

APPLICABILITY OF THE THREE-CONSTANT WILSON EQUATION FOR CORRELATIONS OF STRONGLY NONIDEAL SYSTEMS. I.

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It follows from a comparison among the three-constant Redlich-Kister, Renon-Prausnitz and Wilson equations that the three-constant Wilson equation fulfills best earlier defined requirements on the normal behaviour. Further, values of correlation parameters A_1, A_2 corresponding to different pairs x_0 and $(G11)_{x_0}$ at constant C and related limiting activity coefficients have been calculated. Limits of sets of parameters yielding $\mathcal{G}^E > 0$, $\mathcal{G}^E < 0$ in the whole concentration range, an S-shaped course of $\mathcal{G}^E(x_1)$ as well as an extreme on the $\log \gamma_i(x_1)$ curve have been also established. A convex course of $[\partial^2 \mathcal{G} / \partial x_1^2](x_1)$ has been proved for the case of the two-constant Wilson equation.

In previous works, the applicability of the Redlich-Kister¹ (further denoted as R-K) and Renon-Prausnitz² (NRTL) equations to correlations of systems exhibiting large positive deviations from Raoult's law³⁻⁵ has been investigated. The normal behaviour of these systems has been defined in the following manner:

1) Curve $(QI) = \partial[\mathcal{G}^E / (2 \cdot 303RT)] / \partial x_1$ is a monotonously decreasing function in the concentration interval (0; 1), *i.e.*

$$\partial(QI) / \partial x_1 < 0. \quad (1)$$

2) A less strict condition requires that the molar excess Gibbs energy be positive in the concentration interval (0; 1), *i.e.*

$$\mathcal{G}^E > 0. \quad (2)$$

From the point of view of the course of $(GII)(x_1) = \partial^2[\mathcal{G} / (2 \cdot 303RT)] / \partial x_1^2$, the following cases have been distinguished:

3) Curve $(GII)(x_1)$ is convex in the whole concentration range, *i.e.*

$$\partial^2(GII) / \partial x_1^2 = (GIII) > 0. \quad (3)$$

4) At a nonconvex course of $(GII)(x_1)$, only one extreme (*i.e.* minimum) on this curve has been required.

This work has been aimed at finding for the three-parameter Wilson equation^{6,7}: a) how it fulfills the above given requirements on the normal behaviour, b) how the equation reflects changes in x_0 and $(G11)(x_0)$, c) possible values of limiting activity

coefficients for homogeneous systems, d) its advantages and disadvantages in comparison with the earlier discussed R-K and NRTL equations.

THEORETICAL

The three-parameter equation proposed by Wilson^{6,7} has been used in the form

$$\mathcal{G}^E/(RT) = 2.303Q = -C[x_1 \ln(x_1 + A_1x_2) + x_2 \ln(x_2 + A_2x_1)], \quad (4)$$

where A_1 , A_2 and C are empirical parameters which depend only on temperature and pressure.

The ratio of activity coefficients and higher (for $n > 2$) derivatives of \mathcal{G}^E/RT with respect to composition are given by relations

$$\ln(\gamma_1/\gamma_2) = 2.303(Q1) = C\{\ln[(x_2 + A_2x_1)/(x_1 + A_1x_2)] - A_2/(x_2 + A_2x_1) + A_1/(x_1 + A_1x_2)\}, \quad (5)$$

$$\begin{aligned} \partial^n Q/\partial x_1^n &= (2.303)^{-1} (-1)^n (n-2)! C\{[1 + (n-1)A_2/(x_2 + A_2x_1)] \cdot \\ &\cdot [(A_2 - 1)/(x_2 + A_2x_1)]^{n-1} - [1 + (n-1)A_1/(x_1 + A_1x_2)] \cdot \\ &\cdot [(1 - A_1)/(x_1 + A_1x_2)]^{n-1}\}. \end{aligned} \quad (6)$$

For the second derivative of the Gibbs energy with respect to composition we obtain

$$\begin{aligned} \partial^2(\mathcal{G}^E/RT)/\partial x_1^2 &= 2.303(G11) = (x_1x_2)^{-1} + \\ &+ C\{(A_2 - 1)[(1 + A_2/(x_2 + A_2x_1))/(x_2 + A_2x_1) - \\ &- (1 - A_1)[1 + A_1/(x_1 + A_1x_2)]/(x_1 + A_1x_2)\}. \end{aligned} \quad (7)$$

Limiting activity coefficients are given by relations

$$\lim_{x_1 \rightarrow 0} \log \gamma_1^0 = L1 = C(1 - \ln A_1 - A_2)/2.303, \quad (8)$$

$$\lim_{x_1 \rightarrow 1} \log \gamma_2^0 = L2 = C(1 - \ln A_2 - A_1)/2.303. \quad (9)$$

Effect of x_0 and $(G11)(x_0)$

During investigating the effect of x_0 and $(G11)(x_0)$, the following equations have been solved numerically

$$[\partial^2(\mathcal{G}/RT)/\partial x_1^2]_{x_1=x_0} = 2.303(G11)(x_0) = f_1(x_0, A_1, A_2, C), \quad (10)$$

$$[\partial^3(\mathcal{G}/RT)/\partial x_1^3]_{x_1=x_0} = 0 = f_2(x_0, A_1, A_2, C), \quad (10a)$$

for different values of x_0 , $(G11)(x_0)$ and C . The method of the solution has been described in an earlier work⁴. Results of the calculations for $C = 1$ are given in Tables I–IV. The results for $C > 1$ in a limited extent are at disposal in the Department of Physical Chemistry at the Institute of Chemical Technology.

The dependence of A_2 on A_1 is depicted on Fig. 1 for $(G11)(x_0) = 0$ (critical isotherm) and for different values of x_0 and parameter C . Values of A_1 and A_2 lower than those indicated by the respective C -curve correspond to a system which splits into two phases. It would have been at $A_1 = A_2 = 0$ for $C = 1$.

The dependence of $L1$ or $L2$ as a function of x_0 for different C is on Fig. 2 or 3, resp., for $(G11)(x_0) = 0$ (solid curves) and $(G11)(x_0) = 0.5$ (dashed curves). It is obvious from these figures that higher values of C yield lower values of limiting activity coefficients $L1$ and $L2$ at constant x_0 and $(G11)(x_0)$. If we limit ourselves

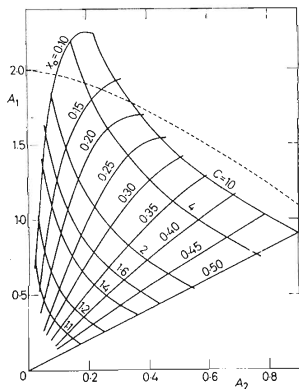


FIG. 1

Limiting Values of A_1 , A_2 , C Securing the Condition of Thermodynamic Stability for the Wilson Equation for Different x_0 and $(G11)(x_0) = 0$

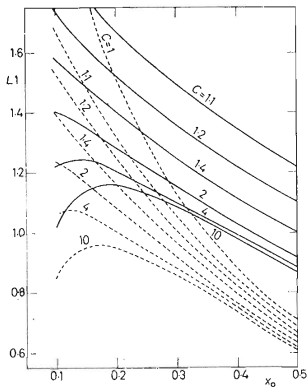


FIG. 2

Dependence of the Logarithm of the Activity Coefficient of the First Component on x_0 and C
 $(G11)(x_0) = 0$, ----- $(G11)(x_0) = 0.5$.

TABLE I

Dependence of the Parameters of the Wilson Equation and Limiting Activity Coefficients on (G11) (x_0) for $x_0 = 0.1, 0.15$ and 0.2

(G11) (x_0)	A_1	A_2	$L1$	$L2$
$x_0 = 0.1$				
1.00	0.00316	1.513	2.252	0.253
0.90	0.00476	1.423	2.135	0.278
0.80	0.00586	1.318	2.093	0.312
0.75	0.00622	1.266	2.090	0.329
0.70	0.00650	1.201	2.093	0.348
0.60	0.00684	1.111	2.115	0.386
0.50	0.00696	0.991	2.155	0.432
0.40	0.00687	0.894	2.210	0.482
0.30	0.00642	0.749	2.299	0.557
0.25	0.00611	0.678	2.352	0.602
0.20	0.00567	0.598	2.420	0.654
0.10	0.00430	0.412	2.623	0.827
0.05	0.00334	0.313	2.772	0.962
$x_0 = 0.15$				
1.00	0.0108	1.492	1.751	0.255
0.90	0.0136	1.389	1.697	0.286
0.80	0.0155	1.282	1.686	0.319
0.75	0.0162	1.229	1.690	0.337
0.70	0.0167	1.175	1.700	0.357
0.60	0.0173	1.063	1.733	0.400
0.50	0.0174	0.950	1.782	0.449
0.40	0.0168	0.828	1.849	0.508
0.30	0.0156	0.699	1.938	0.583
0.25	0.0147	0.628	1.994	0.629
0.20	0.0135	0.553	2.065	0.684
0.10	0.0103	0.375	2.265	0.855
0.05	0.0074	0.259	2.456	1.020
$x_0 = 0.2$				
1.00	0.0251	1.461	1.398	0.258
0.90	0.0295	1.348	1.380	0.292
0.80	0.0323	1.235	1.387	0.328
0.75	0.0336	1.178	1.399	0.348
0.70	0.0341	1.122	1.414	0.369
0.60	0.0346	1.007	1.456	0.416

TABLE I
(Continued)

(G11) (x_0)	A_1	A_2	$L1$	$L2$
0.50	0.0342	0.892	1.513	0.469
0.40	0.0326	0.771	1.585	0.532
0.30	0.0298	0.645	1.679	0.612
0.25	0.0279	0.578	1.738	0.660
0.20	0.0254	0.505	1.809	0.719
0.10	0.0187	0.340	2.015	0.893
0.05	0.0134	0.233	2.205	1.060

to $C = 1$, then the highest values of $L1$ and $L2$ in a homogeneous system may approach infinity at $(G11)(x_0) = 0$. Even at $C > 1$, the Wilson equation enables to reach higher $L1$ values for homogeneous systems in comparison with the R-K and NRTL equations. *E.g.* for $C = 1.1$ or $C = 1.2$ ($x_0 = 0.1$; $(G11)(x_0) = 0$) it follows from Fig. 2 or 3: $L1 = 1.91$, $L2 = 0.62$ or $L1 = 1.73$, $L2 = 0.5$, resp. On the other hand the NRTL equation yields $L1 = 1.5$, $L2 = 0.65$ at the same conditions and at an optimum value $\alpha = 0.6$. The R-K three parameter equation fails completely at these conditions.

Conditions for a Monotonous Course of (Q1) and an S-Shaped Course of \mathcal{G}^E

The monotonous course of (Q1) is closely related to the existence of an extreme on curve (Q1) (x_1) or $\gamma_1(x_1)$, resp. Contradictory or even erroneous conclusions in this respect are found in literature and therefore we will analyze Eq. (4) in detail. Let us investigate the limiting case, *i.e.*

$$\partial(Q1)/\partial x_1 = 0. \quad (11)$$

A small rearrangement of Eq. (6) yields

$$\alpha x_1^2 + \beta x_1 + \gamma = 0, \quad (12)$$

where

$$\alpha = 1 - 2(A_1 + A_2) + (A_1 + A_2)^2 + 2A_1A_2[1 - (A_1 + A_2) + A_1A_2/2],$$

$$\beta = -1 + 4A_1 - 2A_1^2 + A_1A_2[-4 + 2(A_1 + A_2) - A_1A_2],$$

$$\gamma = A_1^2(A_2^2 + 1 - 2/A_1).$$

During solving Eq. (12), the following cases may occur: *A.* Eq. (12) has two solutions for $x_1 \in (0, 1)$. As it is shown in Appendix 1, this case is excluded for the Wilson equation regardless of the value of parameter C . This case would correspond to three extremes on curve $\mathcal{G}^E(x_1)$. *B.* The equation has one solution for $x_1 \in (0, 1)$. One inflexion point is on curve $\mathcal{G}^E(x_1)$ at this composition and the course need not obey condition (2). Eq. (12) may also hold in the case of a zero discriminant

$$D = \beta^2 - 4\alpha\gamma = 0. \quad (13)$$

This case, however, corresponds to an inflexion point with the first derivative equal to zero and it may be inferred from Eq. (13) that this is satisfied for

$$A_2 = 1/A_1 \quad (14a)$$

$$(A_2)_{1,II} = [A_1(3 - 2A_1) \pm 2(A_1 - 1)\sqrt{A_1(A_1 - 1)}] [A_1(4 - 3A_1)]^{-1}. \quad (14b)$$

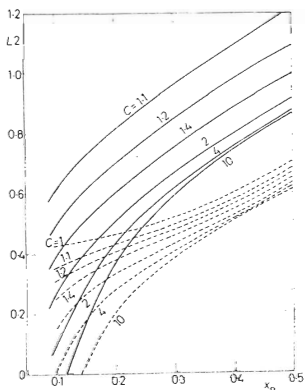


FIG. 3

Dependence of the Logarithm of the Activity Coefficient of the Second Component on x_0 and C

..... (G11) (x_0) = 0, ----- (G11) (x_0) = 0.5.

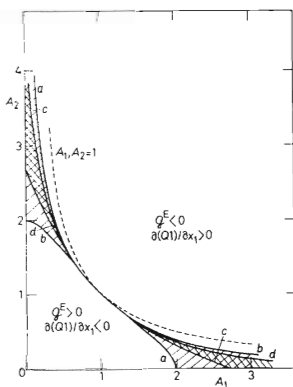


FIG. 4

Sets of Parameters Satisfying Conditions

1 $\mathcal{G}^E > 0$ and $\partial(Q1)/\partial x_1 < 0$, possibly $\mathcal{G}^E < 0$ and $\partial(Q1)/\partial x_1 > 0$ in the whole concentration range 2 set of parameters A_1, A_2 displaying an extreme on the curve $(Q1)(x_1)$, 3 set of parameters yielding an S-shaped course of $\mathcal{G}^E(x_1)$.

TABLE II

Dependence of the Parameters of the Wilson Equation and Limiting Activity Coefficients on (G11) (x_0) for $x_0 = 0.25, 0.3$ and 0.35

(G11) (x_0)	A_1	A_2	$L1$	$L2$
$x_0 = 0.25$				
1.00	0.0500	1.410	1.122	0.263
0.90	0.0558	1.288	1.128	0.300
0.80	0.0594	1.170	1.152	0.340
0.75	0.0605	1.111	1.169	0.362
0.70	0.0611	1.053	1.190	0.385
0.60	0.0611	0.938	1.240	0.435
0.50	0.0592	0.823	1.304	0.493
0.40	0.0556	0.707	1.381	0.561
0.30	0.0500	0.586	1.480	0.645
0.25	0.0464	0.522	1.541	0.696
0.20	0.0420	0.456	1.613	0.757
0.10	0.0303	0.305	1.821	0.937
0.05	0.0214	0.207	2.010	1.112
$x_0 = 0.3$				
1.00	0.091	1.331	0.898	0.270
0.90	0.097	1.204	0.923	0.311
0.80	0.100	1.083	0.960	0.356
0.75	0.101	1.024	0.983	0.380
0.70	0.101	0.967	1.008	0.405
0.60	0.099	0.855	1.066	0.459
0.50	0.095	0.744	1.135	0.521
0.40	0.087	0.635	1.218	0.594
0.30	0.077	0.523	1.320	0.682
0.25	0.079	0.465	1.362	0.736
0.20	0.064	0.404	1.454	0.800
0.10	0.045	0.268	1.665	0.986
0.05	0.032	0.182	1.856	1.160
$x_0 = 0.35$				
1.00	0.155	1.214	0.715	0.282
0.90	0.161	1.088	0.755	0.388
0.80	0.162	0.971	0.803	0.377
0.75	0.161	0.915	0.830	0.403
0.70	0.159	0.861	0.859	0.430
0.60	0.152	0.757	0.923	0.489

TABLE II
(Continued)

0.50	0.142	0.656	0.996	0.555
0.40	0.129	0.557	1.082	0.632
0.30	0.112	0.457	1.187	0.725
0.25	0.102	0.406	1.249	0.781
0.20	0.091	0.352	1.323	0.847
0.10	0.063	0.233	1.534	1.040
0.05	0.044	0.158	1.724	1.217

C. The equation has no solution for $x_1 \in (0, 1)$ and then curve $(Q1)(x_1)$ is either monotonously decreasing and $\mathcal{G}^E(x_1) > 1$ or it is monotonously increasing and $\mathcal{G}^E(x_1) < 0$.

Let us find conditions at which the extreme may appear at concentration limits, i.e. at $x_1 = 0$ and $x_1 = 1$. If the solution should yield $x_1 = 0$, it must hold

$$\gamma = A_1^2(1 + A_2^2 - 2/A_1) = 0 \quad (15)$$

and for $A_1 \neq 0$ we obtain

$$A_2 = \sqrt{(2/A_1 - 1)}. \quad (16)$$

This dependence is on Fig. 4 denoted as *a*.

If the solution is to yield $x_1 = 1$, it must hold on the contrary

$$\alpha + \beta + \gamma = -2A_2 + A_2^2 + A_1^2 A_2^2 = 0 \quad (17)$$

and consequently

$$A_2 = 2/(1 + A_1^2). \quad (18)$$

This dependence is denoted as *b* in Fig. 4 and it is also found as the dashed curve in Fig. 1. The hatched area on Fig. 4 between curves *a* and *b* represents the set of parameters A_1, A_2 (regardless of the value of parameter *C*) yielding an extreme on curve $(Q1)(x_1)$ or an extreme on activity coefficient curves.

As it has been stated earlier, Eq. (12) has only one solution for $x_1 \in (0, 1)$ and, consequently, curve $\mathcal{G}^E(x_1)$ has only one inflexion point. The S-shaped course of $\mathcal{G}^E(x_1)$ (with the consequent change in the sign of \mathcal{G}^E) may occur only for opposite signs at logarithms of limiting activity coefficients. Let us again investigate the cases

for which the limiting values of the activity coefficients equal unity. We obtain for this case from Eqs (8) and (9) (again regardless of the value of parameter C)

$$A_2 = 1 - \ln A_1, \quad (19)$$

$$A_2 = \exp(1 - A_1).$$

TABLE III

Dependence of the Parameters of the Wilson Equation and Limiting Activity Coefficients on (G11) (x_0) for $x_0 = 0.4, 0.45$ and 0.5

(G11) (x_0)	A_1	A_2	$L1$	$L2$
$x_0 = 0.4$				
1.00	0.256	1.051	0.370	0.301
0.90	0.255	0.937	0.620	0.352
0.80	0.249	0.833	0.676	0.405
0.75	0.244	0.784	0.706	0.433
0.70	0.238	0.737	0.738	0.463
0.60	0.222	0.647	0.805	0.526
0.50	0.203	0.561	0.882	0.597
0.40	0.181	0.465	0.970	0.678
0.30	0.154	0.391	1.075	0.775
0.25	0.139	0.347	1.138	0.833
0.20	0.123	0.301	1.212	0.902
0.10	0.084	0.199	1.422	1.098
0.05	0.058	0.135	1.611	1.279
$x_0 = 0.45$				
1.00	0.406	0.841	0.459	0.332
0.90	0.389	0.755	0.516	0.387
0.80	0.367	0.675	0.576	0.445
0.75	0.354	0.638	0.608	0.475
0.70	0.341	0.601	0.641	0.507
0.60	0.311	0.531	0.710	0.574
0.50	0.279	0.462	0.788	0.648
0.40	0.244	0.394	0.876	0.732
0.30	0.205	0.325	0.981	0.883
0.25	0.184	0.289	1.044	0.894
0.20	0.161	0.251	1.117	0.964
0.10	0.109	0.166	1.325	1.166
0.05	0.074	0.113	1.513	1.349

TABLE IV

Dependence of the Parameters of the Wilson Equation and Limiting Activity Coefficients on (G11) (x_0) for $x_0 = 0.5$

(G11) (x_0)	$A_1 = A_2$	$L1 = L2$	(G11) (x_0)	$A1 = A2$	$L1 = L2$
1.00	0.611	0.383	0.40	0.316	0.797
0.90	0.562	0.440	0.30	0.262	0.902
0.80	0.513	0.500	0.25	0.234	0.963
0.75	0.489	0.532	0.20	0.204	1.035
0.70	0.465	0.565	0.10	0.136	1.241
0.60	0.416	0.634	0.05	0.093	1.426
0.50	0.351	0.715			

These dependences are denoted as c and d in Fig. 4. Curve d is also on Fig. 1. The hatched area between both curves represents the set of parameters corresponding to the S-shaped course of $\mathcal{G}^E(x_1)$.

A more concrete representation of the course of \mathcal{G}^E or (Q1) resulting from the three-

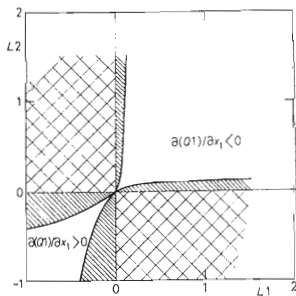


FIG. 5

Sets of Limiting Activity Coefficients Yielding Courses Defined in the Caption to Fig. 4

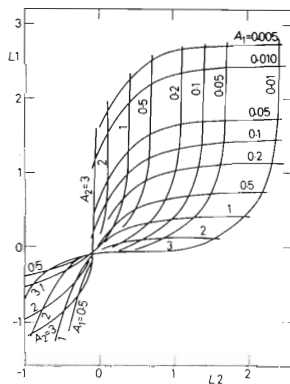


FIG. 6

Values of $L1$ and $L2$ corresponding to pairs A_1, A_2 for $C = 1$

-parameter Wilson equation may be obtained from Fig. 5. This figure contains dependences from Fig. 4 transformed into variables $L1$ and $L2$.

Fig. 5 reveals some limitations of the Wilson equation pointed at by Orye and Prausnitz⁸. The Wilson equation cannot correlate correctly systems exhibiting an extreme on curve (Q1) (x_1) or $\gamma_i(x_1)$ as long as both limiting activity coefficients are greater than 1.359 [= $\exp(1 - \ln 2)$]. Once, however, one activity coefficient is lower than this value (and simultaneously greater than unity), the second one may be arbitrarily large. For activity coefficients lower than unity may the extreme on curve $\gamma_i(x_1)$ occur theoretically at arbitrarily low activity coefficients.

On turning back to strongly nonideal systems, the extreme on curve (Q1) (x_1) may according to the Wilson equation appear, as it is obvious from Fig. 1, only for highly unsymmetrical systems and it is more probable at higher values of (G11) (x_0) and C . The dependence of $L1$ and $L2$ on A_1 and A_2 is on Fig. 6 for $C = 1$.

Conditions Imposed on the Course of (G11) (x_1)

The normal behaviour of (G11) (x_1) has been defined by inequality (3). From Eq. (6) we obtain

$$(G1111) = 2/x_1^3 - 2C(1 - A_1)^3 (x_1 + A_1x_2)^{-3} - 6CA_1(1 - A_1)^3 (x_1 + A_1x_2)^{-4} + 2/x_2^3 - 2C(1 - A_2)^3 (x_2 + A_2x_1)^{-3} - 6CA_2(1 - A_2)^3 (x_2 + A_2x_1)^{-4}. \quad (20)$$

It is shown in Appendix II that condition (3) is always satisfied for $C = 1$. The course of (G11) (x_1) as given by Eq. (4) is always convex for this value of C . The values of (G1111) in unsymmetrical systems at $C > 1$ become negative in a definite concentration range, namely for $x_0 = 0.2$ at $C > 12$; for $x_0 = 0.15$ at $C > 1.33$; for $x_0 = 0.1$ at $C > 1.05$. These values should serve only for orientation and they depend to a certain extent (very little) on values of (G11) (x_0). The occurrence of more extremes on curves (G11) (x_1) is little probable and none were observed in the studied range of x_0 , (G11) (x_0) and C .

CONCLUSIONS

We have calculated parameters A_1 , A_2 , C in the Wilson three-constant equation, which correspond to systems with different values of x_0 and (G11) (x_0). Besides that, the corresponding values of the limiting activity coefficients have been calculated. In contrast to the R-K and NRTL equations, the limiting activity coefficients may reach even infinitely large values. This is one of the reasons which brings about

good results if this equation is used for homogeneous systems. This favourable property is supported by the fact that the equation with values of $C \leq 1$ cannot reproduce the behaviour of systems which are heterogeneous in a certain concentration range. High values of the limiting activity coefficients provided by the R-K and NRTL equations lead to splitting into two liquid phases.

Considerable attention has been paid to the course of $\mathcal{G}^E(x_1)$ and $\partial\mathcal{G}^E/\partial x_1$. The analysis has led to the conclusion that curve $\mathcal{G}^E(x_1)$ can have only two extremes, i.e. it can describe an S-shaped course of $\mathcal{G}^E(x_1)$. Only one inflexion point may appear on curve $\mathcal{G}^E(x_1)$ and this corresponds to an extreme on curves $\gamma_i(x_1)$. A set of parameters has been found (Fig. 4) which yields an extreme on curves $\gamma_i(x_1)$ or an S-shaped behaviour of $\mathcal{G}^E(x_1)$. This set has been transformed and sets of limiting activity coefficients have been found which correspond to $\mathcal{G}^E > 0$; $\mathcal{G}^E < 0$, an S-shaped behaviour of $\mathcal{G}^E(x_1)$ or possibly an extreme on curve $\gamma_i(x_1)$. At the same time it has been found out that at simultaneous occurrence of an extreme on curves $\gamma_i(x_1)$ are the limiting activity coefficients bounded above by a value of 1.355 without being bounded below. It has been proved for the Wilson two-constant equation that it always yields a convex course of $(G11)(x_1)$.

APPENDIX I

Let us investigate whether the quadratic equation (12) can have two roots on the interval (0, 1). It would have to hold in this case

$$0 < \frac{-\beta \pm \sqrt{(\beta^2 - 4\alpha\gamma)}}{2\alpha} < 1. \quad (A-1)$$

As the value of α is always positive, it may be proved by an analysis of relation (A-1) that it holds if and only if the following conditions are satisfied simultaneously:

$$\left. \begin{array}{l} 1) \quad \beta^2 - 4\alpha\gamma \geq 0 \\ 2) \quad 2\alpha + \beta > 0 \\ 3) \quad \alpha + \beta + \gamma > 0 \\ 4) \quad \beta < 0 \\ 5) \quad \gamma > 0 \end{array} \right\} \quad (A-2)$$

It may be shown that for $A_1 < 1$ or $A_1 > 1$ are conditions 4, 5 or 2, 3, respectively, excluded.

APPENDIX II

Let us consider at the beginning the first three terms of Eq. (20)

$$F_1(x_1) = 2/x_1^3 - 2C(1 - A_1)^3(x_1 + A_1x_2)^{-3} - 6CA_1(1 - A_1)^3(x_1 + A_1x_2)^{-4} \quad (A-3)$$

Let us try to find such composition (at non-negative parameters A_1, A_2, C) at which this expression would be equal to zero. After rearranging we obtain

$$A_1^4 + 4A_1^3(1 - A_1)x_1 + 6A_1^2x_1^2(1 - A_1)^2 + 4A_1(1 - A_1)^3x_1^3(1 - C) + x_1^4(1 - A_1)^4(1 - C) = 0. \quad (A-4)$$

This relation simplifies considerably for $C = 1$. Eq. (A-4) reduces in this case to (for $A_1 > 0$)

$$A_1^2 + 4A_1(1 - A_1)x_1 + 6A_1^2x_1^2(1 - A_1)^2 = 0. \quad (A-5)$$

The discriminant of this equation is equal to

$$D = -8A_1^2(1 - A_1)^2, \quad (A-6)$$

it is always negative and consequently no real x_1 exists for which would Eq. (A-4) hold and, followingly, $F_1(x_1)$ can never be equal to zero for $C = 1$. The same results are obtained after similar considerations performed with second three terms of Eq. (19).

Two further negative terms remain in Eq. (A-4) at $C > 1$ and $F_1(x_1)$ may be then not only equal to zero but it can also assume negative values, which was in fact observed.

LIST OF SYMBOLS

A_1, A_2, C	constants in the Wilson equation
\mathcal{G}^E	molar excess Gibbs free energy
(G11) ((G11), (G111))	second (third, fourth) derivative of the molar Gibbs free energy with respect to composition divided by $2 \cdot 303RT$
$L1, L2$	limiting values of the decadic logarithm of the activity coefficient of the i -th component
(G11) (x_0)	ordinate of the minimum on the curve (G11) (x_1)
$Q = \mathcal{G}^E / (2 \cdot 303RT)$	dimensionless molar excess Gibbs free energy
(Q1), (Q11)	first, second derivative of Q with respect to composition
R	universal gas constant
T	absolute temperature
x_i	mole fraction of the i -th component
γ_i	activity coefficient of the i -th component
γ_i^0	limiting activity coefficient of the i -th component
α, β, γ	parameters in Eq. (12)

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