APPLICABILITY OF THE THREE-CONSTANT WILSON EQUATION TO CORRELATIONS OF STRONGLY NONIDEAL SYSTEMS. II.

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A new version of the three-constant Wilson equation has been proposed which connects the two-parameter equation with the first symmetrical term in the polynomial expansion of $\mathscr{G}^E(x_1)$. Some properties of this new modification of the Wilson equation are described.

One disadvantage of the two-parameter Wilson equation from the point of view of correlations of strongly nonideal systems consists in the fact that it yields in contrast to the Redlich–Kister and NRTL equations too high limiting activity coefficients in the vicinity of the critical point without being able to describe simultaneously the heterogeneous region. Wilson[1,2] succeeded partially in removing this disadvantage by adding one multiplication constant C. This procedure, however, leads to further difficulties. As it follows from the expression for $\mathscr{G}^E$ in a multicomponent system

$$\left.\begin{aligned}\mathscr{G}^E/(RT) &= -C\sum_{i=1}^{N} x_i \ln\left(\sum_{j=1}^{N} x_j A_{ij}\right)\\ A_{11} &= A_{22} = \ldots = A_{NN} = 1\end{aligned}\right\} \quad (1)$$

it is necessary that all binary systems be correlated with the same constant C, which weakens considerably this alternative, even though it is possible that values of constant C from the range $1\cdot1 - 1\cdot3$ could perhaps become such universal constants.

An extension of the Wilson equation to correlations of heterogeneous systems may be also performed by connecting the two-constant Wilson equation with another equation for $\mathscr{G}^E$, *e.g.* with the Redlich–Kister equation. If we retain only its first symmetrical term, we obtain

$$\mathscr{G}^E/(RT) = -[x_1 \ln(x_1 + A_1 x_2) + x_2 \ln(x_2 + A_2 x_1)] + B x_1 x_2. \quad (2)$$

where parameter B depends only on temperature and pressure. Relations for different thermodynamic quantities are obtained easily from the relations for the Wilson equation given in the preceding work[3]. As third and higher derivatives of $\mathscr{G}$ resp. Q

TABLE I

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

B	(G11) (x_0)	A_1	A_2	$L1$	$L2$
−0·230	1·0	0·0594	1·170	1·052	0·240
	0·8	0·0611	0·938	1·140	0·335
	0·6	0·0556	0·707	1·281	0·461
	0·5	0·0500	0·586	1·380	0·545
	0·4	0·0420	0·456	1·513	0·657
	0·3	0·0303	0·305	1·721	0·837
	0·2	0	0	∞	∞
−0·115	1·0	0·0558	1·288	1·078	0·250
	0·8	0·0611	1·053	1·140	0·335
	0·6	0·0592	0·823	1·254	0·443
	0·5	0·0556	0·707	1·331	0·511
	0·4	0·0500	0·586	1·430	0·595
	0·3	0·0420	0·456	1·563	0·707
	0·2	0·0303	0·305	1·771	0·887
	0·1	0	0	∞	∞
+0·115	0·8	0·0558	1·288	1·178	0·350
	0·6	0·0611	1·053	1·240	0·435
	0·5	0·0611	0·938	1·290	0·485
	0·4	0·0592	0·823	1·354	0·543
	0·3	0·0556	0·707	1·431	0·611
	0·2	0·0500	0·586	1·530	0·695
	0·1	0·0420	0·456	1·663	0·807
	0·0	0·0303	0·305	1·871	0·987
0·230	0·8	0·0500	1·410	1·222	0·363
	0·6	0·0594	1·170	1·252	0·440
	0·5	0·0611	1·053	1·290	0·485
	0·4	0·0611	0·938	1·340	0·535
	0·3	0·0592	0·823	1·404	0·593
	0·2	0·0556	0·707	1·481	0·661
	0·1	0·0500	0·586	1·580	0·745
	0·0	0·0420	0·456	1·713	0·857
0·345	0·7	0·0500	1·410	1·272	0·413
	0·6	0·0558	1·288	1·278	0·450
	0·5	0·0594	1·170	1·302	0·490
	0·4	0·0611	1·053	1·340	0·535
	0·3	0·0611	0·938	1·390	0·585
	0·2	0·0592	0·823	1·454	0·643
	0·1	0·0556	0·707	1·531	0·711
	0·0	0·0500	0·586	1·630	0·795

TABLE I
(Continued)

B	(G11) (x_0)	A_1	A_2	$L1$	$L2$
0·460	0·6	0·0500	1·410	1·322	0·463
	0·5	0·0558	1·288	1·328	0·500
	0·4	0·0594	1·170	1·352	0·540
	0·3	0·0611	1·053	1·390	0·585
	0·2	0·0611	0·938	1·440	0·635
	0·1	0·0592	0·823	1·504	0·695
	0·0	0·0556	0·707	1·581	0·761
0·576	0·5	0·0500	1·410	1·372	0·513
	0·4	0·0558	1·288	1·378	0·550
	0·3	0·0594	1·170	1·042	0·590
	0·2	0·0611	1·053	1·440	0·635
	0·1	0·0611	0·938	1·490	0·685
	0·0	0·0592	0·823	1·554	0·743
0·619	0·4	0·0500	1·410	1·422	0·663
	0·3	0·0558	1·288	1·378	0·550
	0·2	0·0594	1·170	1·402	0·590
	0·1	0·0611	1·053	1·440	0·635
	0·0	0·0611	0·938	1·640	0·835

with respect to composition do not contain any terms with B, it is possible to use with small changes Tables I—IV from the preceding work[3] even for Eq. (2). Values of A_1, A_2 corresponding in these Tables to certain values of x_0 and (G11) (x_0) will now correspond to values of x_0 and $[(G11)(x_0) - 2B/2\cdot303]$. The values of the limiting activity coefficients will change by $B/2\cdot303$. Table I which represents a part of transformed Table I from the preceding work[3] may serve as an example. We must note that dependences of both $L1$ and $L2$ on parameter B at fixed values of x_0 and (G11) (x_0) pass through a minimum. Thus it is not possible to assess the magnitude of parameter B only from the knowledge of x_0, (G11) (x_0) and the limiting activity coefficient. This equation, which arose by connecting the Wilson equation with the first term of the Redlich–Kister equation, will display properties of both component parts. New results may be expected in cases when both parts have opposite effects.

Eq. (2) will always lead to a convex course of (G11) (x_1) as both the Wilson equation and the added symmetrical term yield always a convex course for (G11) (x_1).

The influence of the additive term on the monotonous behaviour of (Q1) (x_1) or $\mathscr{G}^E$ is rather complex. Answering this question, we must solve the equation

System	x_c	w_c	Ref.
Water–tetrahydrofurane	0·777	0·470	5
Water–tetraethylene glycol diethylether	0·928	0·480	6
Water–1-butanol	0·895	0·675	7
Water–acrolein	0·708	0·438	8
Water–furaldehyde	0·811	0·479	9
Water–β-picoline	0·935	0·736	10

$\partial^2 Q/\partial x_1^2 = 0$, which is in this case of the fourth degree with respect to composition and its analysis is much more complicated. It is however expedient to mention the following special cases:

A. Parameters of the Wilson equation are from the region which corresponds to the monotonously decreasing course of $(Q1)(x_1)$ (see[3]). A positive value of parameter B will exert no influence on this course and the resulting course $(Q1)(x_1)$ will be also monotonously decreasing and $\mathscr{G}^E > 0$. Negative values of B may change this behaviour considerably. With decreasing value of B, one or two extremes appear on curve $(Q1)(x_1)$ (three and more extremes have not been observed in any case). At sufficiently low values of B we may obtain $\mathscr{G}^E < 0$ in the whole concentration range and followingly also a monotonously increasing $(Q1)(x_1)$.

B. Parameters of the Wilson equation are from the set which leads to an extreme on curve $(Q1)(x_1)$ in the region closer to $\mathscr{G}^E > 0$. Sufficiently low and positive values
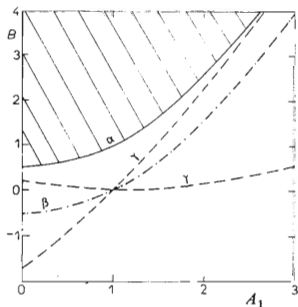

FIG. 1

Definition Region of A_1, B

of B do not exclude the existence of this extreme. The extreme disappears at higher values of B. At negative values of B, the extreme firstly becomes relatively more pronounced (it changes of course its coordinates), still lower values of B may lead to two extremes on curve $(Q1)(x_1)$ and finally very low values of B yield again $\mathscr{G}^E < 0$.

C. Similar trends and their combinations are observed in other cases; these are only qualitative findings and we do not intend to discuss it any further.

It was shown for the Wilson equation that the maximum value of the limiting activity coefficient (supposing that $\partial(Q1)/\partial x_1 = 0$ holds on the given concentration end) might reach $1·355$. Eq. (2) yields, however, for $0 < A_1 < 1$ at similar conditions the value of $1·649$. An arbitrary value of the limiting activity coefficient may be reached with $A_1 > 1$. This problem is discussed in more detail in Appendix.

As it follows from the discussion, the proposed modification of the Wilson equation displays certain advantages over the original version of the three-constant equation, especially in applications to multicomponent systems. Simultaneously, all advantages of the Wilson equation are retained in the new modification. No greater practical experience has been obtained with the new version. It has been applied to one system[4], namely to a 1-butanol–water system at the atmospheric pressure. In comparison with the NRTL equation it reproduces better the composition of conjugated phases but the agreement in the vapour phase composition in the homogeneous region is worse.

It appears that the use of an asymmetrical additive term instead of the symmetrical one would be more suitable, so that the description of the asymmetry may be shared by both parts of the equation. One of possible variants could be

$$\mathscr{G}^E = (\mathscr{G}^E)_{\text{Wilson}} + Dw_1(1 - w_1), \tag{3}$$

where w_1 is the mass or volume fraction. Usefulness of this alternative may be documented by Table II in which compositions of several aqueous systems in the critical point are given. It is seen that the mass fraction is in all cases closer to $0·5$ than corresponding values of the mole fraction.

APPENDIX

Let us limit our considerations to the limiting activity coefficient $L2$, which is given by the relation

$$2·303L2 = L2' = 1 - \ln A_2 - A_1 + B. \tag{A-1}$$

Let us search for maximum or possibly minimum values of $L2$ at the boundary condition

$$(\partial(Q1)/\partial x_1)_{x_1 = 1} = (\partial^2 Q/\partial x_1^2)_{x_1 = 1} = 0. \tag{A-2}$$

It follows from Eqs (*A-1*) and (*A-2*) that

$$A_2 = 2/(1 + A_1^2 - 2B) .$$ (*A-3*)

By substituting Eq. (*A-3*) into (*A-1*) we obtain

$$L2' = 1 - \ln 2 + \ln (1 + A_1^2 - 2B) - A_1 + B .$$ (*A-4*)

It follows from Eq. (*A-4*) that

$$B < (1 + 2A_1^2)/2 .$$ (*A-5*)

The result of an analysis of the dependence $L2' = L2'(A_1, B)$ is on Fig. 1. Curve α bounds the region of validity of relation (*A-5*).

At a fixed value of A_1, $L2'$ assumes its extreme value for B_{extr}, for which it holds

$$B_{extr} = (A_1^2 - 1)/2 .$$ (*A-6*)

Curve A_1, B_{extr} is denoted on Fig. 1 by symbol γ. If we substitute Eq. (*A-6*) into Eq. (*A-4*) we find that on curve β the following relation holds

$$L2' = 0{\cdot}5(A_1 - 1)^2$$ (*A-7*)

On curves γ it holds $L2' = 0$.

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