EVALUATION OF THE INTERACTION
EFFECT IN TERNARY SYSTEMS

by

YI-CHUAN PAN

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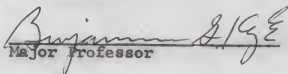submitted in partial fulfillment of the

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INTRODUCTION

For designing extractive or azeotropic distillation systems
a knowledge of ternary vapor-liquid equilibrium data is required.
There is a large number of binary vapor-liquid equilibrium data
in the literature, but few ternary systems. The experimental
determination of vapor-liquid equilibrium data for ternary systems
requires long and detailed experimental work, and is always com-
plicated by inaccuracies in the methods of analysis.

Therefore a simple and systematic method of calculating ac-
tivity coefficients in ternary systems from binary equilibrium
data available for the three binary combinations of components
would be quite useful. Such a method would make possible the re-
liable prediction of vapor-liquid equilibrium data for any ternary
system with the aid of binary vapor-liquid equilibrium data alone,
or at worst, only a relatively small number of experimental mea-
surements on the ternary system.

Several authors have attempted to correlate vapor-liquid
equilibrium data of non-ideal solutions on a semi-empirical basis,
notable among them being Margules (10), van Laar (24), Scatchard
and Hamer (15), Carlson and Colburn (3), White (26), Benedict
et. al. (1), and Wohl (27). Wohl combined all these authors'
attempts into a single, general equation.

This work was concerned mainly with Wohl's Margules three-
suffix equation and whether ternary activity coefficients could be
predicted from binary data alone, or whether a ternary constant was

necessary. Non-aqueous systems, taken from the literature, were used in this investigation.

The Margules binary constants were determined by several methods and every combination was used for the ternary calculations. The activity coefficients of each component, which are calculated by Wohl's Margules equation with various binary constants, were compared with binary and ternary experimental data in order to determine which method for the calculation of binary constants is the best.

Ternary constants were thought to be necessary whenever the average of the absolute value of the deviations of the calculated activity coefficient from the experimental activity coefficient was more than or equal to ten percent. (e.g., $\sum_{i=1}^{n} \frac{|\gamma_i - \gamma_{ei}|}{n\gamma_{ei}} \geq 0.1$)

MATHEMATICAL REPRESENTATION OF ACTIVITY COEFFICIENT

The activity coefficient γ_i may be thought of as the ratio between the apparent vapor-pressure of the ith component in a li-quid solution to its Raoult's law value. In an ideal solution, the activity coefficient of every component equals one, and in any type of solution its value for a particular component approaches one as that component's mole fraction approaches one. In non-ideal solutions activity coefficients are strong function of concentration, but their variation must satisfy the Gibbs-Duhem equation for thermodynamic consistency.

In the preceding section it was mentioned that Wohl generated

several authors' (1, 3, 10, 15, 24, 26, 27) equations from a single general expression relating the activity coefficients as functions of concentration in binary, ternary, and quaternary systems. Using the excess free energy, ΔG^E, as a function of composition, he obtained equations suitable for expressing the activity coefficients of the components as a function of the composition of the mixture.

Wohl expressed ΔG^E in terms of the following expansion;

$$\frac{\Delta G^E}{2.303RT \sum q_i x_i} = \sum_{ij} z_i z_j a_{ij} + \sum_{ijk} z_i z_j z_k a_{ijk} + \sum_{ijkl} z_i z_j z_k z_l a_{ijkl} \quad (2-1)$$

where

ΔG^E is molar excess free energy;

q_i, q_j are the effective volumes of the components i, j;

a_{ij}, a_{ijk}, a_{ijkl}... are empirical constants measuring the interactions in various groups of molecules ij, ijk, ijkl......
The effective volumetric fraction of any component i is defined by the relation,

$$z_i = \frac{q_i x_i}{\sum q_i x_i} \quad (2-2)$$

Equation (2-1) is written as an equation of fourth order. From this equation Wohl's activity coefficient equation of fourth order for component k can be obtained. It is usually found that the higher the order of the equation used, the better it will represent the behavior of the given system, but the more complicated it will become. Practically speaking, the equations of order higher than four are rarely used, and the equations of third order were used in this work.

(A) <u>Binary</u> <u>Systems</u>. An equation of the third order of the form of equation (2-1) can be written for a binary system,

$$\frac{\Delta G^E}{2.303RT} = (x_1 + \frac{q_2}{q_1} x_2)z_2 z_1 \left[z_1 q_1(2a_{12} + 3a_{112}) \right.$$
$$\left. + z_2 q_1(2a_{12} + 3a_{122}) \right]. \tag{2-3}$$

After introducing the new constants,

$$A_{12} = q_1(2a_{12} + 3a_{122})$$
$$A_{21} = q_2(2a_{12} + 3a_{112}) \tag{2-4}$$

equation (2-3) can be written as:

$$\frac{\Delta G^E}{2.303RT} = (x_1 + \frac{q_2}{q_1}x_2)z_2 z_1(A_{21}z_1\frac{q_1}{q_2} + A_{12}z_2). \tag{2-5}$$

Wohl's activity coefficient equation of the third order for a binary system can be obtained from equation (2-5);

$$\log \gamma_1 = z_2^2 \left[A_{12} + 2z_1(A_{21}q_1/q_2 - A_{12}) \right],$$
$$\log \gamma_2 = z_1^2 \left[A_{21} + 2z_2(A_{12}q_2/q_1 - A_{21}) \right] \tag{2-6}$$

On the assumption that $q_2/q_1=1$, equations (2-6) take the form of the three-suffix Margules equations. These equations contain two constants A_{12}, A_{21} which have to be determined from the ex-perimental measurements:

$$\log \gamma_1 = x_2^2 \left[A_{12} + 2x_1(A_{21} - A_{12}) \right],$$
$$\log \gamma_2 = x_1^2 \left[A_{21} + 2x_2(A_{12} - A_{21}) \right]. \tag{2-7}$$

Redlich-Kister equations (13) are rearranged forms of the three-suffix Margules equations:

$$\log \gamma_1 = x_2^2 \left[b_{12} + c_{12}(x_2 + 3x_1) \right],$$
$$\log \gamma_2 = x_1^2 \left[b_{12} + c_{12}(x_1 - 3x_2) \right]. \tag{2-8}$$

The relations between Redlich-Kister and Margules constants are

$$b_{12} = \tfrac{1}{2} (A_{12} + A_{21}), \tag{2-9}$$

$$c_{12} = \tfrac{1}{2}(A_{21} - A_{12}),$$

or

$$A_{12} = b_{12} - c_{12},$$
$$A_{21} = b_{12} + c_{12}. \tag{2-10}$$

(B) <u>Ternary Systems</u>. Wohl's equation of the third order for ternary systems is

$$\begin{aligned}
\log\gamma_1 = {}& z_2^2 \left[A_{12} + 2z_1(A_{21}q_1/q_2 - A_{12}) \right] \\
& + z_3^2 \left[A_{13} + 2z_1(A_{31}q_1/q_3 - A_{13}) \right] \\
& + z_2 z_3 \left[A_{21}q_1/q_2 + A_{13} - A_{32}q_1/q_3 + 2z_1(A_{31}q_1/q_3 - A_{13}) \right. \\
& \left. + 2z_3(A_{32}q_1/q_3 - A_{23}q_1/q_2) - C(1 - 2z_1) \right]. \tag{2-11}
\end{aligned}$$

The equations for $\log\gamma_2$ and $\log\gamma_3$ can be produced by a rotation principle from the subscript triangle.

In order to obtain the equation for $\log\gamma_2$, all subscripts in equation (2-11) are rotated one unit (e.g. $x_1 \to x_2$, $A_{12} \to A_{23}$) and the equation for $\log\gamma_3$ follows from the equation for $\log\gamma_2$ in the same way. The symbols A_{12}, A_{21} and the effective molal volume ratio are the same as in the binary equations. The ternary constants C_1, C_2 and C_3 which have to be determined from ternary data are related by,

$$C_2 = C_1 q_2/q_1,$$
$$C_3 = C_1 q_3/q_1$$

For the Margules three-suffix equation $C_1 = C_2 = C_3$, since $q_1/q_2 = 1$ and $q_1/q_3 = 1$.

The ternary three-suffix Margules equations can be obtained

from equation (2-11):

$$\log\delta_1 = x_2^2 \left[A_{12} + 2x_1(A_{21} - A_{12})\right] + x_3^2 \left[A_{13} + 2x_1(A_{31} - A_{13})\right]$$
$$+ x_2 x_3 \left[A_{21} + A_{13} - A_{32} + 2x_1(A_{31} - A_{13})\right.$$
$$\left. + 2x_3(A_{32} - A_{23}) - C(1 - 2x_1)\right] . \tag{2-12}$$

$\log\delta_2$ and $\log\delta_3$ can be obtained by the rotation principle. These equations are identical algebraically with the three-suffix equations used by Benedict et. al. (1) and ternary Redlich-Kister equations (13). Hala (8) has shown that the Redlich-Kister equation is equivalent to the Margules equation in both binary and ternary form.

DETERMINATION OF CONSTANTS

(A) <u>Binary Margules Constants</u>. The constants A_{12}, A_{21} in Margules equation (2-7) are the terminal values of the curves relating the logarithm of the activity coefficient and the composition of the solution:

$$A_{12} = \lim_{x_1 \to 0} \log\delta_1 ,$$
$$A_{21} = \lim_{x_2 \to 0} \log\delta_2 . \tag{3-1}$$

The values of the constants A_{12}, A_{21} characterize a given binary system, and the determination of these constants has been an important problem in studies of phase equilibria. They could be determined theoretically, but from the view point of practical application they are always determined from experimental data.

The calculation of the constants A_{12}, A_{21} from the known equilibrium composition of the vapor and liquid is the most precise

method. There are two unknowns A_{12} and A_{21} to be determined in
equations (2-7). Mathematically speaking equations (2-7) can be
considered as equations in the two unknowns A_{12} and A_{21} which,
therefore, can be evaluated for each data point. The values of
A_{12} and A_{21} determined in this way are called point values of A_{12}
and A_{21}.

Since Margules equations are linear in the constants, A_{12} and
A_{21} they can also be determined by the method of ordinary least
squares or the weighted least squares method (22, 23).

In this work, the method of ordinary least squares was used in
evaluating the binary Margules constants. This was due to the
fact that no information was available regarding the precision of
experimental measurements and therefore it was assumed that all
points had equal weight.

The constants A_{12} and A_{21} were calculated by computer by app-
lying the method of least squares to four different arrangements
of equations (2-7).

Method 1.

$$\text{var. 1} = \sum_{i=1}^{n} \left[\frac{\log \gamma_1}{(1-x_1)^2} - A_{12} - 2(A_{21} - A_{12})x_1 \right]^2 , \tag{3-2}$$

$$\text{var. 2} = \sum_{i=1}^{n} \left[\frac{\log \gamma_2}{(1-x_2)^2} - A_{21} - 2(A_{12} - A_{21})x_2 \right]^2 , \tag{3-3}$$

Method 2.

$$\text{var. 1} = \sum_{i=1}^{n} \left\{ \log \gamma_1 - (1-x_1)^2 \left[A_{12} - 2(A_{21} - A_{12})x_1 \right] \right\}^2 , \tag{3-4}$$

$$\text{var. 2} = \sum_{i=1}^{n} \left\{ \log \gamma_2 - (1-x_2)^2 \left[A_{21} - 2(A_{12} - A_{21})x_2 \right] \right\}^2 , \tag{3-5}$$

Method 3.

$$\text{var.} = \sum_{i=1}^{n}\left[\frac{\log \gamma_1}{(1-x_1)^2} - A_{12} - 2(A_{21} - A_{12})x_1\right]^2$$
$$+ \sum_{i=1}^{n}\left[\frac{\log \gamma_2}{(1-x_2)^2} - A_{21} - 2(A_{12} - A_{21})x_2\right]^2 , \qquad (3-6)$$

Method 4.

$$\text{var.} = \sum_{i=1}^{n}\left\{\log \gamma_1 - (1-x_1)^2\left[A_{12} - 2(A_{21} - A_{12})x_1\right]\right\}^2$$
$$+ \sum_{i=1}^{n}\left\{\log \gamma_2 - (1-x_2)^2\left[A_{21} - 2(A_{12} - A_{21})x_2\right]\right\}^2 , \qquad (3-7)$$

Method 5.

This method consisted of averaging the point values.

Method 1 is equivalent to the J-plot used by Severns, Sesonske, Perry and Pigford (16), or to Robinson and Gilliland's (14) graphical method. Method 2 is equivalent to plot of $\log \gamma_1$ vs x_1. For showing the differences between method 1 and method 2, the following substitutions in equations (2-7) were made,

$$a_1 = A_{12} , \qquad\qquad a_2 = A_{21} ,$$
$$b_1 = 2(A_{21} - A_{12}) , \qquad b_2 = 2(A_{12} - A_{21}) ,$$
$$r_1 = \log \gamma_1 , \qquad\qquad r_2 = \log \gamma_2 , \qquad (3-8)$$
$$s_1 = (1-x_1)^2 , \qquad\qquad s_2 = (1-x_2)^2,$$

it follows

$$r_1 = (a_1 + b_1 x_1)s_1 , \qquad (3-9)$$
$$r_2 = (a_2 + b_2 x_2)s_2. \qquad (3-10)$$

Rearranging equation (3-9), (3-10)

$$\frac{r_1}{s_1} = a_1 + b_1 x_1 , \qquad (3-11)$$

$$\frac{r_2}{s_2} = a_2 + b_2 x_2 , \qquad (3-12)$$

are obtained.

Using equations (3-9) and (3-10) to obtain a_1, b_1, a_2, b_2 by the method of least squares gives values different from those obtained using equations (3-11) and (3-12). This can be shown by the following

$$\theta_1 = \sum_{i=1}^{n} \left[r_1 - (a_1 + b_1 x_1) s_1 \right]^2 , \tag{3-13}$$

$$\omega_1 = \sum_{i=1}^{n} \left[\frac{r_1}{s_1} - (a_1 + b_1 x_1) \right]^2 , \tag{3-14}$$

Minimum values of θ_1 and ω_1 were found as follows:

By partial differentiation with respect to a_1 and b_1, then setting the partial derivatives equal to zero, the following equations were obtained,

$$\frac{\partial \theta_1}{\partial a_1} = 2 \sum_{i=1}^{n} \left[r_1 - (a_1 + b_1 x_1) s_1 \right] (-s_1) = 0 , \tag{3-15}$$

$$\frac{\partial \theta_1}{\partial b_1} = 2 \sum_{i=1}^{n} \left[r_1 - (a_1 + b_1 x_1) s_1 \right] (-x_1 s_1) = 0 , \tag{3-16}$$

$$\frac{\partial \omega_1}{\partial a_1} = 2 \sum_{i=1}^{n} \left[\frac{r_1}{s_1} - (a_1 + b_1 x_1) \right] (-1) = 0 , \tag{3-17}$$

$$\frac{\partial \omega_1}{\partial b_1} = 2 \sum_{i=1}^{n} \left[\frac{r_1}{s_1} - (a_1 + b_1 x_1) \right] (-x_1) = 0 , \tag{3-18}$$

Rearranging equation (3-15) to (3-18) it follows that

$$\sum r_1 s_1 = a_1 \sum s_1^2 + b_1 \sum x_1 s_1^2 , \tag{3-19}$$

$$\sum r_1 x_1 s_1 = a_1 \sum x_1 s_1 + b_1 \sum x_1^2 s_1^2 , \tag{3-20}$$

$$\sum \frac{r_1}{s_1} = n a_1 + b_1 \sum x_1 , \tag{3-21}$$

$$\sum \frac{r_1}{s_1} x_1 = a_1 \sum x_1 + b_1 \sum x_1^2 , \tag{3-22}$$

Solving equation (3-19) with equation (3-20) a_1 and b_1 were obtained,

$$a_1 = \frac{\left(\sum r_1 s_1 \right) \left(\sum x_1^2 s_1^2 \right) - \left(\sum r_1 x_1 s_1 \right) \left(\sum x_1 s_1^2 \right)}{\left(\sum s_1^2 \right) \left(\sum x_1^2 s_1^2 \right) - \left(\sum x_1 s_1^2 \right) \left(\sum x_1 s_1 \right)} , \tag{3-23}$$

$$b_1 = \frac{\left(\sum s_1^2 \right) \left(\sum r_1 x_1 s_1 \right) - \left(\sum x_1 s_1 \right) \left(\sum r_1 s_1^2 \right)}{\left(\sum s_1^2 \right) \left(\sum x_1^2 s_1^2 \right) - \left(\sum x_1 s_1^2 \right) \left(\sum x_1 s_1 \right)} . \tag{3-24}$$

a_2, b_2 can be obtained by changing subscripts 1 to 2.

Also solving equation (3-21) with equation (3-22) a_1, b_1 were

obtained:

$$a_1 = \frac{(\sum^n \frac{r_1}{s_1})(\sum^n x_1^2) - (\sum^n \frac{r_1}{s_1} x_1)(\sum^n x_1)}{n\sum x_1^2 - (\sum x_1)(\sum x_1)} \quad , \qquad (3\text{-}25)$$

$$b_1 = \frac{n\sum^n \frac{r_1}{s_1} x_1 - (\sum x_1)(\sum \frac{r_1}{s_1})}{n\sum x_1^2 - (\sum x_1)(\sum x_1)} \quad . \qquad (3\text{-}26)$$

a_2 and b_2 were obtained by changing subscripts 1 to 2.

After a_1, b_1, a_2 and b_2 had been determined, A_{12} and A_{21} were calculated, but A_{12} and A_{21} calculated from a_1, b_1 were not necessarily equal to A_{12} and A_{21} calculated from a_2, b_2.

Method 3 was the combination of equation (3-2) and (3-3) and method 4 was the combination of equation (3-4) and (3-5).

Methods 1 and 2 yield two sets of binary constants from a binary system while methods 3, 4 and 5 yield only one set of binary constants. A detailed description of the computer program is presented in the Appendix.

(B) Ternary Constant In the Margules Equation. Wohl (27) defines binary constants in terms of interaction constants

$$A_{12} = 2a_{12} + 3a_{122} \quad ,$$
$$A_{21} = 2a_{12} + 3a_{112} \quad ,$$
$$A_{23} = 2a_{23} + 3a_{233} \quad ,$$
$$A_{32} = 2a_{23} + 3a_{223} \quad , \qquad (3\text{-}27)$$
$$A_{13} = 2a_{13} + 3a_{133} \quad ,$$
$$A_{31} = 2a_{13} + 3a_{113} \quad ,$$

and a ternary constant,

$$C = 3a_{112} + 3a_{133} + 3a_{223} - 6a_{123} \quad , \qquad (3\text{-}28)$$

where a_{112}, a_{133}... are the empirical constants which measure the

interactions in various group of molecules 112, 133...

A new ternary constant C^* was more recently defined by Wohl (28),

$$C^* = \frac{3}{2} (a_{112} + a_{122} + a_{113} + a_{133} + a_{223} + a_{233}) - 6a_{123}.$$

$$(3-29)$$

By application of equation (3-27), it follows

$$C^* - C = \frac{1}{2}(A_{12} - A_{21} + A_{23} - A_{32} + A_{31} - A_{13}) \quad . \qquad (3-30)$$

In this work the older definition of C (27) as given by equation (3-28) was used.

In the ternary three-suffix Margules equation, the ternary constant has its greatest influence on the calculated value of $\log\gamma_k$ when $x_i x_j (1-2x_k)$ has its maximum value. The maximum value of $x_i x_j (1-2x_k)$ occurs for very small values of x_k and equal values of x_i and x_j; the term vanishes when $x_k=\frac{1}{2}$ and reverses its sign for higher values of x_k. The most suitable region of concentration in which to determine the ternary constant from experimental data is the liquid concentration which makes the value of $x_i x_j (1-2x_k)$ as large as possible. In this work, ternary constants were determined by the following procedure.

The ternary constant C was calculated from the binary constants and the experimental value of the ternary activity coefficients from the following equation,

$$C = - \frac{\log\gamma_{ex.} - \log\gamma_{cal.}, \ C=0}{x_i x_j (1-2x_k)} \quad . \qquad (3-31)$$

$\log\gamma_{cal.}, \ C=0$ is the value of $\log\gamma$ calculated with only binary constants. From a given set of experimental data three different

average values of C were evaluated for comparison:

1) using all data points.

2) using only the data points where x is greater than 0.05.

3) using the data points where x is greater than 0.05 as well as $x_i x_j (1-2m_L)$ greater than 0.1.

Concentrations smaller than 0.05 are ignored because of the difficulty in obtaining accurate analysis of the component when the concentration is relatively small and the fact that small errors in the composition result in large variations in the activity coefficient.

The average values of the ternary constants, which were evaluated under the condition 3, were used to obtain a more satisfactory fit in the activity coefficient equation.

A flow diagram and a detailed computer program are shown in the Appendix.

RESULTS AND DISCUSSION

A. General Results. Vapor-liquid equilibrium data for only 11 non-aqueous ternary systems could be found in the literature. Table 1 gives the components of these systems and the references.

Binary constants used in the calculations were obtained by the methods described in a previous chapter or from the literature. These are listed on Table 2. On Figures 1 through 19 the experimental data and the Margules equation are compared for most of the binary pairs comprising the eleven ternary systems. On these figures the solid line is a plot of the Margules equation with

constants evaluated by method 4.

Results of calculations of the three-suffix Margules equation are presented in Tables 4, 5, 6, 7, 8, 12, 13, 14, 15, 16 and 17 which give the ternary constant and the average of the absolute value of the percent deviation of calculated γ with C=0 from the observed γ for each component in the three different cases.

1. Using all data points.
2. Using only the data points where x is greater than 0.05.
3. Using only the data points where x is greater than 0.05 as well as $x_i x_j (1-2x_k)$ greater than 0.1.

When it was found necessary to use a ternary constant the absolute value of the percent deviation of γ calculated with C, from the observed γ for each component was also tabulated.

The calculations were made by computer. In order to ensure that no mistakes were made in the processing or programing, the results were checked by hand calculation for a few systems.

B. Discussion.

System: Benzene - Cyclohexane - Methylcellosolve

Figures 1 and 2 are plots of logγ versus x for the Benzene - Methylcellosolve and Cyclohexane - Methylcellosolve binary systems.

The three-suffix Margules equation fit the data in Figure 1 well but did poorly in Figure 2. The absolute value of error shown in Table 3 is a good indication of how well the data are fitted by the binary Margules equation.

Table 1.   Components of Systems

System No.	Components of System (1)	(2)	(3)	Ref.
1	Benzene	Cyclohexane	Methylcellosolve	(20)
2	Benzene	Cyclohexane	Furfural	(19)
3	Isooctane	Toluene	Furfural	(21)
4	Benzene	Cyclohexane	Acetone	(9)
5	MEK*	n-Heptane	Toluene	(17)
6	Ethylacetate	Benzene	Cyclohexane	(4)
7	Benzene	Cyclohexane	MIBK**	(5)
8	Benzene	Cyclohexane	MEK*	(6)
9	Benzene	Cyclohexane	Trichloroethylene	(12)
10	Benzene	CCl4	Ethanol	(2)
11	CCl4	MEK*	Cyclohexane	(11)

*   Methyl ethyl ketone
**   Methyl isobutyl ketone

Table 2. Margules Binary Constants

System No.	A13	A31	A23	A32	A12	A21	Re-mark
1	0.3278	0.7044	0.7526	1.1910	0.1738	0.1515	a
	0.3100	0.6440	0.6980	0.9750	0.1600	0.1600	b
2	0.2450	0.2830	0.7420	1.0460	0.1600	0.1600	b
	0.2419	0.2528	0.8812	1.0260	0.1738	0.1515	a
3	0.9200	1.0137	0.5232	0.2917	0.1203	0.1017	a
	0.8844	0.9214	0.4832	0.3525	0.1293	0.1453	b
4	0.1107	0.1773	0.8420	0.4010	0.1580	0.1580	b
5	0.1995	0.1184	0.1422	0.1047	0.4965	0.5150	a
	0.1942	0.1202	0.1430	0.0950	0.4894	0.4706	b
6	0.4253	0.3621	0.1364	0.1567	0.0410	0.0328	a
7	0	0	0.1000	0.4100	0.1580	0.1580	b
	0	0	0.0690	0.4421	0.1364	0.1567	a
8	0.1204	0.2685	0.4686	0.4546	0.1364	0.1567	a
9	0	0	0.1100	0.1800	0.1580	0.1580	b
	0	0	0.1026	0.1686	0.1364	0.1567	a
10	0.5850	0.8510	0.6240	0.9570	0.0420	0.0337	a
11	0	0	0.5010	0.4040	0.1600	0.2200	b

a Calculated by method 4.

b From literature.

FIG.1 BENZENE-METHYLCELLOSOLVE SYSTEM

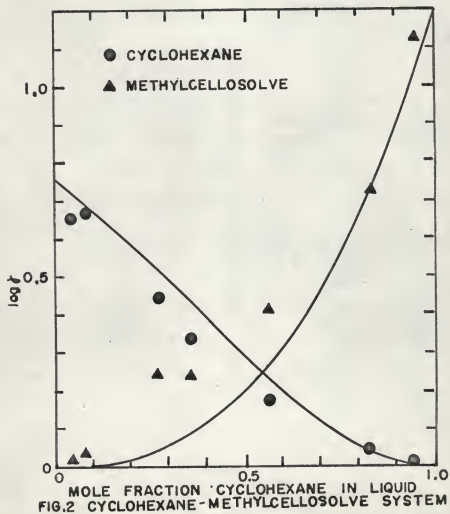FIG.2 CYCLOHEXANE-METHYLCELLOSOLVE SYSTEM
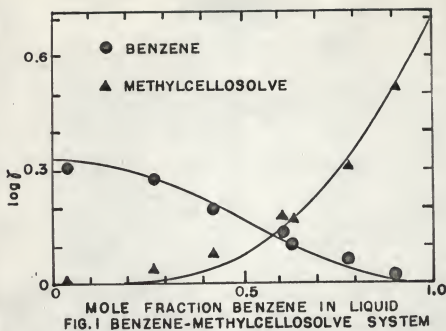
Table 3. Average of the Absolute Value of the Percent Deviation of γ_{cal} from γ_{exp} for Binary Systems

Binary systems	A_{12}	A_{21}	Absolute value of percent error	
			Component 1	Component 2
Benzene - Methylcellosolve	0.3278	0.7044	2.8%	4.5%
Cyclohexane - Methylcellosolve	0.7526	1.1910	10.5%	6.4%
Benzene - Cyclohexane	0.1738	0.1515	0.2%	0.3%

Table 4. Average of the Absolute Value of the Percent Deviation of Ternary γ_{cal} from γ_{exp}

Component	Binary constants from Reference 21		Binary constants by method 4	
	$C = 0$	$C = -1.6$	$C = 0$	$C = -1.5$
Benzene	15.96	6.85	15.50	5.45
Cyclohexane	16.31	13.21	12.60	18.03
Methylcellosolve	13.43	6.28	8.18	10.87

A comparison of the absolute value of the deviation of γ_{cal} with and without C from γ_{exp} is shown in Table 4. It appears that the system needs a ternary constant for more satisfactory ternary activity coefficient calculation. This might be due to the fact that only a few experimental points were presented for

the binary system Cyclohexane - Methylcellosolve and the Margules
binary equation did not correlate the binary data very well. On
the other hand the other two binary systems were fitted quite
well with the Margules equation. The agreement is better using
Thornton and Garner's constants than with computer calculated
constants. Also their ternary constant made the calculated results
more satisfactory.

System: Benzene - Cyclohexane - Furfural

Plots of logγ versus x for the three binary systems, Benzene -
Cyclohexane, Benzene - Furfural, and Cyclohexane - Furfural are
shown in Figures 3, 4, and 5. The binary data for these three
binary systems fit the binary Margules equations fairly well.

Table 5 shows the absolute value of the percent error of the
calculated activity coefficients from the experimentally deter-
mined activity coefficients. These are compared with and with-
out use of a ternary constant. The ternary constant does not
improve the results in activity coefficient calculation very much.
It is evident that a ternary constant is not necessary in the
system.

FIG. 3 BENZENE-CYCLOHEXANE SYSTEM

FIG. 4 BENZENE-FURFURAL SYSTEM

FIG.5 CYCLOHEXANE-FURFURAL SYSTEM
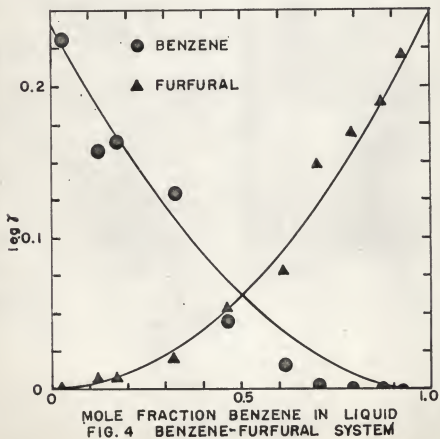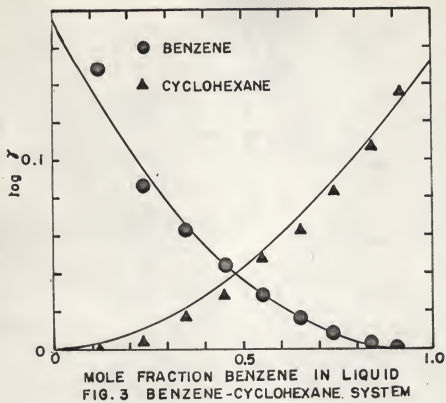
Table 5. Average of the Absolute Value of the Percent Deviation of γ_{cal} from γ_{exp}

Component	Binary constants from Reference 21		Binary constants by method 4	
	$C = 0$	$C=-0.251$	$C = 0$	$C=-0.251$
Benzene	8.14	6.17	9.64	7.14
Cyclohexane	7.17	8.93	9.08	12.11
Furfural	5.15	4.65	7.33	7.21

System: Isooctane - Toluene - Furfural

Figures 6, 7 and 8 are plots of $\log\gamma$ versus x for Isooctane - Toluene, Toluene - Furfural, and Isooctane - Furfural. The binary Margules equation correlates the binary systems reasonably well.

Table 6 shows that the ternary constant C=-0.317 proposed by Thornton and Garner is not much help in correlation of the activity coefficients of the system. The small value of C indicates that activity coefficients in the ternary system could be correlated relatively well without the ternary constant.

Table 6. Average of the Absolute Value of the Percent Deviation of γ_{cal} from γ_{exp}

Component	Binary constants from Reference 21		Binary constant by method 4	
	$C = 0$	$C=-0.317$	$C = 0$	$C=-0.200$
Isooctane	8.17	4.82	6.99	5.09
Toluene	3.38	3.19	5.76	4.18
Furfural	3.50	3.29	4.36	4.63

MOLE FRACTION ISOOCTANE IN LIQUID
FIG.6 ISOOCTANE-TOLUENE SYSTEM

FIG. 7 TOLUENE-FURFURAL SYSTEM

FIG. 8 ISOOCTANE-FURFURAL SYSTEM
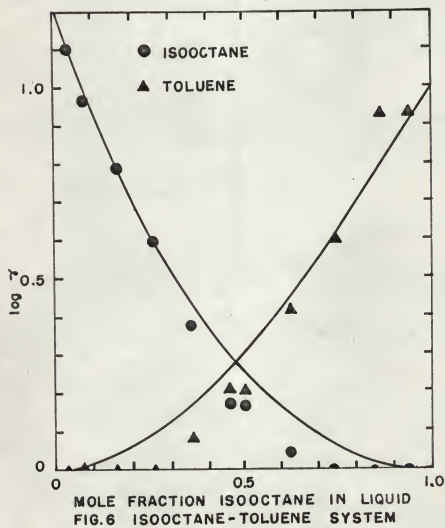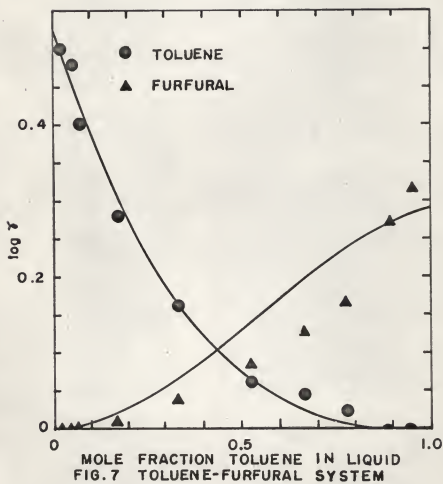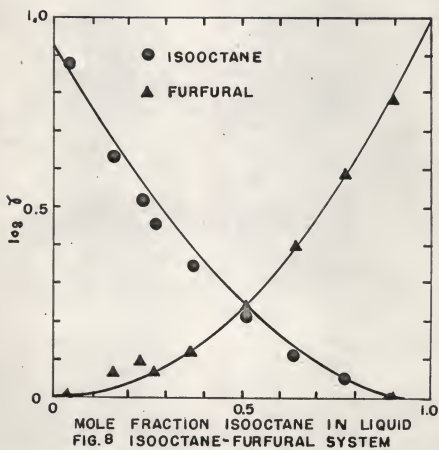
System: Benzene - Cyclohexane - Acetone

Binary constants were not calculated for this system because the binary equilibrium data were reported only in the form of constants in the three-suffix Margules equation.

The ternary constant, C^t, which the investigators of this system used is equivalent to $A_{21} + A_{13} + A_{32} - C$. (i. e. $C = A_{21} + A_{13} + A_{32} - C^t$). Using their reported value of C^t and the above relation, a value of -0.03 was obtained for C. Values of δ_1, δ_2, δ_3 were calculated with and without this ternary constant. The deviation of these calculated δ from experimental γ are shown on Table 7. It can be seen that a ternary constant is not necessary in the three-suffix Margules equations. Furthermore Table 7 shows that if the data points which satisfy the condition x smaller than 0.05 were omitted, the absolute value of the average deviation would be reduced.
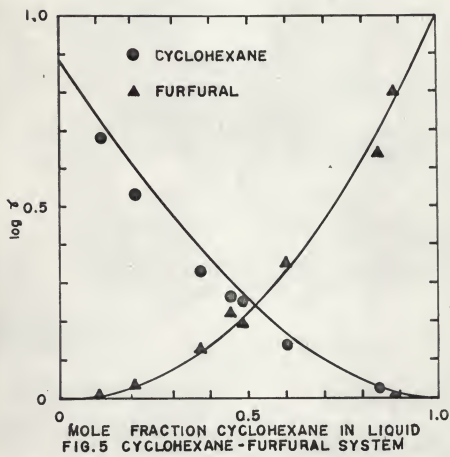
Table 7. Average of the Absolute Value of the Percent Deviation of γ_{cal} from γ_{exp}

Component	All data points			The points where $x > 0.05$	
	No. of data points	Deviation		No. of data points	Dev.
		$C = 0$	$C = -0.03$		$C = 0$
Benzene	60	7.47	7.99	52	6.80
Cyclohexane	60	14.76	14.20	46	11.60
Acetone	60	6.63	6.69	45	5.65

Systems: Methyl ethyl ketone - Heptane - Toluene

Table 8 shows that the average of the absolute value of the percent error of δ for x_3 greater than 0.05 is very much reduced from the average absolute percent error obtained from all data points. This is probably due to the difficulty in obtaining accurate analysis of the component present in relatively small concentrations. Figures 9, 10, and 12 show that the three constituent binaries of the ternary system are excellently represented by the binary Margules equation. The average of the absolute value of the percent error between calculated and experimental δ for these three binary systems is less than 2 percent. These systems are listed on Table 9. The Margules constants determined by several methods are very close to each other. They are listed on Table 10.

Table 8. Average of the Absolute Value of the Percent Deviation of δ for Ternary System

Component	Binary constants from Reference 17				Binary constants by method 4			
	All data		$x > 0.05$		All data		$x > 0.05$	
	No. of data	dev.	No. of data	dev.	No. of data	dev.	No. of data	dev.
Methyl-ethyl-ketone	60	2.10	52	1.56	60	2.76	52	2.22
Heptane	60	2.20	46	1.70	60	2.55	46	2.12
Toluene	60	14.50	45	1.34	60	15.75	45	2.12

The ternary system shows less than 3 percent deviation be-

FIG.9 HEPTANE-TOLUENE SYSTEM

MOLE FRACTION HEPTANE IN LIQUID

FIG.10 MEK-TOLUENE SYSTEM

MOLE FRACTION MEK IN LIQUID
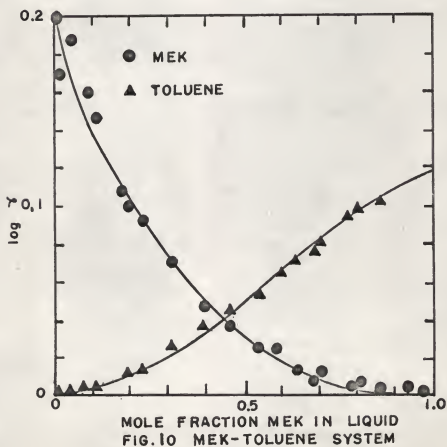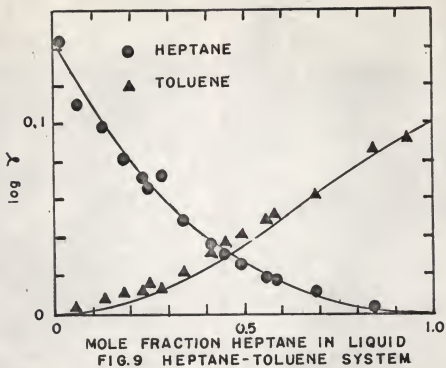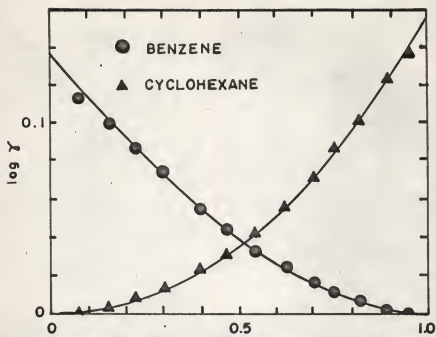
FIG.11 BENZENE-CYCLOHEXANE SYSTEM
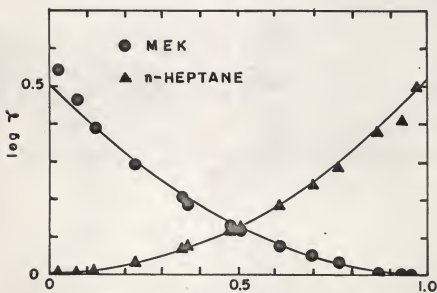
FIG.12 MEK-n-HEPTANE SYSTEM

tween calculated δ and observed δ, therefore no ternary constants
are necessary.

Table 9. Absolute Value of the Percent Deviation
of γ_{cal} from γ_{exp}

	MEK-Toluene		n-Heptane-Toluene		MEK-Heptane	
	A13 0.1995	A31 0.1184	A23 0.1422	A32 0.1047	A12 0.4965	A21 0.5150
Component 1	0.56		0.73		1.26	
Component 2	0.37		0.62		1.21	

Table 10. Margules Binary Constants for the System
MEK - n-Heptane - Toluene

	A13	A31	A23	A32	A12	A21	
Method 1	0.1809	0.1284	0.1207	0.1166	0.3799	0.5293	a
	0.2100	0.0941	0.1710	0.0811	0.5286	0.4240	b
Method 2	0.1811	0.1277	0.1381	0.1114	0.4658	0.5063	a
	0.1990	0.1168	0.1664	0.0993	0.5181	0.4557	b
Method 3	0.2104	0.1280	0.1711	0.1154	0.5214	0.5371	
Method 4	0.1995	0.1184	0.1422	0.1047	0.4965	0.5150	
Method 5	0.1983	0.1172	0.1624	0.1029	0.4927	0.5053	
From Reference 17	0.1942	0.1202	0.1430	0.0950	0.4894	0.4706	

a   determined from γ-x data for component 1.
b   determined from γ-x data for component 2.

System: Ethylacetate - Benzene - Cyclohexane

The binary constants determined by method 4 described in the

previous section are in agreement with those of Chao and Hougen
(4) determined by the method of least squares using a computer.
Their two constant Redlich-Kister equation is equivalent to the
three-suffix Margules equation of Wohl. The constants are present-
ed on Table 11 for comparison.

Table 11. Comparison of Binary Constants

Binary System	From Reference 13				Margules Constants by method 4	
	R-K Constants		Margules Constants			
	b_{12}	c_{12}	A_{12}	A_{21}	A_{12}	A_{21}
Ethylacetate(1) Benzene (2)	0.0369	-0.0041	0.0410	0.0328	0.0410	0.0328
Benzene (1) Cyclohexane(2)	0.1443	0.0100	0.1343	0.1543	0.1364	0.1568
Cyclohexane(1) Ethylacetate(2)	0.3849	-0.0321	0.4170	0.3528	0.4253	0.3621

Figures 11, 13 and 14 are plots of $\log \gamma$ versus composition
for the three binary systems. Agreement is very good over all
concentrations. The ternary three-suffix Margules equation
without the ternary constant gives very good results in correlation
of ternary vapor-liquid equilibrium. The results are shown in
Table 12.

MOLE FRACTION CYCLOHEXANE IN LIQ.
FIG.13 CYCLOHEXANE-ETHYLACETATE

MOLE FRACTION ETHYLACETATE IN LIQ.
FIG.14 ETHYLACETATE-BENZENE SYSTEM
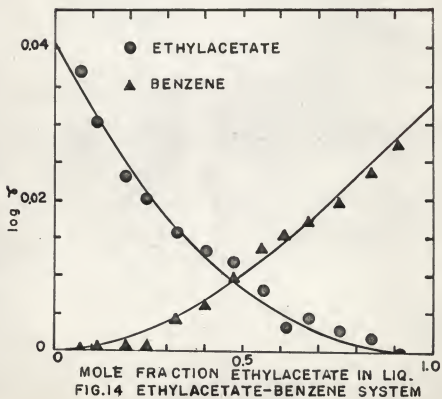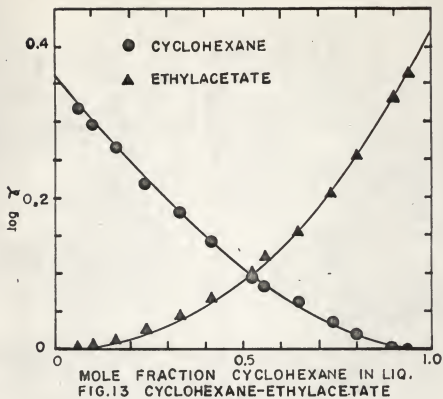
Table 12. Average of the Absolute Value of the Percent
Deviation of γ_{cal} from γ_{exp}

Component	All data		the data where $x > 0.05$		the data where $x > 0.05$, $u < 0.1$	
	No. of data	Dev.	No. of data	Dev.	No. of data	Dev.
Ethylacetate	77	1.14	77	1.14	14	1.87
Benzene	77	0.87	76	0.328	11	1.37
Cyclohexane	77	0.917	77	0.917	17	1.75

This is also in agreement with Chao and Hougen's statement, (4) " No additional constants were required for ternary effects."

System: Benzene - Cyclohexane - Methylisobutylketone

For the Benzene - Cyclohexane system the binary constants were taken from the previous work. Benzene - Methylisobutylketone is nearly an ideal solution and zero can be used for these binary constants.

The binary constants for the Cyclohexane-Methylisobutylketone system were determined. The plot of $\log \gamma$ versus composition is given in Figure 15. An examination of the Figure 15 reveals that this data did not fit the curve well when x_1 approaches zero, this poor correlation might cause more deviation when the binary constants of this system are used in the ternary three-suffix Margules equation to predict the vapor-liquid equilibrium. Deviations of the activity coefficients in the ternary system are presented in Table 13.

FIG.15 CYCLOHEXANE-MIBK SYSTEM
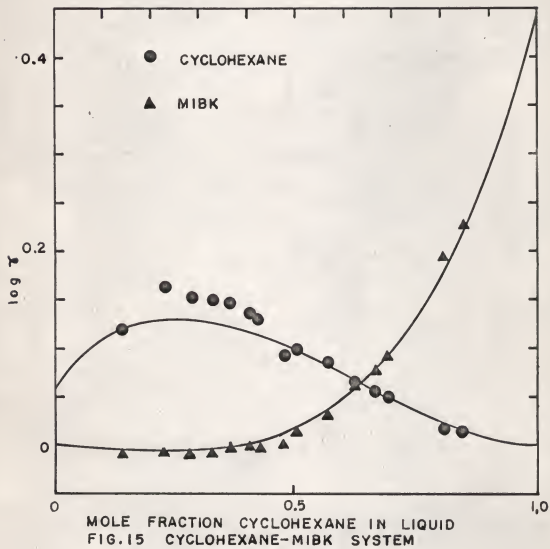
Table 13. Average of the Absolute Value of the Percent
           Deviation of γ_{cal} from γ_{exp}

Component	Binary Constants from Reference 5		Binary Constants by method 4	
	C = 0	C=-0.26	C = 0	C=-0.118
Benzene	3.56	3.98	3.59	3.48
Cyclohexane	9.52	8.37	9.71	8.82
MIBK	6.04	7.47	6.17	6.50

In reference to Table 13, the ternary constant reduced the
deviation of component two, but increased the deviation of the
other two components. From the view point of the total devia-
tion of three components, the ternary constant is not necessary
in this system. It seems that no ternary effect exists. The
above discussion is not in agreement with the statement of Rao
et. al (5). They state " As a first approximation C was assumed
to be zero and the activity coefficients were calculated; good
agreement was not obtained between the calculated and experimental
values. In order to obtain a more satisfactory fit of the data..
C was calculated .... By inserting these seven constants into the
three-suffix Margules equation of Wohl...... The average error
between calculated value and experimental activity coefficient
in γ_1, γ_2 and γ_3 are respectively 2.4 percent, 4 percent, and
4.5 percent. "

This disagreement might be due to the fact that the
calculations performed at K.S.U. were done by computer, whereas
their calculations were probably done by hand. In this work

average deviations are reported as absolute values; deviations
reported by Rao et. al. (5) were most likely averaged algebraically.

System: Benzene - Cyclohexane - Methylethylketone

These three binary systems were correlated very well by the
three-suffix Margules equation. Figures 16 and 17 show plots of
$\log \delta$ against x for two of the binary systems. The plot for
Benzene - Cyclohexane has already been presented in Figure 11.
In Table 14, the deviations for this system are seen to be within
limits of experimental accuracy. Hence the three-suffix Margules
equations represent the data fairly well without the ternary
constant.

Table 14. Average of the Absolute Value of the Percent
Deviation of δ_{cal} from δ_{exp}

Component	All data		The data where $x > 0.05$		The data where $x > 0.05$, $u > 0.1$	
	No. of data	Dev.	No. of data	Dev.	No. of data	Dev.
Benzene	86	5.47	77	4.62	5	2.31
Cyclohexane	86	6.11	78	5.77	14	9.51
MEK	86	7.98	81	7.16	13	11.75

System: Benzene - Cyclohexane - Trichloroethylene

Table 15 shows clearly that for this system the small ternary
constant was of no use in the Margules three-suffix equations.
Furthermore the binary constants exerted more influence than
the ternary constant in predicting vapor-liquid equilibrium in
this ternary system.
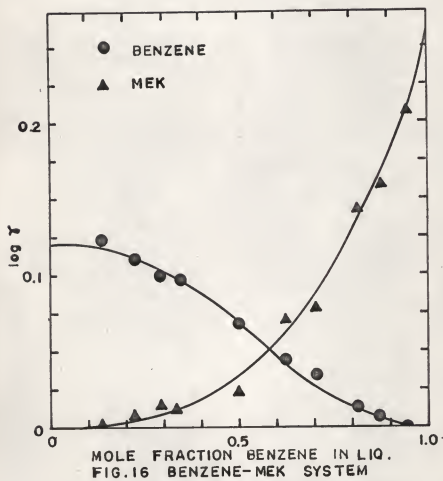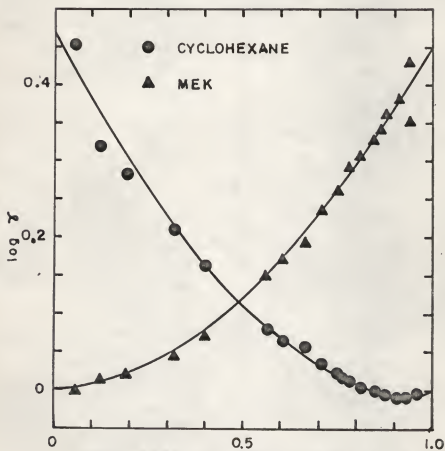
FIG.16 BENZENE-MEK SYSTEM

FIG. 17 CYCLOHEXANE-MEK SYSTEM

In the determination of binary constants, the Benzene - Trichloroethylene system behaves ideally, hence these binary constants are zero.

The constants of the well known system, Benzene - Cyclohexane were previously determined. For the Cyclohexane - Trichloroethylene system, $\log \gamma$ versus x is plotted in Figure 19. The binary Margules equation fits the experimental data fairly well.

Table 15. Average of the Absolute Value of the Percent Deviation of γ_{cal} from γ_{exp}

Component	Binary Constants from Reference 11		Binary Constants by method 4	
	$C = 0$	$C=0.094$	$C = 0$	$C=0.094$
Benzene	2.60	2.69	2.64	2.69
Cyclohexane	3.20	3.28	2.93	3.35
TCE	6.38	5.73	6.24	5.50

System: Benzene - Carbon tetrachloride - Ethyl alcohol

Figures 18, 20 and 21 show plots of $\log \gamma$ versus composition for the three constituent binary systems. It was found that the three-suffix Margules equation correlated the three binary systems well except for a few points which were obviously due to experimental errors.

Using six binary constants in the three-suffix Margules equation, the activity coefficients were calculated for the Benzene - Carbon tetrachloride - Ethyl alcohol system and the deviations from the observed activity coefficient are listed

FIG. 18 ETHANOL-BENZENE SYSTEM

FIG. 19 CYCLOHEXANE-TRICHLOROETHYLENE SYSTEM.

Figure 1 labels:
- CCl₄
- ETHANOL
- log γ
- 0.8
- 0.4
- 0
- 0.5
- 1.0
- MOLE FRACTION CCl₄ IN LIQ.
- FIG. 20 CCl–ETHANOL SYSTEM
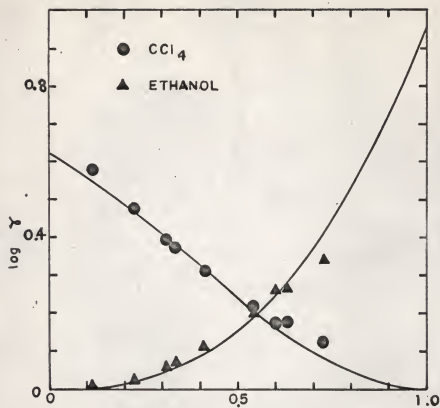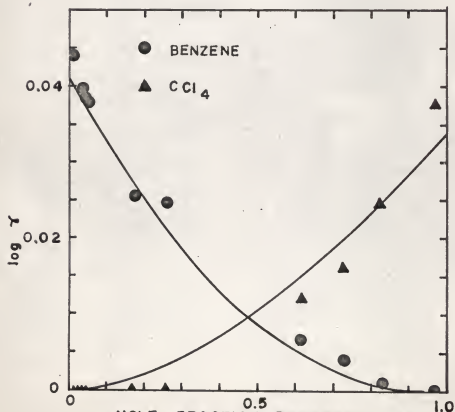
Figure 2 labels:
- BENZENE
- CCl₄
- log γ
- 0.04
- 0.02
- 0
- 0.5
- 1.0
- MOLE FRACTION BENZENE IN LIQ.
- FIG. 21 BENZENE-CCl₄ SYSTEM

in Table 16.

It appears that no ternary constant is necessary in this ternary system. Excluding concentrations less than 0.05 the agreement between calculated γ and observed γ was found even more satisfactory.

Table 16. Average of the Absolute Value of the Percent Deviation of γ_{cal} from γ_{exp}

Component	All data		The data where $x > 0.05$		The data where $x > 0.05$, $u < 0.1$	
	No. of data	Dev.	No. of data	Dev.	No. of data	Dev.
Benzene	51	8.99	44	6.16	37	4.33
CCl$_4$	51	5.93	36	4.55	31	3.56
Ethyl alcohol	51	8.67	41	4.00	39	4.07

System: Carbon tetrachloride-Methylethylketone-Cyclohexane

No binary data have been reported for these systems. However binary Margules constants are available. The ternary activity coefficients were computed by substituting the six binary constants and one ternary constant given by Rao (11) into the three-suffix Margules equation. The deviation from the observed activity coefficients are listed in Table 17.
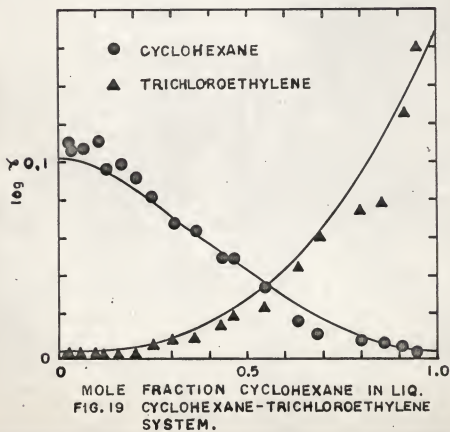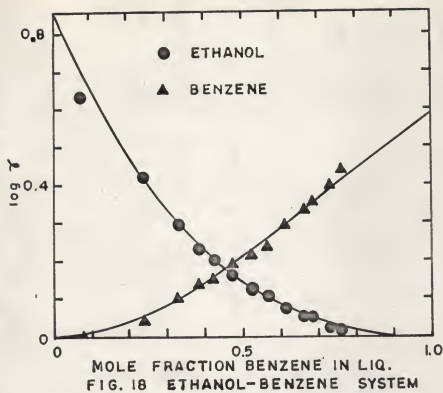
Table 17. Average of the Absolute Value of the Percent
Deviation of γ_{cal} from γ_{exp}

Component	Deviation computed by author		Deviation reported in reference 11
	$C = 0$	$C=-0.314$	$C=-0.314$
CCl_4	5.99	3.28	3.54
MEK	10.14	8.03	4.43
Cyclohexane	6.62	5.83	4.24

In this work the absolute value of the deviations were taken;
whereas Rao did not mention whether his deviations were absolute
or not. In Table 17 all calculations were made with Rao's report-
ed binary constants. The system seems to need a small ternary
constant to make the ternary Margules equation fit the data more
satisfactorily.

CONCLUSION

The results show that if each of the three binary systems comprising the ternary system could be correlated well by the three-suffix Margules equation, the prediction of the ternary relationships could be made without a ternary constant in most cases. The precision of the prediction of an activity coefficient in the ternary system is about the same as in the binary Margules equation fit of the binary data. For example, in the Ethylacetate - Benzene - Cyclohexane system each binary Margules equation fit the data to within one percent, and the ternary activity coefficients were predicted to about one percent error. This should not be the case in a ternary system where one of the three constituent binary systems was not well represented by the Margules equation.

The activity coefficient is sensitive to temperature, but the three-suffix Margules equation still can be applied to isobaric systems where the temperature range in the ternary systems is approximately the same range as in the binary systems. The Methylethylketone - n-Heptane - Toluene system is a good example of this.

Five different ways of determining Margules binary constants were presented. As far as the computer calculation is concerned, method 4 is the best one. The results also show that method 4 is more satisfactory in ternary activity coefficient calculation.

The results indicate that systems which were fitted well without a ternary constant usually showed small deviations from ideal behavior.

ACKNOWLEDGMENT

NOMENCLATURE

A	Binary constant (double subscripts); Antonine constant (single subscripts)
a	Empirical constant
B	Antonine constant
b	Redlich-Kister constant
C	Ternary constant; Antonine constant
c	Redlich-Kister constant
G	Total free energy
n	Number of data points; Number of moles of component
p	Vapor pressure
q	Effective molal volume
R	Gas constant
r	The function defined in Equation (3-8)
s	The function defined in Equation (3-8)
T	Absolute temperature, $^\circ K$
x	mole fraction
z	Effective molal volume fraction
Δ	Increment
ΔG^E	Molar excess free energy
ln	logarithm base e
log	logarithm base 10
var	Sum of squares of deviations of measured values from calculated values
γ	Activity coefficient, standard state taken as pure substance

θ	The function defined in Equation (3-13)
w	The function defined in Equation (3-14)

Subscripts

1	Component 1
2	Component 2
3	Component 3
i	i^{th} component

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APPENDIX

Description of Computer Program

a)

Title: Program for the calculation of Margules constants by the method of least squares.

Computer: IBM 1620 with 60,000 positions of storage.

Program language: Fortran.

Description: The program was used to determine binary Margules constants by the method of least squares. A maximum of 50 data points was provided. The point values of A_{12} and A_{21} at each liquid composition were calculated first. The binary constants were calculated by five methods then these constants were used in equation (2-7) and the average of the absolute value of the percent deviation between calculated and experimental activity coefficient was evaluated for each of the five methods.

Input cards were read in the following order;

Card 1. Title or comment less than 49 characters including blanks in the body of the comment.

Card 2. M, N

M is a fixed point constant showing the type of input activity coefficient data. N is also a fixed point constant representing the number of sets of experimental measurements.

Sample input data cards were arranged as following depending on a fixed point constant M;

for M = 1   Constant pressure with x, y, t

Card 3. A_1, B_1, C_1, A_2, B_2, C_2

Card 4. $\overline{\Pi}$

Card 5. x_1, y_1, t_1
    •   •
    •   •
Card $(4+N)$ x_N, y_N, t_N

for M = 2   constant pressure with x, y, P1, P2

Card 3. Π

Card 4. x_1, y_1, P_{11}, P_{21}
    •   •
    •   •
Card $(3+N)$ x_N, y_N, P_{1N}, P_{2N}

for M= 3   constant temperature with x, y, Π

Card 3. P_1^o, P_2^o

Card 4. x_1, y_1, Π_1
    •   •
    •   •
Card $(3+N)$ x_N, y_N, Π_N

for M = 4 γ are available

Card 3. x_1, y_1, γ_{11}, γ_{21}
    •   •
    •   •
Card $(2+N)$ x_N, y_N, γ_{1N}, γ_{2N}

for M = 5 $\ln \gamma$ are available

Card 3. x_1, y_1, $(\ln \gamma_1)_1$, $(\ln \gamma_2)_1$
    •   •
    •   •
Card $(2+N)$ x_N, y_N, $(\ln \gamma_1)_N$, $(\ln \gamma_2)_N$

for M = 6 $\log \gamma$ are available

Card 3. x_1, y_1, $(\log \gamma_1)_1$, $(\log \gamma_2)_1$

Card 4. x_2, y_2, $(\log \gamma_1)_2$, $(\log \gamma_2)_2$
.   .
.   .
.   .
Card (2+N) x_N, y_N, $(\log \gamma_1)_N$, $(\log \gamma_2)_N$

All output is printed on the console typewriter in the following format:

Title: Benzene - Cyclohexane

The point value of Margules constants,

x_1	A_{12}	A_{21}
....	....	....
....	....	....
....	....	....
Average	....	....

Benzene

	A_{12}	A_{21}	Percent Error
Method 1	....	....	....
Method 2	....	....	....
Method 3	....	....	....
Method 4	....	....	....
Method 5	....	....	....

Cyclohexane

	A_{12}	A_{21}	Percent Error
Method 1	....	....	....
Method 2	....	....	....
Method 3	....	....	....
Method 4	....	....	....
Method 5	....	....	....

Console setting for operation:

Overflow check switch - program

All other check switches - stop

Sense switches 1, 2, 3, 4 - immaterial

BLOCK DIAGRAM FOR USE WITH IBM 1620 FOR COMPUTING MARGULES CONSTANT

START

READ, M, N

M = ?

M = 1 | M = 2 | M = 3 | M = 4 | M = 5 | M = 6

M = 1:
READ, A1, B1, C1, A2, B2, C2
READ, π
X Y T
CALC. γ, log γ
J = N — NO / YES

M = 2:
READ, π
X, Y, P_1, P_2
CALC. γ, log γ
J = N — NO / YES

M = 3:
READ, P_1°, P_2°
READ, X, Y, π
CALC. γ, log γ
J = N — NO / YES

M = 4:
READ X, Y, γ_1, γ_2
CALC. log γ
J = N — NO / YES

M = 5:
READ X, Y, ln γ_1, ln γ_2
CALC. γ, log γ
J = N — NO / YES

M = 6:
READ X, Y, log γ_1, log γ_2
CALC. γ
J = N — NO / YES

1

```
        ┌───┐
        │ I │
        └───┘
          │
          ▼
┌─────────────────────┐
│  CALCULATE POINT    │
│  VALUES OF A₁₂,A₂₁  │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│  CALCULATE A₁₂,A₂₁  │
│  BY EQ.(3-2) TO     │
│  EQ.(3-7)           │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│  CALCULATE AVERAGE  │
│  VALUE OF ABSOLUTE  │
│  DEVIATION USING    │
│  DIFFERENT A₁₂,A₂₁  │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│  PRINT, A₁₂,A₂₁     │
│  PERCENT ERROR      │
│  FOR 5 METHODS      │
└─────────────────────┘
          │
          ▼
      ┌─────────┐
      │  START  │
      └─────────┘
```

CALCULATE POINT VALUES OF A_{12}, A_{21}

CALCULATE A_{12}, A_{21} BY EQ.(3-2) TO EQ.(3-7)

CALCULATE AVERAGE VALUE OF ABSOLUTE DEVIATION USING DIFFERENT A_{12}, A_{21}

PRINT, A_{12}, A_{21} PERCENT ERROR FOR 5 METHODS

START

```
C   DETERMINATION OF MARGULES CONSTANTS BY THE METHOD OF LEAST SQUARES
    DIMENSION SXU(2), GALOC(2,50), U(2,50), SN(2), SU(2), SX(2)
    DIMENSION BA1(2,50), BA2(2,50), BA(2,50), SBA(2), AB(2), SVV(2)
    DIMENSION SVR(2), SRR(2), SUV(2), SUR(2), GAA(2,50), GAB(2,50)
    DIMENSION SVVX(2), SVVXX(2), SGV(2), SGVX(2), CC(2), CD(2), GAC(2,50)
    DIMENSION VAPRO(2), CE(2), CF(2), GCLOC(2,50), GDLOC(2,50)
    DIMENSION A(2), B(2), C(2), PO(2), X(2,50), Y(2,50), T(50), SL(2)
    DIMENSION GA(2,50), GALN(2,50), GALOE(3,50), SXX(2), AA(2), BB(2)
    DIMENSION S2(2), A12(2), A21(2), DEV(2,50), P(2,50), S4(2), S5(2)
    DIMENSION GBLOC(2,50), S3(2), SM(2), GAD(2,50), SV(2), GAE(2,50)
    DIMENSION GELOC(2,50)
1   FORMAT (E12.6)
2   FORMAT (I2, I2)
3   FORMAT ( E12.6, E12.6 )
4   FORMAT ( E12.6, E12.6, E12.6, E12.6 )
5   FORMAT ( E12.6, E12.6, E12.6, E12.6, E12.6 )
6   FORMAT ( E12.6, E12.6, E12.6, E12.6, E12.6, E12.6 )
7   FORMAT(6HMETHOD I4, 2X E12.6, E12.6, E12.6 )
8   FORMAT (12HAVERAGEVALUE E12.6, E12.6 )
9   FORMAT (/17X 3HA12 9X 3HA21 6X 10HPERCENT ER )
10  PAUSE
    READ 16
    READ 2, M, N
    PRINT 16
    GO TO ( 11, 12, 13, 14, 14, 14 ), M
11  READ 6, A(1), B(1), C(1), A(2), B(2), C(2)
12  READ 1, PI
    GO TO 14
13  READ 3, VAPRO(1), VAPRO(2)
14  SO=0.
    SQ=0.
    SR=0.
    SS=0.
    SW=0.
    DO 15 I=1,2
    S1(I)=0.
    S2(I)=0.
    S3(I)=0.
    S4(I)=0.
    S5(I)=0.
    SBA(I)=0.
    SGV(I)=0.
    SGVX(I)=0.
    SN(I)=N
    SM(I)=N
    SU(I)=0.
    SV(I)=0.
    SX(I)=0.
    SXU(I)=0.
    SRR(I)=0.
    SVR(I)=0.
```

```
      SVV(I)=0.
      SVVX(I)=0.
      SVVXX(I)=0.
      SUR(I)=0.
      SUV(I)=0.
  15  SXX(I)=0.
  16  FORMAT (49H THE POINT VALUE OF MARGULES CONSTANTS)                    )
  17  FORMAT (38HTHE POINT VALUE OF MARGULES CONSTANTS)
  18  FORMAT (/5X 2HX1 9X 3HA12 9X 3HA21)
  19  FORMAT ( E12.6, E12.6, E12.6 )
      DO 20 J=1,N
      READ 5, X(1,J), Y(1,J), T(J), P(1,J), P(2,J)
      Y(2,J)=1.-Y(1,J)
  20  X(2,J)=1.-X(1,J)
      DO 33 I=1,2
      DO 33 J=1,N
      GO TO ( 21, 23, 22, 24, 26, 28 ), M
  21  P(I,J)=EXP(2.302585*(A(I)-B(I)/(C(I)+T(J))))
      GO TO 23
  22  P(I,J)=VAPRO(I)
      PI=T(J)
  23  GA(I,J)=PI*Y(I,J)/P(I,J)/X(I,J)
      GO TO 25
  24  GA(I,J)=P(I,J)
  25  GALN(I,J)=LOG(GA(I,J))
      GO TO 27
  26  GALN(I,J)=P(I,J)
      GA(I,J)=EXP(GALN(I,J))
  27  GALOE(I,J)=GALN(I,J)/2.302585
      GO TO 29
  28  GALOE(I,J)=P(I,J)
      GA(I,J)=EXP(2.302585*GALOE(I,J))
  29  U(I,J)=GALOE(I,J)/((1.-X(I,J))**2)
  30  FORMAT (///)
  32  SU(I)=SU(I)+U(I,J)
      SX(I)=SX(I)+X(I,J)
      SXX(I)=SXX(I)+X(I,J)*X(I,J)
   SXU(I)=SXU(I)+X(I,J)*U(I,J)
      SV(I)=SV(I)+(1.-X(I,J))**4
      SVV(I)=SVV(I)+(1.-2.*X(I,J))**2
      SVR(I)=SVR(I)+(1.-2.*X(I,J))**2.*X(I,J)
      SRR(I)=SRR(I)+4.*X(I,J)**2
      SUV(I)=SUV(I)+U(I,J)*(1.-2.*X(I,J))
      SUR(I)=SUR(I)+U(I,J)*2.*X(I,J)
      SVVX(I)=SVVX(I)+(1.-X(I,J))**4*X(I,J)
      SVVXX(I)=SVVXX(I)+(1.-X(I,J))**4*X(I,J)**2
      SGV(I)=SGV(I)+GALOE(I,J)*(1.-X(I,J))**2
      SGVX(I)=SGVX(I)+GALOE(I,J)*(1.-X(I,J))**2*X(I,J)
  33  CONTINUE
      PRINT 30
      PRINT 17
```

```
      DO 50 I=1,2
      DO 49 J=1,N
      GALOE(3,J)=GALOR(1,J)
      BA1(I,J)=GALOR(I,J)/(1.-X(I,J))**2
      BA2(I,J)=2.*X(I,J)*(GALOE(I+1,J)/X(I,J)**2-BA1(I,J))
      BA(I,J)=BA1(I,J)+BA2(I,J)
      IF ( X(I,J)-0.15 ) 35, 36, 34
   34 IF ( X(I,J)-0.85 ) 36, 36, 35
   35 SN(I)=SN(I)-1.
      GO TO 49
   36 SBA(I)=SBA(I)+BA(I,J)
   49 CONTINUE
   50 SBA(I)=SBA(I)/SN(I)
      PRINT 18
      DO 60 J=1,N
   60 PRINT 19, X(1,J), BA(1,J), BA(2,J)
      PRINT 8, SBA(1), SBA(2)
      DO 70 I=1,2
      CC(I)=SV(I)*SVVXX(I)-SVVX(I)**2
      CD(I)=(SGV(I)*SVVXX(I)-SGVX(I)*SVVX(I))/CC(I)
      CE(I)=(SV(I)*SGVX(I)-SGV(I)*SVVX(I))/CC(I)
      CF(I)=CD(I)+0.5*CE(I)
      AA(I)=(SU(I)*SXX(I)-SX(I)*SXU(I))/(SM(I)*SXX(I)-SX(I)*SX(I))
      BB(I)=(SM(I)*SXU(I)-SX(I)*SU(I))/(SN(I)*SXX(I)-SX(I)*SX(I))
   70 AB(I)=AA(I)+0.5*BB(I)
      DTA1=SVV(1)+SRR(2)
      DTA2=SVR(1)+SVR(2)
      DTB2=SRR(1)+SVV(2)
      DTC1=SUV(1)+SUR(2)
      DTC2=SUR(1)+SUV(2)
      A12(1)=(DTC1*DTB2-DTC2*DTA2)/(DTA1*DTB2-DTA2**2)
      A21(1)=(DTA1*DTC2-DTA2*DTC1)/(DTA1*DTB2-DTA2**2)
      DO 80 J=1,N
      SQ=SQ+GALOE(1,J)*X(2,J)**2*(1.-2.*X(1,J))+2.*GALOE(2,J)*X(2,J)*(1,J)**2
      SW=SW+GALOE(1,J)*2.*X(1,J)*X(2,J)**2+GALOE(2,J)*X(1,J)**2*(1.-2.*X(2,J))
      SQ=SQ+X(2,J)**4*(1.-2.*X(1,J))**2+4.*X(1,J)**4*X(2,J)**2
      SR=SR+2.*(1.-2.*X(1,J))*X(1,J)*X(2,J)*(X(2,J)**3-X(1,J)**3)
   80 SS=SS+4.*X(1,J)**2*X(2,J)**4+X(1,J)**4*(1.-2.*X(2,J))**2
      A12(2)=(SQ*SS-SR*SW)/(SQ*SS-SR*SR)
      A21(2)=(SQ*SW-SQ*SQ)/(SQ*SS-SR*SR)
      DO 90 I=1,2
      READ 16
      PRINT 30
      PRINT 16
      DO 85 J=1,N
      GALOE(I,J)=(1.-X(I,J))**2*(AA(I)+BB(I)*X(I,J))
      GBLOC(I,J)=(1.-X(I,J))**2*(CD(I)+CE(I)*X(I,J))
      GCLOC(1,J)=(1.-X(1,J))**2*(A12(1)+2.*(A21(1)-A12(1))*X(1,J))
      GCLOC(2,J)=(1.-X(2,J))**2*(A21(1)+2.*(A12(1)-A21(1))*X(2,J))
      GDLOC(1,J)=(1.-X(1,J))**2*(A12(2)+2.*(A21(2)-A12(2))*X(1,J))
      GDLOC(2,J)=(1.-X(2,J))**2*(A21(2)+2.*(A12(2)-A21(2))*X(2,J))
```

```
      GELOC(1,J)=(1.-X(1,J))**2*(SBA(1)+2.*(SBA(2)-SBA(1))*X(1,J))
      GELOC(2,J)=(1.-X(2,J))**2*(SBA(2)+2.*(SBA(1)-SBA(2))*X(2,J))
      GAA(I,J)=EXP(2.302585*GALOC(I,J))
      GAB(I,J)=EXP(2.302585*GBLOC(I,J))
      GAC(I,J)=EXP(2.302585*GCLOC(I,J))
      GAD(I,J)=EXP(2.302585*GDLOC(I,J))
      GAE(I,J)=EXP(2.302585*GELOC(I,J))
      S1(I)=S1(I)+(((GAA(I,J)-GA(I,J))/GA(I,J))**2)**0.5
      S2(I)=S2(I)+(((GAB(I,J)-GA(I,J))/GA(I,J))**2)**0.5
      S3(I)=S3(I)+(((GAC(I,J)-GA(I,J))/GA(I,J))**2)**0.5
      S4(I)=S4(I)+(((GAD(I,J)-GA(I,J))/GA(I,J))**2)**0.5
   85 S5(I)=S5(I)+(((GAE(I,J)-GA(I,J))/GA(I,J))**2)**0.5
      S1(I)=S1(I)/SM(I)
      S2(I)=S2(I)/SM(I)
      S3(I)=S3(I)/SM(I)
      S4(I)=S4(I)/SM(I)
      S5(I)=S5(I)/SM(I)
      PRINT 9
      I1=1
      I2=2
      I3=3
      I4=4
      I5=5
      TEMP=AA(2)
      AA(2)=AB(2)
      AB(2)=TEMP
      TEMP=CD(2)
      CD(2)=CF(2)
      CF(2)=TEMP
      PRINT 7, I1, AA(I), AB(I), S1(I)
      PRINT 7, I2, CD(I), CF(I), S2(I)
      PRINT 7, I3, A12(1), A21(1), S3(I)
      PRINT 7, I4, A12(2), A21(2), S4(I)
   90 PRINT 7, I5, SBA(1), SBA(2), S5(I)
      GO TO 10
      END
```

b)

Title: Program for the calculation of the ternary constant and
ternary activity coefficients.

Computer: IBM 1620 with 60,000 positions of storage.

Program language: Fortran.

Description: The program was used to calculate the three activity
coefficients in a ternary mixture by Wohl's three-suffix equations.

Provision has been made for a maximum of 60 data points. The
average of the absolute value of the percent deviation between
calculated γ and experimental δ for each component was calculated.
If the ternary constant was zero in the input, the average values
of the ternary constant was calculated for three cases: (1) using
all data points, (2) using only data points where x is greater
than 0.05, and (3) using only data points where $x_1 x_2 (1-2x_3)$ is
greater than 0.1, and x is greater than 0.05. The calculation
starts after setting program switch 1 in the on position and
depressing start key.

The input data should be fed into machine in the following
order:

Card 1.   Comment such as Benzene, Cyclohexane, Acetone C=0
less than 49 characters including blanks in the body of the comment.

Card 2. A_{13}, A_{31}, A_{23}, A_{32}, A_{12}, A_{21}

Card 3.   C, q_2/q_1, q_3/q_1

For Margules equation set $q_2/q_1 = q_3/q_1 = 1$

Having program switch 1 in the on position requires that
additional input data be fed into the machine.

Card 4.   MK, K

Card 5. x_{11}, x_{21}, y_{11}, y_{21}
.   .
.   .
.   .
Card (4+K) x_{1K}, x_{2K}, y_{1K}, y_{2K}

MK is a fixed point constant representing the form of experimental γ input. K is also a fixed point constant representing the number of data points

After all x, y input had been read, the following cards are fed into machine depending on the value of MK:

for MK=1

Card (5+K) Π
Card (6+K) A_1, B_1, C_1
Card (7+K) A_2, B_2, C_2
Card (8+K) A_3, B_3, C_3
Card (9+K) T_1
.   .
.   .
Card (8+2K) T_K

for MK=2

Card (5+K) γ_{11}, γ_{21}, γ_{31}
.   .
.   .
Card (4+2K) γ_{1K}, γ_{2K}, γ_{3K}

for MK=3

Card (5+K) $\ln \gamma_{11}$, $\ln \gamma_{21}$, $\ln \gamma_{31}$
.   .
.   .
Card (4+2K) $\ln \gamma_{1K}$, $\ln \gamma_{2K}$, $\ln \gamma_{3K}$

for MK=4

    Card (5+K) $\log \gamma_{11}$, $\log \gamma_{21}$, $\log \gamma_{31}$

        •   •

        •   •

    Card (4+2K) $\log \gamma_{1K}$, $\log \gamma_{2K}$, $\log \gamma_{3K}$

All output is presented on the console typewriter in the following manner:

Benzene Cyclohexane Acetone C=0

A_{13}	A_{31}	A_{23}	A_{32}	A_{12}	A_{21}
.....	.....	.....	.....	.....	.....

Sum of A   Predicted C

  ....

	Total		x greater than 0.05		u greater than 0.1	
	Data	Error	Data	Error	Data	Error
Component 1.	....	....	....	....	....	....
Component 2.	....	....	....	....	....	....
Component 3.	....	....	....	....	....	....

If C is zero in the input data then the following output is typed,

	Total		x greater than 0.05		u greater than 0.11	
Component 1.	....	....	....	....	....	....
Component 2.	....	....	....	....	....	....
Component 3.	....	....	....	....	....	....

Note: Data = Number of data points
       Error = Absolute values of the average deviation of γ_{cal}
           from γ_{exp}.
       Sum of A = $A_{13} + A_{31} + A_{23} + A_{32} + A_{12} + A_{21}$
       Predicted C = $0.5(A_{21} - A_{12} + A_{13} - A_{31} + A_{32} - A_{23})$

After obtaining the complete output for a system, it may be desired to try a new Margules binary constant or ternary constant.

This can be accomplished through setting sense switch 1 in the off position, which allow one to read in the new constant without reading x, y, and Υ.

Console setting for operation:

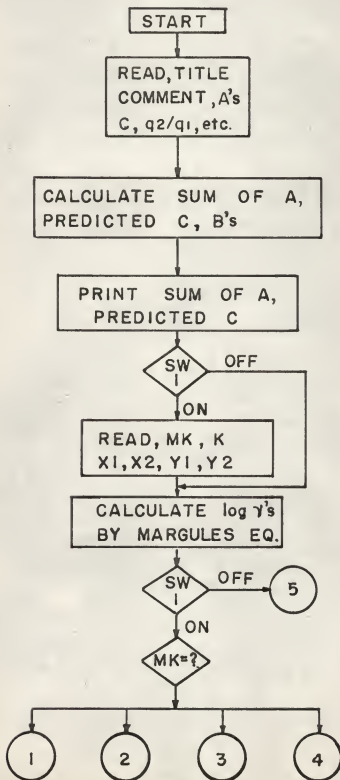Overflow check switches - program

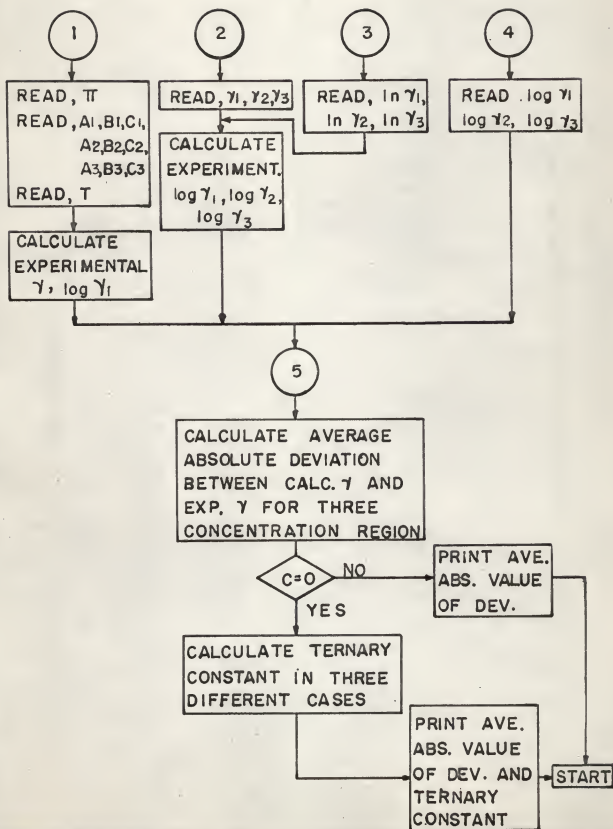All other check switch - stop

Sense switch 1 - on: title card and two constant cards and
x, y, Υ cards.

off: read title card and two constant cards only.

Sense switch 2, 3 and 4 - immaterial.

BLOCK DIAGRAM FOR USE WITH IBM 1620
FOR COMPUTING TERNARY CONSTANTS AND
THE ACTIVITY COEFFICIENT

```
C     CALCULATION OF TERNARY CONSTANT AND ACTIVITY COEFFICIENT
      DIMENSION AA(3),AB(3),AC(3),T(60),P(3,60),GA(3,60),GALN(3,60)
      DIMENSION A(3,3),Q(3,3),B(5,3),X1(3,60),Y(3,60),GA1(3,60),Z1(3,60)
      DIMENSION GALOG(3,60),ERROR(3,60),V(3,60),SK1(3),SK2(3),SK3(3)
      DIMENSION S1(3),S2(3),S3(3),U(3,60),TERNA(3,60),G4(3),S5(3),S6(3)
      DIMENSION GB1(3,60),GC1(3,60),GD1(3,60),G1(3,60)
      DIMENSION SK4(3), SK5(3), SK6(3)
 1    FORMAT ( I2, I2 )
 2    FORMAT ( E12.6, E12.6 )
 3    FORMAT ( E12.6, E12.6, E12.6 )
 4    FORMAT ( E12.6, E12.6, E12.6, E12.6 )
 5    FORMAT (9HCOMPONENT I3, E12.6,E12.6,E12.6,E12.6,E12.6,E12.6 )
 6    FORMAT (E12.6,E12.6, E12.6, E12.6, E12.6, E12.6 )
 7    FORMAT (/5X 3HA13 9X 3HA31 9X 3HA23 9X 3HA32 9X 3HA12 9X 3HA21)
 8    FORMAT (49H                                                     )
 9    FORMAT (///)
 10   PAUSE
      READ 8
      PRINT 8
      PRINT 7
      READ 6, A(1,3),A(3,1),A(2,3),A(3,2),A(1,2),A(2,1)
      PRINT 6, A(1,3),A(3,1),A(2,3),A(3,2),A(1,2),A(2,1)
      READ 3, CA, Q(2,1), Q(3,1)
      IF ( Q(2,1) ) 12, 11, 12
 11   Q(2,1)=A(2,1)/A(1,2)
      Q(3,1)=A(3,1)/A(1,3)
 12   Q(1,1)=1.
      Q(2,3)=Q(2,1)/Q(3,1)
      Q(3,2)=Q(3,1)/Q(2,1)
      Q(1,2)=1./Q(2,1)
      Q(1,3)=1./Q(3,1)
      SA2=A(2,1)+A(1,2)+A(3,2)+A(2,3)+A(1,3)+A(3,1)
      SA1=(A(2,1)-A(1,2)+A(3,2)-A(2,3)+A(1,3)-A(3,1))*0.5
 13   FORMAT ( 12H   SUM OF A 12H PREDICTED C )
      PRINT 13
      PRINT 2, SA2, SA1
 15   FORMAT (22X 5HTOTAL 15X 12HX BIGER 0.05 13X 11HU BIGER 0.1)
 16   FORMAT ( 16X4HDATA 8X5HERROR7X4HDATA8X5HERROR7X4HDATA8X5HERROR)
      DO 27 J=1,3
      L=J+1
      IF (9L-3) 22, 22, 21
 21   L=J+1-3
 22   M=J+2
      IF (M-3) 24, 24, 23
 23   M=J+2-3
 24   B(1,J)=2.*(A(L,J)*Q(J,L)-A(J,L))
      B(2,J)=2.*(A(M,J)*Q(J,M)-A(J,M))
      B(3,J)=A(J,M)+A(L,J)*Q(J,L)-A(M,L)*Q(J,M)-CA*Q(J,L)
      B(4,J)=(CA*Q(J,1)+A(M,J)*Q(J,M)-A(J,M))
 27   B(5,J)=2.*(A(M,L)*Q(J,M)-A(L,M)*Q(J,L))
      IF ( SENSE SWITCH 1 ) 28, 31
```

```
 28   READ 1, MK, K
      DO 29 N=1,K
      READ 4,  X1(1,N),X1(2,N),Y(1,N),Y(2,N)
      X1(3,N)=1.-X1(1,N)-X1(2,N)
 29   Y(3,N)=1.-Y(1,N)-Y(2,N)
      DO 30 J=1,3
      DO 30 N=1,K
 30   Z1(J,N)=X1(J,N)*Q(J,1)/(X1(1,N)+X1(2,N)*Q(2,1)+X1(3,N)*Q(3,1))
 31   CONTINUE
      DO 36 J=1,3
      DO 36 N=1,K
      L=J+1
      IF (L-3) 33, 33, 32
 32   L=L-3
 33   M=J+2
      IF (M-3) 35, 35, 34
 34   M=M-3
 35   GA1(J,N)=Z1(L,N)**2*(A(J,L)+Z1(J,N)*B(1,J))
      GB1(J,N)=Z1(M,N)**2*(A(J,M)+Z1(J,N)*B(2,J))
      GC1(J,N)=Z1(L,N)*Z1(M,N)*(B(3,J)+Z1(J,N)*B(4,J)+Z1(M,N)*B(5,J))
      GD1(J,N)=GA1(J,N)+GB1(J,N)+GC1(J,N)
      G1(J,N)=EXP(2.302585*GD1(J,N))
      U(J,N)=Z1(L,N)*Z1(M,N)*(1.-2.*Z1(J,N))
 36   V(J,N)=(U(J,N)**2)**0.5
      DO 37 I=1,3
      SK1(I)=0.
      SK2(I)=0.
      SK3(I)=0.
      SK4(I)=0.
      SK5(I)=0.
      SK6(I)=0.
      S1(I)=0.
      S2(I)=0.
      S3(I)=0.
      S4(I)=0.
      S5(I)=0.
 37   S6(I)=0.
      IF ( SENSE SWITCH 1 ) 38, 49
 38   CONTINUE
      GO TO ( 39, 43, 45, 47 ), MK
 39   READ 2, PI
      DO 40 I=1,3
 40   READ 3, AA(I), AB(I), AC(I)
      DO 41 N=1,K
 41   READ 2, T(N)
      DO 42 I=1,3
      DO 42 N=1,K
      P(I,N)=EXP(2.302585*(AA(I)-AB(I)/(AC(I)+T(N))))
      GA(I,N)=PI*Y(I,N)/P(I,N)/X1(I,N)
 42   GALOE(I,N)=LOG(GA(I,N))/2.302585
      GO TO 49
 43   CONTINUE
```

```
      DO 44 N=1,K
      READ 3, GA(1,N), GA(2,N), GA(3,N)
      DO 44 I=1,3
44    GALOE(I,N)=LOG(GA(I,N))/2.302585
      GO TO 49
45    CONTINUE
      DO 46 N=1,K
      READ 3, GALN(1,N), GALN(2,N), GALN(3,N)
      DO 46 I=1,3
      GALOE(I,N)=GALN(I,N)/2.302585
46    GA(I,N)=EXP(GALN(I,N))
      GO TO 49
47    CONTINUE
      DO 48 N=1,K
      READ 3, GALOE(1,N), GALOE(2,N), GALOE(3,N)
      DO 48 I=1,3
48    GA(I,N)=EXP(2.302585*GALOE(I,N))
49    CONTINUE
      DO 53 I=1,3
      DO 53 N=1,K
      ERROR(I,N)=(((GA(I,N)-G1(I,N))/GA(I,N))**2)**0.5
      IF ( X1(I,N)-0.05 ) 52, 52, 50
50    S2(I)=S2(I)+ERROR(I,N)
      SK2(I)=SK2(I)+1.0
      IF ( V(I,N)-0.1 ) 52, 51, 51
51    S3(I)=S3(I)+ERROR(I,N)
      SK3(I)=SK3(I)+1.0
52    S1(I)=S1(I)+ERROR(I,N)
53    SK1(I)=SK1(I)+1.0
      PRINT 9
      PRINT 15
      PRINT 16
      DO 54 I=1,3
      S1(I)=S1(I)/SK1(I)
      S2(I)=S2(I)/SK2(I)
      S3(I)=S3(I)/SK3(I)
54    PRINT 5, I, SK1(I), S1(I), SK2(I), S2(I), SK3(I), S3(I)
      IF (CA) 10, 60, 10
60    CONTINUE
      DO 64 I=1,3
      DO 64 N=1,K
      TERNA(I,N)=(GALOE(I,N)-GD1(I,N))/U(I,N)*(-1.)
      IF ( X1(I,N)-0.05 ) 63, 63, 61
61    S4(I)=S4(I)+TERNA(I,N)
      SK4(I)=SK4(I)+1.0
      IF ( V(I,N)-0.1 ) 63, 62, 62
62    S5(I)=S5(I)+TERNA(I,N)
      SK5(I)=SK5(I)+1.0
63    S6(I)=S6(I)+TERNA(I,N)
64    SK6(I)=SK6(I)+1.0
      PRINT 9
      PRINT 65
```

```
      PRINT 15
65    FORMAT ( 16HTERNARY CONSTANT )
      DO 66 I=1,3
      S4(I)=S4(I)/SK4(I)
      S5(I)=S5(I)/SK5(I)
      S6(I)=S6(I)/SK6(I)
66    PRINT 5, I, SK6(I),S6(I),SK4(I),S4(I),SK5(I),S5(I)
      GO TO 10
      END
```

EVALUATION OF THE INTERACTION
EFFECT IN TERNARY SYSTEMS

by

YI-CHUAN PAN

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Department of Chemical Engineering

KANSAS STATE UNIVERSITY
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Major Professor

ABSTRACT

The purpose of this work is to use Wohl's ternary Margules three-suffix equations to evaluate the activity coefficients in ternary systems. Binary constants for the equations were obtained from the three constituent binary systems. Using the method of least squares, several methods of determining binary constants were evaluated. Inserting these six independent binary constants into the Margules equation a ternary constant was evaluated using the observed ternary activity coefficients. Eleven non-aqueous ternary systems, found in the literature, were used to determine the need for a ternary constant.

All calculations were made by the IBM 1620 computer and the computer programs for determination of Margules binary constants and calculation of ternary activity coefficients are presented.

The results show that if the constituent binary systems can be well represented by the Margules equation, the ternary system can be represented using the three-suffix Margules equations without a ternary constant. The precision of the prediction of activity coefficients in the ternary system is about the same as the precision with which binary activity coefficients are represented by the Margules equation.