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A PRELIMINARY STUDY OF THE THERMODYNAMIC LIMITATIONS OF THE NRTL/LEMF EQUATIONS

BY

ROBERT PETRIE

A THESIS

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THE REQUIREMENTS FOR THE DEGREE
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A PRELIMINARY STUDY OF THE THERMODYNAMIC LIMITATIONS OF THE NRTL/LEMF EQUATIONS

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A Preliminary Study of the
Thermodynamic Limitations of the NRTL/LEMF Equations

Abstract

Analytical evaluations of the second and third derivatives of the molar Gibbs energy of mixing for the NRTL/LEMF equations indicate distinct zones of miscible and inmiscible prediction.

These calculations for a number of different α's have produced approximate miscibility limits for both NRTL/LEMF energy parameters and infinite dilution activity coefficients of a given system.

Introduction

Phase equilibria equations relating temperature, composition and component activity coefficients provide the basis for the design of separation processes such as distillation and extraction. The approach of the system design to actual unit operation is basically a function of these equations' accuracy in describing phase equilibrium. Over the years, many phase equilibria equation forms have been suggested by investigators, including Van Laar, Wohl, Black, Scatchard, and Margules (1,2).

In 1964, G.M. Wilson (3) proposed a novel theory of liquid phase interactions based on his own conceived idea of local mole fractions. He developed a two-parameter per binary system expression which was able to describe miscible systems with accuracies surpassing those of previous equations. However, the expression could not handle inmiscible cases.

At the University of California, Berkeley, in 1968, H. Renon and J.M. Prausnitz (4) extended Wilson's theory, in conjunction with R.L. Scott's two-liquid concept (5), to generate the non-random two-liquid or NRTL equation. This expression was able to describe both miscible and inmiscible systems with remarkable accuracy. In the course of their derivation, the authors introduced a third parameter, alpha or α, which was hypothesized by Renon to be related to the nonrandomness of the liquid phase. The authors proposed guidelines for the choice of α based on the qualitative physics of a system and its components. However, these rules were unclear at times and resulted in ambiguity as to which of the three available alphas, 0.20, 0.30 or 0.47, to use.

In 1971, Marina and Tassios (6) found that the use of a single alpha, -1. 0, in the NRTL equation yielded comparable accuracy for miscible and improved performance for immiscible cases, in relation to the original expression. Based on a new derivation, these investigators called this relationship the LEMF (local effective mole fraction) equation and transformed the NRTL equation into a true two-parameter phase equilibria model.

Recently a group of Czech researchers led by J.P. Novak have stated, through private communication and published findings, that the use of any particular value of α restricts the applicability of the NRTL equation (7, 8, 9).

They have also presented data which illustrates thermodynamic restraints for both positive and negative alphas. In the case of the LEMF expression, they contend that systems exhibiting the following conditions cannot be described with thermodynamic consistency:

$$0.35 \angle \xi \angle 0.40$$

where $\xi = |x_0 - 0.5|$

and

$$G\,11 = \left.\frac{\partial^2 \Delta g^m}{\partial x^2}\right]_{T,P}$$

$$\left.\frac{\partial G\,11}{\partial x_1}\right]_{x_1 = x_0} = 0$$

Δg^m = molar Gibbs energy of mixing

They also state that water-polar substance systems very often have ξ's in the range of 0.20 to 0.40 and therefore are subject to this restriction. In effect, these investigators hold that the NRTL/LEMF equations may, under certain circumstances, predict phase separations where only a single phase exists. As a result of this work, it was decided to examine the thermodynamics of the NRTL/LEMF equations with the purpose of elucidating the miscible and immiscible prediction limits for a number of alphas. It was also hoped that sufficiently clear correlations might be provided to insure the choice of a "miscible alpha" for a given system; use of this alpha would guarantee that no erroneous phase separation be predicted for a truly homogeneous system.

Background

Wilson, NRTL/LEMF Equations

Through his concept of local mole fractions, Wilson developed the following expression:

$$\frac{x_{21}}{x_{11}} = \frac{x_2}{x_1} \exp\left[-(g21-g11)/RT\right] \qquad (1)$$

where

x_{ij} = the local mole fraction of molecules i which are in the immediate proximity of molecule j

g_{ij} = energies of interaction between an i-j pair of molecules; parameters

x_i = the overall mole fraction of component i in the mixture.

He then generated a relationship for the excess Gibbs energy through comparison with the Flory-Huggins model of athermal mixtures,

$$G^E/RT = x_1 \ln (Z_{11}/x_1) + x_2 \ln (Z_{22}/x_2) \qquad (2)$$

where Z_{ij} are local volume fractions obtained from equation (1) or,

$$Z_{11} = \frac{x_1}{x_1 + x_2 (v_2/v_1) \exp(-(g21-g11)/RT)} \qquad (3)$$

$$Z_{22} = \frac{x_2}{x_2 + x_1 (v_1/v_2) \exp(-(g12-g22)/RT)} \qquad (4)$$

where v_i = molar volume of component i.

Differentiations of equation (2) yield the appropriate component activity coefficients.

Renon and Prausnitz utilized Scott's two-liquid theory of binary mixtures to derive a modification of equation (1) in which they introduced a nonrandomness mixing factor, alpha or α :

$$\frac{x_{21}}{x_{11}} = \frac{x_2}{x_1} \exp\left[-\alpha(g21-g11)/RT \right] \qquad (5)$$

By using the following relationships,

$$x_{21} + x_{11} = 1 \qquad (6)$$

and

$$x_{12} + x_{22} = 1 \qquad (7)$$

and comparison with Guggenheim's quasichemical theory, (10), they arrived at the proceeding excess Gibbs energy expression,

$$G^E = x_1 x_{21}(g21-g11) + x_2 x_{12}(g12-g22) \qquad (8)$$

which, upon full expansion, becomes,

$$\frac{G^E}{RT} = \frac{x_1 x_2}{RT}\left[\frac{(g21-g11)\ \exp\left[-\alpha(g21-g11)/RT\right]}{x_1 + x_2\ \exp\left[-\alpha(g21-g11)/RT\right]} + \frac{(g12-g22)\ \exp\left[-\alpha(g12-g22)/RT\right]}{x_2 + x_1\ \exp\left[-\alpha(g12-g22)/RT\right]} \right] \qquad (9)$$

This is the nonrandom two-liquid or NRTL equation. Differentiations of equation (9) for the respective components provide the corresponding activity coefficients:

$$\ln \gamma_1 = x_2^2 \left[\frac{\left[(g21-g11)/RT\right] \exp\left[-2\alpha(g21-g11)/RT\right]}{\left[x_1 + x_2 \exp\left[-\alpha(g21-g11)/RT\right]\right]^2} + \frac{\left[(g12-g22)/RT\right] \exp\left[-\alpha(g12-g22)/RT\right]}{\left[x_2 + x_1 \exp\left[-\alpha(g12-g22)/RT\right]\right]^2} \right] \quad (10)$$

$$\ln \gamma_2 = x_1^2 \left[\frac{\left[(g12-g22)/RT\right] \exp\left[-2\alpha(g12-g22)/RT\right]}{\left[x_2 + x_1 \exp\left[-\alpha(g12-g22)/RT\right]\right]^2} + \frac{\left[(g21-g11)/RT\right] \exp\left[-\alpha(g21-g11)/RT\right]}{\left[x_1 + x_2 \exp\left[-\alpha(g21-g11)/RT\right]\right]^2} \right] \quad (11)$$

With g12 = g21.

These are the expressions which are able to describe both homogeneous and hetergeneous systems with fine overall accuracy.
In actuality the energy parameters are obtained through regression with the existing data.

Originally, Renon and Prausnitz (11, 12) recommended use of one of the following alphas, 0.20, 0.30, or 0.47, according to the nature of the system and components. They grouped liquid mixtures into seven categories according to polarity, association, etc., and suggested specific alpha values for each. However, at times the rules for alpha selection became ambiguous and were difficult to apply. As a result, Marina and Tassios investigated the whole question of this nonrandomness value.

Through a study of fifty-five binary and eleven ternary systems, these authors concluded that a single alpha of -1.0 resulted in comparable accuracy for miscible cases and improved accuracy for immiscible systems when compared to the original NRTL equation (13). Since a negative alpha was not consistent with Renon's hypothesis of its physical significance, Marina undertook a new derivation, with the final equation resulting in an identity with equation (9). The new equation with $\alpha = -1.0$ was termed the LEMF or local effective mole fraction expression.

Confirmation of Immiscibility Problem

Seven published water-polar material binary systems, all miscible, were chosen in an effort to confirm the existence of the immiscibility breakdown phenomenon for the NRTL/LEMF equations. Binary, isothermal data were selected because of its ease of handling in the calculations. Besides confirmation of the problem, it was expected that the seven cases would provide a data base from which to examine any results of the investigations into the thermodynamics of the respective equations. Four of the systems were checked for thermodynamic consistency. Two of the cases corresponded to binaries which were mentioned by Novak et.al., as being inconsistent with the LEMF expression ; the 3-methylpyridine-water and the tetrahydrofuran-water binaries. The thermodynamic consistency test used was a familiar form of the Gibbs-Duhem equation, in terms of activity coefficients :

$$\int_0^1 \ln {}^{\gamma_1}\!/_{\gamma_2} \, d x_1 = 0 \qquad (12)$$

Equation (12) is approximately true at constant temperature conditions; by plotting experimental data of γ_1/γ_2 versus x from 0 to 1.0, the net area of the graph should be close to zero. The following table lists the results of the consistency test, where all percentages are relative to the smallest area, positive or negative, measured:

TABLE I

Thermodynamic Consistency of Systems

SYSTEM	3-methylpyridine-water	3-methylpyridine-water	tetrahydrofuran-water	4-methylpyridine-water
	@ 69.86°C	@ 89.83°C	@ 50°C	@ 69.86°C
% Error	8.8	8.6	1.1	2.6

It was concluded from these low relative errors that these data were thermodynamically consistent.

Table II lists the system, chosen alphas, and the corresponding activity coefficient standard deviations (SD's) which were observed in the NRTL/LEMF equations. A table of typical system parameters is shown in the Appendix. Standard deviations were calculated as relative error according to the following expression :

$$SD = \left[\frac{\sum_{i=1}^{N} \left[\frac{\gamma_{1\,cal} - \gamma_{1\,obs}}{\gamma_{1\,obs}} \right]_i^2 + \left[\frac{\gamma_{2\,cal} - \gamma_{2\,obs}}{\gamma_{2\,obs}} \right]_i^2}{2N - 1} \right]^{0.5} \qquad (13)$$

Where N equals the number of experimental data points. The capital "M" or "I" after each SD value indicates whether the particular value of α predicted phase miscibility or immiscibility, respectively. Miscibility was assumed at equal or increasing vapor compositions in the increasing "ψ" direction. (Note that this criterion, however, is an approximate measure of miscibility predictions. It is possible that within a range not covered by the existing data "y" would decrease. The only rigorous test is use of equation 16 1) with the parameter values obtained by regression of the experimental data.) Table III presents a list of experimental and predicted y's, at α =0.3, for the 3-methylpyridine- water binary and gives examples of both miscible and immiscible data.

---

1) to be discussed

NOTE: Numbers in parentheses refer to bibliography sources.

TABLE II

NRTL/LEMF Equation Performance

Acetone-water		3-Methylpyridine-water		3-Methylpyridine-water		Water-pyridine		Tetrahydrofuran-water		Water-Thioazole		4-Methylpyrid water	
25°C		69.86°C		89.83°C		80.05°C		50°C		90°C		69.86°C	
α	SD	α	SD	α	SD	α	SD	α	SD	α	SD	α	SD
0.6	.0757 M	0.72	.1678 M	0.72	.1767 M	0.7	.0943 M	0.7	.2586 M	0.6	.0901 M	0.7	.1069 M
0.5	.0702 M	0.7	.1533 I	0.7	.1633 M	0.6	.0718 M	0.6	.1694 M	0.5	.0497 M	-1.0	.1849 I
0.5*	.0678 M	0.6	.0710 I	0.6	.0847 I	0.5	.0744 M	0.5	.0607 I	0.47	.0405 M		
0.7	.0687 M	0.5	.0581 I	0.5	.0500 I	0.47	.0772 M	0.47	.0364 I	0.3	.0093 I		
0.8	.0692 M	0.47	.0713 I	0.47	.0600 I	0.3	.0948 I	0.3	.0579 I	0.2	.0120 I		
1.0	.0706 M	0.3	.1295 I	0.3	.1269 I	0.2	.1038 I	0.2	.0747 I	-1.0	.0201 M		
1.5	.0759 M	0.2	--- --	0.2	.1835 M	-0.5	.1139 M	-0.5	.0620 I	-3.0	.1289 M		
2.0	.0838 M	0.1	.1680 I	-0.5	.1618 I	-0.7	.0928 M	-0.9	.0304 I				
2.5	.0955 M	-0.5	.1802 I	-1.0	.1049 I	-0.8	.0871 M	-1.0	.0257 I				
3.0	.1110 M	-0.7	.1535 I	-1.4	.2428 M	-1.0	.0827 M	-1.1	.0250 I				
		-0.8	.1419 I	-1.5	--- --	-1.5	.0812 M	-1.2	.0286 I				
		-1.0	.1224 I	-1.6	.0954 I	-2.0	.0736 M	-1.3	.0353 I				
		-1.5	.0966 I	-1.8	.0872 I	-2.5	.0732 M	-1.4	.0435 I				
		-2.0	.0937 I	-2.0	.0785 I	-3.0	.0916 M	-1.5	.0524 I				
		-2.5	.0731 I	-2.5	.0603 I	-10.0	.2655 M	-1.7	.0709 I				
		-3.0	.0592 I	-3.0	.0581 I			-1.8	.0800 I				
		-4.0	.0763 I	-4.0	.0937 I			-2.0	.0978 I				
		-4.5	.0961 I	-5.0	.1353 I			-3.0	.1723 I				
		-5.0	.1162 I	-6.0	.1699 I			-4.0	.2259 I				
		-6.0	.1525 I	-7.0	.1978 I			-10.0	.3709 I				
		-7.0	.1826 I	-10.0	--- --								
		-10.0	.2446 I										
(15)		(14)		(14)		(15)		(7)		(15)		(14)	

*Figures from here down are negative figures

TABLE III

Basis for Predicting Phase Separations
(Data from 3 MP-water system at 89.83°C)

ψ (3 MP)	Y (EXPERIMENTAL)	Y (PREDICTED, α =0.3
.00306	.04263	.034
.0187	.1048	.121
.0605	.1119	.150
.0941	.1120	.135
.1371	.1123	.117
.1900	.1135	.106
.2410	.1157	.101
.3018	.1210	.102
.3748	.1309	.110
.4267	.1403	.119
.4614	.1488	.127
.5388	.1685	.148
.5976	.1900	.170
.7118	.2508	.230
.7818	.2948	.284
.9747	.7947	.764

The experimental y's show a constantly increasing pattern with rising ψ , illustrating miscible behavior. The predicted y's, however, increase initially then decrease and increase again, being indicative of immiscible systems.

Figure I is a plot of these data.

As Table II shows, both 3-methylpyridine binaries and the tetrahydrofuran binary were erroneously described as heterogeneous by the original-alpha NRTL and LEMF equations except for a single value of alpha (α = 0.20 for 3-methylpyridine @ 89.83°C). In addition the LEMF failed for the 4-methylpyridine system and two values of the original NRTL (0.20 and 0.30) brokedown for both the thioazole and pyridine binaries. Although the first three binaries mentioned are indeed borderline homegeneous cases, as seen in Table IV, the mispredictions of a phase separation by the NRTL/LEMF equations were confirmed. Table V presents the "best" vapor composition predictions obtained for these systems which still yielded a phase split. Very good agreement is apparent between experimental and predicted y's, neglecting the false heterogeneity. An interesting observation from Table II is the failure to predict homogeneity even up to alphas of -10.0 for these three "worst" binaries. In the reverse direction, miscibility was obtained for these three binaries individually at either 0.60, 0.70 or 0.72. The overall results from all systems suggested that an alpha of perhaps 0.70 or 0.72 would satisfy a majority of situations where lower alphas yielded a phase split prediction. However, it was also noticed that a considerable increase in activity coefficient standard deviation appears to be a by-product of shifting to higher alphas (see Table II). An analysis of this alpha-activity coefficient standard deviation relationship is beyond the scope of this work. Figure II presents perhaps the most

FIGURE I - BASIS FOR PREDICTING PHASE SEPARATIONS

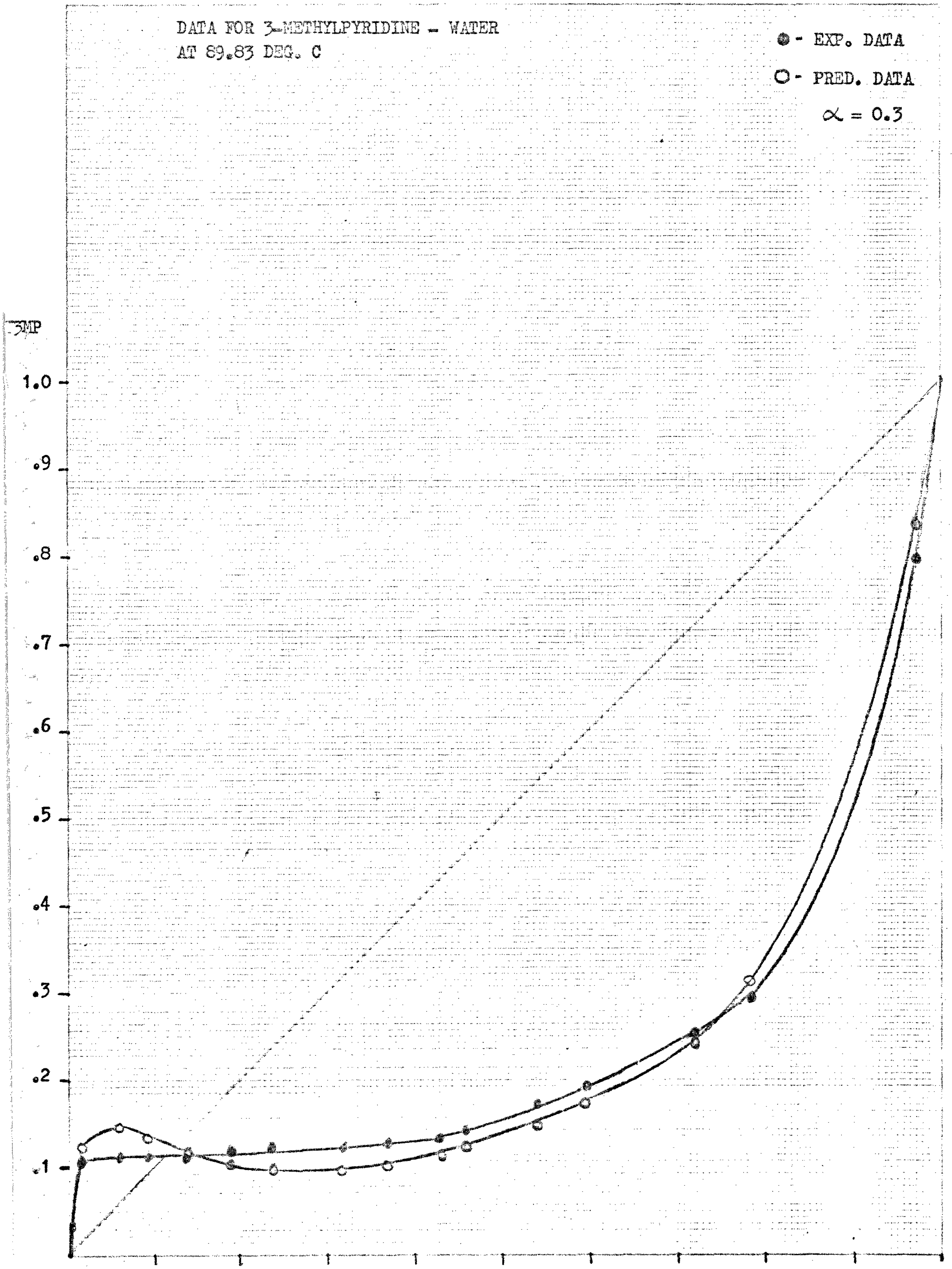

TABLE IV

"Borderline" Homogeneous Systems - Actual Data

3-methylpyridine-water @ 69.86°C		3-methylpyridine-water @ 89.83°C		tetrahydrofuran-water @ 50°C	
X	Y	X	Y	X	Y
.00223	.03445	.00306	.04263	.028	.700
.0167	.0996	.0187	.1048	.038	.745
.0484	.1068	.0605	.1119	.046	.767
.0777	.1071	.0941	.1120	.075	.781
.1239	.1071	.1371	.1123	.1165	.797
.1606	.1075	.1900	.1135	.183	.800
.2028	.1090	.2410	.1157	.228	.802
.2604	.1126	.3018	.1210	.264	.800
.3225	.1207	.3748	.1309	.354	.802
.3884	.1314	.4267	.1403	.441	.803
.4428	.1444	.4614	.1488	.531	.805
.4954	.1575	.5388	.1685	.611	.810
.5923	.1932	.5976	.1900	.698	.820
.6869	.2395	.7118	.2508	.765	.832
.7754	.3039	.7818	.2948	.798	.840
.9770	.8027	.9747	.7947	.868	.865
				.888	.870
				.922	.901
				.956	.936
				.979	.965

TABLE V - COMPOSITION ACCURACY OF IMMISCIBLE PREDICTIONS

SYSTEM	3-METHYLPYRIDINE-WATER @ 69.86°C		3-METHYLPYRIDINE-WATER @ 89.83°C		TETRAHYDROFURAN-WATER @ 50°C	
	$\alpha = 0.5$, SD (γ) =.0581		$\alpha = 0.5$, SD (γ) =.0500		$\alpha = -1.1$, SD (γ)=.0250	
	Y_{3MP}(EXP.)	Y_{3MP}(PRED.)	Y_{3MP}(EXP.)	Y_{3MP}(PRED.)	Y_{THF}(EXP.)	Y_{THF}(PRED.)
	.03445	.029	.04263	.038	.700	.706
	.0996	.110	.1048	.116	.745	.743
	.1068	.124	.1119	.126	.767	.762
	.1071	.114	.1120	.114	.781	.794
	.1071	.103	.1123	.106	.797	.806
	.1075	.100	.1135	.104	.800	.806
	.1090	.100	.1157	.106	.802	.803
	.1126	.104	.1210	.113	.800	.800
	.1207	.113	.1309	.125	.802	.796
	.1314	.126	.1403	.136	.803	.797
	.1444	.138	.1488	.145	.805	.801
	.1575	.153	.1685	.166	.810	.808
	.1932	.187	.1900	.188	.820	.819
	.2395	.235	.2508	.245	.832	.832
	.3039	.303	.2948	.299	.840	.841
	.8027	.809	.7947	.779	.865	.867
					.870	.878
					.901	.901
					.936	.933
					.965	.964

drastic example of this situation for the tetrahydrofuran-water system; the actual data and predicted results at $\alpha = 0.6$ and 0.7 are plotted. A full investigation would be needed to quantitatively determine the effect of higher alphas on composition predictions.

Although not directly related to the purpose of this investigation, Figure III presents the SD-alpha relationship of the available miscible data for the three systems acetone, pyridine and thioazole, respectively. Use of $\alpha = -1.0$ for all three cases yields a miscible, accurate representation of the actual data.

Thermodynamics of Phase Instability

A single liquid phase will split itself into two phases if, upon doing so, it can lower its overall molar Gibbs energy. Mathematically, this phase separation or instability then requires that the second derivative of the molar Gibbs energy of mixing-composition function be negative for at least one value of ψ in the range 0 to 1. In equation form, this means

$$\left.\frac{\partial^2 G^E}{\partial \psi^2}\right]_{T,\,P} < 0 \qquad (14)$$

It is also a mathematical fact that the minimum, maximum and inflection points of the second derivative of the Gibbs energy-composition relation ship are described by this energy's third derivative, with respect to concentration or,

$$\left.\frac{\partial^3 G^E}{\partial \psi^3}\right]_{T,\,P} = 0 \qquad (15)$$

where $\psi = \psi_o$ at this point.

FIGURE II – EFFECT OF HIGHER α'S ON COMPOSITION PREDICTION

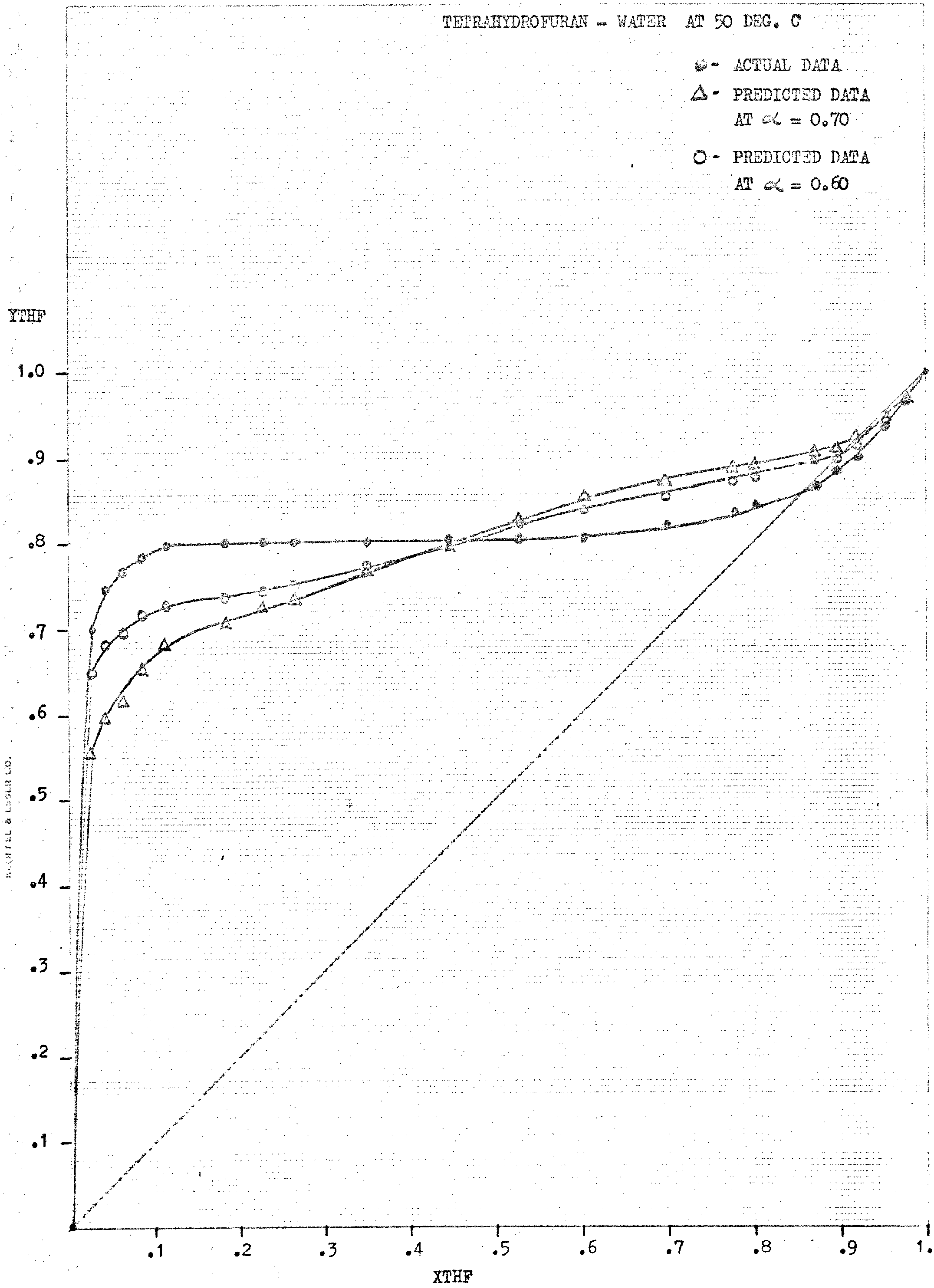

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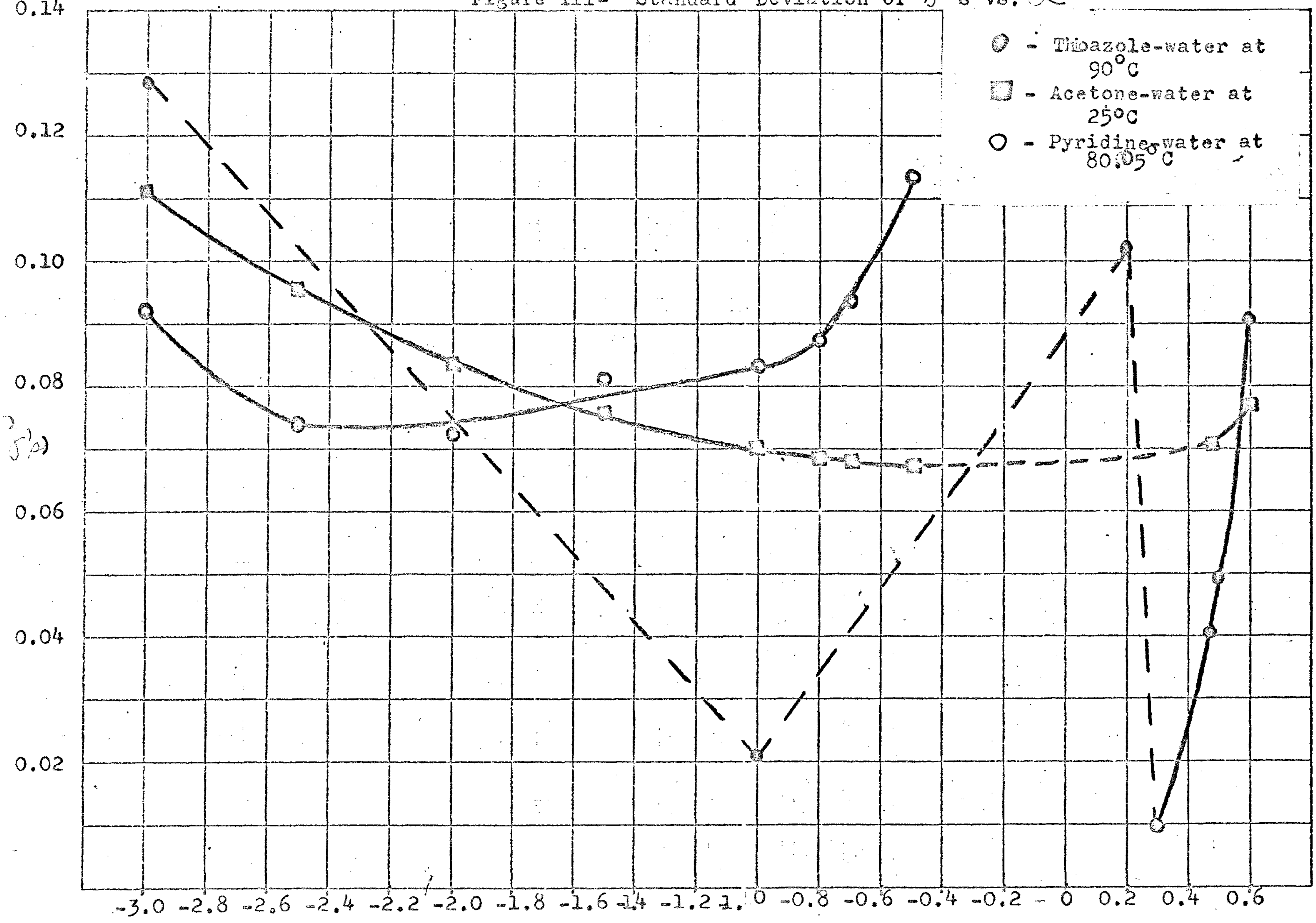
Figure III- Standard Deviation of γ's vs. α



Theoretically, therefore, if a given Gibbs energy function could be evaluated for its various parameters, subject to satisfying equation (15), then the second derivative of this function, with these same parameters, would indicate whether a phase split will be predicted, i.e., equation (14) would be satisfied.

Renon and Prausnitz (11) have shown that substitution of the NRTL expression, equation (9), into equation (14) yields the following:

$$\frac{\left[-2\ (g21-g11)/RT\right]\left[\exp\left[-\alpha(g21-g11)/RT\right]\right]^{2}}{\left[\psi_1+\psi_2\ \exp\left[-\alpha(g21-g11)/RT\right]\right]^{3}}$$

$$+\frac{\left[-2\ (g12-g22)/RT\right]\left[\exp\left[-\alpha(g12-g22)/RT\right]\right]^{2}}{\left[\psi_2+\psi_1\ \exp\left[-\alpha(g12-g22)/RT\right]\right]^{3}}$$

$$+\frac{1}{\psi_1}+\frac{1}{\psi_2}<0 \qquad (16)$$

Evaluations by others of equation (15) for the NRTL equation, to date have involved numerical methods. Novak, et.al., have stated this procedure as their course, in various communications. (7, 8, 9). However, by insertion of equation (16) into equation (15), a rather straightforward, analytical differentiation can be performed to generate the following expression :

$$\frac{\left[6(g21-g11)/RT\right]\;\left[\exp\left[-\alpha(g21-g11)/RT\right]\right]^{2}\times\left[1-\exp\left[-\alpha\,(g21-g11)/RT\right]\right]}{\left[\psi_{1}+\psi_{2}\;\exp\left[-\alpha(g21-g11)/RT\right]\right]^{4}}$$

$$+\frac{\left[6(g12-g22)/RT\right]\;\left[\exp\left[-\alpha(g12-g22)/RT\right]\right]^{2}\times\left[\exp\left[-\alpha(g-12-g22)/RT\right]-1\right]}{\left[\psi_{2}+\psi_{1}\;\exp\left[-\alpha\frac{(g12-g22)}{RT}\right]\right]^{4}}$$

$$+\left[\frac{1}{\psi_{2}}\right]^{2}-\left[\frac{1}{\psi_{1}}\right]^{2}=0 \qquad (17)$$

Equations (16) and (17) therefore provide a complete explanation of the prediction performance of the NRTL/LEMF equations.

With the setting of the parameters α and g12-g11 and g21-g22, the latter differences obtained by regression of the experimental data, evaluation of equation (17) will yield an $\psi = \psi_{o}$ value. This value with the chosen parameters then may be put into equation (16) and this expression calculated. If this calculated value is a negative number a phase separation will be predicted; if positive, a completely homogeneous phase is to be expected.

Solutions of Second and Third Derivatives

One possible procedure for evaluating equations (16) and (17) might involve a choice of alpha and the more or less random choosing of the energy parameters for the purpose of generating generalized charts. However, a more reasonable and systematic approach involves the use of the NRTL/LEMF activity coefficients, equations (10) and (11). By letting $x_1 \rightarrow 0$ in equation (10) and $x_2 \rightarrow 0$ in equation (11), infinite dilution activity coefficients are obtained which are functions solely of alpha and the parameters,

$$\ln \underset{x_1 \rightarrow 0}{\gamma^o_1} = (g12-g11)/RT + \left[(g21-g22)/RT\right] \exp\left[-\alpha\,(g21-g22)/RT\right] \qquad (18)$$

and

$$\ln \underset{x_2 \rightarrow 0}{\gamma^o_2} = (g21-g22)/RT + \left[(g12-g11)/RT\right] \exp\left[-\alpha\,(g12-g11)/RT\right] \qquad (19)$$

Now, for a chosen alpha and set of infinite dilution activity coefficients, the parameters can be determined. Therefore, simultaneous solution of equations (18) and (19), at set coefficients and alpha, yields a pair of parameters, which are related to the set values. One advantage of this method is the easy access to the infinite dilution activity coefficients of a system, which, it was hoped, would allow for similarly easy reference to the generalized charts, which were proposed.

Equation (17) is first used by substituting the calculated parameters and chosen alpha into the equation and then solving for $x = x_0$ meeting the equality. Finally, this x_0 value, alpha and the parameters are inserted into equation (16) and the second derivative evaluated, which signifies whether or not a phase separation will be predicted. The results of following this procedure are presented in the proceeding section.

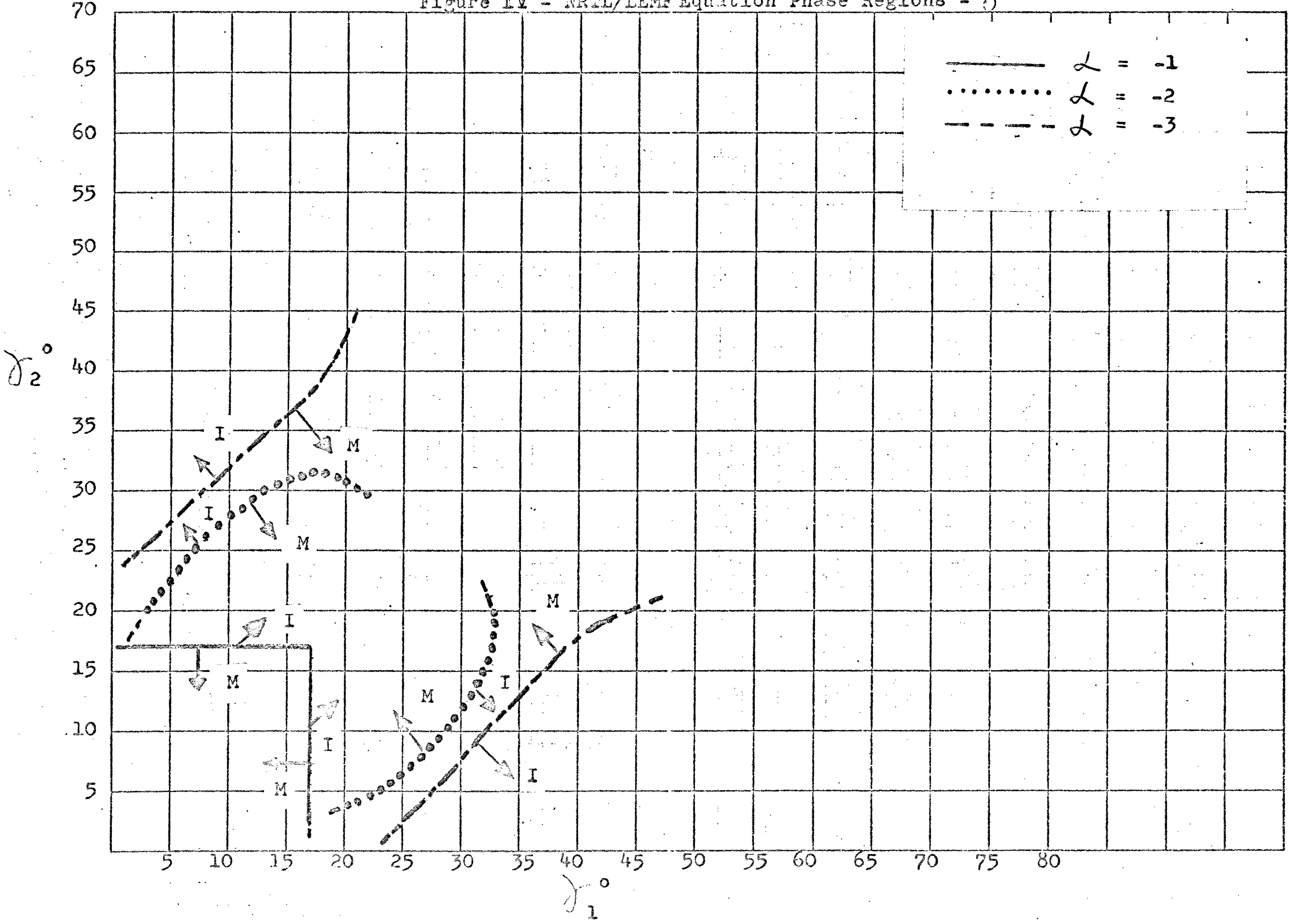
Generalized Curves and Results

In carrying out the method described above, a large number of infinite dilution activity coefficients were used to generate an equal number of parameter pairs. These parameters were calculated in temperature independent form, g12-g11/RT and g21-g22/RT.

To date, the following alphas have been investigated : -3.0, -2.0, -1.0, 0.2, 0.3, 0.47 and 0.7. The first two values were suggested by the overall good SD values obtained with the systems as well as the desire to explore the negative alpha region. The final value of 0.7 was chosen since all binaries examined, except one, could be accurately described as being miscible with this alpha. The remaining values are either the original NRTL alphas or the LEMF modification. The main result of following the calculated scheme described was the discovery of approximate miscible and immiscible prediction zones for each alpha, except one, which will be discussed later.
Figures IV and V present generalized curves signifying miscible and immiscible regions for each α as a function of limiting activity coefficient. Figures VI and VII show these areas as a function of the parameters corresponding to these activity coefficients. As a direct result of the forms of the equations and axes' scales, each of the plots is symmetrical, i.e. one side of any given curve is a mirror image of its extension on the opposite side of the 45° line. In order to reasonably illustrate the results with respect to graph scale, the positive and negative alphas were plotted together, respectively, on both the limiting activity coefficient and parameter constructions.

It must be pointed out that only the sections shown on the enclosed graphs could be constructed with any degree of reliability. Additional data points outside the line extensions of the various alphas were obtained, however, the lack of clarity between homogeneous and heterogeneous zones dictated the present terminations of the lines. Even so, a large degree of interpolation and extrapolation entered into the drawing of the figures.

Figure IV - NRTL/LEMF Equation Phase Regions - γ°



NO. 36.401. 14 BY 20 7/16" BLACK DIVISIONS,
70 BY 100 BLUE DIVISIONS.

codex GRAPH PAPER ® IN STOCK DIRECT FROM CODEX BOOK CO. INC. NORWOOD, MASS. 02062
PRINTED IN U.S.A.

Figure V. - NRTL Equation Phase Regions - γ°_s

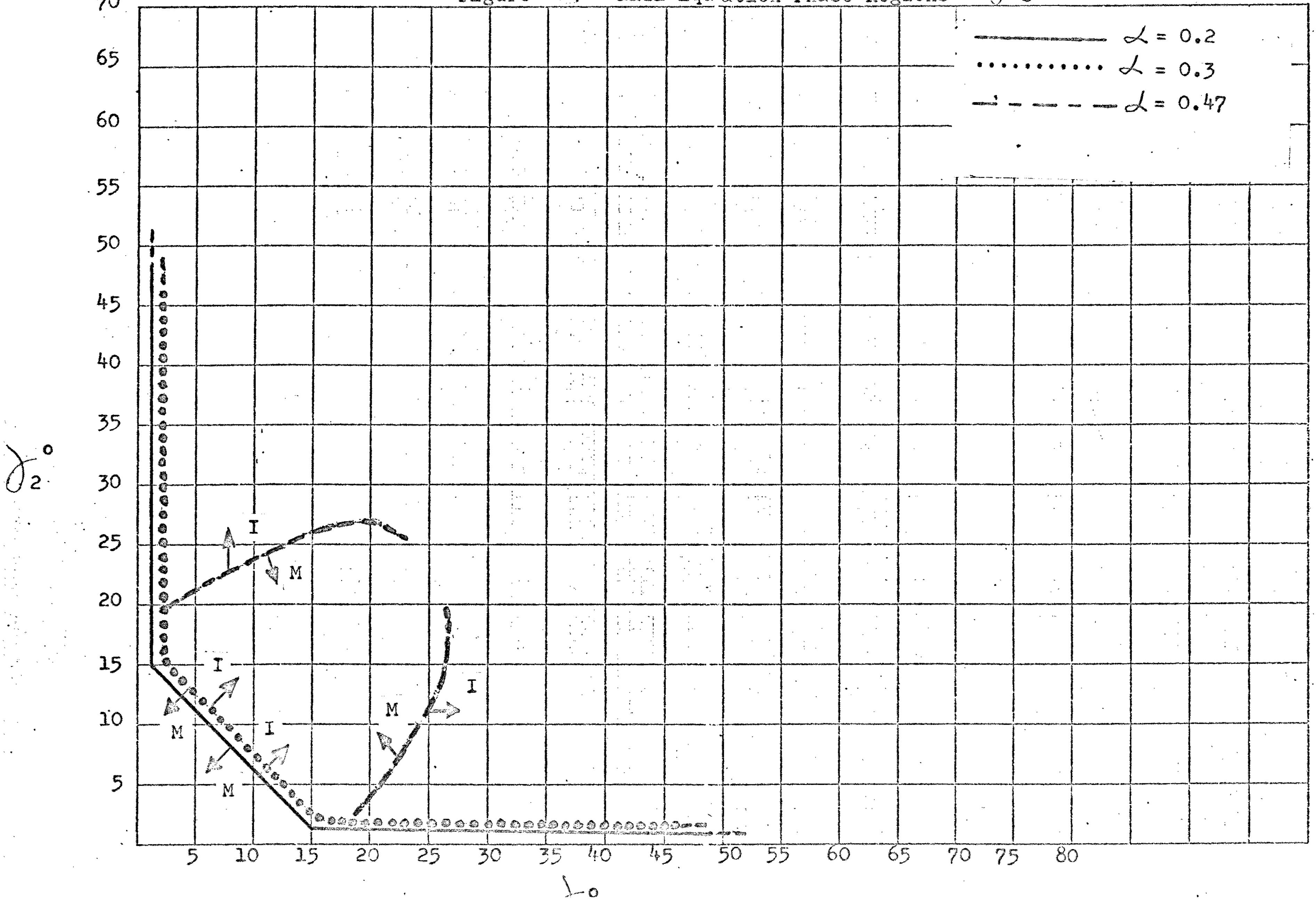


FIGURE VI -NRTL/LEMF EQUATION PHASE REGIONS - PARAMETERS

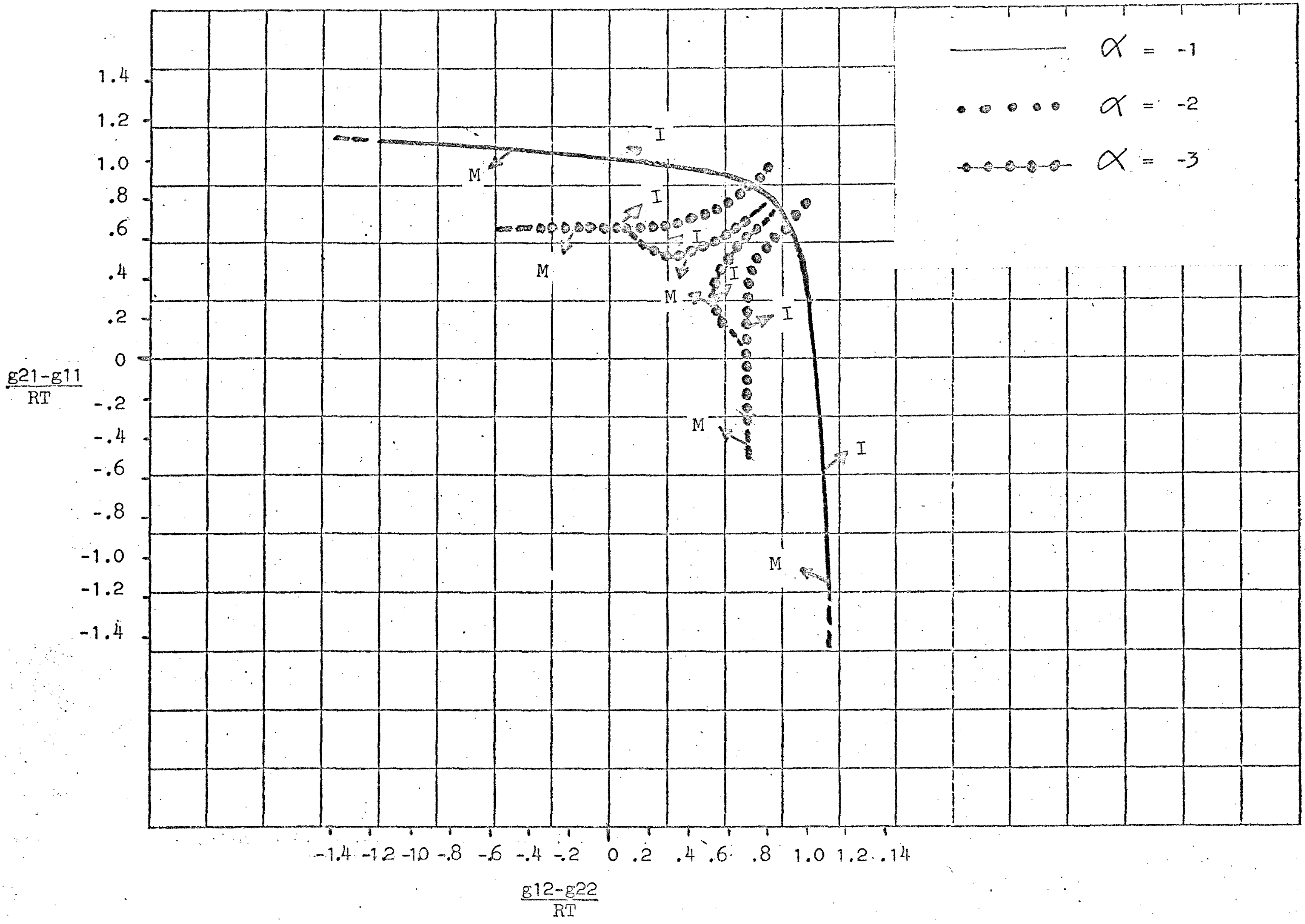


FIGURE VII - NRTL EQUATION PHASE REGIONS - PARAMETERS

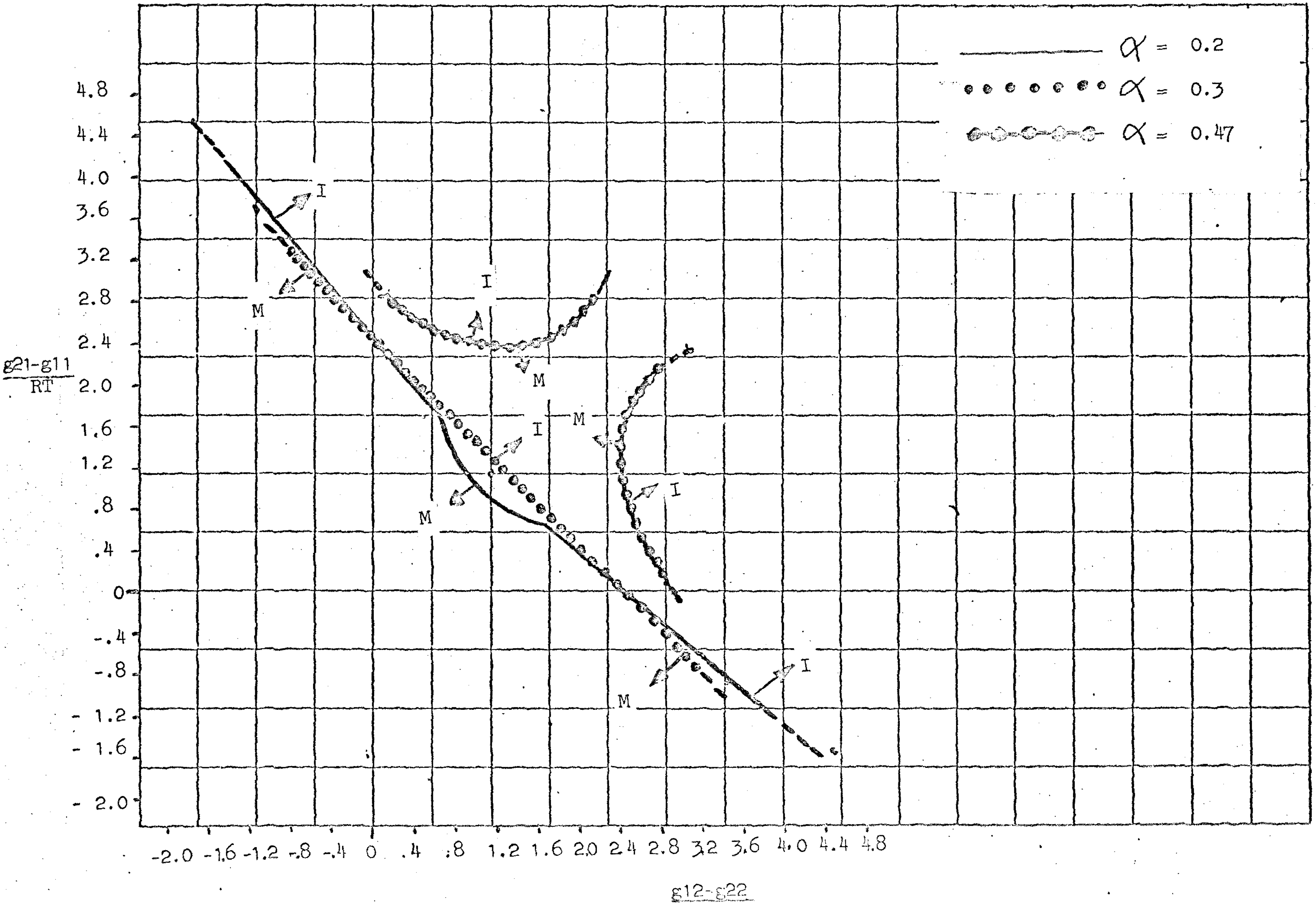


Figure IV indicates the range of miscible predictability for decreasing negative alphas. The alpha of -1.0 supplied the most well defined and complete phase differentiation of the three negative alphas. Departing from the somewhat limited yet distinct miscible/immiscible behavior of α = -1.0, parameters of -2.0 and -3.0 exhibit expanded miscible ranges but with corresponding increased uncertainty near the line ends. A similar situation exists in Figure V with three of the four positive alphas. Constants of 0.20and 0.30 produce clearly defined phase areas while α = 0.47 shows a somewhat less definite region change at high limiting activity coefficients near the 45° line. Results from investigations into α = 0.70 indicated miscible predictions for virtually all limiting activity coefficients. Those data points which represented a phase separation were not sufficient in number to justify drawing of a definite line.

Figures VI and VII which were based on the parameters, parallel the findings shown in the corresponding limiting activity coefficient graphs, to a degree. Figure VI, containing the negative alphas, indicates that α = -1.0 appears to have a wider parameter miscibility range than either α = -2.0 or -3.0.

However, this situation is reversed if, instead of the "base" parameters, the products of alpha and the parameters are plotted. This adjustment is reasonable since, although the equation contains the parameter term alone, it also contains exponential functions of the alpha-parameter product. As in Figure IV, the more negative alphas again have less definition in their graph constructions. Figure VII, illustrates basically the same behaviour observed in Figure V; increasing positive alphas again seem to cover enlarged miscibility ranges once the alpha-parameter products are taken into account. Also, an increasing uncertainty in the phase cross-over line accompanies the increasing positive alphas.

Suggested Procedures for Use of Graphs

There are a choice of routes to follow in determining whether use of a given alpha in the NRTL equation will yield a miscible or immiscible prediction. The available experimental data for a given system may be regressed for a specific alpha to obtain the parameters which may, in turn, be checked with the appropriate alpha-parameter plot. This procedure would entail calculation of (g12-g11)/RT and (g21-g22)/RT for the system parameters and temperature.

If immiscibility is indicated, then a change in alpha to a "more miscible alpha", according to the graphs, may eliminate the problem. Obviously, experience and a degree of certainty should enter into the decision that the case being studied is actually homogeneous over the entire concentration range before forcing the equations to predict homogeneity. Another alternative for guaranteeing miscibility is to obtain the system's limiting activity coefficients from the available data and to consult the appropriate graphs for a suitable alpha. No recalculations are needed in this approach. Of course, the "guarantee" is dependent on the accuracy of the limiting activity coefficients. It is suggested that both of the above approaches be applied to systems as independent checks on each other.

Also, parameters may be generated from the system's limiting activity coefficients and the parameter graphs referred to for a satisfactory alpha, as in the first procedure mentioned. However, it should be stated that the parameters found in the two manners have been found to differ, sometimes substantially, and these differences may be sufficient to affect opposite phase predictions. As a result, it is again recommended that total-data-regression parameters be given the most weight since the alternate procedure of generating parameters relies on a single, sometimes highly extrapolated data point, the limiting activity coefficient. A final "choice" is to evaluate the Gibbs energy second and third derivative equations for a given alpha. However, if the differentials indicate heterogeneity, this procedure will offer no direction as to reselecting an alpha.

Correlation of Graphs with Table II Systems

Table VI lists the Table II binaries with the system infinite dilution activity coefficients and corresponding phase results from consulting Figures IV and V. The parameter phase results are shown for only α = 0.30 and -1.0 as an example of the method. Unfortunately not enough regression data results were obtained to construct reasonably confident extensions of many of the lines for the various alphas that would enable highly non-ideal systems to be predicted. These situations are typified by the tetrahydrofuran-water and methylpyridine-water binaries in Table II. The phase predictions contained in parentheses are therefore only expected circumstances based on limited data; at this point in developing these graphs, these data suggest line extensions for all alphas similar to those seen with α = 0.20 and 0.30. This, of course, will need be confirmed by future work.

Overall, there appears to be only reasonable agreement between the actual phase predictions based on the total data

TABLE VI - Phase Predictions Based on Figures IV, V, VI and VII

	*Acetone-water @25°C	3-Methylpyridine Water @ 69.86°C	3-Methylpyridin water @ 89.83°C	*Water-pyridine @ 80.05°C	Tetrahydrofuran-water @ 50°C	*Water-thioazole @ 90°C	4-Methylpyridine-water @ 69.86°C
γ_1^o	6	70.81	64.72	3.5	21.98	3.5	61.56
γ_2^o	4	2.75	2.59	21	8.85	17	2.61
γ^o graphs							
α							
0.47	M	(I)	(I)	M	M**	M	(I)
0.30	M	(I)	(I)	I	I	I	(I)
0.20	M	(I)	(I)**	I	I	I	(I)
-1.0	M	(I)	(I)	I**	I	M	(I)
-2.0	M	(I)	(I)	M	M**	M	(I)
-3.0	M	(I)	(I)	M	M**	M	(I)
rameter graphs							
α							
0.30	--	I	I	I	I	I	--
1.0	M	I	I	I**	I	M	I

*Approximate Limiting Activity Coefficient Values

**Discrepancies with Total Data Regression Results (Table II) for the systems and the predictions resulting from the limiting activity coefficients. The discrepancies are,

1) The pyridine-water system where, at α = -1.0. The total data regression shows miscible behavior while use of the γ^{o}'s indicates a phase separation.

2) The 3-methylpyridine-water binary at 89.83°C; use of α = 0.2 points to an expected phase separation while Table II, results indicate a single, homogeneous phase.

3) The tetrahydrofuran-water system's total data regression yields phase separations, among other values, at α = -2.0, -3.0 and 0.47. Miscible behavior is predicted by use of the limiting activity coefficients.

It is thought that these inconsitencies are due to a combination of inaccuracies in the graphs themselves and the limiting coefficients, as explained earlier. Unfortunately the last two systems are extremely borderline miscible cases.

Also included in Table VI, are some partial results obtained from consulting the parameter graphs with total data regression parameters. The only discrepancy is in the water-pyridine binary at α = -1.0, a phase separation being predicted while the total data regression indicates miscible system behavior. The actual regression results are listed here:

γ_2	Y_2
.892	.714
.815	.585
.747	.501
.724	.476
.541	.339
.424	.287
.336	.262
.216	.247
.109	.247 *
.073	.241
.046	.219
.002	.022

1 2
Water-pyridine
@ 80.05°C

Regression results at
α = -1.0

According to the phase designation rules on page 10, this system is termed miscible. However, the extreme closeness to immiscibility at the asterisked data points suggests that in fact this system might show a phase split at an intermediate value of γ Thus the discrepancy may in fact not be real but only apparent.

Discussion and Conclusions

The confirmation of the miscibility limitations for the NRTL/LEMF has led to investigations into their thermodynamics. Analytical differentiation of the molar Gibbs energy of mixing allows rigorous determination of the miscible/immiscible regions of the NRTL equation for both positive and negative alphas. Preliminary graphs have been constructed which show definite one and two-phase areas for both limiting activity coefficients and energy parameter variables at these alphas. Only fair agreement exists between phase predictions based on these plots and total data regressions for the systems studied. Possible explanations are included in the text. The choice of alphas to insure miscible prediction may be based on a number of approaches, however, use of a suitable alpha may result in extremely large standard deviations for activity coefficients and consequently, predicted compositions.

Much refinement remains to be done on these basic plots; fortunately, the main limitation appears to be computer size, speed and availability. Worthwhile future work might include clarification of the miscible/immiscible envelope for any alpha through simultaneous solution of the second and third derivatives of the molar Gibbs energy of mixing with both expressions set equal to zero. One of the three parameters, g12-g11, g-21-g22 or α would be preset with the remaining two obtained by the equations' solution. The figures contained in this present work would provide direction in the envelope construction.

Nomenclature

Δg^m, G^E - molar Gibbs energy of mixing

G11 - second derivative of molar Gibbs energy of mixing

x_{ij} - local mole fraction of molecules i around molecule j

g_{ij} - interaction energy parameter between an i - j molecular pair

x_i - overall mole fraction of component i

Z_{ij} - local volume fraction of molecules i around molecule j

v_i - molar volume of component i

R - gas constant

T - absolute temperature

α - nonrandomness parameter, alpha

γ_i - activity coefficient of component i

SD - standard deviation in activity coefficient prediction

N - number of experimental data points

γ_i^o - limiting (infinite dilution) activity coefficient of component i

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APPENDIX

TEMPERATURE-INDEPENDENT* PARAMETERS AND PHASE PREDICTIONS BASED ON γ°'s

$\alpha = 0.20$

γ_2°	γ_1°	g21-g11	g12-g22
.4	.8	-1.595	1.374 M
.4	1.0	-1.578	1.360 M
.6	.6	-.249	-.249 M
.6	1.2	-1.105	.994 M
.6	1.5	-1.095	.987 M
.6	1.8	-1.100	.991 M
2	4	2.243	-.827 M
2	5	2.634	-.862 M
2	6	2.919	-.935 M
2	12	3.878	-1.088 M
2	14	4.018	-1.106 I
2	20	4.416	-1.133 I
4	4	.745	.745 M
4	6	1.559	.245 M
4	8	2.056	.023 M
4	10	2.405	-.100 M
4	12	2.670	-.179 M
4	16	3.062	-.274 I
5	20	3.042	-.046 I
5	25	3.321	-.100 I
5	40	3.870	-.176 I
5	50	4.118	-.198 I
6	6	.984	.984 M
6	9	1.667	.597 M
6	12	2.108	.409 I
6	15	2.428	.298 I
6	18	2.676	.225 I
6	36	3.536	.048 I
6	60	4.111	.015 I
7	70	4.113	.139 I
8	8	1.160	1.160 I
8	12	1.780	.833 I
8	16	2.189	.667 I
8	24	2.726	.500 I
10	10	1.300	1.300 I
10	15	1.882	1.011 I
10	20	2.271	.861 I
10	25	2.560	.768 I
10	30	2.788	.706 I
12	12	1.417	1.418 I
12	24	2.349	1.017 I
14	14	1.519	1.518 I
14	21	2.056	1.276 I
14	28	2.420	1.148 I
14	35	2.693	1.067 I

*NOTE: The values listed under g21-g11 and g12-g22 on this page and proceeding ones are, in effect, temperature independent or g21-g11/RT and g12-g22/RT.

α = 0.20

γ_2°	γ_1°	g21-g11	g12-g22
14	42	2.911	1.013 I
15	15	1.564	1.564 I
18	18	1.687	1.687 I
18	36	2.548	1.360 I
18	54	3.023	1.238 I
20	40	2.605	1.449 I
22	44	2.658	1.529 I
34	68	2.922	1.898 I
38	76	2.993	1.993 I
40	80	3.027	2.037 I

α = 0.30

2	12	3.016	-.530 M
2	14	3.264	-.533 M
2	16	3.399	-.534 I
2	18	3.514	-.532 I
2	20	3.615	-.529 I
4	4	.773	.773 M
4	6	1.381	.474 M
4	8	1.767	.346 M
4	12	2.263	.239 M
4	20	2.829	.176 I
4	40	3.535	.162 I

α = 0.30

γ_2°	γ_1°	g21-g11	g12-g22
5	40	3.348	.383 I
5	50	3.568	.386 I
6	18	2.370	.628 I
6	12	1.908	.715 I
6	24	2.682	.592 I
6	36	3.104	.589 I
6	60	3.614	.570 I
7	70	3.665	.726 I
8	8	1.229	1.230 M
8	12	1.717	1.054 I
8	16	2.047	.972 I
8	24	2.491	.900 I
10	15	1.853	1.240 I
10	20	2.172	1.171 I
10	30	2.608	1.108 I
12	24	2.284	1.334 I
14	21	2.080	1.525 I
14	28	2.386	1.472 I
14	42	2.833	1.430 I
15	15	1.687	1.692 I
15	30	2.432	1.536 I
16	40	2.708	1.571 I
18	18	1.833	1.833 I

$\alpha = 0.30$

γ_2°	γ_1°	g21-g11	g12-g22
18	36	2.562	1.703 I
18	45	2.791	1.682 I
18	54	2.977	1.672 I
20	30	2.343	1.836 I
20	40	2.640	1.800 I
20	60	3.052	1.774 I
22	22	1.995	1.995 I
22	33	2.417	1.921 I
22	44	2.712	1.889 I
22	55	2.939	1.874 I
34	68	3.066	2.304 I
38	76	3.160	2.413 I
40	80	3.205	2.464 I

$\alpha = 0.47$

γ_2°	γ_1°	g21-g11	g12-g22
2	6	1.878	-.083 M
2	12	2.563	-.075 M
2	14	2.707	-.065 M
2	18	2.937	-.046 M
2	20	3.302	-.036 I
4	6	1.297	.681 M
4	8	1.611	.631 M
4	12	2.030	.604 M

$\alpha = 0.47$

γ_2°	γ_1°	g21-g11	g12-g22
4	16	2.317	.607 M
4	20	2.534	.616 M
4	40	3.198	.675 I
5	25	2.650	.847 I
5	20	2.432	.834 M
5	30	2.827	.861 I
5	35	2.976	.875 I
5	40	3.104	.888 I
5	45	3.217	.900 I
5	50	3.318	.912 I
6	12	1.855	1.016 M
6	18	2.262	1.015 M
6	24	2.546	1.023 I
6	36	2.941	1.054 I
6	60	3.436	1.109 I
7	70	3.548	1.276 I
8	8	1.361	1.361 M
8	12	1.777	1.309 M
8	16	2.068	1.297 M
10	15	1.964	1.522 M
10	20	2.251	1.522 M
10	25	2.474	1.529 I
10	30	2.654	1.540 I

α = 0.47

γ_2°	γ_1°	g21-g11	g12-g22
10	40	2.939	1.564 I
10	50	3.159	1.587 I
12	24	2.413	1.709 M
14	21	2.269	1.858 M
14	28	2.555	1.870 I
14	42	2.960	1.903 I
15	15	1.929	1.929 M
15	30	2.622	1.944 I
16	16	1.992	1.992 M
16	40	2.907	2.031 I
18	18	2.108	2.108 M
18	36	2.801	2.139 I
18	45	3.024	2.160 I
18	54	3.207	2.180 I
20	30	2.619	2.231 I
20	40	2.908	2.254 I
20	60	3.314	2.298 I
20	80	3.603	2.333 I
22	22	2.311	2.311 M
22	33	2.717	2.333 I
22	44	3.006	2.359 I
22	55	3.230	2.383 I
30	60	3.336	2.706 I

α = 0.47

γ_2°	γ_1°	g21-g11	g12-g22
40	60	3.362	2.997 I
40	80	3.653	3.033 I
	α = 0.70		
2	2	.394	.394 M
2	12	2.288	.232 M
2	14	2.430	.250 M
2	6	1.639	.173 M
2	18	2.660	.280 M
2	20	2.757	.293 M
2	16	2.552	.266 M
2	60	3.779	.425 M
2	70	3.924	.441 M
4	4	.906	.906 M
4	6	1.320	.862 M
4	8	1.608	.865 M
4	20	2.507	.953 M
4	40	3.186	1.044 M
4	12	2.007	.894 M
5	20	2.480	1.172 M
5	35	3.034	1.247 M
5	40	3.167	1.265 I
5	45	3.284	1.280 I

$\alpha = 0.70$

γ_2°	γ_1°	g21-g11	g12-g22
5	50	3.389	1.294 M
6	18	2.366	1.340 M
6	12	1.962	1.295 M
6	24	2.653	1.378 M
6	36	3.058	1.432 M
6	60	3.569	1.498 M
8	8	1.556	1.556 M
8	12	1.962	1.583 M
8	16	2.251	1.614 M
8	24	2.659	1.666 M
8	20	2.490	1.867 M
10	25	2.716	1.897 M
10	30	2.827	1.922 M
10	50	3.418	1.990 M
12	24	2.693	2.076 M
14	21	2.574	2.215 M
14	42	3.279	2.309 M
14	28	2.876	2.254 M
15	15	2.241	2.241 M
15	30	2.946	2.334 M
16	16	2.315	2.314 M
16	40	3.246	2.438 M
18	18	2.449	2.450 M
18	36	3.156	2.544 M
18	45	3.382	2.573 M
18	54	3.567	2.597 M
18	48	3.447	2.581 M
20	30	2.984	2.626 M
20	40	3.276	2.665 M
22	22	2.681	2.681 M
22	33	3.094	2.736 M
22	44	3.386	2.775 M
22	55	3.613	2.803 M
34	68	3.888	3.270 M
38	76	4.016	3.396 M
40	80	4.074	3.454 M
26	52	3.579	2.966 M

$\alpha = -1.0$

γ_2°	γ_1°	g21-g11	g12-g22
.4	.4	-.589	-.589 M
.4	.8	.144	-1.082 M
.4	1.0	.345	-1.416 M
.6	.6	-.293	-.293 M
.6	1.2	.527	-1.404 M
.6	1.5	.690	-1.887 M

α = -1.0

γ_2°	γ_1°	g21-g11	g12-g22	γ_2°	γ_1°	g21-g11	g12-g22
				6	60	.418	1.156 I
.6	1.8	.813	2.343 M	6	36	.457	1.071 I
.8	.8	-.118	-.118 M	6	24	.489	.995 I
2	2	.296	-.296 M	6	15	.530	.892 M
2	4	0	.693 M	8	8	.693	.693 M
2	5	-.097	.781 M	8	16	.634	.884 M
2	6	-.186	.848 M	8	20	.618	.934 I
2	12	-.677	1.076 M	8	24	.605	.973 I
2	14	-.686	1.101 M	7	70	.480	1.170 I
2	16	-.693	1.123 M	9	18	.665	.903 I
2	18	-.700	1.141 I	10	10	.743	.743 M
2	20	-.706	1.157 I	10	15	.712	.852 M
4	4	.527	.518 M	10	20	.692	.919 I
4	6	.450	.680 M	10	25	.678	.967 I
4	8	.408	.772 M	10	30	.667	1.003 I
4	10	.378	.835 M	12	12	.781	.781 M
4	12	.354	.882 M	12	18	.754	.883 I
5	5	.578	.578 M	12	24	.736	.947 I
5	20	.419	.974 I	12	30	.724	.992 I
4	40	.210	1.127 I	12	36	.714	1.027 I
5	40	.354	1.105 I	14	14	.812	.812 M
5	50	.335	1.142 I	14	21	.787	.909 I
6	18	.513	.934 I	14	35	.760	1.014 I

$\alpha = -1.0$				$\alpha = -2.0$			
γ_2°	γ_1°	g21-g11	g12-g22	γ_2°	γ_1°	g21-g11	g12-g22
14	28	.772	.970 I				
14	42	.751	1.048 I				
15	15	.825	.825 M				
15	30	.787	.981 I	.6	1.8	.604	-2.531 M
16	16	.838	.838 M	2	6	.111	.555 M
16	24	.815	.931 I	2	12	.033	.658 M
16	32	.801	.990 I	2	14	.018	.677 M
16	40	.789	1.033 I	2	16	0	.693 M
16	48	.781	1.065 I	2	20	-.027	.719 I
18	18	.860	.860 I	4	4	.419	.419 M
18	45	.815	1.049 I	4	6	.397	.506 M
20	20	.879	.879 I	4	8	.385	.557 M
20	30	.859	.967 I	4	12	.368	.617 M
20	40	.847	1.023 I				
22	22	.896	.896 I	4	20	.351	.680 M
22	33	.877	.981 I	4	40	.330	.750 I
22	44	.865	1.036 I	5	25	.405	.697 I
22	55	.856	1.075 I	5	35	.397	.731 I
24	24	.911	.911 I	5	45	.391	.755 I
26	26	.925	.925 I	5	40	.394	.744 I
34	68	.945	1.095 I	5	50	.389	.764 I
38	76	.964	1.110 I	6	18	.456	.656 M
40	80	.973	1.116 I	6	24	.689	.449 M

$\alpha = -2.0$

γ 2°	γ 1°	g21-g11	g12-g22	
6	12	.604	.467	M
6	36	.440	.730	I
6	60	.430	.776	I
7	70	.461	.786	I
8	8	.533	.533	M
8	12	.522	.596	M
8	16	.515	.635	M
8	24	.507	.682	M
10	15	.555	.621	M
10	20	.549	.657	M
10	25	.545	.683	M
10	30	.542	.702	I
10	40	.537	.730	I
12	24	.574	.687	M
10	50	.534	.752	I
14	21	.599	.657	M
14	28	.594	.690	M
14	42	.588	.731	I
15	15	.614	.614	M
15	30	.603	.696	M
16	16	.621	.621	M
16	40	.608	.724	I
18	18	.634	.634	M
18	36	.625	.712	I
18	45	.622	.734	I
20	20	.646	.646	M
20	40	.637	.721	I
20	60	.632	.759	I
22	22	.656	.656	M
22	33	.651	.701	I
22	44	.647	.729	I
22	55	.645	.750	I
25	50	.661	.740	I
34	68	.692	.765	I
38	76	.703	.773	I
40	80	.707	.777	I

$\alpha = -3.0$

γ_2^0	γ_1^0	g21-g11	g12-g22	
4	.8	-.153	-.820	I
4	1.0	.052	-.977	M
6	.6	.390	-.390	M
6	1.8	.567	-3.618	I
6	1.5	.410	-1.915	M
6	1.2	.234	-.983	M
2	4	.181	.383	M
2	5	.168	.415	M
2	8	.144	.471	M
2	10	.134	.494	M
2	6	.158	.438	M
2	12	.126	.510	M
2	14	.119	.524	M
2	16	.113	.535	M
2	18	.108	.544	M
2	20	.103	.552	M
4	4	.355	.355	M
4	8	.339	.451	M
4	10	.335	.474	M
4	6	.345	.416	M
5	10	.373	.471	M
5	25	.360	.550	M
5	30	.358	.563	I
5	35	.356	.573	I
5	45	.353	.589	I
5	40	.355	.582	I
5	50	.352	.596	I
6	18	.392	.522	M
6	36	.385	.573	I
6	60	.380	.605	I
7	14	.416	.499	M
7	70	.401	.613	I
8	8	.439	.439	M
8	12	.434	.482	M
8	16	.431	.509	M
8	24	.436	.542	M
8	32	.425	.563	I
8	20	.429	.528	M
10	15	.457	.501	M
10	20	.455	.525	M
10	30	.451	.556	M

α =-3.0

γ 2°	γ 1°	g21-g11	g12-g 22	γ 2°	γ 1°	g21-g11	g12-g22
10	40	.449	.576 I				
10	50	.447	.590 I	25	50	.533	.585 I
10	60	.446	.601 I	25	75	.531	.609 I
12	24	.472	.538 M	30	30	.549	.549 M
14	14	.492	.492 M	34	68	.555	.602 M
14	42	.484	.577 M	40	80	.565	.611 I
14	28	.486	.549 M				
15	15	.497	.497 M				
15	60	.488	.599 I				
16	16	.503	.503 M				
16	40	.496	.579 M				
15	30	.492	.553 M				
18	18	.512	.512 M				
18	27	.509	.544 M				
18	36	.507	.565 M				
18	45	.506	.580 M				
20	30	.518	.551 M				
20	40	.516	.572 I				
22	22	.527	.527 M				
22	33	.525	.558 M				
22	55	.522	.591 M				
20	60	.514	.597 I				

ADDITIONAL RESULTS

These parameter values were chosen to aid in refining the actual I - M boundary for the various alphas; the second and third derivatives (third set equal to zero) of the excess Gibbs energy of mixing were evaluated directly from them.

$\alpha = 0.2$

g21-g11/RT	g12-g22/RT	2nd der.	g21-g11/RT	g12-g22/RT	2nd der.
2.934	-.293	-.174 I	.587	1.614	.178 M
2.347	.147	-.133 I	.293	1.760	.471 M
.587	1.760	-.035 I	.440	1.467	.645 M
1.174	1.174	-.089 I	1.174	.880	.356 M
1.174	1.320	-.301 I	1.027	1.027	.351 M
.587	2.054	-.459 I			

$\alpha = 0.3$

g21-g11/RT	g12-g22/RT	2nd der.	g21-g11/RT	g12-g22/RT	2nd der.
-.293	1.760	1.920 M	1.320	1.320	-.086 I
-.293	2.934	.194 M	.587	2.054	-.068 I
.147	2.347	.220 M	.587	1.614	.471 M
.587	1.760	.293 M	.293	2.347	-.030 I
1.174	1.174	.241 M	.440	2.201	-.053 I
1.174	1.320	.074 M	.440	2.054	.139 M

$\alpha = 0.47$

1.760	1.760	.374 M	2.347	2.934	.733 M
1.760	2.347	.107 M	1.760	2.641	-.236 I
1.174	2.347	.074 M	1.174	2.494	-.095 I
.587	2.347	.323 M	.587	2.494	.135 M
.587	2.641	-.086 I	1.760	2.567	-.135 I
2.347	2.347	.274 M	2.054	2.641	-.159 I

$\alpha = -1.0$

g21-g11/RT	g12-g22/RT	2nd der.	g21-g11/RT	g12-g22/RT	2nd der.
1.174	1.174	.624 M	-.880	1.100	1.034 M
.880	.880	-.131 I	.587	.587	1.229 M
1.027	.587	-1.002 I	.880	.734	.033 M
-.880	1.027	1.774 M	.293	.880	.645 M
-.587	1.174	-1.016 I	.293	1.027	-.658 I
-1.174	1.247	-.693 I	.293	1.174	3.067 I
1.218	-1.174	-.099 I	.652	.971	-.501 I *)
.968	.653	-.477 I	.734	.734	.525 M
-.880	1.174	-.085 I	.807	.807	.192 M
-.587	1.027	1.212 M	.844	.844	.033 M
.477	-1.174	.035 M	.867	.867	-.062 I
.880	.587	.211 M	-.293	1.027	.050 M

*) THF-H_2O system parameters

$\alpha = -2.0$

g21-g11/RT	g12-g22/RT	2nd der.	g21-g11/RT	g12-g22/RT	2nd der.
-.147	.734	-.237 I	.147	.660	.968 M
.734	.734	1.095 M	.440	.660	.714 M
-.147	.587	2.396 M	.587	.660	.683 M
.293	.660	.803 M	.697	.697	1.154 M
.697	.734	1.127 M	.587	.770	-2.498 I

$\alpha = -3.0$

.367	.587	-1.631 I	.550	.587	2.000 M
.550	.624	2.006 M	.440	.587	-1.625 I
.550	.550	2.004 M	.147	.514	1.614 M
.514	.587	1.533 M	.293	.514	1.514 M
.220	.403	2.492 M			

VAPOR PRESSURE DATA FOR SYSTEMS

	1 2	1 2	1 2
SYSTEM	Acetone-water @ 25°C	3-methylpyridine-water @ 69.86°C	3-methylpyridine-water @ 89.83°C
P1 (mm Hg)	229.6	60.05	134.4
P2 (mm Hg)	23.7	232.3	522.4

	1 2	1 2	1 2
SYSTEM	Water-pyridine @ 80.05°C	Tetrahydrofuran-water @ 50°C	Water-thioazole @ 90°C
P1 (mm Hg)	355.0	439.55	526.0
P2 (mm Hg)	238.9	92.49	320.0

	1 2
SYSTEM	4-methylpyridine-water @ 69.86°C
P1 (mm Hg)	57.6
P2 (mm Hg)	232.3

NOTE: Pressure data for all binaries were taken directly from the system data sources as listed in the bibliography. The THF-water binary pressures were calculated from the following Antoine constants, also from its data source, reference 7

CONSTANT	THF	WATER
A	6.99589	7.96681
B	1202.7	1668.2
C	226.3	228.

EXAMPLE OF TYPICAL SYSTEM PARAMETER RESULTS

	ACETONE-WATER @ 25°C		3-METHYLPYRIDINE-WATER @ 69.86°C		3-METHYLPYRIDINE-WATER @ 89.83°C		PYRIDINE-WATER @ 80.05°C	
α	-1.0	-2.0	-1.0	-2.0	-1.0	-2.0	-1.0	-2.0
SD (γ)	.0706	.0838	.1224	.0937	.1049	.0785	.0827	.0736
g12-g11/RT	.665	.676	-.965	.072	-1.022	.143	1.220	.696
g21-g22/RT	.665	.498	1.256	.778	1.280	.776	1.172	.205

	TETRAHYDROFURAN WATER @ 50°C		THIOAZOLE-WATER @ 90°C		4-METHYLPYRIDINE-WATER @ 69.86°C	
α	-1.0	-2.0	-1.0	-3.0	-1.0	0.7
SD (γ)	.0257	.0978	.0201	.1284	.1849	.1069
g12-g11/RT	.652	.578	.995	.557	-.930	3.445
g21-g22/RT	.971	.723	.208	.324	1.244	1.212

COMPUTER PROGRAMS

The following programs, NLREGR and GIBTH, were used in this work. NLREGR is a non-linear regression program generating g21-g11/RT and g12-g22/RT from a given system's experimental data. Additionally, predicted vapor compositions are obtained.

GIBTH is a root-finding program solving first equation (17), the Gibbs third derivative, and then evaluating equation (16), the second derivative. Typical results are also attached.

```
      PROGRAM NLREGR
      DIMENSION XT(10),X(10,10),Y(10),JJ(10),A(10,10)
      DIMENSION G1OUT(25),G2OUT(25),PRESS(25)
      COMMON T,TS,VA,VB,X1(25),X2(25),G1OBS(25),G2OBS(25),N,G1MCAL
     1G2MCAL(25),II,ALPHA
      MREAD=5
      MWRTE=6
      DO 490 I=1,10
      XT(I) = 0.0
      Y(I) = 0.0
      JJ(I) = 0
      DO 490 J=1,10
      A(I,J) = 0.0
      X(I,J) = 0.0
  490 CONTINUE
      READ (MREAD,188) ISWTH
  188 FORMAT (I5)
      READ (MREAD,88) N,T,VA,VB,ALPHA,M,L,E,DX,M1,XT(1),XT(2),PO1,
   88 FORMAT (I2,4F5.0,2I2,2F5.0,I2,4F5.0)
  491 DO 90 I=1,N
      READ (MREAD,89) X1(I),X2(I),G1OBS(I),G2OBS(I),PRESS(I)
      G1OUT(I) = G1OBS(I)
      G2OUT(I) = G2OBS(I)
   90 CONTINUE
   89 FORMAT (2F5.0,3F10.0)
   91 M3=N+3
      WRITE(MWRTE,500)
  500 FORMAT(1H1,10X,'NON-LINEAR REGRESSION INPUT DATA'/)
      WRITE(MWRTE,510)N,T,VA,VB
  510 FORMAT(1X,'N=',12X,I3/1X,'T=',5X,F10.3/1X,'VA=',4X,F10.3/1X,
     14X,F10.3)
      WRITE(MWRTE,520)ALPHA,M,L,E
  520 FORMAT(1X,'ALPHA= ',F10.3/1X,'M=',12X,I3/1X,'L=',12X,I3/1X,'
     1,F10.3)
      WRITE(MWRTE,530)DX,M1,XT(1),XT(2)
  530 FORMAT(1X,'DX=',4X,F10.3/1X,'M1=',11X,I3/1X,'XT(1)= ',F10.3/
     1(2)= ',F10.3/)
      IF (ISWTH-2) 492,493,493
  492 WRITE(MWRTE,540)
  540 FORMAT(1X,'NO',9X,'X1',11X,'X2',11X,'G1',11X,'G2'/)
      WRITE(MWRTE,550)(I,X1(I),X2(I),G1OBS(I),G2OBS(I),I=1,N)
  550 FORMAT(1X,I2,1X,F12.3,1X,F12.3,1X,F12.3,1X,F12.3)
  493 L1C=0
      IF(L.LE.0)GO TO 50
      IHC = M1 + 1
      EN = M
      EN = EN * 1.5
      L1 = L
      L = -L
      L2 = (3 * M) / 2 + 5
```

```
      K3 = 2
      IF(M.GE.3)K3 = 3
      K4 = K3 - 1
      G = K3 * 2
      G = 1.0 / G
      DO 100 I=1,M
  100 X(I,1) = XT(I)
      GO TO (700,710),ISWTH
  700 CALL FN(Y(1),XT)
      GO TO 720
  710 CALL TN (Y(1),XT)
  720 DO 106 J=2,M1
      XT(J-1) = XT(J-1) + DX
      DO 104 I=1,M
  104 X(I,J) = XT(I)
      IF (ISWTH-2) 721,722,722
  721 CALL FN(Y(J),XT)
      GO TO 723
  722 CALL TN(Y(J),XT)
  723 XT(J-1)=X(J-1,1)
  106 CONTINUE
      L2C = 0
      FLG = 1.0
      GO TO 50
  108 L1C = L1C + 1
      IF(L1C.GE.L1)GO TO 400
   50 YL = 1.0E38
      YH = - YL
      Y2 = YH
      Y3 = YL
      DO 110 J=1,M1
      IF(Y(J).LT.YH)GO TO 1091
      Y2 = YH
      I2 = IH
      YH = Y(J)
      IH = J
      GO TO 109
 1091 IF(Y(J).LT.Y2)GO TO 109
      Y2 = Y(J)
      I2 = J
  109 IF(Y(J).GT.YL)GO TO 1101
      Y3 = YL
      I3 = IL
      IL = J
      YL = Y(J)
      GO TO 110
 1101 IF(Y(J).GT.Y3)GO TO 110
      Y3 = Y(J)
      I3 = J
  110 CONTINUE
```

```
      L2C = L2C + 1
      IF(L2C.LT.L2)GO TO 111
      L2C = 0
      JJ(1) = IL
      JJ(2) = I2
      JJ(3) = I3
      DO 60 K1=1,K3
      J1 = JJ(K1)
      DO 60 K2=K1,K3
      J2 = JJ(K2)
      S = 0.0
      DO 55 I=1,M
   55 S = S + (X(I,J1) - X(I,IH)) * (X(I.J2) - X(I,IH))
   60 A(K1,K2) = S
      D = A(1,1) * A(2,2) - A(1,2)**2.0
      GO TO(62,61),K4
   61 D1 = A(1.1) * A(2,3) - A(1,2) *A(1,3)
      D = ((A(1,1) * A(3,3)-A(1,3)**2.0)*D-D1*D1) / (A(1,1) * 9.0)
   62 D = (D / 4.0)**G
      IF(D.LT.E)GO TO 65
      FLG = 1.0
      GO TO 111
   65 IF(FLG.LT.0.0)GO TO 400
      FLG = -1.0
  111 DO 115 I=1,M
      XT(I) = 0.0
      DO 112 J=1,M1
      IF(J.NE.IH)XT(I) = XT(I) + X(I,J)
  112 CONTINUE
  115 XT(I) = (3.0 * XT(I) + X(I,I2) - X(I,IL)) / EN - X(I,IH)
  121 IF (ISWTH-2) 771,724,724
  771 CALL FN(YT,XT)
      GO TO 725
  724 CALL TN(YT,XT)
  725 IF (YT.GE.Y2)GO TO 167
      IHC = M1 + 1
      IF(YT.GE.YL)GO TO 140
      YTT = YT
      DO 135 I=1,M
  135 XT(I) = 1.5 * XT(I) - 0.5 * X(I,IH)
      IF (ISWTH-2) 726,727,727
  726 CALL FN(YT,XT)
      GO TO 728
  727 CALL TN(YT,XT)
  728 IF(YT.LE.YL)GO TO 140
      DO 138 I=1,M
  138 X(I,IH) = (2.0 * XT(I) + X(I,IH)) / 3.0
      Y(IH) = YTT
      GO TO 108
  140 DO 142 I=1,M
```

```
  142 X(I,IH) = XT(I)
      Y(IH) = YT
      GO TO 108
  167 IHC = IHC - 1
      IF(IHC.EQ.0)GO TO 300
      IF(YT.GE.YH)GO TO 173
      DO 168 I=1,M
      XS = XT(I)
      XT(I) = X(I,IH)
  168 X(I,IH) = XS
  173 DO 174 I=1,M
  174 XT(I) = 0.75 * X(I,IH) + 0.25 * XT(I)
      IF(ISWTH-2) 729,730,730
  729 CALL FN (YT,XT)
      GO TO 731
  730 CALL TN (YT,XT)
  731 IF(YT.GT.YH)GO TO 180
      Y(IH) = YT
      DO 175 I=1,M
  175 X(I,IH) = XT(I)
      GO TO 108
  180 DO 185 J=1,M1
      IF(J.EQ.IL)GO TO 185
      DO 182 I=1,M
      XT(I) = (X(I,J) + X(I,IL)) / 2.0
  182 X(I,J) = XT(I)
      IF(ISWTH-2) 732,733,733
  732 CALLFN(Y(J),XT)
      GO TO 185
  733 CALL TN(Y(J),XT)
  185 CONTINUE
      GO TO 108
  300 IHC = 2 * M1
      IF(M.GE.3)GO TO 350
      S = 0.0
      DO 302 I=1,M
      X(I,M+2) = X(I,IH) - X(I,IL)
      X(I,M+3) = X(I,IH) - X(I,I3)
  302 S = S + X(I,M+2)**2.0
  303 S = SQRT(S)
      U = -X(2,M+2) / S
      X(2,M+2) = X(1,M+2) / S
      X(1,M+2) = U
      S = X(1,M+2) * X(1,M+3) + X(2,M+2) * X(2,M+3)
      DO 305 I=1,M
  305 X(I,M+2) = X(I,M+2) * S
  306 DO 307 I=1,M
  307 XT(I) = X(I,IH) + X(I,M+2)
      IF (ISWTH-2) 734,735,735
  734 CALL FN(YT,XT)
```

```
      GO TO 736
  735 CALL TM(YT,XT)
  736 DO 309 I=1,M
  309 XT(I) = X(I,IH) - X(I,M+2)
      IF (ISWTH-2) 737,738,738
  737 CALL FH(YTT,XT)
      GO TO 739
  738 CALL TM(YTT,XT)
  739 IF (YTT.LE.YT) GO TO 320
      DO 311 I=1,M
  311 XT(I) = X(I,IH) + X(I,M+2)
      YTT = YT
  320 Y(IH) = YTT
      DO 321 I=1,M
  321 X(I,IH) = XT(I)
      GO TO 108
  350 DO 352 I=1,M
      XT(I) = X(I,IH) - X(I,IL)
      X(I,M+2) = X(I,IH) - X(I,I2)
  352 X(I,M+3) = X(I,IH) - X(I,I3)
      S = 0.0
      S1 = 0.0
      DO 355 I=1,M
      S = S + XT(I)**2.0
  355 S1 = S1 + X(I,M+3)**2.0
      S = SQRT(S)
      S1 = SQRT(S1)
      S2 = 0.0
      DO 357 I=1,M
      XT(I) = XT(I) / S
      S2 = S2 + XT(I) * X(I,M+2)
  357 X(I,M+3) = X(I,M+3) / S1
      DO 360 I=1,M
  360 X(I,M+2) = X(I,M+2) - XT(I) * S2
      S1 = 0.0
      DO 362 I=1,M
  362 S1 = S1 + X(I,M+2)**2.0
      S1 = SQRT(S1)
      DO 365 I=1,M
  365 X(I,M+2) = X(I,M+2) / S1
      S1 = 0.0
      S2 = 0.0
      DO 367 I=1,M
      S1 = S1 + XT(I) * X(I,M+3)
  367 S2 = S2 + X(I,M+2) * X(I,M+3)
      DO 370 I=1,M
  370 X(I,M+2) = S * (S1 * XT(I) + S2 * X(I,M+2) - X(I,M+3))
      GO TO 306
  400 S = Y(1)
      Y(1) = Y(IL)
```

```
      Y(IL) = S
      DO 402 I=1,M
      XT(I) = X(I,IL)
      X(I,IL) = X(I,1)
  402 X(I,1) = XT(I)
      WRITE(MWRTE,560)
  560 FORMAT(/1X,'NON-LINEAR REGRESSION RESULTS'/)
      L=L+51
      WRITE(MWRTE,565) L
  565 FORMAT (1X,'ITERATION=',I5/)
      IF (ISWTH-2) 602,601,601
  602 WRITE (MWRTE,568) PO1,PO2
  568 FORMAT (1X,'PRESSURE OF X1=',F12.5//1X,'PRESSURE OF X2=',F12.
  601 WRITE (MWRTE,570) YT,XT(1),XT(2)
  570 FORMAT(1X,'STANDARD DEVIATION= ',F12.4//1X,'G12-11=',12X,F13.4
     1,'G12-22=',12X,F13.4//)
      IF (ISWTH-2) 603,600,600
  603 WRITE(MWRTE,572)
  572 FORMAT(/T12,'G1',13X,'G1',13X,'G1',13X,'G2',13X,'G2',13X,'G2')
      WRITE (MWRTE,574)
  574 FORMAT(1X,'NO',T7,'OBSERVED',T22,'PREDICTED',T37,'DEVIATION',T
     1'OBSERVATION',T67,'PREDICTED',T83,'DEVIATION'/)
      DO 578 I=1,N
      G1X = G1OUT(I) - G1MCAL(I)
      G2X = G2OUT(I) - G2MCAL(I)
      WRITE(MWRTE,576)I,G1OUT(I),G1MCAL(I),G1X,G2OUT(I),G2MCAL(I),G2
  576 FORMAT(1X,I2,1X,6(F12.5,3X))
  578 CONTINUE
      WRITE (MWRTE,580)
  580 FORMAT (//1X,'NO',T17,'X1',T37,'Y1',T56,'X2',T77,'Y2',T91,'PRE
     1E'/)
      DO 595 I=1,N
      Y1=(G1MCAL(I)*X1(I)*PO1)/PRESS(I)
      Y2=(G2MCAL(I)*X2(I)*PO2)/PRESS(I)
      RAW=Y1+Y2
      Y1=Y1/RAW
      Y2=Y2/RAW
      WRITE (MWRTE,585) I,X1(I),Y1,X2(I),Y2,PRESS(I)
  585 FORMAT (1X,I2,T9,5(F12.3,8X)/)
  595 CONTINUE
  600 CALL GIBB (XT)
      WRITE (MWRTE,888)
  888 FORMAT(1H1,'***END OF JOB***'/)
      STOP
      END
```

```
      SUBROUTINE FN(Y,XT)
      DIMENSION G1CAL(25),G2CAL(25),UNEX1(25),UNEX2(25),XT(10)
      COMMON T,TS,VA,VB,X1(25),X2(25),G1OBS(25),G2OBS(25),N,G1MCAL
     1G2MCAL(25),II,ALPHA
      U1=XT(1)
      U2=XT(2)
      YS=0.
      V1=VA
      V2=VB
      RT = 1.987 * (273.2 + T)
      G2111 = U1 / RT
      G1222 = U2 / RT
      E2111 =  EXP(-ALPHA * G2111)
      E1222 = EXP(-ALPHA * G1222)
      DO 6 K=1,N
      D2111 = (X1(K) + X2(K) * E2111)**2.0
      D1222 = (X2(K) + X1(K) * E1222)**2.0
      UNEX1(K) =(X2(K)**2.0)*(((G2111*(E2111**2.0))/D2111)+((G1222
     1)/D1222))
      UNEX2(K) =(X1(K)**2.0)*(((G1222*(E1222**2.0))/D1222)+((G2111
     1)/D2111))
      G1CAL(K)=EXP(UNEX1(K))
      G2CAL(K)=EXP(UNEX2(K))
      Y=(((G1CAL(K)-G1OBS(K))/G1OBS(K))**2)+(((G2CAL(K)-G2OBS(K))/
     1K))**2)
      YS=YS+Y
      Z=2*N
      G1MCAL(K)=G1CAL(K)
      G2MCAL(K)=G2CAL(K)
    6 CONTINUE
      STDEV=SQRT(YS/(Z-1.))
      Y=STDEV
   10 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE TN(Y,XT)
      DIMENSION G1CAL(25),G2CAL(25),UNEX1(25),UNEX2(25),XT(10)
      COMMON T,TS,VA,VB,X1(25),X2(25),G1OBS(25),G2OBS(25),N,G1NCAL
     1G2NCAL(25),II,ALPHA
      U1=XT(1)
      U2=XT(2)
      YS=0,0
      RT=1.987*(273,2+T)
      G2111=U1/RT
      G1222=U2/RT
      E2111=EXP(-ALPHA*G2111)
      E1222=EXP(-ALPHA*G1222)
      D2111=(X1(1)+X2(1)*E2111)**4.0
      D1222=(X2(1)+X1(1)*E1222)**4,0
      F2111=E2111**2.0
      F1222=E1222**2,0
      THRDV=(6.0*G2111*F2111/D2111)*(1.0-E2111)+(6.0*G1222*F1222/D1
     1(E1222-1.0)+1.0/(X1(1)**2.0)-(1.0/(X2(1)**2.0))
      Y=THRDV
      Y=Y+YS
      RETURN
      END
```

```
      PROGRAM GIBTH
      DIMENSION TITLE(18),X1(3),X2(3),THRDV(3),D2111(3),D1222(3)
      NREAD=5
      NWRTE=6
    8 READ(NREAD,10) NUM,TITLE
   10 FORMAT (I2,18A4)
      IF (NUM) 12,12,3
   12 READ (NREAD,1) (X1(I),I=1,2),ALPHA,U1,U2,T
    1 FORMAT (3F5.0,3F10.0)
      WRITE (NWRTE,10) NUM,TITLE
      WRITE (NWRTE,4)
    4 FORMAT (4X,'X1',2X,'X1',2X,'ALPHA',2X,'U1',5X,'U2',2X,'T')
      WRITE (NWRTE,7) X1(1),X1(2),ALPHA,U1,U2,T
    7 FORMAT (4X,F4.2,2X,F4.2,4X,F5.2,1X,F8.2,2X,F8.2,3X,F6.2)
      RT=1.987*(273.2+T)
      G2111=U1/RT
      G1222=U2/RT
      E2111=EXP(-ALPHA*G2111)
      E1222=EXP(-ALPHA*G1222)
    6 DO 2 I=1,2
   28 X2(I)=1.0-X1(I)
      D2111(I)=ABS((X1(I)+X2(I)*E2111))**4.0
      D1222(I)=ABS((X2(I)+X1(I)*E1222))**4.0
      F2111=E2111**2.0
      F1222=E1222**2.0
    2 THRDV(I)=(6.0*G2111*F2111/D2111(I))*(1.0-E2111)+(6.0*G1222*F1222/D
     11222(I))*(E1222-1.0)-1.0/(X1(I)**2.0)+(1.0/(X2(I)**2.0))
   22 SLOPE=(THRDV(1)-THRDV(2))/(X1(1)-X1(2))
      B=THRDV(1)-SLOPE*X1(1)
      X1NEW=-B/SLOPE
      X1(3)=X1NEW
      X2(3)=1.0-X1(3)
      D1222(3)=ABS((X2(3)+X1(3)*E1222))**4.0
      D2111(3)=ABS((X1(3)+X2(3)*E2111))**4.0
      THRDV(3)=(6.0*G2111*F2111/D2111(3))*(1.0-E2111)+(6.0*G1222*F1222/D
     11222(3))*(E1222-1.0)-1.0/(X1NEW**2.0)+(1.0/((1.0-X1NEW)**2.0))
      IF (ABS(THRDV(3))-.01) 9,9,16
   16 IF (THRDV(1)) 30,30,31
   30 IF (THRDV(3)) 32,32,33
   32 X1(1)=X1NEW
      GO TO 6
   33 X1(2)=X1NEW
      GO TO 6
   31 IF (THRDV(3)) 33,33,32
    9 X1(2)=X1NEW
      X2(2)=1.0-X1(2)
      GBLF=((E2111**2.0)/((X1(2)+(X2(2)*E2111))**2.0))*(-2.0*G2111)/(X1(
     12)+(X2(2)*E2111))
      GBFT=((E1222**2.0)/((X2(2)+(X1(2)*E1222))**2.0))*(-2.0*G1222)/(X2(
     12)+(X1(2)*E1222))
```

```
      SECDE=GBLF+GBRT+(1./X1(2))+(1./X2(2))
      WRITE (MWRTE,11) THRDV(1),THRDV(3),SLOPE,B,X1NEW,SECDE
   11 FORMAT (6(2X,F10.3))
      GO TO 8
    3 WRITE(MWRTE,13)
   13 FORMAT (1H1,'END OF JOB'//)
      STOP
      END
```

Table II Miscible Predictions

The following computer print-outs were obtained for the tetrahydrofuran-water and 3-methylpyridine binaries at α values yielding miscible predictions.

THF-H_2O

@ 50°C

20 pt

$\alpha = +0.7$

```
N=            20
T=        50.000
VA=       40.000
VB=       40.000
ALPHA=     0.700
M=             2
L=            50
E=         0.080
DX=      100.000
M1=            3
XT(1)=     0.001
XT(2)=     0.001

NO        X1           X2           G1          G2

 1      0.028        0.972       17.245       1.012
 2      0.038        0.962       16.048       1.031
 3      0.046        0.954       14.544       1.012
 4      0.075        0.925        9.962       1.076
 5      0.117        0.883        6.854       1.094
 6      0.183        0.817        4.430       1.179
 7      0.228        0.772        3.577       1.240
 8      0.264        0.736        3.087       1.316
 9      0.354        0.646        2.316       1.489
10      0.441        0.559        1.869       1.719
11      0.531        0.469        1.564       2.039
12      0.611        0.389        1.376       2.409
13      0.698        0.302        1.229       2.963
14      0.765        0.235        1.146       3.582
15      0.798        0.202        1.113       3.980
16      0.868        0.132        1.005       5.146
17      0.888        0.112        1.035       5.827
18      0.922        0.078        1.027       6.341
19      0.956        0.044        1.017       7.178
20      0.979        0.021        1.009       8.109

NON-LINEAR REGRESSION RESULTS

ITERATION=    1

PRESSURE OF X1=   439.6 009

PRESSURE OF X2=    92.49001

STANDARD DEVIATION=        0.2586

G12-11=                 1450.6398

G12-22=                 1177.8911


          G1              G1            G1            G2            G2             G2
NO     OBSERVED       PREDICTED     DEVIATION    OBSERVATION    PREDICTED      DEVIATION

 1     17.245 0        9.37811       7.86689       1.01200       1.00716        0.00484
 2     16.048 0        8.06120       7.98681       1.03100       1.01236        0.01864
 3     14.544 0        7.22367       7.32033       1.01200       1.01723       -0.00523
 4      9.962 0        5.19739       4.76461       1.07600       1.03878        0.03722
 5      6.854 0        3.71209       3.14191       1.09400       1.07596        0.01804
 6      4.430 0        2.63259       1.79741       1.17900       1.14175        0.03725
 7      3.577 0        2.25856       1.31844       1.24000       1.18764        0.05236
 8      3.087 0        2.05505       1.03195       1.31600       1.22470        0.09130
 9      2.316 0        1.73523       0.58077       1.48900       1.31984        0.16916
10      1.869 0        1.55073       0.31827       1.71900       1.42095        0.29805
11      1.564 0        1.41594       0.14806       2.03900       1.54848        0.49052
12      1.376 0        1.31913       0.05687       2.40900       1.70200        0.70700
13      1.229 0        1.22623       0.00277       2.96300       1.95650        1.00650
14      1.146 0        1.16007      -0.01407       3.58200       2.27805        1.30395
15      1.113 0        1.12906      -0.01606       3.98000       2.51038        1.46962
16      1.005 0        1.06814      -0.06314       5.14600       3.32411        1.82189
17      1.035 0        1.05252      -0.01752       5.82700       3.69635        2.13065
18      1.027 0        1.02889      -0.00189       6.34100       4.59590        1.74510
19      1.017 0        1.01057       0.00643       7.17800       6.07839        1.09961
20      1.009 0        1.00267       0.00633       8.10900       7.69592        0.41308

NO            X1             Y1             X2              Y2             PRESSURE

 1          0.028          0.560          0.972           0.440           303.200

 2          0.038          0.599          0.962           0.401           359.800

 3          0.046          0.619          0.954           0.381           383.400

 4          0.075          0.658          0.925           0.342           420.500

 5          0.117          0.684          0.883           0.316           440.400

 6          0.183          0.711          0.817           0.289           445.400

 7          0.228          0.727          0.772           0.273           447.000

 8          0.264          0.741          0.736           0.259           447.800

 9          0.354          0.774          0.646           0.226           449.400

10          0.441          0.804          0.559           0.196           451.100

11          0.531          0.831          0.469           0.169           453.500

12          0.611          0.853          0.389           0.147           456.200

13          0.698          0.873          0.302           0.127           459.800

14          0.765          0.887          0.235           0.113           463.400

15          0.798          0.894          0.202            .106           464.800

16          0.868          0.909          0.132           0.091           465.400

17          0.888          0.915          0.112           0.085           464.300

18          0.922          0.926          0.078           0.074           462.100

19          0.956          0.945          0.044           0.055           456.400

20          0.979          0.967          0.021           0.033           450.000
```

THF-H_2O

@ 50°C

20 DATA POINTS

α = +0.6

```
        NON-LINEAR REGRESSION INPUT DATA

N=            20
T=        50,000
VA=       40,000
VB=       40,000
ALPHA=     0,600
M=             2
L=           .50
E=         0,080
DX=      100,000
MI=            3
XT(1)=     0,001
XT(2)=     0,001

NO         X1          X2          G1          G2

 1       0,028       0,972      17,245       1.012
 2       0.038       0.962      16.048       1.031
 3       0.046       0.954      14.544       1.012
 4       0.075       0.925       9,962       1.076
 5       0.116       0.883       6,850       1.079
 6       0.183       0.817       4,430       1.179
 7       0.228       0.772       3,577       1.240
 8       0.264       0,736       3,087       1.316
 9       0.354       0.646       2.316       1.489
10       0.441       0.559       1.869       1.719
11       0.531       0.469       1.564       2.039
12       0.611       0.389       1.376       2.409
13       0.698       0.302       1.229       2.963
14       0.765       0.235       1.146       3.582
15       0.798       0.202       1.113       3.980
16       0.868       0.132       1.005       5.146
17       0.888       0.112       1.035       5.827
18       0.922       0.078       1.027       6.341
19       0.956       0.044       1.017       7.178
20       0.979       0.021       1.009       8.109

NON-LINEAR REGRESSION RESULTS

ITERATION=    1

PRESSURE OF X1=   439,60001

PRESSURE OF X2=    92,49000

STANDARD DEVIATION=        0,1694

G12-11=               1697,6603

G12-22=               1198,3092

          G1            G1           G1            G2             G2.          G2
NO     OBSERVED     PREDICTED    DEVIATION    OBSERVATION    PREDICTED     DEVIATION

 1     17,24500     13,86488      3,38012       1,01200       1,00843       0,00357
 2     16,04800     11,60244      4,44557       1,03100       1,01457       0,01643
 3     14,54400     10,19672      4,34728       1,01200       1,02032      -0,008 2
 4      9,96200      6,92018      3,04162       1,07600       1,04582       0,03018
 5      6,85000      4,65439      2,19961       1,09400       1,09007       0,00393
 6      4,43000      3,10097      1,32903       1,17900       1,16929       0,00971
 7      3,57700      2,58504      0,99196       1,24000       1,22532       0,01468
 8      3,08700      2,30968      0,77732       1,31600       1,27106       0,04494
 9      2,31600      1,88479      0,43121       1,48900       1,39068       0,09832
10      1,86900      1,64441      0,22459       1,71900       1,52105       0,19795
11      1,56400      1,47212      0,09188       2,03900       1,68877       0,35023
12      1,37600      1,35165      0,02435       2,40900       1,89255       0,51645
13      1,22900      1,24033     -0,01133       2,96300       2,22941       0,73359
14      1,14600      1,16465     -0,01865       3,58200       2,64923       0,93277
15      1,11300      1,13045     -0,01745       3,98000       2,94790       1,03210
16      1,00500      1,06602     -0,06102       5,14600       3,96441       1,18159
17      1,03500      1,05021     -0,01521       5,82700       4,41530       1,41170
18      1,02700      1,02693      0,00007       6,34100       5,47278       0,86822
19      1,01700      1,00958      0,00742       7,17800       7,13062       0,04738
20      1,00900      1,00237      0,00663       8,10900       8,84089      -2,73189

                                        NORM                                  NORM
NO            X1                Y1       Y1          X2               Y2       Y2       PRESSURE      Y TOTAL

 1          0,028             0,563  ~~.694~~ .653  0,972            0,299    .347      303,200     ~~.8350~~ .8620

 2          0,038             0,539  ~~.686~~ .682  0,962            0,251    .318      359,800      .790

 3          0,046             0,538   .696         0,954            0,235    .304      383,400      .773

 4          0,075             0,543   .718         0,925            0,213    .282      420,500      .756

 5          0,116             0,541   .728         0,883            0,202    .272      440,400      .743

 6          0,183             0,560   .739         0,817            0,198    .261      445,400      .758

 7          0,228             0,580   .747         0,772            0,196    .253      447,000      .776

 8          0,264             0,599   .756         0,736            0,193    .244      447,800      .792

 9          0,354             0,653   .779         0,646            0,185    .221      449,400      .838

10          0,441             0,707   .802         0,559            0,174    .198      451,100      .881

11          0,531             0,758   .824         0,469            0,162    .176      453,500      .920

12          0,611             0,796   .842         0,389            0,149    .158      456,200      .946

13          0,698             0,828   .860         0,302            0,135    .140      459,800      .963

14          0,765             0,845   .872         0,235            0,124    .128      463,400      .969

15          0,798             0,853   .878         0,202            0,118    .122      464,800      .971

16          0,868             0,874   .894         0,132            0,104    .106      465,400      .978

17          0,888             0,883   .899         0,112            0,099    .101      464,300      .982

18          0,922             0,901   .914         0,078            0,085    .086      462,100      .986

19          0,956             0,930   .9~~45~~36     0,044            0,064    .064      456,400      .994

20          0,979             0,959   .962         0,021            0,038    .038      450,000      .997
```

3-methylpyridine-H_2O

C 89.83°C

16 pts

α = +0.2

```
                NON-LINEAR REGRESSION INPUT DATA

N=              16
T=          89,830
VA=         40,000
VB=         40,000
ALPHA=       0,200
M=               2
L=              50
E=           0,080
DX=        100,000
M1=              3
XT(1)=       0,001
XT(2)=       0,001

NO          X1           X2           G1           G2

 1        0,003        0,997       56,783        1.007
 2        0,019        0,981       24,210        1.014
 3        0,060        0,939        8,038        1.057
 4        0,094        0,906        5,173        1.096
 5        0,137        0,863        3,559        1.150
 6        0,190        0,810        2,596        1.224
 7        0,241        0,759        2,080        1.299
 8        0,302        0,698        1,723        1.392
 9        0,375        0,625        1,473        1.50
10        0,427        0,573        1,354        1.588
11        0,464        0,539        1.301        1.640
12        0,539        0,461        1,193        1.770
13        0,598        0,402        1.141        1.859
14        0,712        0,288        1,094        2.07
15        0,782        0,218        1,035        2.282
16        0,975        0,025        1,040        2,662

NON-LINEAR REGRESSION RESULTS

ITERATION=    1

PRESSURE OF X1=   134,39999

PRESSURE OF X2=   522,40002

STANDARD DEVIATION=        0,1835

G12-11=                 2150,0291

G12-22=                 -397,7101


         G1              G1             G1              G2              G2            G2
NO    OBSERVED        PREDICTED      DEVIATION      OBSERVATION      PREDICTED      DEVIATION

 1    56,78300        11,94563       44,83737        1,00700         1,00006        0,00694
 2    24,21000        10,01580       14,19420        1,01390         1,00199        0,01191
 3     8,03830         6,61431        1,42399        1,05690         1,01904        0,03786
 4     5,17270         4,99336        0,17934        1,09600         1,04322        0,05278
 5     3,55920         3,68809       -0,12889        1,15000         1,08515        0,06485
 6     2,59570         2,73019       -0,13449        1,22350         1,15049        0,07301
 7     2,08000         2,17062       -0,09062        1,29870         1,22499        0,07371
 8     1,72300         1,75557       -0,03257        1,39200         1,32523        0,06677
 9     1,47290         1,45596        0,01694        1,50830         1,45740        0,05090
10     1,35360         1,31932        0,03428        1,58830         1,55638        0,03192
11     1,30050         1,24847        0,05203        1,63970         1,62665        0,01305
12     1,19320         1,14396        0,04924        1,76980         1,77479       -0,00499
13     1,14120         1,09160        0,04960        1,85880         1,88720       -0,02840
14     1,09430         1,03328        0,06102        2,07710         2,09063       -0,01353
15     1,03500         1,01535        0,01965        2,28220         2,20053        0,08167
16     1,03980         1,00010        0,03970        2,66240         2,42236        0,24004

                                                          Norm
NO            X1                 Y1                 X2     Y2          Y2              PRESSURE

 1           0,003              0,009  .009         0,997  .991        0,951            547,800   .960
 2           0,019              0,043  .046         0,981  .954        0,885            580,600   .928
 3           0,060              0,092  .097         0,939  .903        0,856            584,100   .948
 4           0,094              0,108  .113         0,906  .887        0,845            584,100   .953
 5           0,137              0,116  .122         0,863  .878        0,838            584,000   .954
 6           0,190              0,119  .125         0,810  .875        0,834            584,000   .953
 7           0,241              0,121  .127         0,759  .873        0,834            582,300   .955
 8           0,302              0,123  .128         0,698  .872        0,837            577,600   .960
 9           0,375              0,129  .133         0,625  .867        0,840            566,800   .969
10           0,427              0,137  .140         0,573  .860        0,842            553,300   .977
11           0,464              0,144  .146         0,539  .854        0,844            542,000   .988
12           0,539              0,162  .163         0,461  .837        0,834            512,800   .996
13           0,598              0,182  .181         0,402  .819        0,822            482,400   1.004
14           0,712              0.237  .239         0,288  .761        0,754            417,400   .991
15           0,782              0,289  .298         0,218  .702        0,680            368,900   .969
16           0,975              0,764  .803         0,025  .197        0,187            171,400   ~~.954~~ .951
```

3-methylpyridine -H_2O

@89.83°C 16 dpts

α = +0.72

```
NON-LINEAR REGRESSION INPUT DATA

N=          16
T=      89.830
VA=     40.000
VB=     40.000
ALPHA=   0.720
M=           2
L=          50
E=       0.080
DX=    100.000
M1=          3
XT(1)=   0.001
XT(2)=   0.001

NO        X1          X2          G1          G2

 1      0.003       0.997      56.783       1.007
 2      0.019       0.981      24.210       1.014
 3      0.060       0.939       8.038       1.057
 4      0.094       0.906       5.173       1.096
 5      0.137       0.863       3.559       1.150
 6      0.190       0.810       2.596       1.224
 7      0.241       0.759       2.080       1.299
 8      0.302       0.698       1.723       1.392
 9      0.375       0.625       1.473       1.508
10      0.427       0.573       1.354       1.588
11      0.464       0.539       1.301       1.640
12      0.539       0.461       1.193       1.770
13      0.598       0.402       1.141       1.859
14      0.712       0.288       1.094       2.077
15      0.782       0.218       1.035       2.282
16      0.975       0.025       1.040       2.662

NON-LINEAR REGRESSION RESULTS

ITERATION=    1

PRESSURE OF X1=   134.39999

PRESSURE OF X2=   522.40002

STANDARD DEVIATION=        0.1767

G12-11=                 2227.1067

G12-22=                  700.3625

         G1           G1          G1           G2            G2          G2
NO    OBSERVED     PREDICTED   DEVIATION   OBSERVATION   PREDICTED   DEVIATION

 1    56.78320     29.92270    26.86030     1.00700       1.00025     0.00674
 2    24.21000     14.97136     9.23864     1.01390       1.00767     0.00623
 3     8.03830      5.29743     2.74087     1.05690       1.04857     0.00833
 4     5.17270      3.45793     1.71477     1.09600       1.08598     0.01002
 5     3.55920      2.51364     1.04556     1.15000       1.13138     0.01862
 6     2.59570      2.00383     0.59187     1.22350       1.18185     0.04165
 7     2.08000      1.75009     0.32991     1.29870       1.22623     0.07247
 8     1.72300      1.56972     0.15328     1.39200       1.27655     0.11545
 9     1.47290      1.43150     0.04140     1.50830       1.33780     0.17050
10     1.35360      1.35927    -0.00567     1.58830       1.38486     0.20344
11     1.30050      1.31659    -0.01609     1.63970       1.42070     0.21900
12     1.19320      1.24032    -0.04712     1.76980       1.50839     0.26141
13     1.14120      1.19005    -0.04885     1.85880       1.59287     0.26593
14     1.09430      1.10816    -0.01386     2.07710       1.82523     0.25187
15     1.03500      1.06722    -0.03222     2.28220       2.04050     0.24170
16     1.03980      1.00121     0.03859     2.66240       3.35147    -0.68907

NO          X1               Y1               X2               Y2          PRESSURE

 1        0.003            0.023            0.997            0.977          547.800

 2        0.019            0.068            0.981            0.932          580.600

 3        0.060            0.077            0.939            0.923          584.100

 4        0.094            0.078            0.906            0.922          584.100

 5        0.137            0.083            0.863            0.917          584.200

 6        0.190            0.093            0.810            0.907          584.000

 7        0.241            0.104            0.759            0.896          582.300

 8        0.302            0.120            0.698            0.880          577.600

 9        0.375            0.142            0.625            0.858          566.800

10        0.427            0.158            0.573            0.842          553.300

11        0.464            0.170            0.539            0.833          542.300

12        0.539            0.198            0.461            0.802          512.600

13        0.598            0.222            0.402            0.778          482.400

14        0.712            0.278            0.288            0.722          417.000

15        0.782            0.325            0.218            0.675          368.900

16        0.975            0.748            0.025            0.252          171.400
```

3-methylpyridine-H_2O

C 89.83

16

α = -1.4

```
            NON-LINEAR REGRESSION INPUT DATA

N=            16
T=        69.830
VA=       40.000
VB=       40.000
ALPHA=    -1.400
M=             2
L=            50
E=         0.002
DX=      100.000
M1=            3
XT(1)=     0.001
XT(2)=     0.001

NO         X1            X2            G1          G2

 1        0.003         0.997        56.763       1.007
 2        0.019         0.981        24.210       1.014
 3        0.060         0.939         8.038       1.057
 4        0.094         0.906         5.173       1.096
 5        0.137         0.863         3.559       1.150
 6        0.190         0.810         2.596       1.224
 7        0.241         0.759         2.060       1.299
 8        0.302         0.698         1.723       1.392
 9        0.375         0.625         1.473       1.508
10        0.427         0.573         1.354       1.588
11        0.464         0.539         1.301       1.640
12        0.539         0.461         1.193       1.770
13        0.598         0.402         1.141       1.859
14        0.712         0.288         1.094       2.277
15        0.782         0.216         1.035       2.282
16        0.975         0.025         1.040       2.662
FORTP0400S EXP CALLED WITH EXPONENT GREATER THAN 87.
NAME      SEQ
FN        02219
MAIN.     00118

FORTP0400S EXP CALLED WITH EXPONENT GREATER THAN 87.
NAME      SEQ
FN        00219
MAIN.     00118


NON-LINEAR REGRESSION RESULTS

ITERATION=     1

PRESSURE OF X1=    134.39999

PRESSURE OF X2=    522.40002

STANDARD DEVIATION=        0.2428

G12-11=               -742.9023

G12-22=                776.7400


          G1            G1            G1            G2            G2            G2
NO     OBSERVED     PREDICTED     DEVIATION    OBSERVATION    PREDICTED     DEVIATION

 1    56.76300       9.97305      46.80995      1.00700       1.00008       0.00692
 2    24.21000       7.93711      16.27289      1.01390       1.00256       0.01134
 3     8.03830       4.84987       3.18843      1.05690       1.02262       0.03428
 4     5.17270       3.59411       1.57859      1.09600       1.04840       0.04760
 5     3.55920       2.67834       0.88086      1.15000       1.08913       0.06087
 6     2.59570       2.05677       0.53893      1.22350       1.14632       0.07718
 7     2.06000       1.71129       0.36871      1.29670       1.20534       0.09336
 8     1.72320       1.46185       0.26115      1.39200       1.27767       0.11433
 9     1.47290       1.28401       0.18869      1.50830       1.36455       0.14375
10     1.35360       1.20287       0.15073      1.58830       1.42523       0.16307
11     1.30250       1.16052       0.13998      1.63970       1.46667       0.17303
12     1.19320       1.09716       0.09604      1.76980       1.55110       0.21870
13     1.14120       1.06451       0.07669      1.85680       1.61377       0.24503
14     1.09430       1.02615       0.06815      2.07710       1.72843       0.34867
15     1.03500       1.01318       0.02182      2.28220       1.79414       0.48806
16     1.03900       1.00013       0.03967      2.66240       1.95825       0.70415

NO            X1                Y1                 X2                 Y2            PRESSURE

 1          0.003             0.008   008        0.997              0.951   992      547.800

 2          0.019             0.034   037        0.981              0.885   963      580.600

 3          0.060             0.068   073        0.939              0.859   927      584.100

 4          0.094             0.078   084        0.906              0.849   916      584.100

 5          0.137             0.085   092        0.863              0.841   908      584.000

 6          0.190             0.090   098        0.810              0.831   902      584.000

 7          0.241             0.095   104        0.759              0.821   896      582.300

 8          0.302             0.103   113        0.698              0.807   887      577.600

 9          0.375             0.114   127        0.625              0.786   873      566.800

10          0.427             0.125   140        0.573              0.771   860      553.300

11          0.464             0.134   ~~156~~ 127  0.539              0.761   850      542.000
                                      150
12          0.539             0.155   178        0.461              0.729   825      512.800

13          0.598             0.177   201        0.402              0.703   799      482.400

14          0.712             0.235   274        0.288              0.623   726      417.400

15          0.782             0.289   343        0.218              0.554   657      368.900

16          0.975             0.764   835        0.025              0.151   165      171.400
```

3-methylpyridine - H_2O
@ 89.83°C
16 dpt

$\alpha = +0.70$

```
            NON-LINEAR REGRESSION INPUT DATA

N=              16
T=          89,830
VA=         40,000
VB=         40,000
ALPHA=       0,700
M=               2
L=              50
E=           0,080
DX=        100,000
MI=              3
XT(1)=       0,001
XT(2)=       0,001

NO          X1            X2            G1            G2

 1        0,003         0,997        56,783         1,007
 2        0,019         0,981        24,210         1,014
 3        0,060         0,939         8.038         1,057
 4        0,094         0,906         5.173         1,096
 5        0,137         0,863         3.559         1,150
 6        0,190         0,810         2.596         1,224
 7        0,241         0,759         2.080         1,299
 8        0,302         0,698         1.723         1,392
 9        0,375         0,625         1.473         1,508
10        0,427         0,573         1.354         1,586
11        0,464         0,539         1.301         1,640
12        0,539         0,461         1,193         1,770
13        0,598         0,402         1,141         1,859
14        0,712         0,288         1.094         2,077
15        0,782         0,218         1,035         2,282
16        0,975         0,025         1,040         2,662

NON-LINEAR REGRESSION RESULTS

ITERATION=     1

PRESSURE OF X1=   134,39999

PRESSURE OF X2=   522,40002

STANDARD DEVIATION=          0,1633

G12-11=                   2302,1440

G12-22=                    697,8329


         G1             G1            G1             G2            G2             G2
NO    OBSERVED      PREDICTED     DEVIATION     OBSERVATION    PREDICTED      DEVIATION

 1    56,78300       33,24452      23,53848       1,00700       1,00027        0,00673
 2    24,21000       16,15493       8,05507       1,01390       1,00792        0,00598
 3     8,03830        5,50411       2,53419       1,05690       1,05039        0,00651
 4     5,17270        3,54615       1,62655       1,09600       1,08903        0,00697
 5     3,55920        2,55545       1,00375       1,15000       1,13583        0,01417
 6     2,59570        2,02580       0,56990       1,22350       1,18776        0,03574
 7     2,08000        1,76376       0,31624       1,29870       1,23342        0,06528
 8     1,72300        1,57817       0,14483       1,39200       1,26518        0,12682
 9     1,47290        1,43636       0,03654       1,50830       1,34819        0,16011
10     1,35360        1,36245      -0,00885       1,58630       1,39660        0,19170
11     1,30050        1,31886      -0,01836       1,63970       1,43345        0,20625
12     1,19320        1,24118      -0,04798       1,76980       1,52349        0,24631
13     1,14120        1,19019      -0,04899       1,85880       1,61004        0,24876
14     1,09430        1,10759      -0,01329       2,07710       1,84702        0,23008
15     1,03500        1,06661      -0,03161       2,28220       2,06524        0,21696
16     1,03980        1,00119       0,03861       2,66240       3,37227       -0,70987

NO              X1               Y1               X2                Y2             PRESSURE

 1            0,003            0,026            0,997             0,974             547,800

 2            0,019            0,073            0,981             0,927             580,600

 3            0,060            0,080            0,939             0,920             584,100

 4            0,094            0,080            0,906             0,920             584,100

 5            0,137            0,084            0,863             0,916             584,000

 6            0,190            0,093            0,810             0,907             584,000

 7            0,241            0,105            0,759             0,895             582,300

 8            0,302            0,120            0,698             0,880             577,600

 9            0,375            0,141            0,625             0,859             566,800

10            0,427            0,157            0,573             0,843             553,300

11            0,464            0,169            0,539             0,831             542,000

12            0,539            0,197            0,461             0,803             512,800

13            0,598            0,220            0,402             0,780             482,400

14            0,712            0,276            0,288             0,724             417,400

15            0,782            0,323            0,218             0,677             368,900

16            0,975            0,746            0,025             0,254             171,400
```

3-methylpyridine-H_2O

@ 69.86°C

16 pts

$\alpha = +0.72$

```
              NON-LINEAR REGRESSION INPUT DATA

N=            16
T=        69,860
VA=       40,000
VB=       40,000
ALPHA=     0,720
M=             2
L=            50
E=         0,080
DX=      100,000
M1=            3
XT(1)=     0,001
XT(2)=     0,001

NO        X1          X2          G1          G2

 1      0.002       0.998      61.900       1.002
 2      0.017       0.983      25.455       1.010
 3      0.048       0.952       9.484       1.043
 4      0.078       0.922       5.927       1.076
 5      0.124       0.876       3.715       1.132
 6      0.161       0.839       2.877       1.181
 7      0.203       0.797       2.307       1.240
 8      0.260       0.740       1.847       1.325
 9      0.322       0.678       1.577       1.414
10      0.388       0.612       1.393       1.51.
11      0.443       0.557       1.302       1.584
12      0.495       0.505       1.225       1.663
13      0.592       0.408       1.145       1.796
14      0.687       0.313       1.085       1.956
15      0.775       0.225       1.043       2.13.
16      0.977       0.023       0.982       2.651

NON-LINEAR REGRESSION RESULTS

ITERATION=     1

PRESSURE OF X1=    60.05000

PRESSURE OF X2=   232.30000

STANDARD DEVIATION=         0.1678

G12-11=                  2166.1880

G12-22=                   654.4839


         G1          G1          G1           G2          G2          G2
NO    OBSERVED    PREDICTED   DEVIATION   OBSERVATION  PREDICTED   DEVIATION

 1    61.90000    33.92091    27.97910     1.00230     1.00015     0.00215
 2    25.45500    16.52401     8.93099     1.01000     1.00672     0.00328
 3     9.48400     6.47166     3.01234     1.04300     1.03722     0.00578
 4     5.92700     4.02095     1.90605     1.07600     1.07029     0.00571
 5     3.71500     2.64880     1.06620     1.13200     1.12021     0.01179
 6     2.87700     2.18639     0.69061     1.18100     1.15607     0.02493
 7     2.30700     1.89050     0.41650     1.24000     1.19368     0.04632
 8     1.84700     1.65981     0.18719     1.32500     1.24096     0.08404
 9     1.57700     1.50952     0.06748     1.41400     1.29005     0.12395
10     1.39300     1.40107    -0.00807     1.51100     1.34399     0.16701
11     1.30200     1.33229    -0.03029     1.58400     1.39292     0.19108
12     1.22500     1.27646    -0.05146     1.66300     1.44660     0.21640
13     1.14500     1.19094    -0.04594     1.79600     1.57158     0.22442
14     1.08500     1.12237    -0.03737     1.95400     1.74686     0.20714
15     1.04300     1.06951    -0.02651     2.13200     1.99345     0.13855
16     0.98240     1.00099    -0.01859     2.65100     3.31101    -0.66001

NO          X1            Y1            X2            Y2          PRESSURE

 1        0.002         0.019         0.998         0.981         240.600

 2        0.017         0.067         0.983         0.933         256.300

 3        0.048         0.076         0.952         0.924         258.100

 4        0.078         0.076         0.922         0.924         258.200

 5        0.124         0.080         0.876         0.920         258.100

 6        0.161         0.086         0.839         0.914         258.100

 7        0.203         0.094         0.797         0.906         257.800

 8        0.260         0.109         0.740         0.891         256.500

 9        0.322         0.126         0.678         0.874         253.100

10        0.388         0.146         0.612         0.854         247.200

11        0.443         0.164         0.557         0.836         239.700

12        0.495         0.183         0.505         0.817         231.400

13        0.592         0.222         0.408         0.778         210.800

14        0.687         0.267         0.313         0.733         186.900

15        0.775         0.324         0.225         0.676         159.800

16        0.977         0.769         0.023         0.231          71.800
```

DATA & DATA SOURCES

The following pages list the data and data sources used in the work.

VAPOR-LIQUID EQUILIBRIUM in THE 4MP-WATER SYSTEM AT 69.86°C

X4MP	Y4MP	P,mmHg
0.0000	0.0000	232.3
0.00155	0.0210	236.7
0.0141	0.0819	251.0
0.0683	0.0948	254.1
0.1094	0.0958	253.7
0.1925	0.0993	252.8
0.2640	0.1059	250.5
0.3201	0.1140	246.9
0.4069	0.1317	237.1
0.4967	0.1569	222.3
0.5953	0.1939	201.9
0.8379	0.3735	132.6
1.0000	1.0000	57.6

Source: Andon. R.J.L., Cox, J.D., Herington, E.F.G., Trans. Far. Soc., 53, 410 (1957).

VAPOR-LIQUID EQUILIBRIUM in THE 3MP-WATER SYSTEM AT 89.83°C

X3MP	Y3MP	P,mmHg
0.0000	0.0000	522.4
0.00306	0.04263	547.8
0.0187	0.1048	580.6
0.0605	0.1119	584.1
0.0941	0.1120	584.1
0.1371	0.1123	584.0
0.1900	0.1135	584.0
0.2410	0.1157	582.3
0.3018	0.1210	577.6
0.3748	0.1309	566.8
0.4267	0.1403	553.3
0.4614	0.1488	542.0
0.5388	0.1685	512.8
0.5976	0.1900	482.4
0.7118	0.2508	417.4
0.7818	0.2948	368.9
0.9747	0.7947	171.4
1.0000	1.0000	134.4

Source: Andon, R.J.L., Cox, J.D., Herington, E.F.G., Trans. Far. Soc., 53, 410 (1957)

VAPOR-LIQUID EQUILIBRIUM in THE 3MP-WATER SYSTEM AT 69.86°C

X3MP	Y3MP	P,mmHG
0.0000	0.0000	232.2
0.00223	0.03445	240.6
0.0167	0.0996	256.3
0.0484	0.1068	258.1
0.0777	0.1071	258.2
0.1239	0.1071	258.1
0.1606	0.1075	258.1
0.2028	0.1090	257.8
0.2604	0.1126	256.5
0.3225	0.1207	253.1
0.3884	0.1314	247.2
0.4428	0.1444	239.7
0.4954	0.1575	231.4
0.5923	0.1932	210.8
0.6869	0.2395	186.9
0.7754	0.3039	159.8
0.9770	0.8027	71.8
1.0000	1.0000	60.05

Source: Andon, R.J.L., Cox, J.D., Herington, E.F.G., Trans, Far.Soc.,
53, 410 (1957)

VAPOR-LIQUID EQUILIBRIUM in THE WATER-PYRIDINE SYSTEM AT 80.05°C

XH20	YH20	P,mmHG
0.00	0.00	238.9
0.1082	0.3488	312.9
0.1853	0.4738	344.7
0.2527	0.5544	367.8
0.2758	0.5600	373.8
0.4587	0.6654	415.2
0.5759	0.7122	431.0
0.6636	0.7440	439.1
0.7842	0.7558	441.0
0.8912	0.7646	437.9
0.9268	0.7765	432.7
0.9542	0.7822	428.9
0.9982	0.9755	356.8
1.000	1.000	355.0

Source: Chu, J.C., Wang, S.L., Levy, S.L., Paul, R.,
"Vapor Liquid Equilibrium Data" Ref. 273, J.W. Edwards,
Publisher, Inc. Ann Arbor, Mich. (1956)

VAPOR-LIQUID EQUILIBRIUM IN THE THIOAZOLE-WATER SYSTEM AT 90°C

XH2O	YH2O	P, mmHg
0.0	0.0	320
0.015	0.076	340
0.10	0.356	450
0.18	0.494	530
0.35	0.644	645
0.50	0.697	684
0.62	0.715	693
0.72	0.716	695.5
0.76	0.716	694.5
0.90	0.723	689.5
0.95	0.761	658
0.98	0.860	601
1.00	1.00	526

Source: Chu, J.C., Wang, S.L., Levy, S.L., Paul, R., "Vapor Liquid Equilibrium Data" Ref. 56, J.W. Edwards, Publisher, Inc. Ann Arbor, Mich. (1956).

VAPOR-LIQUID EQUILIBRIUM in THE ACETONE-WATER SYSTEM AT 25.00°C

XACET	YACET	P,mmHG
0.0	0.0	23.7
0.01936	0.5234	50.1
0.0289	0.6212	61.8
0.04495	0.7168	81.3
0.0556	0.7591	91.9
0.0939	0.8351	126.1
0.0951	0.8416	126.6
0.1310	0.8618	144.3
0.147	0.8768	150.6
0.1791	0.8782	159.8
0.2654	0.8856	176.1
0.3538	0.8954	184.4
0.5808	0.9158	199.1
0.7852	0.9421	213.5
1.00	1.00	229.6

Source: Chu, J.C., Wang, S.L., Levy, S.L., Paul, R,. "Vapor Liquid Equilibrium Data", Ref. 17, J.W. Edwards, Publisher, Inc. Ann Arbor, Mich. (1956)

VAPOR-LIQUID EQUILIBRIUM in THE THF-WATER SYSTEM AT 50°C

XTHF	YTHF	P. TORR
0.028	0.700	303.2
0.038	0.745	359.8
0.046	0.767	383.4
0.075	0.781	420.5
0.1165	0.797	440.4
0.183	0.800	445.4
0.228	0.802	447.0
0.264	0.800	447.8
0.354	0.802	449.4
0.441	0.803	451.1
0.531	0.805	453.5
0.611	0.810	456.2
0.698	0.820	459.8
0.765	0.832	463.4
0.798	0.840	464.8
0.868	0.865	465.4
0.888	0.870	464.3
0.922	0.901	462.1
0.956	0.936	456.4
0.979	0.965	450.0

Source: Suska, J., Novak, J.P., Matous, J., Pick, J.
Collection Czech. Chem. Comm. 37,2664, (1972)

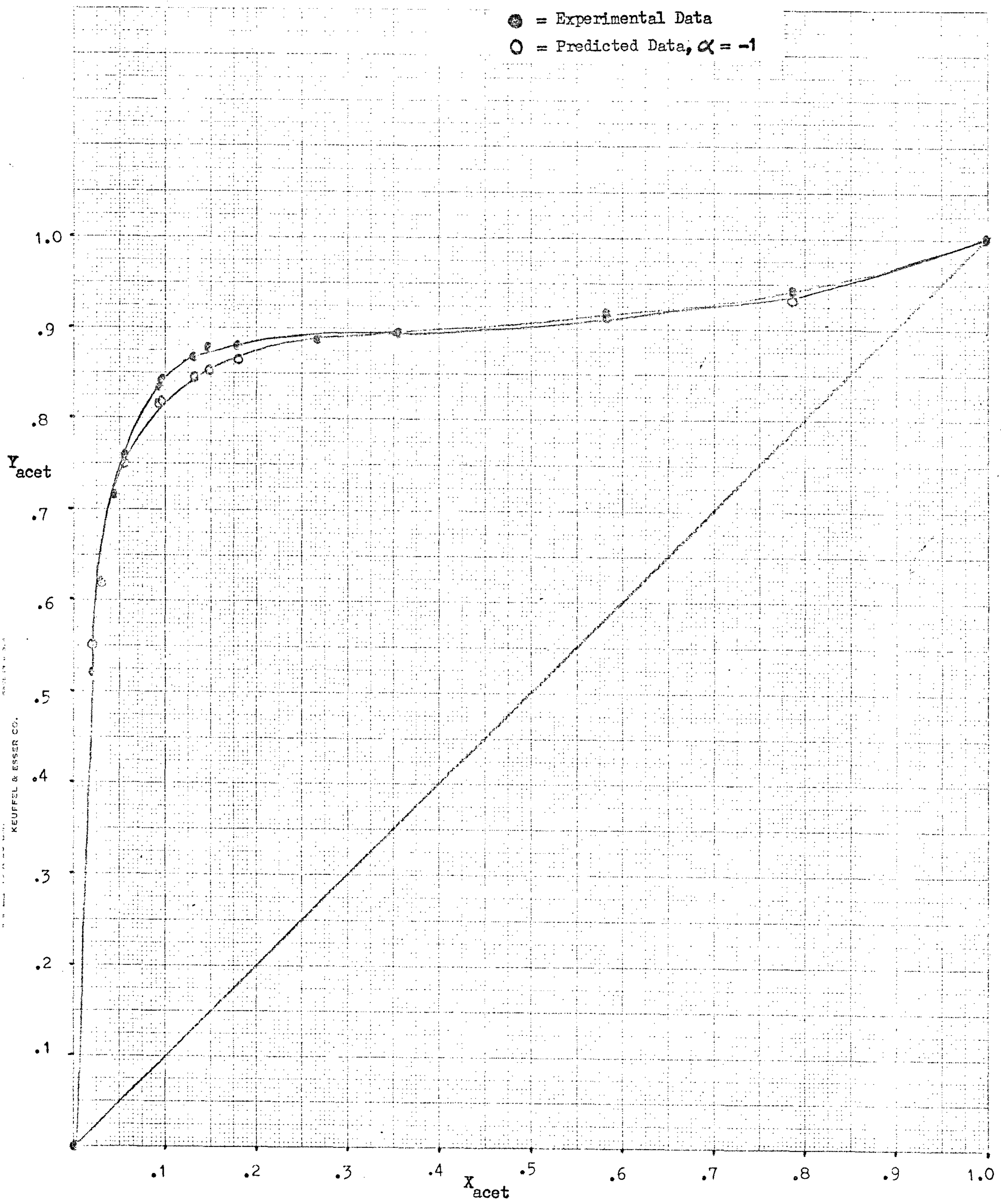
X,Y PLOTS OF EXPERIMENTAL & PREDICTED DATA

The following graphs provide comparisons between the experimental and predicted vapor compositions of the following systems:

THIOAZOLE - WATER AT 90°C
WATER - PYRIDINE AT 80.05°C
ACETONE - WATER AT 25°C

The predicted data was obtained using an $\alpha = -1$; (see Figure III).

Comparison of Experimental and Predicted Data
Acetone-Water at 25°C.



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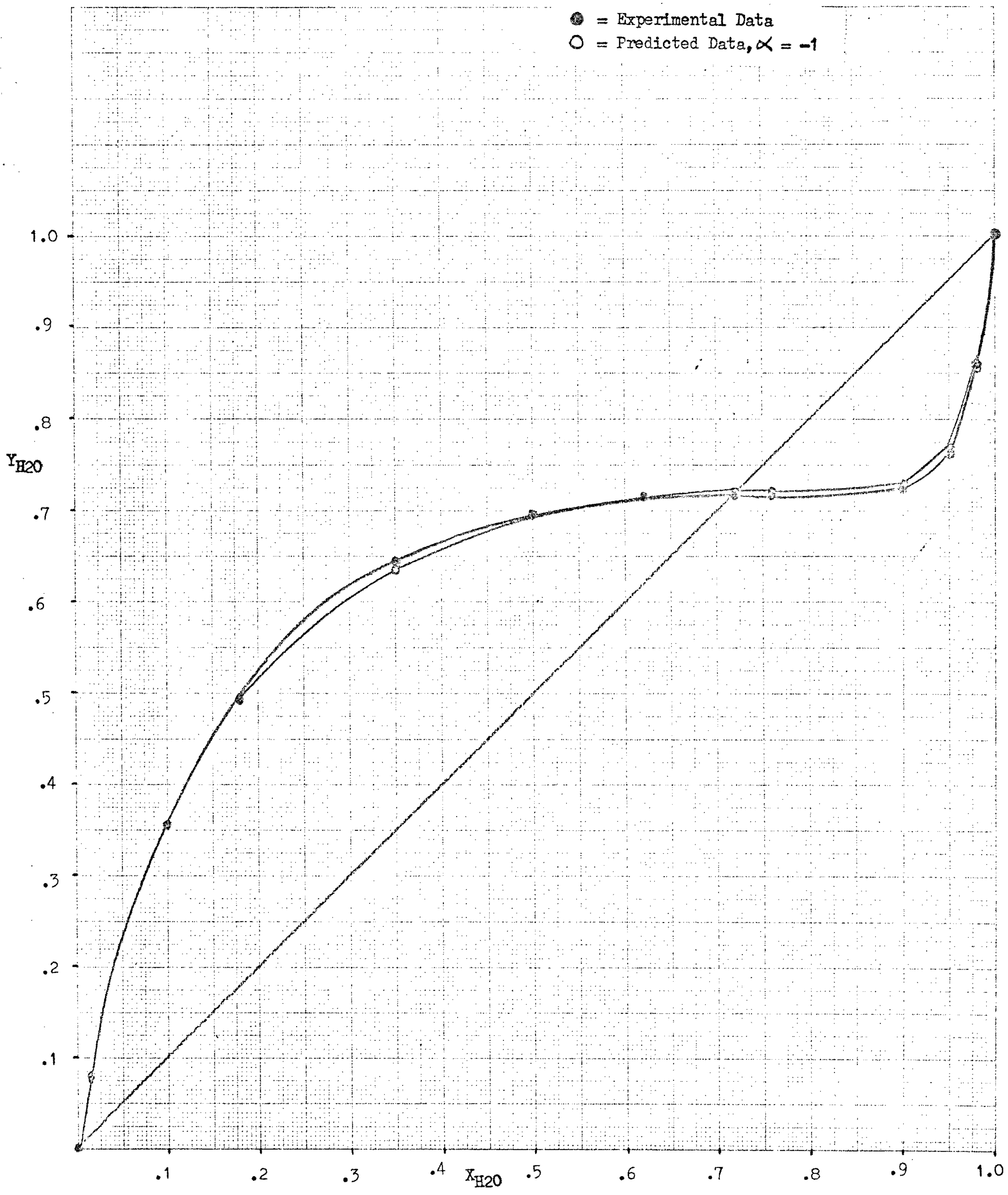
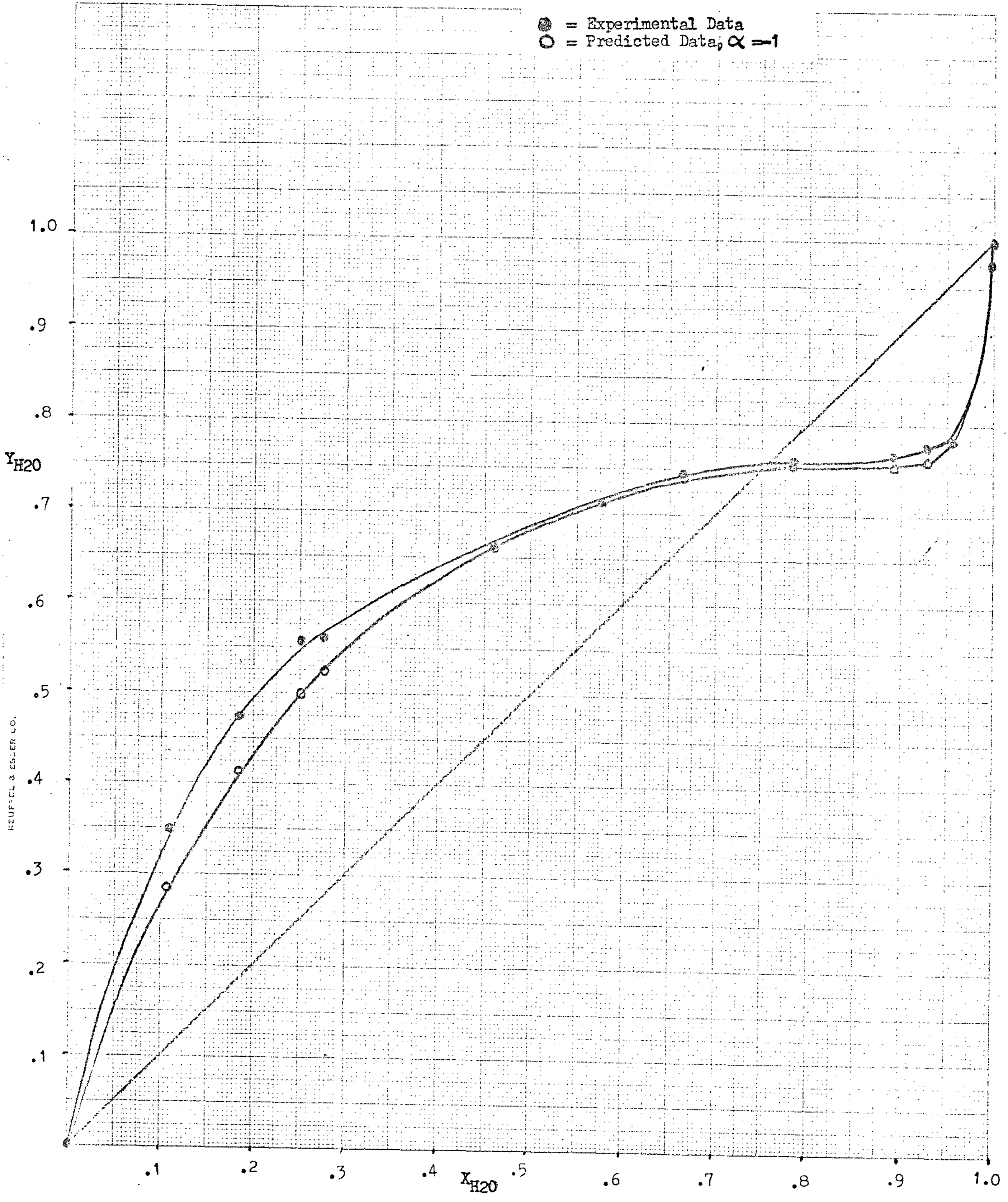
Comparison of Experimental and Predicted Data
Thioazole-Water at 90°C.



Comparison of Experimental and Predicted Data
Water-Pyridine at 80.05°C.



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