - (1-B)z^2 + (A-3B^2-2B)z - (AB-B^2-B^3) = 0 \quad (44c)$$

$$T^{(i+1)} = \frac{v-b}{R} \left[p + \frac{a\alpha}{v^2 + 2bv - b^2} \right] \quad (44d)$$

Parametri

$$a = \frac{\Omega_a R^2 T_c^2}{P_c} \quad (45)$$

$$b = \frac{\Omega_b RT_c}{P_c} \quad (46)$$

$$\Omega_a = 0.45724 \quad (47)$$

$$\Omega_b = 0.07780 \quad (48)$$

$$\alpha = \left(1 + \kappa \left(1 - \sqrt{T_r}\right)\right)^2 \quad (49)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (50)$$

za vodik: $\alpha = 1.202 \exp(-0.30288T_r)$ (GRABOSKI-DAUBERT) (51)

$$A = \frac{a\alpha p}{R^2 T^2} \quad (52)$$

$$B = \frac{bp}{RT} \quad (53)$$

Koeficijent fugacitvnosti čiste tvari

$$\ln \phi = z - 1 - \ln(z - B) - \frac{A}{2\sqrt{2}B} \ln\left(\frac{z + (\sqrt{2} + 1)B}{z - (\sqrt{2} - 1)B}\right) \quad (54)$$

$$\ln \varphi = \ln \frac{v}{v-b} - \frac{a\alpha}{bRT} \frac{v+b(1+\sqrt{2})}{2\sqrt{2}} \ln \frac{v+b(1+\sqrt{2})}{v+b(1-\sqrt{2})} + (z-1) - \ln z \quad (55)$$

Koeficijent fugacitvnosti komponente u smjesi

$$\ln \hat{\varphi}_i = \frac{B_i}{B} (z-1) - \ln(z-B) + \frac{A}{2.828B} \left[\frac{B_i}{B} - \frac{2}{a\alpha} \sum_{j=1}^{nK_0} y_j (a\alpha)_{ij} \right] \ln \left(\frac{z + (\sqrt{2} + 1)B}{z - (\sqrt{2} - 1)B} \right) \quad (56)$$

SMJESE (SOAVE-REDLICH-KWONG I PENG ROBINSON)

Unakrsni parametri

$$(a\alpha)_{ij} = (1 - k_{ij}) \sqrt{(a\alpha)_i (a\alpha)_j} \quad (57)$$

$$k_{ij} = 0$$

(ZA PAROVE UGLJIKOVODIK - VODIK)

$$k_{ii} = 0$$

Pravila miješanja

$$(a\alpha)_M = \sum \sum y_i y_j (a\alpha)_{ij} \quad (58)$$

$$b_M = \sum y_i b_i \quad (59)$$

$$A_M = \sum \sum y_i y_j A_{ij} \quad (60)$$

$$B_M = \sum y_i B_i \quad (61)$$

Lee-Keslerova korelacija

$$z = z^{(0)}(T_r, p_r) + \omega z^{(1)}(T_r, p_r) \quad (62)$$

Funkcije odstupanja

$$\left(\frac{h^\circ - h}{RT_K} \right) = \left(\frac{h^\circ - h}{RT_K} \right)^{(0)} + \omega \left(\frac{h^\circ - h}{RT_K} \right)^{(1)} \quad (63)$$

$$\left(\frac{s^\circ - s}{R}\right) = \left(\frac{s^\circ - s}{R}\right)^{(0)} + \omega \left(\frac{s^\circ - s}{R}\right)^{(1)} - \ln \frac{p^\circ}{p} \quad (64)$$

Gibbs-Duhemova rovnice

$$\sum n_i d\bar{y}_i = 0 \quad (65)$$

$$\sum x_i d\bar{y}_i = 0$$

Tablica 1. Termodinamički podaci

Rbr	Formula	Naziv_hrv	M	T _{sl}	T _{lv}	T _c	p _c	v _c	Z _c	ω
4	Ar	argon	39,9	83,8	87,3	150,8	48,7	74,9	0,291	0,001
48	He	helij-4	4,0		4,3	5,2	2,3	57,4	0,302	-0,365
54	NO	dušik(II)-oksid	30,0	109,5	121,4	180,0	64,8	57,7	0,250	0,588
55	NO2	dušik(IV)-oksid	46,0	251,9	294,3	431,0	101,0	167,8	0,473	0,834
56	N2	dušik	28,0	63,3	77,4	126,2	33,9	89,8	0,290	0,039
58	Ne	neon	20,2	24,5	27,1	44,4	27,6	41,6	0,311	-0,029
59	O2	kisik	32,0	54,4	90,2	154,6	50,4	73,4	0,288	0,025
60	O2S	sumpor(IV)-oksid	64,1	197,7	263,2	430,8	78,8	122,2	0,269	0,256
76	H2	vodik (normalni uvjeti)	2,0	14,0	20,4	33,2	13,0	65,1	0,306	-0,218
77	H2O	voda	18,0	273,2	373,2	647,3	221,2	57,1	0,235	0,344
78	H2S	sumporovodik	34,1	189,6	213,5	373,2	89,4	98,6	0,284	0,081
94	CCl4	ugljik(IV)-klorid	153,8	250,0	349,9	556,4	45,6	275,9	0,272	0,193
97	CO	ugljik(II)-oksid	28,0	68,1	81,7	132,9	35,0	93,2	0,295	0,066
99	CO2	ugljik(IV)-oksid	44,0	216,6		304,1	73,8	93,9	0,274	0,239
103	CHCl3	kloroform	119,4	209,6	334,3	536,4	53,7	238,9	0,293	0,218
112	CH3Cl	metil-klorid	50,5	115,4	249,1	416,3	67,0	138,9	0,269	0,153
116	CH4	metan	16,0	90,7	111,6	190,4	46,0	99,2	0,288	0,011
117	CH4O	metanol	32,0	175,5	337,7	512,6	80,9	118,0	0,224	0,556
137	C2HCl3	trikloreten	131,4	186,8	360,4	572,0	50,5	256,0	0,265	0,213
140	C2H2	acetilen	26,0		188,4	308,3	61,4	112,7	0,270	0,190
146	C2H3Cl	vinil-klorid	62,5	119,4	259,8	425,0	51,5	169,0	0,265	0,122
155	C2H4	etilen	28,1	104,0	169,3	282,4	50,4	130,4	0,280	0,089
157	C2H4Cl2	1,1-dikloreten	99,0	176,2	330,5	523,0	50,7	236,0	0,275	0,240
158	C2H4Cl2	1,2-dikloreten	99,0	237,5	356,7	566,0	53,7	225,0	0,259	0,278
165	C2H5Cl	etil-klorid	64,5	136,8	285,5	460,4	52,7	199,0	0,274	0,191
168	C2H6	etan	30,1	89,9	184,6	305,4	48,8	148,3	0,285	0,099
170	C2H6O	etanol	46,1	159,1	351,4	513,9	61,4	167,1	0,240	0,644
186	C3H4	propin	40,1	170,5	249,9	402,4	56,3	164,0	0,275	0,215
191	C3H5Cl3	1,2,3-trikloropropan	147,4	258,5	429,0	651,0	39,5	348,0	0,250	0,310
193	C3H6	ciklopropan	42,1	145,7	240,3	397,8	54,9	163,0	0,274	0,130
194	C3H6	propen	42,1	87,9	225,5	364,9	46,0	181,0	0,274	0,144
196	C3H6O	acetone	58,1	178,2	329,2	508,1	47,0	209,0	0,232	0,304
204	C3H7Cl	propil-klorid	78,5	150,4	320,4	503,0	45,8	254,0	0,278	0,235
205	C3H7Cl	izopropil-klorid	78,5	156,0	308,9	485,0	47,2	230,0	0,269	0,232
206	C3H8	propan	44,1	85,5	231,1	369,8	42,5	203,0	0,281	0,153
236	C4H8	1-buten	56,1	87,8	266,9	419,6	40,2	240,0	0,277	0,191
237	C4H8	cis-2-buten	56,1	134,3	276,9	435,6	42,0	234,0	0,271	0,202
238	C4H8	trans-2-buten	56,1	167,6	274,0	428,6	39,9	238,0	0,266	0,205
240	C4H8	izobuten	56,1	132,8	266,2	417,9	40,0	239,0	0,275	0,194
253	C4H9Cl	1-klorbutan	92,6	150,1	351,6	542,0	36,8	312,0	0,255	0,218
254	C4H9Cl	2-klorbutan	92,6	141,8	341,4	520,6	39,5	305,0	0,280	0,300
258	C4H10	n-butan	58,1	134,8	272,7	425,2	38,0	255,0	0,274	0,199
259	C4H10	izobutan	58,1	113,6	261,4	408,2	36,5	263,0	0,283	0,183
311	C5H12	n-pentan	72,2	143,4	309,2	469,7	33,7	304,0	0,263	0,251
312	C5H12	2-metilbutan	72,2	113,3	301,0	460,4	33,9	306,0	0,271	0,227

Tablica 2. Vrijednosti parametara interakcije k_{ij} za Soave-Redlich-Kwong (SRK) i Peng-Robinson (PR) jednađbe stanja

	CO ₂		H ₂ S		N ₂		CO	
	SRK	PR	SRK	PR	SRK	PR	SRK	PR
metan	0.093	0.092			0.028	0.031	0.032	0.03
etilen	0.053	0.055	0.085	0.083	0.08	0.086		
etan	0.136	0.132			0.041	0.052	-0.028	-0.023
propen	0.094	0.093			0.090	0.090		
propan	0.129	0.124	0.088	0.088	0.076	0.085	0.016	0.026
izobutan	0.128	0.120	0.051	0.047	0.094	0.103		
n-butan	0.143	0.133			0.07	0.08		
izopentan	0.131	0.122			0.087	0.092		
n-pentan	0.131	0.122	0.069	0.0630	0.088	0.100		
n-heksan	0.118	0.110			0.150	0.150		
n-heptan	0.110	0.110			0.142	0.142		
n-dekan	0.130	0.114						
ugljik(IV)- oksid			0.099	0.097	-0.032	-0.017		
cikloheksan	0.129	0.105						
benzen	0.077	0.077			0.153	0.164		
toluen	0.113	0.106						

SIMBOLI

a	parametar u RK, SRK ili PR jednadžbi stanja
A	parametar u RK, SRK ili PR jednadžbi stanja
b	parametar u RK, SRK ili PR jednadžbi stanja
B	parametar u RK, SRK ili PR jednadžbi stanja
k	parametar interakcije u SRK ili PR jednadžbi stanja
M	molarna masa (g mol^{-1})
n_{Ko}	broj komponenti
p	tlak (bar)
R	opća plinska konstanta ($\text{bar cm}^3 \text{mol}^{-1} \text{K}^{-1}$)
T	termodinamička temperatura (K)
v	volumen ($\text{cm}^3 \text{mol}^{-1}$)
y	molarni udio
z	koeficijent kompresibilnosti
α	parametar u SRK ili PR jednadžbi stanja
ϕ	koeficijent fugacitivnosti
φ	parcijalni koeficijent fugacitivnosti
κ	parametar u SRK ili PR jednadžbi stanja
ω	Pitzerov koeficijent acentričnosti
Ω_a	konstanta u RK, SRK ili PR jednadžbi stanja
Ω_b	konstanta u RK, SRK ili PR jednadžbi stanja

Podoznake

c	kritična veličina
i, j	oznaka komponente
id	idealni plin
m	mixture, smjesa
pc	pseudokritična veličina
r	reducirana veličina
sl	solid-liquid, ravnoteža krutina-kapljevina
vl	vapor-liquid, ravnoteža para-kapljevina