

LIQUID-VAPOUR EQUILIBRIUM. LI.*

CORRELATION OF LIQUID-VAPOUR EQUILIBRIUM DATA
OF STRONGLY NON-IDEAL SYSTEMS

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Received June 21st, 1971

With the homogeneous systems which exhibit sufficiently great deviations from Raoult's law, it occurs that the constants of the expansion used, obtained by a standard method do not fulfil the conditions of the thermodynamic stability and consequently they lose physical significance. The method is proposed which restricts the possibility of obtaining such constants. The procedure is demonstrated on the Redlich-Kister equation.

The standard method of the evaluation and correlation of the phase vapour-liquid equilibria is usually carried out in terms of the activity coefficients defined by the relation

$$P y_k v_k = \gamma_k x_k f_k^{01}, \quad (1)$$

where γ_k is the activity coefficient of the k -th component, P pressure, T temperature, y_k and x_k mole fraction of the k -th component in the vapour and liquid phase, resp., v_k fugacity coefficient in the vapour phase, f_k^{01} fugacity of the pure k -th component in the liquid state at the temperature and pressure of the system.

From empirical and semi-empirical relations for the dependence of the excess Gibbs energy G^E on composition, the relations follow for the logarithm of the ratio of the activity coefficients which contain adjustable constants. These constants are usually evaluated from measured data by the least squares method minimizing the deviations of the logarithms of the activity coefficients (or their ratio) or the deviations in the vapour phase composition. With homogeneous systems which show great positive deviations from the Raoult law, the constants may be obtained by the above-said standard procedure which have no physical significance, because they are at variance with the condition of thermodynamic stability, *i.e.*¹⁻³

$$(\partial^2 G / \partial x_1^2)_{T,P} \geq 0. \quad (2)$$

(The equality sign holds, in a strict sense, only for the critical point.) This fact is due to *a*) the existence of experimental errors, *b*) the rounding-off errors during computation, *c*) an empirical character of the relations for G^E . For the time being it is difficult to judge mutually these three

* Part L: This Journal 37, 375 (1972).

factors, especially because we do not know the real dependence $G^E = G^E(x)$ in an analytical form. The course of the dependence of thermodynamic functions on composition in the critical region is very flat⁴ and $(\partial^2 G/\partial x_1^2)_{T,P}$ is very small. The systems considered in this work behave analogously (see below Figs 5 and 6). The quantity $(\partial^2 G/\partial x_1^2)_{\text{cor}}$ determined from an empirical relation and from the constants evaluated by the standard correlation of measured data tends to the oscillation about the real dependence and can twice or several times intersect the x -axis (*i.e.* $(\partial^2 G/\partial x_1^2) = 0$) (Fig. 4). In such system, two or more liquid phases should exist. If a homogeneous system is correlated, it is evident that such constants are without both physical and practical sense. As it follows from the relations given in Appendix, the $y-x$ diagram constructed by means of such constants shows the course that is schematically represented in Fig. 1 and that cannot be used at all for calculating the distillation column.

The above-said phenomenon can be elucidated well by the following example. Let us have the data on vapour-liquid equilibrium at the liquid-liquid critical temperature at our disposal. By correlating these, though very accurate data by the standard method, we never get exactly such course that conforms to the reality, *i.e.* $(\partial^2 G/\partial x_1^2)_{T,P} > 0$ for all $x_1 \neq (x_1)_c$ and $(\partial^2 G/\partial x_1^2)_{T,P} = 0$ for $x_1 = (x_1)_c$, where $(x_1)_c$ is the composition corresponding to the critical point. The dependence of the Gibbs energy on composition and consequently the constants must necessarily correspond either to the homogeneous system ($(\partial^2 G/\partial x_1^2)_{\text{cor}} > 0$ for all x_1) or to the heterogeneous one (in a certain concentration interval the relation $(\partial^2 G/\partial x_1^2)_{\text{cor}} < 0$ is valid). The first case occurs always on correlating the data by the Wilson equation⁵ which cannot describe the critical isotherm.

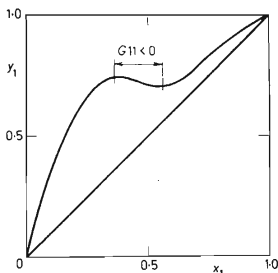


FIG. 1

$y-x$ Dependence for Thermodynamically Unstable System

THEORETICAL

To eliminate this phenomenon, we proposed the method given below which is demonstrated on the Redlich-Kister equation⁶ for excess molar Gibbs energy

$$G^E/2.303RT = x_1 x_2 [b + c(x_1 - x_2) + d(x_1 - x_2)^2 + e(x_1 - x_2)^3 + \dots], \quad (3)$$

where b, c, d, e are constants independent of composition. For the logarithm of the ratio of activity coefficients and for second and third derivative of the Gibbs energy with respect to the composition, the following relations can be derived

$$\log \gamma_1/\gamma_2 = b(x_2 - x_1) + c(6x_1x_2 - 1) + d(x_1 - x_2)(8x_1x_2 - 1) + e(x_1 - x_2)^2(10x_1x_2 - 1) + \dots, \quad (4)$$

$$(\partial^2[G/(2 \cdot 303RT)]/\partial x_1^2)_{T,P} = G11 = 0.4343/(x_1x_2) - 2b - 6c(x_1 - x_2) + d(48x_1x_2 - 10) + 2e(x_1 - x_2)(40x_1x_2 - 7) + \dots, \quad (5)$$

$$(\partial^3[G/(2 \cdot 303RT)]/\partial x_1^3)_{T,P} = G111 = 0.4343(1/x_2^2 - 1/x_1^2) - 12c - 48d(x_1 - x_2) + 12e(40x_1x_2 - 9) + \dots \quad (6)$$

Let us investigate, for several special cases, what conditions must the constants of Eq. (3) fulfil in order that the inequality (2) may be satisfied. If we limit ourselves to the constant b , then, on comparing Eqs (5) and (2), we obtain $b < 0.8686$. For the case of arbitrary number of constants in Eq. (3) but when limiting to the composition $x_1 = x_2 = 0.5$, we get $b - d < 0.8686$ by combining Eqs (5) and (2). This condition is necessary, but its fulfilment does not eliminate the possibility that Eq. (2) will not be satisfied for another composition. For the four-suffix Margules equation, the last inequality turns into $A_{12} + A_{21} - D_{12} < 1.7372$.

An orientating (but less accurate) answer can be obtained from Fig. 2. In this figure, the curves of constant values of d are plotted from -0.6 to 0.6 by steps 0.2 in dependence on b and c . On the side of the curve $d = \text{const.}$ marked by points

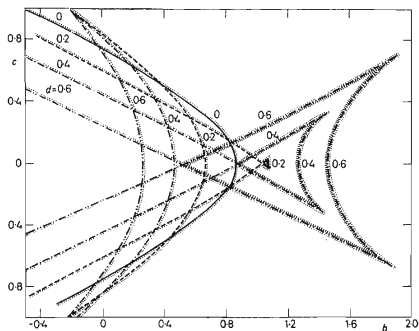


FIG. 2

Limiting Values of b , c Satisfying Conditions of Thermodynamic Stability for Various Values of d

(strokes), two (four) liquid phases can exist in the system at the given temperature and pressure. When constructing this diagram, it was proceeded according to Boberg and White⁷.

Principle of Method

It is evident from the discussion that with the standard correlation, the fundamental experimental fact is not respected, namely, that the given system is homogeneous. In the method proposed, we make use of this fact and we get out of the course of the G_{11} curve determined in advance from experimental data according to one of the relations given in Appendix. In Fig. 3 this course of the dependence of G_{11} on composition is represented schematically. Let us assume that this curve has the minimum value $(G_{11})_{x_0}$ at the point x_0 . Then at this point, according to Eqs (5) and (6), the relations must hold

$$(G_{11})_{x_0} = 0.4343/[x_0(1-x_0)] - 2b - 6c(2x_0-1) + d[48x_0(1-x_0) - 10] + 2e(2x_0-1)[40x_0(1-x_0) - 7] + \dots, \quad (7)$$

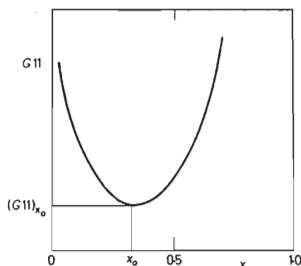


FIG. 3
Dependence of G_{11} on Composition

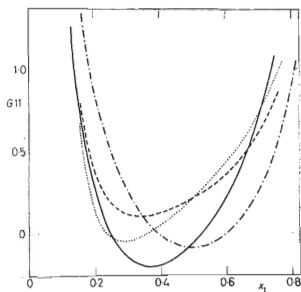


FIG. 4
Dependence of G_{11} on Composition Established on the Basis of Constants Determined from Experimental Vapour-Liquid Equilibrium Data in the Ethanol(1)-Cyclohexane(2) System: --- b 0.9084; — b 0.8959, c -0.1722; b 0.8738, c -0.1532, d 0.1196; - - - b 0.8640, c -0.0975, d 0.1035, (x_0 0.34, $(G_{11})_{x_0}$ 0.1).

$$0 = (G11)_{x_0} = 0.4343[1/(1 - x_0)^2 - 1/x_0^2] - 12c - 48d(2x_0 - 1) + 12e[40x_0(1 - x_0) - 9] + \dots \quad (8)$$

Eq. (8) is the consequence of the fact that the function $G11$ has an extreme at the point x_0 . When combining Eqs (4), (7) and (8), we obtain the relation for logarithm of the activity coefficients ratio that does not contain the constants b , c any more but instead of them the predetermined values x_0 and $(G11)_{x_0}$. From experimental data on the vapour-liquid equilibrium the further constants d , e , ... can be then optimized in the usual way. Upon determining them, it is possible to calculate the constants b , c , too, from Eqs (7) and (8). The calculation was programmed in the Algol language for the computer Hewlett-Packard.

Verification of Method

The procedure proposed was verified using the systems ethanol-n-heptane (isothermal data⁸ at 70°C) and ethanol-cyclohexane (isobaric data at 760 Torr⁹). With both systems the constants are obtained that do not fulfil the condition (2) on determining the constants of the Redlich-Kister equation with the standard procedure by minimizing the deviations of the activity coefficients ratio. In Fig. 4 the course of $(G11)_{cor}$ calculated from Eq. (5) with constants b ; b, c ; b, c, d , is represented as a function of composition of the ethanol-cyclohexane system. When calculating the activity coefficients according to Eq. (1), the ideal behaviour of the vapour phase was assumed.

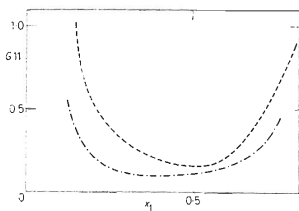


FIG. 5

Dependence of $G11$ on Composition in the Ethanol(1)-n-Heptane(2) System

Dependence determined from curve:

----- $P - x$ (Eq. (A-4) with $z^E = 1$), - - - - -; $y - x$ (Eq. (A-9)).

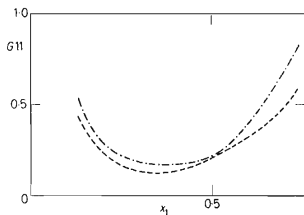


FIG. 6

Dependence of $G11$ on Composition in the Ethanol(1)-Cyclohexane(2) System

Dependence determined from curve: - - - - -

$t - x$ (Eq. (A-12)), - - - - -; $y - x$ (Eq. (A-13)); heats of vaporization¹¹ $\Delta H_{v1} = 9400$ cal/mol, $\Delta H_{v2} = 7200$ cal/mol were used for the calculation.

TABLE I
Vapour-Liquid Equilibrium in the Ethanol(1)-n-Heptane(2) System at 70°C

x_1	y_1	P_{exp}	Δy_1^a	Δy_1^b
0.0567	0.4685	500.3	0.0065	0.0002
0.1180	0.5531	614.3	-0.0179	-0.0112
0.1573	0.5790	648.0	-0.0199	-0.0080
0.2575	0.6000	689.6	-0.0242	-0.0074
0.3633	0.6114	705.9	-0.0155	-0.0027
0.4290	0.6213	712.1	-0.0043	0.0031
0.5069	0.6241	715.7	-0.0004	-0.0009
0.5968	0.6280	717.7	0.0014	-0.0070
0.6648	0.6383	717.7	0.0057	-0.0082
0.7174	0.6483	717.7	0.0067	-0.0090
0.8090	0.6483	713.8	-0.0246	-0.0381
0.8200	0.6516	704.9	-0.0171	-0.0398
0.8640	0.6713	693.4	-0.0381	-0.0463
0.8940	0.7293	676.5	-0.0103	-0.0144
0.9250	0.8013	651.8	0.0181	0.0188
0.9564	0.8639	610.0	0.0165	0.0212
0.9827	0.9211	569.4	-0.0058	-0.0011
<i>Mean deviations</i>			<i>0.0140</i>	<i>0.0140</i>

^a Correlated by the classical method with three constants b 0.9365, c -0.0606, d 0.0635, the minimum value of G_{11} -0.05 at x_1 0.305. ^b Correlated by the new proposed method b 0.9091, c -0.0617, d 0.1315, the determined parameters x_0 0.34, $(G_{11})_{x_0}$ 0.1. ($\Delta y_1 = y_1, \text{exp} - y_1, \text{calc}$)

The $P - x$ (or $t - x$) and $y - x$ diagrams were constructed on the basis of the measured data of these systems and the derivatives needed for the calculation of G_{11} were determined from the smoothed course by the mirror method¹⁰. The calculated dependences of G_{11} on concentration are shown in Figs 5 and 6. It appears that the values G_{11} determined from $P - x$ and $y - x$ curves (or $t - x$ and $y - x$ ones) differ each other. These differences are due to the inaccuracy in the determination of the derivatives and the experimental errors. Considering that the values x_0 and $(G_{11})_{x_0}$ cannot be determined uniquely, the program was arranged so that it was possible to change these values and according to them to find out the deviations in the activity coefficients ratio and in the vapour phase composition. This dependence, as for the ethanol-cyclohexane system, is represented in Fig. 7. The results of the correlation by the standard method and by the new proposed one are presented in Table I and II.

TABLE II
Vapour-Liquid Equilibrium in the Ethanol(1)-Cyclohexane(2) System at a Pressure of 760 Torr

x_1	y_1	°C	Δy_1^a	Δy_1^b
0.020	0.175	73.99	-0.024	0.001
0.030	0.302	69.08	0.054	0.012
0.065	0.358	66.94	0.004	0.031
0.081	0.363	66.08	-0.015	0.008
0.086	0.365	66.37	-0.021	0.002
0.125	0.388	65.59	-0.029	-0.003
0.151	0.396	65.23	-0.031	-0.020
0.206	0.408	65.12	-0.027	-0.025
0.258	0.415	64.93	-0.021	-0.025
0.283	0.418	64.87	-0.017	-0.024
0.315	0.426	64.84	-0.008	-0.018
0.366	0.430	64.78	-0.004	-0.017
0.403	0.431	64.77	-0.004	-0.018
0.431	0.431	64.77	-0.005	-0.017
0.444	0.438	64.78	0.001	-0.014
0.500	0.443	64.81	0.000	-0.015
0.557	0.455	64.88	0.003	-0.011
0.613	0.460	65.01	-0.005	-0.018
0.621	0.458	64.99	-0.009	-0.022
0.678	0.475	65.25	-0.010	-0.020
0.738	0.505	65.56	-0.006	-0.012
0.763	0.496	66.03	-0.030	-0.033
0.776	0.515	65.93	-0.018	-0.020
0.781	0.598	66.40	-0.039	-0.041
0.809	0.545	66.90	-0.013	-0.012
0.833	0.578	67.20	0.000	0.002
0.853	0.595	67.98	-0.004	0.000
0.881	0.623	68.86	-0.011	-0.005
0.898	0.653	69.44	-0.007	-0.000
0.909	0.678	70.11	-0.002	0.006
0.929	0.725	71.42	0.003	0.011
0.951	0.778	72.48	-0.002	0.006
<i>Mean deviations</i>			0.013	0.017

^a Correlated by the classical method with three constants b 0.8738, c -0.1532, d 0.1196, the minimum value of G_{11} -0.037 at x_1 0.283. ^b Correlated by the new proposed method b 0.8640, c -0.0975, d 0.1035, the determined parameters x_0 0.34, $(G_{11})_{x_0}$ 0.1.

CONCLUSION

The method proposed for calculating the constants of the G^E expansion is suitable for strongly non-ideal systems with great positive deviations from the Raoult law. In case of the Redlich-Kister expansion, its use is simple. With relations for G^E that are nonlinear with respect to constants, it is necessary to choose more complicated mathematical methods (nonlinear regression, if need be together with the method of the Lagrange multipliers). Further, it is necessary to call attention to the fact that Eq. (8) is the necessary condition for the minimum of G_{11} but not the sufficient one. With some systems it was found that the constants b, c, d obtained are of such sort that G_{11} has a local maximum at the point x_0 . In this case either those three constants are not enough to characterize the given system or that expansion is not suitable for the given system

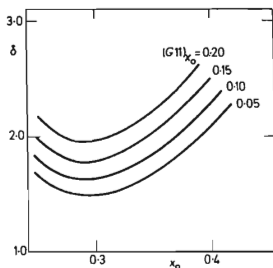


FIG. 7

Dependence of Mean Deviation δ , % in the Vapour Phase Composition on x_0 and $(G_{11})_{x_0}$ for the Ethanol(1)-Cyclohexane(2) System

APPENDIX

Relations for Calculating G_{11} from Vapour-Liquid Equilibrium Data

Isothermal data. In this case the relation holds

$$G_{11} = 0.4343/(RT) \cdot (\partial P/\partial x_1)_T \cdot \Delta V_{\text{vap}}/(y_1 - x_1), \quad (A-1)$$

where the differential vaporization volume ΔV_{vap} is given by

$$\Delta V_{\text{vap}} = V^E - V^l - (y_1 - x_1) (\partial V/\partial x_1)_{T,P}^l. \quad (A-2)$$

The V^E and V^l are molar volumes of the mixture in the vapour and liquid phase. Supposing that

$$V^E \gg V^l \quad (A-3)$$

and $(\partial V/\partial x_1)_{T,P}^I$ is comparable with V^I ,

Eq. (A-1) turns into

$$G11 = 0.4343z^{\#}(\partial P/\partial x_1)_T/[P(y_1 - x_1)], \quad (A-4)$$

where $z^{\#}$ is the compressibility factor of saturated vapour. The value of $(\partial P/\partial x_1)$ must be determined from the experimental $P - x$ dependence by a numerical or graphical differentiation. The use of this relation practically fails in the vicinity of azeotropic point (where extremely accurate data are required). From Eq. (A-4) it is also evident that at the pressure about $P \sim 1$ atm, the effect of the real behaviour of the vapour phase ($z^{\#} \in \langle 0.9 - 1.0 \rangle$) is very small, but it always reduces the value of $G11$ in comparison with the ideal behaviour (however it can never change the sign of $G11$).

The quantity $G11$ can be determined from the isothermal $y - x$ data according to the relation

$$G11 = 0.4343/(RT) \cdot (\partial^2 G/\partial y_1^2)_T^{\#} (\partial y_1/\partial x_1)_T \cdot \Delta V_{\text{vap}}/\Delta V_{\text{cond}}, \quad (A-5)$$

where ΔV_{cond} is the differential condensation volume that is given by a relation analogous to Eq. (A-2) and $(\partial^2 G/\partial y_1^2)_T^{\#}$ is the second-order derivative of the Gibbs energy with respect to the composition in the vapour phase. On limiting to the region of low pressures (where the second virial coefficient is sufficient for expressing the pressure - volume - temperature behaviour) and assuming the validity of Eq. (A-3) we get from Eq. (A-5) after rearrangement

$$G11 = [0.4343/(y_1 y_2) - 0.8686\delta_{12} \cdot P/(RT)] \cdot (\partial y_1/\partial x_1)_T \cdot \frac{(RT/P) + B_{11}y_1 + B_{22}y_2 + \delta_{12}y_1y_2}{(RT/P) + B_{22} + y_1^2\delta_{12} + x_1[B_{11} - B_{22} + \delta_{12}(y_2 - y_1)]}. \quad (A-6)$$

The B_{11} and B_{22} are virial coefficients of pure components, B_{12} is the cross virial coefficient and δ_{12} is given by

$$\delta_{12} = 2B_{12} - B_{11} - B_{22}. \quad (A-7)$$

On the assumption of the validity of the Amagat law ($\delta_{12} = 0$), Eq. (A-6) is simplified, thus

$$G11 = 0.4343(y_1 y_2)^{-1} \cdot (\partial y_1/\partial x_1)_T \cdot \frac{(RT/P) + B_{11}y_1 + B_{22}y_2}{(RT/P) + B_{22} + x_1(B_{11} - B_{22})}. \quad (A-8)$$

In the case of the ideal behaviour of the vapour phase we obtain

$$G11 = 0.4343(y_1 y_2)^{-1} \cdot (\partial y_1/\partial x_1)_T. \quad (A-9)$$

Unlike Eq. (A-4) this relation may be used even in the vicinity of azeotropic point.

Isobaric data. In this case the relation holds

$$G11 = -0.4343 \cdot (\partial T/\partial x_1)_P/[RT^2(y_1 - x_1)] \cdot \Delta H_v, \quad (A-10)$$

where ΔH_v is differential heat of vaporization. Neglecting the heats of mixing in both phases and the effect of pressure on enthalpy we obtain from Eq. (A-10)

$$G11 = -0.4343 \cdot (\partial T/\partial x_1)_P/[RT^2(y_1 - x_1)] (y_1 \Delta H_{v1} + y_2 \Delta H_{v2}), \quad (A-11)$$

where ΔH_{v1} and ΔH_{v2} are the heats of vaporization of pure substances at the given temperature.

From the isobaric $y - x$ data, the quantity G_{11} can be determined according to the relation

$$G_{11} = 0.4343(y_1 y_2)^{-1} \cdot (\partial y_1 / \partial x_1)_P \frac{y_1 \Delta H_{v1} + y_2 \Delta H_{v2}}{x_1 \Delta H_{v1} + x_2 \Delta H_{v2}}, \quad (A-12)$$

that holds under the same assumptions as Eq. (A-11).

We thank Dr A. Malijevský for suggestive discussions and his interest in this work.

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