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Pitzer-Debye-Huckel

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Pitzer-Debye-

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Huckel

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SCLC

$$I_x = 1/2 \sum X_i Z_i^2 \quad (1)$$

$$A_\phi = \frac{1}{3} \left(2\pi N_0 \frac{d_w}{1000} \right)^{3/2} \left(\frac{e^2}{DkT} \right)^{3/2} \quad (2)$$

$\frac{gr}{cm^3}$ d_w N_0
 $k \text{ (J.Cm)}^{1/2}$ e
 $^\circ K$ $T \text{ } \frac{J}{^\circ K}$
 D

$$D = 78.3 + a x_n \quad (3)$$

x_n a

$$\frac{G^E}{RT} = \frac{G^{E,LR}}{RT} + \frac{G^{E,SR}}{RT} \quad (4)$$

$$\ln \gamma_n^{el} = A.B. \left[-\frac{3}{2} (78.3 + a x_n)^{-5/2} \cdot a (1 - x_n) I_x^{1/2} - \frac{1}{2} \rho \left(\frac{I_x^{3/2}}{1 + \rho I_x^{1/2}} \right) \times (78.3 + a x_n)^{-3/2} \right] \quad (5)$$

LR

SR

Pitzer- ()
 : [] **Debye- Huckel** ()

$$g^{ex,el} / RT = - \left(\sum n_k \right) \left(\frac{1000}{M_s} \right)^{1/2} \left(4A_\phi I_x / \rho \right) \ln \left(1 + \rho I_x^{1/2} \right) \quad (6)$$

ρ M_s

B A

k-i

α ($g_{ij}=g_{ji}$)

/

()

a

c

n

g_{ji} g_{ki}

j-i

$$A = \frac{1}{3} \left(\frac{2\pi N_0 d_w}{1000} \right)^{1/2} \times \left(\frac{e^2}{kT} \right)^{3/2} \quad ()$$

$$B = - \left(\frac{1000}{M_s} \right)^{1/2} \cdot \frac{4}{\rho} \quad ()$$

n_i

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x_n **x_m** **x_c** **x_a**

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$$\ln \gamma_i^{el*} = A.B. \left[-\frac{3}{2} (78.3 + a x_n) \right]^{-5/2} \cdot a \cdot x_n \cdot I_x +$$

$$\frac{1}{2} z_i^2 (78.3 + a x_n)^{-3/2} \cdot \ln(1 + \rho I_x^{0.5}) +$$

$$\rho \cdot (78.3 + a x_n)^{-3/2} \cdot \frac{\frac{1}{2} z_i^2 - \frac{1}{2} I_x^{3/2}}{(1 + \rho I_x^{0.5})}$$

$$x_{im} = \frac{x_i G_{immm}}{x_a G_{anmm} + x_c G_{cnmm} + x_n G_{nmm} + x_m}$$

i=a,c,n,m

()

z_i

$$x_{in} = \frac{x_i G_{innn}}{x_a G_{ann} + x_c G_{cnn} + x_m G_{mnn} + x_n}$$

i=a,c,n,m

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NRTL

$$x_{ic} = \frac{x_i G_{ic,nc}}{x_m G_{mcnc} + x_a G_{ac,nc} x_n}$$

i=a,n,m

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$$x_{ia} = \frac{x_i G_{ia,na}}{x_m G_{mana} + x_c G_{ca,na} x_n}$$

i=c,n,m

NRTL

$$\frac{x_{ji}}{x_{ki}} = \frac{x_j}{x_k} G_{ji,ki} \quad ()$$

$$G_{ji,ki} = \exp(-\alpha \tau_{ji,ki}) \quad ()$$

$$\tau_{ji,ki} = -(g_{ji} - g_{ki}) / RT \quad ()$$

$$g^{(a)} = z_a (x_{ma} g_{ma} + x_{ca} g_{ca} + x_{na} g_{na}) \quad ()$$

$$g^{(c)} = z_c (x_{mc} g_{mc} + x_{ac} g_{ac} + x_{nc} g_{nc}) \quad ()$$

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$$g^{(m)} = x_{am} g_{am} + x_{cm} g_{cm} + x_{nm} g_{nm} + x_{mm} g_{mm}$$

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$$g^{(n)} = x_{an} g_{an} + x_{cn} g_{cn} + x_{mn} g_{mn} + x_{nn} g_{nn}$$

$$g_{am} = g_{cm} = g_{an} = g_{cn} \quad ()$$

τ

x_m

x_n

:

$$\tau_{m\grave{a}ca} = \tau_{n\grave{a}ca} = \tau_{m\grave{c}ac} = \tau_{n\grave{c}ac} = \tau_1 \quad ()$$

x_a

$$\tau_{am} = \tau_{cm} = \tau_2 \quad ()$$

x_c

$$\tau_{an} = \tau_{cn} = \tau_3 \quad ()$$

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$$\tau_{nm} = \tau_4 \quad ()$$

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$$\tau_{mn} = \tau_5 \quad ()$$

$$\begin{aligned} \frac{g^{ex,lc}}{RT} = & x_m (x_{am} \tau_{am} + x_{cm} \tau_{cm} + x_{nm} \tau_{nm}) + \\ & x_n (x_{an} \tau_{an} + x_{cn} \tau_{cn} + x_{mn} \tau_{mn}) + \\ & x_a z_a (x_{ma} \tau_{ma,ca} + x_{na} \tau_{na,ca}) + \\ & x_c z_c (x_{mc} \tau_{mc,ac} + x_{nc} \tau_{nc,ac}) \end{aligned}$$

τ_4, τ_3, τ_2

τ_5

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$$\tau_5 = \tau_3 - \tau_2 + \tau_4 \quad ()$$

τ

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$$\begin{aligned} \frac{g^{ex,lc}}{RT} = & \left(\frac{x_m}{(x_a + x_c) G_2 + x_n G_4 + x_m} \right)^* \\ & ((x_a + x_c) G_2 \tau_2 + x_n G_4 \tau_4) + \\ & \left(\frac{x_m}{(x_a + x_c) G_3 + x_m G_5 + x_m} \right)^* \\ & ((x_a + x_c) \tau_3 G_3 + x_m \tau_5 G_5) + \\ & \frac{x_a z_a \tau_1 (x_m + x_n)}{(x_m + x_c G_1 + x_m)} + \frac{x_c z_c \tau_1 (x_m + x_n)}{(x_m + x_a G_1 + x_n)} \end{aligned}$$

$$x_{am} z_a = x_{cm} z_c \quad ()$$

$$x_{an} z_a = x_{cn} z_c \quad ()$$

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$$g_{am} = g_{cm} \quad ()$$

$$g_{an} = g_{cn} \quad ()$$

-

$$x_{cc} = x_{aa} = 0$$

$$\begin{aligned}
 \ln \gamma_n^{ic*} = & \frac{(x_a + x_c)G_2G_4x_m(\tau_4 - \tau_2) - \tau_4G_4x_m^2}{(x_a + x_c)G_2 + x_nG_4 + x_m} + \\
 & \frac{(x_a + x_c)\tau_3G_3 + x_m\tau_5G_5}{(x_a + x_c)G_3 + x_mG_5 + x_n} + \\
 & \frac{\tau_1x_aZ_ax_cG_1}{(x_m + x_cG_1 + x_n)^2} + \frac{\tau_1x_cZ_cx_aG_1}{(x_m + x_aG_1 + x_n)^2} - \\
 & x_c \left(\frac{(-\tau_2G_2x_mG_4(x_nG_4 + x_m) + G_2x_m\tau_4G_4(x_nG_4 - x_m))}{(x_nG_4 + x_m)^3} + \right. \\
 & \left. \frac{(\tau_3G_3x_mG_5(x_mG_5 + x_n) + G_3x_m\tau_5G_5(x_mG_5 - x_n))}{(x_mG_5 + x_n)^3} \right) - \\
 & x_a \left(\frac{(-\tau_2G_2x_mG_4(x_nG_4 + x_m) + G_2x_m\tau_4G_4(x_nG_4 - x_m))}{(x_nG_4 + x_m)^3} + \right. \\
 & \left. \frac{(\tau_3G_3x_mG_5(x_mG_5 + x_n) - G_3x_m\tau_5G_5(x_mG_5 - x_n))}{(x_mG_5 + x_n)^3} \right)
 \end{aligned}$$

$a, \tau_4, \tau_3, \tau_2, \tau_1$

$$\begin{aligned}
 g^{ex*,ic} / RT = & \left(\frac{x_m}{(x_a + x_c)G_2 + x_nG_4 + x_m} \right)^* \\
 & \frac{(x_a + x_c)G_2\tau_2 + x_nG_4\tau_4}{x_m} + \\
 & \left(\frac{x_m}{(x_a + x_c)G_3 + x_mG_4 + x_n} \right)^* \\
 & \frac{(x_a + x_c)\tau_3G_3 + x_m\tau_5G_5}{x_aZ_a\tau_1(x_n + x_m)} + \frac{x_cZ_c\tau_1(x_n + x_m)}{(x_m + x_cG_1 + x_n) + (x_m + x_aG_1 + x_n)} - \\
 & x_c \left(\frac{(\tau_2G_2x_m(x_nG_4 + x_m) - G_2x_mx_n\tau_4G_4)}{(x_nG_4 + x_m)^2} + \right. \\
 & \left. \frac{(\tau_3G_3x_n(x_mG_5 + x_n) - G_3x_nx_m\tau_5G_5)}{(x_mG_5 + x_n)^2} + \tau_1Z_c \right) - \\
 & x_a \left(\frac{(\tau_2G_2x_m(x_nG_4 + x_m) - G_2x_mx_n\tau_4G_4)}{(x_nG_4 + x_m)^2} + \right. \\
 & \left. \frac{(\tau_3G_3x_n(x_mG_5 + x_n) - G_3x_nx_m\tau_5G_5)}{(x_mG_5 + x_n)^2} + \tau_1Z_a \right)
 \end{aligned}$$

$\tau_5, \tau_4, \tau_3, \tau_2, \tau_1$
 G_5, G_4, G_3, G_2, G_1
 τ

MATLAB

Nelder-Mead

6.1

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$$\sigma_{\ln \gamma_n} = \left[\frac{\sum (\ln \gamma_{n,\text{exp}} - \ln \gamma_{n,\text{cal}})^2}{N} \right]^{0.5} \quad ()$$

exp

cal

N

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- : A
- : B
- : C
- : D
- : E
- : F

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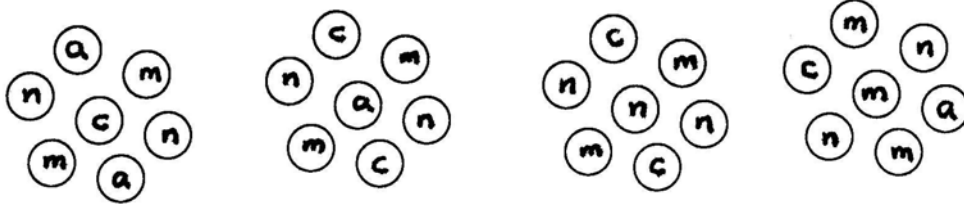
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SYSTEM	T	τ_1	τ_2	τ_3	τ_4	a	N	σ
A	303	13.799	-14.14	-14.64	0.2782	-11.88	19	0.07
	313	7.92	-15.19	-15.58	0.271	-10.83	19	0.07
	323	8.177	-15.97	-16.24	0.258	-12.22	19	0.08
	333	7.47	-16.08	-16.47	0.258	-8.58	19	0.05
B	303	8.16	-15.03	-15.26	0.268	-11.16	19	0.1
	313	10.57	-15.56	-15.8	0.252	-11.54	19	0.08
	323	9.16	-16.28	-16.52	0.253	-10.87	19	0.11
	333	10.62	-16.46	-16.63	0.248	-11.44	19	0.1
C	303	15.62	-12.13	-12.27	0.151	-16.5	16	0.07
	313	15.23	-12.15	-11.97	0.068	-13.6	16	0.07
	323	10.68	-12.7	-12.99	0.0151	-20.2	16	0.08
D	303	7.04	-11.21	-11.02	-0.028	-14.4	16	0.02
	313	6.94	-11.51	-11.29	0.0255	-13.86	16	0.02
	323	7.85	-12.88	-12.98	0.215	-16.08	16	0.04
E	303	8.99	-14.73	-16.08	0.2508	-23.01	17	0.15
	313	13.94	-15.28	-16.4	0.2548	-29	17	0.13
	323	7.5026	-14.57	-15.79	0.232	-17.46	17	0.06
F	303	9.96	-13.39	-13.21	0.1	-14.106	17	0.04
	313	11.612	-14.02	-14.23	0.183	-14.74	17	0.05
	323	11.48	-14.33	-14.52	0.2058	-16.007	17	0.04

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System	T (K)	error(%)
A	303	5.1865
	313	5.523
	323	6.799
	333	5.43
B	303	8.38
	313	6.27
	323	7.52
	333	7.81
C	303	4.21
	313	4.52
	323	7.08
D	303	3.15
	313	1.62
	323	2.47
E	303	7.64
	313	9.17
	323	4.017
F	303	4.47
	313	4.8
	323	3.3
average(error)=5.46		



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