APPLICABILITY OF THE THREE-CONSTANT REDLICH–KISTER EQUATION TO CORRELATION OF STRONGLY NON-IDEAL SYSTEMS* **

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On the basis of the course of the log (γ_1/γ_2) and $\partial^2(\mathscr{G}/2\cdot303RT)/\partial x_1^2 = $ G11 (x_1) curves, various definitions of "normal" system were proposed. By means of them the limits of applicability of the two-constant and three-constant Redlich–Kister equation were determined. For orientation it is possible to use the following rules: The one-constant Redlich–Kister equation may be applied to systems with $x_0 = 0\cdot5$; the two-constant one to systems with $x_0 \in \langle 0\cdot4, 0\cdot6 \rangle$; the three-constant one to systems with $x_0 \in \langle 0\cdot3, 0\cdot7 \rangle$, where x_0 is the coordinate of minimum of the dependence G11(x_1). The applicability of the Redlich–Kister equation can be found out as well in terms of the values of limiting activity coefficients. Not even the three-constant Redlich–Kister equation is able to describe the behaviour of a homogeneous system with higher value of $\lim_{x_2\to 0} \log \gamma_2$ than $\sim 1\cdot2$ with only one minimum on the G11(x_1) curve. Besides, a test is proposed in the work which allows to predetermine the possibility of successful application of the three-constant Redlich–Kister equation when knowing the position of minimum on the G11(x_1) curve regardless of the mentioned definitions of "normal" system.

As to the systems which exhibit large positive deviations from Raoult's law it is important to investigate the quantity $\partial^2(\mathscr{G}/2\cdot303RT)/\partial x_1^2$ which will be denoted, in short, by G11, for in a homogeneous system, according to the theory of thermodynamic stability, it must hold[1-3]

$$\text{G11} \geqq 0 \,. \qquad (1)$$

Schematic course of G11(x_1) is presented in Fig. 1.

In case of systems which are already at the end of limited miscibility, G11 is relatively small in the vicinity of the minimum and its dependence on composition is very flat. Sometimes it occurs[4] that a system behaving in this manner is not described in qualitatively correct way by the empirical relation for $\mathscr{G}^E$ in terms of its parameters determined by correlation, *i.e.* the relation is obtained by correlating which does not fulfil Eq. (*1*) in the whole concentration range. The fundamental problem of correlation of measured data is the application of a respective empirical or semi-empirical equation. The adequacy of equation is judged practically only by the agreement of directly measured and calculated values. Such a way of judging the equation or computed parameters is insufficient for the very reason that it refers, among others, to the given set of data only. We

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assume that every system makes different demands on the empirical relation for $\mathscr{G}^E$ and not every relation is sufficiently flexible to describe the given facts. If we want to use a certain equation, we should use the proper number of constants with different systems, provided that the equation allows it. Usual statistical tests defining the corresponding number of adjustable parameters need not always give a unique answer[5,6], apart from the fact that they consider the significance of the number of parameters with respect to the minimized quantity without taking into account, at least qualitatively, the course of derivatives.

In this work, the applicability of the three-constant Redlich–Kister equation[7] to strongly non-ideal systems is defined on keeping the qualitative characteristics of the course of $\log (\gamma_1/\gamma_2) = Q1(x_1)$ and $G11(x_1)$, above all the position of minimum on the curve $G11(x_1)$, i.e. the values of x_0, $(G11)_{x_0}$. When analyzing this equation, we got out of the relation

$$\mathscr{G}^E/(2\cdot303RT) = Q = x_1 x_2 [b + c(x_1 - x_2) + d(x_1 - x_2)^2] . \tag{2}$$

Further relations needed for analyzing are given in Appendix.

In further considerations we will get out of the knowledge of the concentration dependence of G11, or strictly speaking, of the position of its minimum (Fig. 1). The relations for the determination of G11 on the basis of measured vapour–liquid equilibrium data can be found in the literature[1–3] and are summarized in previous paper[4]. Let us assume that G11 takes its minimum value $(G11)_{x_0}$ at the composition $x_1 = x_0$. We suppose x_0 to be from the interval 0 to 0·5. At this composition the conditions must be fulfilled

$$(G11)_{x_1 = x_0} = (G11)_{x_0} , \tag{3}$$
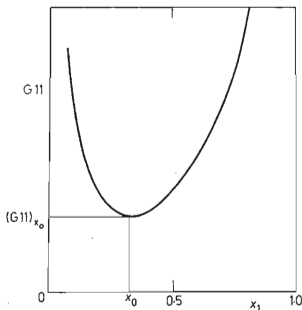
$$(G111)_{x_1 = x_0} = 0 . \tag{4}$$

Fig. 1

Schematic Representation of G11 on Composition

The parameters b, c can be determined from conditions (3) and (4) according to the relations

$$c = (1 - 2x_0) \{4d - 0.0362/[x_0^2(1 - x_0)^2]\}, \tag{5}$$

$$b = -\tfrac{1}{2}(G11)_{x_0} + 0.2171[x_0(1 - x_0)]^{-1} - 0.1085(1 - 2x_0)^2 \cdot$$
$$\cdot x_0^{-2}(1 - x_0)^{-2} + d[7 - 24x_0(1 - x_0)]. \tag{5a}$$

By substituting Eqs (5) and (5a) into Eq. (2) we obtain, for the ratio of activity coefficients, the relation

$$\log(\gamma_1/\gamma_2) = Q1 =$$
$$= \{0.6514/[x_0(1 - x_0)] - [9.212x_0^2(1 - x_0)^2]^{-1} - 0.5(G11)_{x_0}\}(x_2 - x_1) +$$
$$+ (2x_0 - 1)(6x_1x_2 - 1)[27.636x_0^2(1 - x_0)^2]^{-1} +$$
$$+ d\{(x_2 - x_1)[7 - 24x_0(1 - x_0)] - 4(6x_1x_2 - 1)(2x_0 - 1) +$$
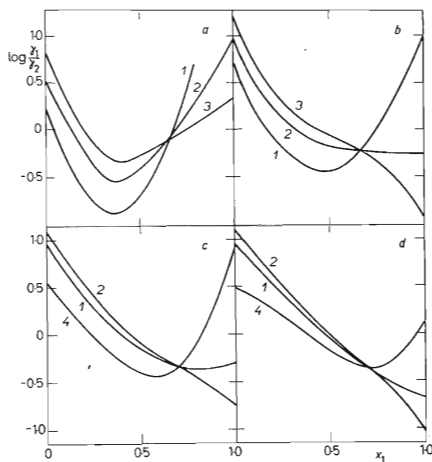$$+ (x_1 - x_2)(8x_1x_2 - 1)\} = f_1 + df_2. \tag{6}$$

Fig. 2

Dependence of $\log(\gamma_1/\gamma_2)$ on x_1 for Various x_0, d and $(G11)_{x_0} = 0$
a) $x_0 = 0.16$, b) $x_0 = 0.20$, c) $x_0 = 0.30$, d) $x_0 = 0.40$. $1\ d = 0$, $2\ d = 0.2$, $3\ d = 0.3$, $4\ d = -0.1$.

The relations for $\mathscr{G}^E$, G11, and G111 are presented in Appendix again.

Course of Curves $\log(\gamma_1/\gamma_2)$

Now we are investigating the concentration dependence of $\log(\gamma_1/\gamma_2)$ (to shorten the record we will use the denotation Q1), *i.e.* the relation (6) in dependence on the parameters x_0, $(G11)_{x_0}$, d. In Figs 2 and 3a, the calculated dependences are represented for $x_0 = 0.4$, 0.3, 0.2, 0.16, 0.25 and for $(G11)_{x_0} = 0$ (the critical isotherm) and for different values of parameter d. On the other hand, in Fig. 4 the experimental course of Q1 is represented for three systems being close to limited miscibility for various values of x_0. The systems in question are as follows: 2-methyl-2-butene–acetonitrile[10] with experimental values $x_0 \sim 0.4$ and $(G11)_{x_0} \sim 0.05$, tetrahydrofuran––water[11] with $x_0 \sim 0.24$ and $(G11)_{x_0} \sim 0.01$, and 2-methylpyridine–water[9] with $x_0 = 0.1$ and $(G11)_{x_0} \sim 0.005$. It is evident from Fig. 2 that with a decrease in x_0 (at fixed d and $(G11)_{x_0}$), the minimum appears on curves Q1 first and further, at higher concentrations, Q1 takes even positive values, which would correspond to an S-shaped dependence of $\mathscr{G}^E$ on composition. On comparing the courses of Q1 in Fig. 2 with those determined experimentally (Fig. 4), it is evident that the calculated courses are not "normal" in some cases. For our further considerations let us define two following "normal" courses of the $Q1(x_1)$ curves:

1. The curve Q1 is a monotone decreasing function in whole concentration range, *i.e.*
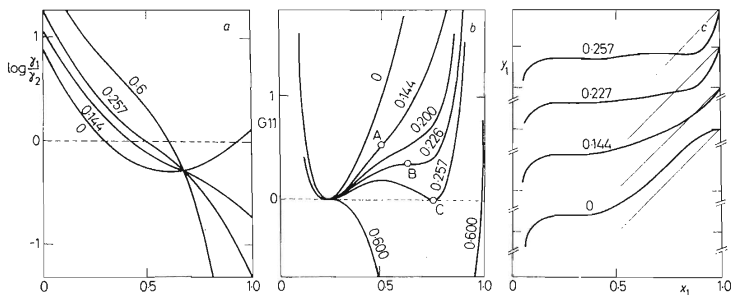
$$\partial(Q1)/\partial x_1 \leqq 0 . \tag{7}$$

Fig. 3

Dependence of $\log(\gamma_1/\gamma_2)$, G11 and γ_1 on Composition of the Liquid Phase for Systems with $x_0 = 0.25$ and $(G11)_{x_0} = 0$ and with Different Values of the Parameter d

As to the systems with high positive deviations from Raoult's law verging towards limited miscibility, it must hold in the vicinity of x_0:

$$G11 < (G11)^* = 0.4343/(x_1 x_2), \tag{8}$$

where $(G11)^*$ is the value of G11 which would correspond to the ideal system. For G11 we can also write

$$G11 = (G11)^* + \partial^2 Q/\partial x_1^2 = 0.4343/(x_1 x_2) + \partial(Q1)/\partial x_1. \tag{9}$$

With respect to Eqs (8) and (9) the ratio of activity coefficients must decrease with x_1 in the vicinity of x_0. We will understand "normal" systems as such which keep this property in whole concentration range. It follows from the Gibbs–Duhem equation that the condition (7) is in binary system equivalent to the requirement $\partial \log \gamma_i / \partial x_i \leqq 0$.

By combining the relations (7) and (A-8) (see Appendix) we get

$$48d(x_1 - x_0)^2 - 0.4343(1 - 2x_0)(x_1 - x_0)/[(x_0^2(1 - x_0)^2] +$$
$$+ 0.4343/[x_0(1 - x_0)] - (G11)_{x_0} \geqq 0. \tag{10}$$

It follows from the discussion of Eq. (10) that for $x_0 \leqq x_D$ the relation must be valid

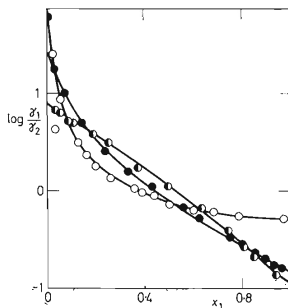$$d \geqq d_D, \tag{11}$$

where

Fig. 4

Experimental Dependence of log (γ_1/γ_2) for Three Systems

◐ 2-Methyl-2-butene(1)–acetonitrile(2), ● tetrahydrofuran(1)–water(2), ○ 2-methylpyridine(1)–water(2).

$$d_D = 0.4343(1 - 2x_0)^2 \left\{192x_0^3(1 - x_0)^3 \left[1 - 2.303(G11)_{x_0} x_0(1 - x_0)\right]\right\}^{-1}$$

$$(11a)$$

and for $x_0 \geqq x_D$ it must hold

$$d \geqq d_1,$$ (12)

where

$$d_1 = \left[(G11)_{x_0} + 0.4343(1 - 3x_0) x_0^{-2}(1 - x_0)^{-1}\right]/\left[48(1 - x_0)^2\right]. \quad (12a)$$

The composition x_D is given by the relation

$$4x_D - 1 - 4.606(G11)_{x_0} (1 - x_D) x_D^2 = 0. \quad (12b)$$

For $(G11)_{x_0} = 0$ we get $x_D = 0.25$ by solving Eq. $(12b)$ and for $(G11)_{x_0} = 0.5$ we obtain $x_D = 0.283$.

The minimum values of the parameter d warranting the monotone course of Q1, calculated from Eq. $(11a)$ or $(12a)$ are given in Fig. 5 and are denoted by d_{mon}.

2. In this work we discuss systems with positive deviations from Raoult's law for which holds

$$\mathscr{G}^E > 0. \quad (13)$$

From this point of view we can define the "normal" systems as such systems which satisfy the relation (13) in whole concentration range. Unlike the first case an extreme is admitted on the curve $Q1 = Q1(x_1)$ but the course must not be such that $\mathscr{G}^E$ should take negative values. This requirement can be expressed by*

$$\lim_{x_1 \to 1} Q1 = \lim_{x_1 \to 1} \log (\gamma_1/\gamma_2) = -\log \gamma_2^0 = 0. \quad (14)$$

From Eqs (6) and (14) we get that in this case the equation must hold

$$d \geqq d_s = \left\{3 (G11)_{x_0} x_0^2(1 - x_0)^2 + 0.4343[2 - x_0 - 9x_0(1 - x_0)]\right\} \cdot$$
$$\cdot \left\{24x_0^2(1 - x_0)^2 \left[3 - 2x_0 - 6x_0(1 - x_0)\right]\right\}. \quad (15)$$

The values of d_s for various x_0 and $(G11)_{x_0}$ are given in Fig. 5. If the nonequality (15) was not fulfilled the dependence $\mathscr{G}^E = \mathscr{G}^E(x_1)$ would show an S-shaped course.

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*   The case $\lim\limits_{x_1 \to 0} Q1 = 0$, contingently local extremes which would be at variance with Eq. (13) are considered less probable and they will not be discussed further.

Course of G11 Curves

In Figs 2 and 3a the curves $Q1 = Q1(x_1)$ are plotted for various values of the para-
meter d. It is evident at first sight that higher values of the parameter d make this
course "more normal" (compared both with the experimentally found course (Fig. 4)
and with the above-mentioned definitions). For example at $x_0 = 0.2$ the value
$d = 0.2$ causes that the ratio of activity coefficients is already a monotone decreasing
function. With lower values of x_0 the parameter d must be still higher. Let us examine
now how the quantity G11 responds to various values of d at constant x_0 and $(G11)_{x_0}$.
The effect of the parameter d, not only on the course of Q1, G11, but also on the
composition of the vapour phase (the calculation was carried out for the vapour
pressure ratio $P_1^0/P_2^0 = 3$ and the ideal behaviour of the vapour phase) can be seen
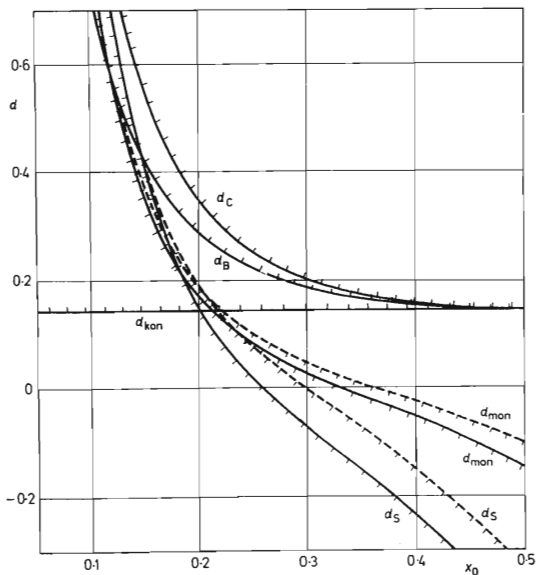in Figs $3a - 3c$ $(x_0 = 0.25, (G11)_{x_0} = 0)$.

FIG. 5
Limiting Values of Parameter d in Dependence on x_0
——— $(G11)_{x_0} = 0$,   — — — $(G11)_{x_0} = 0.5$.

According to the course of G11(x_1) (Fig. 3b), the following limiting values of parameter d will be distinguished:

A. The curve G11 is convex in whole concentration range, i.e. it holds:

$$[\partial^2 G11/\partial x_1^2] = G1111 \geqq 0 . \tag{16}$$

From Eq. (A-5) it follows that d must fulfil the relation

$$d \leqq d_{kon} = 0\cdot4343/3 = 0\cdot1447 . \tag{17}$$

It has not been hitherto known exactly how far the relation (16) is justified with homogeneous systems; Eq. (16) holds, however, at the critical point[1−3].

B. At the point B (Fig. 3b) at which holds

$$[\partial G11/\partial x_1]_{x_1 = x_B} = [\partial^2 G11/\partial x_1^2]_{x_1 = x_B} = 0 \tag{18}$$

the value of d_B is given by the relation

$$d_B = (0\cdot4343/48) \left[x_B^{-3} + (1 - x_B)^{-3} \right] , \tag{19}$$

where x_B is given by the equation

$$\left[(1 - 2x_0) x_B^2 (1 - x_B)^2 - (1 - 2x_B) x_0^2 (1 - x_0)^2 \right] x_0^{-2} (1 - x_0)^{-2} + \\ + \left[x_B^3 + (1 - x_B)^3 \right] (x_0 - x_B) \left[x_B (1 - x_B) \right]^{-1} = 0 . \tag{20}$$

The values of d_B in dependence on x_0 are given in Fig. 5.

C. At still higher values of d, a further local minimum appears on the curve G11. In this case the equations must be satisfied:

$$x_1 = x_C > x_0 , \\ (G11)_{x_1 = x_C} = (G11)_C , \\ (G111)_{x_1 = x_C} = 0 . \tag{21}$$

On combining Eqs (A-8), (A-9) and (21) we get

$$(G11)_C = (G11)_{x_0} + 0\cdot4343(x_0 - x_C) \left\{ x_0^{-1} (1 - x_0)^{-1} \left[(2x_0 - 1) \cdot \right. \right. \\ \left. \cdot x_0^{-1} (1 - x_0)^{-1} + (1 - x_0 - x_C) x_C^{-1} (1 - x_C)^{-1} \right] + \\ \left. + \tfrac{1}{2} \left[(2x_C - 1) x_C^{-2} (1 - x_C)^{-2} + (1 - 2x_0) x_0^{-2} (1 - 2x_0)^{-2} \right] \right\} . \tag{22}$$

Eq. (22) is simplified very much in the special case when it holds

$$(G11)_C = (G11)_{x_0} .$$ (23)

From Eq. (22) after rearrangement $(x_C = 1 - x_0)$ we then obtain

$$d_C = (0.4343/48) x_0^{-2}(1 - x_0)^{-2} .$$ (24)

The values of d_C determined by the relation (24) are summarized in Fig. 5. We assume that the number of systems which would exhibit properties corresponding to this alternative is small. On the y–x curves such behaviour should become evident by three inflex points (Fig. 3c with $d = 0.25$). With these systems the existence of two
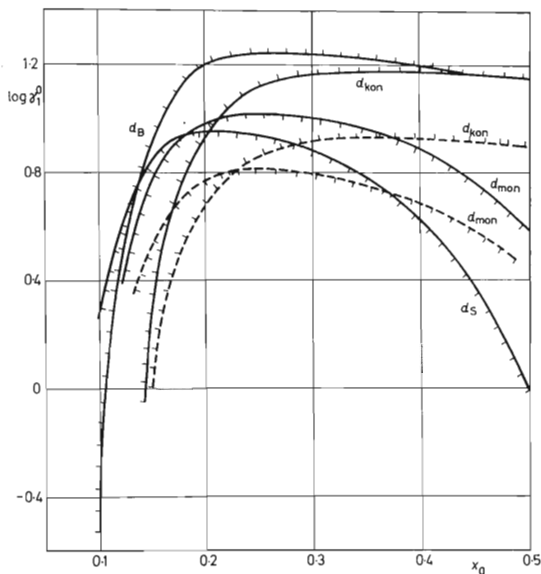

FIG. 6

Permitted Values of $\log \gamma_1^0$ in Dependence on x_0 for Various Values of Parameter d

——— $(G11)_{x_0} = 0$,   — — — $(G11)_{x_0} = 0.5$.

azeotropes contingently even two different heterogeneous regions (as far as $(G11)_{x_0} < 0$) would be possible.

D. At still higher values of d the minimum at the point x_C becomes deeper and can have even negative values. At yet higher values of d it occurs that the point $x_1 = x_0$ is changed into the inflex point and finally a maximum appears at the point x_0. These alternatives will not be investigated.

Limits of Applicability of the Three-Constant Redlich–Kister Equation

Let us investigate first the applicability of the two-constant equation, *i.e.* the case $d = 0$. In this special case the function f_1 in Eq. (6) gives directly the logarithm of the ratio of activity coefficients and the course of G11 is always convex. On the basis
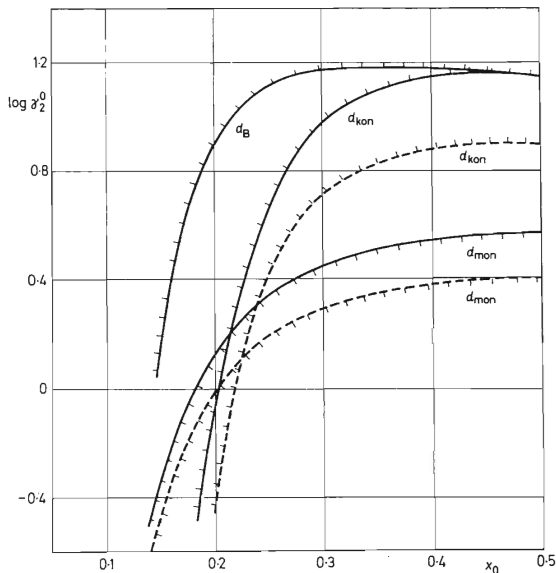

Fig. 7

Permitted Values of $\log \gamma_2^0$ in Dependence on x_0 for Various Values of Parameter d

——— $(G11)_{x_0} = 0$,   — — — $(G11)_{x_0} = 0.5$.

of Figs 2, 3 and 5 and of the foregoing discussion it is possible to draw the following conclusions:

A. From the alternatives given in Fig. 2, f_1 has the form which fulfils the condition (7) only at $x_0 = 0.4$, *i.e.* the course of Q1 is a monotone decreasing function. From the relation (*11a*) we get that at $(G11)_{x_0} = 0$ or $(G11)_{x_0} = 0.5$ it will be always like that as far as $x_0 > 0.333$ or $x_0 > 0.362$, respectively. In case that x_0 is lower than the given values and the course of the ratio of activity coefficients is monotone decreasing, it is not to be assumed that the two-constant equation will be sufficient.

B. If the measured data fulfil the less rigid condition (*13*), *i.e.* there is a local minimum on the curve Q1 not leading, however, to an S-shaped course of the $\mathcal{G}^E$ curve, it is possible to show, using Eq. (*15*) (and it follows from Fig. 5, too) that in
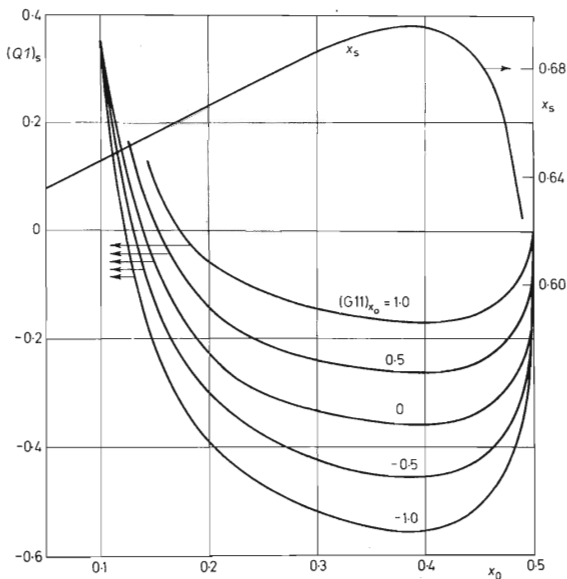

FIG. 8

Values of x_s and $[\log (\gamma_1/\gamma_2)]_s$ in Dependence on x_0 and $(G11)_{x_0}$

this case the least value of x_0 which may be still described by the two-constant equation is $x_0 = 0.26$ at $(G11)_{x_0} = 0$ or $x_0 = 0.28$ at $(G11)_{x_0} = 0.5$.

C. An interesting feature of the relation (*6*) is the fact that at higher values of $(G11)_{x_0}$, *i.e.* in case of a "more homogeneous" and at first sight more easily correlatable systems, less "normal" courses of the ratio of activity coefficients are obtained in sense of the requirements of Eqs (*11*) and (*13*). It means that the systems with $(G11)_{x_0} < 0$, *i.e.* heterogeneous systems behave, as for the Redlich–Kister equation, "more normal" and can be more easily correlated.

The applicability of the three-constant Redlich–Kister equation is connected closely with the possible values of the parameter *d*. It follows from the foregoing discussion that the parameter *d*, with respect to the course of Q1, cannot be arbitrarily small and, with respect to the course of G11, arbitrarily large. The above defined limiting parameters are represented in Fig. 5. It is evident from the figure that at $(G11)_{x_0} = 0$ (the critical isotherm) and at the monotone course of Q1 and the convex course of G11, the equation cannot be applied to systems with $x_0 < 0.235$. The range of applicability still decreases with higher values of $(G11)_{x_0}$. Further alternatives for $(G11)_{x_0} = 0$ or $(G11)_{x_0} = 0.5$ can be as well determined using this figure.

More clear idea of the applicability of the Redlich–Kister equation can be sometimes provided in terms of the limiting values of activity coefficients which are given in Figs 6 and 7 for differently defined parameters *d*. From the figures it is again possible to read the maximum and minimum values of the limiting activity coefficients $\log \gamma_1^0$ and $\log \gamma_2^0$ for various values of x_0 and $(G11)_{x_0}$.

The limits of applicability of the Redlich–Kister equation which can be read from Fig. 5 are the maximum possible ones. We assume, however, that some difficulties will occur in actual cases already for $x_0 < 0.4$ with the two-constant equation and for $x_0 < 0.3$ for the three-constant one. For the systems with $x_0 < 0.3$ it is necessary to use more constants. However, in contradistinction of Kehlen[8] we do not suppose that in such cases it would not be possible to use the Redlich–Kister equation at all.

In foregoing discussion we defined the minimum and maximum values of the parameter *d* for the given x_0 and $(G11)_{x_0}$ and the minimum and maximum values of limiting activity coefficients on the basis of requirements on the course of the curves Q1 and G11. It may occur that a system will fulfil these criteria but in spite of it the use of the three-constant Redlich–Kister equation will not be successful. To judge this alternative the following test can serve which is independent of the value of parameter *d*. It follows from Figs 2 and 3*a* that the curves Q1 at the given x_0 and $(G11)_{x_0}$ intersect at a certain point whose parameters are denoted by $x_1 = x_s$; $[\log (\gamma_1/\gamma_2)]_{x_1 = x_s} = (Q1)_s$. It follows from Eq. (*6*) that this case occurs as far as the equation

$$f_2 = 0 \tag{25}$$

is fulfilled.

On solving this equation we get

$$x_s = x_0 + \sqrt[3]{(0.25 + 0.5x_0 - 1.5x_0(1 - x_0) - x_0^3)}. \qquad (26)$$

In Fig. 8 the dependence of x_s on x_0 is represented together with the value of the ratio of activity coefficients corresponding to this point of intersection, *i.e.* $(Q1)_s$. It is evident that in case of systems for which the experimentally found logarithm of the ratio of activity coefficients at $x_1 = x_s$ would not correspond to the value read from Fig. 8 (with respect to experimental errors), the Redlich–Kister equation with three constants is not to be used. In some cases the reverse procedure is more evident, when we look for $(G11)_{x_0}$ for a given $\log(\gamma_1/\gamma_2)$. As far as the given requirements are not fulfilled (the proposed test represented in Fig. 8 or the limiting activity coefficients exceed the limits defined in Figs 6 and 7) it is possible to assume the failure of the three-constant Redlich–Kister equation when correlating those systems, which was stated in the foregoing paper[4].

In case of the systems with $x_0 < 0.3$ it is probably necessary to use higher number of constants. When optimizing them, we meet with another difficulty for it is not possible to expect that we will be successful in obtaining, by usual calculation procedures, such a set of constants which would exhibit smooth (*i.e.* without inflex points) course of $\mathscr{G}$ and its derivatives. Let us consider the following extreme case of the ten-constant Redlich–Kister equation. In case of Q1 (Eq. $(A-2)$) with the value of all constants equal to one, the maximum contribution of single addends will be in absolute value the same (at $x_1 = 0$ or $x_1 = 1$). In case of the second to fourth derivatives the limiting maximum contribution of the i-th order derivatives, Δ_i, of single terms is given in Table I. Provided that we require the contribution of the third term in the expression for the second-order derivative to be comparable with the value of the first term, it should hold $|C_3|/|C_1| = |d|/|b| = 1/5$, and so on. If we consider still higher derivatives we should get even stricter limitations. The least-

TABLE I
Maximum Contributions of Single Terms of the Redlich–Kister Expansion to the i-th Order Derivative of Q with Respect to Composition

j	1	2	3	4	5	6	7	8	9	10
Δ_1	1	1	1	1	1	1	1	1	1	1
Δ_2	2	6	10	14	18	22	26	30	34	38
Δ_3	0	12	48	108	192	300	432	588	768	1 002
Δ_4	0	0	96	480	1 344	2 280	5 280	8 736	13 440	20 684

square method itself and from it derived numerical procedures for determining constants do not enable us to hold the constants in corresponding limits. The results of such correlation are then the curves of derivatives of $\mathscr{G}$ which are often without any physical meaning.

Appendix I

From Eq. (2) we get

$$\mathscr{G}^{E}/(2\cdot303RT) = Q = x_1 x_2 \sum_{j=1}^{s} C_j (x_1 - x_2)^{j-1}, \qquad (A\text{-}1)$$

$$\partial Q/\partial x_1 = \mathrm{Q1} = \log(\gamma_1/\gamma_2) = \sum_{j=1}^{s} C_j (x_1 - x_2)^{j-2} [2(j+1)x_1 x_2 - 1], \qquad (A\text{-}2)$$

$$\partial^2(\mathscr{G}/(2\cdot303RT))/\partial x_1^2 = \mathrm{G11} = 0\cdot4343/(x_1 x_2) +$$
$$+ 2 \sum_{j=1}^{s} C_j (x_1 - x_2)^{j-3} [1 - 2j + 2j(j+1)x_1 x_2], \qquad (A\text{-}3)$$

$$\partial^3(\mathscr{G}/(2\cdot303RT))/\partial x_1^3 = \mathrm{G111} = 0\cdot4343(x_1 - x_2)/(x_1^2 x_2^2) +$$
$$+ 4 \sum_{j=1}^{s} C_j (x_1 - x_2)^{j-4} (j-1)[2j(j+1)x_1 x_2 - 3(j-1)], \qquad (A\text{-}4)$$

$$\partial^4(\mathscr{G}/(2\cdot303RT))/\partial x_1^4 = \mathrm{G1111} = 0\cdot8686(x_1^{-3} + x_2^{-3}) +$$
$$+ 16 \sum_{j=1}^{s} C_j (x_1 - x_2)^{j-5} (j-1)[x_1 x_2 j(j+1)(j-2) -$$
$$- 2(j-2)(j-3/2)], \qquad (A\text{-}5)$$

where s denotes the number of constants. On using three constants and substituting for $C_1(C_1 = b)$, $C_2(C_2 = c)$ and $C_3(C_3 = d)$ from Eqs (5) and (6) into the relations $(A\text{-}1) - (A\text{-}4)$ we get these relations

$$Q = x_1 x_2 \{ -\tfrac{1}{2}(\mathrm{G11})_{x_0} + 0\cdot2171[x_0(1-x_0)]^{-1} +$$
$$+ (2x_0 - 1)[13\cdot818x_0^2(1-x_0)^2]^{-1}[(1+x_1)/3 - x_0] +$$
$$+ d[7 - 24x_0(1-x_0) - 4(2x_0 - 1)(x_1 - x_2) + (x_1 - x_2)^2]\}, \qquad (A\text{-}6)$$

$$\mathrm{Q1} = \log(\gamma_1/\gamma_2) = \{0\cdot6514x_0^{-1}(1-x_0)^{-1} - [9\cdot212x_0^2(1-x_0)^2]^{-1} -$$
$$- \tfrac{1}{2}(\mathrm{G11})_{x_0}\}(x_2 - x_1) + (2x_0 - 1)(6x_1 x_2 - 1)[27\cdot636x_0^2(1-x_0)^2]^{-1} +$$
$$+ d\{(x_2 - x_1)[7 - 24x_0(1-x_0)] - 4(6x_1 x_2 - 1)(2x_0 - 1) +$$
$$+ (x_1 - x_2)(8x_1 x_2 - 1)\} = f_1 + \mathrm{d}f_2, \qquad (A\text{-}7)$$

$$\mathrm{G11} = (\mathrm{G11})_{x_0} + 0\cdot4343(x_0 - x_1)\{(1 - x_0 - x_1)[x_1 x_2 x_0(1-x_0)]^{-1} +$$
$$+ (2x_0 - 1)[x_0^2(1-x_0)^2]^{-1}\} - 48d(x_0 - x_1)^2, \qquad (A\text{-}8)$$

$$\mathrm{G111} = 0\cdot4343(x_1 - x_2)/(x_1^2 x_2^2) - (2x_0 - 1)x_0^{-2}(1-x_0)^{-2} +$$
$$+ 96\mathrm{d}(x_0 - x_1). \qquad (A\text{-}9)$$

LIST OF SYMBOLS

b, c, d	
C_1, C_2, C_3	parameters of Redlich–Kister equation
$\mathscr{G}$	molar Gibbs energy
$\mathscr{G}^E$	molar excess Gibbs energy
G11 (G111, and so on)	second-order (third-order, and so on) derivative of molar Gibbs energy with respect to the composition, devided by $2 \cdot 303 RT$
$(G11)_{x_0}$	ordinate of minimum of $G11(x_1)$ curve
$Q = \mathscr{G}^E/(2 \cdot 303 RT)$	dimensionless excess Gibbs energy
Q1 (Q11)	first-order (second-order) derivative of Q with respect to composition
$(Q1)_s$	value of Q1 corresponding to $x_1 = x_s$
R	gas constant
T	absolute temperature
x_i	mole fraction of component i
x_0	coordinate of minimum of $G11$-x_1 curve
x_s	composition defined by the relation (25)
γ_i	activity coefficient of component i
γ_i^0	limiting activity coefficient of component i

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