Modeli koeficijenta aktivnosti

Ekscesna Gibbsova energija

Idealna otopina
u simetričnim sustavima

$$v^{\mathrm{id}} = \sum x_i v_i$$

$$h^{\mathrm{id}} = \sum x_i h_i$$

$$s^{\mathrm{id}} = \sum x_i s_i - R \sum x_i \ln x_i$$

$$g^{\mathrm{id}} = \sum x_i g_i + RT \sum x_i \ln x_i$$

$$g = g^{\mathrm{id}} + g^{\mathrm{ex}}$$

$$g = \sum x_i g_i + RT \sum x_i \ln x_i + RT \sum x_i \ln \gamma_i$$

$$g^{\mathrm{ex}} = RT \sum x_{\mathrm{i}} \ln \gamma_{\mathrm{i}}$$

Eksperimentalno određivanje koeficijenta aktivnosti i ekscesne Gibbsove energije

Koligativna svojstva

Povišenje vrelišta

$$\ln \gamma_1^{\mathrm{L}} = \frac{\Delta h^{\mathrm{isp}}}{R}\left(\frac{1}{T} - \frac{1}{T^{\bullet}}\right) - \ln\left(1 - x_2^{\mathrm{L}}\right)$$

Sniženje ledišta

$$\ln \gamma_1 = \frac{\Delta h^{\mathrm{talj}}}{R}\left(\frac{1}{T} - \frac{1}{T^{\bullet}}\right) - \ln\left(1 - x_2\right)$$

Osmotski tlak

$$\ln \gamma_1 = -\frac{M_1 g \Delta z}{RT} - \ln\left(1 - x_2\right)$$

Eksperimentalno određivanje koeficijenta aktivnosti i ekscesne Gibbsove energije

Iz ravnoteže para-kapljevina

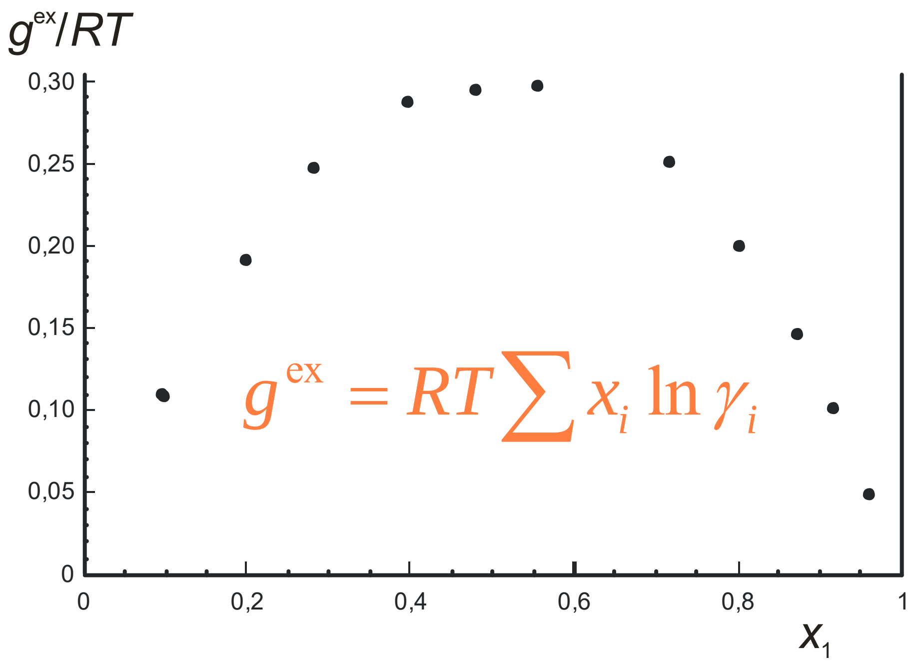
DIJAGRAM VRENJA

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^{L} p_i^{\bullet}}{p} \exp\left[\frac{v_i^{L}\left(p - p_i^{\bullet}\right)}{RT}\right]$$

$$\log\left(p_i^{\bullet}/\mathrm{bar}\right) = A - \frac{B}{T/\mathrm{K} + C - 273{,}15} \qquad v_i^{L} = \frac{M_i}{\rho_i^{L}}$$

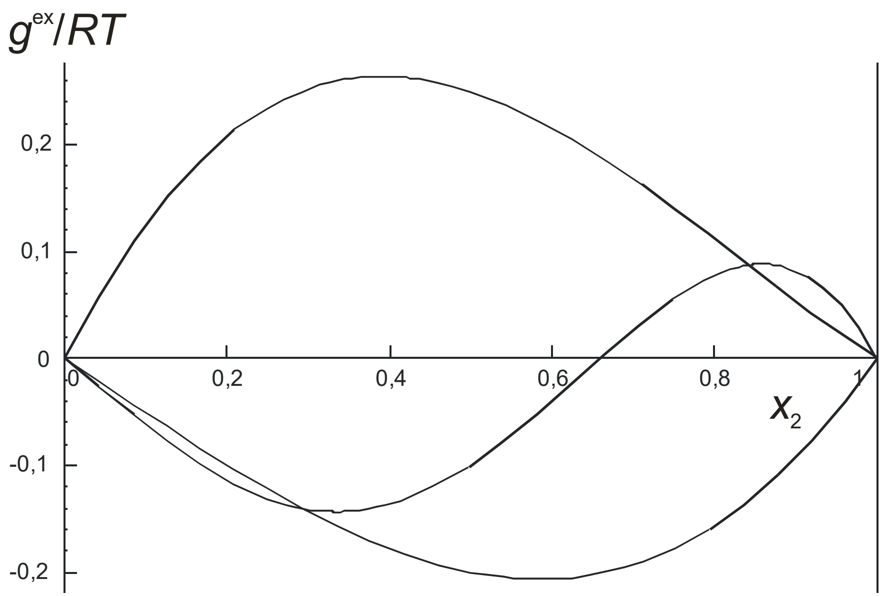
x_1	y_1	p/Pa	γ_1	γ_2	g^{ex}/RT
0,0950	0,2820	66900	2,60	1,02	0,1096
0,0980	0,2880	67020	2,58	1,02	0,1086
0,1970	0,4190	75870	2,11	1,06	0,1907
0,2820	0,4840	80780	1,81	1,12	0,2469
0,3950	0,5500	84660	1,54	1,21	0,2867
0,4790	0,5970	86430	1,41	1,29	0,2949
0,5560	0,6260	87580	1,29	1,42	0,2965
0,7160	0,6970	88150	1,12	1,81	0,2508
0,8030	0,7480	87250	1,06	2,15	0,1994
0,8720	0,8040	85530	1,03	2,52	0,1452
0,9160	0,8540	83430	1,02	2,79	0,1020
0,9610	0,9170	80300	1,002	3,29	0,0488

n-heksan(1) – 2-butanon (2), 60°C, Hanson i suradnici



$$g^{ex} = RT\sum x_i \ln \gamma_i$$

Empirijski polinomni modeli



Redlich-Kister (1948)

A=1; *B*=0,5; *C*=0

A=-0,8; *B*=0,3; *C*=0

A=-0,4; *B*=-1; *C*=0,8

$$\frac{g^{ex}}{RT} = x_1 x_2 \left[A + B\left(x_1 - x_2\right) + C\left(x_1 - x_2\right)^2 + \cdots \right]$$

$$\ln \gamma_1 = x_2^2 \left[A + B\left(3x_1 - x_2\right) + C\left(x_1 - x_2\right)\left(5x_1 - x_2\right) \right]$$

$$\ln \gamma_2 = x_1^2 \left[A + B\left(x_1 - 3x_2\right) + C\left(x_1 - x_2\right)\left(x_1 - 5x_2\right) \right]$$

Empirijski polinomni modeli

Simetrični Margules

$$\frac{g^{\text{ex}}}{RT} = A x_1 x_2$$

$$\ln \gamma_1 = A x_2^2$$

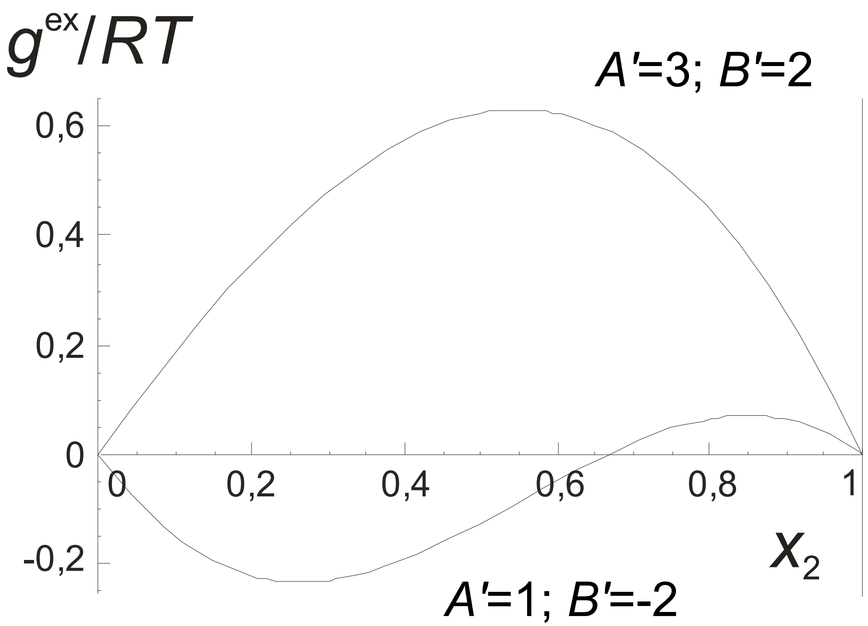
$$\ln \gamma_2 = A x_1^2$$

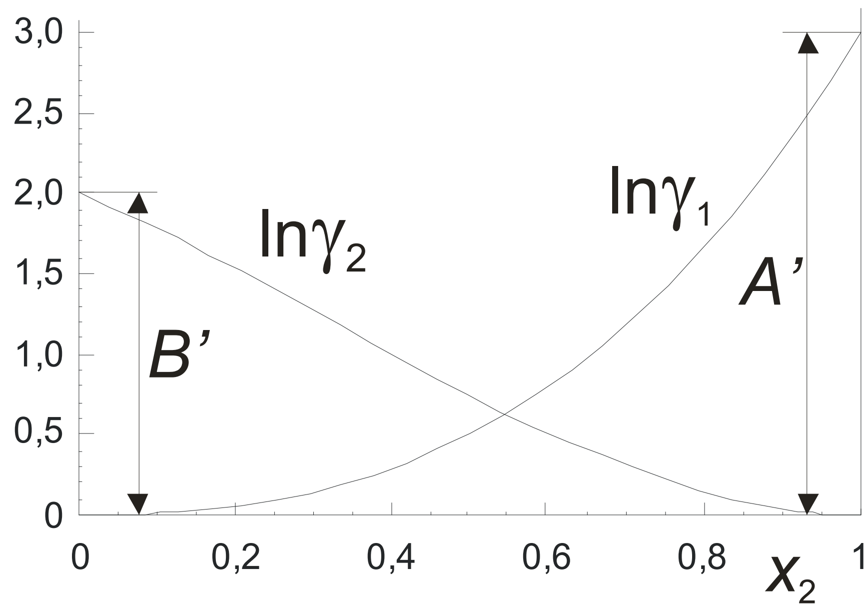
Margules (1895)

$$\frac{g^{\text{ex}}}{RT} = x_1 x_2 \left[A' x_2 + B' x_1 \right]$$

$$\ln \gamma_1 = \left[A' + 2\left(B' - A' \right) x_1 \right] x_2^2$$

$$\ln \gamma_2 = \left[B' + 2\left(A' - B' \right) x_2 \right] x_1^2$$





Empirijski polinomni modeli

Virijalna ekspanzija, Wohl (1946)

$$\frac{g^{ex}}{RT\left(x_1r_1+x_2r_2\right)}=2a_{12}\varphi_1\varphi_2+3a_{112}\varphi_1^2\varphi_2+3a_{122}\varphi_1\varphi_2^2+$$
$$+4a_{1112}\varphi_1^3\varphi_2+4a_{1222}\varphi_1\varphi_2^3+6a_{1122}\varphi_1^2\varphi_2^2+\cdots$$

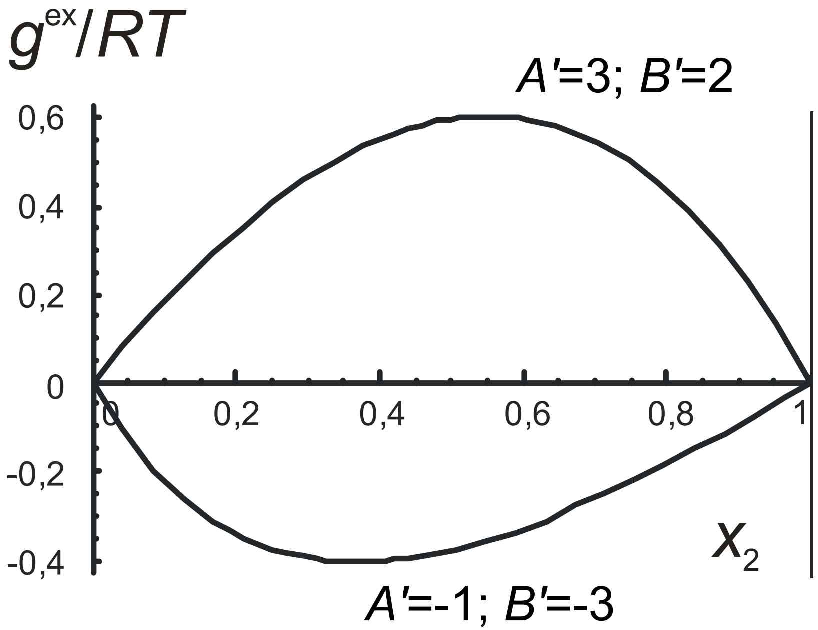
$$\varphi_i=\frac{x_ir_i}{x_1r_1+x_2r_2}$$

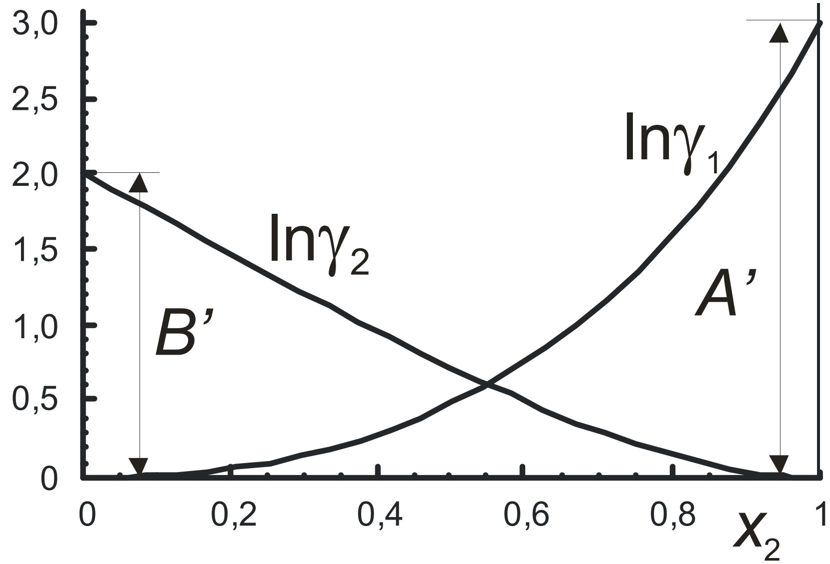
Volumni udio

Van Laar (1910) iz vdW jednadžbe

$$\frac{RT}{g^{ex}}=\frac{1}{A'x_1}+\frac{1}{B'x_2}$$

$$\ln\gamma_1=\frac{A'}{\left(1+\frac{A'x_1}{B'x_2}\right)^2}\qquad \ln\gamma_2=\frac{B'}{\left(1+\frac{B'x_2}{A'x_1}\right)^2}$$



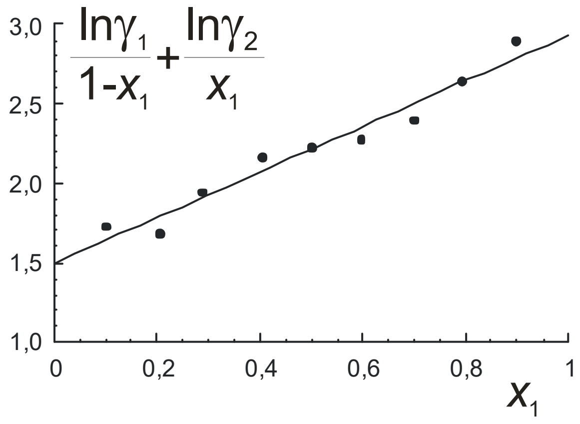


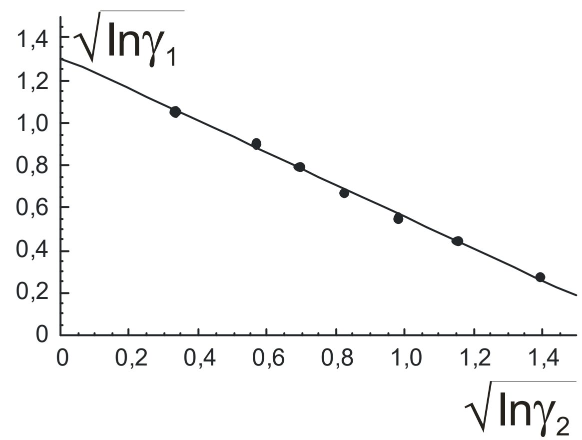
Određivanje parametara

Linearna regresija

$$\frac{\ln\gamma_1}{1-x_1}+\frac{\ln\gamma_2}{x_1}=A'+(B'-A')x_1$$

$$\sqrt{\ln\gamma_1}=\sqrt{A'}-\sqrt{\frac{A'}{B'}}\sqrt{\ln\gamma_2}$$





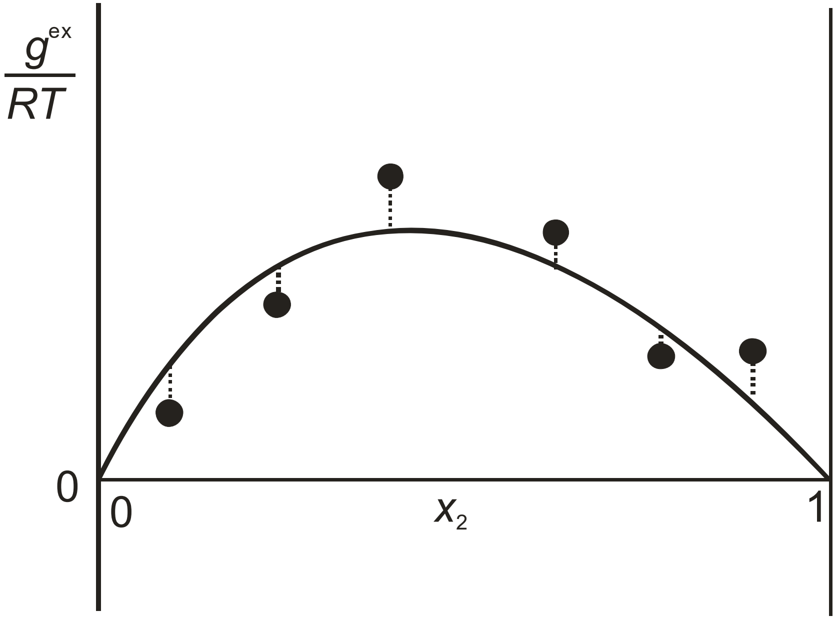
x_1	y_1	p/Pa	γ_1	γ_2
0,1008	0,5204	14450	5,731	0,978
0,2052	0,6304	16750	3,952	0,989
0,2902	0,6468	17680	3,027	1,117
0,4059	0,6490	18390	2,258	1,379
0,5017	0,6576	18590	1,871	1,621
0,5984	0,6632	18520	1,576	1,971
0,7013	0,6687	18550	1,358	2,612
0,7950	0,6732	18730	1,218	3,790
0,8970	0,6895	18250	1,077	6,983

model	Margules	van Laar
$A'=\ln\gamma_1^{\infty}$	1,496	1,706
$B'=\ln\gamma_2^{\infty}$	2,931	3,045

cikloheksan(1) – etanol(2), 25°C, Washburn i Handorf

Određivanje parametara

Neinearna regresija



$$r = \left(\frac{g^{ex}}{RT}\right)_{\text{mod}} - \left(\frac{g^{ex}}{RT}\right)_{\text{exp}}$$

$$OF = \sum_{i=1}^{nd} r_i^2 = \sum_{i=1}^{nd} \left[\left(\frac{g^{ex}}{RT}\right)_{\text{mod}} - \left(\frac{g^{ex}}{RT}\right)_{\text{exp}} \right]_i^2$$

$$\left(\frac{\partial OF}{\partial A'}\right)_{\text{r}} = 0$$

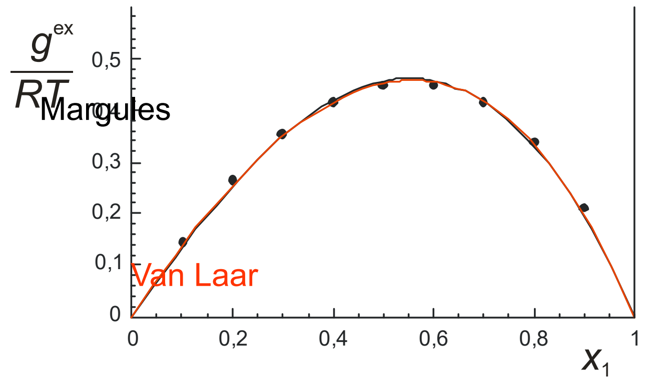
$$\left(\frac{\partial OF}{\partial B}\right)_{\text{r}} = 0$$

Određivanje parametara

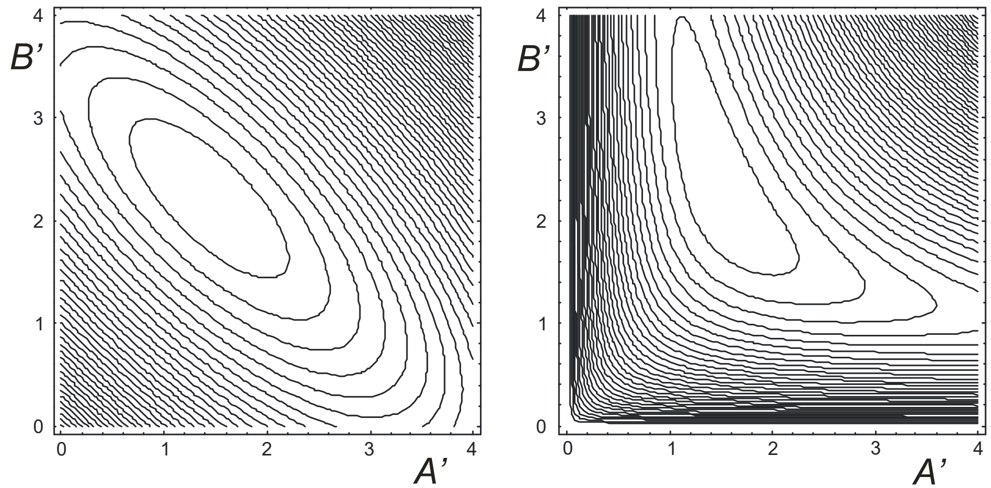
Neinearna regresija

x_1	y_1	p/Pa	γ_1	γ_2	$(g^{ex}/RT)_{exp}$
0,1000	0,3970	11930	3,734	1,015	0,145
0,2000	0,5300	14200	2,967	1,059	0,263
0,3000	0,5940	15430	2,409	1,136	0,353
0,4000	0,6320	16120	2,008	1,255	0,415
0,5000	0,6580	16470	1,709	1,430	0,447
0,6000	0,6720	16590	1,465	1,727	0,448
0,7000	0,6880	16650	1,290	2,198	0,415
0,8000	0,7000	16600	1,145	3,161	0,339
0,9000	0,7400	16160	1,048	5,333	0,209

benzen(1) – etanol(2), 25°C, Smith i suradnici



$$OF = \sum_{i=1}^{nd} r_i^2 = \sum_{i=1}^{nd} \left[\left(\frac{g^{ex}}{RT} \right)_{mod} - \left(\frac{g^{ex}}{RT} \right)_{exp} \right]_i^2$$



Teorijski modeli

Načelo razdvajanja doprinosa

$$g^{\mathrm{ex}} = h^{\mathrm{ex}} - Ts^{\mathrm{ex}}$$

$$\ln \gamma = \ln \gamma^{h} + \ln \gamma^{s}$$

$$\gamma = \gamma^{h} \cdot \gamma^{s}$$

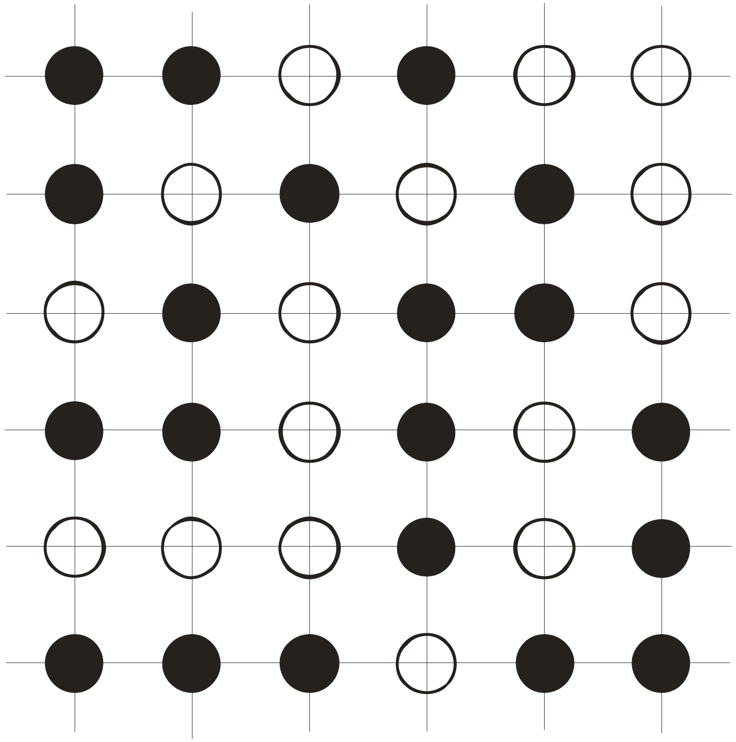
Regularne otopine

$$\left|Ts^{\mathrm{ex}}\right| << \left|h^{\mathrm{ex}}\right|$$

$$g^{\mathrm{ex}} \approx h^{\mathrm{ex}}$$

Scatchard i Hildebrand (1935)

Rešetkasti model



$$v^{\mathrm{ex}} = 0$$

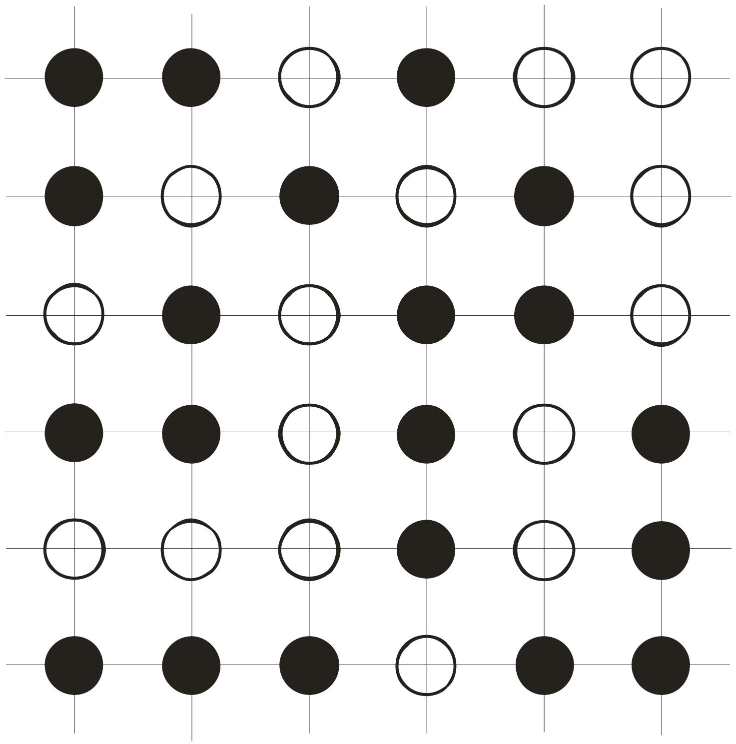
$$s^{\mathrm{ex}} = 0$$

$$s^{\mathrm{m}} = -R\sum_{\mathrm{i}=1}^{\mathrm{nk}} x_{\mathrm{i}} \ln x_{\mathrm{i}}$$

Scatchard i Hildebrand

Teorija regularnih otopina

Rešetkasti model



$$h^{\mathrm{m}} = h^{\mathrm{ex}} < Ts^{\mathrm{m}}$$

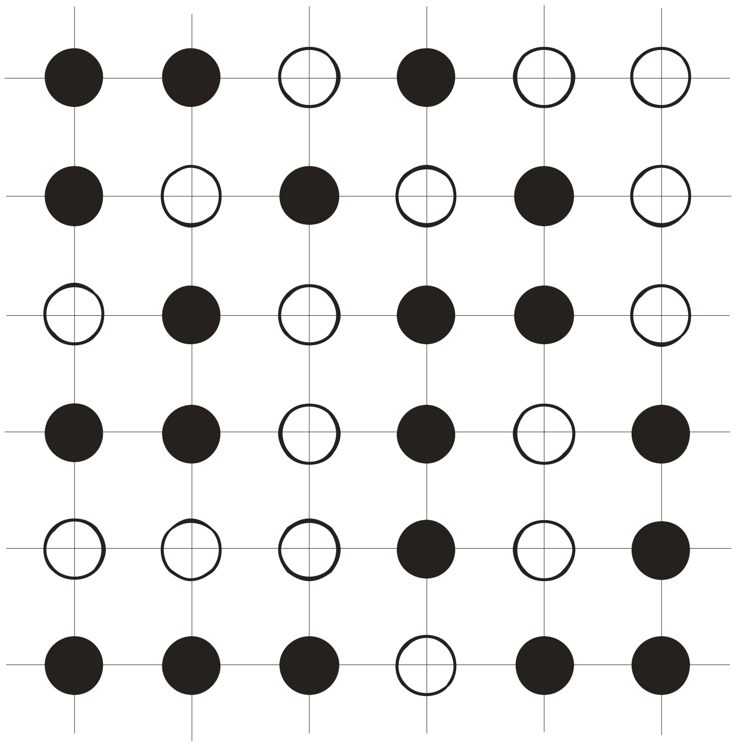
$$H^{\mathrm{ex}} = B\frac{n_1 v_1 \cdot n_2 v_2}{n_1 v_1 + n_2 v_2}$$

$$\frac{h^{\mathrm{ex}}}{RT} = Bv^{\mathrm{ref}}\varphi_1\varphi_2$$

Scatchard i Hildebrand

Teorija regularnih otopina

Rešetkasti model



Interakcijski parametar

$$h^{ex} = u^{ex} + pv^{ex} = u^{ex}$$

$$c_{ii} = \frac{u_i}{v_i}$$

$$B = c_{11} + c_{22} - 2c_{12}$$

$$c_{12} = \sqrt{c_{11}c_{22}}$$

$$B = \left(\sqrt{c_{11}} - \sqrt{c_{22}}\right)^2$$

Parametar topljivosti

$$\delta = \sqrt{\frac{u}{v}}$$

Scatchard i Hildebrand

$$h^{\mathrm{m}} = h^{\mathrm{ex}} = g^{\mathrm{ex}} = RT\left(x_1 \ln\gamma_1 + x_2 \ln\gamma_2\right) > 0$$

$$\ln\gamma_1 = \frac{v_1}{RT}\varphi_2^2\left(\delta_1 - \delta_2\right)^2$$

$$\ln\gamma_2 = \frac{v_2}{RT}\varphi_1^2\left(\delta_1 - \delta_2\right)^2$$

$$g^{\mathrm{m}} = h^{\mathrm{m}} - Ts^{\mathrm{m}}$$

$$h^{\mathrm{m}} < Ts^{\mathrm{m}}$$

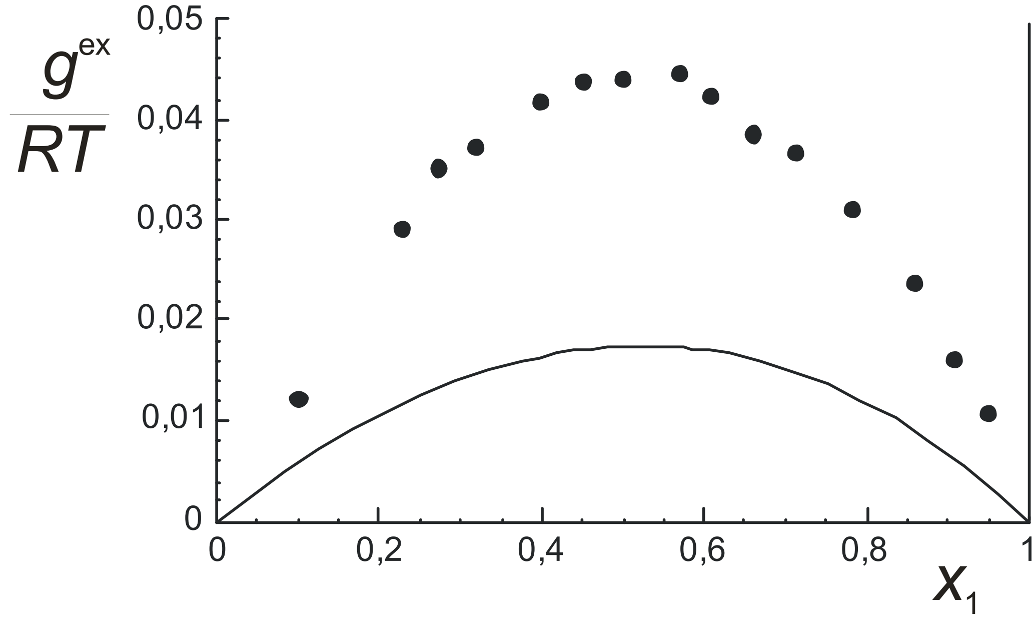
Alifatski ugljikovodici		**Klorirani ugljikovodici**	
metan	11,0	metil klorid	19,8
etan	12,3	metilen klorid	19,8
propan	13,1	kloroform	19,0
n-butan	13,9	tetraklorugljik	17,6
n-pentan	14,3	etil klorid	18,8
n-heksan	14,9	**Eteri**	
n-heptan	15,3	dimetileter	18,0
n-dekan	13,5	dietileter	15,1
cikloheksan	16,8	tetrahidrofuran	18,6

Scatchard i Hildebrand

Primjer

kloroform(1) – tetraklorugljik(2), 25°C, McGlashan i suradnici

x_1	y_1	p/Pa	γ_1	γ_2	$g^{ex}/RT\cdot 10^2$
0,1006	0,1828	16710	1,160	0,997	1,220
0,2280	0,3545	18420	1,094	1,011	2,915
0,2731	0,4080	19030	1,086	1,018	3,521
0,3185	0,4580	19560	1,074	1,021	3,727
0,3982	0,5377	20490	1,057	1,033	4,181
0,4516	0,5869	21090	1,047	1,043	4,380
0,5006	0,6292	21600	1,037	1,053	4,393
0,5689	0,6896	22380	1,036	1,058	4,447
0,6096	0,7192	22730	1,024	1,073	4,222
0,6608	0,7603	23220	1,020	1,077	3,857
0,7133	0,7994	23750	1,017	1,091	3,668
0,7842	0,8485	24380	1,007	1,124	3,099
0,8592	0,9026	25080	1,006	1,139	2,365
0,9074	0,9331	25430	0,999	1,206	1,618
0,9488	0,9658	25840	1,005	1,133	1,069



$$\frac{g^{ex}}{RT} = \frac{h^{ex}}{RT} = \frac{B}{RT}\frac{x_1 v_1^{\bullet} \cdot x_2 v_2^{\bullet}}{x_1 v_1^{\bullet} + x_2 v_2^{\bullet}}$$

$$B = \left(\delta_1 - \delta_2\right)^2$$

Flory Huggins (1941-42)

Atermalne otopine

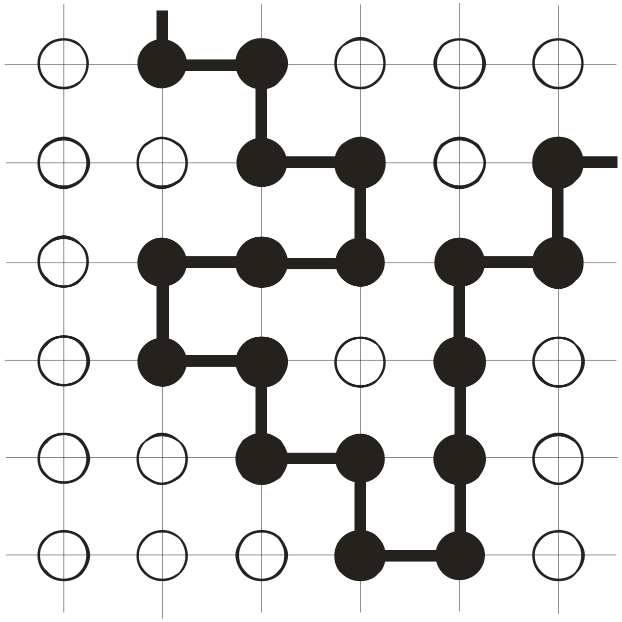
$$\left|Ts^{\text{ex}}\right| >> \left|h^{\text{ex}}\right|$$

$$g^{\text{ex}} \approx -Ts^{\text{ex}}$$

Regularne otopine

$$\left|Ts^{\text{ex}}\right| << \left|h^{\text{ex}}\right|$$

$$g^{\text{ex}} \approx h^{\text{ex}}$$



$$S^{\text{C}} = -k\left(N_1 \ln \frac{N_1}{N_1 + zN_2} + N_2 \ln \frac{zN_2}{N_1 + zN_2}\right)$$

$$s^{\text{C}} = -R\left(x_1 \ln \varphi_1 + x_2 \ln \varphi_2\right) \qquad s^{\text{M,id}} = -R\left(x_1 \ln x_1 + x_2 \ln x_2\right)$$

$$s^{\text{ex}} = s^{\text{C}} - s^{\text{M,id}} \qquad s^{\text{ex}} = -R\left(x_1 \ln \frac{\varphi_1}{x_1} + x_2 \ln \frac{\varphi_2}{x_2}\right)$$

Flory Huggins

$$\frac{g^{ex}}{RT} = (x_1 + zx_2)\chi\varphi_1\varphi_2 + \left(x_1 \ln\frac{\varphi_1}{x_1} + x_2 \ln\frac{\varphi_2}{x_2}\right)$$

$$\ln\gamma_1 = \ln\frac{\varphi_1}{x_1} + \varphi_2\left(1 - \frac{1}{z}\right) + \chi\varphi_2^{\,2}$$

$$\ln\gamma_2 = (1 - z)\varphi_1 + \ln\frac{\varphi_2}{x_2} + \chi\varphi_1^{\,2}$$

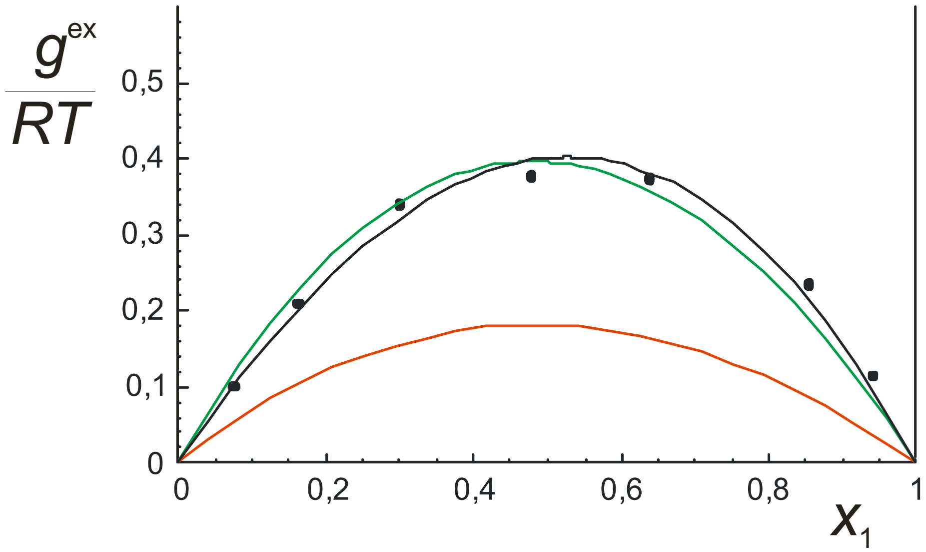
Flory-Hugginsov parametar međudjelovanja

$$\chi = \frac{Bv_1}{RT} \qquad \chi = \chi_0 + \frac{v_1}{RT}(\delta_1 - \delta_2)^2$$

Primjer

benzen(1) – izopropanol(2), 25°C, Olsen i Washburn

x_1	y_1	p/Pa	γ_1	γ_2
0,0760	0,3650	8850	3,352	1,010
0,1640	0,5300	11200	2,854	1,046
0,3000	0,6350	13310	2,221	1,152
0,4790	0,7120	14110	1,654	1,295
0,6380	0,7450	14450	1,330	1,690
0,8540	0,7950	14530	1,066	3,388
0,9410	0,8770	13930	1,024	4,822



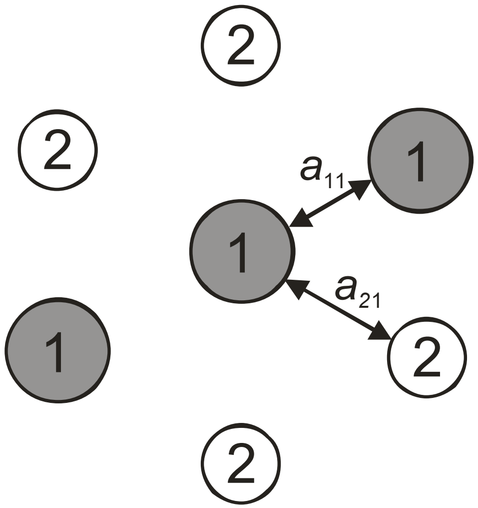
Scatchard-Hildebrand, δ_1=18,8 (MPa)^{0,5} i δ_2=23,5 (MPa)^{0,5}

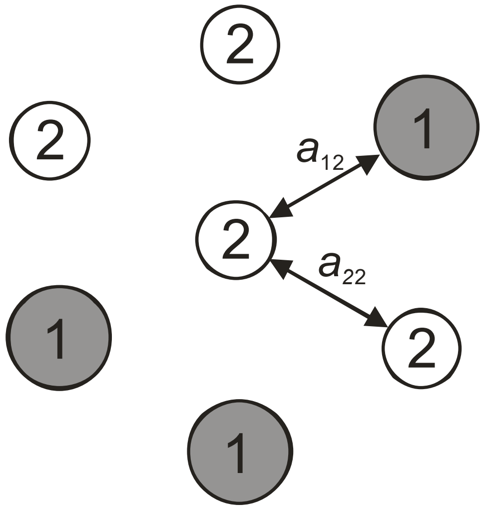
Flory-Huggins, χ=0,928

Flory-Huggins, χ=0,631+0,635x_1

Wilsonov model

Wilson (1958, 1964)





$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left(-\frac{\lambda_{12}}{RT}\right)$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp\left(-\frac{\lambda_{21}}{RT}\right)$$

$$\lambda_{12} = a_{21} - a_{11}$$
$$\lambda_{21} = a_{12} - a_{22}$$

Potencijalne energije međudjelovanja

Stanični model – *two liquid*

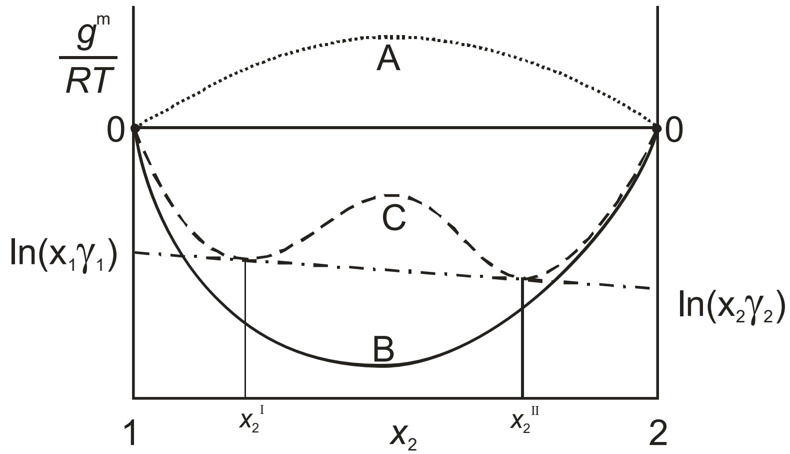
$$\frac{g^{\text{ex}}}{RT} = -x_1 \ln\left(x_1 + \Lambda_{12} x_2\right) - x_2 \ln\left(\Lambda_{21} x_1 + x_2\right)$$

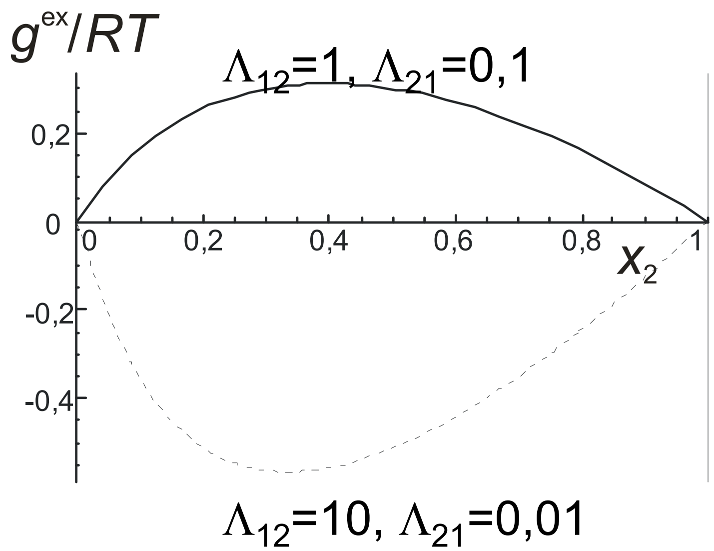
$$\ln \gamma_1 = -\ln\left(x_1 + \Lambda_{12} x_2\right) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2}\right) \qquad \ln \gamma_2 = -\ln\left(\Lambda_{21} x_1 + x_2\right) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2}\right)$$

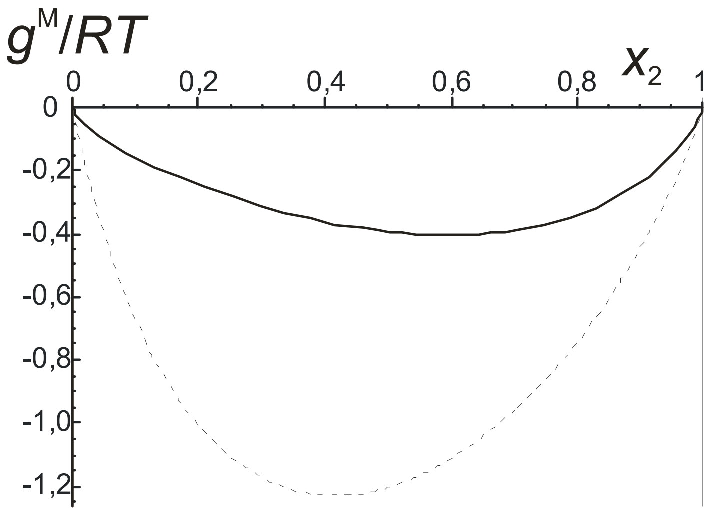
Wilsonov model

Za potpuno mješljive kapljevine

$$\frac{g^{M}}{RT} = x_1 \ln \frac{x_1}{x_1 + \Lambda_{12} x_2} + x_2 \ln \frac{x_2}{\Lambda_{21} x_1 + x_2}$$



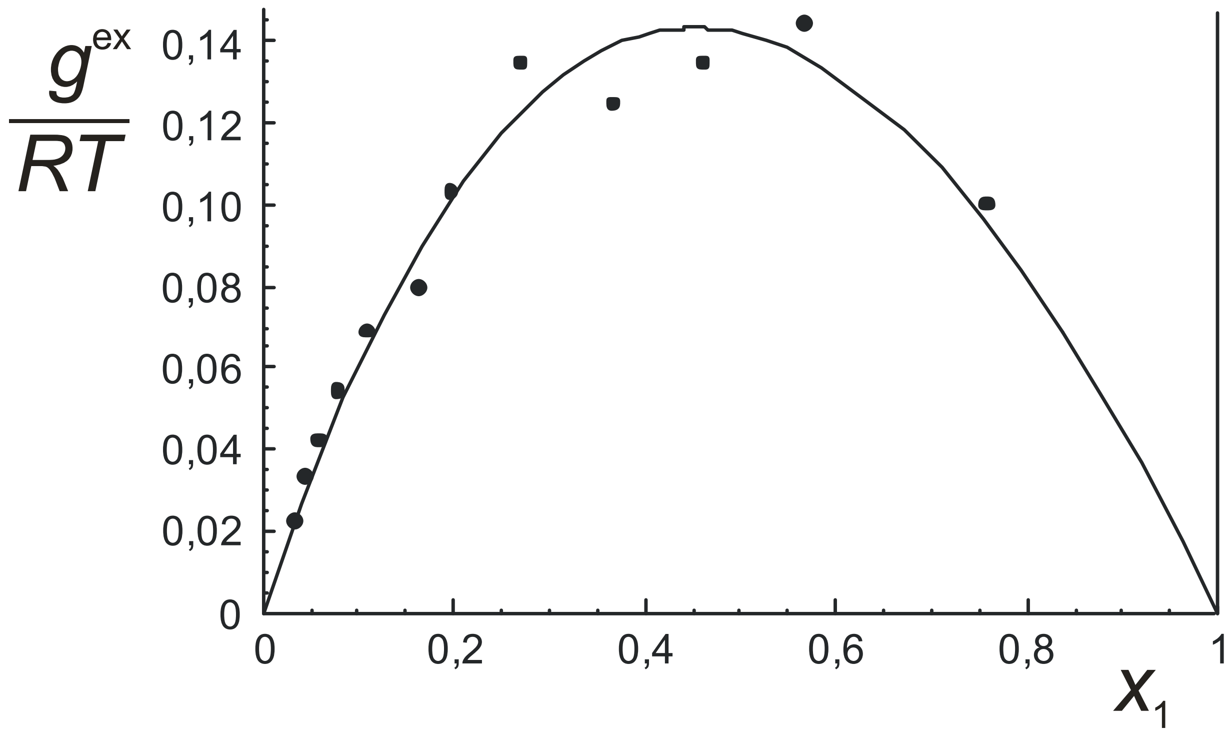




Wilsonov model

metanol(1) – voda(2), 60°C, Broul i suradnici

x_1	y_1	p/Pa	γ_1	γ_2
0,0343	0,2106	24480	1,778	1,003
0,0446	0,2699	26250	1,879	1,005
0,0594	0,3312	28220	1,861	1,006
0,0793	0,3920	30490	1,783	1,009
0,1092	0,4714	33960	1,734	1,010
0,1634	0,5698	38900	1,605	1,003
0,1961	0,5989	41260	1,491	1,032
0,2705	0,6699	47090	1,380	1,068
0,3670	0,7462	52770	1,269	1,061
0,4619	0,7889	57480	1,161	1,130
0,5665	0,8223	62250	1,069	1,279
0,7582	0,9010	71760	1,009	1,473



Wilsonov model

Za prijenos podataka iz dvokomponentnih u višekomponentne sustave

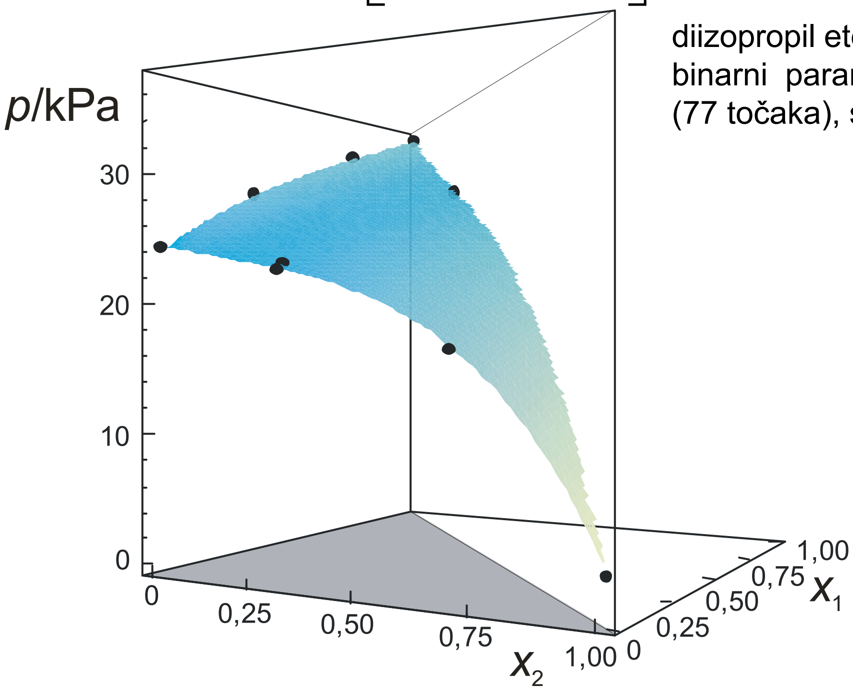
$$\ln \gamma_i = 1 - \ln \sum_{j=1}^{nk} x_j \Lambda_{ij} - \sum_{k=1}^{nk} \frac{x_k \Lambda_{ki}}{\sum_{j=1}^{nk} x_j \Lambda_{kj}}$$

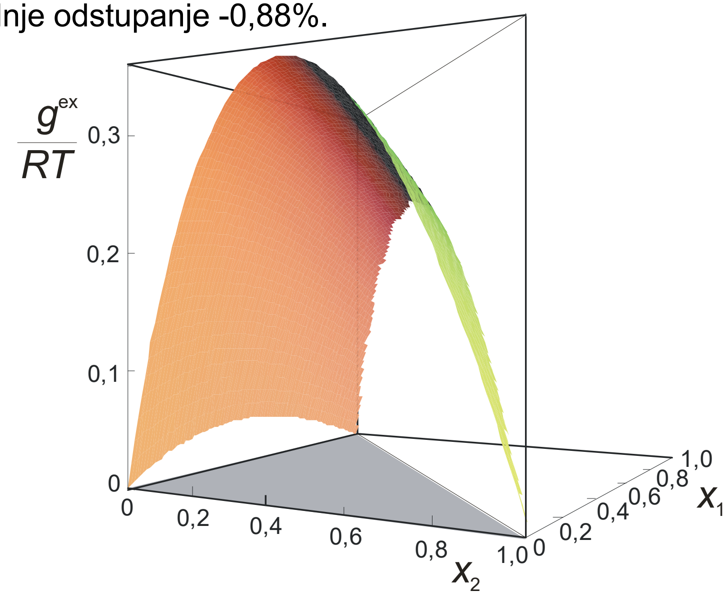
$$\frac{g^{\mathrm{ex}}}{RT} = -\sum_{i=1}^{nk} x_i \ln \sum_{j=1}^{nk} x_j \Lambda_{ij}$$

$$p = \sum_{i=1}^{nk} \gamma_i^{\mathrm{L}} x_i p_i^{\bullet} \exp\left[\frac{v_i^{\mathrm{L}}\left(p - p_i^{\bullet}\right)}{RT}\right]$$

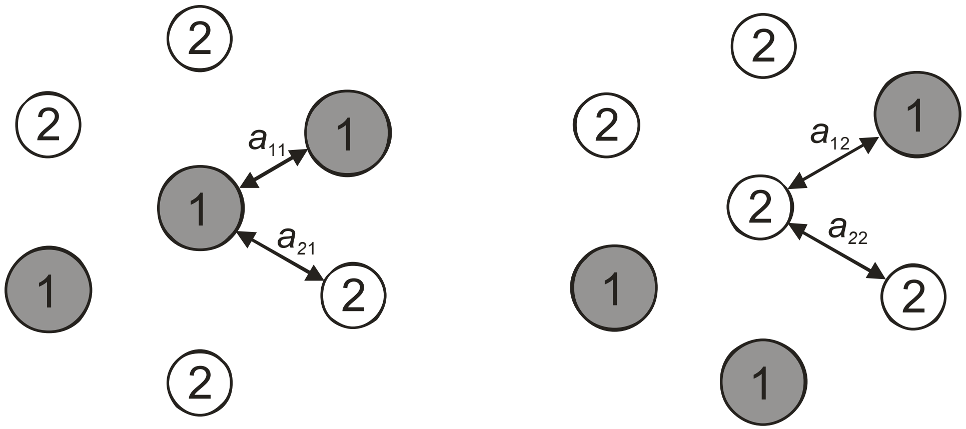
$$\frac{g^{\mathrm{ex}}}{RT} = -\begin{bmatrix} x_1 \ln\left(x_1 + x_2\Lambda_{12} + x_3\Lambda_{13}\right) + \\ + x_2 \ln\left(x_1\Lambda_{21} + x_2 + x_3\Lambda_{23}\right) + \\ + x_3 \ln\left(x_1\Lambda_{31} + x_2\Lambda_{32} + x_3\right) \end{bmatrix}$$

diizopropil eter(1) – 1-butanol(2) – benzen pri 40°C, binarni parametri R.M.Villamañán i suradnici (77 točaka), srednje odstupanje -0,88%.





Model NRTL



Zamijeniti *a* s *g* –
Gibbsove energije međudjelovanja

$$g^{ex} = x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_1 G_{12} + x_2} \right]$$

$$\tau_{12} = (g_{12} - g_{22})/RT$$

$$\tau_{21} = (g_{21} - g_{11})/RT$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12})$$

$$G_{21} = \exp(-\alpha_{12}\tau_{21})$$

Interakcijski parametri
Parametri neslučajnosti

$$\ln\gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_1 G_{12} + x_2)^2} \right]$$

$$\ln\gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_1 G_{12} + x_2} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]$$

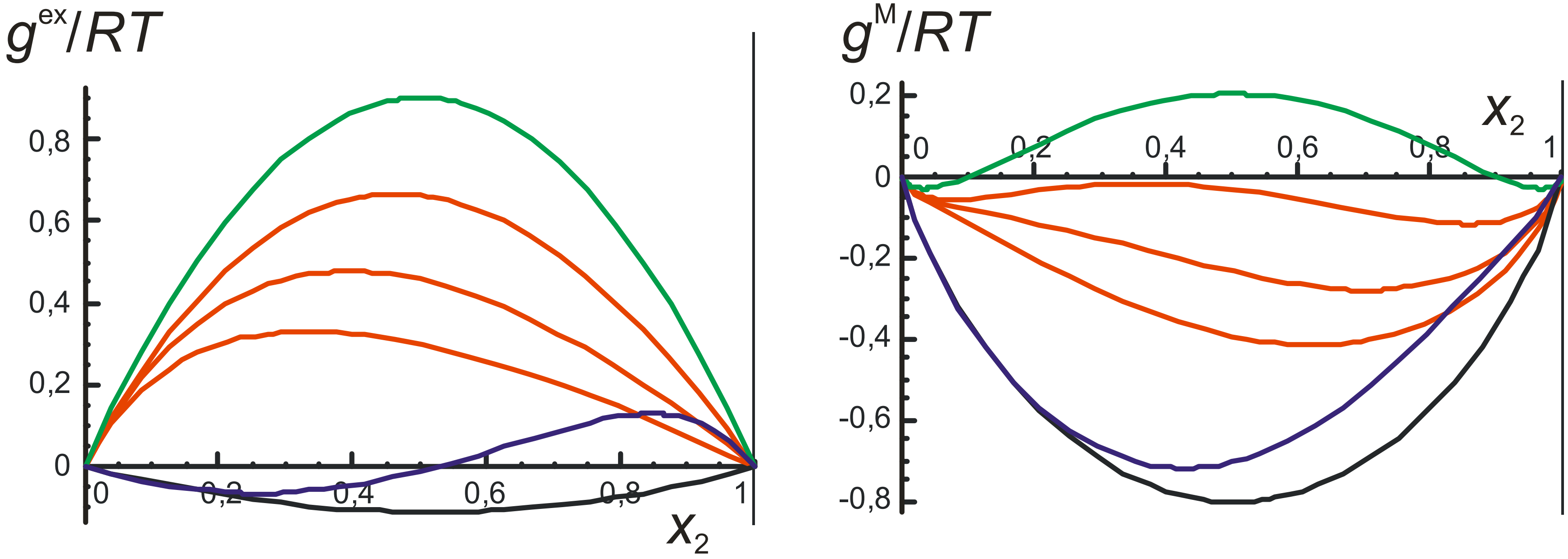
$$A_{12} = (g_{12} - g_{22})/R$$

$$A_{21} = (g_{21} - g_{11})/R$$

Temperaturna ovisnost

Model NRTL

Za opis djelimice mješljivih sustava



τ_{12}=-0,5; τ_{21}=0,1; α_{12}=0,3

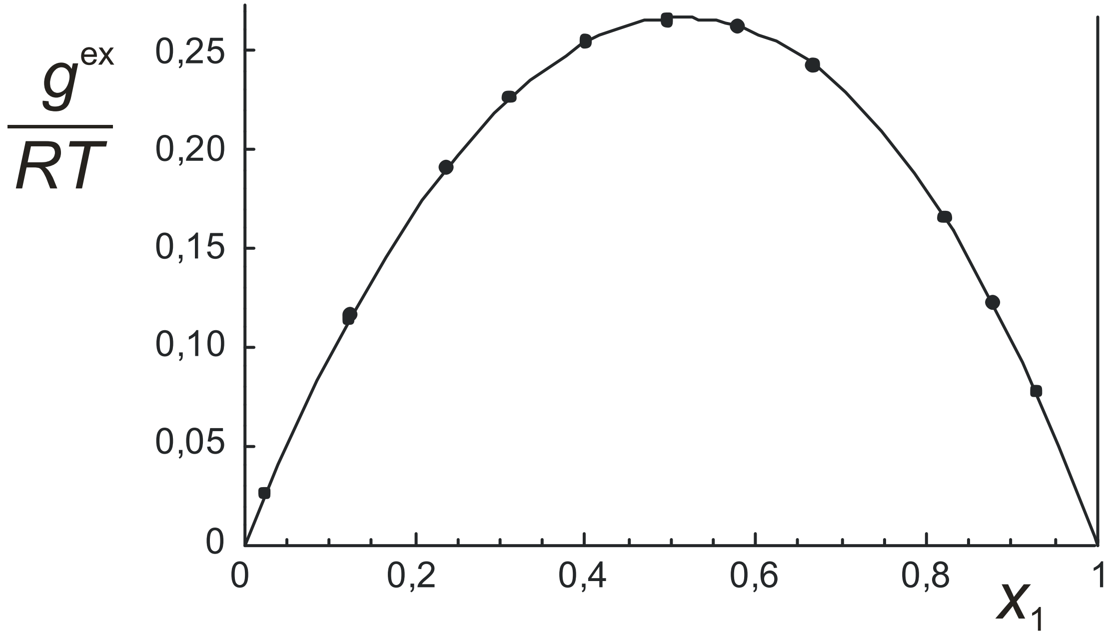
τ_{12}=2; τ_{21}=2; α_{12}=0,1)

τ_{12}=-2,3; τ_{21}=5,8; α_{12}=0,2.

τ_{12}=3; τ_{21}=0,1. α_{12}= 0,5; 0,3 i 0,1.

Model NRTL

x_1	y_1	p/Pa	γ_1	γ_2
0	0	79210		
0,0251	0,0436	80990	2,529	1,003
0,1238	0,1744	85820	2,173	1,021
0,1259	0,1773	85940	2,175	1,021
0,2376	0,2730	88460	1,827	1,065
0,3117	0,3212	88990	1,648	1,108
0,4014	0,3720	88820	1,479	1,176
0,4963	0,4199	87770	1,335	1,276
0,5791	0,4641	86160	1,241	1,385
0,6671	0,5103	83810	1,152	1,556
0,8213	0,6318	76240	1,054	1,983
0,8777	0,7061	71370	1,032	2,166
0,9280	0,7886	66360	1,014	2,461
1,0000	1,0000	55610		



metanol(1) – metil acetat(2), 50°C, Bernatova i suradnici

Model NRTL

Za prijenos podataka iz dvokomponentnih u višekomponentne sustave

$$\ln \gamma_i = \frac{\sum_{j=1}^{nk} x_j \tau_{ji} G_{ji}}{\sum_{l=1}^{nk} x_l G_{li}} + \sum_{j=1}^{nk} \frac{x_j G_{ij}}{\sum_{l=1}^{nk} x_l G_{lj}} \left(\tau_{ij} - \frac{\sum_{m=1}^{nk} x_m \tau_{mj} G_{mj}}{\sum_{l=1}^{nk} x_l G_{lj}} \right)$$

$$\frac{g^{\mathrm{ex}}}{RT} = \sum_{i=1}^{nk} x_i \left(\frac{\sum_{j=1}^{nk} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{nk} G_{ki} x_k} \right)$$

Model UNIQUAC

UNIversal QUAsi-Chemical theory

$$g^{\mathrm{ex}} = g^{\mathrm{C}} + g^{\mathrm{R}}$$

$$\ln\gamma_i = \ln\gamma_i^{\mathrm{C}} + \ln\gamma_i^{\mathrm{R}}$$

$$\gamma_i = \gamma_i^{\mathrm{C}}\gamma_i^{\mathrm{R}}$$

Načelo razdvajanja doprinosa

$$\Theta_i = \frac{x_i q_i}{\sum_{j=1}^{nk} x_j q_j} \qquad \Phi_i = \frac{x_i r_i}{\sum_{j=1}^{nk} x_j r_j}$$

Oblik čestica $\dfrac{\Theta_i}{\Phi_i} = \dfrac{q_i}{r_i}\dfrac{\sum_{j=1}^{nk} x_j r_j}{\sum_{j=1}^{nk} x_j q_j}$

$$\frac{g^{\mathrm{ex,C}}}{RT} = \sum_{i=1}^{nk} x_i \ln\frac{\Phi_i}{x_i} + \frac{z}{2}\sum_{i=1}^{nk} q_i x_i \ln\frac{\Theta_i}{\Phi_i}$$

Flory Huggins

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$$

$$\ln\gamma_i^{\mathrm{C}} = \ln\frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln\frac{\Theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum_{j=1}^{nk} x_j l_j$$

Model UNIQUAC

UNIversal QUAsi-Chemical theory

$$\frac{g^{\text{ex,R}}}{RT} = -q_1 x_1 \ln\left(\Theta_1 + \Theta_2 \tau_{21}\right) - q_2 x_2 \ln\left(\Theta_2 + \Theta_1 \tau_{12}\right)$$

$$\frac{g^{\text{ex,R}}}{RT} = -\sum_{i=1}^{nk} q_i x_i \ln\left(\sum_{j=1}^{nk} \Theta_j \tau_{ji}\right)$$

$$\tau_{ij} = \exp\left(-\frac{u_{ij} - u_{jj}}{RT}\right)$$

$$\ln \gamma_i^{\text{R}} = q_i \left(1 - \ln \sum_{j=1}^{nk} \Theta_j \tau_{ji} - \sum_{j=1}^{nk} \frac{\Theta_j \tau_{ij}}{\sum_{k=1}^{nk} \Theta_k \tau_{kj}}\right)$$

$$A_{ij} = \frac{u_{ij} - u_{jj}}{R}$$

Interakcijski parametri

Model UNIFAC

Korelativni i prediktivni modeli – koja je njihova razlika?

UNIquac Functional group Activity Coefficient

Kombinatorni doprinos – kao kod UNIQUAC-a

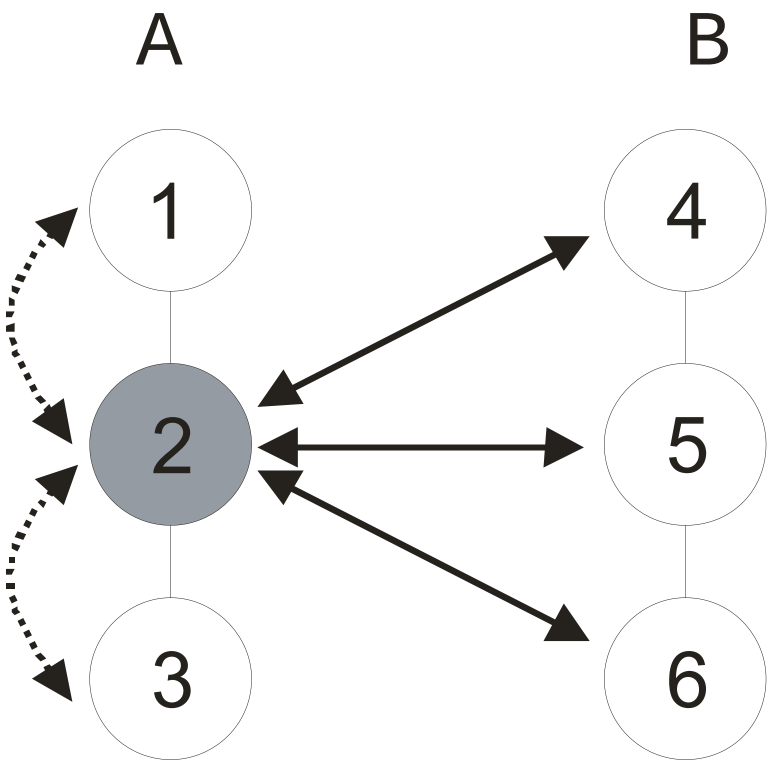
$$q_i = \sum_{k=1}^{ng} \nu_{ki} Q_k$$

$$r_i = \sum_{k=1}^{ng} \nu_{ki} R_k$$

Model UNIFAC

Rezidualni doprinos – otopina strukturnih grupa

$$\ln \gamma_i^{\mathrm{R}} = \sum_{k=1}^{ng} \nu_{ki} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)} \right)$$



$$\ln \Gamma_k = Q_k \left(1 - \ln \sum_{m=1}^{ng} \Theta_m \psi_{mk} - \sum_{l=1}^{ng} \frac{\Theta_l \psi_{kl}}{\sum_{m=1}^{ng} \Theta_m \psi_{ml}} \right)$$

$$\ln \Gamma_k^{(i)} = Q_k \left(1 - \ln \sum_{m=1}^{ng} \Theta_m^{(i)} \psi_{mk} - \sum_{l=1}^{ng} \frac{\Theta_l^{(i)} \psi_{kl}}{\sum_{m=1}^{ng} \Theta_m^{(i)} \psi_{ml}} \right)$$

Model UNIFAC

Rezidualni doprinos – otopina strukturnih grupa

$$\Theta_m = \frac{Q_m X_m}{\sum_{l=1}^{ng} Q_l X_l}$$

$$\Theta_l^{(i)} = \frac{Q_l X_l^{(i)}}{\sum_{m=1}^{ng} Q_m X_m^{(i)}}$$

Interakcijski parametar

$$\psi_{mk} = \exp\left(-\frac{a_{mk}}{T}\right)$$

$$X_m = \frac{\sum_{i=1}^{nk} x_i \nu_{mi}}{\sum_{i=1}^{nk}\left(x_i \sum_{j=1}^{ng} \nu_{ji}\right)}$$

$$X_l^{(i)} = \frac{\nu_{li}}{\sum_{m=1}^{ng} \nu_{mi}}$$

$$a_{mk} \neq a_{km}$$

$$a_{kk} = 1$$

Model ASOG

Analytical Solution Of Groups

$$g^{\mathrm{ex}} = g^{\mathrm{S}} + g^{\mathrm{G}}$$

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{S}} + \ln \gamma_i^{\mathrm{G}}$$

$$\gamma_i = \gamma_i^{\mathrm{S}} \gamma_i^{\mathrm{G}}$$

Kombinatorni doprinos

$$\Phi_i = \frac{x_i \nu_i}{\sum_{j=1}^{nk} x_j \nu_j}$$

$$r_i = \frac{\Phi_i}{x_i} = \frac{\nu_i}{\sum_{j=1}^{nk} x_j \nu_j}$$

$$\ln \gamma_i = 1 + \ln r_i - r_i$$

Flory-Huggins

Model ASOG

Rezidualni doprinos

$$\ln \gamma_i^{G} = \sum_{k=1}^{ng} \nu_{ki} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)} \right)$$

$$\ln \Gamma_k = 1 - \ln \sum_{l=1}^{ng} X_l A_{kl} - \sum_{l=1}^{ng} \frac{X_l A_{lk}}{\sum_{m=1}^{ng} X_m A_{lm}}$$

$$\ln \Gamma_k^{(i)} = 1 - \ln \sum_{l=1}^{ng} X_l^{(i)} A_{kl} - \sum_{l=1}^{ng} \frac{X_l^{(i)} A_{lk}}{\sum_{m=1}^{ng} X_m^{(i)} A_{lm}}$$

$$X_l = \frac{\sum_{j=1}^{nk} x_j \nu_{lj}}{\sum_{j=1}^{nk} \left(x_j \sum_{l=1}^{ng} \nu_{lj} \right)} \qquad X_l^{(i)} = \frac{\nu_{li}}{\sum_{m=1}^{ng} \nu_{mi}}$$

$$A_{kl} = \exp\left(m_{kl} + \frac{n_{kl}}{T} \right)$$

$$A_{kl} \neq A_{lk}$$

$$A_{kk} = 1$$