APPLICABILITY OF THE VAN LAAR EQUATION TO CORRELATION OF STRONGLY NON-IDEAL SYSTEMS*

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Dedicated to Professor E. Hála on the occasion of his 60th birthday.

The performed analysis of the van Laar equation and its comparison with the results of analyses of the Redlich–Kister, NRTL and Wilson equations demonstrate that the Redlich–Kister equation is applicable only to slightly asymmetric systems. The van Laar and NRTL equations have approximately the same range of applicability, the NRTL equation with a suitable choice of the parameter α allowing to attain higher limiting activity coefficients. For moderately asymmetric systems, the Wilson equation provides higher activity coefficients than other two-parameter equations but lower than the three-parameter ones. On the contrary, for very asymmetric systems, the Wilson equation allows to reach on the whole the highest limiting activity coefficients.

In our foregoing works, we dealt with the applicability of the Redlich–Kister[1], NRTL (ref.[2,3]) and Wilson[4] equations for the description of strongly non-ideal systems. In this work, the analysis of applicability of the van Laar equation and furthermore its comparison with the equations mentioned above are carried out.

Like in the previous works, we will pursue the systems with positive deviations from the Raoult law here. With respect to the number of extremes and points of inflexion on the curve $Q(x_1) = G^E/RT$ we will distinguish these variants (Fig. 1):

I) There is one extreme on the curve Q (*i.e.* a maximum in the case of positive deviations from the Raoult law) and no point of inflexion. The curve $\partial Q/\partial x_1 = Q1 = \ln(\gamma_1/\gamma_2) = f(x_1)$ has in this case the monotonous course.

II) There is one extreme and one point of inflexion on the curve Q (Fig. 1*b*). This behaviour is less frequent. On the curve $Q1 = \ln(\gamma_1/\gamma_2)$ and on the curves of activity coefficients of components there is an extreme (at the composition which corresponds to the point of inflexion). Both the Redlich–Kister and NRTL equations, when applied to asymmetric systems, have a tendency, as it was found out formerly, to approximate the systems pertaining to the first group by the course which belongs to this variant[1-4].

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III) There exist two extremes and one point of inflexion on the curve Q, that means that we get an S-shaped course of G^E. This course is very rare for excess Gibbs energy but for other thermodynamic quantities, it is comparatively more frequent (*e.g.* H^E or V^E). There is an extreme on the curve $Q1 = \ln(\gamma_1/\gamma_2)$ in this case and besides the limiting values of logarithms of activity coefficients have opposite signs.

It is possible to define yet further variants which could be illustrated by examples but they are seldom common.

From the point of view of the course of $G11 = \partial^2(G^M/RT)/\partial x_1^2$ we will distinguish these alternatives:

a) The course of the $G11 = f(x_1)$ curve is convex, *i.e.*

$$\partial^2 G11/\partial x_1^2 = \partial^4(G^M/RT)/\partial x_1^4 = G1111 > 0 \tag{1}$$

holds in the entire concentration range. It is *e.g.* the curve *c* in Fig. 2.

b) The curve $G11(x_1)$ is not convex in the entire concentration range but between two points of inflexion which delimit the concave part, $\partial G11/\partial x_1 > 0$ holds. See *e.g.* the curve *d* in Fig. 2.

In our work[1] yet further alternatives were defined, however, these will not be used here.

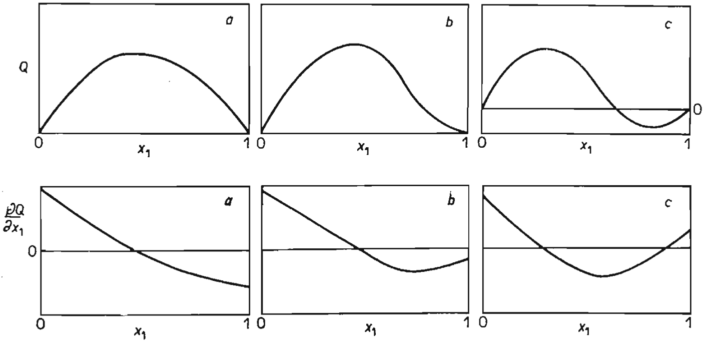


FIG. 1

Dependence of Q and $\partial Q/\partial x_1 = \ln \gamma_1/\gamma_2$ on Composition for Three Different Variants Differing in the Number of Extremes and Points of Inflection

Relations Used

The van Laar three-constant equation is hereafter used in the form

$$Q = G^E/RT = (x_1 + x_2 B/A)\, z_1 z_2 (A - D z_1 z_2)\,, \tag{2}$$

where

$$z_1 = x_1/(x_1 + x_2 B/A)\,; \quad z_2 = 1 - z_1 = x_2(B/A)/(x_1 + x_2 B/A)\,. \tag{2a}$$

The first to fourth derivative of the dimensionless excess Gibbs energy Q with respect to the composition is given by the relations

$$\begin{aligned} \partial Q/\partial x_1 = Q1 = \ln(\gamma_1/\gamma_2) &= (1 - B/A)\, z_1 z_2 (A - D z_1 z_2) + \\ &+ (z_2 - z_1)(B/A)(A - 2D z_1 z_2)/(x_1 + x_2 B/A)\,, \end{aligned} \tag{3}$$

$$\partial^2 Q/\partial x_1^2 = Q11 = 2(B/A)^2 \left[D(6 z_1 z_2 - 1) - A\right]/(x_1 + x_2 B/A)^3\,, \tag{4}$$

$$\begin{aligned} \partial^3 Q/\partial x_1^3 = Q111 &= 6(B/A)^2 (B/A - 1)\left[D(6 z_1 z_2 - 1) - A\right]/(x_1 + x_2 B/A)^4 + \\ &+ 12(B/A)^3 D(z_2 - z_1)/(x_1 + x_2 B/A)^5\,, \end{aligned} \tag{5}$$

$$\begin{aligned} \partial^4 Q/\partial x_1^4 &= 96(B/A)^3 (B/A - 1)\, D(z_2 - z_1)/(x_1 + x_2 B/A)^6 + \\ &+ 24(B/A)^2 (B/A - 1)^2 \left[D(6 z_1 z_2 - 1) - A\right]/(x_1 + x_2 B/A)^5 - \\ &- 24(B/A)^4 D/(x_1 + x_2 B/A)^7\,. \end{aligned} \tag{6}$$

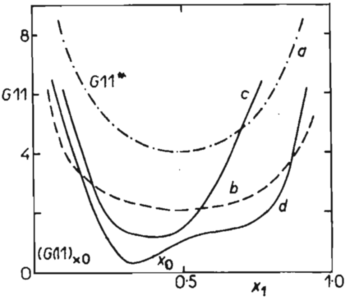


FIG. 2

Dependence of G11 on Composition for Some Special Cases

a Ideal solution, *b* strongly non-ideal solutions, *c* example of real course of G11 (convex), *d* example of non-convex course of G11.

The limiting activity coefficients are given by the relations

$$L1 = \lim_{x_1 \to 0} \ln \gamma_1 = \lim_{x_1 \to 0} \partial Q/\partial x_1 = A\,, \tag{7a}$$

$$L2 = \lim_{x_1 \to 1} \ln \gamma_2 = B\,. \tag{7b}$$

Course of G^E/RT

A very important conclusion follows from Eqs (*7*), viz. that the van Laar equation is not able to describe the S-shaped course of $G^E = f(x_1)$ and therefore the values of logarithms of limiting activity coefficients cannot have opposite signs. The constants A, B must not have opposite signs because then it would hold $x_1 + x_2B/A = 0$ at a certain composition and Q would not be defined. Null[6] removes this defect by a modification of the van Laar equation.

Let us investigate now the conditions under which a point of inflexion can occur on the $Q(x_1)$ curve. At the point of inflexion, $\partial^2 Q/\partial x_1^2 = 0$ must hold and so we get from Eq. (*4*)

$$D(6z_1z_2 - 1) = A\,. \tag{8}$$

It is evident from this relation that the point of inflexion can in no case occur for the case of the two-constant equation which may be therefore applicable only to the description of the systems which belong to the first variant. The composition $(z_1)_{\mathrm{infl.}} = z$ which corresponds to the point of inflexion is given by the relation

$$(z)_{1,2} = 0{\cdot}5\{1 \pm \sqrt{[1 - (2/3)(A/D + 1)]}\}\,. \tag{9}$$

From the analysis of Eq. (*9*) follows that the two points of inflexion will be in the interval $z \in \langle 0, 1 \rangle$ if

$$-1 < A/D < 1/2\,. \tag{10}$$

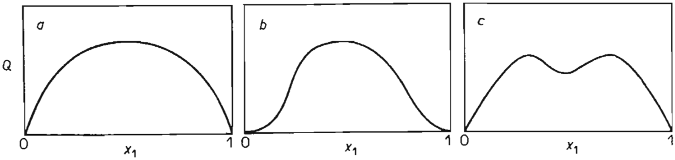


FIG. 3

Possible Courses of Q for van Laar Equation
a $-1 \leqq D/A \leqq 2$; *b* $D/A \leqq -1$; *c* $D/A \geqq 2$.

According to the magnitude of D/A we get three courses of Q which are illustrated in Fig. 3. As it is evident from Fig. 3, the variants *b*) and *c*) have not been considered in the beginning. The authors do not know a case of the system which would correspond to Fig. 3*b*. The course shown in Fig. 3*c* should occur in the methyl isopropyl ketone–water system[10]. Considering that in correlations we usually get $|D| < A$, the van Laar equation behaves "more naturally" from this point of view than the Redlich–Kister or NRTL equations.

The applicability of an empirical equation for G^E is considerably influenced by possible values of limiting activity coefficients. Let us investigate what values L1 and L2 pertain to strongly non-ideal systems. The term "strongly non-ideal system" is intended to mean such a system whose value $[\partial^2(G^M/RT)/\partial x_1^2]_{x_1=x_2} = (G11)_{x_0} < (1/2)(G11)^* = (1/2)\, x_0^{-1}(1 - x_0)^{-1}$, where $(G11)^*$ is the value which corresponds to the ideal system at a composition $x_1 = x_0$ (Fig. 2).

To determine the values $L1$ and $L2$ (or A, B) for different values of x_0 and $(G11)_{x_0}$ it is necessary to solve this system of equations

$$(G11)_{x_0} = 1/[x_0(1 - x_0)] + (\partial^2 Q/\partial x_1^2)_{x_1=x_0}\,, \qquad (11a)$$

$$(\partial\, G11/\partial x_1)_{x_1=x_0} = 0 = (2x_0 - 1)/[x_0^2(1 - x_0)^2] + \partial^3 Q/\partial x_1^3)_{x_1=x_0}\,. \qquad (11b)$$

On solving this system of equations by means of the Newton method for different values of x_0, $(G11)_{x_0}$ and D, the parameters A, B have been obtained which represent $L1$ and $L2$ at the same time. Part of the results is given in Table I and in Fig. 4.

In Fig. 5 we present the limiting values of A on B and A on $\ln(A/B)$ resp., which represent the boundary between homogeneous and heterogeneous system. From estimated parameters A, B according to Hildebrand and Scatchard[7] (Eq. (*12*)), it is

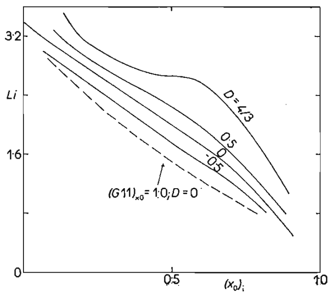


FIG. 4

Values of Limiting Activity Coefficients in Dependence on $(x_0)_i$ for Different Values of D (except curve *a*)

For $i = 1$, $x_0 = (x_0)_i$ and $Li = L1 = A$, for $i = 2$, $x_0 = (1 - x_0)_i$ and $Li = L2 = B$.

possible to determine by means of these graphs whether the substances will be partially or completely miscible. The estimation of parameters A, B according to Hildebrand and Scatchard is given by the relations

$$A = V_2\varphi_1^2(\delta_1 - \delta_2)^2/(RT)\,, \tag{12a}$$

$$B/A = V_1/V_2\,, \tag{12b}$$

where V_1 and V_2 are the molar volumes in the liquid phase and δ_1 and δ_2 the so-called solubility parameters, φ_1 is the volume fraction of the first component.

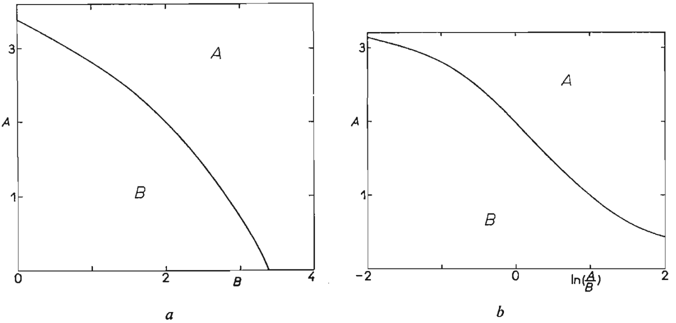
Before passing to a more detailed discussion we will analyze one special case which can be solved analytically. Let us consider $(G11)_{x_0} = 0$ (critical isotherm) and the two-constant van Laar equation, *i.e.* $D = 0$. Under these assumptions the system of equations (*11*), after inserting from Eqs (*4*) and (*5*), reduces to the form

$$0 = 1/[x_0(1 - x_0)] - (2B^2/A)\,[x_0 + (1 - x_0)\,B/A]^{-3}\,, \tag{13a}$$

$$0 = (2x_0 - 1)/[x_0^2(1 - x_0)^2] - (B/A)^2\,(B/A - 1)\,[x_0 + (1 - x_0)\,B/A]^{-4}\,. \tag{13b}$$

By solving we get

$$A/B = (1 - x_0)/[x_0(2 - x_0)]\,, \tag{14a}$$



a

b

FIG. 5

a Limiting Values of A, B Delimiting Homogeneous System, *b* Limiting Values of A in Dependence on the Ratio of Molar Volumes in Eq. (*12*) which Delimit Homogeneous System

A Heterogeneous; B Homogeneous.

$$A = L1 = (27/2)\,(1 - x_0)/[(1 + x_0)\,(2 - x_0)^2]\,, \tag{14b}$$

$$B = L2 = (27/2)\,x_0/[(1 + x_0)\,(2 - x_0)]\,. \tag{14c}$$

As it follows from Eqs (*14*), we get the final values of A, B even for the case $x_0 \to 0$.

TABLE I

Dependence of $A = \ln \gamma_1^\infty$, $B = \ln \gamma_2^\infty$ on x_0, $(\mathrm{G11})_{x_0}$ and D

D	$(\mathrm{G11})_{x_0}$	A	B	A	B
		$x_0 = 0{\cdot}5$		$x_0 = 0{\cdot}4$	
−1	0	1·500	1·500	1·802	1·318
	1	1·000	1·000	1·297	0·892
	2	0·500	0·500	0·793	0·495
0	0	2·000	2·000	2·260	1·722
	1	1·500	1·500	1·782	1·248
	2	1·000	1·000	1·327	0·790
1	0	2·500	2·500	2·649	2·257
	1	2·000	2·000	2·225	1·666
	2	1·500	1·500	1·982	0·961
4/3	0	2·666	2·666	2·717	2·566
	1	2·166	2·166	2·290	1·943
	2	1·666	1·666	2·258	0·955
		$x_0 = 0{\cdot}3$		$x_0 = 0{\cdot}2$	
−1	0	2·092	1·087	2·392	0·804
	1	1·629	0·760	2·000	0·597
	2	1·192	0·474	1·659	0·421
0	0	2·515	1·409	2·778	1·042
	1	2·090	1·015	2·429	0·779
	2	1·734	0·659	2·152	0·551
1	0	2·839	1·904	3·070	1·428
	1	2·477	1·360	2·757	1·057
	2	2·362	0·787	2·629	0·687
4/3	0	2·888	2·185	3·122	1·628
	1	2·527	1·583	2·803	1·220
	2	2·620	0·799	2·774	0·740

TABLE I

(*Continued*)

		A	B
		$x_0 = 0{\cdot}1$	
−1	0	2·682	0·451
	1	2·437	0·374
	2	2·214	0·306
0	0	3·060	0·587
	1	2·828	0·485
	2	2·627	0·395
1	0	3·297	0·810
	1	3·114	0·668
	2	2·941	0·532
4/3	0	3·443	0·914
	1	3·166	0·760
	2	2·993	0·608

This is in abrupt contrast to the formerly discussed equations. The maximum value of $L1$ is equal 2 for a homogeneous symmetric system ($x_0 = 0{\cdot}5$) but in an extreme unsymmetric case (for $x_0 \rightarrow 0$), it can attain as much as the value of $L1 = 27/8 = 3{\cdot}375$ or $\gamma_1^\infty = 29{\cdot}2$. As it follows from Eq. (*12*), the last case is to be realized physically in case of $V_1/V_2 \rightarrow 0$, *i.e.* for instance in a mixture of polymer with low-molecular solvent.

Let us consider now the three-constant van Laar equation with $x_0 = 0{\cdot}5$ and $(\mathrm{G11})_{x_0} = 0$, *i.e.* a system at the critical temperature with $x_{\mathrm{crit.}} = 0{\cdot}5$. Let us investigate the effect of parameter D on the value of limiting activity coefficients without getting an extreme on their concentration dependences. In this case the non-equality (*10*) must be fulfilled. Let us assume that $D = 2\alpha A$ from which at $\alpha = 1$ and $\alpha = -1/2$, we get, respectively, the upper and lower value of D ensuring the monotonous courses of activity coefficients in their dependence on composition. By combining Eq. (*11a*) (Eq. (*11b*) is fulfilled for $x_0 = 0{\cdot}5$ when $A = B$) with Eq. (*5*) we have

$$0 = 4 + 2[2\alpha A(1/2 - A)]\,,$$

or

$$A = 2/(1 - \alpha)\,. \tag{15}$$

For $\alpha \rightarrow 1$ we get $A \rightarrow \infty$ and for $\alpha \leqq -1/2$ on the contrary $A = 4/3$. It means that by choosing a sufficiently high value of D, we can attain an arbitrarily high value of the activity coefficient on critical isotherm retaining the monotonous course. As it will be shown below, however, the value of D is limited from above by the requirement of convex course of $\mathrm{G11}(x_1)$. On the other hand the lowest activity coefficients, when retaining the monotonous course, are obtained at $D = -4/3$.

Course of $\mathrm{G11} = f(x_1)$

It remains to investigate the course of the curve $\mathrm{G11}(x_1)$ which corresponds to the alternatives mentioned. We have not succeeded in rearranging Eq. (*1*) so as to be able to answer this question directly and therefore we have proceeded by way of trial. On the basis of the parameters obtained, the values of G1111 have been calculated for compositions $x_1 = 0{\cdot}05, \ldots, 0{\cdot}95$. Negative value of G1111 at some compositions indicates a non-convex course of $\mathrm{G11}(x_1)$. On the basis of the calculations performed it is possible to draw these conclusions:

In symmetric system ($A = B$), the maximum value of D which still ensures the convex course equals 4/3 regardless of the value of $(\mathrm{G11})_{x0}$. For other cases it is possible to read the limiting values of D in Fig. 6 for $(\mathrm{G11})_{x_0} = 0$ and $(\mathrm{G11})_{x_0} = 2{\cdot}0$. It follows from the figure that the two-constant van Laar equation is applicable for $x_0 \in (0{\cdot}195, 0{\cdot}805)$. Higher values of D extend the limits of applicability a little but the values $D > 4/3$ can be recommended only exceptionally.

It has been found in the calculations that at non-convex course of $\mathrm{G11}(x_1)$ (the range of $D \in \langle -1, 4/3 \rangle$ has been investigated), the formation of additional extremes on the curve $\mathrm{G11}(x_1)$ does not take place, which is a substantial difference from the Redlich–Kister or NRTL equations. On the other hand this fact prevents from using the van Laar equation for systems which would exhibit two critical points even if the course in Fig. 3*c* would indicate it.

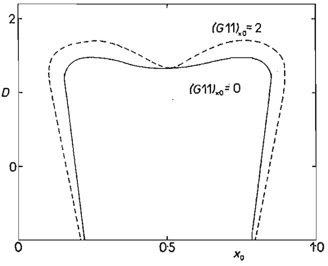


FIG. 6

Region of D Ensuring Convex Course of G11 in Dependence on x_0

DISCUSSION

From the point of view of the value of attainable limiting activity coefficients, the Redlich–Kister, van Laar, NRTL and Wilson equations are compared in Figs 7 and 8. The values of maximum limiting activity coefficients have been chosen so that the monotonous course of activity coefficients and convex course of $G11(x_1)$ may be retained.

The maximum possible values of limiting activity coefficients in dependence on x_0 for $(G11)_{x_0} = 0$, *i.e.* on the critical isotherm are given in Fig. 7. It is evident from the figure that the two-constant Redlich–Kister equation has the lowest range of applicability ($x_0 \in \langle 0{\cdot}333, 0{\cdot}666 \rangle$) which is somewhat extended by higher value of d (the maximum value of d which retains the convex course of G11 is $d_{\text{con}} = 1/3$). On the contrary, the van Laar equation is applicable not only in a wider range of x_0 but also provides higher values of limiting activity coefficients in asymmetric systems.

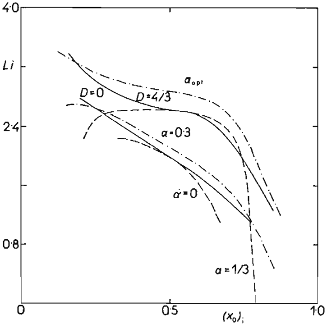


FIG. 7

Maximum Values of Limiting Activity Coefficients in System with $(G11)_{x_0} = 0$ in Dependence on $(x_0)_i$ for van Laar, Redlich–Kister and NRTL Equations

Course of curves outside the marked regions does not ensure monotonous dependence of activity coefficients or convexity of G11. ---- Redlich–Kister eq. ($d = 0$ and $d = 1/3$), ——— van Lear eq. ($D = 0$ and $D = 4/3$), -·-·- NRTL eq. ($\alpha = 0{\cdot}3$, $\alpha = \alpha_{\text{opt}}$), -o-o- Wilson eq.

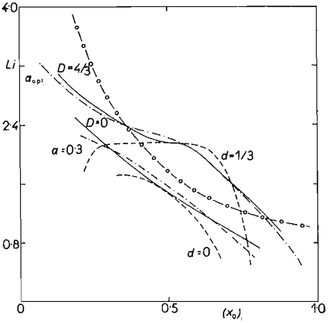


FIG. 8

Maximum Values of Limiting Activity Coefficients in System with $(G11)_{x_0} = 1{\cdot}0$ in Dependence on $(x_0)_i$ for van Laar, Redlich–Kister, NRTL and Wilson Equations

Course of curves outside the marked regions does not ensure monotonous dependence of activity coefficients or convexity of G11 (see also Fig. 7).

The NRTL equation with $\alpha = 0{\cdot}3$ is comparable to a certain extent with the two-constant van Laar equation. The optimum choice of α, however, allows to obtain higher limiting activity coefficients (at $x_0 = 0{\cdot}1$ it must be $\alpha \sim 0{\cdot}55$). The Wilson equation is practically inapplicable on the critical isotherm and would provide infinite activity coefficients.

The fact that the van Laar equation is more suitable for asymmetric systems than the Redlich–Kister or Margules ones is proved by calculations due to Brian[9] who used the van Laar and Margules equations with two constants to describe heterogeneous systems. For asymmetric systems, the Margules equation failed completely.

The obtained values for the case of $(G11)_{x_0} = 1{\cdot}0$ are illustrated in Fig. 8. Here it is possible to draw analogous conclusions. The three-constant equations are able to describe approximately equally high values of activity coefficients in case of not very much asymmetric systems. This fact extends the previously presented knowledge[8], according to which in weakly non-ideal systems the differences among the descriptions by single equations are very small, to the systems with high deviations from ideal behaviour but relatively symmetric. It is interesting that the activity coefficients determined from the Wilson equation lie approximately in the middle of the interval which is given by the zero value of the third parameter and the maximum possible one ensuring at the same time the convex course of $G11(x_1)$.

The possible values of activity coefficients according to single equations differ considerably unless x_0 is from the range of 0·3 to 0·65. First of all fails the Redlich–Kister equation. The van Laar equation with $D = 4/3$ is applicable for $x_0 \in (0{\cdot}15, 0{\cdot}85)$. Analogously behaves the NRTL equation where not even $\alpha \approx 0{\cdot}8$ ensures the convex course unless x_0 is from the interval 0·15 to 0·85. The far highest values of limiting activity coefficients allows, however, the Wilson equation. Therefore we assume that good experience with this equation is just due to this fact.

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