VAPOUR LIQUID EQUILIBRIUM - PRACTICAL AND THEORETICAL STUDIES.

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SUMMARY

Vapour liquid equilibrium data have been obtained at a constant pressure of 760 mm Hg. for the binary systems ethyl acetate-n-butanol, n-butanol-n-butyl acetate using a modified Cathala flow still.
The liquid and vapour samples were analysed by both gas liquid chromatography and refractive index measurements.

The data has been shown to be thermodynamically consistent by the methods of Ulrichson and Stevenson, Samuels and Van Ness and Byer and has been fitted to several of the better known activity coefficient equations such as the Wilson and NRTL. It has been demonstrated that the level of random error inherent in the analytical procedures can have a significant effect on the correlation parameters obtained during data reduction.

The Cathala still has been shown to be as good as conventional stills for the acquisition of equilibrium data.

An attempt has been made to model the behaviour of systems containing acetic acid as one component. The procedure involved was to compute correction factors in the manner of Marek for the association of the acid to dimers. Use was made of a concentration dependent equilibrium constant which was related to overall activity coefficients obtained from an equation such as the Wilson or NRTL.
Data reduction by the Barker method using these equations corrected for association resulted in a marked improvement. This method was applied to approximately 27 systems containing acetic acid, the majority of which were found to be consistent by the test of Van Ness and Byer. Extension to the prediction of tie lines in the partially miscible system acetic acid-water-toluene yielded no discernable improvements compared with using the uncorrected NRTL equation.

The subject matter in this thesis forms the basis of two papers accepted for publication in Chemical Engineering Science and the Transactions of the Institute of Chemical Engineers.

THERMODYNAMIC CONSISTENCY ACETIC ACID ASSOCIATION.

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CONTENTS

CHAPTER PAGES

1. INTRODUCTION. 1 - 11

2. THE THEORY OF VAPOUR LIQUID EQUILIBRIUM 12 - 42

   2.1 Basic Thermodynamic relations ..... 13 - 15

   2.2 The gas phase .... 16 - 17

   2.3 The liquid phase .... 17 - 20

   2.4 The equilibrium relationship ...... 20 - 24

   2.5 Gas phase models .... 20 - 28

   2.6 Liquid phase models .... 28 - 42

3. THE DETERMINATION AND CALCULATION OF VAPOUR LIQUID EQUILIBRIUM DATA 43 - 68

   3.1 Introduction .... 43 - 44

   3.2 Distillation methods 44

   3.3 Circulation methods .... 45 - 48

   3.4 Flow methods .... 48 - 49

   3.5 Static methods .... 50 - 51

   3.6 Other methods .... 51 - 53

   3.7 Total pressure methods .... 54 - 68

4. THERMODYNAMIC CONSISTENCY 69 -101

   4.1 Area tests .... 71 - 80

   4.2 Slope tests .... 81 - 84

   4.3 Statistical tests .... 85 - 97

   4.4 Barker type tests .... 97 -100

5. VAPOUR LIQUID EQUILIBRIUM WITH ASSOCIATION IN BOTH PHASES. 102 -126

   5.1 Introduction ....102 -105

   5.2 Modes of Association .... 105 -106

CONTENTS(CONTINUED)

CHAPTER PAGES

5.3 Correlation of data from systems containing acetic acid............. 107 - 108

5.4 Calculation of correction factors.. 108 - 117

5.5 Thermodynamic consistency in systems involving dimerisation .... 118 - 120

5.6 Extension to multicomponent V.L.E. and L/L equilibrium .... 121 - 123

5.7 Systems under investigation .... 124 - 126

6. EXPERIMENTAL WORK 127 - 149

6.1 Description of Cathala still ...... 128 - 139

6.2 Determination of V.L.E. data ...... 140 - 145

6.3 Operation of the still .... 146 - 147

6.4 Sources of error in Cathala still . 148 - 149

7. DISCUSSION OF RESULTS 150 - 176

7.1 Application of consistency tests to Cathala still data .... 150 - 162

7.2 Examination of experimental multicomponent results 162

7.3 Modelling of the system acetic acid-toluene .... 163 - 166

7.4 Modelling of other systems containing acetic acid .... 167 - 174

7.5 Comparison of various models used in the reduction of V.L.E. data ... 175

7.6 Prediction of liquid-liquid equilibrium in system acetic acid-toluene-water .... 175 - 176

8. CONCLUSIONS AND RECOMMENDATIONS 177 - 191

8.1 Analysis of experimental work ..... 177 - 179

8.2 Modelling of acetic acid association179 - 183

8.3 Multicomponent V.L.E. for ethyl acetate-ethanol-n-butanol-n-butyl acetate.183

CONTENTS (Continued)

CHAPTER. PAGES.

8.4 Prediction of liquid-liquid equilibrium in system acetic acid-toluene-water 184-185

8.5 Comparison of Wilson, NRTL and UNIQUAC equations 185-186

8.6 Recommendations for future work 186-191

REFERENCES 192-222

LIST OF SYMBOLS 223-225

APPENDIX A1

Manual of computer programs................ 226-268

APPENDIX A2

Detailed deviation of correction factors...... 269-272

APPENDIX A3

New model applied to systems containing acetic acid 273-358

APPENDIX A4

Wilson, NRTL and UNIQUAC parameters 359-397

CONTENTS (Continued)

CHAPTER. PAGES.

APPENDIX A5

Pure component properties and vapour pressures 389-397

APPENDIX A6

Experimental results..... 398-414

APPENDIX A7

Miscellaneous results including tie line predictions.............. 415-431

LIST OF FIGURES.

FIG.		FACING PAGE.
1	Equilibrium still of Raal, Code and Best.	47
2	Dew point and Bubble point curves.	51
3	Apparatus of Kato Konishi and Hirata.	52
4	Apparatus of Hermsen and Prausnitz.	55
5	Apparatus of Gibbs and Van Ness.	57
6	Total pressure apparatus of Jenkins and Smith.	58
7	Simple apparatus of Jenkins and Smith.	58
8	Overall layout of Cathala still.	128
9	Layout of vapouriser and super-heater.	129
10	Diagrammatic cross section of modified Cathala still.	130
11	Details of liquid cooler.	136.
12	Details of vapour condenser/ cooler.	137
13	Layout of chromatography apparatus.	142

LIST OF FIGURES (CONTINUED)

FIG. FACING PAGE.

14 Layout of liquid preheater. 128

15 x-y diagram for system n-butanol-n-butyl-acetate. 150

16 x-y diagram for refractive index and G.L.C. results systems ethyl acetate-n-butyl acetate and n-butanol-n-butyl acetate. 150

17 $(y-x)$ vs x for system etyl acetate n-butyl acetate. 151

18 $(y-x)$ vs x for system n-butanol-n-butyl acetate. 151

19 Deviation plot for system n-butanol-n-butyl acetate using 4 suffix Margules equation. 153

20 a. F(a.b) test for system ethyl acetate-n-butyl acetate. 156

b. F(a,b) test for system n butanol-n-butyl acetate. 156

21 Analysis of least squares residuals, system ethyl acetate n-butyl acetate, 4 suffix Margules equation. 158

LIST OF FIGURES (CONTINUED)

FIG.		FACING PAGE
22	Experimental vs calculated vapour compositions for ternary system ethyl acetate-n-butyl acetate n-butanol.	162
23	Experimental vs calculated vapour compositions for quarternary system ethanol-ethyl acetate-n-butanol-n-butyl acetate.	162
24	Acetic acid-toluene system, Pressure and vapour composition deviation plots for the isothermal data of Meehan and Zawidski at 70°C with vapour phase correction only.	163
25	Deviation plots for acetic acid-toluene system using 3 parameter NRTL equation with vapour correction only. Isothermal data of Zawidski (80°C), Meehan (50°C) and Markuzin and Pavlova (30°C).	163

LIST OF FIGURES (CONTINUED)

FIG.		FACING PAGE
26	Deviation plot for acetic acid-toluene system using Wilson equation and 3 approaches. 1. Vapour correction only. 2. Composition independent association constant. 3. Composition dependent association constant. Isothermal data of Meehan at 50°C.	163
27	Deviation plots for system acetic acid-toluene. Wilson equation and three approaches on isothermal data of Markuzin and Pavlova at 30°C.	165
28	Deviation plots for system acetic acid-toluene. Wilson equation and three approaches on isothermal data of Meehan at 70°C.	165
29	Deviation plots for system acetic acid-toluene. Wilson equation and three approaches on isothermal data of Zawidski at 69.94°C.	166

LIST OF FIGURES (CONTINUED)

FIG. FACING PAGE.

30 Deviation plots for system acetic acid-toluene. Wilson equation and three approaches on isothermal data of Zawidski at 80.05°C. 166

31 Deviation plots for system acetic acid-benzene. Wilson equation on isothermal data of Meehan at 30°C. 167

32 Equilibrium constant, k_m vs mole fraction acetic acid (x) for hydrocarbon systems. 168

33 Heat of mixing, h_m vs mole fraction acetic acid x for acetic acid toluene at 20°C using Wilson equation. 169

34 H_m vs x for acetic acid-toluene at 20°C using 3 parameter NRTL equation. 169

35 H_m vs x for acetic acid-benzene at 20°C using Wilson equation. 169

LIST OF FIGURES (CONTINUED)

FIG.		FACING PAGE.
36	H_m vs x for acetic acid-benzene at 20°C using 3 parameter NRTL equation.	169
37	H_m vs x for acetic acid-n-heptane at 20°C using Wilson equation.	169
38	H_m vs x for acetic acid-n-heptane at 20°C using 3 parameter NRTL equation.	169
39	Equilibrium constant, k_m vs mole fraction acetic acid, x for trichloroethylene.	170
40	Deviation plots for system acetic acid-water at 69.9°C using 2 approaches. 1. Vapour phase correction only. 2. Using liquid phase model. 3 parameter NRTL equation.	171
41	Deviation plots for system acetic acid-water at 79.9°C using 2 approaches and 3 parameter NRTL equation.	171
42	Deviation plots for acetic acid-water at 89.9°C using 2 approaches and 3 parameter NRTL equation.	171

LIST OF FIGURES (CONTINUED)

FIG.		FACING PAGE.
43	Activity coefficients for system acetic acid-water corrected and uncorrected.	171
44.	Ln V_1/V_2 vs x for acetic acid-water.	171
45	Deviation plots for acetic acid-water at 70 mm Hg. Using 2 approaches with 3 parameter NRTL equation.	171
46	Deviation plots for acetic acid-water at 200 mm Hg. Using 2 approaches with 3 parameter NRTL equation.	171
47	Correction factors, ε_A and ε_B vs x for system acetic acid-water.	171
48	Deviation plots for acetic acid-water at 760 mm Hg. Using 2 approaches and 3 parameter NRTL equation.	171
49	Equilibrium constant, km vs x for isothermal acetic acid-water systems.	171
50	Km vs x for acetic acid-water systems at 760 mm Hg.	171

LIST OF FIGURES (CONTINUED)

FIG. FACING PAGE

51 Deviation plots for system acetic acid-methanol. Using Wilson equation and 2 approaches. 172

52 Deviation plots for system acetic acid-ethanol. Using Wilson equation and 2 approaches. 172

53 Deviation plots for system acetic acid-n-butanol. Using 2 approaches with Wilson equation. 172

54 Activity coefficients in system acetic acid-toluene at 30°C Corrected and uncorrected values. 172

55 Ln V_1/V_2 vs x for acetic acid-toluene. Corrected and uncorrected cases. 172

56 Correction factors, δ_A and δ_B vs x for system acetic acid-toluene. 172

57 Equilibrium constant, K_m vs mole fraction acetic acid, x for alcohols. 173

58 Deviation plots for system acetic acid-ethyl acetate. Wilson equation with 2 approaches. 173

59 Activity coefficients for acetic acid-methanol, acetic acid-ethanol. Corrected and uncorrected values. 173

LIST OF FIGURES (CONTINUED)

FIG. FACING PAGE.

60 Correction factors, δ_A and δ_B for acetic acid-ethanol. 174

61 Equilibrium constant, K_m vs x for ethyl acetate. 174

62 Deviation plots for acetic acid-acetone. Using 3 parameter NRTL equation and 2 approaches. 174

63 Km vs x for ketones. 174

64 Deviation plot acetic acid-ethyl ether. Using 2 approaches with Wilson equation. 174

65 Km vs x for acetic acid-ethyl ether. 174

66 Tie lines at 30°C from 3 parameter NRTL for system acetic acid-toluene-water. No account taken of association. 175

67 Tie lines at 60°C from 3 parameter NRTL equation. 175

68 Tie lines at 30°C from UNIQUAC equation for system acetic acid-toluene-water. No account taken of reaction. 175

LIST OF FIGURES (CONTINUED).

FIG.		FACING PAGE.
69	Tie lines at 60°C from UNIQUAC equation.	175
70	Tie lines at 30°C from 3 parameter NRTL equation for system acetic acid-water-toluene association taken into account.	175
71	Flow diagram - JF4LIQLIQ.	234
72	Flow diagram - subroutine ROSEN.	235
73	Flow diagram - Subroutine VIRIAL.	237
74	Flow diagram - Subroutine LIQP.	239
75	Flow diagram - Subroutine PCLCA.	240
76	Flow diagram - Subroutine XMODEL/VAPFIT.	241
77	Input data layout JF4LSQMKA.	242
78	Flow diagram - JF4 VAPFIT.	243
79	FLOW DIAGRAM JF4LSQMKA.	244.

LIST OF FIGURES (CONTINUED)

FIG.		FACING PAGE.
80	Input data layout JF4LIQLIQ.	245
81	Flow diagram JF4LSQFIT.	249
82	Flow diagram subroutine XMODEL.	249
83	Flow diagram subroutine ETACAL(a).	253
84	Flow diagram subroutine ETACAL(b).	253
85	Flow diagram subroutine DELCAL.	254
86	Flow diagram JF4LSQSOL.	256
87	Flow diagram JF4ERRAN.	257
88	Input layout for JF4ERRAN.	257
89	Flow diagram subroutine ERRAN.	261
90	Input layout for JF4LSQSPL.	262

PLATE

1	**Cathala Still apparatus**	128

INTRODUCTION.

The determination of the vapour phase composition that exists in equilibrium with a liquid phase is of fundamental importance in chemical engineering. The continuing improvements in design techniques for equipment such as distillation columns and absorption towers, place an increasing emphasis on the accuracy with which the vapour phase composition can be calculated. Although work in this field has been in progress for many years it is still not possible to predict vapour liquid equilibrium data from pure component properties alone. There have been some advances in prediction of activity coefficients at infinite dilution from the contributions of structural groups such as the approach of Derr and Deal (D5) but in general, if accurate data is required recourse must be made to experimental techniques. However a considerable degree of experimental skill is required and furthermore complete determination of data across the ranges of pressure, temperature and composition of interest is a time consuming process. These factors have led to the numerous attempts to design equilibrium stills whereby vapour liquid equilibrium data may be obtained rapidly and accurately but by reference to published data it is evident that each type of still can be the source of various errors which need not have the same importance in all systems to be investigated.

Some of the sources of error in vapour liquid equilibrium data cannot be detected experimentally and classical thermodynamics is used to assist in detecting such errors. This is accomplished by applying the Gibbs-Duhem relationship in one of its forms to the data, and such an application is commonly called a consistency test. Although the Gibbs-Duhem equation has been used in many different ways and for many different purposes, the limitations on its use in terms of what it can or cannot do appears to have been little discussed in the literature. Neither is there any apparent agreement on how best to use the Gibbs-Duhem equation to detect experimental errors.

The most common application of the Gibbs-Duhem equation is to data where all of the unknown variables are experimentally measured. Such data may be determined by a variety of methods, an example of which is the flow method or in particular the Cathala flow still. The principle of the flow still is that boiling liquid is brought into intimate contact with vapour and allowed to come to equilibrium. The two phases are then separated and the temperature, pressure, vapour and liquid compositions are determined when the conditions in the still are no longer changing with time. The potential sources of error with this type of experimental procedure are well known and apply in general to other experimental procedures with only minor differences. These sources of error can be divided into two broadly different types :

1. Random measurement errors.

2. Systematic errors.

Both of these types of error are always present to some extent in experimental data. The random measurement errors such as those associated with uncertainties in the temperature, pressure and composition measurements can be estimated, and to some extent controlled while the experiment is in progress. The systematic errors, however, are a result of unknown errors associated with the experimental procedure or with the design of the experimental apparatus and cannot therefore be estimated before the data are taken. Systematic errors arise, for example, from the system under investigation not achieving equilibrium or from entrainment of liquid in the vapour space by too rapid boiling. Such errors are effectively detected only by means of a consistency test.

Another possible source of error arises in applications of the Gibbs-Duhem equation. This equation contains, in addition to the vapour-liquid equilibrium variables, terms which depend on the heat of mixing or the volume change of mixing. Since these terms must be measured by separate experimental procedures and since such data are relatively scarce in the literature, they are often neglected in consistency tests. It is difficult to estimate the error incurred by neglecting the heat or volume change of mixing and thus a positive conclusion about the accuracy of the data may not be obtainable.

The fact that experimentally determined vapour-liquid equilibrium data will not precisely satisfy the Gibbs-Duhem equation has generally been recognised. However, no universally accepted criterion is available for declaring a set of data "accurately measured". One aim of this work is to identify a procedure which will indicate, with some level of confidence, whether a set of vapour-liquid data exhibit no more error than that expected from random measurement errors.

The first step in selecting a procedure is to examine the existing published consistency tests for ease and accuracy of application. One of the most promising tests is due to Ulrichson and Stevenson (U1), derived from the local area test of Stevenson and Sater (S12) by applying the propagation of error equation. This yields a formula for the error bounds (or confidence region) which establishes the effect of random measurement error on the consistency test. In addition this test involves statistical techniques which indicate the probability of a given random distribution in the test results arising only from normally distributed random measurement errors. A set of data with known uncertainties in the measured variables may then be accepted as free from systematic errors if the probability is high, e.g., the chances are greater than 1 in 10 that only random measurement error exists. Conversely, further analysis may be required if the probability is low that only random measurement error exists. In this context the terms consistent or inconsistent have no meaning.

Data for which the consistency test results are non-random or random with a low probability of containing only measurement error, may be treated in several ways. Firstly the data may be rejected as being of unacceptably low accuracy or more probably the effect of neglected terms in the test equation would be investigated and new estimates of the uncertainty in the measured variables sought. However, a value judgement is still required to reach a final conclusion.

Should a set of vapour-liquid equilibrium data tested by this procedure be found to be free from systematic error then the level of random error associated with the data set may be used to determine the effect of this error on the end use for which the data were obtained. For example by applying the propagation of error formula, it is possible to develop confidence limits for the effect of random measurement error on calculated activity coefficients.

It will be shown later that in fact no single consistency test is adequate on its own to analyse a set of vapour-liquid equilibrium data since different tests are affected by systematic and random error in different ways. In addition to the local area test, it will also be shown that the propagation of error formula in conjunction with the overall area test of Samuels is capable of detecting systematic error across the composition range which may be missed by the local area test. It was found to be best to use the above two tests together with the Van Ness test on the residuals obtained from a Barker type fit on the experimental data. This last test, though easier to interpret than some other tests, has the disadvantage of assuming a particular solution to the Gibbs-Duhem equation raising the additional possibility that failure to satisfy the test may be due to inadequacy of the liquid phase model. This last objection has been overcome by Christiansen and Fredenslund (C8) who used the method of orthogonal collocation to calculate equilibrium vapour compositions from P-T-X data for binary systems which they then compared with experimental values to obtain an indication of thermodynamic consistency.

These tests were utilised to analyse the performance and shortcomings of a Cathala flow still although the additional refinement of orthogonal collocation was not used.

The Cathala flow still was designed for the express purpose of determining vapour-liquid equilibrium data in reactive systems, and has been used extensively for this purpose. Mamers (M4) used a modified Cathala still to investigate vapour-liquid equilibrium in the acetic acid - acetic anhydride - water system while more recently, as part of a programme of work on distillation with chemical reaction, Davies, Jenkins and Jeffreys (D3) determined vapour-liquid equilibrium data for the quaternary system ethanol-n-butanol-ethyl acetate-n-butyl acetate and its constituent ternary and binary systems. They used the same modified Cathala still, even though no reaction took place in the absence of the catalyst, because as a flow still it enabled the data to be obtained rapidly, an important advantage in view of the large number of data points to be determined. A proposed extension of the above distillation work to a system of industrial importance made necessary the future determination of data for a strongly reactive mixture.

Despite the widespread use of the Cathala still, no detailed study of its performance appears to have been reported. Accordingly it was thought necessary to make measurements of vapour-liquid equilibria on a number of typical non-reactive systems and to obtain enough data for the previously discussed statistically based thermodynamic consistency tests to be used. Hence the reliability of the still could be assessed before its use on the more difficult multicomponent system and its constituent binaries.

In the earlier work of Davies et al (D3) some discrepancies had been evident in three of the binary systems. As these three systems provided examples of near ideal, moderately non-ideal and azeotropic systems they were chosen as the test systems. The opportunity was taken to investigate at the same time the effect of analytical uncertainty on the reliability and consistency of the data. Thus for two of the systems, the vapour and liquid samples were analysed both by refractive index and by a rapid gas-liquid chromatographic method, to give two data sets with different levels of random measurement error. Application of statistical consistency tests should give results that reflected these different error levels. Further, any systematic deviations in the data ought to be detected. However, the results obtained will be seen to raise considerable doubts as to the general usefulness of consistency tests.

There are industrially important systems, however, for which the application of consistency tests indicate systematic error regardless by what method the data were obtained or how carefully the variables are measured. One such example is the system acetic acid-toluene for which data exist over a wide temperature and pressure range. The reasons for this anomaly are due to reactions of the components in the liquid and vapour phase. In particular solvation, the formation of complexes, and association to the dimer and possibly higher polymers, as in the case of acetic acid all cause apparent inconsistency.

Phase equilibria in systems showing association in one or more phases has been studied for a considerable time. The early work of Marek (M6) and the classical work of Prigogine and Defay (P10) are typical examples.

Although their work presented methods of dealing with association in both phases, it has been the practice of most workers to ignore liquid phase association and to use the activity coefficients to account for any non-idealities, but to correct the vapour phase fugacity for association. This is probably because it is possible to make certain simplifying assumptions for the vapour phase which are not justified for the liquid phase. The assumptions allow a straightforward calculation of the necessary correction factors. In particular the association constant for dimerisation in the vapour phase is normally assumed to be independent of composition and to be equal to the value of the association constant for the pure associating substance. In the liquid phase however, spectroscopic measurements indicate that the association is a function of composition (P10). This taken with the fact that reasonable correlations have been obtained using corrections only for vapour phase association has led to the general failure to take liquid phase association into account.

As will be shown later development of a liquid phase model incorporating a concentration dependent equilibrium constant considerably improves the correlation and consistency of data for systems containing acetic acid.

A further use for these studies was in the development of a computer programme for the prediction of the tie-lines and binodal curve for the system acetic acid-toluene-water. The need for this had arisen in connection with research in this department into the optimisation of a mixture-settler chain for the solvent extraction of acetic acid from water using toluene. The new approach will be shown to give little improvement over methods employing the NRTL and UNIQUAC equations alone.

2.0 The Theory of Vapour-Liquid Equilibrium.

In order to predict the composition of two phases in equilibrium it is necessary to provide precise criteria for the equilibrium state.

One useful criterion is given by the relationship :

$$\mu_i^A = \mu_i^B \qquad (2.1)$$

where μ_i^P is the chemical potential of component i in phase P and is defined by :

$$\mu_i = \frac{\partial G}{\partial n_i} \quad T,\ P,\ nj \text{ for } i \neq j \qquad (2.2)$$

It can be described as the change in Gibbs free energy, G, of a phase when one mole of component i is added to it without changing the composition. The implications of equation 2.1 are that for each component i in each phase no driving force for mass transfer exists.

However if this criterion is to be of use it is necessary to relate the value of the chemical potential to the concentrations of component, i in each phase. This may be accomplished by making use of the exact relationships provided by thermodynamics.

2.1 Basic Thermodynamic relations.

For a closed system for which the only form of energy that changes is the internal energy, U, the first law of thermodynamic may be expressed as :

$$du = q - w \qquad (2.3)$$

where q and w represent the heat added to and the work done by the system respectively. For a reversible process doing expansion work only, eqn. (2.3) may be re-written as :

$$du = TdS - PdV \qquad (2.4)$$

where T is the absolute temperature, S the entropy, P the pressure and V the volume. Two other important thermodynamic properties are the enthalpy, H and the free energy G defined as follows :

$$H = U + PV \qquad (2.5)$$

and $$G = H - TS \qquad (2.6)$$

On differentiation we have :

$$dH = du + PdV + VdP \qquad (2.7)$$

and $$dG = dH - TdS - SdT \qquad (2.8)$$

combining (2.7) and (2.8) with (2.4) in an appropriate fashion gives :

$$dH = TdS + VdP \qquad (2.9)$$

and $$dG = SdT + VdP \qquad (2.10)$$

A further extremely important relationship is the Gibbs-Duhem relationship :

$$SdT - VdP + \Sigma n_i . d\mu_i = 0 \qquad (2.11)$$

For dT = 0 and dP = 0 this reduces to the restricted Gibbs-Duhem relationship :

$$\Sigma\, n_i \, .\, d\mu_i = 0 \tag{2.12}$$

Two further relationships which enable this effects of temperature and pressure on phase equilibria to be established are given by :

$$\left.\frac{\partial\,(\mu_i/T)}{\partial\, T}\right|_{P,\, n_i,\, n_j} = \frac{-\bar{H}i}{T^2} \tag{2.13}$$

$$\left.\frac{\partial\,(\mu_i)}{\partial P}\right|_{T,\, n_i,\, n_j} = \bar{V}i \tag{2.14}$$

where $\bar{H}i$ and $\bar{V}i$ are respectively the partial molar enthalpy and partial molar volume of i in a mixture defined as :

$$\bar{V}i = \left.\frac{\partial V}{\partial n_i}\right|_{T,\, P,\, n_j} \qquad i \neq j \tag{2.15}$$

$$\bar{H}i = \left.\frac{\partial H}{\partial n_i}\right|_{T,\, P,\, n_j} \qquad i \neq j \tag{2.16}$$

2.2 The gas phase.

The gas phase whether considered as ideal or real or as a mixture of components ideal or real may be modelled in two different ways. Firstly an equation of state may be used such as the classical relation for an ideal gas :

$$PV = nRT \qquad (2.17)$$

or for example the Van der Waals equation for real gases. These may be called direct models. Among other equations for real gases is the virial equation which will be considered later.

The second method, here designated as indirect models relates the chemical potential defined at the same temperature. For a single ideal gas this may be written :

$$\mu(P,T) = \mu^{o}(T) + RT \ln \frac{p}{p^{o}} \qquad (2.18)$$

where p^{o} is defined as 1 standard atmosphere$\equiv 1.01325 \times 10^{5}$ Nm^{-2}.

For the real gas mixture case this becomes :

$$\left.\begin{aligned} &\mu_i\ (P,T) = \mu_i^{\circ}\ (T) + RT\ \ln \frac{f_i}{f_i^{\circ}} \\ &\text{with } \frac{f_i}{P_i} \longrightarrow 1.0 \text{ as } P_i \longrightarrow 0 \end{aligned}\right\} \quad (2.19)$$

f_i is the fugacity of component i in the real gas mixture. f_i^{o} is the standard state fugacity of i, defined as being 1 standard atmosphere. μ_i (T) is now the standard state chemical potential of pure i at a pressure where $f_i = 1$. Equation (2.19) is conveniently rewritten as :

$$\mu_i = \mu_i^* + RT\ \ln f_i \quad (2.20)$$

$$\frac{f_i}{P_i} \longrightarrow 1.0 \text{ as } P_i \longrightarrow 0$$

2.3 The Liquid Phase.

An advantage of the indirect approach for the vapour phase is that conceptually similar models can be set up for the ideal and non-ideal liquid cases. For an ideal solution the chemical potential is written as :

$$\mu_i = \mu_i^* + RT \ln x_i \qquad (2.21)$$

where μ_i^* is a function of temperature and pressure only. For the non-ideal case the equation is modified by the introduction of the activity coefficient, Vi which may be a function of pressure, temperature and liquid compositions i.e. :

$$\mu_i = \mu_i^* + RT \ln x_i + RT \ln Vi \qquad (2.22)$$

μ_i^* is chosen either so that Vi tends to 1.0 as x_i tends to 1.0 and is thus the Gibbs free energy per mole of pure i or such that $Vi \longrightarrow 1.0$ as $x_i \longrightarrow 0$, the so-called infinite dilution standard state.

In dealing with the general case of a non-ideal liquid mixture it has been found useful to define a property of the system known as the Gibbs excess function or property g^E :

$$\text{For a mixture} \quad G(\text{mixture}) = \Sigma\, G_i n_i \qquad (2.23)$$

or separating ideal from non-ideal G(mixture.) $= \sum G_i^{ideal} n_i + g^E$ (2.24)

Dividing by the total number of moles in the mixture we have :

$$\frac{G(\text{mixture})}{\Sigma n_i} = \sum_i \overline{Gi}^{\,ideal} x_i + \frac{g^E}{\Sigma n_i} \qquad (2.25)$$

where g^E in the excess free energy, which can be expressed as a polynomial containing empirically determined coefficients, relating g^E to composition. This holds for any other thermodynamic property.

From equations (2.23),(2.24) and (2.25) it is possible to express the excess Gibbs free energy g^E in terms of compositions and activity coefficients in the form :

$$g^E = RT \sum n_i . \ln Vi \qquad (2.26)$$

Furthermore the activity coefficients can be expressed in terms of g^E as :

$$\ln Vi = \frac{1}{RT}\left(\frac{\partial nTg^E}{\partial ni}\right)_{nj\ j \neq i} \qquad (2.27)$$

where $n^T = \Sigma n_i$.

To relate Vi to x_i requires a knowledge of g^E as a function of composition. There have been numerous attempts to achieve this which will be discussed in a later section.

2.4 The Equilibrium relationship.

Thus replacing the chemical potentials in equation (2.1) by the vapour and liquid phase models outlined previously the equilibrium relationship may be expressed as :

$$\mu_i{}^* + RT \ln Vi\ x_i = \mu_i{}^o + RT \ln f_i \qquad (2.28)$$

(dropping all unnecessary labels, etc).

or $$Vi\ x_i \exp\left(\frac{\mu_i{}^* - \mu_i{}^o}{RT}\right) = f_i \qquad (2.29)$$

A fugacity coefficient may be defined as :

$$\phi_i = f_i / P_i \qquad (2.30)$$

where Pi is the partial pressure of i defined as :

$$P_i = y_i P \qquad (2.31)$$

Therefore f_i may be replaced in equation (2.32) by :

$$\phi_i \quad y_i \; P \qquad (2.33)$$

and equation (2.29) becomes :

$$V_i \; x_i \; \exp \left(\frac{\mu_i{}^* - \mu_i{}^\circ}{RT} \right) = \phi_i \quad y_i \quad P \qquad (2.34)$$

where $(\mu_i{}^* - \mu_i{}^\circ)$ is the difference in Gibbs function between the pure liquid i at P and T of the solution and the pure vapour i at the T of the solution and a fugacity of 1 atm.

To evaluate this quantity consider first the pure vapour i in equilibrium with the pure liquid i at the T of the solution and at a pressure Psi which is the saturated vapour pressure of i at T. Writing the equilibrium relationship for this as :

$$\mu_i^V = \mu_i^L \tag{2.35}$$

or $\mu_i^* (T, P_{si}) + RT \ln V_i x_i$

$$= \mu_i^o + RT \ln f_{si} (P_{si}) \tag{2.36}$$

Recalling that $V_i \longrightarrow 1.0$ as $x_i \longrightarrow 1.0$ gives :

$$\mu_i^* (T, P_{si}) = \mu_i^o + RT \ln f_{si} (P_{si}) \tag{2.37}$$

and equation (2.36) thus becomes :

$$V_i \, x_i \, f_{si} (P_{si}) \exp \left(\frac{\mu_i^* (T,P) - \mu_i^* (T,P_{si})}{RT} \right) = \O_i \cdot y_i \, P \tag{2.38}$$

To evaluate $\mu_i^* (T,P) - \mu_i^* (T,P_{si})$ the thermodynamic relation :

$$\left(\frac{\partial \mu_i^*}{\partial P} \right)_T = V_i^L \tag{2.39}$$

gives $\mu_i^* (T,P) - \mu_i^* (T, P_{si})$

$$x \quad = \quad \int_{P_{si}}^{P} V_iL \, dP$$

Substituting into equation (2.38) and replacing f_{si} (P_{si}) by $\emptyset_{si}$ (P_{si}) yields :

$$V_i \, x_i \, \emptyset_{si} \, (P_{si}) \, P_{si} \exp \left[\frac{1}{RT} \int_{P_{si}}^{P} V_iLdP \right] = \emptyset_i \, (p_i) \, y_i \, P \qquad (2.40)$$

where the subscripts denote the pressure at which the $\emptyset_i$'s are calculated.

Equation (2.40) may be simplified if certain assumptions are made. For example if the vapour phase is assumed to be ideal in all respects then $\emptyset_i = \emptyset_{si} = 1$ and the exponential term may be neglected and equation (2.40) may be written :

$$V_i \, x_i \, P_{si} = y_iP \qquad (2.41)$$

Further if the liquid solution is assumed to be ideal then Vi = 1.0 and (2.41) reduces to Raoults Law:

$$x_i \, P_{si} \quad = \quad y_iP \qquad (2.42)$$

The various quantities may be evaluated as shown in chapter 3, but the use of the equilibrium relationship to predict multicomponent vapour liquid equilibrium often requires an expression for the relationship between the activity coefficient and liquid composition.

2.5 Gas phase models

As has been stated before, models of the real gas are of direct and indirect types. The direct models consist of an equation of state, often a modified version of the ideal gas law, while the indirect model replaces the pressure of the gas by a 'dummy property', the fugacity.

There have been many hundreds of equations of state produced since Van der Waals' modification of the ideal gas law. However no one equation of state is adequate to represent PVT data over the wide range of conditions which may be encountered but all the equations that have been used are based upon either the Van der Waals or the virial equation.

In 1873 Van der Waals proposed two modifications to the ideal gas law to allow for attractive and repulsive forces between the molecules in a gas. Thus he replaced V by (V-b) where b is a constant allowing for the volume of the molecules, and increased the pressure term by an 'internal pressure' allowing for the attractive forces between molecules. This he suggested was proportional to the square of the density. The equation of state then becomes :

$$\left(P + \frac{n^2a}{V^2}\right) (V-nb) = nRT \qquad (2.43)$$

As might be expected this equation is good only at regions where the real gas is nearly ideal. For the regions where the real gas behaves as a dense fluid the equation becomes inadequate due to the assumption of a hard sphere model for the molecules. The equation however forms the basis of many other equations some of which are discussed later.

The virial equation however was initially proposed to fit PVT data empirically, but it has since been shown that it has a firm basis in statistical mechanics. This has shown exact relationships between the virial coefficients and the intermolecular potential describing the forces between molecules. The equation is given by :

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots \qquad (2.44)$$

where B, C and D are respectively the second, third and fourth virial coefficients and Z the compressibility factor. They are functions of temperature and composition, but not of pressure. Although considerable data are available on second virial coefficients, relatively little is known about the third and virtually nothing about fourth and higher virial coefficients so that a truncated form is normally used. This means that for practical purposes use of the virial equation is limited to the pressure range for which the equation, truncated after the third term provides an acceptable approximation. This generally means a pressure limit corresponding to a density nearly equal to the critical density.

An alternative form of the virial equation presents the expansion of Z as a power series in P.

$$Z = 1 + B^1P + C^1P^2 + D^1P^3 + \ldots \qquad (2.45)$$

Equation (2.45) is widely used in its truncated form :

$$Z = 1 + \frac{BP}{RT} \qquad (2.46)$$

This form is a sufficiently good approximation at low pressures to have many useful engineering applications.

To obtain the parameters in the Van der Waals equation the equation must be fit to PVT data. The virial coefficients however can be deduced from several different correlations, all of the corresponding states types. One of the most useful of these is that of Pitzer and Curl (P4) which will be further discussed in Appendix A1.

The most successful development of the Van der Waals equation using only two adjustable constants is the equation of Redlich and Kwong (R9) given by :

$$P = \frac{RT}{V-b} - \frac{a}{T^{\frac{1}{2}}V(V+b)} \qquad (2.47)$$

where a and b are constants related to the critical temperature, Tc and critical pressure Pc by :

$$a = \Omega_a \frac{R^2 T_c^{2.5}}{Pc} \quad \text{and } b = \Omega_b \frac{RTc}{Pc} \qquad (2.48)$$

where Ωa and Ωb are proportionality constants. This equation and modifications of it are quite powerful and can be used at pressures higher than those applicable to equation (2.44).

A large number of equations have forms which can be shown to be related to that of the virial equation. An example is the Benedict-Webb-Rubin (B6), (B7), (B8) equation which represents satisfactorily volumetric properties of non polar gases and liquids to densities about 1.8 times the critical. However use of this equation requires extensive experimental data to determine the constants and the main use of these types of equation is in the fitting and smoothing of experimental PVT data. For prediction purposes equations of the Redlich-Kwong type are of more use.

2.6 Liquid phase models.

There have been numerous models produced to relate the excess Gibbs free energy, gE, to liquid phase composition but there have been two main lines of approach. Since

$$g^E = h^E - Ts^E \qquad (2.49)$$

the first approach is that of the theory of "regular solutions" in which it is assumed that $S^E = 0$ and the non ideality is entirely due to the excess enthalpy h^E. If however it is assumed that it is the entropy of mixing that is non-ideal so that $h^E = 0$ then the liquid mixture is regarded as "athermal".

Considering the theory of regular solutions, the most general expression has been derived by Wohl (W7) who expanded g^E as a power series as follows :

$$\frac{gE}{2.303RT \Sigma q_i x_i} = \sum_{ij} ZiZja_{ij} + \sum_{ijk} ZiZjZka_{ijk} + \ldots \quad (2.50)$$

If particular assumptions are made about the quantities qi, Zi then various well known expressions such as the Scatchard and Hamer (S7) Van Laar (V1) and Margules (M7) equations are obtained. For instance for a binary mixture, setting $q1/q2 = 1.0$ in the Wohl expansion and carrying out the differentiation indicated in equation (2.27), gives the 3 suffix Margules equations :

$$\ln V_1 = x_2^2 \left(A + 2x_1 (B-A)\right) \quad (2.51a)$$

$$\ln V_2 \equiv x_1^2 \left(B + 2x_2 (A-B)\right) \quad (2.51b)$$

Similarly if q2/q1 = A/B then the modified third order Van Laar equation of Carlson and Colburn (C2) is obtained i.e.

$$\ln V_1 = \frac{A}{\left(1 + \frac{A}{B}\frac{x1}{x2}\right)^2} \qquad \ln V_2 = \frac{B}{\left(1 + \frac{Bx_2}{Ax_1}\right)^2} \qquad (2.52)$$

These equations, and others based on the Wohl expansion are difficult to apply to multicomponent systems since the constants refer only to binary interactions between pairs of molecules.

If one of the equations is to be used in a ternary system then this requires the evaluation and use of a ternary constant which is difficult since ternary and higher ordered data are scarce. Another disadvantage is that these equations do not relate the activity coefficients to the effect of temperature or pressure so that the constants obtained during data reduction are functions of temperature and pressure. Although the effects of pressure are small on the liquid phase at conditions remote from the critical or at low pressures the same cannot be said of temperature effects and the above quantities are thus restricted in their applicability. However their simplicity and the fact they have been found to apply to quite a variety of mixtures has led to considerable usage. Further the constants can be estimated from a single pair of infinite dilution activity coefficients.

Another approach based on regular solution theory overcomes the disadvantage of higher order constants in multicomponent mixtures. This requires only one constant per component known as the Hildebrand solubility parameter (H10). This parameter is related to the energy required to take a model from the ideal gas state to the liquid state. The equation is written :

$$\ln Vi = \frac{\upsilon i \ (\delta i - \bar{\delta})^2}{RT} \qquad (2.53)$$

where δi is the solubility parameter given by $\sqrt{\Delta Ei/\upsilon i}$ and Ei is the energy required to vaporise one mole of i to infinite volume and $\bar{\delta}$ is the volume average solubility parameter for the liquid mixture and is given by $\bar{\delta} = \Sigma z_i \delta$ where $z_i = \upsilon i x_i / \Sigma x_i \upsilon i$. This assumes no volume change in mixing. Apart from the multicomponent advantage and the fact that the parameter may be deduced from pure component properties, this model has no advantage over the other methods based on the same assumptions such as the Van Laar equations, and only holds at all well for non polar compounds of similar size.

Other equations which have been used based on the same ideas have been reported by Black (B10) who presented a modified version of the Van Laar equations and Abbott and Van Ness (A1) who describe the use of four- and five- suffix Margules equations.

A further method of representing g^E as a function of composition has been proposed by Redlich and Kister (R5) and consists of a series expansion in compositions and does not depend on assumptions as to whether the solution is regular or athermal and is therefore very general and as such widely used. The expansion is :

$$g^E = x_1x_2 \left(A + B(x_1-x_2) + C(x_1-x_2)^2 + D(x_1-x_2)^3 + \ldots\right) \tag{2.54}$$

The constants A, B, C and D are all temperature dependent and determined from experimental data and the expression can be shown to be equivalent to the Margules equations.

Klaus and Van Ness (K7) have pointed out that g^E

as a function of composition is well represented by orthogonal functions.

If the following equations for γ_1 and γ_2 i.e.

$$\ln \gamma_1 = \frac{g^E}{RT} + x_2 \left(\frac{d(g^E/RT)}{dx_1} \right) - \frac{x_2}{RT} \left(V \left(\frac{dP}{dx_1} \right) - \sum_{i=1}^{2} x_i V_i{}^{\circ} \left(\frac{dPi^{\circ}}{dx_1} \right) \right) + \frac{x_2 h^E}{RT^2} \left(\frac{dT}{dx_1} \right) \qquad (2.55)$$

and $$\ln \gamma_2 = \frac{g^E}{RT} - x_1 \left(\frac{d(g^E/RT)}{dx_1} \right) + \frac{x_1}{RT} \left(V \left(\frac{dP}{dx_1} \right) - \sum_{i=1}^{2} x_i V_i{}^{\circ} \left(\frac{dPi^{\circ}}{dx_1} \right) \right) - \frac{h^E x_1}{RT^2} \left(\frac{dT}{dx_1} \right) \qquad (2.56)$$

are substituted into the equilibrium relationship :

$$P = \frac{x_1 \; V_1 \; f_i{}^{\circ}}{\phi_1} + \frac{x_2 \; V_2 \; f_2{}^{\circ}}{\phi_2} \qquad (2.57)$$

then a differential equation in g^E results.

Christiansen and Fredenslund (C8) have used the method of orthogonal collocation to solve this differential equation. The unknown function is approximated by an orthogonal polynomial and values of g^E are determined by successive approximations at selected points, these points being the zeroes of a Jacobi polynomial. The collocation abscissas were chosen to be the roots of Legendre polynomials. This method has given good results for high pressure vapour liquid equilibria.

As an alternative to the preceding models is the approach which assumes that the excess enthalpy of mixing, h^E, is zero. The original athermal solution model is due to Flory (F2), (F3) and Huggins (H20) and (H21) who proposed the following expression to deal with polymer solutions :

$$g^E = \sum x_i \ln \frac{z_i}{x_i} \quad \text{where } z_i = \frac{x_i V_i}{\sum_i x_i V_i} \tag{2.58}$$

which assumes that $v_i = \bar{V}_i$ which implies no volume change on mixing. They introduced the concept of local mole fraction, x_{12} which is related to overall mole fraction by :

$$\frac{x_{12}}{x_{11}} = \frac{x_2 \exp(-g_{12}/RT)}{x_1 \exp(-g_{11}/RT)} \tag{2.59}$$

where the terms exp $(-g_{12}/RT)$ are Boltzmann factors and g_{11} and g_{12} are proportional to the 1-1 and 1-2 interaction energies. A similar relation holds for x_{21}. Wilson (W5) modified the expression z_i to local volume fraction based on the same idea and substituted this into the Flory-Huggins expression for g^E. Differentiating this expression he produced the following model for the activity coefficients in a multicomponent mixture :

$$\ln \gamma_k = \ln (\sum_j x_j \Lambda_{kj}) + 1 - \sum_i \frac{x_i \Lambda_{ik}}{\sum_j x_j \Lambda_{ij}} \qquad (2.60)$$

As can be seen only binary parameters are needed for multicomponent mixtures and the Wilson equation has been shown to be sufficient for a wide range of mixtures. There is one important exception and that is the mixtures which exhibit partial immiscibility, which makes it in this respect inferior to the Van Laar equation.

Wilson (W5) tried to overcome this by the introduction of a third parameter, c. However, unless the binary constants cij are the same for all binary cij pairs the equations cannot be generalised to multicomponent mixtures. Another advantage of the Wilson parameters defined by :

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left(-\frac{(\lambda_{12}-\lambda_{11})}{RT}\right) \quad (2.61a)$$

and

$$\Lambda_{21} = \frac{v_1}{v_2} \exp\left(-\frac{(\lambda_{21}-\lambda_{22})}{RT}\right) \quad (2.61b)$$

where $(\lambda_{12}-\lambda_{11})$ and $(\lambda_{21}-\lambda_{22})$ are the adjustable parameters, is that they have been shown to be only weakly temperature dependent (O2), (C14) and can thus be extrapolated across a wider temperature range than equations such as the Margules.

In an attempt to overcome these defficiencies Renon and Prausnitz (R12) have combined this approach with Scotts two-liquid theory to give the NRTL equation, which gives for the activity coefficient for a component, i :

$$\ln \gamma_i = \frac{\sum_{j}^{m} \tau_{ji} G_{ji} x_j}{\sum_{i}^{m} G_{li} x_i} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{i=1}^{m} G_{ij} x_i} \left[\tau_{ij} - \frac{\sum_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\sum_{i=1}^{m} G_{ij} x_i} \right] \quad (2.62a)$$

where

$$\tau_{ij} = \frac{g_{ij} - g_{ii}}{RT} \quad (2.62b)$$

$$\text{and } G_{ij} = \exp(-\alpha \tau_{ij}) \qquad (2.62c)$$

(gij-gii) are adjustable parameters, 2 per binary while α is a third parameter chosen according to mixture type from rules presented by Renon and Prausnitz or fitted as a third parameter to experimental data. This equation is not restricted in application to miscible systems only. However the parameters are highly temperature dependent and for successful extrapolation usually require additional parameters of the form (A6).

$$g_{21} - g_{11} = c_1 + D_1 \ (T-273.15) \qquad (2.63a)$$

$$g_{12} - g_{22} = c_2 + D_2 \ (T-273.15) \qquad (2.63b)$$

$$\alpha_{12} = \alpha_{21} = \alpha^{0} + \alpha^{T} \ (T-273.15) \qquad (2.63c)$$

in which a linear relation with temperature is assumed. However in this form the NRTL equation has been used successfully to correlate excess enthalpy as well as excess free energy data.

A drawback arises however in that selection of a value for α is not entirely straightforward. Once again only binary parameters are required for multicomponent prediction or correlation.

A nine parameter NRTL equation has also been successfully used (N1) in which a quadratic temperature dependence of the parameters is assumed.

Bruin and Prausnitz (B18) modified the NRTL equation by introducing local volume fractions in place of local mole fractions. They found however that this offered no significant improvement except for aqueous systems or systems where the molar volumes of the components differed strongly. By introducing a physically reasonable approximation they were able to reduce the number of adjustable parameters from two to one. Compared with two parameter equations there is a certain loss of accuracy in fitting, but in many cases this is small. Mixtures with strong association and solution effects such as alcohols-alkanes, alcohols-carbon tetra-chloride and alcohols-chloroform are notable exceptions. However while the fit is not as good as that obtained with the original 2 parameter NRTL equation, it is still superior to the Van Laar equation with two adjustable parameters.

However the problem of choosing a value for α still remains. Marina and Tassios (M8) (M9) eliminated the ambiguity by replacing α by -1. They called it the local effective mole fraction (LEMF) equation. The LEMF and NRTL equations yielded the same accuracy in correlating binary activity coefficients for 55 systems and, in predicting ternary vapour liquid equilibria from binary data was at least as good as the NRTL with the value of α set according to the rules of Renon and Prausnitz. For prediction of ternary liquid-liquid equilibrium for systems containing one partially miscible binary, the LEMF equation gives better results than the NRTL equation (M9).

Tassios (T7) has also proposed a modification to the Wilson equation to make it a single parameter expression. This involved using the molar-energy of vapourization to characterize the like pair interactions λii leaving λij as the sole adjustable parameter for the binary pair.

Other examples of two parameter equations based on the local composition concept are the Orye equation (O3), which was derived by introducing local volume fractions in the entropic and enthalpic parts of the Flory-Huggins equation and the enthalpic Wilson equation developed by Bruin based on a quasi-lattice model of a multicomponent solution developed by Guggenheim. These two equations are applicable to systems showing limited miscibility and have a built in temperature dependence of the activity coefficients. Although these two equations are superior to the Van Laar equation and to the Wilson equation in systems near to phase separation or showing phase separation, they are not as good as the Wilson model in normal circumstances.

Palmer and Smith (P2) presented a new local composition equation based on the two-liquid theory of Scott. They used entropic weighting function in their equation but Nagata (N3) has shown that it is inferior to the Wilson equation in vapour-liquid equilibrium data reduction for completely miscible systems.

McCann (M12) extended the approach of Bruin based on Guggenheim's quasi-lattice model to derive a three parameter equation using the same two adjustable parameters as the Wilson equation plus a further parameter K. By setting K=0 the Wilson equation results and K=1 gives the Orye equation. The enthalpic Wilson equation can also be deduced from it. This equation is applicable to systems showing partial miscibility although it appears to offer no significant advantage over the Wilson and NRTL equations. By considering the results obtained during data reduction McCann suggests that a value of K=0.1 be assigned and used it during all his subsequent work.

Abrams and Prausnitz (A2), generalized Guggenheim's quasi-chemical analysis through introduction of the local area fraction as the primary concentration variable. The effects of molecular size and shape are introduced through fixed parameters determined from tables in Bondi (B13). The resulting universal quasi-chemical (UNIQUAC) equation contains no more than two adjustable parameters per binary and it is applicable to a wide range of mixtures. Extension to multicomponent mixtures requires no higher parameters. In experimental vapour-liquid equilibrium data reduction for 220 binary systems the goodness of fit is about the same for the UNIQUAC equation, the NRTL equation and the Wilson equation. Further when binary parameters alone are used to predict ternary vapour-liquid equilibria, all three equations are essentially similar in prediction accuracy. While the UNIQUAC equation provides no major improvement over the Wilson equation for vapour-liquid equilibria in completely miscible systems it can also represent liquid-liquid equilibrium for multicomponent mixtures.

Binary systems in which solvation or association effects are present are usually difficult to represent with the previously discussed models. There have been a variety of special models proposed to deal with these effects such as that of Wiehe and Bagley (W4) and Kretschmer-Wiebe (K10). Most of these approaches have been developed to correlate data for systems containing alcohols but a different treatment originating with Marek and Standart (M6) is further developed in chapter 5 to deal with association in solutions containing acetic acid.

3. The Determination and Calculation of Vapour Liquid Equilibrium data.

3.1 INTRODUCTION.

Since the early work of Zawidski (Z1) on positive and negative deviations from Raoults Law, there have been numerous attempts to develop experimental techniques that will yield thermodynamically consistent vapour-liquid equilibrium data. The magnitude of the task may be judged from the variety of types of apparatus that have been described in the literature and at present no still has been constructed that is capable of yielding completely consistent data for all types of systems which may need to be determined.

There have been a number of different methods proposed whereby equilibrium data may be determined and these can be broadly classified into the following groups :

1. Differential distillation methods.
2. Circulation methods.
3. Flow methods.
4. Static methods.
5. Other methods.
6. Total pressure methods.

Early work on these approaches has been extensively reviewed by Hala et al (H2) while Jenkins (J4) in 1963 critically surveyed techniques within these groups at that period. In consequence only a brief discussion of the principles and associated problems of each method will be attempted in relation to early work in this field and instead detailed consideration will be confined to the advances of the last few years.

3.2 Distillation method.

As the name implies this method involves merely placing a large charge in a boiling flask and removing liquid and vapour samples at equilibrium and determining their composition. Though the oldest and simplest of methods there are a large number of possible sources of serious error, not the least of which is the fact that removing the liquid and vapour samples alters the composition. This is partly overcome by using a large charge which can be a disadvantage in itself.

There are few techniques based on this approach nowadays although Ramalho et al (R4) have proposed a similar technique in which a simple distillation is performed with the continuous determination of the vapour or liquid composition, the other composition being deduced from the material balance.

3.3 Circulation methods.

These methods are the most widely used and there has been a wide variety of designs embodying the principles of this method. They are best used for low and medium pressure work, for at higher pressures, control of the system becomes a problem since liquid becomes entrained in the recirculating vapour and flash evaporation of the condensate, as it returns to the reboiler, occurs. This is because as the pressure rises the vapour phase pressure approaches the partial pressure and the enthalpy of vapourization is reduced.

The common principle of operation is as follows. Vapour from a boiling mixture passes to a condenser where it is totally condensed and returned through a condensate receiver and a non-return device (usually a weir or a cock) to the boiling vessel. It has been shown by Hala (H2) and Erdos (E3) that when steady state has been reached the system is at equilibrium, providing superheating and partial condensation do not occur.

The types of circulation still that have been constructed fall into two classes.

1. Stills with vapour phase circulation only.
2. Stills with circulation of both liquid and vapour phases.

The first equilibrium still which functioned satisfactorily was constructed by Othmer (O4). The original design contained a number of weaknesses and there have been a number of modifications by Othmer himself (O6) (O7) and others (B20). These types are still commonly used and, for reduced pressures a Jones (J9) (A4) or modified Jones still (T8) gives reliable results even down to 0.5 mm Hg. They are also useful if the constituent components of the system under investigation differ greatly in density, conventional circulation stills often giving poor results under these conditions.

The main advantage of these stills is the excellent mixing and intimate contact of vapour bubbles with the surrounding liquid in the equilibrium chamber. However, these are counterbalanced by difficulty in measuring the boiling temperature and maintaining adiabatic operation of the equilibrium chamber. Furthermore uneven heating of the equilibrium chamber may produce vertical temperature gradients.

The need to improve temperature measurements has led to the proposal of a number of stills incorporating both liquid and vapour circulation. The main feature of these versions such as proposed by Gillespie (G5) and his subsequent modifications (E17) (F1) (M15) is the incorporation of a Cottrell pump which permits very precise temperature measurement. The mixing and vapour-liquid contact characteristics are however, not as satisfactory as stills with vapour phase recirculation only and partial condensation of the vapour may occur particularly in the region of the thermocouple. Other stills based on this principle have been proposed by Otsuki and Williams (O9) and Dvořák and Boublik (D10). The majority of these types of stills require a charge of the order of 250-750 cm^3 though there are versions (E2) that require as little as 30 cm^3.

The most advanced circulation still is probably that of Raal, Code and Best (R1). The layout of the still is illustrated in fig. 1 and attempts to combine the good mixing characteristics of the vapour phase only circulation stills with a novel adaptation of the Cottrell pump. Liquid is heated in the lower portion of B by the main heater and vapour bubbles are formed in such a way that the small annular space between A and B acts as a Cottrell pump, propelling a mixture of

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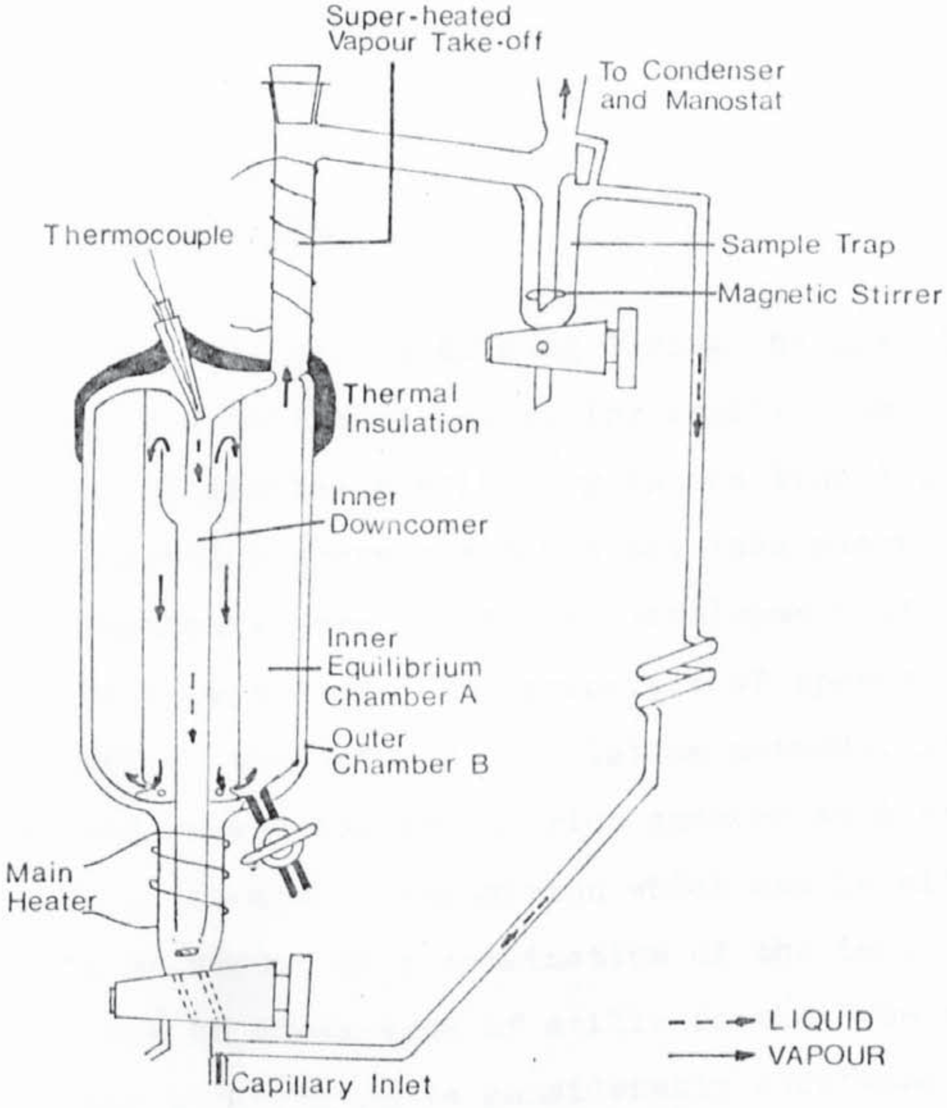


Figure 1

Equilibrium Still of Raal, Code & Best

vapour and liquid onto the jacketed thermocouple while maintaining the inner chamber at the temperature of the boiling liquid.

3.4 Flow methods.

The difficulties arising during the use of circulation stills for measuring equilibrium data in systems of limited miscibility in the liquid phase, and in systems where reactions may take place between the components have led to the development of the dynamic flow method. The principle of operation, in contrast to that of the circulation methods, is that the feed enters the equilibrium chamber as a steady stream of constant composition which can be either liquid or vapour or a combination of the two. A major advantage of these type of stills is that the time taken to reach equilibrium is considerably shortened but good results depend to a very large extent on the proper functioning and control of the feed equipment for the superheated vapour and preheated liquid.

The first modern still employing this method was due to Colburn (C12). The feed consisted entirely of vapour of given composition prepared by mixing the vapours of the individual pure constituents which are vapourised in separate boiling vessels. In contrast the flow still proposed by Cathala (C3) (C4) employed two separate feeds. One is the superheated vapour, the second is preheated liquid. The superheated vapour is fed from below to the mixing chamber which contains two sintered glass discs to promote good mixing between the two phases. The preheated liquid feed enters between the two plates and the combined vapour/liquid mixture passes up into the equilibrium chamber where it impinges on to a thermometer well. The suitability of this still for reactive and heat sensitive mixtures arises from the low residence time in the reboiler. Mamers (M4) modified the original still for his work on the acetic acid-acetic anhydride-water system, Davies, Jenkins and Jeffreys (D3) also used this version for their work on the quaternary system ethanol-n-butanol-n-butyl acetate-ethyl acetate.

Vilim, Hala, Pick and Fried (V7) have described a simpler still based on the same principle. In their version the feed is partially vapourised in a heated tube and the liquid vapour mixture impinges on to a thermometer well. The vapour and liquid are then separated, condensed, cooled and analysed.

Though flow stills have the disadvantage of requiring large amounts of feed the rapidity with which data may be acquired makes their use attractive even for non-reactive systems.

3.5 Static methods.

In this method the solution is charged into a closed and evacuated vessel, which is placed into a constant temperature bath. The vessel with its contents is agitated until equilibrium between the phases is reached. The pressure is measured and samples of the liquid and vapour phases withdrawn and analysed. Although simple in principle the method is often quite difficult in practice, requiring careful degassing of the components. Also removing the gas sample for analysis can cause great difficulties. Gas chromatography is normally used since the vapour phase sample must be kept small.

Wichterle and Hala (W3) have developed a method based on this principle using small quantities and having a very small vapour sample which although rapid in operation does not yield results of comparable accuracy to the classical methods. Wichterle and Boublikova (W2) later produced a rapid technique suitable for the direct measurement of the dependence of partial pressures on concentration. This was achieved by not waiting for equilibrium to be reached between the two phases since the ratio of concentrations of the two components in the gaseous phase is invariant with time.

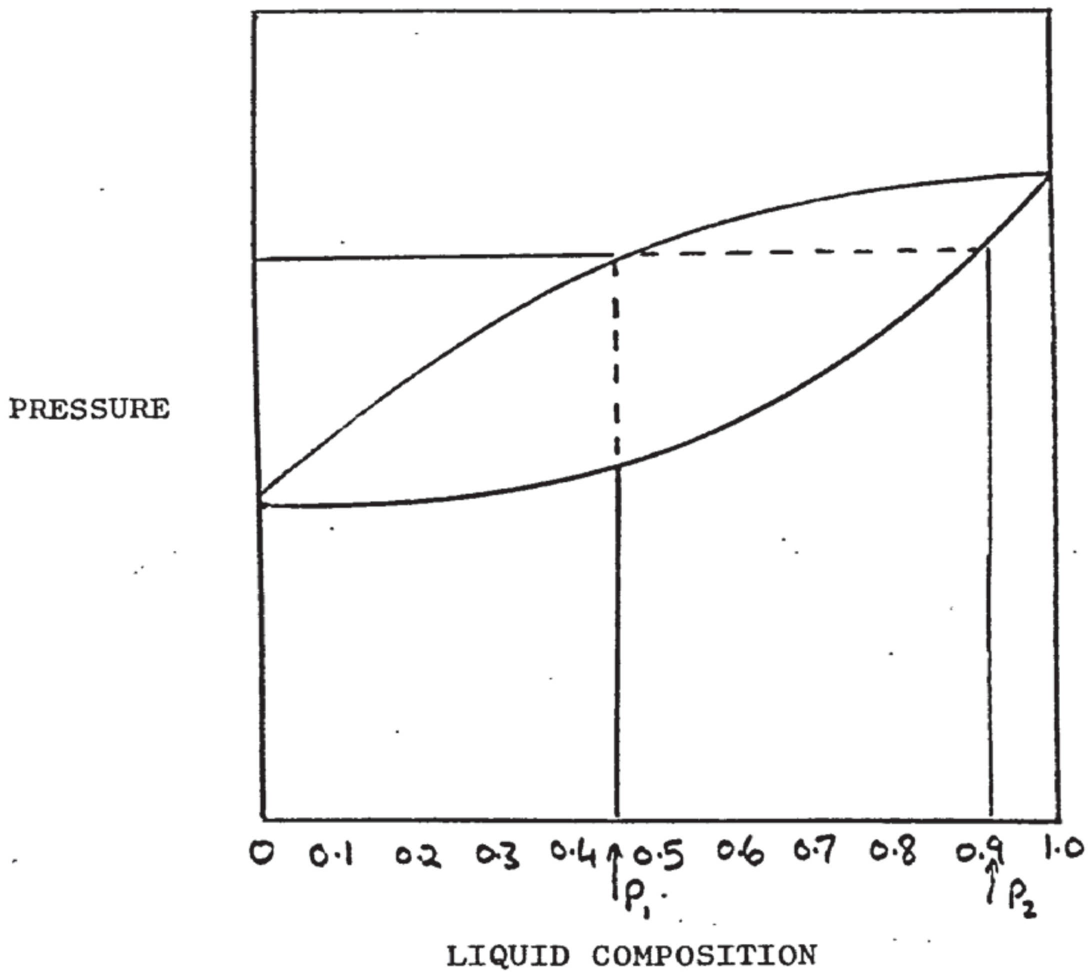
This implies that the rates of vaporisation of components (which do not differ sizeably) are approximately equal, a fact which has been verified experimentally. Difficulties arise with this method however, especially in eradicating condensation in the sampling circuit which is at the same temperature as the equilibrium cell.

Maffido and Vidal (M2) have improved this technique by reducing the risk of condensation, as long as the equilibrium temperature at which equilibrium is achieved is lower than the ambient temperature.

3.6 Other methods.

The dew point and bubble point technique is an indirect static method. The dew point is the condition whereat a small amount of liquid is in equilibrium with the vapour while at the bubble point an infinitely small amount of vapour is in equilibrium with the liquid. If the dew point and bubble point curves can be constructed as shown in fig. 2 then lines drawn at constant pressure P will cut them and the intersections will give the composition of liquid and vapour in equilibrium at P.

FIG. 2 DEW POINT AND BUBBLE POINT CURVES



Kojima et al (K8) designed a novel apparatus in which however, it was necessary to analyse the sample. It was also difficult to measure the dew point at the precise composition desired and the bubble points needed determination by separate methods.

Ebulliometers to measure isobaric bubble points have been proposed by several workers (M7) (C13) (S19) but dew points must be determined separately.

To enable measurement of isobaric dew and bubble points Kato, Konishi and Hirata (K2) initially proposed a flow type apparatus. This has proved difficult to operate at the accurate composition desired and this led them to design the new apparatus shown in fig 3. The principal components are a dew point still, D, a bubble point still, B, and a feeder F. The vapour from D does not return to that still but enters after condensation. The internal construction of both stills is almost similar to that of the flow type of ebulliometer. The boiling vapour-liquid mixture rises through the Cottrell lift and flushes to the thermometer well and the liquid flows from B to D through the connecting capillary tube C. The procedure of operation is as follows. A prepared solution is charged from

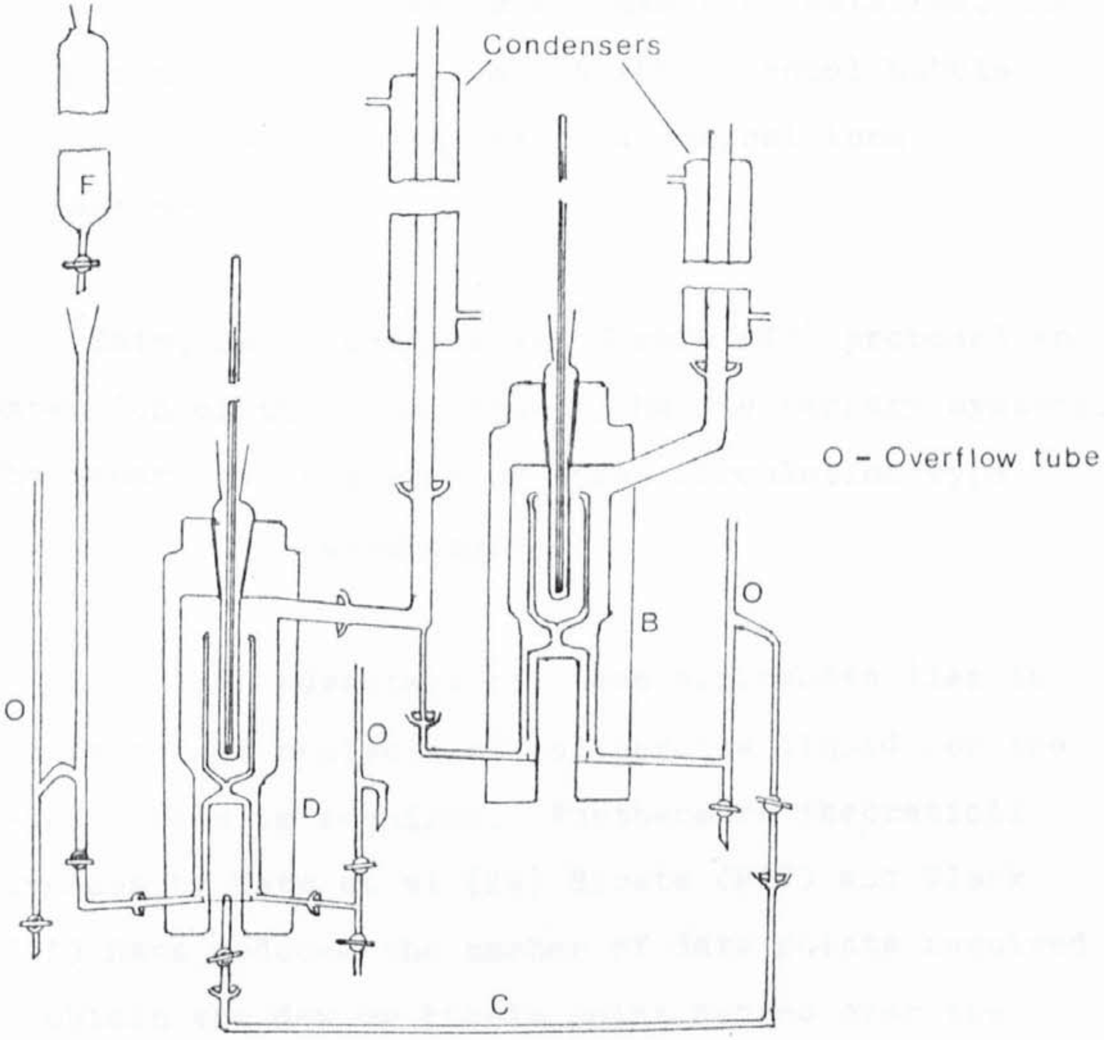


Figure 3
Apparatus of Kato, Konishi & Hirata

feeder F, and the liquid is boiled in the dew point still D, and the bubble point still, B. It can be shown that, when steady state has been attained, the temperature in stills B and D should equal bubble point and dew point at the feed compositions respectively.

Kato, Sato, Konishi and Hirata (K3) proposed an extension of this technique to handle ternary systems. The apparatus consisted of three circulation type stills for the measurements.

The main advantage of these approaches lies in the fact that analysis of neither the liquid nor the vapour phase is required. Furthermore theoretical advances by Kato et al (K4) Hirata (H12) and Clark (C11) have reduced the number of data points required to obtain the dew or bubble point curves over the whole composition range to four.

An approach useful at very low concentrations of one component has been described by Dalager (D1). This method is based on the use of radioactive traces as the component in low concentration is added partly in an isotopic form. He used a modified Thornton (T10) equilibrium still and determined data for the systems methanol-water and ethanol-water.

3.7 Total pressure methods.

The disadvantage of the earlier methods described has led to the increasing popularity of total pressure techniques. These normally involve the direct determination in a static cell of the temperature, total pressure and composition of the liquid phase, while the vapour phase is determined by calculation. Mackay and Salvador (M1) have made a comparison of the accuracy of vapour-liquid equilibrium data obtained from vapour compositions, measured directly and computed from vapour pressure data. They assumed standard errors in x, y, P and T measurements and compared the inaccuracies with the computed y method.

They concluded that in general computed vapour compositions are more accurate than measured ones except in azeotropic regions.

Methods for computing vapour compositions will be discussed later but experimentally two forms of apparatus have been used. One is a static method using a form of isoteniscope while the other is a circulation still technique using an ebulliometer.

In the first case Holtzlander and Riggle (H17) and Rose and Williams (R15) both used a modified form of the Smith-Menzies isoteniscope. The liquid phase compositions were determined by chemical analysis. Ljúnglin and Van Ness (L12) employed a glass cell which was almost completely filled with liquid. The pressure was measured by means of a minature transducer which allowed the cell to be light and portable. The liquid composition was determined by successive weighings. The composition of the liquid was not significantly affected by vapourisation as the vapour phase was small. In this way analysis of the phases was avoided.

Hermsen and Prausnitz (H8) used the apparatus shown in fig. 4. This consisted of two identical isoteniscope assemblies each consisting of a metallic vapour pressure cell, sampling bulb and null manometer. The composition of the liquid phase was determined by withdrawing samples with a hypodermic syringe and analysing by refractive index measurement. This method has also been employed by Jose, Phillipe and Clechet (J10) who modified the equipment to enable the temperature to be controlled to within 0.001°C and improved the degassing procedure.

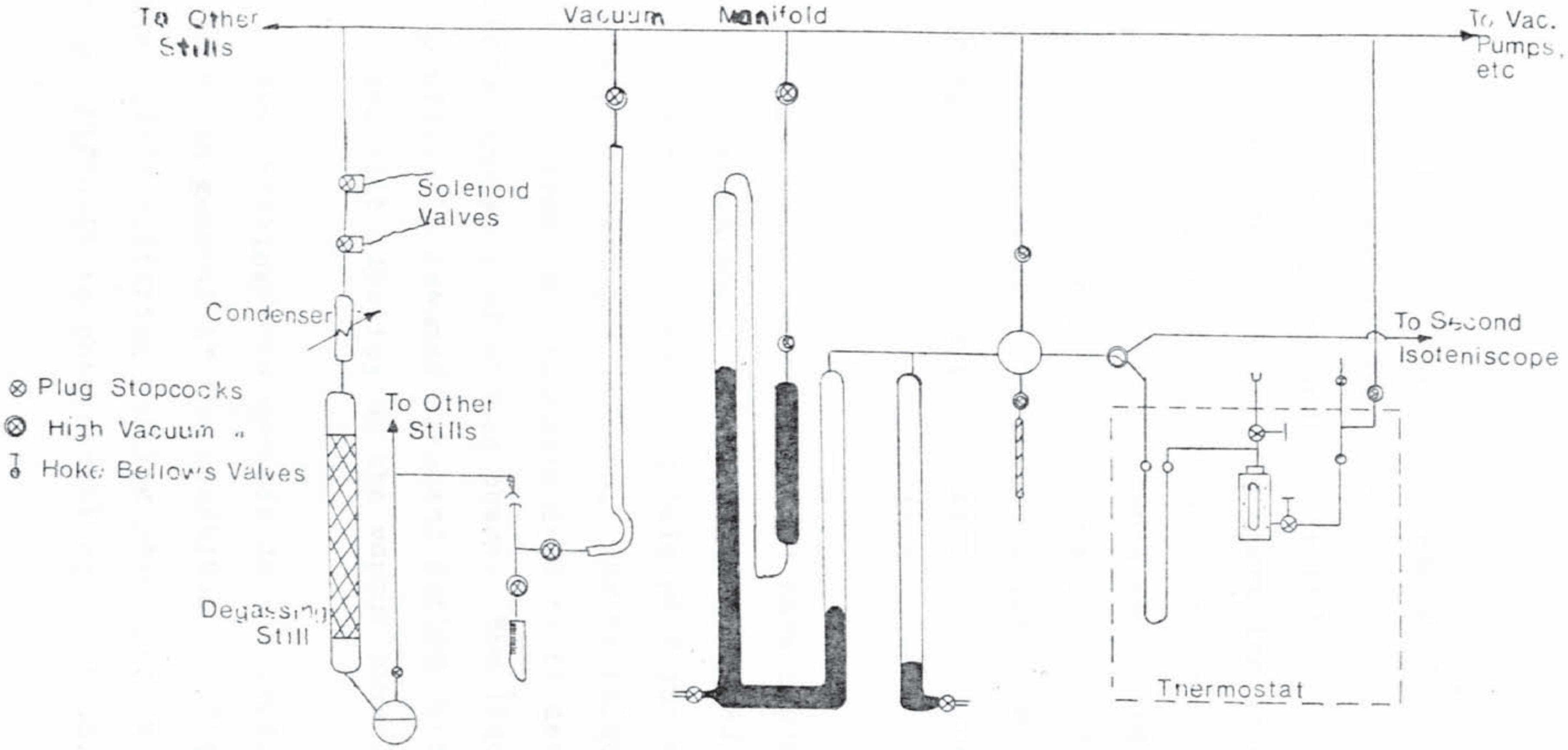


Figure 4
Total Pressure Apparatus of Hermsen & Prausnitz

The ebulliometric method was initially developed by Swietoslawski (S18). Versions of this method have been used by Redlich and Kister (R7) and Prengle and Palm (P9). The principle of operation is effectively that of the circulating still where the condensed vapour is returned to the liquid phase and where the main concern is the precise measurement of the boiling point of the liquid. The vapour pressure is measured by comparison with a pure component boiling at the same temperature in an identical unit.

Jakubrowsky and Norman (J1) have described a total pressure still based on the modified Swietoslawski ebulliometer of Prengle and Palm with the condensate hold-up reduced to a minimum. The technique enables both isothermal and isobaric data to be determined without analysis of either phase. The liquid composition is assumed constant during operation together with ideality of the vapour phase.

The ebulliometric methods do not produce reliable results in general if the constituents of the mixture have widely differing boiling points, probably because it is difficult to obtain real equilibrium.

Gibbs and Van Ness (G4) have described a novel apparatus based on the principles of the static method. The layout of the apparatus is shown in fig. 5. Liquid solutions of known composition are prepared in a test cell by volumetric metering of degassed liquids from accurate piston injectors. The test cell is immersed in a constant temperature bath and the pressure in the cell determined by a Bourdon gauge when equilibrium has been reached. Using this apparatus it is possible to obtain isothermal data over the whole composition range in one day. The vapour phase composition is deduced from solution of the coexistence equation as described by Van Ness (V5).

Jenkins and Smith (S11) (J11) have developed a similar method. An equilibrium cell of approximately 100 mls capacity is constructed so that a known quantity of A is introduced into it with B being added in successive amounts. The cell is of known volume and the volume of the liquid phase is accurately measured after each addition. The cell is immersed in a constant temperature water bath controlled to 0.001°C, the temperature measurements being made by a platinum resistance thermometer. After allowing the cell to come to equilibrium the pressure is measured and the addition of components continued. High precision pressure

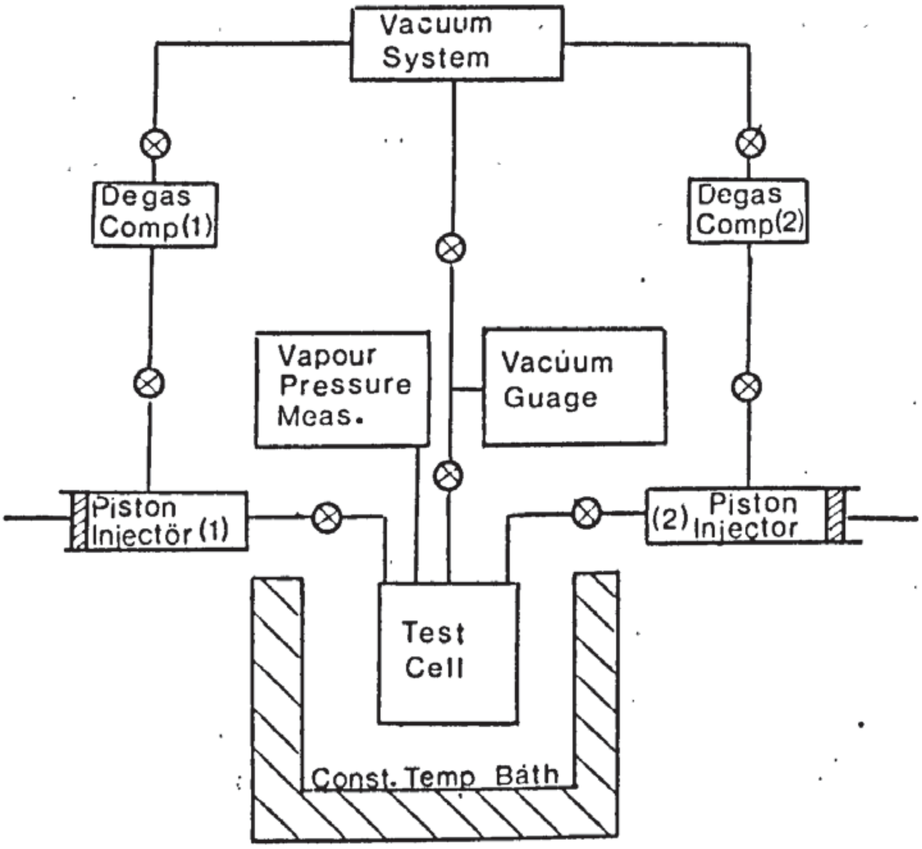
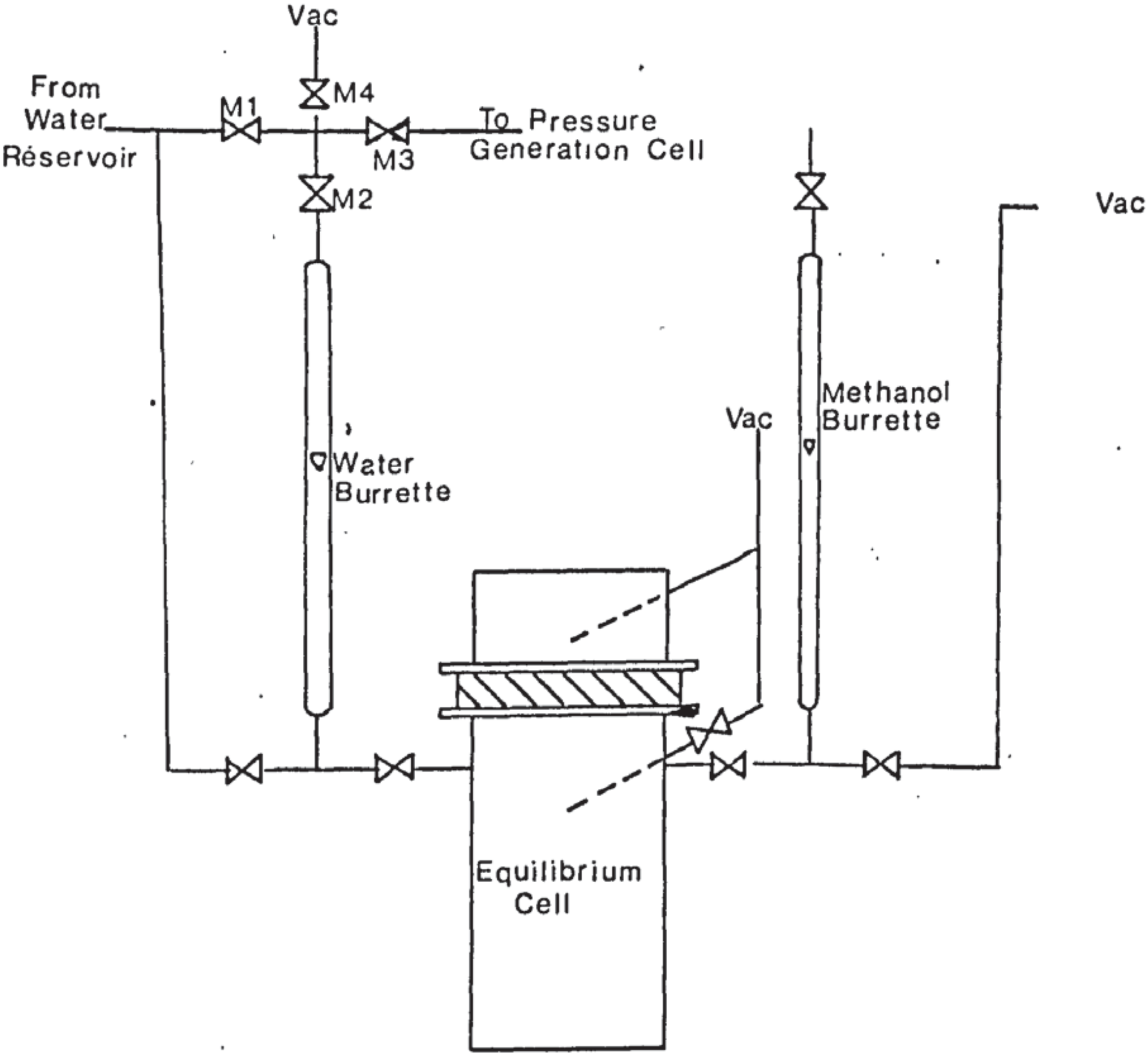


Figure 5
Schematic Diagram of Equipment of Gibbs & Van Ness

measurement and control are required. This has led to the construction of two alternative rigs. The main method achieves the required pressure measurement and control by means of a metallic diaphragm whose position is detected by a transducer. The diaphragm is positioned across the top of the equilibrium cell giving a definite volume to the cell. The diaphragm and transducer are used as null detectors, a high precision bourdon gauge measuring an equalising pressure supplied to the top of the diaphragm. The voltage output from the transducer, zero at rest is used to drive a pressure control system. The layout of this system is shown in fig. 6.

The second approach is illustrated in fig. 7. The equilibrium cell, A, and water burette are arranged to function as a U-tube manometer. A reference bulb, C, containing pure water at the same temperature as the equilibrium cell is connected to the burette in order that the pressure above the burette water is accurately known. The cell pressure is this vapour pressure plus the head difference reflected by the two levels in the burette and cell. The connection between the cell and burette is a fine capilliary tube, preventing back mixing or diffusion of the cell mixture into the burette.



NOT TO SCALE

Figure 6

TOTAL PRESSURE APPARATUS OF JENKINS AND SMITH

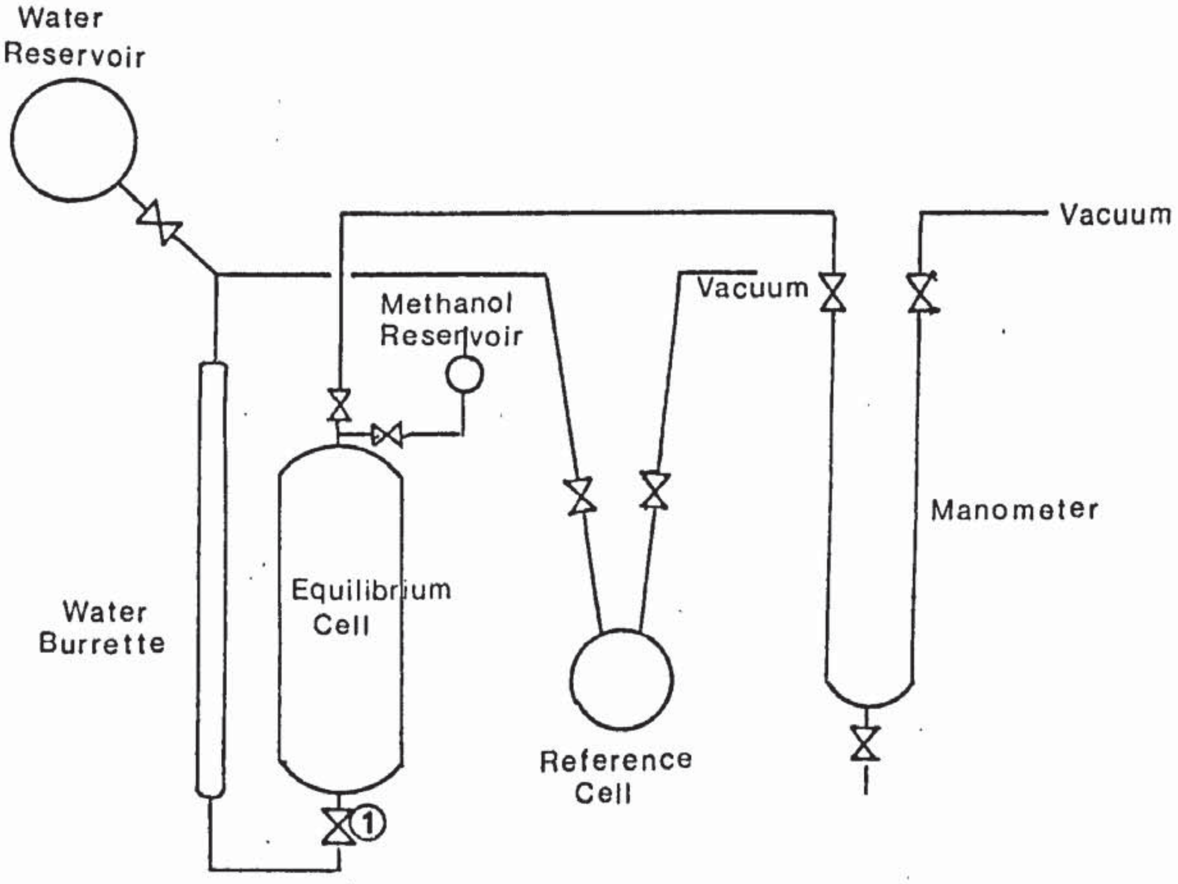


Figure 7

SIMPLE APPARATUS OF JENKINS AND SMITH

A disadvantage of this approach is that the composition of the more volatile component is limited to a very small value and to a limited range. This is because the cell mixture pressure must be less than the small pressure head developed by the burette water otherwise a reverse flow will occur between the cell and burette. A further drawback is that the more volatile component must always be charged to the cell first.

Janaszewski, Oracz and Warycha (J3) have described a total pressure apparatus based on the static method and capable of operating over the range of 25^{o}-50^{o} to an accuracy of 0.003^{o}C. The vapour pressure range is from 10 torr to 600 torr with a precision of 0.2% while the size of the required sample is 2.5 ml. Equilibrium is established by agitation. The equilibrium cell is connected to a mercury manometer. The sample is degassed by connecting the apparatus to a vacuum line through a system of porous plugs. The sample is repeatedly degassed and the pressure read. The pressure corresponding to the sample composition is obtained by extrapolating the series of pressure readings.

Olbroniski (O1) has described the use of absorption to measure compositions in conjunction with the ebulliometric method of Swietoslawski. It is claimed that this enables the composition of the coexisting phases to be rapidly determined and the approach to equilibrium to be monitored.

There have been a number of approaches proposed in the literature for computing compositions from liquid phase compositions, temperature and pressure measurements. They fall into two categories.

Firstly, the direct method involves calculation of vapour compositions by integration of the coexistence equation. This is a first order differential equation derived from the Gibbs-Duhem relationship which relates the composition of the liquid and vapour phases at equilibrium. Another approach is by the stepwise integration procedure of Ho, Boshko and Lu (H14) which is not suitable for systems containing an azeotrope. A detailed review of direct methods has been given by Hala et al (H2).

Recently Nagata and Ohta (N2) reported a procedure using Forsyth orthognal polynomials to correlate the total pressure data in terms of the liquid phase composition. An accurate fit for the highly non-ideal system ethanol-chloroform was obtained. The polynomials however are extremely sensitive to any experimental error which limits the utility of the method for obtaining vapour compositions.

Other methods include the spline-fit technique of Klaus and Van Ness (K6) in which successive cubic equations are fitted to pairs of data points across the composition range subject to constraints that avoid extraneous points of inflection caused by uneveness in the pressure-composition curve, due to random error. Vapour compositions are then calculated directly.

Christianson and Fredenslund (C8) have described a similar method using orthogonal polynomials in their work with high pressure vapour-liquid equilibria.

The alternative approach is known as the indirect method and involves firstly the calculation by some appropriate means of the liquid phase activity coefficients and subsequent calculation of vapour compositions. These methods normally assume a solution to the Gibbs-Duhem equation and involve the adjustment of parameters until the pressure-liquid composition behaviour is reproduced as nearly as possible. These methods avoid numerical integration but the accuracy is dependent upon the analytical form used to express the relationship between the activity coefficient and composition of the liquid phase.

Early indirect procedures such as those of Levy (L3), Carlson and Colburn (C2), Christian (C7), Redlich, Kister and Turnquist (R8), and Prengle and Palm (P9) have been reviewed by Hala et al (H2).

The most commonly used indirect method is due to Barker (B3) who starts from the assumption that the excess free energy can be represented as a polynomial function of composition.

$$\begin{aligned} G^E &= x_1 \mu_1^E + x_2 \mu_2^E \\ &= RT\, x_1 x_2 \left(A + B\,(x_1 - x_2) + C\,(x_1 - x_2)^2 + \ldots\right) \end{aligned} \tag{3.1}$$

This is equivalent to assuming that the Margules equations relate the activity coefficients to composition. The constants A, B and C are adjusted until the total pressure vs composition relationship is reproduced. Having obtained this fit the vapour phase can be calculated directly if ideality is assumed. If not, an iterative procedure must be adopted in which as the new vapour phase composition is calculated it is used to calculate corrections for non-ideality and the cycle repeated. Convergence is rapid with this method.

Diaz Pena (D7) has shown that methods using a function similar to Barkers for G^E do not, in general hold for complex systems involving dipole moments and hydrogen bonding and has suggested that an equation of the form originally proposed by Van Ness

$$G^E = \frac{x_1 x_2}{\sum_{j=1} B_j (x_1 - x_2)^{j-1}} \qquad (3.2)$$

should be used.

The necessity of assuming a functional form for the excess free energy has been overcome by Tao(T1.) Tao's indirect procedure involves calculation of the activity coefficients by integration of an equation resembling the coexistence equation. The procedure although indirect retains the rigour associated with the direct method. A disadvantage of his approach is that it applies only to binary systems.

Mixon, Gumowski and Carpenter (M20) proposed a technique retaining the same degree of rigour as Tao's but able to be generalised to ternary and higher order systems. This involved expressing an equation for the solution vapour pressure in terms of the excess free energy and its composition derivatives. The expression is inverted to give the g^E function that reproduces the observed vapour pressure behaviour and activity coefficients are then deduced from the excess free energy function.

Christiansen and Fredenslund (C8) used a numerical method for solving differential equations, the orthogonal collocation method, to calculate the value of the excess Gibbs free energy at chosen values of liquid composition. From these values, the equilibrium vapour mole fractions corresponding to each experimental liquid mole fraction are calculated. They applied this technique to high pressure systems.

Ramahlo and Delmas (R3) (R2) reported an indirect method employing the 2 constant Redlich-Kister expansion and an iterative procedure to obtain the constants. Although their method was shown to be superior to that of Prengle and Palm convergence was not always obtained and the results sometimes physically meaningless. This may be because of the limitations of the two constant Redlich-Kister expansions. Minh and Ruel (M19) suggested its replacement with an expression involving three constants but it is doubtful whether this gave any real improvement.

Davidson and Smith (D2) have presented a method which does require a thermodynamically consistent polynomial. This may be of advantage in highly non-ideal systems.

Ba Tai, Ramahlo and Kaliaguine (B1) describe a technique incorporating the Wilson equation for predicting isothermal data for binary and ternary systems and for heats of mixing for ternary systems from binary data. This approach was reasonably successful and did not require that the energy parameters be independent of temperature.

Jambon and Clechet (J2) have compared the indirect and direct methods and demonstrated the superior fit accorded by the direct method. They have shown the difficulties that can arise from using an unsuitable activity coefficient relationship. This last fact has inhibited the use of the Barker method although it is a comparatively simple approach. Although there have been many models that have been proposed none seem to be clearly better than the others.

Orye and Prausnitz (02) Sabylin and Aristovich (S1) and Holmes and Van Winkle (H16) compared the Wilson and Van Laar equations and showed the Wilson equation to be superior to the Van Laar equation for many binary and multicomponent mixtures. Neretnieks (N4) also showed the Wilson equation to be superior to the modified Van Laar equation.

Renon and Prausnitz compared the NRTL, Wilson and Heil equations for 12 ternary systems. For moderately non ideal systems all equations gave similar results. They also extended the comparison of the NRTL equation to the 4 suffix Margules equation and were able to demonstrate the superiority of the NRTL equation in this case. Hudson and Van Winkle (H19) tested the Wilson equation on one quinary, three quarternary and 20 ternary systems. Although good results were obtained comparisons were not made with other equations.

Mertl (M18) also showed the NRTL equation to be superior to the 4 suffix Margules equation for 41 ternary and 144 binary systems.

Larson and Tassios (L1) compared the 3 and 4 suffix Margules equations, the Wilson equation and 2 and 3 parameter NRTL equations. They found the 3 and 4 suffix Margules equations appeared to give equal results. The NRTL equation describes non ideal systems better than the Margules, but it is somewhat inferior to the Wilson equation. However for nearly ideal systems the NRTL equation is not as good as the Margules equation. Furthermore they suggested that the best form of the NRTL equation was the two constant version.

Nagata (N1) has predicted data for a large number of systems and concluded that the Wilson model shows better overall performance than the other equations.

McCann (M12) has tested the Wilson, NRTL, Orye, Enthalpic Wilson and modified Orye equation on a wide range of systems. Unfortunately different equations appeared best for each of the various types of systems involved so that no clear cut recommendation for a particular model emerged from his work.

Abrams and Prausnitz (A2) have shown the UNIQUAC equation to be comparable to the NRTL equation and the Wilson equation for vapour equilibrium work.

Because of the large variety of types of system that may be encountered during work on vapour liquid equilibrium and the fact that, as has been shown no single model can adequately represent the various types, the Barker method has not been exploited as a general method for the reduction of P-x data in spite of its attractions. Van Ness and Abbot (A1) have shown however that the five suffix Margules equation and a modified Margules equation can in fact handle a very wide range of systems overcoming the previously discussed disadvantage of the Barker method.

Many of these models have been incorporated in a computer programme JF4LSQMKA which reduces binary vapour-liquid equilibrium data by the Barker method.

Another advantage of the Barker method is that it does not use vapour compositions allowing consistency testing to be carried out on the experimental data as described in the next chapter.

4. THERMODYNAMIC CONSISTENCY.

The classic method of determining vapour-liquid equilibrium data has been to measure the temperature and the pressure of the system and the compositions of the co-existing liquid and vapour phases. The fact that this represents an over-determination of equilibrium has long been recognised and that hence the redundancy in the data set may be utilised to test the internal consistency of the data. However difficulties of interpretation of the test results has led to the proposal of a large number and variety of types of test in the literature each with particular advantages.

All tests however depend on utilising the Gibbs-Duhem relationship in some way or another. This is normally stated as :

$$\sum_{i=1}^{N} n_i \, d\mu_i = V \, dP - S \, dT \qquad (4.1)$$

An expanded form of this equation for the liquid phase as used by Ljunglin and Van Ness (80) is :

$$\sum_{i=1}^{N} x_i \, d \ln f_i + ((H-H^*)/RT^2) \, dT - (V/RT) \, dp = 0. \qquad (4.2)$$

from which they deduced the general co-existence equation for binary systems, viz :

$$AdP + BdT = (y_1-x_1) \, d \ln (V_{1v}/V_{2v}) + ((y_{i} - x_1)/y_1y_2) \, dy_1 \qquad (4.3a)$$

$$\text{where } A = (\Delta V_v + x_1 \, Y_{1v} + x_{2v} - V_1)/RT \qquad (4.3b)$$

$$B = -(\Delta H_v + x_1 \, H_{1v} + x_2 \, H_{2v} - H_1)/RT^2 \qquad (4.3c)$$

so called because it relates the liquid and vapour phases that co-exist at equilibrium.

These equations are the basis for the consistency tests considered. There has been another equation proposed by Tao (T5) (T6) (T4) and by Lee and Edmister (L2) involving fugacities and phase enthalpy differences. However uncertainties in calculating derivatives required in this equation renders this test of doubtful value and it is not considered further.

The tests so far proposed may be divided into four types as follows :

a) Area tests.
b) Slope tests.
c) Statistical tests.
d) Barker type tests.

These will now be considered in more detail.

4.1 Area Tests.

These tests appear to be the most popular and widely used in the literature. They are based on an integral form of the Gibbs-Duhem relationship and Herrington (H6) and Redlich and Kister (R5) have independently presented one in the form :

$$\int_0^1 \ln \frac{V_1}{V_2} \, dx_1 = 0 \qquad (4.4)$$

Its application depends on the fact that the curve of $\ln V_1/V_2$ vs x_1 crosses the $\ln V_1/V_2 = 0$ line and for perfectly consistent data the areas above and below this line should be equal. The deviation from equality is then used as a measure of consistency. The obvious disadvantage of this method is that errors in ln V_1/V_2 above and below the line tend to cancel out. Bonne (B14), Van Ness (V3) and Techo (T9) have criticised this test on the grounds that data are required over the whole range of composition for implementation, compensating errors are not detected and that for binary data temperature and pressure cannot be held constant while varying composition. Herrington (H7) has considered the latter problem and has developed criteria for deciding whether the data are consistent or not without the need for evaluating the heat of mixing term. The area test has been the subject of further discussion. In particular Broughton and Brearly (B15) assumed that the product RT ln Vi was independent of temperature and that the heat of mixing term could be neglected by integrating this product for isobaric data but Van Ness (V3) among others has disputed this. Black (B10) and Black, Derr and Papadopoulos (B11) in a discussion of liquid phase models and consistency tests have demonstrated that the area test is insensitive to errors in total pressure measurement and temperature. This is because in the ratios of the activity coefficients V_1/V_2 the total pressure cancels out and temperature errors appear as a ratio through vapour pressures. Because of this Byer and Van Ness (B21) have pointed out that the test will be sensitive to scatter in the x-y data but will show nothing about the internal consistency of such data. Black (B10) has proposed that a smooth plot of $\sqrt{\ln V_1}$ vs $\sqrt{\ln V_2}$ would indicate accurate temperature and pressure measurements with the simultaneous satisfaction of the area test showing consistency.

Further developments of the area test used small integration intervals and are essentially point by point comparisons. They have been applied to both binary and multicomponent systems. For the latter the Gibbs-Duhem equation may be restated as :

$$\sum_{i=1}^{N} x_i d\ln V_1 + (\Delta Hm/RT^2)\, dT - (\Delta Vm/RT)\, dP = 0 \qquad (4.5)$$

which in turn may be integrated by parts to give :

$$Q(b)-Q(a) - \sum_{i=1}^{N} \int_a^b \ln V_i \, dx_i + \int_{Tb}^{Ta} (\Delta H/RT^2)\, dT - \int_{Pb}^{Pa} (\Delta V/RT)\, dP = 0 \qquad (4.6)$$

However to evaluate the integrals in this equation some path has to be chosen. Herington (H5) (H7) used integration along a path where the ratio of two mole fractions was a constant. He assumed in this case that the heat and volume of mixing terms were negligble. This assumption was also made by Krishnamurty and Rao (K11) who proposed integration with one mole fraction constant. Li and Lu (L4) chose to use short linear paths such that T and P were approximately constant while Prausnitz and Snider (P8) described a general method for multicomponent systems involving holding x_i/x_1 constant for i = 2,3 .... N-1. Mc Dermott and Ellis (M13) modified the method of Li and Lu by using the trapezoidal rule to compare points by pairs. All these methods however suffer from the defect that no criteria have been presented for relating the deviation of eqn. (4.6) from zero to the quality of the data. This is a serious ommission since even if data contains only random error the value of equation (4.6) is unlikely to be zero. Another approach is to rearrange the area test as shown in equation (4.7) :

$$\ln V_2 = - \int_{\ln V1a}^{\ln V1b} \left(\frac{x_1}{x_2} \right) d \ln V_1 \qquad (4.7)$$

This can be used as a consistency test if the $\ln V_2$ data are known. Unfortunately the error in $\ln V_1$ data at low concentrations of x_1 is carried through the whole composition range and cannot be used to give a true point by point comparison at each of the $\ln V_2$ data points.

Tao (T2) (T3) has considered the problem of propagation of error from low x_1 and has proposed using a combination of a slope test, to be discussed in the next section and an integral test. An important feature of his proposals is the inclusion of an analysis of the effect of random experimental error. Tao defined the quantities Q and Z as follows :

$$Q = \sum x_i \ln V_i \qquad (4.8)$$

$$Z = A(x_1) + B(x_1) + \sum K_i \ln V_i \qquad (4.9)$$

where $A(x_1) = -\dfrac{(\Delta H)}{RT^2}\dfrac{dT}{dx_1}$ and $B(x_1) = \dfrac{(\Delta V)}{RT}\dfrac{dP}{dx_1}$

and K_i is the finite difference approximation to the slope :

$$\text{i.e.} \quad K_i = \frac{dx_i}{dx_1} = \frac{(x_{ia} - x_{ib})}{(x_{1a} - x_{1b})} \qquad (4.10)$$

Since Z and Q can be calculated from experimental data and are related as :

$$Z = \frac{dQ}{dx_1} \text{ and } \quad Q(x_{1b}) - Q(x_{1a}) = \int_{x_{1a}}^{x_{1b}} Z dx_1 \qquad (4.11)$$

it is possible to obtain two sets of Z and Q values. The difference in the two sets then constitutes the consistency test. Tao then defined error bounds in the form :

$$\frac{E(V_i)}{V_i} \quad \frac{E(P)}{P} \qquad \frac{E(T)}{P_{si}} \quad \frac{dp_{si}}{dT} \qquad \frac{1}{y_i} \quad \frac{1}{x_i} E(x_1) \qquad (4.12a)$$

$$E(Q) = \sum (x_i \frac{E(V_i)}{V_i} - E(x) \ln V_i) \qquad (4.12b)$$

$$E(Z) = \sum K_i \frac{E(V_i)}{V_i} \qquad (4.12c)$$

where for example ± E(Z) represents the maximum error in Z. Provided the Q and Z differences fall within the error bounds defined by (4.12a, b) and (4.12c) the data can be considered consistent.

Stevenson and Sater (S12) have suggested the direct application of equation (4.6) but proposed that it should be set equal to a function $f(x_1)$ instead of zero. The deviation of $f(x_1)$ should then give an indication of the inaccuracy of the data. They pointed out the advantage of a point by point test in that it can reveal local inconsistency and demonstrated that summing the $f(x_1)$ values from $x_1 = 0$ resulted in much of the sensitivity to local inconsistency being lost.

Chang and Lu (C6) combined Tao and Stevenson and Sater's techniques in developing maximum error bounds for a local area test. They defined an expression similar to that of Stevenson and Sater and generated error bounds D from the total derivative of d defined below, using ± E(x), ± E(P) and E(T) to replace dx_i, dy_i, dP and dT each of which represent the maximum measurement errors in each of the variables x, y, P and T.

$$d = \sum_{1}^{N} (x_{1a} + x_{1b}) (\ln (K_{ib}/K_{ia}) - \ln (\phi ia\ Pa/\phi ib\ Pb) - \int_{P_a}^{P_b} (Vil/RT)dP - \int_{T_a}^{T_b} ((hiv-\bar{H}il)/RT^2)dT \qquad (4.13)$$

where: $K_i = y_i/x_i$

ϕ_i = fugacity coefficient of component i.

V_{il} = partial molar liquid volume of component i.

h_{iv} = ideal gas enthalpy of component i in vapour state.

$\bar{H}_{il}$ = partial molar liquid enthalpy of component i in the soln.

The test then consists of testing the data in pairs by comparing d with the absolute value of D. If it is larger then the experimental point used in calculating d is considered inconsistent. A disadvantage of this procedure is that errors in x and y are not considered separately. The use of maximum measurement errors may also obscure small systematic errors and prevent application of the statistical criteria to be discussed later.

Further discussions of the integral test have been presented by Her~~r~~ington (H6), Deshpande and Lu (D6) and Lu and Jones (L10).

Samuels (S3) has examined the overall area test to determine whether the results of this test may be used to provide a quantitative estimate of the level of error in the set of activity coefficients under investigation. He defined the area defect, Δ , as

$$\Delta = -\int_{x_1 = 0}^{x_1 = 1} \left(\ln \frac{V_1}{V_2} - \frac{\Delta Hm}{RT^2} \frac{dT}{dx_1} + \frac{\Delta Vm}{RT} \frac{dP}{dx_1} \right) dx_1 \qquad (4.14)$$

and has shown that if the activity coefficients ratio V_1/V_2 is multiplied by $1 + \Delta$ then the overall area test can be satisifed exactly. In this way an indication of the average error in the ratio of the activity coefficients can be obtained by examination of the value of Δ although individual errors in the activity coefficients cannot be determined. He has demonstrated using this method that two sets of data which when tested by other criteria appear to be of widely differing accuracy are in fact closely comparable. He goes on to suggest that a decision as to whether the data are consistent within the limits defined by the experimental uncertainties in the measured coefficients or not can be made by considering the scatter in the curve of :

$$\left(\ln \frac{V_1}{V_2} - \left(\frac{\Delta Hm}{RT_2} \right) \left(\frac{dT}{dx_1} \right) \right) \text{ vs } x_1 \qquad (4.15)$$

If the scatter is greater than the value of Δ obtained previously then the data can be accepted as consistent.

In conclusion Redlich, Kister and Turnquist (R8) showed that the overall area test could not distinguish between two sets of data taken by different experimenters even though the data differed significantly, because of the compensating effect noted earlier.

4.2 Slope Tests.

Slope tests in the various forms that have been proposed constitute a much stricter examination for thermodynamic consistency than area tests. As an illustration Prausnitz (P7) has pointed out that if the data set satisfies the slope test at every point then it will also satisfy the area test but the converse is not true.

Early applications of the slope test (B5) utilised the Duhem-Margules in the form :

$$x_1 \frac{d \ln p_1}{dx_1} = x_2 \frac{d \ln p_2}{dx_2} \qquad (4.16)$$

This assumes ΔH and ΔV to be zero and the vapour phase to be an ideal gas. Redlich and Kister (R6) replaced this by :

$$x_1 \frac{d \ln V_1}{dx_1} + x_2 \frac{d \ln V_2}{dx_2} = 0 \qquad (4.17)$$

which removes the ideal vapour phase assumption. The procedure involved is to plot the logs of the activity coefficients, obtained experimentally against x_1 and estimate the slopes graphically. The difficulties inherent in such measurements have precluded the widespread use of these equations but they do provide conditions by which grossly inaccurate data may be identified and these have been summarised by Her~~r~~ington (H7) and Lu (L11) among others.

A similar approach has been discussed by Van Ness (V4), Van Ness and Mrazek (V2) and Prausnitz (P7) which involves plotting Q defined as :

$$Q \quad = \quad \Delta G^E/RT \quad = \sum_{i=1}^{N} x_i \ln V_i \qquad (4.18)$$

against x_1 as abscissa. To obtain the value of $\ln V_1$ at a point a tangent is drawn which is extrapolated to intersect with the ordinate at $x_1 = 1$ at which the required value can be read off. Success of this method is dependent on the curvature of Q against x_1 and the lengths of extrapolation required for small and large x_1. Van Ness and Mrazek (V2) have used a plot of Q/x_1x_2 against x_1. The advantage of this is that the curvature is usually less and the length of extrapolation is shorter. Van Ness has pointed out, however, that random errors must be small to establish a smooth curve and that it is only a positive test in that if the experimental and derived values do not agree then the data can only be rejected as inconsistent.

Techo (T9) has devised a slope test for binary isothermal data with negligible volume of mixing, by writing the excess chemical potential in terms of virial coefficients, B_{ii} :

$$\text{i.e.}\quad RT \ln V_1 = RT \ln (Py_1/p_1x_1) + (B_{11} - V_1)(P - p_1) + B_{12}Py_2^2 \qquad (4.19)$$

with a similar expression for component 2 where V_i are the liquid molar volumes. Partial differentiation and substitution into equation (4.19) gives :

$$\underline{RT} - (B_{11} - \upsilon_1)x_1 + (B_{22} - \upsilon_2)x_2 + B_{12}(y_2^2x_1 - y_1^2x_2)$$

$$\frac{dP}{dy_1} + RT((x_1-y_1)/y_1y_2) + 2B_{12}P(y_1 - x_1) = 0 \qquad (4.20)$$

All the terms in equation (4.20) are experimentally determined except the derivative dP/dy_1, and the virial coefficients. The virial coefficients may be evaluated in a number of ways while in order to calculate the derivative, Techo used orthogonal polynomials to represent P = P(x) and y = y(x). The order of these polynomials is determined by the requirements that the deviation from the null value in equation (4.20) should be a minimum. The test for consistency is then simply an examination of the deviation from zero. Because P and y are fixed at values of x = 0 and 1 the consistency of the data may be checked as near the endpoints as desired which is a significant advantage over slope tests which use the activity coefficients directly. A serious disadvantage of this approach is the possible occurence of extraneous inflection points that occur with higher order polynomials with resulting false indications of consistency or inconsistency. Techo also proposed a maximum limit for accurately measured data in terms of the sums of squares of the deviations obtained from equation (4.20).

The limiting slopes of the P, T, y and V curves with respect to liquid composition have also been the subject of discussion in several papers (G3) (H18) (V5) as regards the correlation, prediction and testing of vapour-liquid equilibrium data.

In conclusion although slope tests provide extremely rigorous tests for thermodynamic consistency practical difficulties in calculating the quantities involved render them of limited value.

4.3 Statistical Tests.

It is possible to distinguish between two types of error associated with experimental measurements. Firstly there is random error owing to small fluctuations in operating equipment and to analytical procedures. Secondly there is systematic error due to equipment malfunction such as faulty pressure measuring equipment. Random error is impossible to eliminate entirely but can usually be accounted for by statistical averaging techniques. Systematic error however cannot be so treated and unless it is small must cause the data set obtained experimentally to be rejected. It is the aim of thermodynamic consistency tests to detect systematic error, but as noted in connection with slope tests random error may render this impossible if it is of the same order as the systematic error. In other words data may be rejected as inconsistent because the random error gives large deviations in the consistency test. It is an important feature of the tests to be described in this section that an attempt has been made to define error bounds due to random error alone and to analyse whether the deviations found in consistency test results are due to any significant systematic error.

As described earlier both Tao (T3) and Chang and Lu (C6) have attempted to define error bounds but these are difficult to interpret.

Ulrichson and Stevenson (U1) have developed a consistency test based on the local area test of Stevenson and Sater (S12) and have described an error analysis to be used in conjunction with it. The local area test may be written as :

$$f(x) = \sum_{i=1}^{N} \int_a^b x_i \, d\ln V_i + \int_a^b (\Delta H/RT^2) dT - \int_a^b (\Delta V/RT) dP \tag{4.21}$$

To evaluate the integral between two points a and b requires a numerical integration technique. Since most integration formulae require several points, each one equally spaced, which is difficult to obtain with experimental data, they used the trapezoidal rule. Equation (4.21) may be rewritten :

$$f(a,b) = \sum_{i=1}^{N} {}^1/_2 \, (x_{ia} + x_{ib}) \ln (V_{ib}/V_{ia}) + \int_a^b (\Delta H/RT^2) \, dT - \int_a^b (\Delta V/RT) \tag{4.22}$$

The use of the trapezoidal rule may lead to significant error for systems in which the activity coefficients are highly unsymmetrical unless a large number of data points are obtained with corresponding small intervals a-b. If this is not so Ulrichson and Stevenson have derived a correction which may be applied to equation (4.22). They have applied the propagation of error formula i.e. :

$$\text{if} \quad \phi = f(z_1, z_2, z_3) \tag{4.23}$$

$$\text{then } S_\phi^2 = \sum \left(\frac{\partial \phi}{\partial z}\right)^2 Sz_i^2 \tag{4.24}$$

where S_ϕ^2 is the variance of the dependent variable ϕ and Sz_i^2 are the variances of the independent variables Z_i to the equation (4.22) to estimate the variance Sf of a series of f(a,b) values in terms of the variances of the experimentally measured values (Sx, Sy, Sp, ST). For a binary application of equation (4.24) to equation (4.22) results in :

$$S_f^2 = Kx^2Sx^2 + Ky^2Sy^2 + Kp^2Sp^2 + K_T^2S_T^2 \tag{4.25}$$

where the K's are a function of composition, temperature and pressure defined as follows :

Thus if the variances of the composition, pressure and temperature measurements are known or can be estimated, the variance of the series of f(a,b) values obtained from the consistency test can be calculated. From this variance, confidence limits may be established for a plot of f(a,b) against x_1.

For example if there is no systematic error in the measured data set to which the test is being applied 68.3% of the f(a,b) values will be smaller in absolute value than the standard deviation of S_f and should be randomly distributed about zero provided the data set is very large and that the distribution of f (a,b) can be described as normal. If the number of data points approaches infinity then exactly half the f (a,b) values should be positive and the other half negative. When a finite number of data points is taken, this is equivalent to taking a finite sample of values from an infinite population. The probability of obtaining a given fraction of these points within a specified confidence limit can be calculated from the binomial expansion. If the percentage of those f (a,b) values which lie within a given confidence limit is denoted by p_f the variance of p_f may be calculated from :

$$S_{pf}^{2} = q\ (100-q)/N \qquad (4.27)$$

where q = 50 for the 50% confidence region and 68.3 for the 68.3% confidence region. Thus 95% confidence limits for pf are given by ± 2S pf or :

$$pf = q \pm 2\sqrt{q(100-q)/N} \qquad (4.28)$$

This may be interpreted as meaning that if there is only random error present there is less than a 1 in 20 chance of selecting a sample of N data points for which pf, calculated from the ratio of f(a,b) values lying within a given confidence limit, q, to the total, is less than q-2Spf or greater than q + 2Spf. If the values of pf calculated from the data set lie outside these limits then three possibilities exist. Firstly this may be the 1 in 20 data set, secondly the variances of the experimentally measured variables are incorrectly estimated, or, that in addition to random error the data set contains systematic error. An inspection of a plot of f(a,b) against x_i will aid in distinguishing between the last two possibilities. If systematic errors are present then provided these are of a sufficient order of magnitude compared with the random error, they will be revealed by non-random trends in the f(a,b) values. If there is only random error present they should be evenly distributed about zero. If there are a sufficient number of f(a,b) values (of the order of 25 or 30) it is possible to apply the chi-square test i.e. :

$$\chi^2 = 4\,(N_+ - N/2)^2/N \qquad (4.29)$$

where N_+ is the number of positive values of f(a,b). The probability is less than 1 in 20 of obtaining a chi-square greater than 3.84 so for any values larger than that the possibilities of systematic error should be investigated. If the estimated variances are incorrect then the f(a,b) values should appear randomly scattered but lie significantly outside the confidence limits. The estimates must then be increased until the correct proportion of f(a,b) values lies within a given confidence limit. If it is suspected that the data set constitutes the 1 in 20 case then the investigator has little option but to determine more data points.

The variances of the experimentally measured variables may be used to establish confidence limits for the activity coefficients. Recalling that, for the ideal vapour phase case :

$$V_i = \frac{y_i P}{x_i\, P_{si}} \qquad (2.41)$$

and applying the propagation of error formula (4.24) to (2.41) gives :

$$\frac{S_{Vi}^{2}}{Vi^{2}} = \frac{S_{xi}^{2}}{xi^{2}} + \frac{S_{yi}^{2}}{yi^{2}} + \frac{S_{p}^{2}}{p^{2}} + \left(\frac{d \ln P_{si}}{dT}\right)^{2} S_{T}^{2} \tag{4.28}$$

The results in the preceding sections however all require a normal distribution of f(a,b) values. The quantity f(a,b) is calculated however from products, ratios and logarithms of the variables containing random error i.e. x, y, P and T. To check this assumption Ulrichson and Stevenson simulated V.L.E. data and added normally distributed random error to the variables. This was repeated 200 times. If the f(a,b) values were normally distributed 68.3% of them would lie within ± Sf with a variance given by equation (4.25). Their results indicated that the distribution of f(a,b) is sufficiently near normal for the test procedure to be applied. They used the 3 suffix Margules equation to generate the simulated activity coefficients but repeating the procedure with the Wilson equation gives similar results. Using simulated data Ulrichson and Stevenson were also able to examine the effects of random measurement error in the various variables on the overall results obtained for the consistency test. They were able to demonstrate that the effect of random error on x is significantly less than the effect of error in other variables so that if the measuring techniques for x and y have equal uncertainties the consistency test will be significantly affected only by the uncertainty in y for x values between 0.1 and 0.9. Also it was shown that if the system under investigation contains an azeotrope the consistency test is unaffected by errors in y so that very accurate data may be indicated near the azeotrope when in fact the opposite may be the case. The errors in pressure and temperature appear approximately linear across the composition range and affect the consistency test only if they are quite large. Finally they showed that the consistency test does not necessarily reflect the uncertainty in the activity coefficient. As an example they showed that it is possible to obtain very small values for f(a,b) but the confidence limits obtained for the activity coefficient from equation (4.28) may be very large.

As an extension of the preceding procedure Samuels, Ulrichson and Stevenson (S4) have applied the approach to the overall area test. They have shown that it is possible to obtain the total area defect by summing the values of f(a,b) found from the local area test. Furthermore it is possible to define an expression for the variance of the overall area test by summing the variances of the f(a,b) values, Sf. The advantage of this procedure is that it is possible to detect small systematic errors which may not be picked up by the local area test. However, the local area test is superior in assessing the contribution of individual points to the area defect, and in cases where a few particular points contribute a large fraction of the total area defect it is better suited to assist in deciding whether those points can be ignored. They conclude that a combination of the two is the most valuable procedure.

Renon (R10)has noted that the true value of each measured variable is unknown. Only the mean value of the variable is known with at most the standard deviation obtained from reproducibility tests. The random errors present in each measurement generate random error in the residuals formed by the difference between the measured and calculated variable. The principle of maximum likelihood maximises the probability of the residuals of the measured quantities being equal to the experimental error.

Renon makes the following assumptions :

1) Errors in each measured quantity are independent in different experiments.

2) The statistical distribution of the error in each variable is normal.

This maximum probability occurs when the parameters in the datafit minimize the quadratic form, S given by :

$$S = \sum_{1}^{N} \bar{r}_i^{\,t} \; \overline{\text{VAR}}^{\,-1} \left(\bar{r}_i \right) \bar{r}_i \qquad (4.29)$$

where $\overline{\text{VAR}}\,(\bar{r}_i)$ is the variance-convariance matrix of residuals vector $\bar{r}_i$. The diagonal terms of this matrix equal the error variance $\sigma^2(r_i)$ in residual r_i which is the mean value of the quantity $(\delta r r_i)^2$ when a large number of measurements are made for the same experiment i.

As noted by Noton (N7) the best method of solution is by Gauss-Newton iteration because linearization of S which leads to solving:

$$\overline{A} \quad \overline{\Delta C} = \overline{B} \qquad (4.30)$$

directly gives the Variance-Covariance matrix of optimal parameters VAR (C). The estimation of the matrix is given by the inversion of A in the last iteration steps :

$$\text{VAR} \ \overline{(C)} = \overline{A}^{-1} \qquad (4.31)$$

The eigenvectors of the matrix give the linear by independent combination of the parameters while the corresponding eigen-values are the variances of these combinations.

The predicted value of each variable is obtained by minimizing d^2 defined by :

$$d^2 = \sum_{i=1}^{4} \frac{(Z_i^{\exp} - Z_i)^2}{V^2(Z_i)} \qquad (4.32)$$

where $V^2 (Z_i)$ is proportional to the variance $\sigma^2 (Z_i)$ of the experimental variable Z_i. Lagrangian multipliers are used to account for the constraints imposed by the equilibrium conditions. The consistency test consists of plotting $Z_i^{exp}-Z_i^{calc}$ against x_i for each variable. If systematic error is present then non-random trends will emerge from the plots. If random error only is present then the points will be evenly distributed about the zero axis but if the standard deviations are very different from the assumed σ's then the assumed experimental errors were incorrect. A disadvantage of this approach is that non-random trends may be caused by an inadequate model rather than any deficiencies in the data.

4.4 Barker type tests.

Van Ness, Byer and Gibbs (B21) have outlined a similar test to that of Renon. After reviewing methods of data reduction and demonstrating that only 3 out of the 4 experimentally measured variables x, y, P and T are needed by any particular method, they proposed that the fourth may be used in a consistency test.

The procedure is to reduce the data by some method and to calculate values of the redundant variable. A residual is formed by taking the difference between the calculated and experimental values of the variable and this is plotted against liquid composition. Inconsistency is then indicated by non-random trends in the plot. If the data is perfectly consistent and contains random error only then the residuals will be scattered randomly about the $\Delta = 0$ axis.

In the same paper they also analyse the effect of random measurement error on the calculated thermodynamic functions and have derived expressions for confidence limits for the various forms of functions used in the data reduction procedure such as $g/x_1 x_2$ or ln V_1/V_2, after the manner of Ulrichson and Stevenson (U1).

Although as discussed in the previous chapter Van Ness used numerical methods such as the spline fit procedure in his early work Abbott and Van Ness (A1) have applied Barker's method to reduction of P-x-T data and utilised y in the consistency test. As described earlier they used various forms of the Margules equation to provide analytical expressions for G^E as a function of composition and a minimization technique was used to fit the calculated pressure to the experimental pressure by adjusting the parameters in the representation equation. A value of y was then calculated and compared with the experimental value as mentioned previously and the residual plotted against x. Non-random trends indicate inconsistency but the possibility also arises that they may also be due to the inability of the representation equation to model the system adequately. However Abbott and Van Ness (A1) have shown that this drawback may be overcome by using an equation with a sufficient number of parameters and demonstrated its effectiveness for the highly non-ideal system, n-pentanol-n-hexane. An additional plot required with the residuals plot is a plot of the residuals of the variables being minimized, (P in the case of a Barker fit) against x to show that the data has been fit to within the limits of experimental error. Van Ness (B21) claims that this test constitutes the purest and most meaningful of all the possible comparison tests available.

Christiansen and Fredenslund (C8) in their work on high pressure vapour liquid equilibrium used a similar approach. They used orthogonal collocation to solve for G^E and hence obtained the activity coefficients.

They went on to calculate vapour compositions and used the difference between y calc and y exptl as a consistency test, using the criterion of Christianson (C9).

If $| y(\text{calc}) - y(\text{exptl}) | \leq \Delta x_i + \Delta y_i$ where Δx_i and Δy_i are the experimental uncertainties in the liquid and vapour compositions, then the data is consistent. If not, either the data is inconsistent or the methods of calculating fugacities, molar volumes or enthalpies are erroneous.

Conclusion.

From the preceding discussion it appears that the most suitable form of consistency test for analysing the performance of the Cathala still as a method of data acquisition would be a conjunction of the Ulrichson and Stevenson test (U1) and the Samuels, Ulrichson and Stevenson (S4) test. For assessing improvements in the model of systems containing acetic acid a Barker fit with the analysis of the residuals was adopted. The last technique was also employed in the analysis of the Cathala still data. Accordingly the first two tests were programmed as programme JF4ERRAN details of which are given in Appendix A1. Also the analysis of residuals test was incorporated in the data fitting programme JF4LSQMKA to be used in conjunction with the various models incorporated therein.

Application of the local area test requires heat and volume of mixing data. Since the experimental work was carried out at low pressures it was assumed that the volume of mixing term may be neglected. This is a common assumption in the literature but the same does not unfortunately apply to the heat of mixing terms. For the systems under consideration there does not appear to be any data in the literature. However, Orye (O3) has shown that the Wilson equation may be used to give a reasonable if rough estimation of the heat or mixing for non-associated solutions. Further details are given in Appendix A1.

5. Vapour Liquid Equilibrium with Association in Both Phases.

5.1 Introduction.

There have been a considerable number of papers reporting experimental determination of systems containing acetic acid as the associating component. The work of Carli et al (C1), Liszi (L7) (L8) (L9), Meehan and Murphy (M17) and Chueh (C10) are typical.

However application of standard consistency tests to the data has led to apparent inconsistency due to the phenomenon of association in both liquid and vapour phases. The early work of Marek (M6) and the classical work of Prigogine and Defay (P10) have presented methods of dealing with association in both phases, but it has been the practice of most workers to ignore liquid phase association and to use the activity coefficients to account for any non-idealities, and to correct only the vapour phase fugacity for association. This is probably because it is possible to make certain simplifying assumptions for the vapour phase which are not justified for the liquid phase. These assumptions allow a straightforward calculation of the necessary correction factors. In particular the association constant for dimerisation in the vapour phase is normally assumed to be independent of composition and to be equal to the value of the association constant for the pure associating substance. In the liquid phase, however, spectroscopic measurements indicate that the association is a function of composition (P10). This taken with the fact that reasonable correlations have been obtained using corrections only for vapour phase association, has led to the general failure to attempt to take liquid phase association into account.

An exception to this has been the work of Garner, Ellis and Pearce (G1) who used variable molecular weights to correlate data for acetic acid -benzene, acetic acid-water and other systems. Bourne (B14) and Herington have also adopted this approach. They found for some systems this procedure gave satisfactory results but not for others. Their approach however was based on the assumption that the degree of association was independent of the concentration of acetic acid in the binary mixture. Liszi (L8) working with the acetic acid-carbon tetrachloride system used dieletric measurements to establish the relative concentrations of acetic acid monomer, dimer and carbon tetrachloride in an isothermal mixture of varying nominal concentrations of acetic acid at 20°C. From this he deduced an expression relating the law of mass action equilibrium constant, k, to the nominal concentration of carbon tetrachloride in the solution. He then utilised this expression to predict vapour composition and the total pressure of the acetic acid-carbon tetrachloride system at 20°C. Comparison with experiment yielded excellent results. Extension to systems containing acetic acid and benzene, heptane and toluene (L9) however was not so successful indicating that the association of acetic acid is influenced by the nature of the non-reacting component and that correlations obtained from one system cannot generally be extended to other systems. Barton and Hsu (B4) in their work on the solubility of non-polar gases in carboxylic acids presented an expression for the variation of the equilibrium constant with composition based on the quasi lattice theory of Sarolea-Mathot (S5). This involves the calculation of interaction energies between the monomer, dimer and gas molecules. They also indicated how these energies may be estimated and successfully predicted the solubility of 29 gases in acetic, proprionic and other members of the homologous series.

5.2 Modes of Association.

Although association is known to take place in both the liquid and vapour phase in solutions containing the lower members of the fatty acid family, there is some disagreement as to the degree of polymerisation (T12) (N6) (J6). It has been generally accepted that the reaction $2\,A \rightleftharpoons A_2$ takes place but Ritter and Simons (R13) postulate in addition the formation of a tetramer. For the equilibrium constants of the polymerization reactions they give the following expressions for the vapour phase :

$$\ln K_d = \ln \frac{Pt}{Pm^2} = -23.98925 + \frac{7285.38}{T} \qquad (5.1a)$$

$$\ln K_t = \ln \frac{Pt}{Pm^4} = -54.07022 + \frac{13548.41}{T} \qquad (5.1b)$$

with the units of K_d in $(\text{mm Hg})^{-1}$ and $(\text{mm Hg})^{-3}$ respectively. Chueh (C10) and Potter et al (P5) on the other hand consider that only the dimer and the trimer are formed. The equilibrium constants reported by Potter are given by :

$$\log K_{2A} = \log \frac{Pd}{Pm^2} = -10.322 + \frac{3083}{T} \qquad (5.2a)$$

$$\log K_{3A} = \log \frac{Ptrim}{Pm^3} = -18.984 + \frac{5080}{T} \qquad (5.2b)$$

and are also applicable to the vapour phase only. For the liquid phase Freedman (F7) has determined values of the monomer - dimer association constant using an ultrasonic absorption technique on pure acetic acid at various temperatures and Barton and Hsu (B4) correlated his results by the following relationship for the equilibrium constant :

$$\ln K_o = \frac{3131}{T} - 6.5197 \qquad (5.3)$$

where T in all the preceding equations is in ^{o}K. Marek (M6) on the other hand has ignored the formation of higher polymers and has assumed that dimerisation is the only reaction taking place in both phases.

5.3 Correlation of data from systems containing acetic acid

The normal procedure for a binary data set is to utilise the one of the usual integrated forms of the Gibbs-Duhem equation such as the Wilson equation (W5), NRTL in various forms (R12) and the UNIQUAC equation (A2) to correlate the variation of the activity coefficient with composition as outlined in chapter 2. This approach does not give satisfactory results for systems containing acetic acid and it has been found necessary to multiply the vapour phase fugacity coefficient by a correction factor to allow for vapour phase association. This procedure usually allows the previous equations to be used as above but since the effect of the dimerisation is to make the liquid phase behaviour appear unduly complex none of these equations may be capable of modelling this behaviour exactly. An alternative approach is to model the dimerisation in some explicit way and a number of different approaches may be adopted. Either the effect of concentration of acetic acid in the binary mixture is known by other measurements such as spectroscopic or dielectric methods and so can be taken directly into account, as was done on a limited scale by Liszi (L68), or a more general model can be set up which relates the dimerisation (or association) equilibrium constant in the binary mixture to that of the pure associating substance (here acetic acid). This represents an extension of the work of Marek and Standart (M6).

The difficulty in correcting for association in the liquid phase is that it cannot be assumed that the equilibrium constant for the dimerisation in pure acetic acid is the same in the binary mixture or that it is independent of concentration of acetic acid. As was noted previously this assumption is justified in the vapour phase rendering calculation of the necessary vapour phase corrections a simple matter.

5.4 Calculation of correction factors

Marek and Standart (M6) and Prigogine and Defay (P10) among others have both presented relationships for the correction factors to be applied to the overall concentrations and activity coefficients.

In the treatment of Marek and Standart, the liquid-phase association is handled by considering the 'Law of Mass Action' constant, $K = \varepsilon_2/\varepsilon_1$ where ε_1 and ε_2 are the 'true' mole fractions of the monomer and dimer of acetic acid in the liquid phase. Prigogine and Defay's treatment is based on the concept of an ideal associated liquid and has been modified for non-ideality other than that due to association by Francesconi and Trevissoi (F5) in the development of a consistency test.

While Marek and Standart noted that the thermodynamic equilibrium constant K^T was defined as:

$$K^T = \frac{\gamma_2}{\gamma_1^2} \cdot \frac{\varepsilon_2}{\varepsilon_1^2} \qquad (5.4)$$

they made no use of this in their treatment of the liquid phase behaviour, and in the way K varied with concentration. In this work their approach is extended by utilising the fact that since k^T is defined in terms of the standard states of the reacting components, it must be independent of concentration. However, before introducing this concept explicitly into the analysis, the necessary relationships between the differing activity coefficients of the various species will be developed.

Marek and Standart presented the following modified equilibrium relationship in systems of associating components. For the associating component A (acetic acid).

$$PY_A \; Z_A \; \varnothing_A = p_{AO} \; x_A \; \delta_A \; \gamma_A \qquad (5.5)$$

Where Y_A and x_A are nominal vapour and liquid mole fractions, p_{AO} is the vapour pressure of the overall mixture of monomers and dimers, P is the total pressure, γ_A is the nominal activity coefficient and Z_A and δ_A are vapour and liquid phase correction factors defined by :

$$Z_A = \frac{1 + \sqrt{1 + 4\,K_A\,p_{AO}}}{1 + \sqrt{4KPY_A\,(2-Y_A)}} \qquad (5.6)$$

Where K_A - association constant at pressure p_{AO} in acetic acid vapour.

K - association constant at pressure P in acetic acid vapour.

$$\text{and} \quad \delta_A = \frac{1 + \sqrt{1 + 4k_A}}{1 + \sqrt{1 + 4k x_A\,(2-x_A)}} \qquad (5.7)$$

k_A - association constant in pure acetic acid liquid.

k - association constant in liquid mixture.

ϕ_A is the overall fugacity coefficient defined by

$$\phi_A = \phi_1/\phi_{1A} \qquad (5.8)$$

ϕ_1 - fugacity coefficient for the monomer in the mixture vapour.

ϕ_{1A} - fugacity coefficient for the monomer pure acetic acid vapour.

ALSO

$$\gamma_A = \frac{\gamma_1}{\gamma_{1A}} \qquad (5.9)$$

Where γ_1 and γ_{1A} are similarly defined.

For the non associating component B Marek and Standart have

$$PY_B \phi_B Z_B = p_{BO} x_B \delta_B \gamma_B \qquad (5.10)$$

Where the symbols have a similar meaning except that the correction factors Z_B and δ_B are defined as follows:

$$Z_B = \frac{2\left[1 - Y_A + \sqrt{1 + 4KPY_A\ (2-Y_A)}\right]}{(2-Y_A)\ \left[1 + \sqrt{1 + 4KPY_A\ (2-Y_A)}\right]} \qquad (5.11)$$

and $$\delta_B = \frac{2\ \left[1 - \chi_A + \sqrt{1 + 4k\chi_A\ (2-\chi_A)}\right]}{(2-\chi_A)\ \left[1 + \sqrt{1 + 4k\chi_A\ (2-\chi_A)}\right]} \qquad (5.12)$$

Provided the values for the association constants in the pure associating substances are known the application of correction factors is straightforward. As stated previously for the vapour phase, K is assumed to be independent of composition so that $K = K_A$, obtained from equation (5.2) and Z_A and Z_B can be evaluated directly. For the liquid phase this assumption is not justified so that many workers have set

$$\delta_A = \delta_B = 1$$

and correlated data correcting for vapour phase association only.

In this work an attempt is made to overcome this problem as follows. It is first of all necessary to establish a relationship between the activity coefficient of the dimer in the mixture γ_2 to the overall activity coefficient γ_A obtained from one of the activity coefficient models used during the data fit. The procedure of Marek and Standart is extended by utilising the following expressions.

$$K_A = \frac{\eta_{2A}}{p_{AO}\eta_{1A}^2} \quad \text{where} \quad \eta_{1A} + \eta_{2A} = 1 \tag{5.13}$$

$$k_A = \frac{\varepsilon_{2A}}{\varepsilon_{1A}^2} \quad \text{where} \quad \varepsilon_{1A} + \varepsilon_{2A} = 1 \tag{5.14}$$

(Where η_{1A} and η_{2A} are the true mole fractions of monomer and dimer in the vapour phase of pure acetic acid and ε_{1A} and ε_{2A} those for the liquid phase), and, giving the equilibrium relationship for the pure acetic acid dimer in terms of nominal mole fractions of acetic acid :

$$PY_A\, z_A^{1}\, \phi_A^{1} = p_{AO}\, x_A\, \delta_A^{1}\, \gamma_A^{1} \tag{5.15}$$

Where $\phi_A{}^1 = \phi_2 / \phi_{2A}$ and $\gamma_A{}^1 = \gamma_2/\gamma_{2A}$

and

$$Z_A{}^1 = \frac{Y_A \left[(4KP + {}^1/_{Y_A} - 2KPY_A) - \sqrt{{}^1/_{Y_A}{}^2 + \frac{8KP}{Y_A} - 4KP} \right] K_A p_{AO}}{(KPY_A{}^2 + 4KP - 4KPY_A)\ (2K_A p_A O + 1 - \sqrt{4K_A p_{AO}} + 1)}$$

(5.16)

$$\delta_A{}^1 = \frac{x_A \left[(4k + {}^1/x_A - 2kx_A) - \sqrt{{}^1/x_A{}^2 + 8k/x_A - 4k} \right] (k_A)}{(k_A{}^2 + 4 \quad - 4k_A)\ (2k_A + 1 - \quad 4k_A + 1)}$$

(5.17)

The detailed derivation of these equations is given in Appendix A2.

It is necessary to relate $\gamma_A{}^1$ to γ_A.

Dividing (5.15) by (5.5) gives :

$$\frac{PY_A\ Z_A{}^1\ \phi_A{}^1}{PY_A\ Z_A\ \ \phi_A} = \frac{P_{AO} X_A\ \delta_A{}^1\ \gamma_A{}^1}{P_{AO} X_A\ \delta_A{}^1\ \gamma_A} \qquad (5.18)$$

$$\text{OR } \gamma_A^1 = \frac{Z_A^1}{Z_A} \frac{\phi_A^1}{\phi_A} \frac{\delta_A}{\delta_A^1} \gamma_A \tag{5.19}$$

Since $\gamma_A^1 = \gamma_2/\gamma_{2A}$ this may be written :

$$\gamma_2 = \frac{Z_A^1}{Z_A} \frac{\phi_A^1}{\phi_A} \frac{\delta_A}{\delta_A^1} \gamma_A \gamma_{2A} \tag{5.20}$$

$$\gamma_1 = \gamma_A \gamma_{1A} \tag{5.21}$$

For the vapour phase it has been customary, as was pointed out above, to assume that K, the association constant in the mixture is equal to that for the pure vapour. For the liquid phase, this is not as valid an assumption. The liquid phase association constant for the pure component was defined above as $k_A = \varepsilon_{2A}/\varepsilon^2_{1A}$. As already noted this, however, is not the thermodynamic equilibrium constant for the association which is given by

$$k^T = \frac{\gamma_{2A} \varepsilon_{2A}}{\gamma^2_{1A} \varepsilon_{1A}} \tag{5.22}$$

OR $$k_A^T = \frac{\gamma_{2A}}{\gamma^{2}_{1A}} k_A \qquad (5.23)$$

Now the equilibrium mole fractions in the mixture are given by :

$$k^T = \frac{\gamma_2}{\gamma_1^2} \frac{\varepsilon_2}{\varepsilon_1^2} \qquad (5.24)$$

OR $$= \frac{\gamma_2}{\gamma_1^2} k \qquad (5.25)$$

Since $k^T = k_A^T$ then

$$\frac{\gamma_2}{\gamma_1^2} k = \frac{\gamma_{2A}}{\gamma_{1A}^2} k_A \qquad (5.26)$$

Thus (5.26) may be rewritten as :

$$k = \frac{\gamma_1^2}{\gamma_2} \frac{\gamma_{2A}}{\gamma_{1A}^2} k_A \qquad (5.27)$$

Substituting the previously derived expressions for γ_1 and γ_2 gives :

$$k = \frac{\gamma_{2A}}{\gamma_{1A}^{2}} \; k_A \; \frac{\gamma_A^{2} \; \gamma_{1A}^{2}}{\dfrac{z_A^{1}}{z_A} \; \dfrac{\phi_A^{1}}{\phi_A} \; \dfrac{\delta_A}{\delta_A^{1}} \; \gamma_A \; \gamma_{2A}} \qquad (5.28)$$

$$= \frac{\gamma_{2A}}{\gamma_{1A}^{2}} \; k_A \, \beta \; \frac{\gamma_A^{2} \; \gamma_{1A}^{2}}{\gamma_A \; \gamma_{2A}} \qquad (5.29)$$

i.e. $k = k_A \cdot \beta \cdot \gamma_A$ (5.30)

where :

$$\beta = \frac{z_A}{z_A^{1}} \; \frac{\phi_A}{\phi_A^{1}} \; \frac{\delta_A^{1}}{\delta_A} \qquad (5.31)$$

Hence in any calculation of the correction factors an iterative procedure can be adopted where initially k can be set equal to k_A, obtained from equation (5.3) the values of β and γ_A can be calculated, a new k obtained and the calculation repeated. This may be organised in a number of ways depending on the overall computation being carried out.

5.5 Thermodynamic consistency in systems involving Dimerisation.

As mentioned in chapter 4, the wide range of proposed thermodynamic consistency tests in the literature share as their starting point, the Gibbs-Duhem equation, which in one form may be expressed as :

$$\sum_i x_i \ d\ln \gamma_i = \frac{\overline{Vm}}{RT} dP + \frac{\overline{Hm}}{RT^2} dT \qquad (5.32)$$

As previously described this equation has been employed for the consistency testing of vapour-liquid equilibrium data in a number of different ways, such as area tests, (H6), local area tests (S12) slope tests (V2) and Barker fit tests (B21).

Consistency tests have been applied to systems in which dimerisation occurs (largely mixtures containing acetic acid) by Meehan and Murphy (M17), Francesconi and Trevissoi (F5) and Francesconi and Cojutti (F4).

The procedure adopted in this work is effectively the simultaneous correlation and thermodynamic consistency testing of experimental data for various systems with a number of alternative models of the liquid phase, by use of the Barker method (B3) as outlined in chapter 3. It will be recalled that in the Barker method, an integrated form of the Gibbs-Duhem equation is used to relate the activity coefficients to the mole fractions in a binary mixture. The parameters in the integrated equation are adjusted by a least-squares fitting-through-optimisation procedure until a minimum error between experimental and calculated total pressures or y values is obtained. Byer and Van Ness (B21) and others (V6), (C8) have pointed out that a good indication of the consistency of the data can be obtained if the difference between the calculated and experimental values of the variable <u>not</u> used in the data fit is examined for each data point. This is a rigorous test, being more severe than the forms of the area test used by Meehan and Murphy (M17) in their acetic acid toluene data and by Francesconi and Cojutti (F4) on the data of Zawidski (Z1). Meehan and Murphy imply that they concluded that their data were consistent, while Francesconi and Cojutti concluded that the data of Zawidski were consistent.

As with all consistency tests, the final conclusion depends on a value judgement. The experimental y values are the data most likely to contain the largest error, and so these are excluded from the data-fit and used for the consistency test. Should an appreciable random or systematic deviation occur between the (y^{calc}) and (y^{exp}) values, then there are three possibilities as discussed in chapter 4.

1. The data set is completely unreliable and must be discarded.

2. The y values only are in error and the remaining data are acceptable.

3. If the Barker method has been used then the liquid phase model used may not be capable of adequately representing the liquid phase behaviour.

As one of the objectives of this work is to compare the various models for the liquid phase, the Barker method was used to fit the data by each of the models in turn. A plot of the deviations in y^{calc} and y^{exp} against composition for each of the models simultaneously provides a consistency test and also enables the performances of the models to be compared.

5.6 Extension to multicomponent V.L.E. and L/L equilibrium.

The calculation of multicomponent vapour-liquid equilibrium in systems containing acetic acid is straightforward. Each additional component requires an extra correction factor for the vapour phase and an extra factor for the liquid phase. The factors are identically equal to Z_B and δ_B in the binary case. The correction factors for the acetic acid are dependent only on the nominal mole fractions of acetic acid in the multicomponent mixture. Thus if one of the activity coefficient models is used in one of the computational procedures due to Prausnitz et al (P6) such as programme BUBLT the pure component parameter k_A and K_A may be obtained from equations (5.3) and (5.2) and the equilibrium constant k calculated from equation (5.30).

An extra iteration loop will be required for either the liquid or vapour correction factors depending on whether it is the liquid or vapour composition that is being calculated. Further details are being given in Appendix A1.

Liquid-liquid equilibrium calculations are also reasonably straightforward. It has been shown (N8) for an n component mixture that if two liquid phases exist then the following relationship holds

$$(\gamma_i x_i)^{I} = (\gamma_i x_i)^{II} \quad i = 1, \ldots n \qquad (5.34)$$

For a system containing acetic acid and two other components such as water and toluene, the above equations may be written

$$(\varepsilon_1 \gamma_1)^{I} = (\varepsilon_1 \gamma_1)^{II} \quad - \text{ monomer} \qquad (5.35a)$$

$$(\varepsilon_2 \gamma_2)^{I} = (\varepsilon_2 \gamma_2)^{II} \quad - \text{ dimer} \qquad (5.35b)$$

$$(\varepsilon_W \gamma_W)^{I} = (\varepsilon_W \gamma_W)^{II} \quad - \text{ water} \qquad (5.35c)$$

$$(\varepsilon_T \gamma_T)^{I} = (\varepsilon_T \gamma_T)^{II} \quad - \text{ toluene} \qquad (5.35d)$$

As in the case of binary vapour-liquid equilibrium ε_1, ε_2, ε_W and ε_T, can be replaced by an expression involving the nominal mole fraction of acetic acid. These expressions are presented in Appendix 1.

Equations (5.35) a, b, c, d can thus be rewritten as follows :

$$(x_A \delta_A \gamma_A)^I = (x_A \delta_A \gamma_A)^{II} \quad \text{- monomer} \qquad (5.36a)$$

$$(x_A \delta_A^1 \gamma_A^1)^I = (x_A \delta_A^1 \gamma_A^1)^{II} \quad \text{- dimer} \qquad (5.36b)$$

$$(x_W \delta_W \gamma_W)^I = (x_W \delta_W \gamma_W)^{II} \quad \text{- water} \qquad (5.36c)$$

$$(x_T \delta_T \gamma_T)^I = (x_T \delta_T \gamma_T)^{II} \quad \text{- toluene} \qquad (5.36d)$$

Where $$\delta_A = \left[\frac{\sqrt{1 + 4k (2-x_A)} - 1}{2(2-x_A) k x_A} \right] \qquad (5.37)$$

$$\delta_A^1 = \left[\frac{4k + 1/x_A - 2k x_A - \sqrt{1/x_A^2 + 8k/x_A - 4k}}{2(k x_A^2 + 4k - 4k x_A)} \right] \qquad (5.38)$$

$$\delta_T = \delta_W = \left[\frac{1 + 4k(2-x_A) - \sqrt{1 + 4k x_A (2-x_A)}}{2k(2-x_A)^2} \right] \qquad (5.39)$$

and $\gamma_A = \gamma_1$, $\gamma_A^1 = \gamma_2$. These relationships apply to both phases.

5.7 Systems under investigation

The previously derived relationships were applied to many binary systems containing acetic acid. In all cases the saturated vapour pressures were calculated from the extended Antoine equation.

$$\ln P = C_1 + \frac{C_2}{C_3+T} + C_4T + C_5T^2 + C_6 \ln T \quad (5.45)$$

with P in atmospheres and T the absolute temperature K. The constants were obtained by a least squares fit on vapour pressure data as described in Appendix A1. Van Ness (B21) has pointed out the importance of accurate vapour pressures in the correlation of vapour-liquid equilibrium data.

1. The Acetic acid - toluene binary

There is available a considerable range of data for this system. The oldest is that of Zawidski (Z1) at 69.94°C and 80.05°C. Markuzin and Pavlova (M10) obtained isothermal data at 30°C and Meehan (M16) obtained such data at 50°C and 70°C. Volpicelli and Zizza (V8) obtained isobaric data at 50mm Hg, while Haughton (H3) worked at 760mm Hg.

All these obtained complete sets of X-Y-P-T data so that consistency tests can be applied to them. Liszi (L8) obtained data at 20°C but did not report the total pressure, hence his data is not of use in this work. This system was chosen initially since toluene is a non-polar, non associating compound and should not present too complex liquid phase behaviour.

2. The Acetic acid-water system.

This is an extremely important system both industrially and theoretically, and an enormous amount of data has been reported. Mostly it is isobaric data at 760 mm Hg (S8) (B16) (R14) (12) and (G2). However Othmer (08) reported data over a range of pressures from 20 mm Hg to 2053 mm Hg, while Arich and Tagliavani (A5) reported isothermal data at 70°C, 80°C and 90°C. The behaviour of this system is considerably more complex than that of acetic acid - toluene. This is because the structure of water is extremely complicated with extensive hydrogen bonding and its behaviour and physical properties have been the subject of an extensive monograph (F6) as well as other work.

There is experimental evidence that it exists as a hemihydrate (H9) and so should provide a more severe test for the new approach. Another system investigated is the system acetic acid - dimethylacetamide (C1) which has so far defied attempts to model using equations such as the Wilson or NRTL equations, probably on account of hydrogen bonding and other specific interactions in the liquid phase.

A complete list of systems investigated is given in Appendix A3.

The ternary liquid-liquid equilibrium system acetic acid - toluene - water has been reported by Woodman (W6), Salem (S2) and Pitt (P3) at a range of temperatures between 20°C and 80°C. The tie lines and two phase envelope were calculated using the program described in Appendix A1, both using the new approach and the NRTL and UNIQUAC equations. Parameters for the toluene water system were calculated from mutual solubilities by means of the programme, JF4LSQSOL described in Appendix A1.

6.0 Experimental Work.

Introduction.

In order to assess the performance of the Cathala flow still using the consistency tests discussed in chapter 4, it was necessary to obtain experimental data on a number of systems each of which provided examples of a different type of behaviour.

Three of the systems investigated by Davies (D4) had shown some discrepancies and as these three systems provided examples of near ideal, moderately non-ideal and azeotropic behaviour they were chosen as the test systems. The opportunity was taken to investigate at the same time the effect of analytical uncertainty on the reliability and consistency of the data. Thus for two of the systems, two different analytical procedures were used to give two data sets with different levels of measurement error.

The apparatus used was based on the still used by Mamers (M4) and modified by Davies (D4) and the rapid time taken to reach equilibrium with it facilitated the determination of the large number of data points needed to make statistical comparisons.

The equipment is described in more detail in this chapter.

6.1 Description of the Cathala Still

6.1.1. The General Layout

The general layout of the equipment is illustrated in plate 1 and in fig 8. The purified components were stored in four 5 litre aspirators mounted overhead to obtain a good pressure head. The liquid stream flowed down through feed control valves (1) and was metered by Fisher & Porter flowraters (2) situated in the lines. After passing through the flowraters the liquid streams were mixed and fed into a liquid preheater (3), fig.14 of 250 watt nominal heat input. The liquid feed was heated to just below its boiling point, the temperature being measured by a Chromel-Alumel thermocouple situated just prior to the exit from the preheater. The liquid stream then passed onto the lower of two sieve plates in the mixing chamber (4) where it encountered the superheated vapour.

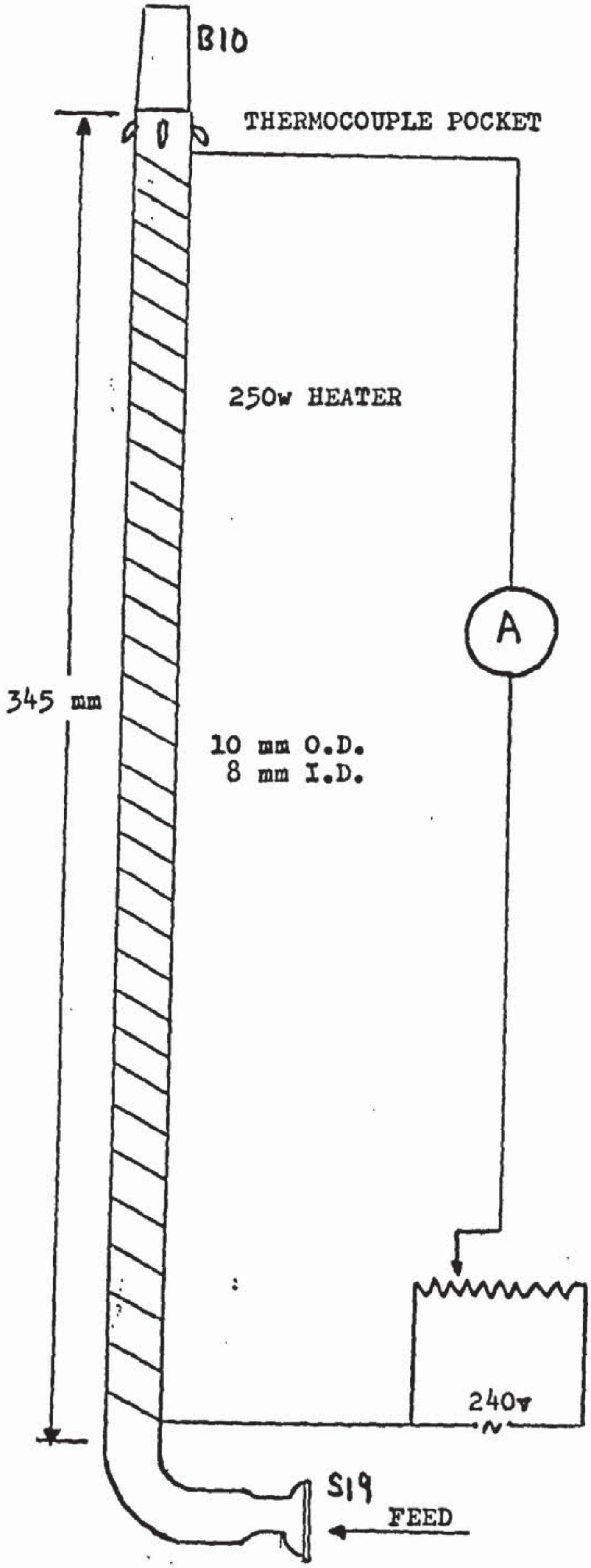


FIG. 14
LIQUID PREHEATER

NOT TO SCALE

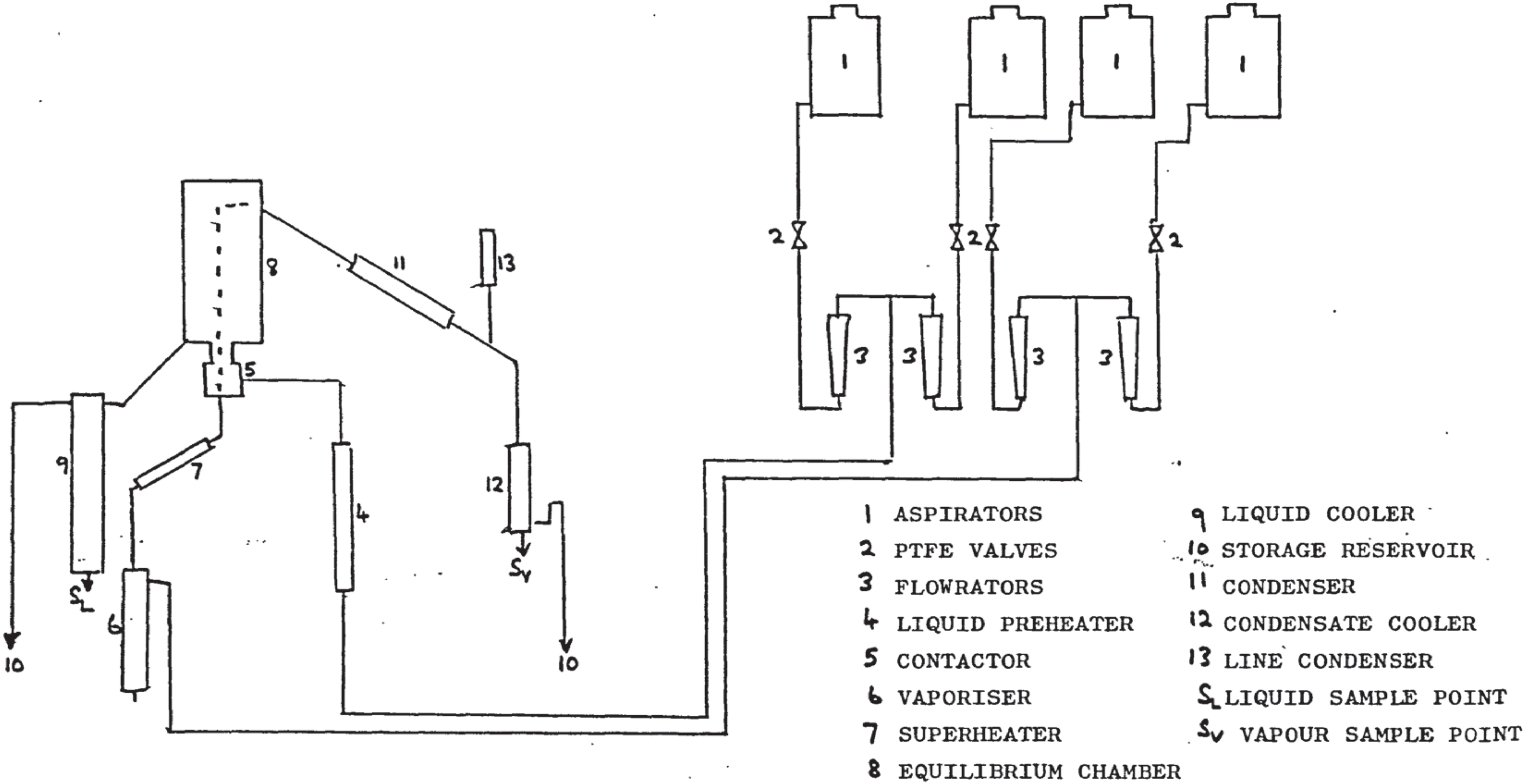
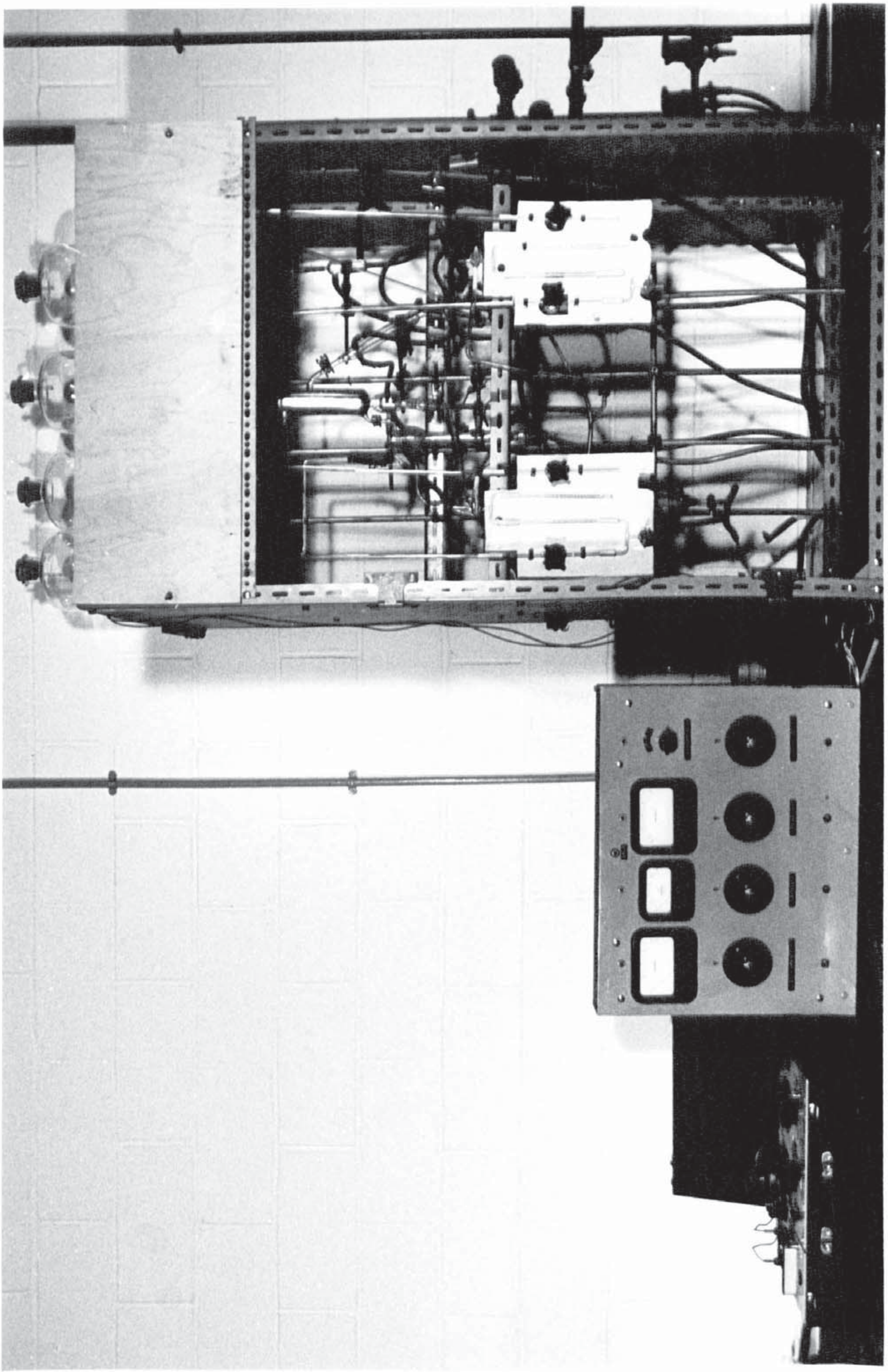


FIG. 8 APPARATUS LAYOUT

PLATE 1

CATHALA STILL APPARATUS



The liquid feed to the vapour (5) from the storage aspirators was controlled and metered in the same manner as the liquid feed to the preheater, and entered into the top of a vertically mounted dropwise film vaporiser, containing stainless steel Oldershaw packing. The heat input to the vaporiser was controllable up to 500 watts and the temperature of the saturated vapour leaving was measured by means of a Chromel-Alumel thermocouple inside a well, which protruded into the exit vapour stream. The vapour then passed into a 100 watt superheater (6), inclined at 15 degrees to the horizontal, to assist drainage as shown in fig 9. The superheater was adjusted to raise the vapour temperature by 10^{o}, the outlet temperature of the vapour being monitored by another Chromel-Alumel thermocouple situated just before the equilibrium chamber.

The superheated vapour was then fed into the base of the mixing chamber and bubbled through the preheated liquid feed. The vapour-liquid mixture then passed up into the equilibrium chamber (7), where equilibrium was approached by passing the mixture up through a vigreux tube at the top which it impinged upon a thermocouple well containing a Chromel-Alumel thermocouple.

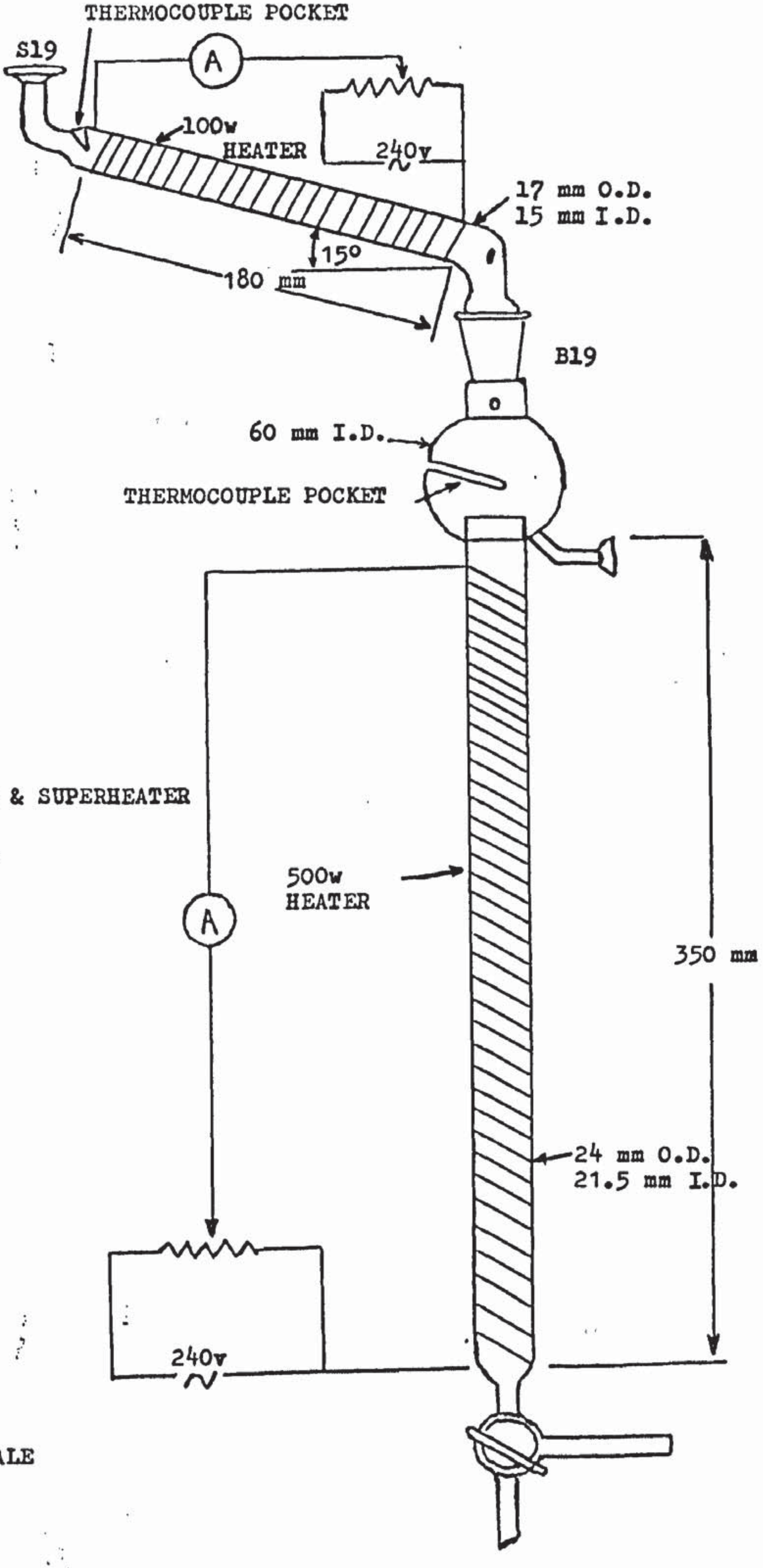


FIG. 9
VAPORISER & SUPERHEATER

NOT TO SCALE

The equilibrium mixture was separated in the de-entrainer section of the still (see fig 10) which was contained within a thermal shield.

The whole of the equilibrium chamber was surrounded by a silvered-evacuated jacket which together with the mixing chamber was well lagged.

The equilibrium liquid phase, separated out in the de-entrainer, flowed into the liquid cooler (8), and thence to a storage reservoir. Samples were removed from the small tap situated at the bottom of the cooler. The equilibrium vapour phase after separation from the liquid, passed out of the still to a condenser (9) and then to a condensate cooler (10), a tap at the base of which provided a sample of the condensed vapour. The remainder flowed to the storage reservoir. The entire rig was capable of operating under pressure or vacuum conditions. Pressure lines were connected to the vapour condenser through a line condenser (11), to the exit from the liquid cooler and to the product storage lines. Pressure control was effected by an Edwards Pressure controller model V.P.C.1., working against the pressure in a surge tank, in conjunction with a water manometer. The entire rig was shielded from draughts by being placed in a plywood cabinet.

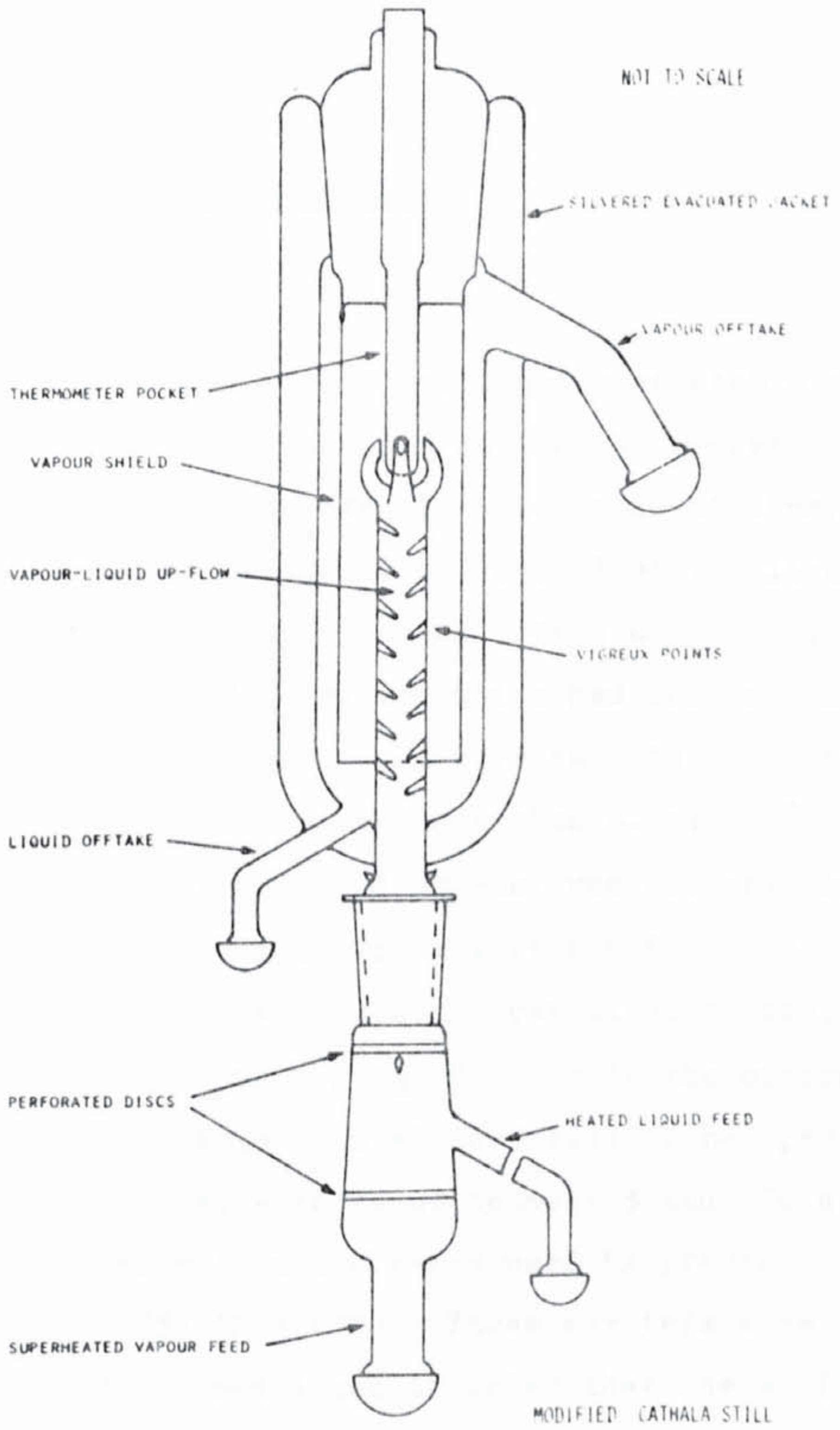


Fig. 10 - Diagrammatic cross section of Modified Cathala Still

6.1.2. The feed system

It was extremely important that stable flow conditions be maintained during the operation of the still for periods of at least 20 minutes, and for this reason close control of the liquid feed flowrates is required. This was achieved by using P.T.F.E. valves which had both a coarse and fine adjustment, and were capable of controlling the flow rates down to less than 0.5ml min^{-1}. Metering of the liquid streams was accomplished by four 1/16" diameter bore Fisher & Porter flowraters containing stainless steel floats, two of which had a range 0-10 while the others were 0-16. This enabled the still to be operated with liquid flow rates of between 3 and 12mls min^{-1} which lies within the range used by previous workers (C3) (M5) (C5). Three way taps were situated in feed lines in order that the equipment could be drained or vented.

To avoid contamination of the feed components all connections were of P.T.F.E. tubing or ball and socket glass joints.

6.1.3 The liquid preheater

This consisted of a 35cm long straight glass tube of internal diameter 0.8cm. The heat input was provided by a coil of resistance wire wrapped around the tube, capable of a maximum output of 250 watts. The thermocouple was situated in a well protruding into the liquid flow at the top of the tube.

6.1.4 The Vaporiser and Superheater

The construction of the vaporiser and superheater are illustrated in fig 9. The vaporiser consisted of a tube 35cm long and 1.7cm diameter, wrapped around with resistance wire calculated to give a maximum heat output of 500 watts. A drain tap at the base of the tube gave an outlet by which excess feed could be drained to the storage reservoir in cases where only partial vaporisation occurred. At the top of the tube was situated a glass bulb containing the feed entrance pipe together with a weir to ensure an even distribution of the feed liquid.

The wall of the bulb contained the thermocouple well, whilst the whole of the tube was fitted with stainless steel Oldershaw packing to increase the available heat transfer area.

The superheater was connected to the top of the vaporiser by a B19 ground glass joint and consisted of a 18cm long tube of 1.7cm diameter inclined at 15° to the horizontal to facilitate drainage. The heat input was again a resistance coil of maximum output 100 watts.

All the heaters were connected to 'Variac' variable transformers situated in a control panel to the left of the main apparatus.

Davis (D4) has calculated the holdups in the vaporiser and liquid preheater to be between 2 and 3 minutes for flowrates of between 8 and 12ml min^{-1} which is approximately one third of the residence time for Cathala's second still, whilst the residence time in the superheater was calculated to be of the order of a few seconds only.

6.1.5. The Equilibrium Still

The lower part of the equilibrium still consisted of a detachable mixing chamber containing the two parallel sieve plates of 1.6cm and 2.4cm diameter, each plate containing 52 0.05cm diameter holes. The superheated vapour entered through the base of the contactor and bubbled through the preheated liquid, which entered between the two sieve plates. The mixture of vapour and liquid flowed up through the vigreux column shown in fig 10 before passing out through the four discharge port holes onto the thermocouple well situated so that it just fitted into the discharge head of the vigreux column. The vigreux column was surrounded by a thermal shield of 2.6cm diameter which reached nearly to the bottom of the equilibrium chamber. The vapour offtake line was situated at the top of the equilibrium chamber and inclined at 60° to the horizontal to assist drainage of any precondensate into the vapour product receiver system, whilst the liquid exit line ran from the base of the chamber as shown in the figure.

By adjusting the back pressure on the liquid overflow line, it was possible to maintain the equilibrium liquid level at the base of the equilibrium chamber thus preventing any escape of vapour along the line. The whole equilibrium chamber was enclosed within a silvered evacuated jacket to eliminate as far as possible any partial condensation of the equilibrium vapour. Originally the still was surrounded by a 150 watt resistance heater, but this was dispensed with since it was felt that this would set up thermal stresses which may have contributed to a fracture which appeared in an earlier still. Instead the equipment was thoroughly lagged and completely enclosed in a cabinet to avoid draughts. Subsequent operating experience indicated that these precautions were sufficient.

6.1.6 The liquid cooler and vapour condenser/cooler system

An outline of the liquid cooler is shown in fig 11. The liquid flowed from the base of the still through a spiral coil connected to a 44cm long downcomer tube. From the exit at the base of the cooler the liquid passed up over the outside surfaces of the coil and tube, and thence through the outlet port situated at the top of the cooler, opposite the inlet port and at the higher level. Cooling was by means of water circulating in the outer jacket whilst the area available for heat transfer was approximately $30cm^2$.

Sampling of the liquid phase was achieved by opening the top at the base of the cooler which was connected to a capillary tube which extended approximately two thirds of the way up the downcomer. This arrangement avoided any backmixing at the base of the cooler and minimised the liquid hold up.

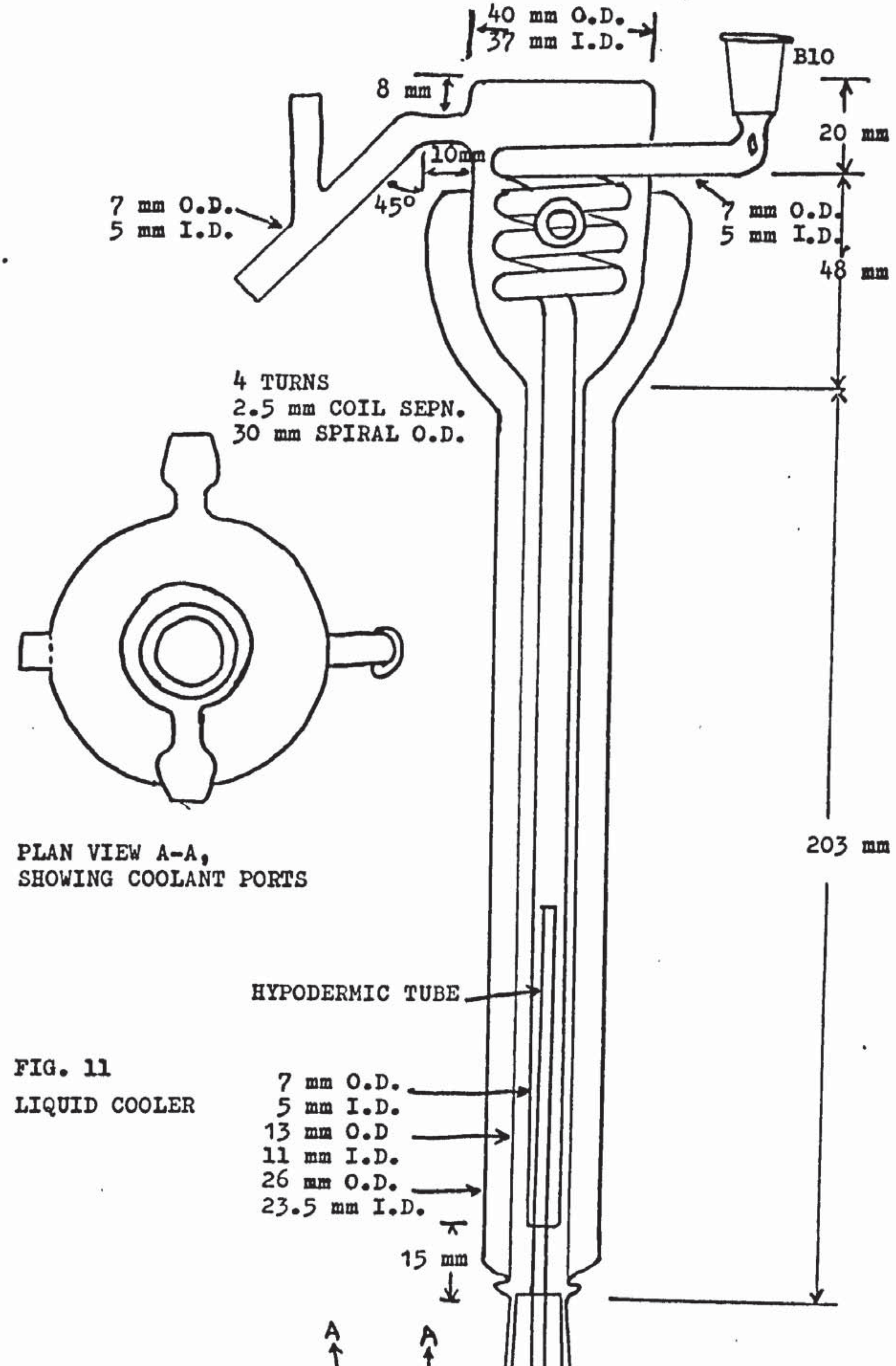


FIG. 11

LIQUID COOLER

NOT TO SCALE

The vapour passed to a water cooled double surface condenser inclined at 60° to the horizontal. The heat transfer area was calculated to be $95cm^2$. A condensate cooler was attached to the base of the condenser which also acted as a product sampling reservoir as shown in fig 12. The height of the liquid in the cooler was controlled by a capillary outlet weir and samples were taken from a tap at the base of the cooler connected to a capillary tube which extended approximately to one half of the liquid level. The base of the condenser was connected to the pressure control system through a small line condenser, which prevented any vapour leakage.

The overflow lines from the liquid cooler, the condensate cooler and the vaporiser drain point were all connected and fed into a 10 litre product storage reservoir which was vented to the pressure controller system.

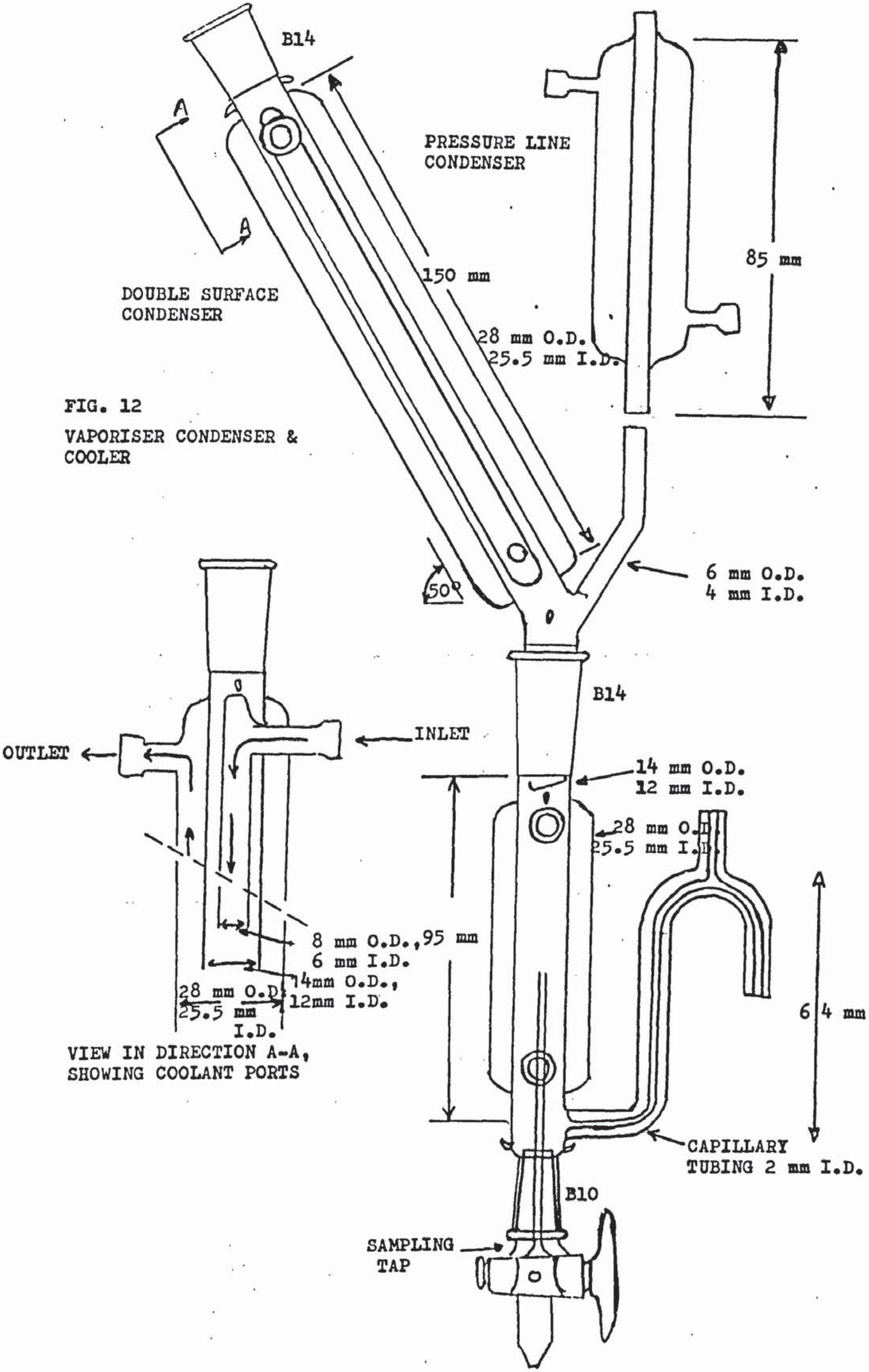


FIG. 12

VAPORISER CONDENSER & COOLER

6.1.7 Pressure Control and Temperature measurement.

Since it was desired to operate the still at a constant pressure of 760mm of mercury during the experimental programme it was necessary to provide a means of adjusting the pressure on the occasions when the barometer gave readings other than 760.

If it was necessary to reduce the pressure, a water ejector capable of pulling a vacuum of nearly 20cm of mercury was connected to the 15 litre surge tank or conversely an air bleed was applied when the atmospheric pressure was less than 760mm. The surge tank pressure was controlled by an Edwards pressure controller model V.P.C.1, and the changes monitored by a water manometer. Control was possible to less than 0.1mm of mercury.

The equilibrium boiling temperature was measured by means of a Chromel-Alumel thermocouple situated in an oil filled pocket in the top of the equilibrium chamber.

The cold junction was immersed in crushed ice contained in a Dewar flask and the output voltage measured by a Pye potentiometer. The thermocouple was capable of measurement to within 0.02°K which was found to be adequate. The thermocouple was calibrated against a factory supplied thermocouple of known voltage/temperature characteristics.

Both thermocouples were placed in a small oil bath containing a resistance heater and the readings of the potentiometer noted at various temperatures. A similar procedure was followed with the three other thermocouples used to monitor the temperature in the various parts of the equipment. These had a common cold junction of crushed ice contained in another Dewar flask and the outputs were fed via a multipoint switch to the Pye potentiometer which was used to measure the temperature.

6.2 Determination of V.L.E. data

6.2.1. The preparation of the materials

The starting materials used were 'Analar' Ethyl Acetate, Butyl Acetate and n-Butanol. Twenty five litres of each component were first distilled in a fifty plate, one inch diameter Oldershaw column at a high reflux ratio until a product was obtained whose refractive index and boiling point were in close agreement with literature values (see Appendix A6). In addition the purity of each component was checked by injection into a chromatograph using stainless steel columns packed with 10% W/W polyethylene glycol (PEG 400) on 100-120 mesh celite support. The absence of any peaks at a very low attenuation, other than the one due to the required component was taken as confirmation of purity.

6.2.2. The methods of analysis

In previous work with the Cathala still, Davis (D4) used a Gas-Liquid Chromatograph with a Flame Ionization Detector as the method of analysis. In order to determine whether the anomalous results obtained for two of the systems investigated could be due to errors in the analysis it was decided to use the same equipment and to also analyse the samples by their refractive index.

6.2.3. Analysis by Refractive index

The samples were analysed using a high accuracy Abbe' refractometer with Sodium D light capable of reading to five figures. Temperature control was by means of water circulating from an external water bath whose temperature was kept constant with a temperature controller. Refractive index/composition plots at 25°C were prepared for the systems Ethyl Acetate-n-Butanol, n-Butyl Acetate-n-Butanol, Ethyl Acetate-n-Butyl Acetate and are listed in Appendix A6.

6.2.4 Analysis by Gas Liquid Chromatography

In his work, Davies (D4) employed an internal standardisation technique using iso-octane (2,2,4 trimethylpentane) as a reference compound. Since this was found to give satisfactory results, it was decided that the same method would be used.

The equipment is shown in fig 13. Argon was used as the carrier gas, and was passed through two 0.25 inch I.D. stainless steel columns five feet long, packed with 10% w/w polyethylene glycol (PEG 400) on 100-120 mesh celite support contained in a constant temperature oven, controlled by a temperature programming unit. A hydrogen/air flame was burnt in each detector head. The carrier gas flowrate was set to 40ml min^{-1} as was that of the hydrogen. The air flowrate was set at 500ml min^{-1} giving an air : hydrogen ratio of 15:1 necessary to minimise condensation in the detectors. Control of the flowrates was by means of pressure gauge regulators attached to the gas cylinders and by flow restrictors situated on top of the oven.

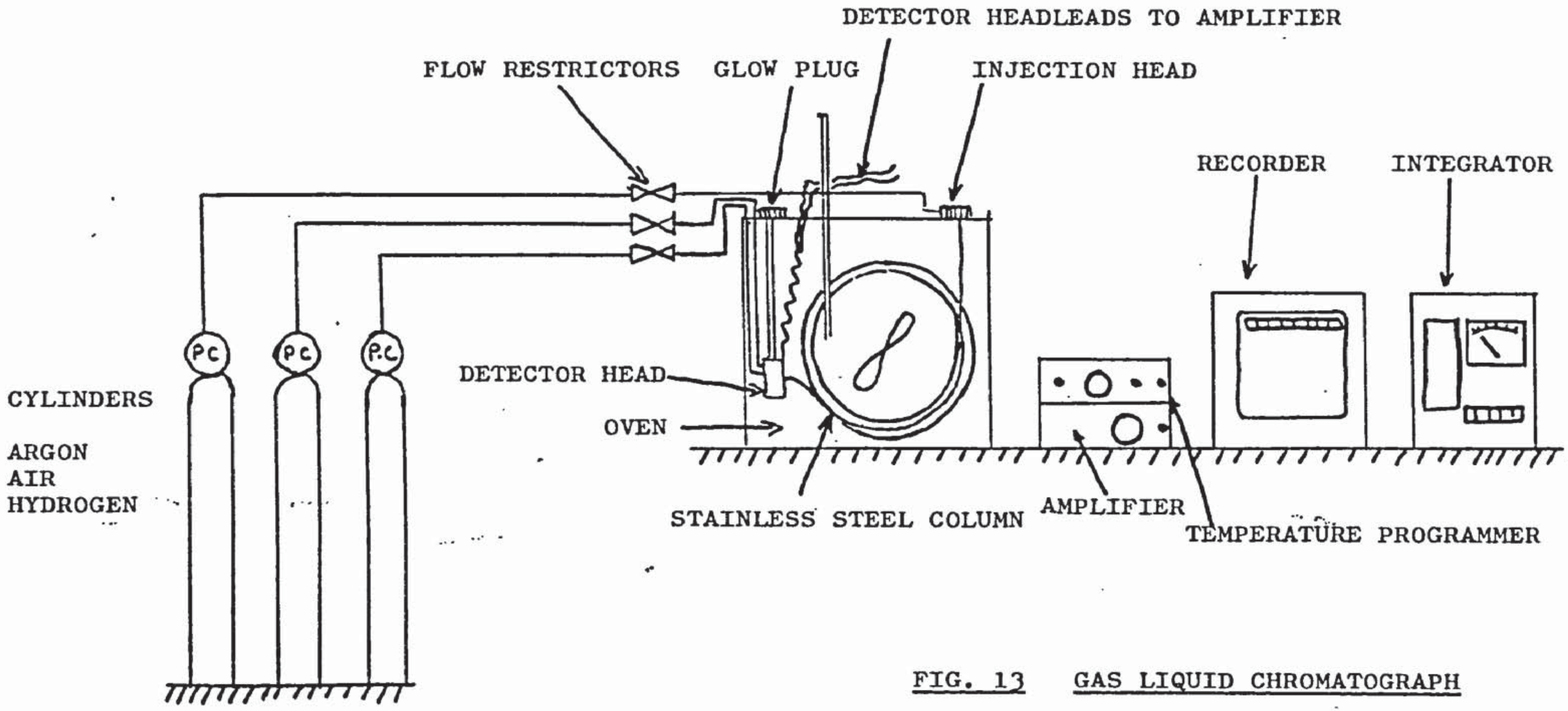


FIG. 13 GAS LIQUID CHROMATOGRAPH

It was also found that improved control could be obtained by placing needle valves in the gas feed lines. The hydrogen, air and argon pressure regulations were calibrated for flow rate against gauge pressure over a range 0-700ml min^{-1} for air and 0-200ml min^{-1} for argon and hydrogen using a bubble flowmeter. To prevent base-line drift and recorder-pen fluctuations, it was thought necessary to use high purity air, white spot hydrogen and commercial-grade argon.

The concentrations of the components were measured by means of a Flame Ionisation Detector, the output from which was fed to a Kent recorder and a Kent Chromolog Integrator.

Prior to use it was necessary to calibrate the chromatograph and to evaluate the response factors of the compounds to be used with respect to iso-octane.

To evaluate the response factors, a sample was made up of 10gms of the compound and 1.67gms of iso-octane. A 0.1μL sample was injected into the chromatograph and the resulting peak areas recorded.

This was repeated ten times and average values of the peak areas taken. By setting the response factors of the reference compound to unity the response factor of the compound may be calculated. This was repeated for all compounds.

Having obtained the response factors of all the compounds, it was then possible to calibrate the chromatograph. Binary samples of the components ethyl acetate, butyl acetate and butyl alcohol were made up weighing in total 10 gms each. 1.67 gms. of iso-octane was added to each sample and 0.1 μL of the resulting mixture injected into the chromatograph. This was repeated ten times for each of the samples and average values of the peak areas recorded. For each component the quantity $fxAx/\sum fA$ was calculated. Where :

fx - response factor of component x.
Ax - peak area of component x.
$\sum fA$ - sum of peak area times response factors for all components in the sample.

From these results a calibration curve of $fxAx/\sum fA$ against weight % present in the sample could be constructed.

However it was found that the factor $f_xA_x/\sum fA$ was directly equal to the weight fraction of the component in the sample. This was also observed by Davies and other workers. The worst error in making this assumption was found to be ± 2.0% at extreme concentrations, whilst the smallest was found to be of the order of ± 0.2%.

To analyse a sample the gas flow rates were set at the specified values and the temperature of the oven controlled at 100°C. The attenuation switch was set at 50×10^3 which was the same as that used during the calibrations and which gave on-scale peaks over the entire concentration ranges. 3mls of the sample were taken and added to 0.42 gms. of iso-octane in a sample bottle. The mixture was shaken and 0.1μL was injected in the chromatograph using a 0-1.0μL syringe. The peak areas were noted from the integrator and the procedure repeated to ensure reproducibility. The time taken to analyse a sample was a maximum of seven minutes.

The response factors were periodically re-evaluated as these change gradually with time.

6.3 Operation of the Still.

After ensuring that the overhead reservoirs contained sufficient liquid, the liquid feed lines were cleared of any entrapped air bubbles. Crushed ice was placed in the thermocouple cold junction flasks and the thermocouple potentiometer switched on and allowed to warm up for at least an hour prior to the commencement of the experimental run. The barometric pressure was noted and the pressure controller was adjusted to give an absolute pressure of 760 mm of mercury in the apparatus.

The feed was passed into the vaporiser and the heater input adjusted to give complete vaporisation. The vapour passed up through the superheater where the input was adjusted with the aid of the thermocouple to raise its temperature by 10 degrees. Superheated vapour was blown through the apparatus for 5-10 minutes to warm up the vigreux column and the de-entrainer surfaces. Preheated liquid feed heated to just below its boiling point was then introduced onto the lower of the two plates in the contactor.

When the temperature in the equilibrium chamber remained steady within ± $0.05^{o}C$ it was assumed that the system had reached equilibrium.
After 10 minutes of steady operation, samples of liquid and vapour condensate were taken for analysis and the equilibrium temperature noted.

After removal of the samples, the feed streams were altered in a manner such that whilst the overall flows to the vaporiser and liquid pre-heater remained approximately the same, their compositions were different. This procedure enabled adjustment of the heaters to be kept to a minimum. The system was then allowed to come to equilibrium again.

Flow rates of both liquid and vapour streams were maintained between 3 and 12ml min^{-1} which was the range used by Davies (D4), Marek (M5) and Cathala (C5).

6.4 Sources of error in the Cathala Still

Consideration of the structure of the Cathala still shows that there exists a number of features which may lead to thermodynamically inconsistent results. It was a primary aim of this work to show that these effects, although impossible to eliminate entirely, do not render the Cathala still unsuitable as a means of obtaining equilibrium data.

The first major possibility is that although the system reaches an apparently stationary state, this may not correspond to true equilibrium since the contact time is very small. In order to check the assumption of equilibrium, the still was operated with the vapour feed richer in the more volatile component and vice-versa. Provided equilibrium is attained in the still, the points obtained by both procedures should lie on the same curve. A second possibility is that liquid droplets may be entrained by the vapour. It was hoped that due to turbulence and the change in the direction of the vapour stream that the majority of the entrainment would be eliminated due to coalescence on the thermal shield and the de-entrainer walls. To minimise errors due to partial condensation of the equilibrium vapour phase the whole of the equilibrium chamber was enclosed in a silvered evacuated jacket and the external surface of the entire still well lagged. The co-current passage of the vapour and liquid together with the mixing effect caused by the vigreux points would, it was hoped, eliminate any error due to the existence of concentration gradients in the boiling liquid. Errors in the sampling of the liquid phase due to backmixing were minimised by taking the sample from two thirds of the way up the downcomer tube and allowing the still to operate for more than 10 minutes at the steady state. Finally, however, carefully the heater inputs were adjusted it, was impossible to eliminate entirely small fluctuations in the vapour and feed flowrates.

7. Discussion of Results.

7.1 Application of consistency tests to Cathala still data.

The experimental vapour liquid equilibrium data is given in tables - with the graphs of vapour composition against liquid phase composition shown in figs. 15-18. The data for the system ethyl acetate-n-butanol is in close agreement with that of Davies et al (D3) but shows considerable scatter. In the n-butanol-n-butyl acetate system an azeotrope was detected at a concentration of 72.6 mole % n-butanol, in contrast to the value reported by Brunjes and Furnas (B19) of 72.9 mole % and Sheinker and Persleni's (S9) value of 78.0 mole %. However the azeotropic boiling point was found to be 117.2°C at 760 mm Hg against the former's 116.5°C and the latter's 116.9°C. The azeotropic data was confirmed by direct measurement in the Oldershaw column. For ethyl acetate-n-butyl acetate, the only available data for comparison is that of Davies et al (D3). The slightly anomalous values they reported could be attributed to the use of the three term Antoine equation with slightly erroneous constants. Before correlating the data with one of the previously discussed liquid phase models, consistency tests were carried out to check for the presence of systematic error. The tests used were Ulrichson and Stevenson's (U1) modification of the local area test of Stevenson and Sater (S12) and a version of the Herington test (H5) due to Samuels (S4). In addition the data was tested during the Barker fit of the data to the liquid phase model by the method suggested by Van Ness (B21) and others. Because the different data sets exhibit different levels of random error and also may deviate systematically from each other, this analysis should give some indication not only of the reliability of the Cathala flow still but also that of the consistency tests used.

Figures 17 and 18 are $y-x$ against x plots for the two systems ethyl acetate-n-butyl acetate and n-butanol-n-butyl acetate. Both the data based on refractive index analysis and those obtained by G.L.C. analysis are shown. The ethyl acetate-n-butyl acetate system plot shows that the refractive index data lie very well on the smooth curve. The G.L.C. results, as expected show a higher random error. Further, a curve drawn through them would not be identical with that drawn through the refractive index points. An examination of the same plot for the azeotropic system n-butanol-n-butyl acetate, shows first that the differences $y-\chi$ are much smaller for this system and record that there is a higher level of random error in the refractive index data in this system. Since the two pure components have refractive indices that lie closely together this is to be expected. The azeotrope compositions are not the same for the two methods of analysis (refractive index 72.6%, G.L.C. 72.2%). Since the higher figure was confirmed by the separate tests in the Oldershaw column, this indicates the possibility of systematic deviations between the data sets. An inspection of the plot shows a marked deviation above the azeotrope and less well marked deviations elsewhere. One rogue G.L.C. point may also be noted.

Fig. 16 is a plot of y versus χ for the azeotropic system n-butanol-n-butyl acetate. Here the refractive index data alone are plotted, with the limited of Brunjes and Furnas (B19) and Sheinker and Persleni (S9) included to enable a comparison between those data and the data of this work to be made. As already noted, the azeotrope composition and normal boiling temperature obtained from the vapour-liquid equilibrium experiments with

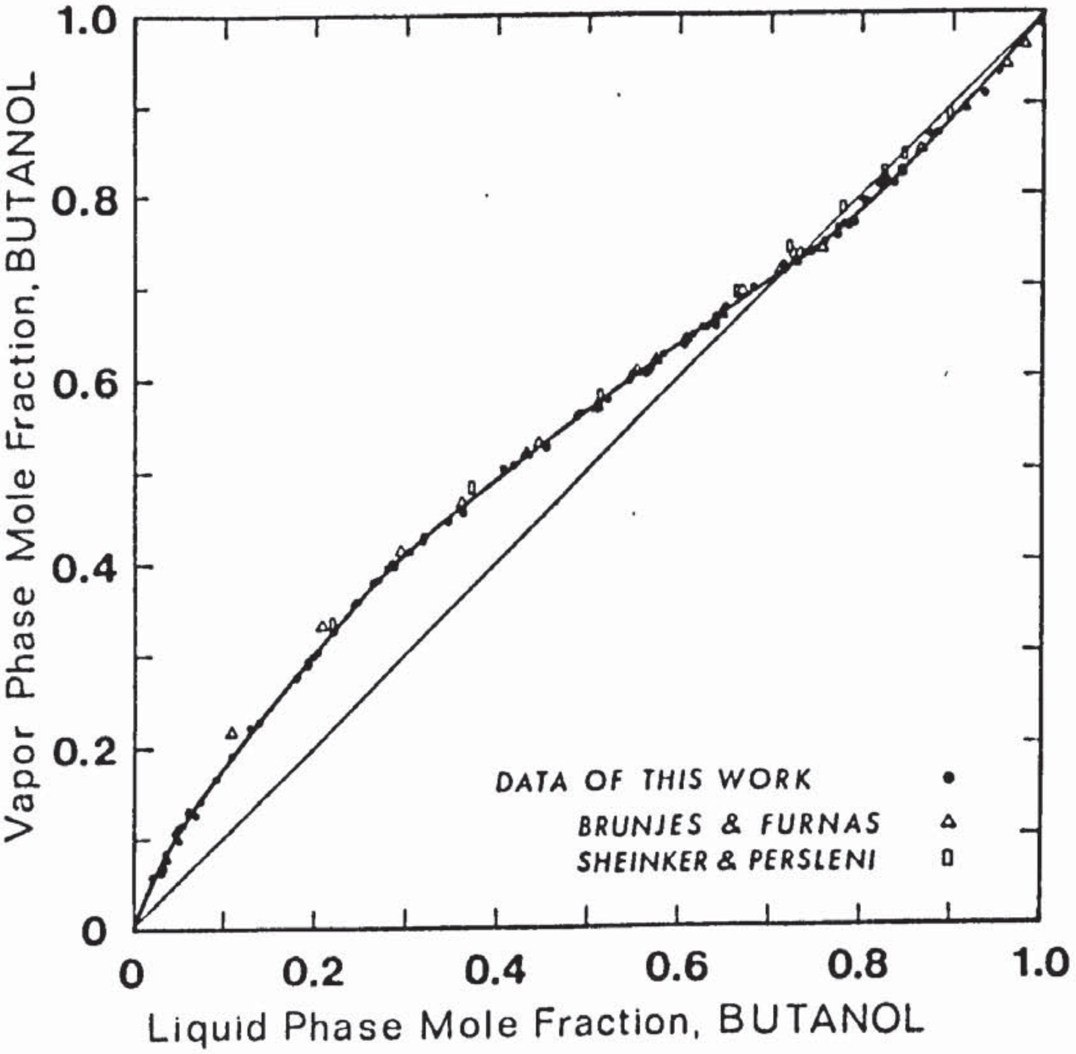


Fig. 15 - Plot of vapour phase mole fraction y against liquid phase mole fraction, x for the system n-butanol - n-butyl acetate

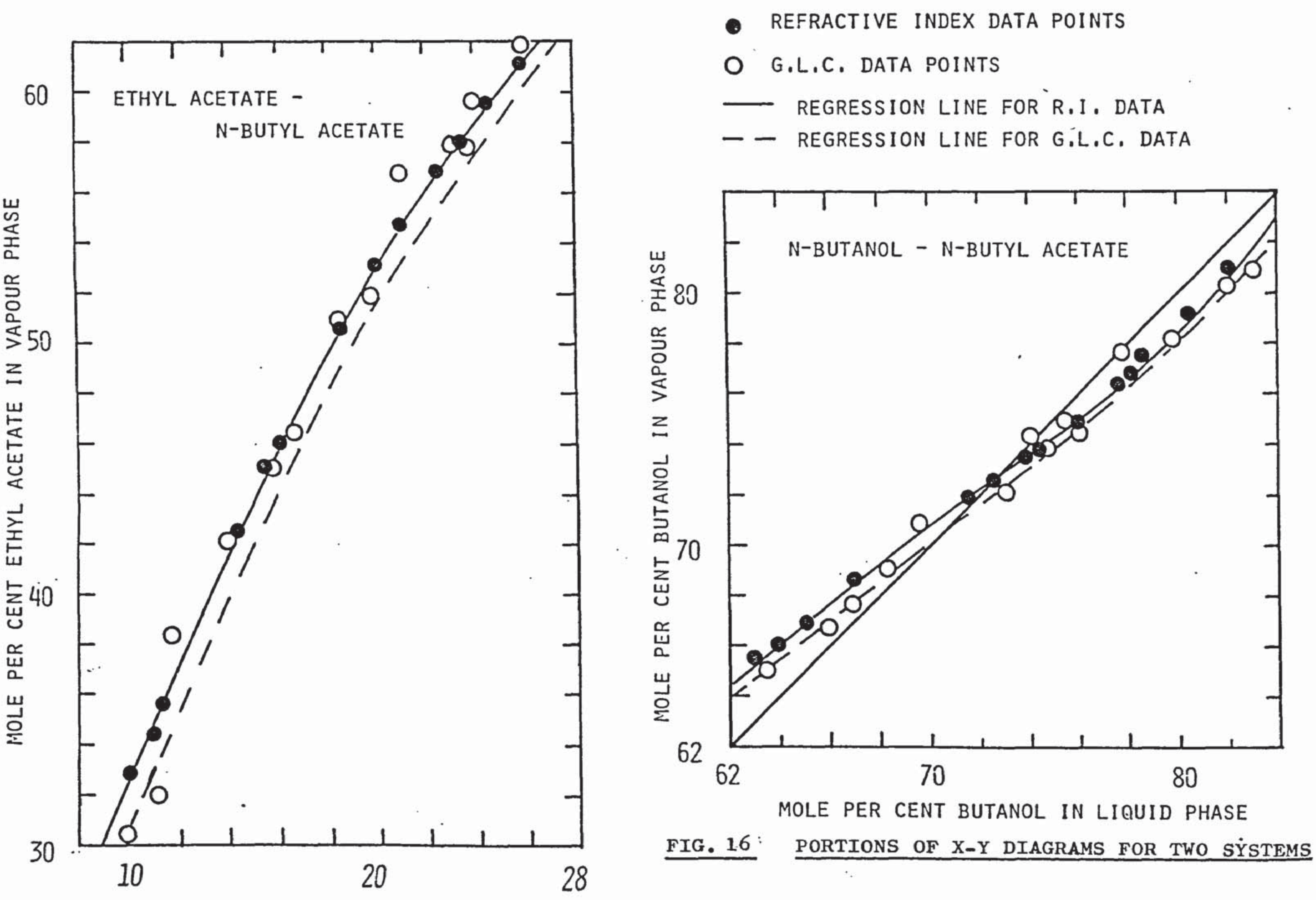


FIG. 16 PORTIONS OF X-Y DIAGRAMS FOR TWO SYSTEMS

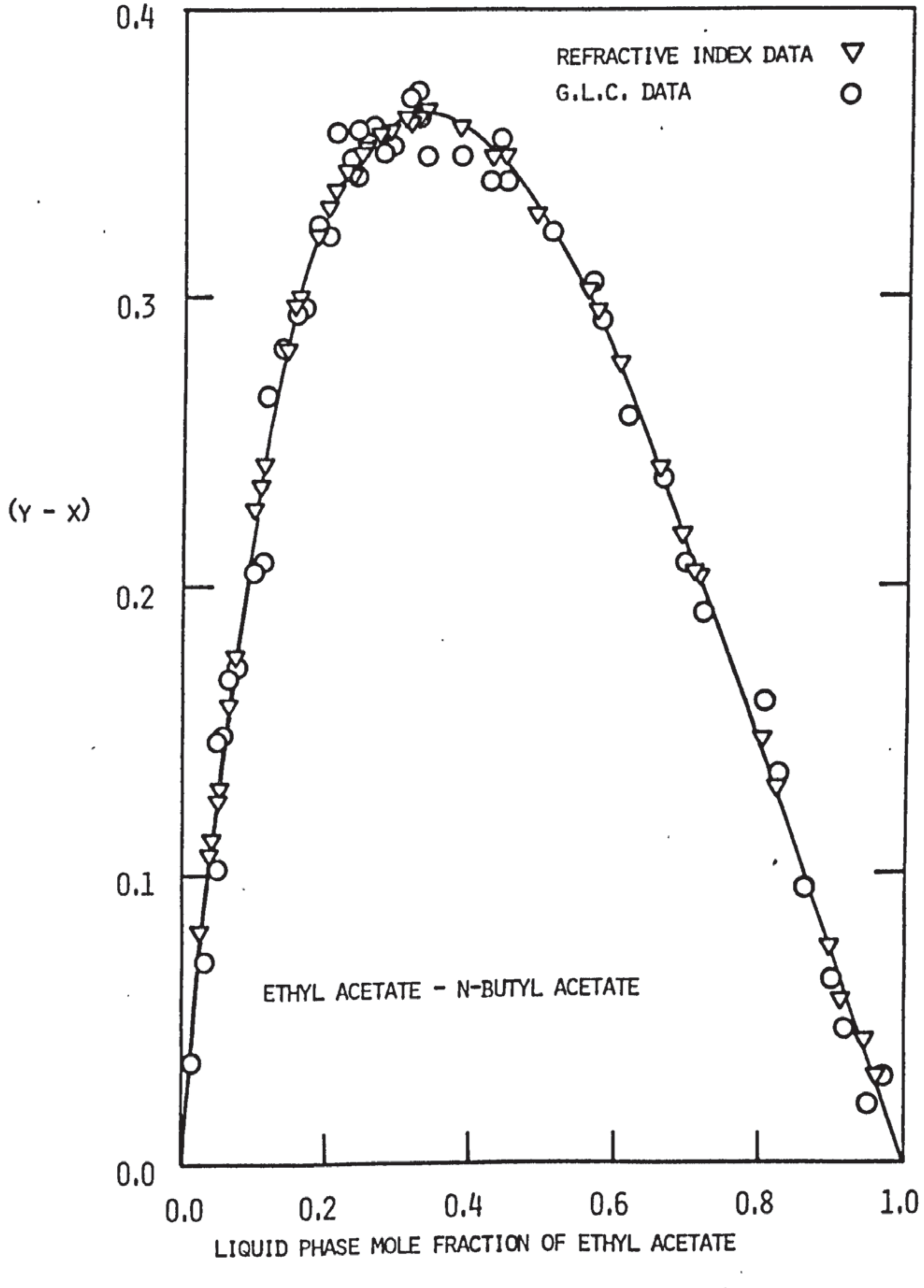


FIG. 17 (y-x) vs. x PLOT FOR ETHYL ACETATE - N-BUTYL ACETATE (SYSTEM 1)

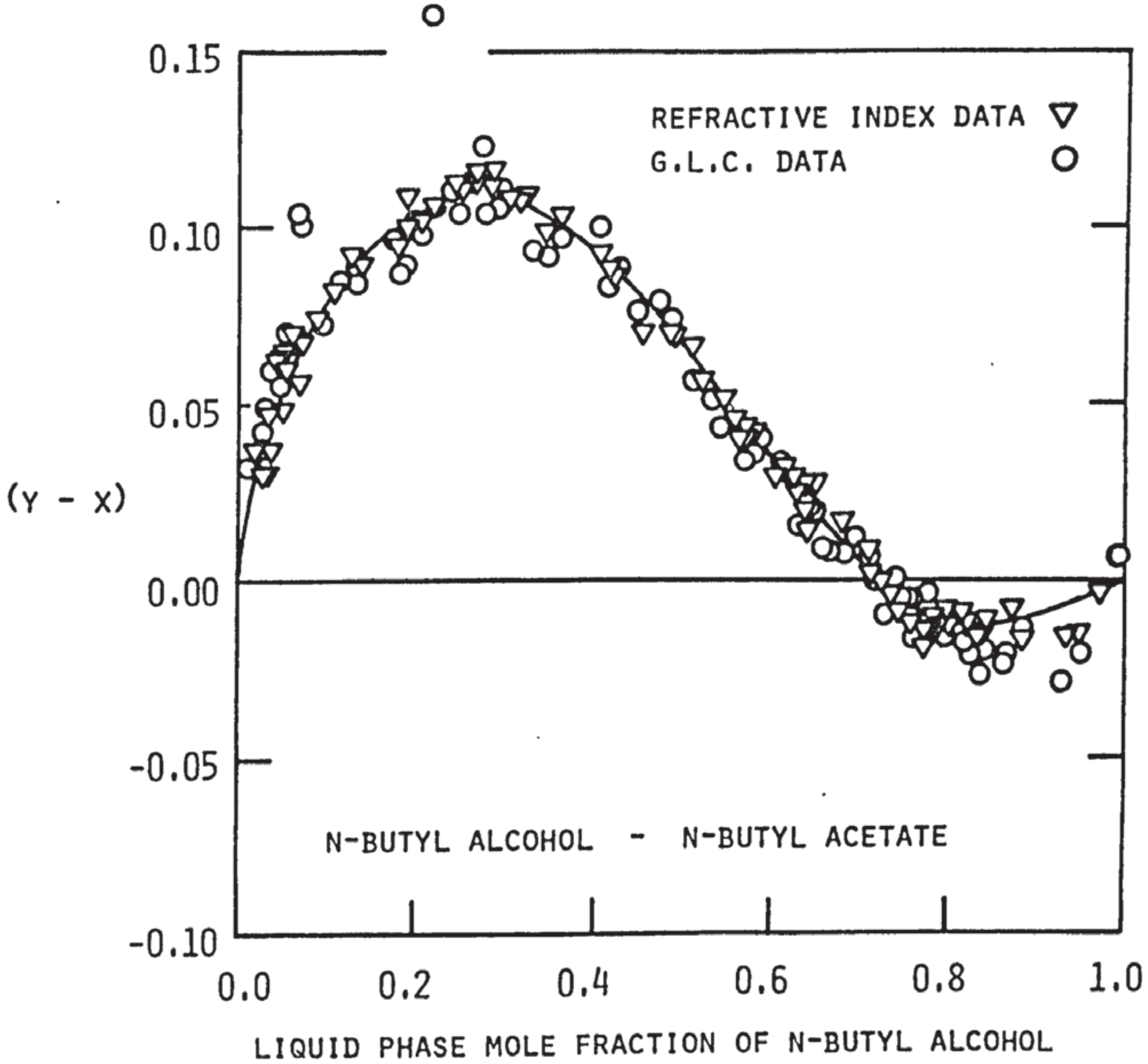
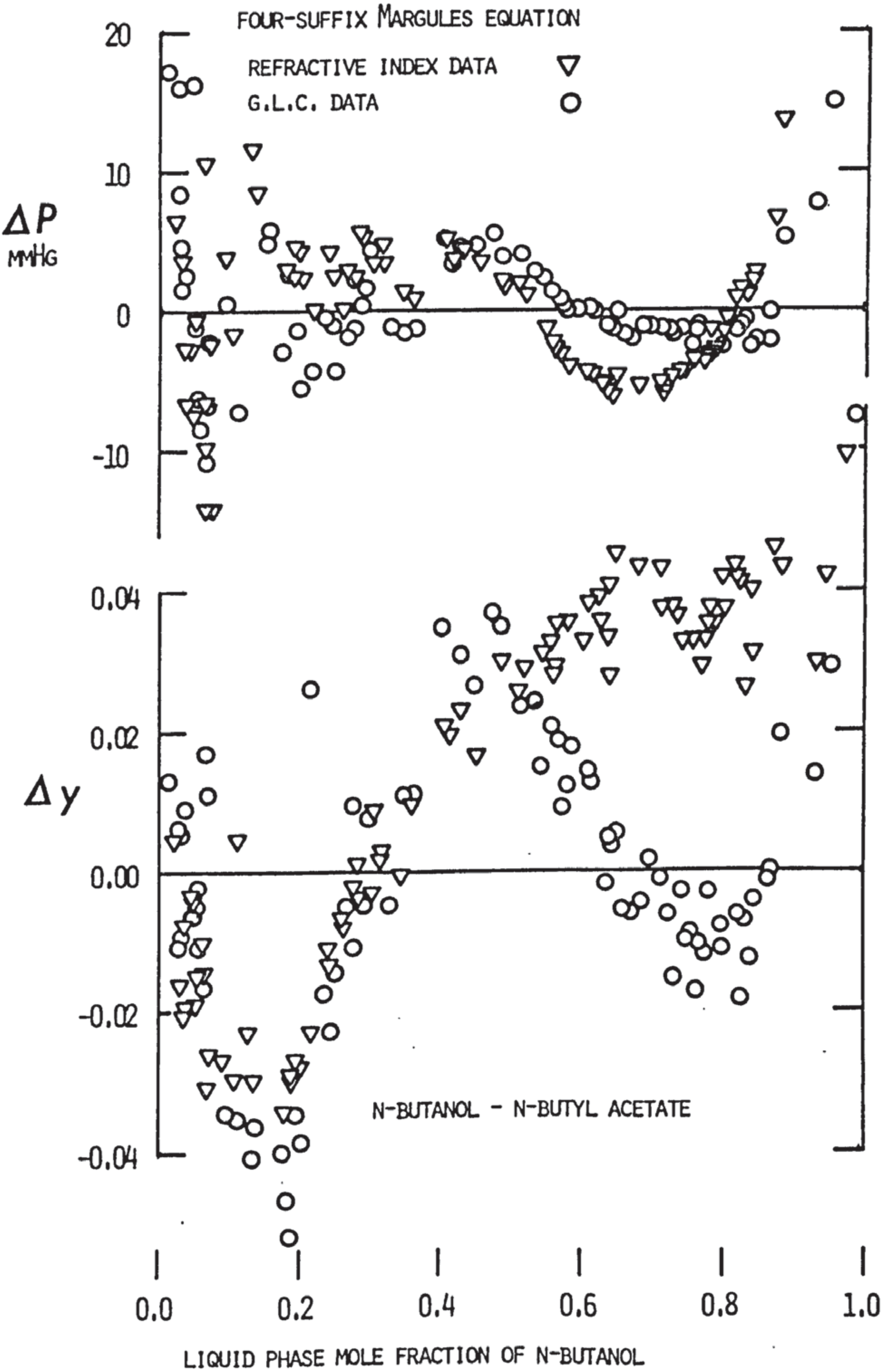


FIG. 18 (y-x) vs. x PLOT FOR N-BUTANOL - N-BUTYL ACETATE (SYSTEM 2) refractive index analysis are virtually identical with those obtained in the confirmation experiments on the 50 plate Oldershaw still. Comparison of the azeotrope conditions with those found by the other workers shows that in one case the boiling temperatures are close, but the composition is different from that obtained here and for the other the converse is true.

Application of the consistency tests should give results that reflect the different levels of random error for the various data sets. Essentially there exists in the data sets four different levels of random error, the level of error being least for the ethyl acetate-n-butyl acetate refractive index data ~~and greatest for the two sets of refractive index data~~, and greatest for the two sets of G.L.C. data.

The remaining figures are plots of the results of the consistency tests. In carrying out the first test (the F (a,b) test) the volume change on mixing term was neglected, and the enthalpy of mixing was calculated by the method of Orye (O3) from the Wilson parameters obtained in the Barker fit (B3) of the data used for the third test.

FIG. 19 ΔP AND Δy PLOTS FOR N-BUTANOL - N-BUTYL ACETATE



All the three tests were implemented by computer programmes developed for this work. In these vapour phase behaviour is modelled by the methods presented by Prausnitz et al (P6). The Barker fits were carried out with seven activity coefficient equations - Wilson, two and three parameter NRTL, UNIQUAC and the three Margules equations discussed by Van Ness (A1). Marginally better fits were obtained with the four suffix Margules equation. The values obtained for correlation parameters are summarised in Table A7.1. It will be noted that the different levels of random error embodied in the respective analytical techniques have a marked effect on the values obtained for the correlation parameters. For the systems ethyl acetate-n-butanol and ethyl acetate-n-butyl acetate all the equations correlated the refractive index data almost equally well. This is probably because the ethyl acetate-butyl acetate system is nearly ideal and the ethyl acetate-n-butanol data are of poor quality. In these circumstances the more complex NRTL and UNIQUAC equations offer no advantage over the Margules equation. However for the n-butanol-n-butyl acetate system the 3 parameter NRTL equation was significantly better.

The data obtained by G.L.C. based analysis provided different conclusions. The ethyl acetate-butyl acetate system was best fitted by the three parameter NRTL equation. This is possibly accounted for by the level of random error in the G.L.C. analysis giving the appearance of complex liquid phase behaviour. The n-butanol-n-butyl acetate system produces similar but not so pronounced trends.

The refractive index data was considerably better correlated than the G.L.C. data. This is confirmed by fig. 15 wherein portions of the V.L.E. curve for the ethyl acetate-butyl acetate and butanol-butyl acetate systems are reproduced showing the regression lines fitted to the G.L.C. and refractive index using the Wilson model. It can be seen that the G.L.C. regression line gives a deviation in calculated vapour composition from the experimental composition of approximately 1.5%. For the butanol-butyl acetate system the difference is not so large but the regression line predicts an azeotrope at a composition approximately 2% less than that obtained experimentally. It can be seen from Table A7.2 that for the systems containing butanol, correlating the data with alpha as an adjustable parameter produces values greater than the range 0.2 - 0.47 considered by Renon and Prausnitz (R11) to be physically significant. Taken with evidence from the consistency tests to be discussed later, it was felt that these values could possibly be due to liquid phase association effects in n-butanol. The ethyl acetate-butyl acetate showed no such behaviour, the values of alpha being close to the value of 0.3 fixed in the 2 parameter equation.

The results of applying the F (a,b) test to the system ethyl acetate-n-butyl acetate are shown in fig. 20. It can be seen immediately that the F (a,b) values are randomly distributed about the zero line. On closer examination it can be seen that the accuracy of the pressure and temperature measurements is such that their standard deviation contribute very little to that in F (a,b) which substantially depends on Sy. The analytical repeatability is 0.001 mole fraction, but it would not be reasonable to set Sy = 0.001 since this would make no allowance for random errors due to the remainder of the experimental procedure. Samuels et al (S4) used a value of 0.002 as typical of Sy obtained in work with recirculation stills. If this value is used here (which implies that the Cathala still + analytical technique combination of this work is equivalent to the typical recirculation still + analytical technique combinations of other workers), then the S_F ban plotted is obtained. Only 9 data points lie outside this band, with 80% of the total of

FIG. 20a RESULTS OF F(a,b) TEST FOR ETHYL ACETATE - N-BUTYL ACETATE

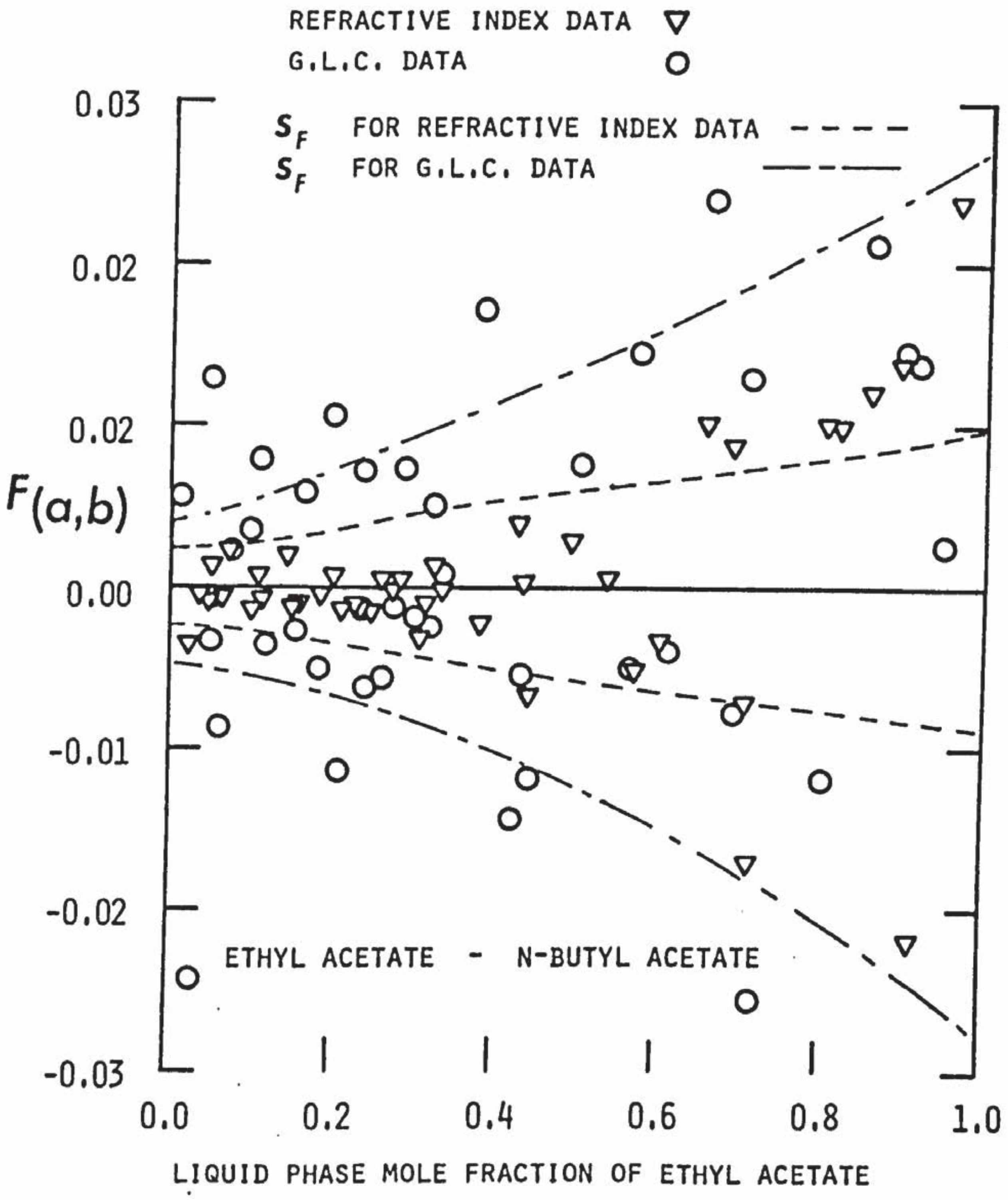
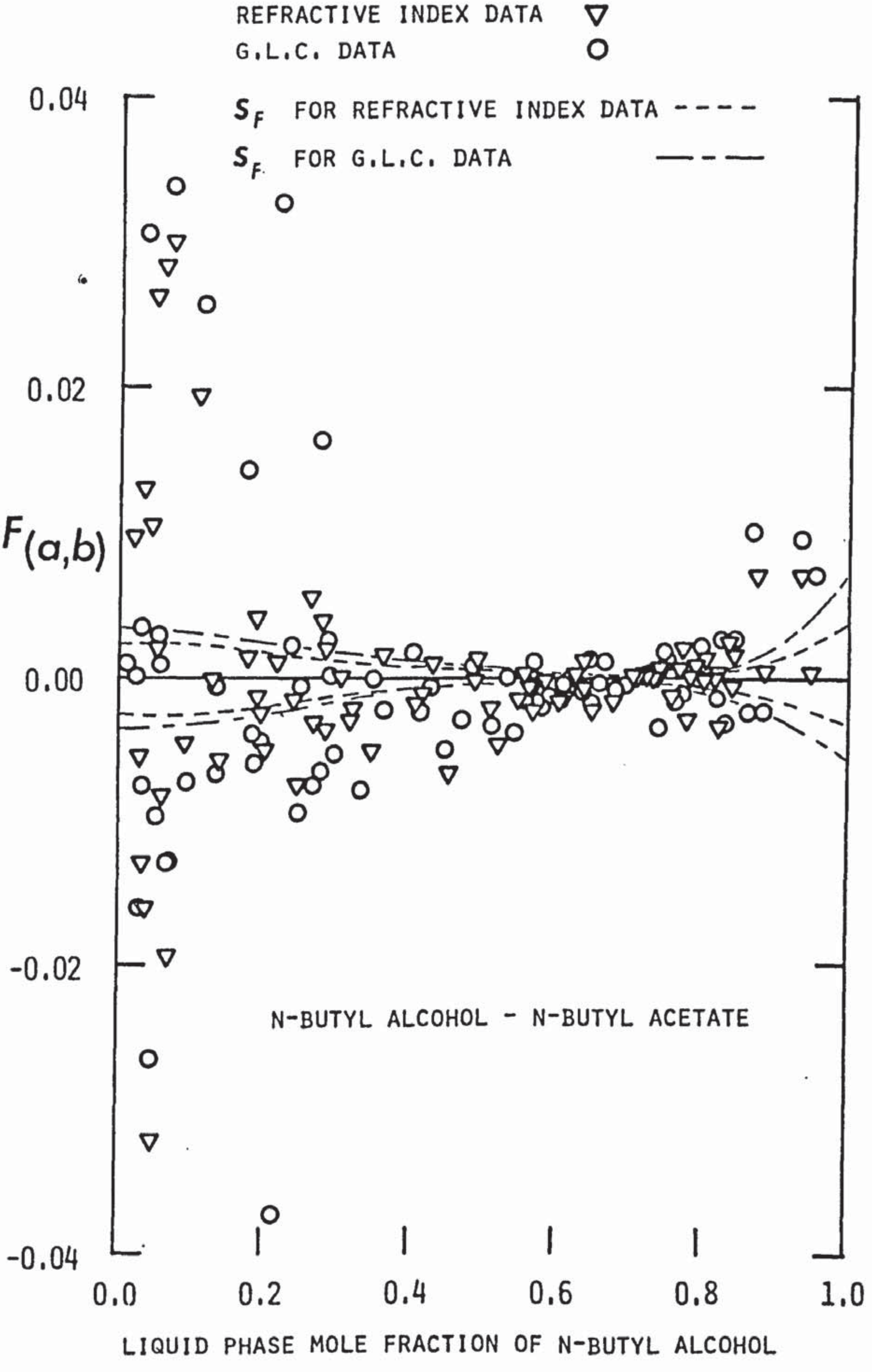


FIG. 20b RESULTS OF F(a,b) TEST FOR N-BUTANOL - N-BUTYL ACETATE



46 within it. Hence the F (a,b) test may be said to be satisfied for the refractive index data. Those values which do lie outside the band do so at one end of the concentration range and a slight broadening of the band (equivalent to Sy of 0.003) would bring all but three points within the band. Since all the data points in the low ethyl acetate range lie inside the band (which is statistically highly improbable), Sy may well be as low as 0.001 in this area. In any event, it can be concluded that the performance of the Cathala still on this system is as good as that of any other equilibrium still. For the data obtained by G.L.C. analysis, the standard deviations must be set at a higher value, one of Sy = 0.004 gives the error band shown. Once again the data appear to meet the test. The two sets of data as shown in fig. 20, are in general agreement, with slight systematic divergences at the two extremes of the concentration range and in the middle of the range - but the divergence is at worst no greater than the uncertainty in y of ± 0.002. It is not surprising, therefore, that the consistency test gives no indication of any such divergence. Comparison of the F(a,b) plots of this work with those of Samuels et al (S4) shows that the spread of the F(a,b) values is quite typical. (The lower F (a,b) values of this work are due to adjacent data points being closer.) The $\sum_{j}$ Fj test is

clearly satisfied by the data, the random variations in F (a,b) cancel out.

Similar conclusions may be drawn from the deviation plot test (B21). The goodness of fit on the pressure for both refractive index and G.L.C. data sets is similar to that shown by Abbott et al (A1) for the three binaries they considered, the fit on the vapour composition for the refractive index data is also comparable to theirs and shows no marked systematic deviation. The G.L.C. data pressure fit is almost as good as that for the refractive index data, but the overall higher level of random uncertainty in this data is reflected in the y-deviation plot. Here again no systematic deviation can be detected. Abbott (A1) et al concluded that while some degree of inconsistency existed in the data examined, the data was reasonably reliable. The same may therefore be said of the data of this work. The Cathala still can be assumed to give results comparable to those of other workers.

For the system n-butanol-n-butyl acetate the results of the F (a,b) test shown in fig. 20 are less clear cut. Again, the values of F (a,b) are randomly distributed above and below the zero line, for both

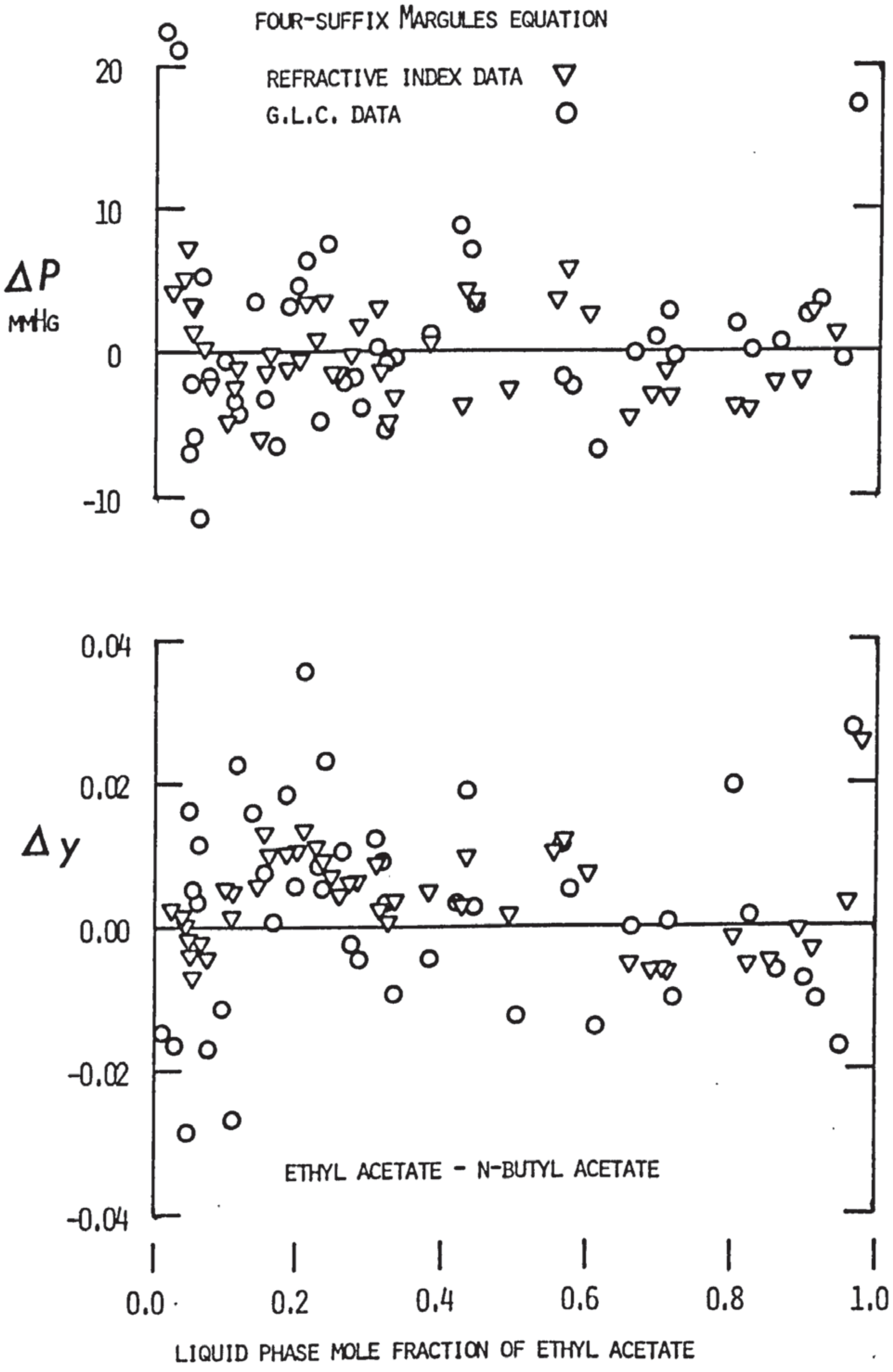


FIG. 21 ΔP AND Δy PLOTS FOR ETHYL ACETATE - N-BUTYL ACETATE

data sets. But the Sf band is much narrower, due to the lower relative volatility in this system, and to the fact that the distance between data points is so small. Only in the middle of the composition range can the F (a,b) values be considered as at all lying in the expected 3 Sf band (corresponding to the 99% confidence band). The Sf values shown here were calculated with standard deviations in Sy of 0.003 for the refractive index data (reflecting the smaller refractive index difference of the two components), and of 0.004 for the G.L.C. data as before.

The data at the two extremes, then, exhibit a degree of thermodynamic inconsistency, but the source of this inconsistency appears to be random in nature. The $\sum_j Fj$ test is in fact satisfied by these data. As a check on the application of the F (a,b), it was rerun with only 46 data points, spread throughout the range, without an attempt to select only the best data. This confirmed the results obtained with all the data. Fig. 21 sets out the deviations obtained from the Barker fit to the data sets for this system. The pressure fit shows a larger random variation at the lower end of the composition range than for the first system, reflecting the greater uncertainty in the analysis and this parallels the results of the F (a,b) test. But the scatter appears to be random. In the rest of the composition range random error is absent and the deviations follow a sinusoidal pattern. This same trend is evident throughout the y deviation plot for the refractive index data. This plot shows very marked devations in the vapour composition.

Van Ness (V6) has demonstrated that an artificially introduced systematic error in the y values shows up clearly in the y deviation plot, and a similar systematic error in y, with an approximately linear dependence, say on $(y-x)$, would account for the deviation observed here. This would indicate some systematic malfunction for the still, such as incomplete separation of liquid and vapour. But since no such deviation is apparent for the other system, with y values even further removed from the x values, this seems an improbable explanation.

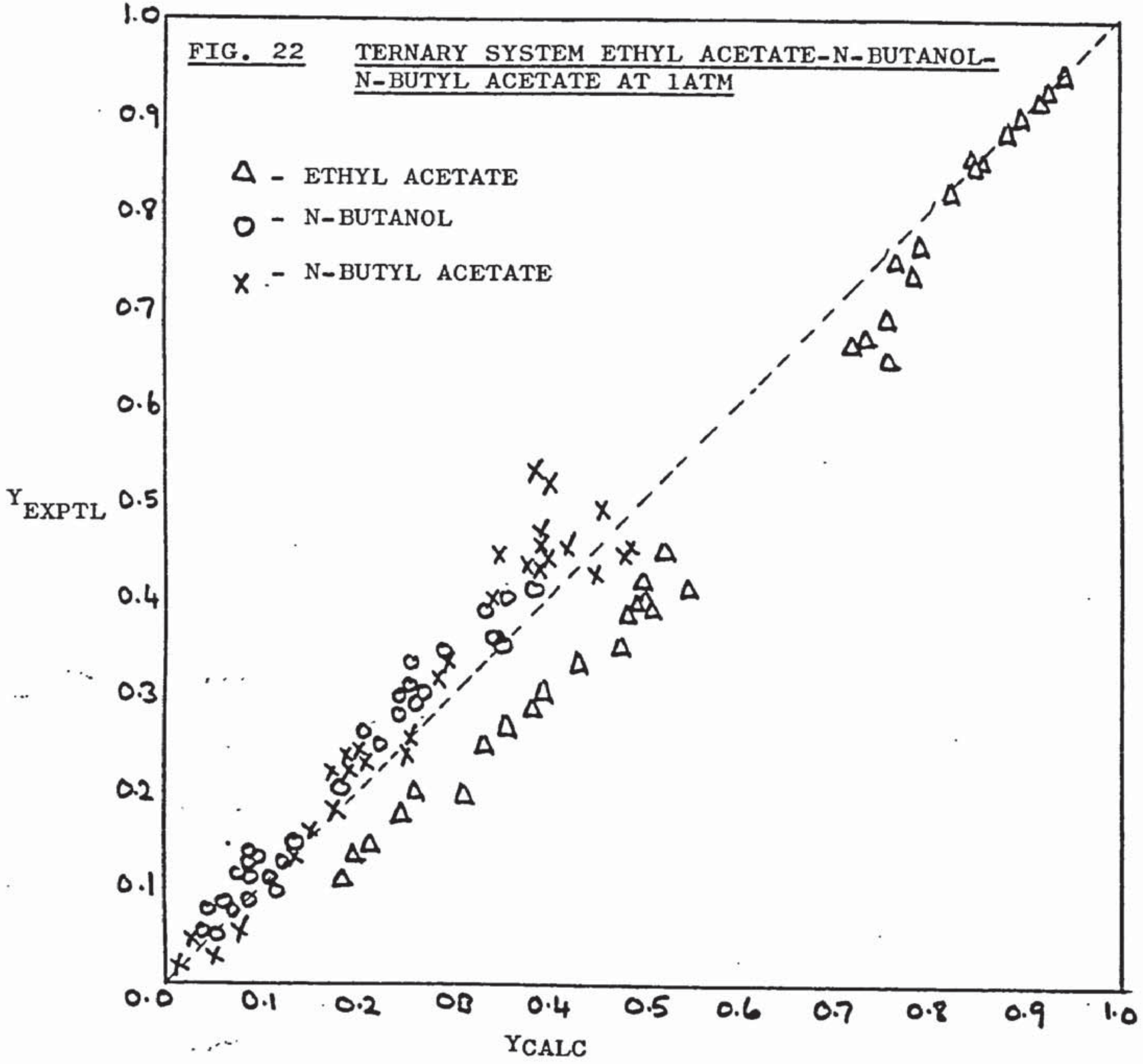
As will be discussed later a similar systematic deviation in the y values when fitting vapour liquid equilibrium data for the toluene-acetic acid system by the Barker method is apparent. There are known association effects in this system and it seems that a similar phenomen is occuring in this system. There is considerable literature on association in alcohols (N5) (K10) (W4) but this point has not been pursued further.

The G.L.C. data shows the same trend, but the effect is less pronounced and the y deviations follow a different and at first, more consistent, trend. The test, then, has distinguished between the two sets of data, but not in any really useful sense. In the absence of any experience of the application of this test to associating mixtures it might well have been deduced that the refractive index data was grossly inconsistent - a contention not supported by the F (a,b) test. The G.L.C. data would have appeared to be the more consistent over a great part of the composition range, a possibility not supported either by the direct evidence available from the (yχ) /plot or by that from the experiments confirming the azeotrope composition. The difference between the two data sets noticeable on the (y-χ) plot have not clearly shown up in either consistency test, but this may well be due to both sets having too high a degree of random error. If either set alone were available the F (a, b) test would suggest that the data at the two extremes ought to be omitted from any subsequent fitting procedure. The y deviation or Barker fit test would give a more problematic conclusion. The G.L.C. set might well have been accepted as being of reasonable reliability, while the refractive index data could well have been judged to show a systematic error which in fact it does not have.

7.2 Examination of experimental multicomponent results.

Figs. 22 and 23 are plots of y (experimental) against y (calculated) for the ternary system ethyl acetate-n-butanol-n-butyl acetate and the quaternary system ethyl acetate-ethanol-n-butanol-n-butyl acetate. The experimental data was determined by Davies et al (D4) while the calculated data was predicted using the Wilson equation from the binary data of Davies and this work. It is evident that there is some disagreement indicating possibly that the experimental data is in error or that the Wilson equation does not represent the system adequately. In view of earlier comments as to the complex behaviour of n-butanol it is felt that it is probably the latter case.

FIG. 22 TERNARY SYSTEM ETHYL ACETATE-N-BUTANOL-N-BUTYL ACETATE AT 1ATM



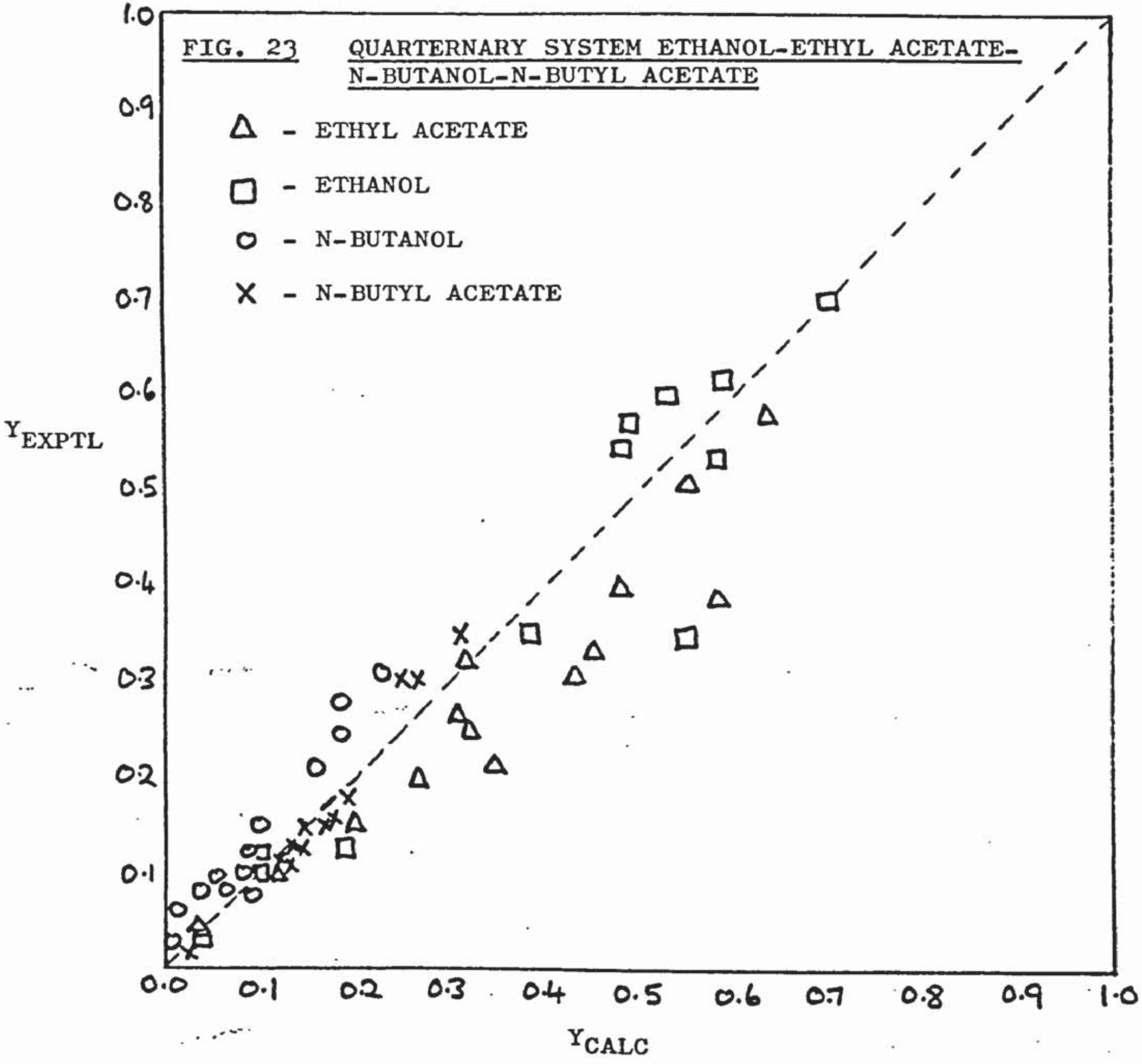


FIG. 23 QUARTERNARY SYSTEM ETHANOL-ETHYL ACETATE-N-BUTANOL-N-BUTYL ACETATE

7.3 Modelling of the system acetic acid - toluene.

Another system in which association is known to cause anomalies is the acetic acid-toluene system. A representative set of results in which various approaches to modelling this system are tested is presented in figs. 24 to 27. In the initial stages, the four liquid phase equations (Wilson, two and three parameter NRTL, UNIQUAC) were fitted to all the data available, without any liquid phase corrections for association. Figures 24 and 25 present the results of this stage. Fig. 24 shows the data of Zawidski at 69.94°C and of Meehan at 70°C. As mentioned above both sets of data have been tested for consistency by other methods, and are also the only duplicated sets. In this plot the fits obtained from all four equations are presented. It is immediately apparent that each equation performs equally well. The fit to total pressure is reasonably good since ± 0.5 kPa corresponds to about ± 1.6% (the approximate ± 1.0% error band is shown). The discrepancies observed in y are, on the other hand, quite substantial, and show little random error. Both the systematic variation of the Δ P and of the Δ y suggests either that the data is

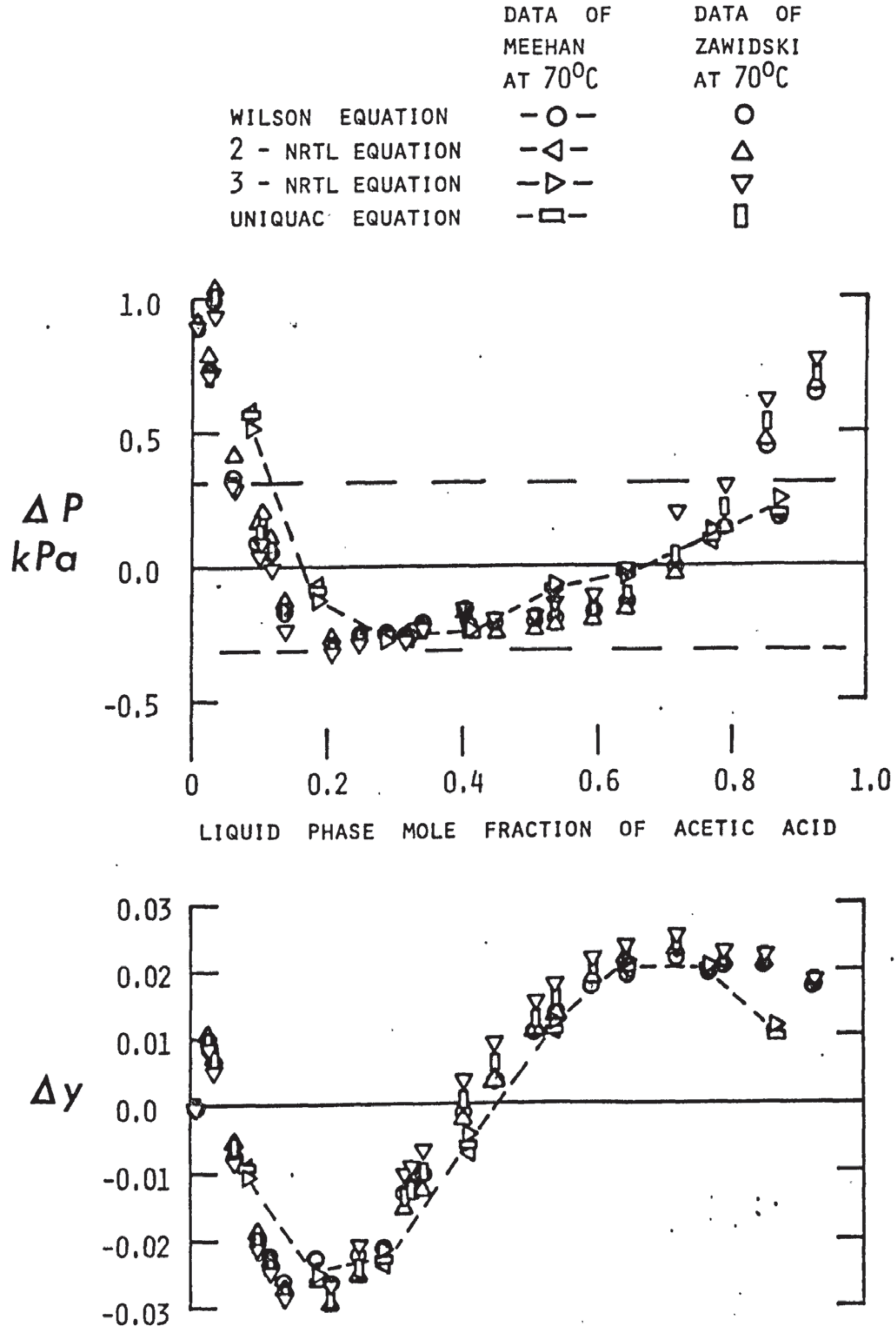


FIG. 24 PRESSURE AND VAPOUR COMPOSITION DEVIATION PLOTS FOR THE 70°C DATA OF MEEHAN AND ZAWIDSKI. VAPOUR PHASE CORRECTION ONLY. FOUR LIQUID PHASE MODELS.

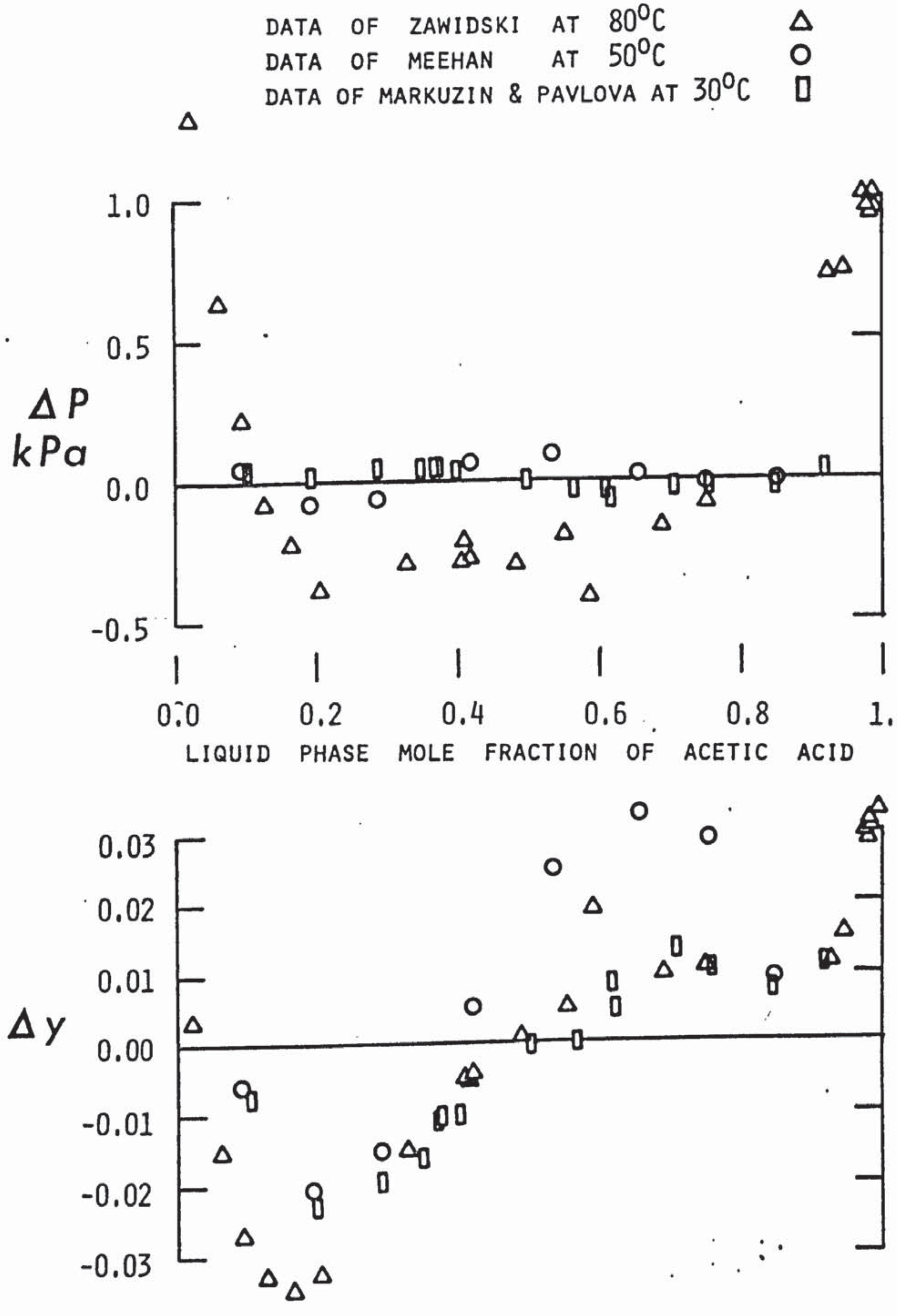


FIG. 25 DEVIATION PLOTS FOR THE DATA OF ZAWIDSKI (80°C), MEEHAN (50°C) AND MARZUKIN AND PAVLOVA (30°C). VAPOUR PHASE CORRECTION ONLY. THREE-PARAMETER NRTL EQUATION.

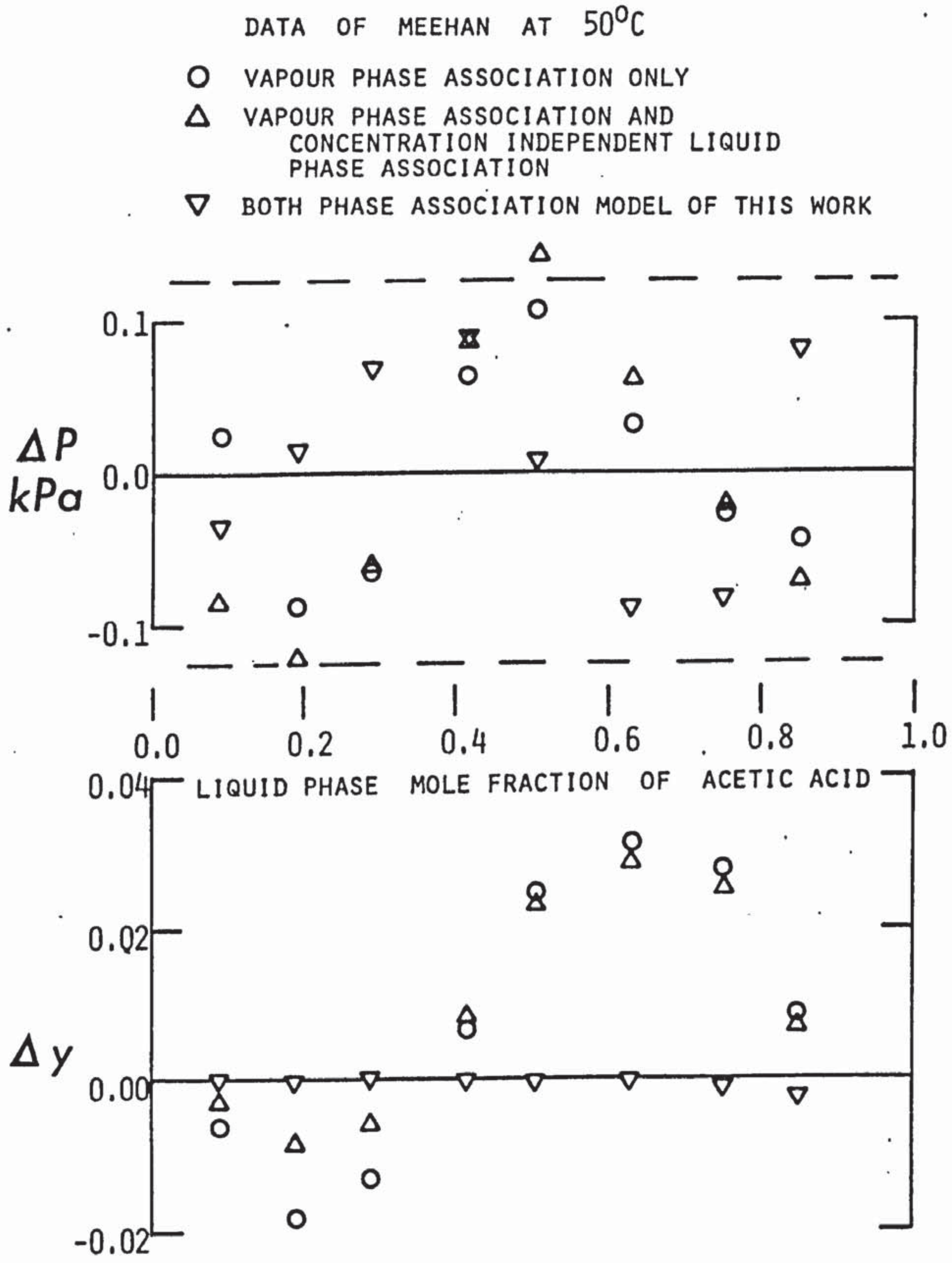


FIG. 26 DEVIATION PLOTS FOR THE DATE OF MEEHAN AT 50°C. COMPARISON OF MODELS WITH NO LIQUID PHASE CORRECTION, COMPOSITION INDEPENDENT ASSOCIATION CONSTANT, AND COMPOSITION DEPENDENT ASSOCIATION CONSTANT. WILSON EQUATION.

not consistent or that the model used in the Barker fit does not represent the liquid phase behaviour well enough. It should be noted that the data of Zawidski and those of Meehan were gathered some 65 years apart, by different techniques. If systematic error were the cause of the discrepancies it would not be expected to give practically identical deviations in the results from two such diverse data sets. This strongly suggests that the liquid phase model without association is, indeed, inadequate. This conclusion is strengthened by fig. 25.

In fig. 25, the results of fitting all the remaining isothermal data by the three parameter NRTL equations are presented. The same systematic deviations in y occur over the whole temperature range, and are quite marked for the 50°C data of Meehan, where a good fit on the pressure is obtained. This strengthens the supposition that the models used for the fits are inadequate. When a similar fit was applied to the data of Haughton at 750 mm Hg, the pressure fit was only marginally acceptable, and the deviations in y did not show that same pattern. As Haughton indicated that some of his pressures were only approximate, the pressure data in his data-set may be more unreliable than the y values and the data should be discarded. This does not mean that his x-y values should be rejected but does mean that his data set as a whole cannot be tested for thermodynamic consistency and is not of use in this work.

The fit obtained for the data of Volpicelli and Zizza was extremely bad. But the only data given in their paper have been calculated from the actual data obtained, and a comparison of their x-y plot for the toluene-acetic acid system with the tabulated values shows a marked difference. The activity coefficients produced in the fit bear no resemblance to those obtained by them. Hence while their original data may well be accurate, their published data appear to be erroneous. Accordingly their data were not used in this work.

The next figures (figs. 26 and 27) present the results of data fits using the three models - vapour phase association only, vapour phase plus constant liquid phase association, and vapour phase plus the concentration dependent k derived above. Fig. 26 gives the results from Meehan's data at 50°C using the Wilson equation.

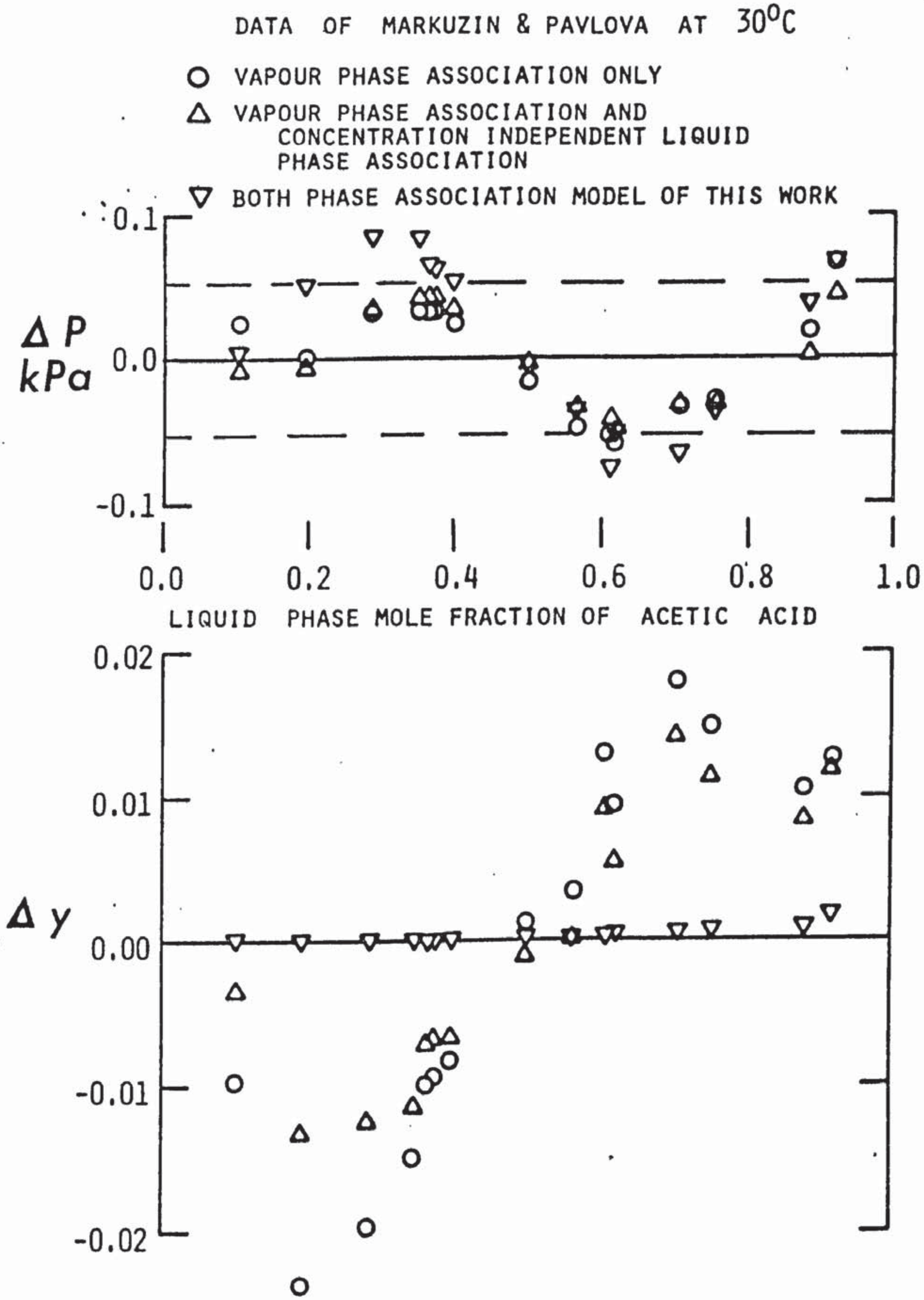


Fig. 27 Deviation plots for the data of Markuzin and Pavlova at 30°C. Comparison of the three approaches to the liquid phase. Wilson equation.

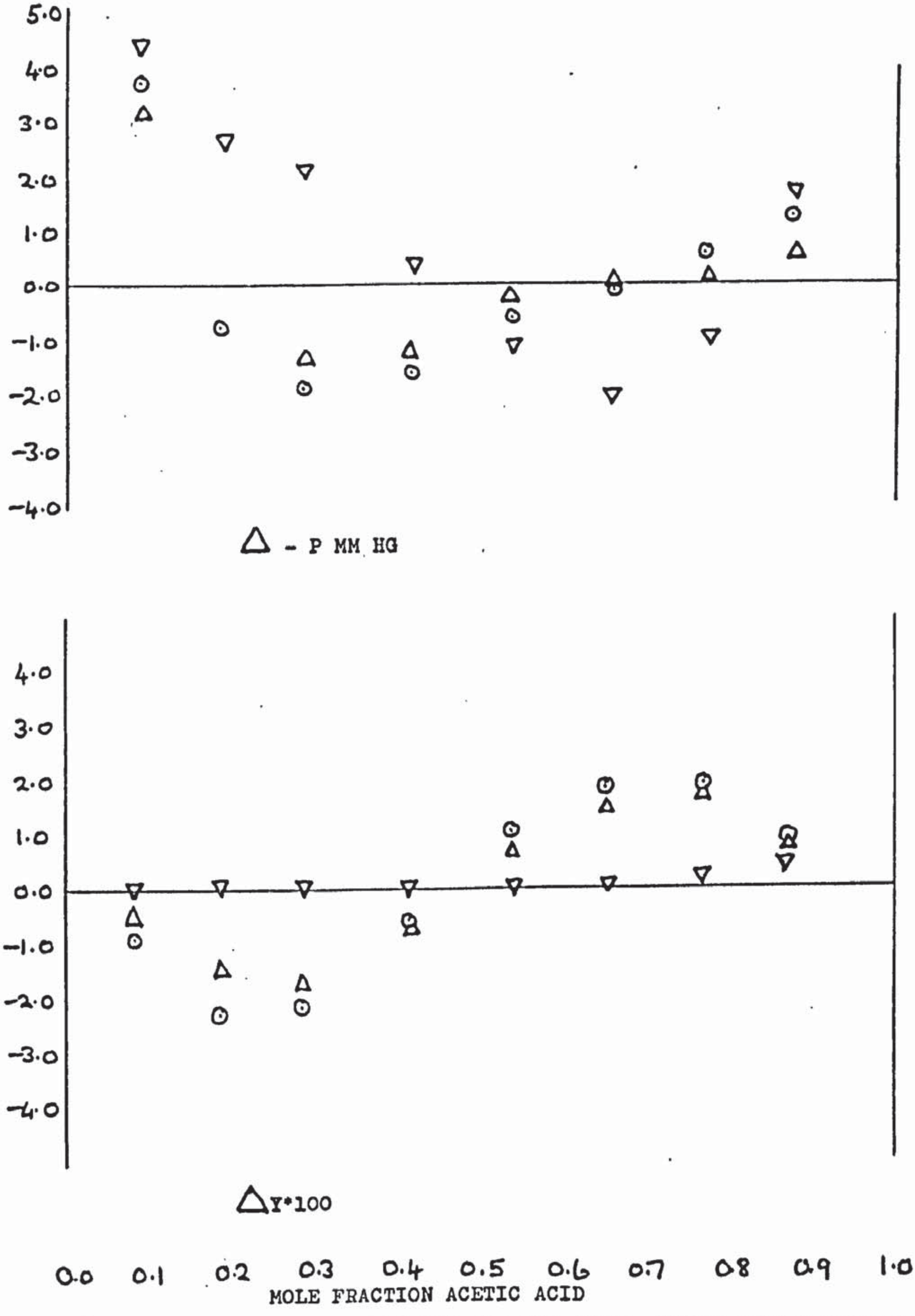


FIG. 28 SYSTEM ACETIC ACID-TOLUENE AT 70°C (M15) USING WILSON EQUATION

⊙ VAPOUR CORRECTION ONLY, △ USING K_0 ONLY, ▽ CONCENTRATION DEPENDENT K

The results are striking. Use of a concentration independent κ_A gives some improvement of the Δ_y, but the use of concentration dependent κ_m gives an equally good fit on the ΔP, with practically no error on the vapour phase mole fractions. The results for Markuzin and Pavlova confirm this (fig.27). Note that the pressure fit is more random in nature. An adapted form of Liszi's relationship (L8) for κ gave results virtually identical with the $\kappa = \kappa_A$ case. Figs. 28 to 30 show similar results for the remaining isothermal data.

It may be concluded that first an adequate model of the liquid phase behaviour is only obtained if a concentration dependent liquid phase association constant is used.

Secondly, since when this extended model is used the vapour phase composition differences $y^{exp}-y^{calc}$ become small and of the same order as the likely analytical uncertainties, it may be concluded that the isothermal data available in the literature is in fact consistent to within its experimental accuracy.

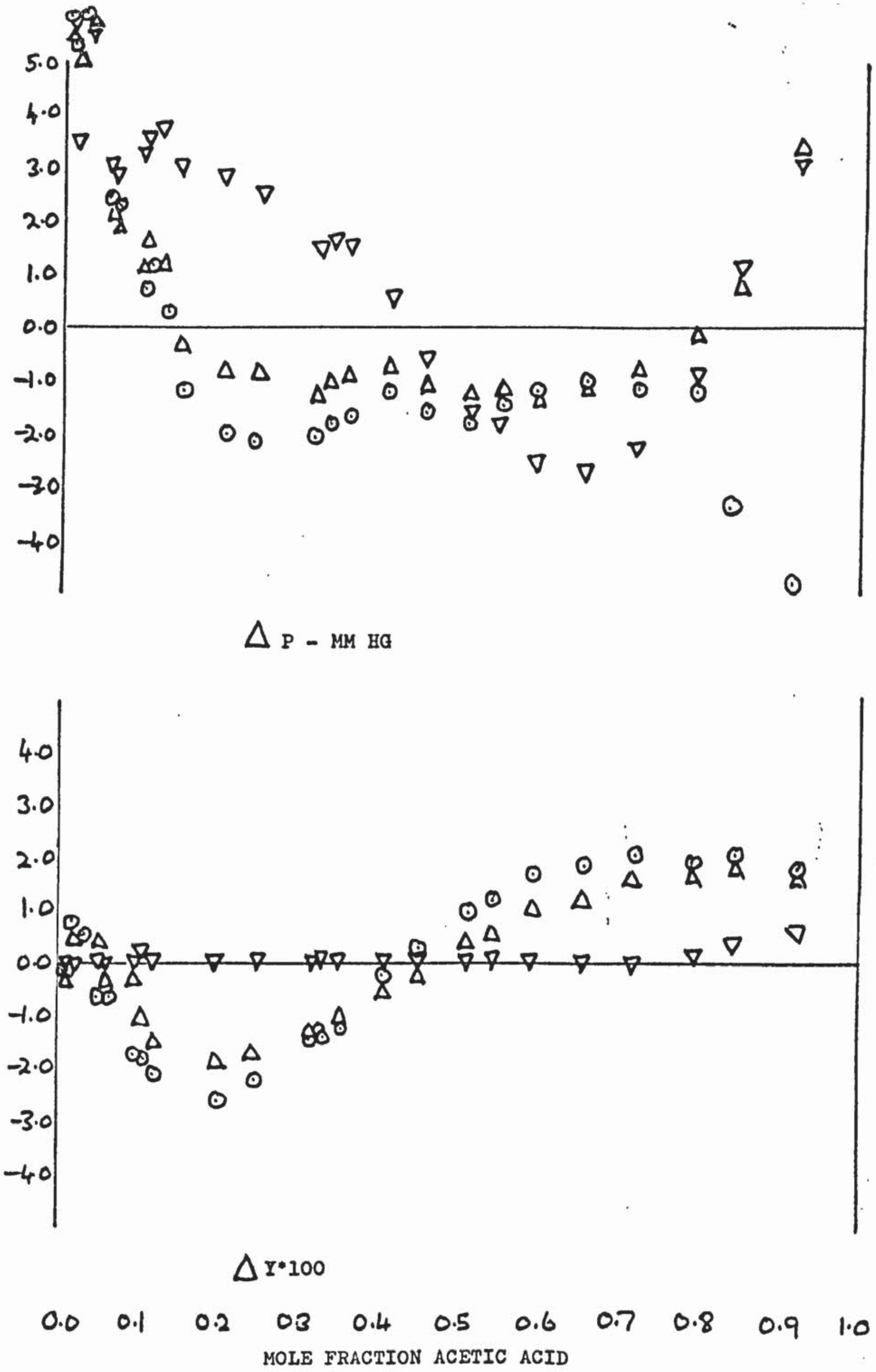


FIG. 29 SYSTEM ACETIC ACID - TOLUENE AT 69.94°C (Z1) USING WILSON EQN

⊙ VAPOUR CORRECTION ONLY, △ USING K_0 ONLY,

▽ USING LIQUID PHASE MODEL

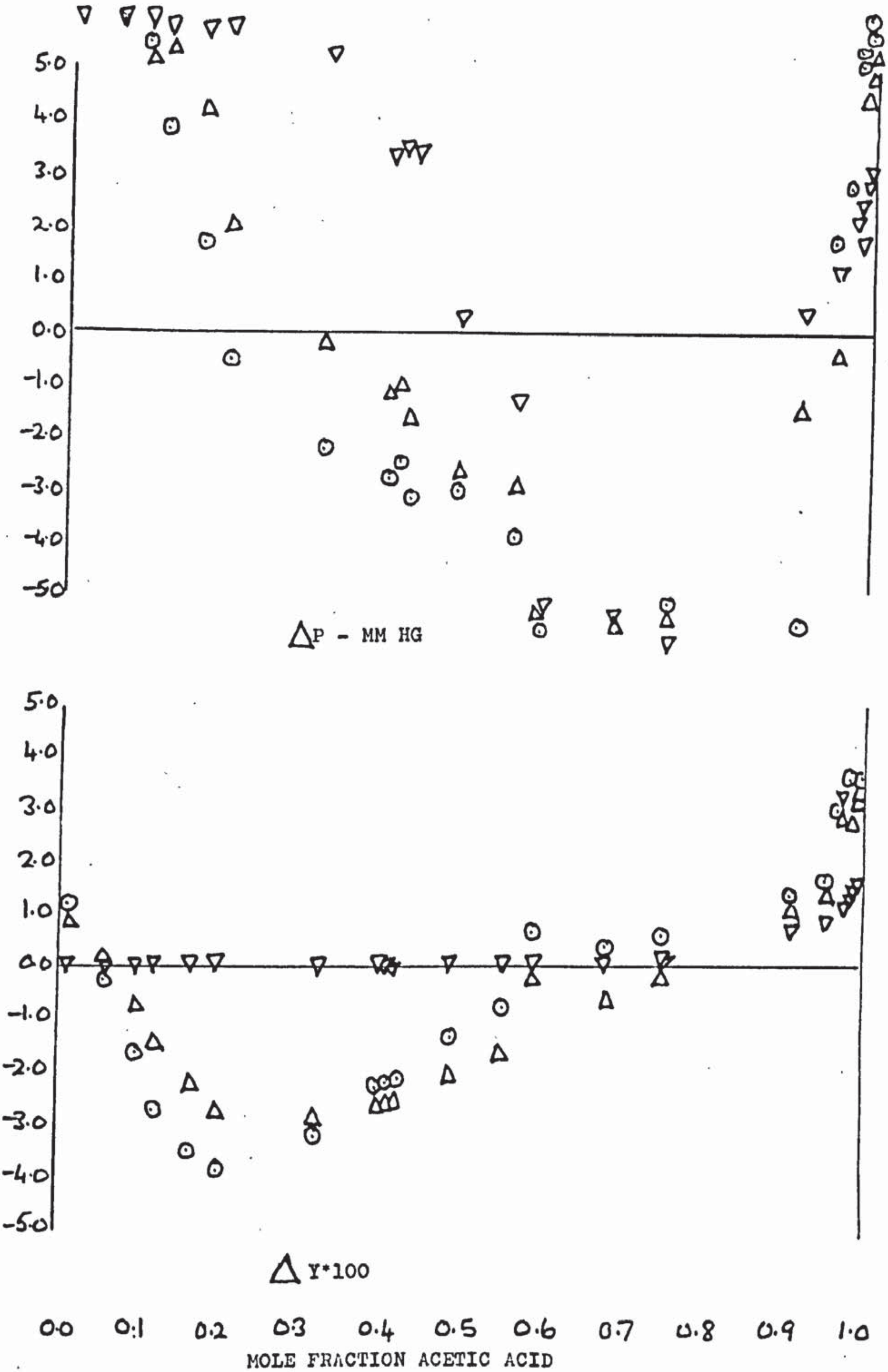


FIG. 30 SYSTEM ACETIC ACID-TOLUENE AT 80.05°C (Z1) USING WILSON EQUATION

⊙ VAPOUR CORRECTION ONLY, △ USING K_0 ONLY, ▽ CONCENTRATION DEPENDENT K

7.4 Modelling of other systems containing acetic acid.

Extension to systems of acetic acid and other hydrocarbons yields similar results. The isothermal data of Meehan for the system acetic acid-benzene at 30, 50 and 70°C when correlated using the vapour phase correction only and the various Gibbs-Duhem models appears to be consistent and accurately measured. Nevertheless the same non-random trend is evident which is eliminated only when the concentration dependent, K_m is used in the correction factors. Results for acetic acid-benzene at 30°C comparing the two approaches are shown in fig. 31. The isothermal data of Werner (W1) at 20°C shows similar results and also the data of Zawidski (Z1) at 49.99°C. This latter data set agrees well with that of Meehan at 50°C although it contains rather more random error. The isobaric data of Othmer (O8) and Garner, Ellis and Pearce (G1) at 760 mm mercury give very bad results when correlated with the vapour phase correction only and although significant improvement is obtained with the new model, the fit obtained is still not satisfactory. It is possible that these two data sets are inconsistent.

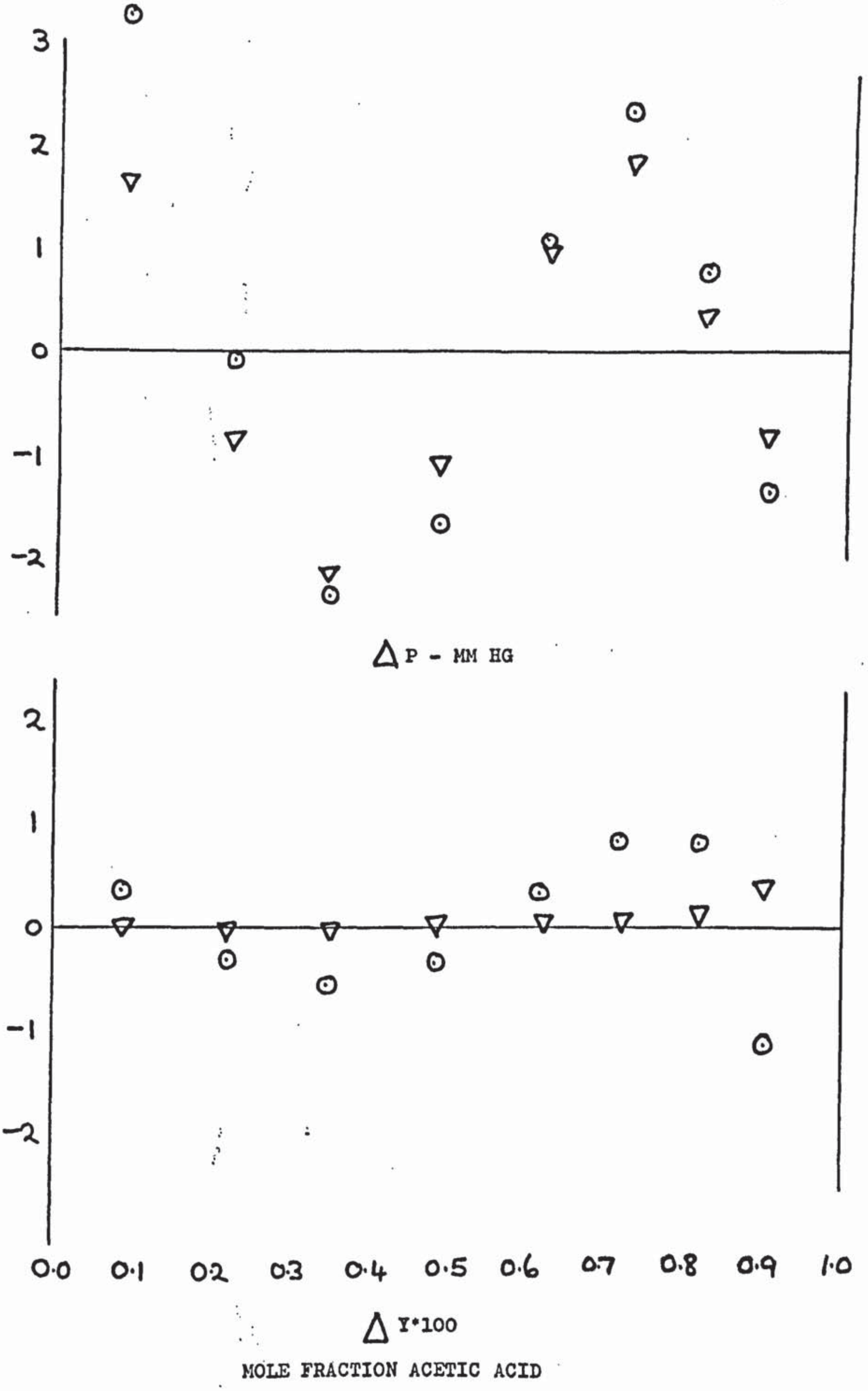


FIG. 31 SYSTEM ACETIC ACID-BENZENE AT 30 CENT (M15), USING WILSON EQUATION

⊙ VAPOUR PHASE CORRECTION ONLY, ▽ LIQUID PHASE MODEL

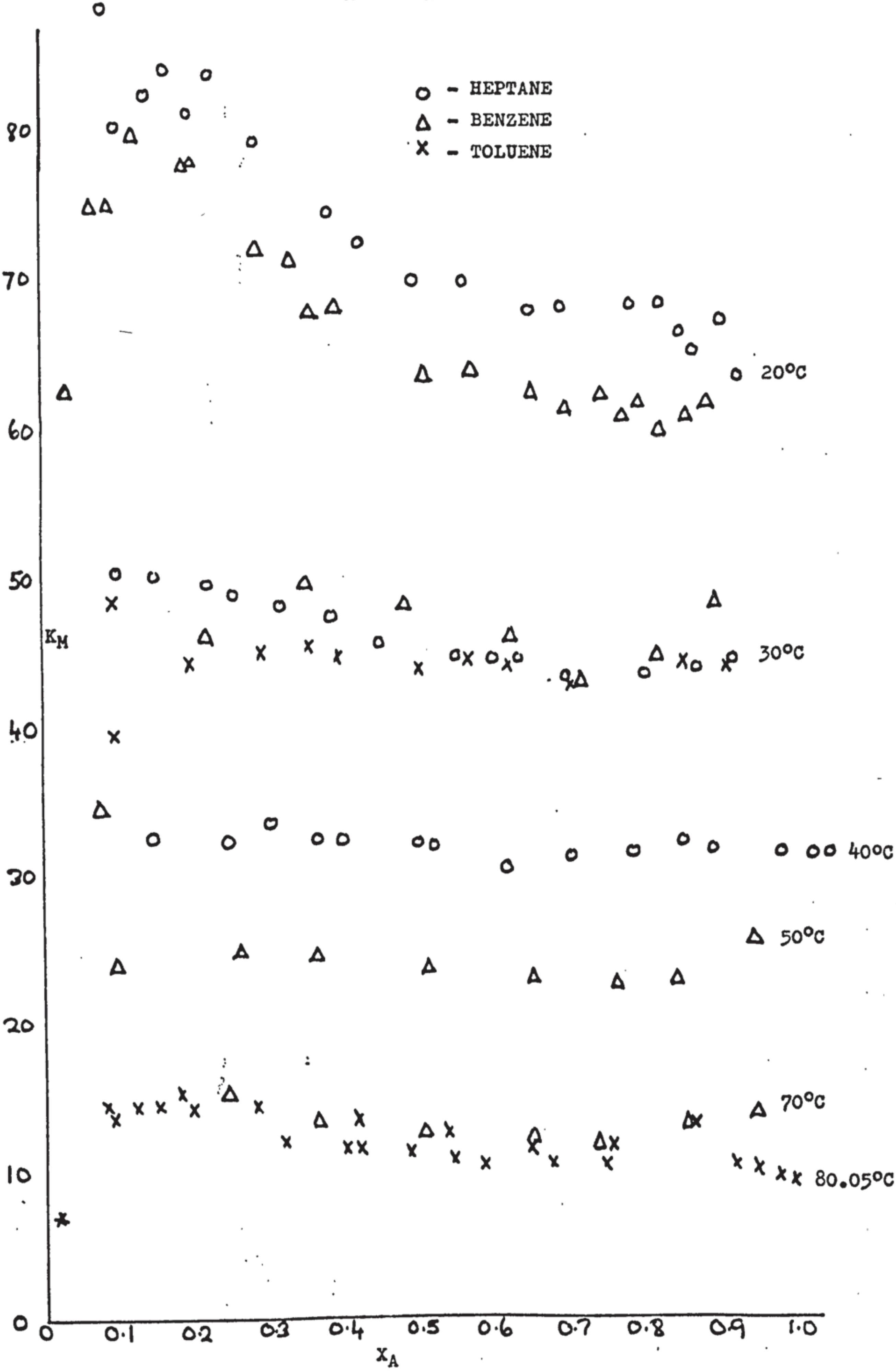
For the system acetic acid-n-heptane the isothermal data of Markuzin and Pavlova at 30°C, 40°C and 50°C, and Werner at 20°C are very well correlated with the vapour phase correction only. Application of concentration dependent correction factors further improve the results and the data is probably consistent and of high quality.

The data sets (B2) (M5) for the systems acetic acid-p-xylene and acetic acid-ethybenzene show significant non-random trends, even using the new model and may not be consistent. Similarly data for acetic acid-n-octane (S10) shows a non-random trend in the Δ y values at low values of acetic acid concentration. This data may be marginally inconsistent.

Finally the data of Zieborak (Z2) for the system acetic acid-n-decane is improved by the new approach and is probably consistent.

It can be seen that the relatively simple systems of acetic acid and hydrocarbons are considerably improved by using a concentration dependent liquid phase association constant, k_m, figs. 32 show plots

FIG. 32 EQUILIBRIUM CONSTANT, K_M V X_A FOR ACETIC ACID-HYDROCARBON SYSTEMS

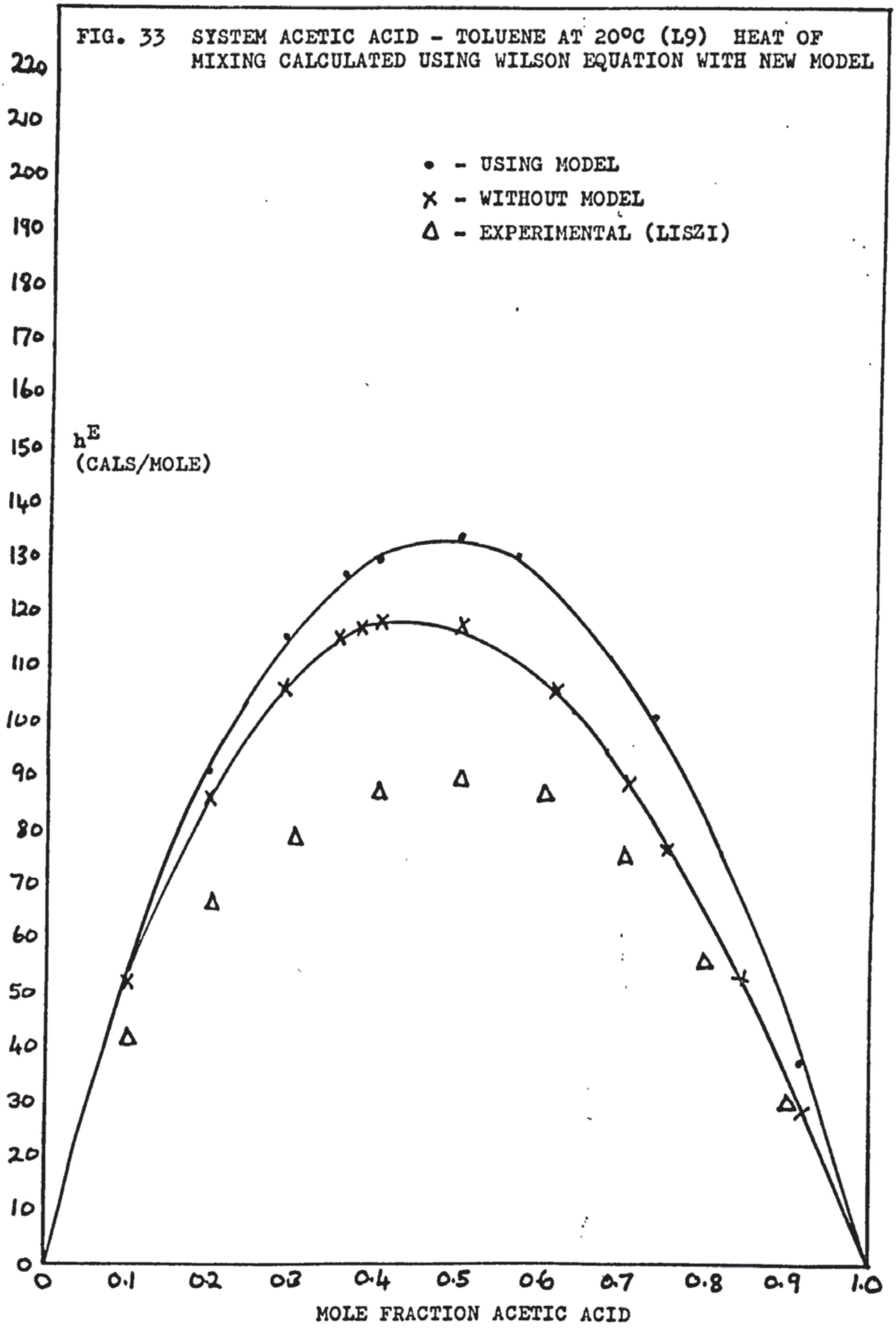


of k_m against liquid phase composition for the various systems. It will be noticed immediately, that for hydrocarbon systems the shapes of the curves are similar. This may be possible to produce a correlation of k_m against x in the manner of Liszi (L9) for different classes or compound. It will be seen later that this is true for all the classes of systems considered such as acetic acid-alcohols.

Another interesting feature of acetic acid-hydrocarbon systems is that parameters obtained during the fits to the isothermal data using the new model give predictions of the heat of mixing that are in quite close agreement with experimental data and in all cases a significant improvement over parameters obtained using the vapour phase correction only. This is particularly striking with the NRTL equation which normally requires temperature dependent parameters fitted across a wide range of conditions to give a good prediction. Figs. 33 to 38 show the results for acetic acid-toluene, acetic acid-benzene and acetic acid n-heptane all at 20°C.

The systems containing acetic acid and chlorinated hydrocarbons show identical results with the plots of

FIG. 33 SYSTEM ACETIC ACID - TOLUENE AT 20°C (L9) HEAT OF MIXING CALCULATED USING WILSON EQUATION WITH NEW MODEL



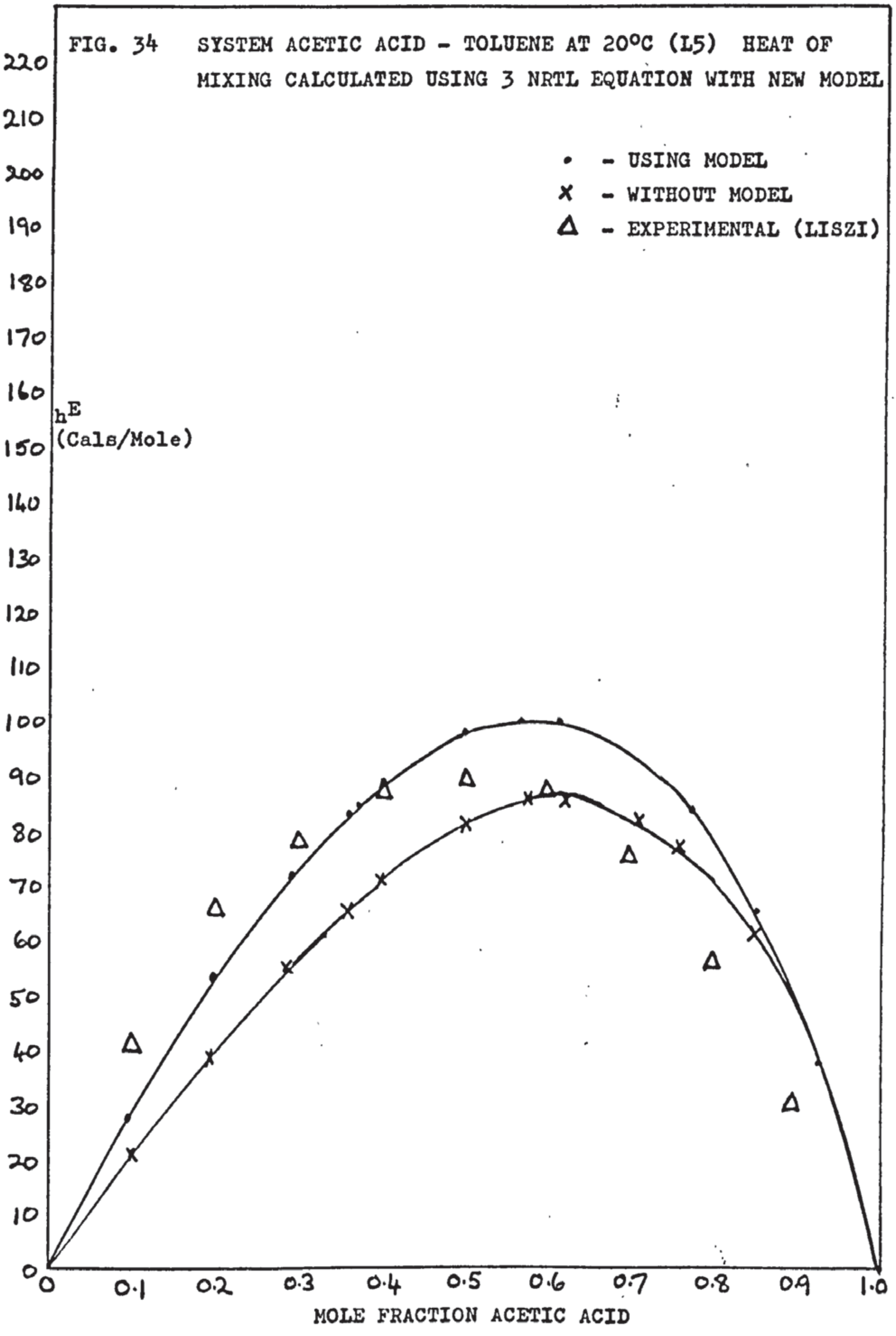
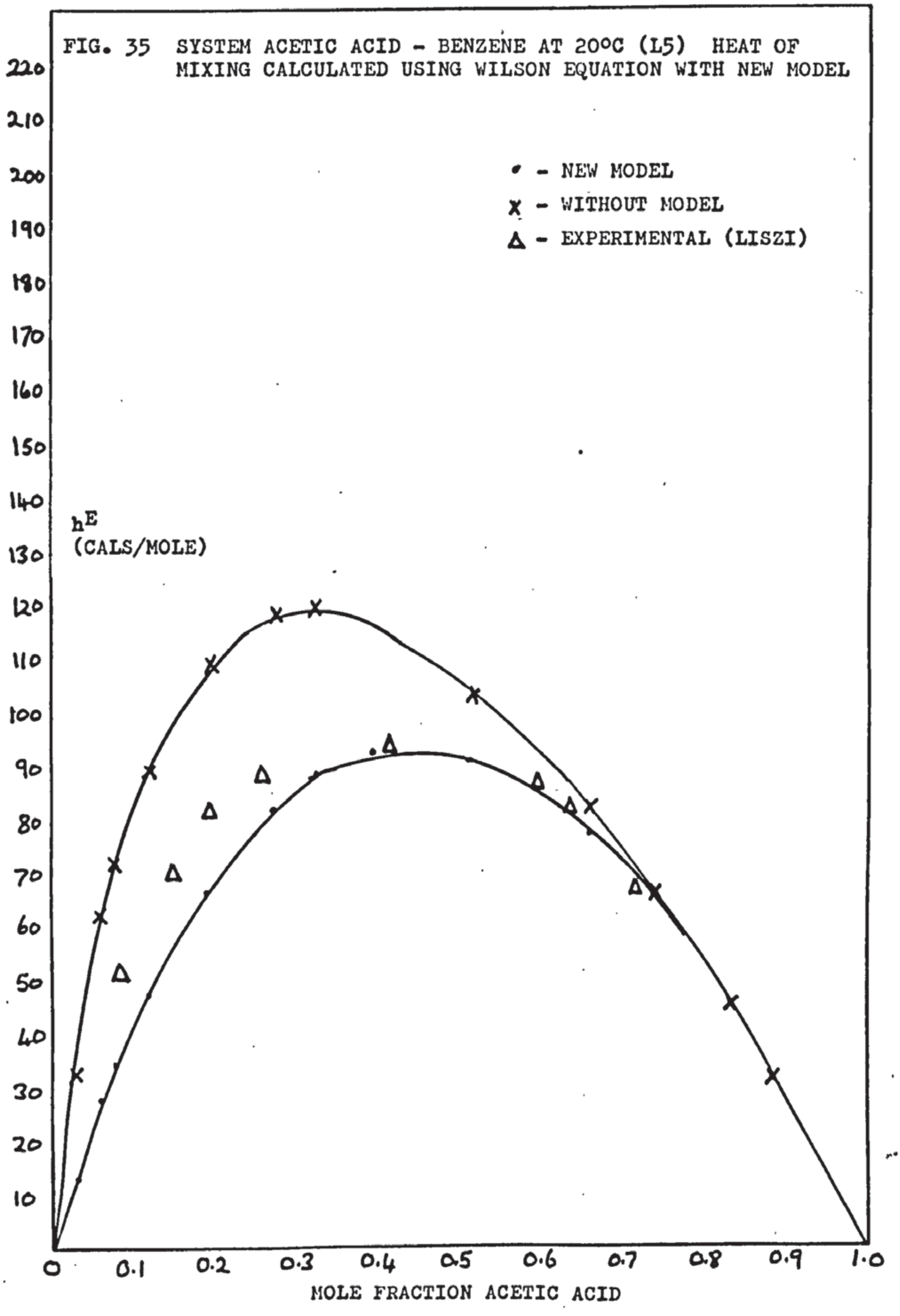


FIG. 34 SYSTEM ACETIC ACID - TOLUENE AT 20°C (L5) HEAT OF MIXING CALCULATED USING 3 NRTL EQUATION WITH NEW MODEL

FIG. 35 SYSTEM ACETIC ACID - BENZENE AT 20°C (L5) HEAT OF MIXING CALCULATED USING WILSON EQUATION WITH NEW MODEL



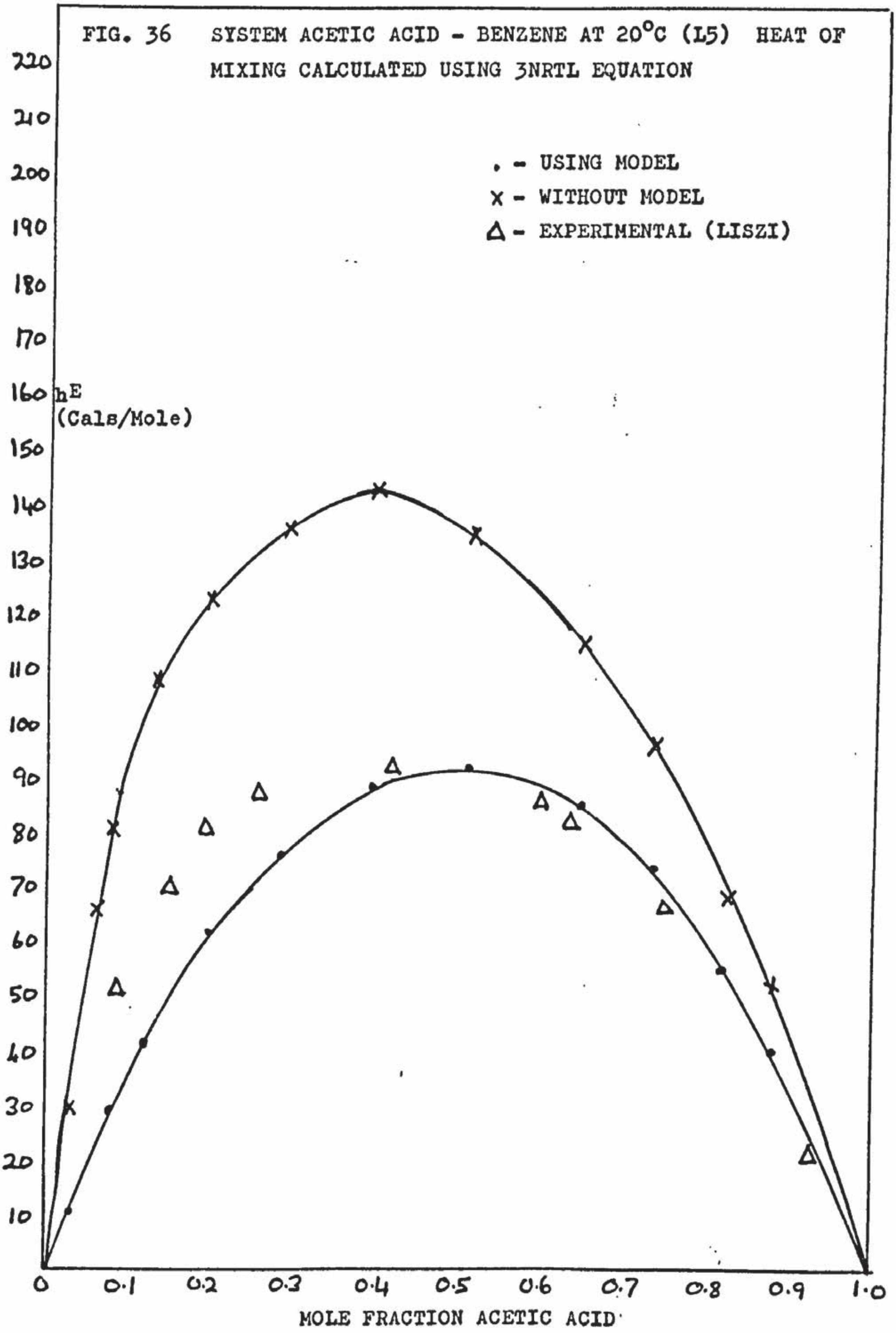


FIG. 36 SYSTEM ACETIC ACID - BENZENE AT 20°C (L5) HEAT OF MIXING CALCULATED USING 3NRTL EQUATION

FIG. 37 SYSTEM ACETIC ACID - N-HEPTANE AT 20°C (L5) HEAT OF MIXING CALCULATED USING WILSON EQUATION WITH NEW MODEL

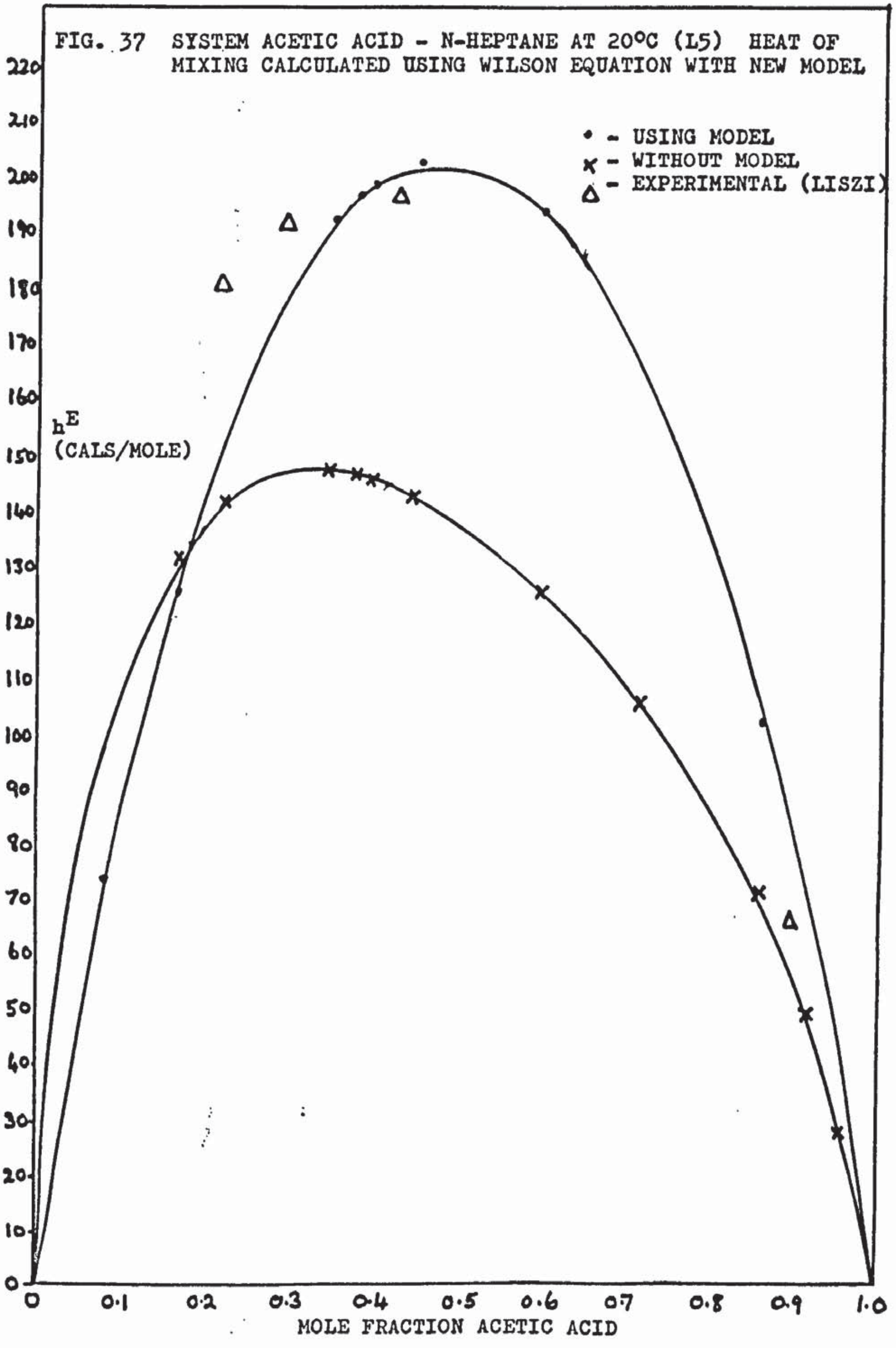
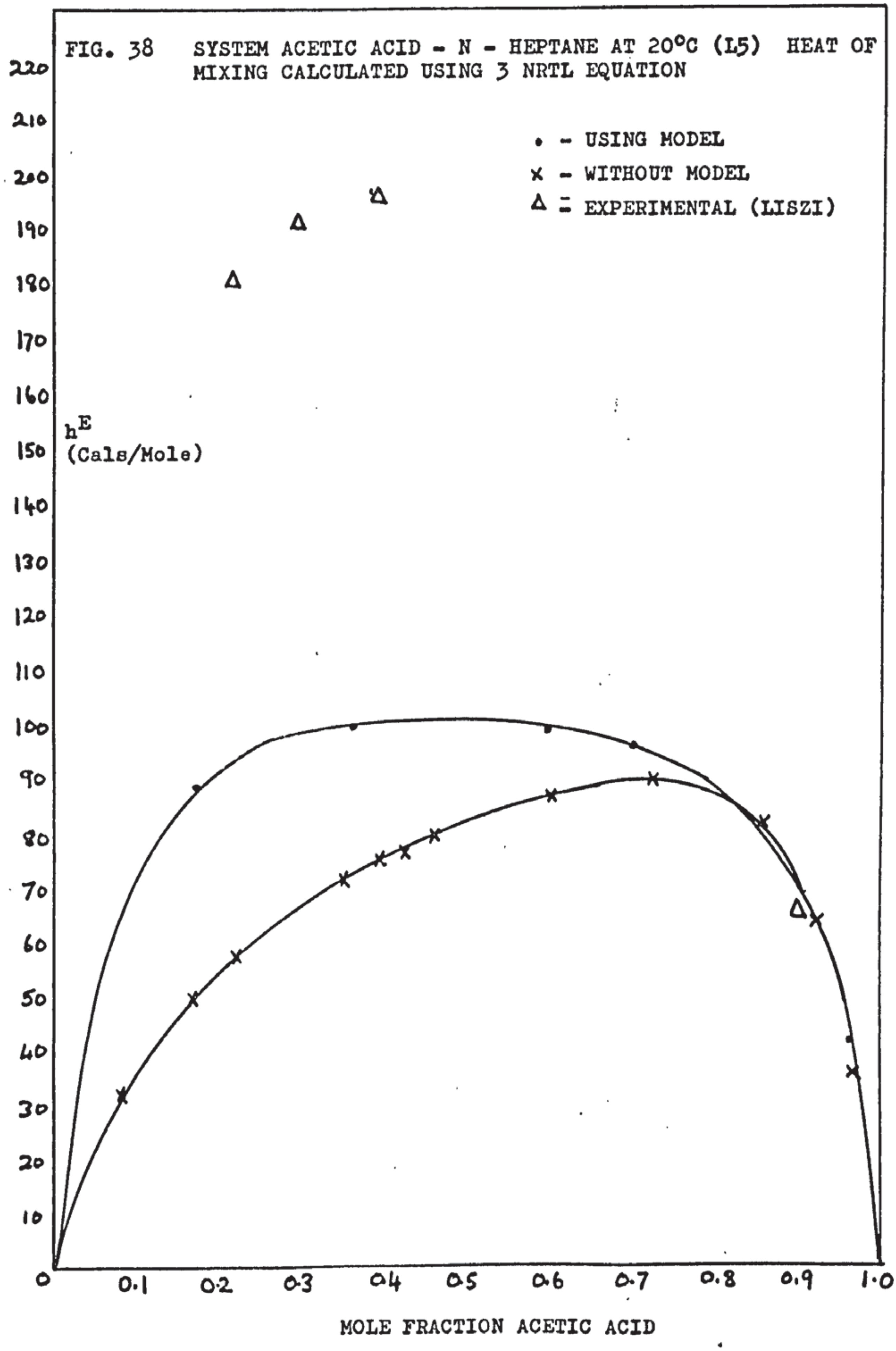


FIG. 38 SYSTEM ACETIC ACID - N - HEPTANE AT 20°C (L5) HEAT OF MIXING CALCULATED USING 3 NRTL EQUATION



k_m vs x shown in fig. 39 showing similar behaviour to the ordinary hydrocarbon systems. Although the acetic acid-trichloroethylene data of Cojutti (F4) seems to contain a fair amount of random error the data is probably consistent. The same may be said of the isothermal data of Liszi for the system acetic acid-carbon tetrachloride at 20°C. The acetic acid-chloroform data of Kenny, however, is improved by using a concentration dependent k but still shows non-random trends. In this case the data may either be inconsistent or there may be other effects not taken into account by the model. For this class of compound the use of concentration dependent correction factors greatly improves the correlation also.

The results obtained for the system acetic acid-water also show a substantial improvement when a concentration dependent correction factor is employed for the liquid phase activity coefficients. Although this improvement is not in general as great as that obtained with acetic acid-hydrocarbon systems, it is still marked. The more complex structure of water and the possibility of association between water and acetic acid molecules probably accounts for the slightly less

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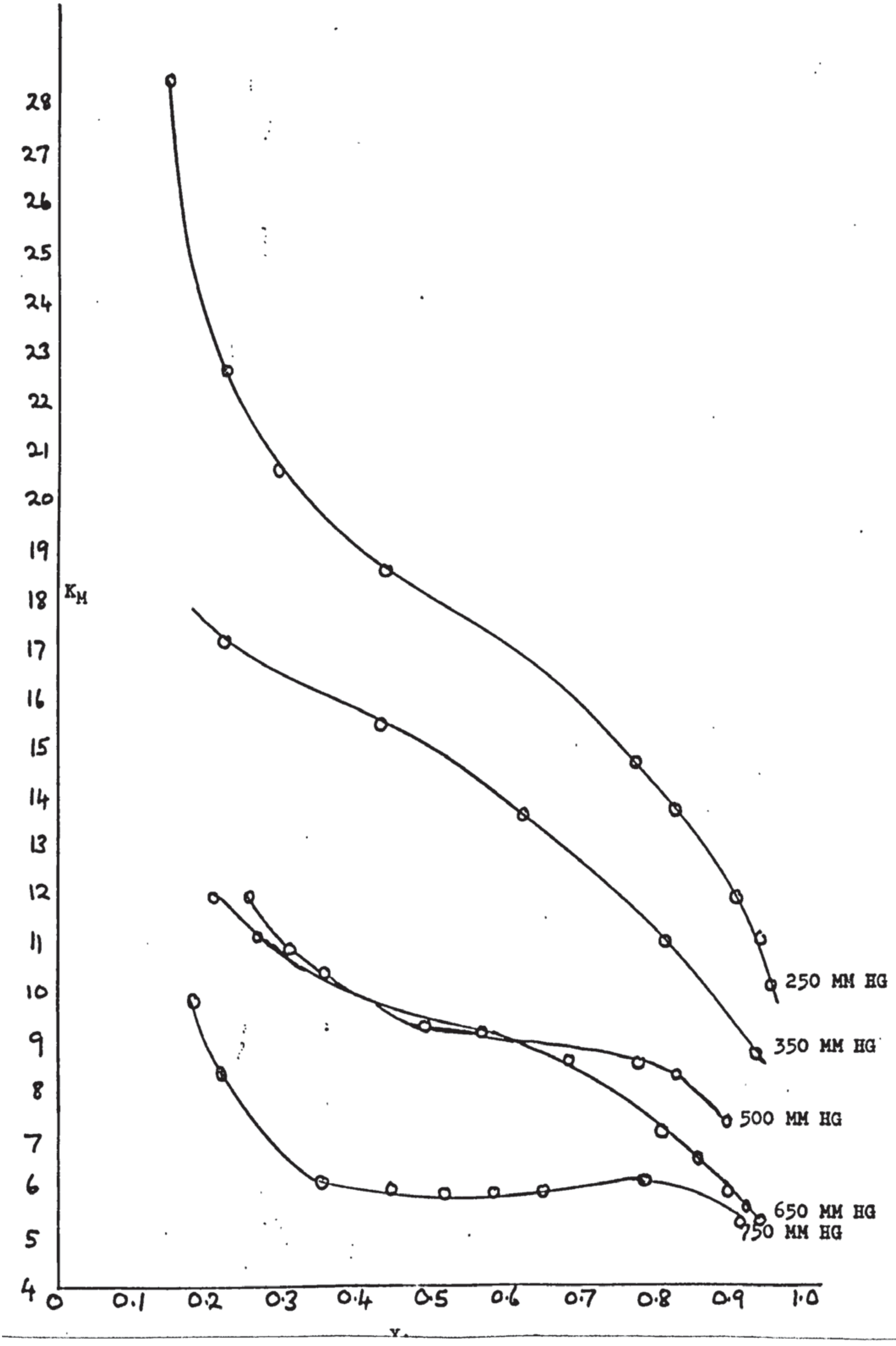
FIG. 39

EQUILIBRIUM CONSTANT, K_M V X_A FOR ACETIC ACID - TRICHLOROETHYLENE



accurate results but nevertheless the improvement is striking. It was found using the vapour phase correction only, for instance, that the Wilson equation does not give a very good fit to any of the data sets. However correcting the activity coefficients for association yields a substantial improvement.

All the data sets appear to be consistent when correlated with the new model with exception of the data of Riveng (R14) at 760 mm and that of Brown and Ewald (B16) at 760 mm which shows a pronounced non-random trend in the mid portion of the concentration range. Figs. 40 to 48 show the results of a Barker fit in the isothermal data of Arich and Tagliavani (A5) at 69.7 amd 89.9°C and on the isobaric data of Ito (12) at 70mm, 200 mm and 760 mm Hg. using the vapour phase correction only with the various Gibbs-Duhem equations and also with the liquid phase correction. The correlation parameters obtained with the new model are given in table A7.2. Figs. 49 to 50 show plots of k_m against x for the isothermal and isobaric systems. It can be seen that once again they are of a similar pattern to each other although different to the plots for acetic acid-hydrocarbon systems.

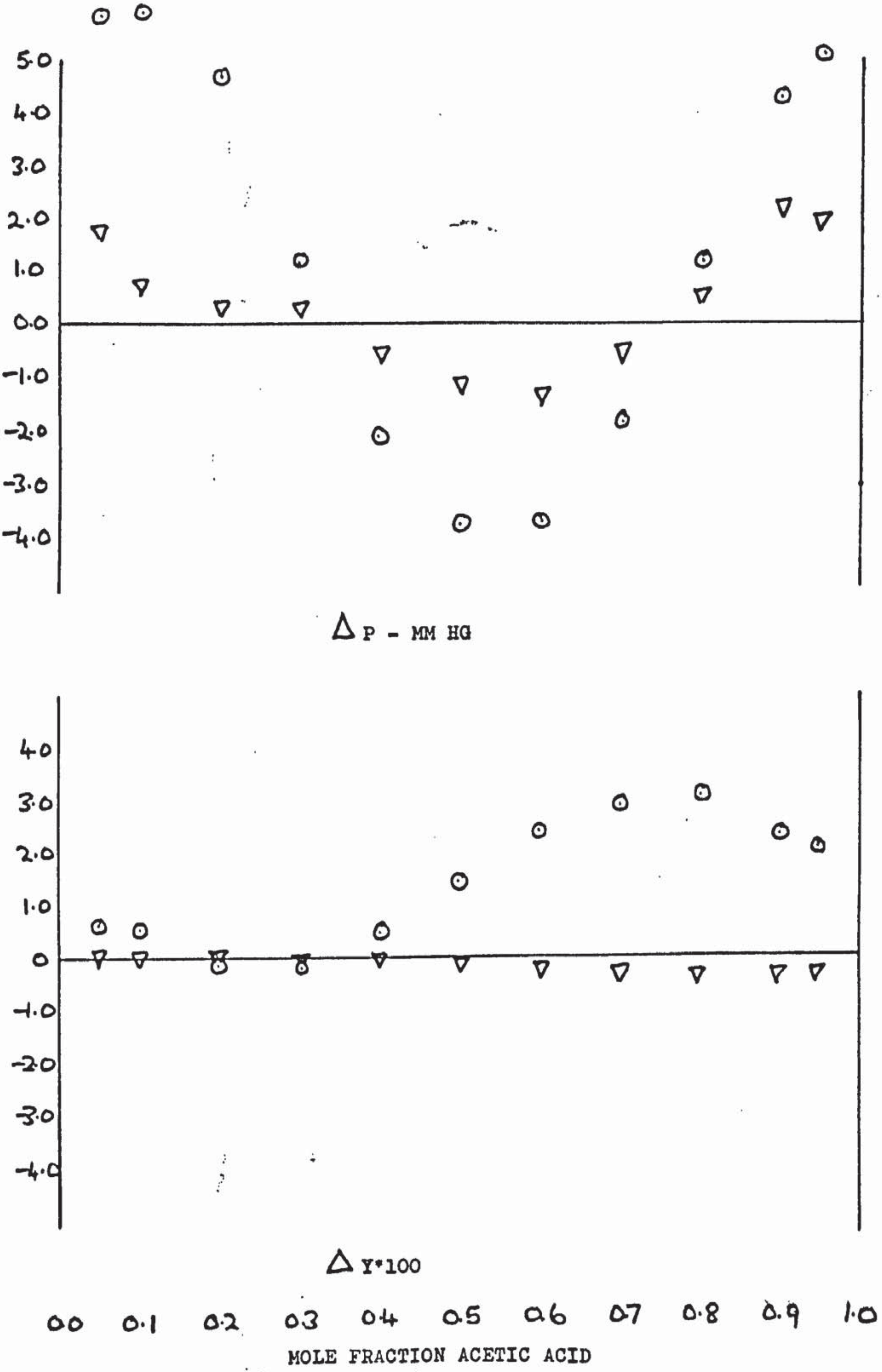


FIG. 41 SYSTEM ACETIC ACID-WATER AT 79.9°C (A5), 3 NRTL EQUATION
⊙ VAPOUR PHASE CORRECTION ONLY, ∇ LIQUID PHASE MODEL

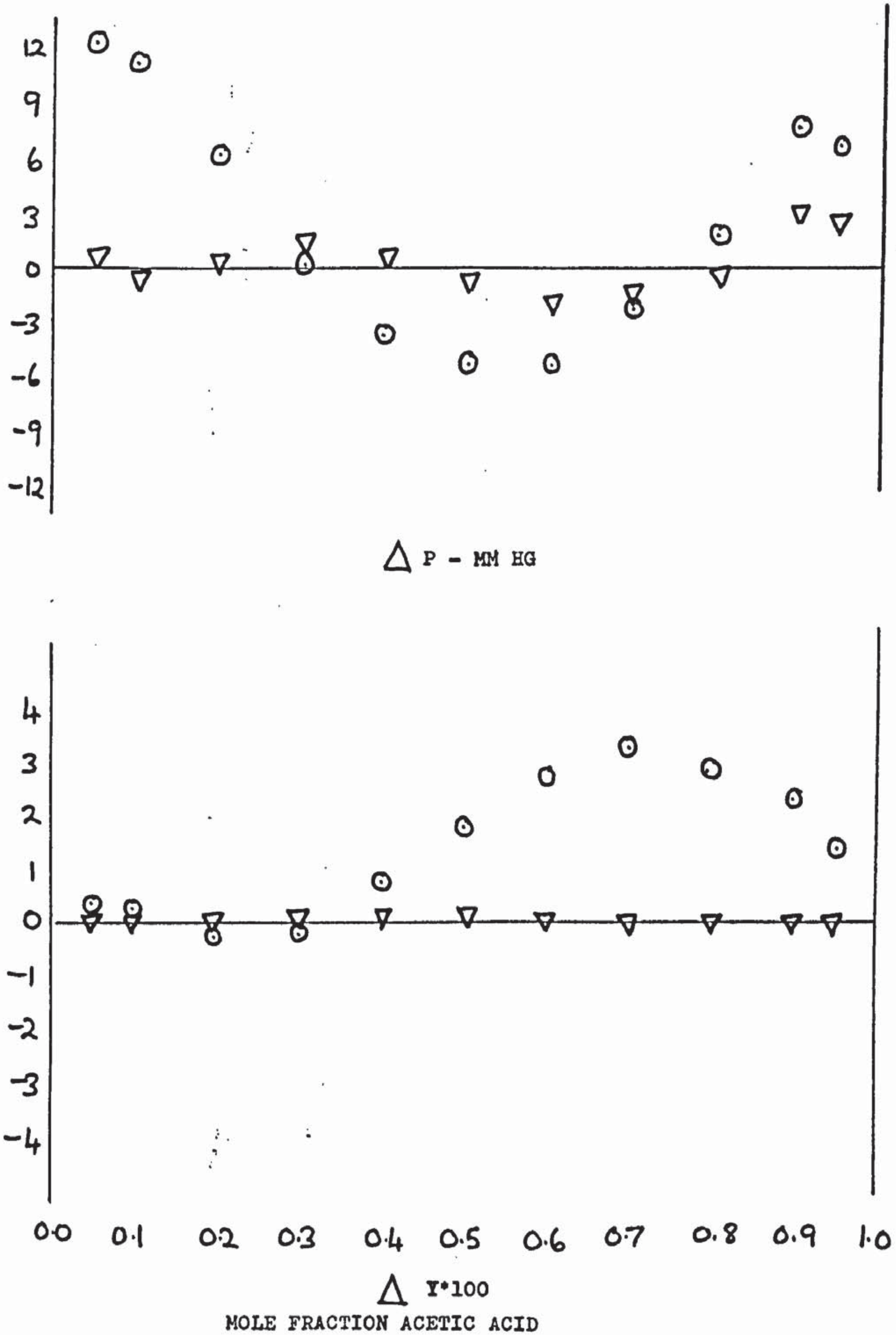


FIG. 42 SYSTEM ACETIC ACID-WATER AT 89.9 CENT (A5), 3 NRTL EQUATION
⊙ VAPOUR PHASE CORRECTION ONLY, ▽ LIQUID PHASE MODEL

FIG. 43 SYSTEM ACETIC ACID - WATER AT 89.9°C

ACTIVITY COEFFICIENTS

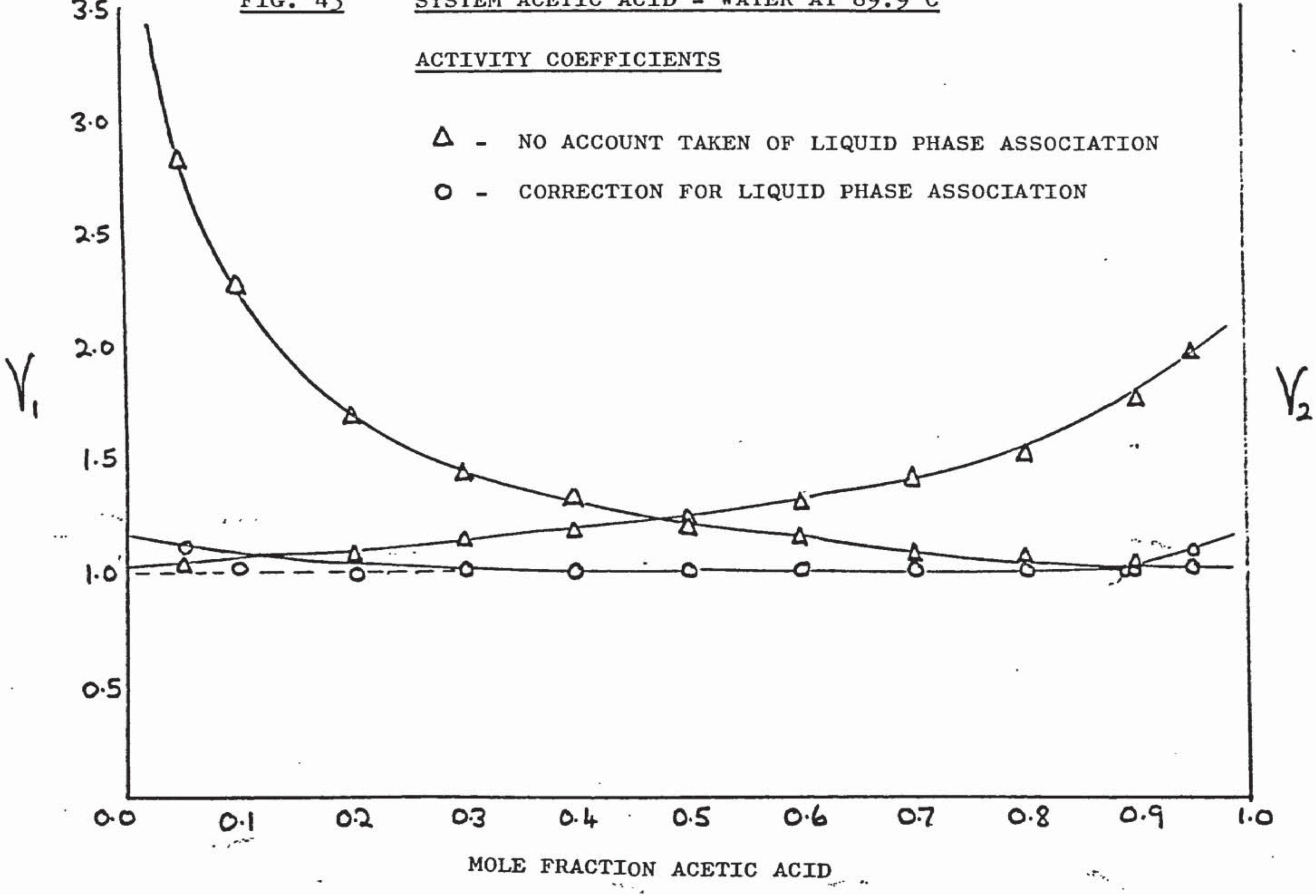
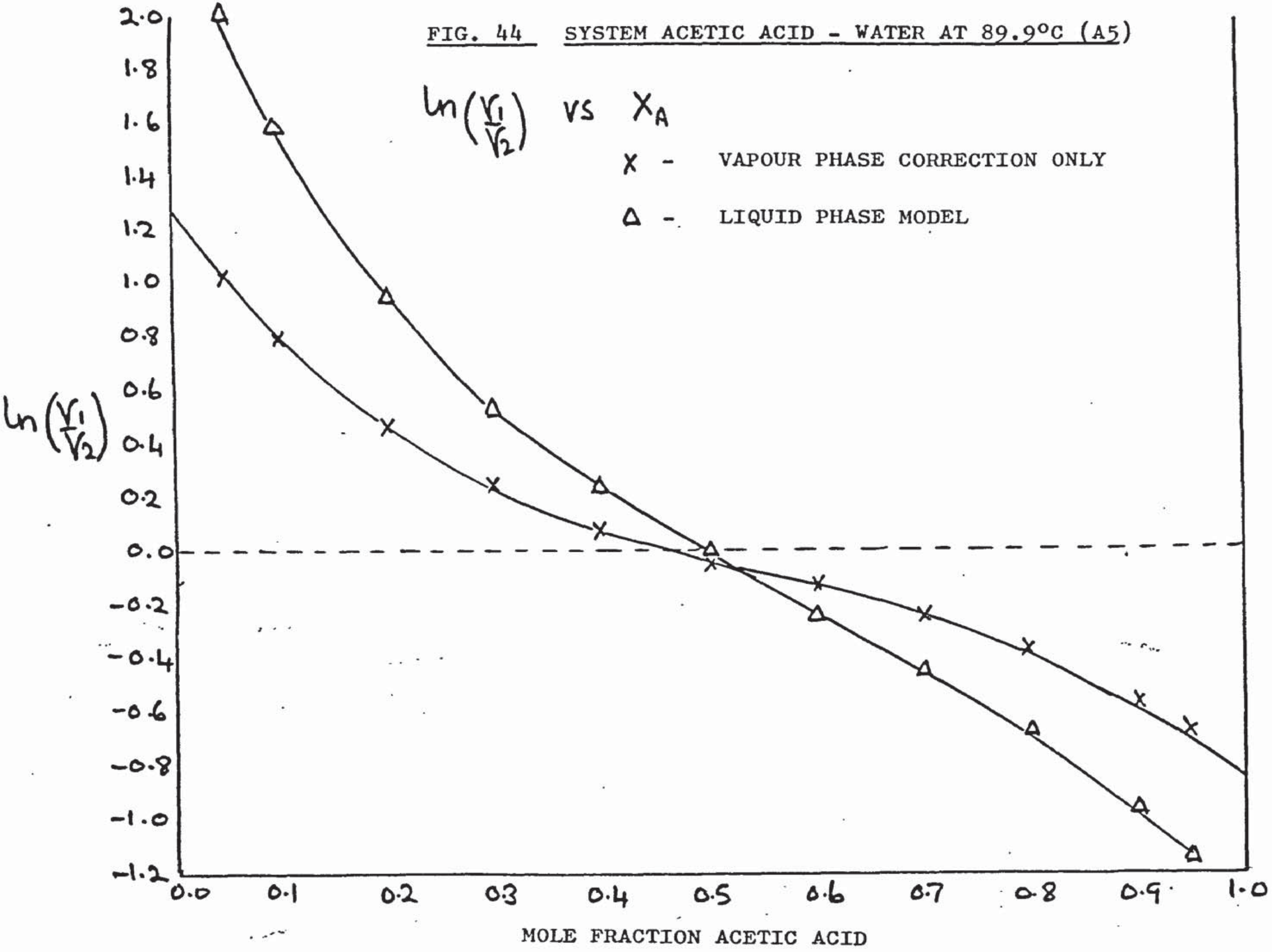
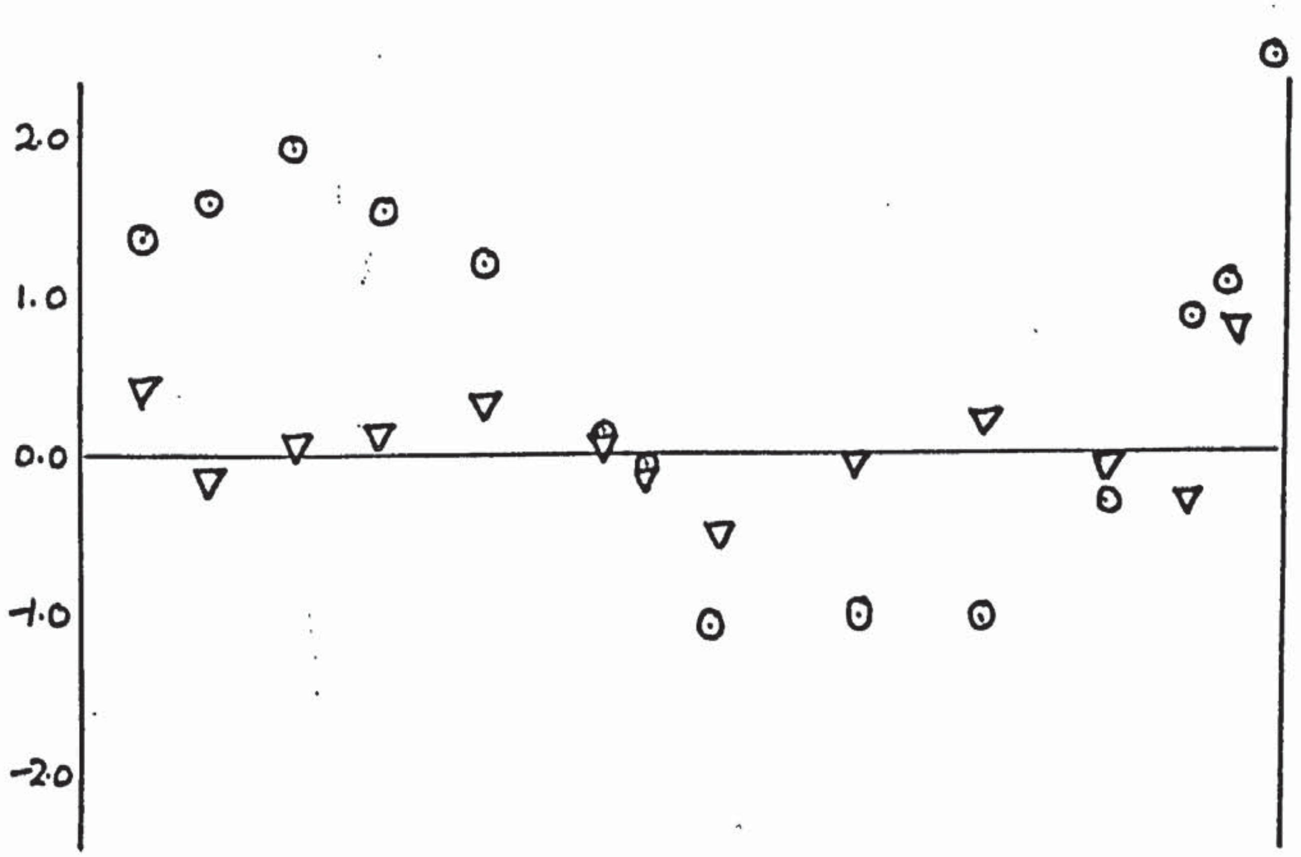
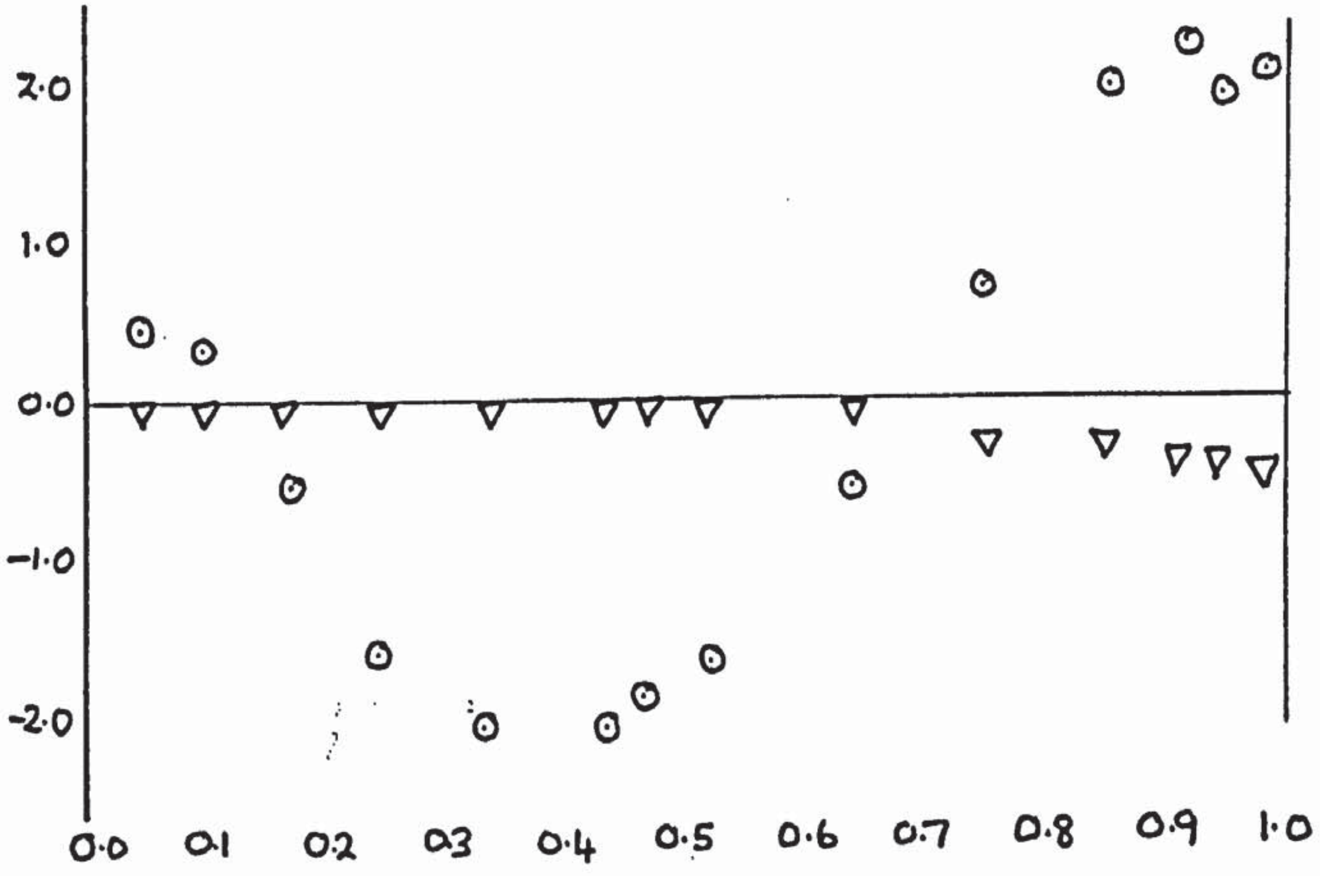


FIG. 44 SYSTEM ACETIC ACID - WATER AT 89.9°C (A5)





ΔP - MM HG



ΔY*100

MOLE FRACTION ACETIC ACID

FIG. 45 SYSTEM ACETIC ACID-WATER AT 70 MM HG (I2), 2 APPROACHES 3 NRTL EQN

⊙ VAPOUR PHASE CORRECTION ONLY, ▽ LIQUID PHASE MODEL

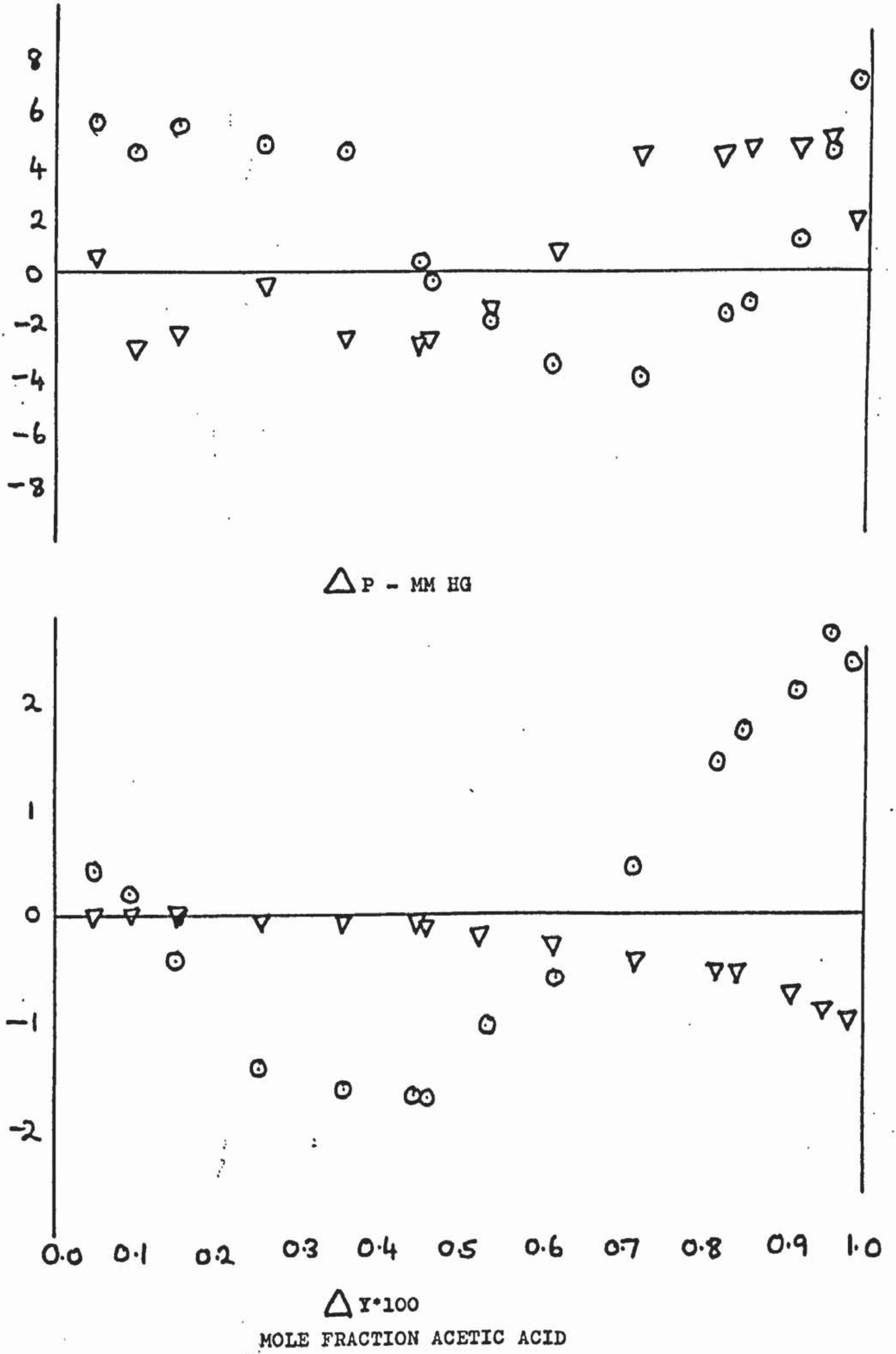


FIG. 46 SYSTEM ACETIC ACID-WATER AT 200 MM HG (I2), 2 APPROACHES 3 NRTL EQN

⊙ VAPOUR PHASE CORRECTION ONLY, ▽ LIQUID PHASE MODEL

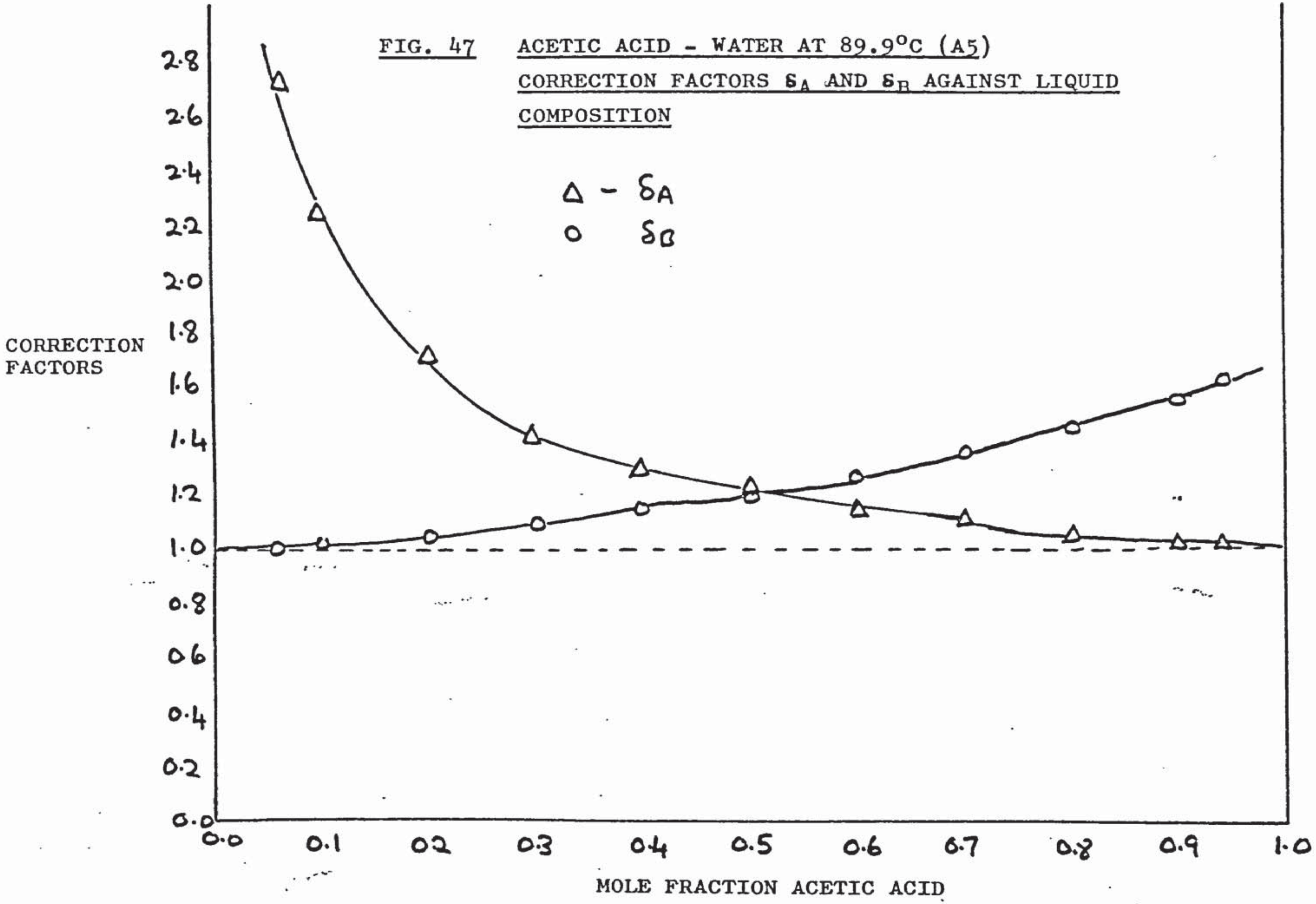
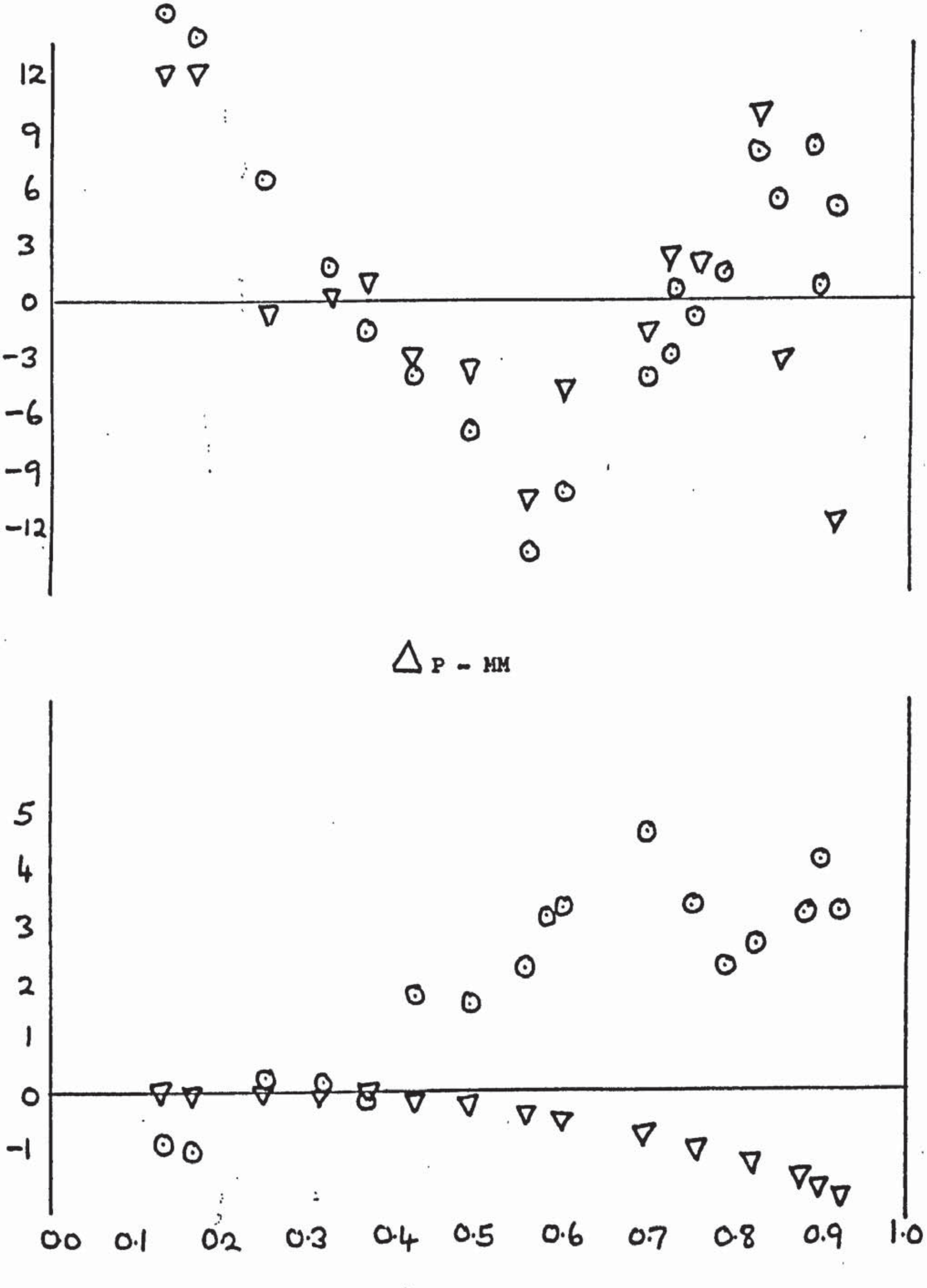


FIG. 47 ACETIC ACID - WATER AT 89.9°C (A5)
CORRECTION FACTORS δ_A AND δ_B AGAINST LIQUID COMPOSITION



MOLE FRACTION ACETIC ACID

FIG. 48 SYSTEM ACETIC ACID-WATER AT 760 MM (55), 3 NRTL EQUATION

⊙ VAPOUR PHASE CORRECTION ONLY, ▽ LIQUID PHASE MODEL

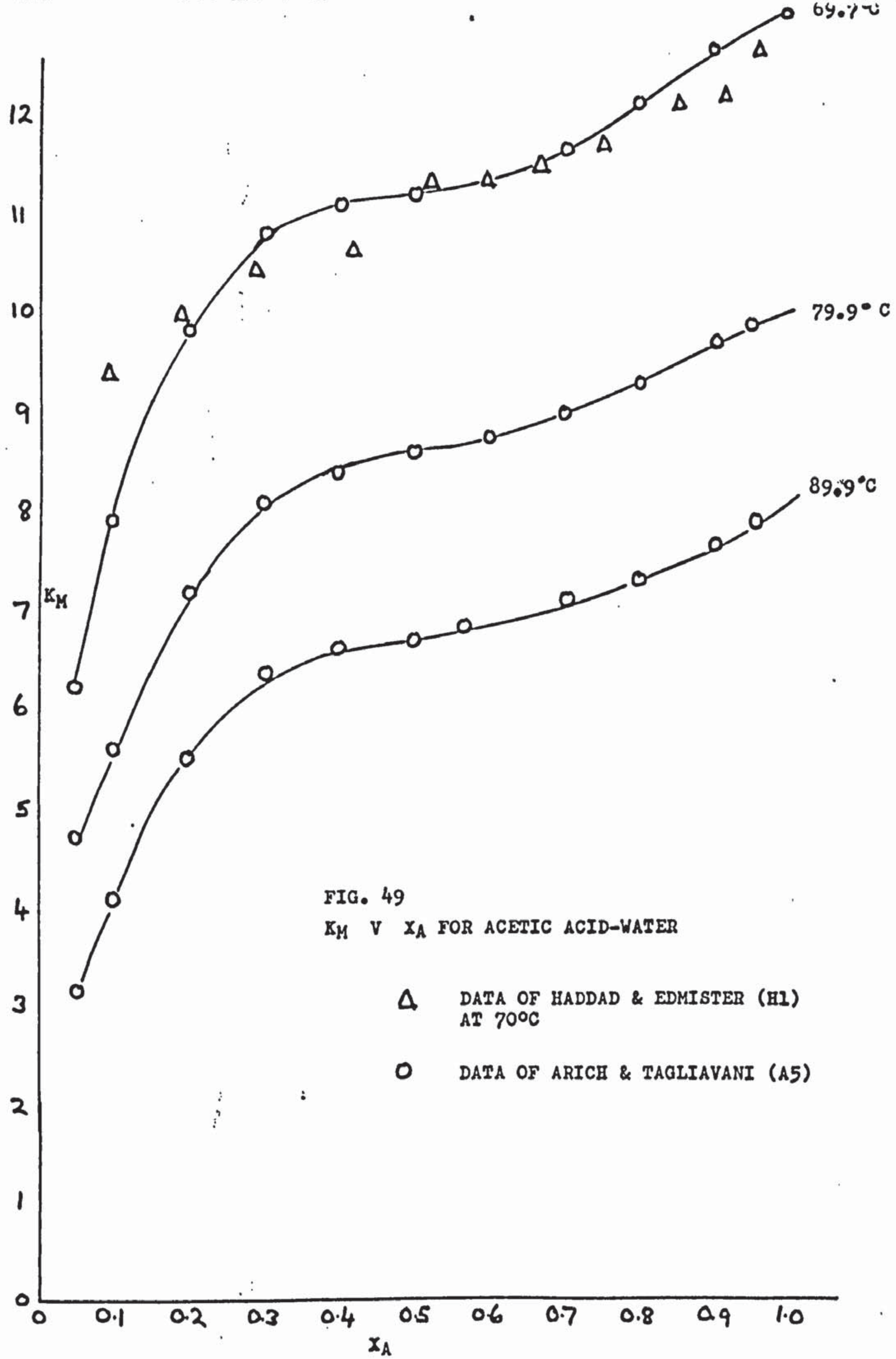
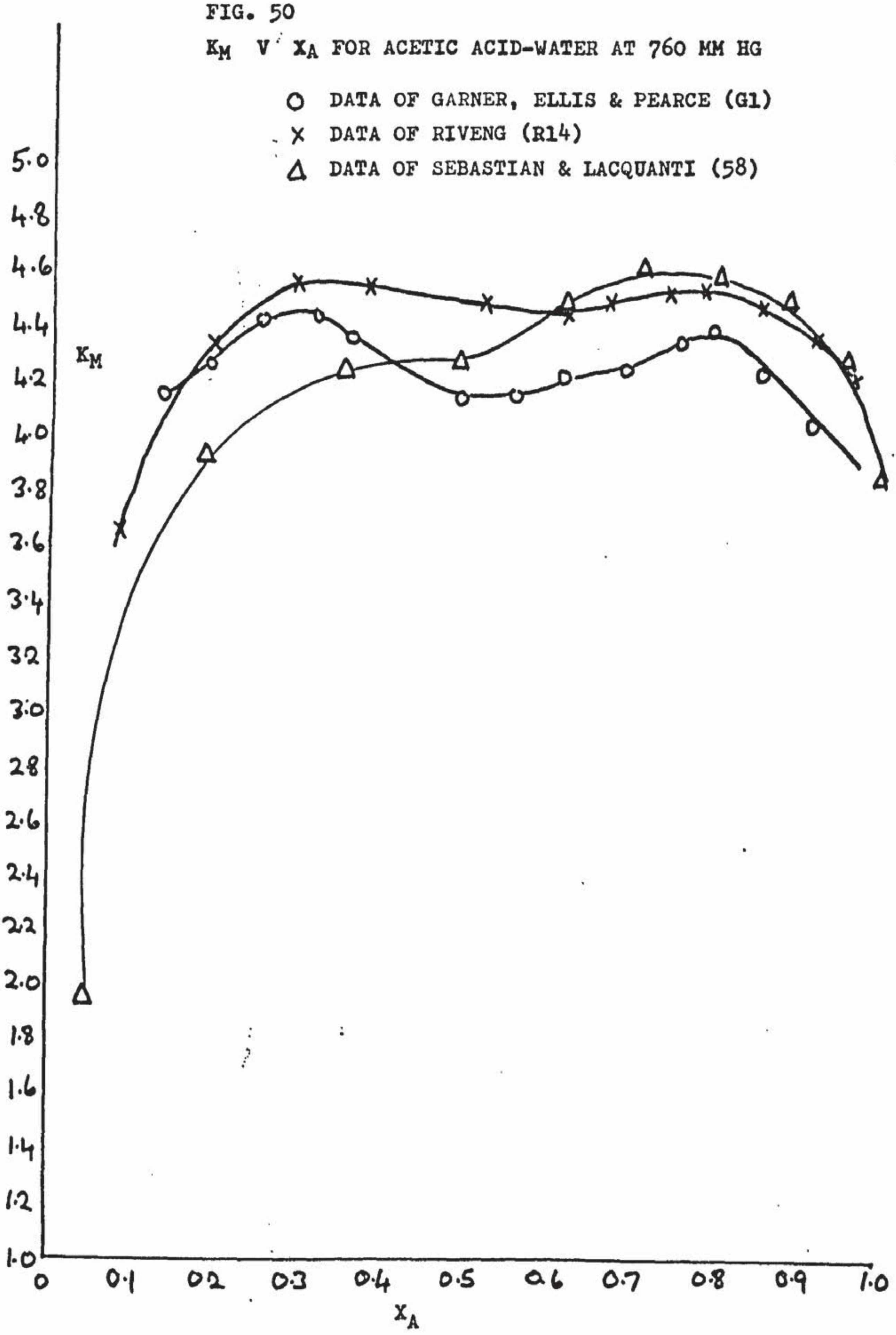


FIG. 49

K_M V x_A FOR ACETIC ACID-WATER

FIG. 50

K_M V X_A FOR ACETIC ACID-WATER AT 760 MM HG



Similar conclusions are obtained when the two approaches are applied to the data sets dealing with the system acetic acid-alcohols and acetic acid-esters. There is considerably more random error in the data especially in that of Amer-Azega (A3). Also the results of applying the new approach are in general only marginally better and in the case of the system acetic acid-iso butanol at 706 mm Hg. reported by Amer-Azega the fit is slightly worse. The systems acetic acid-n-butanol and acetic acid-tert butanol are very badly correlated with both approaches. The complex behaviour of alcohols is well known and there have been many attempts using specially derived models (N5) (W4) (K10) to deal with systems of which an alcohol is a component. This may account for the indifferent results obtained, but, since the data of Ruis (R17) for acetic acid-methanol, ethanol, n-propanol, and n-butanol does not give such bad results as the data sets of Amer-Azega it may be that the latter are inconsistent. Once again plots of the concentration dependent equilibrium constant, k_m, against liquid phase mole fraction show similar behaviour for all the data sets (see fig. 57). The results of the Barker fit are shown in figs. 51 to 56 for various systems in which the

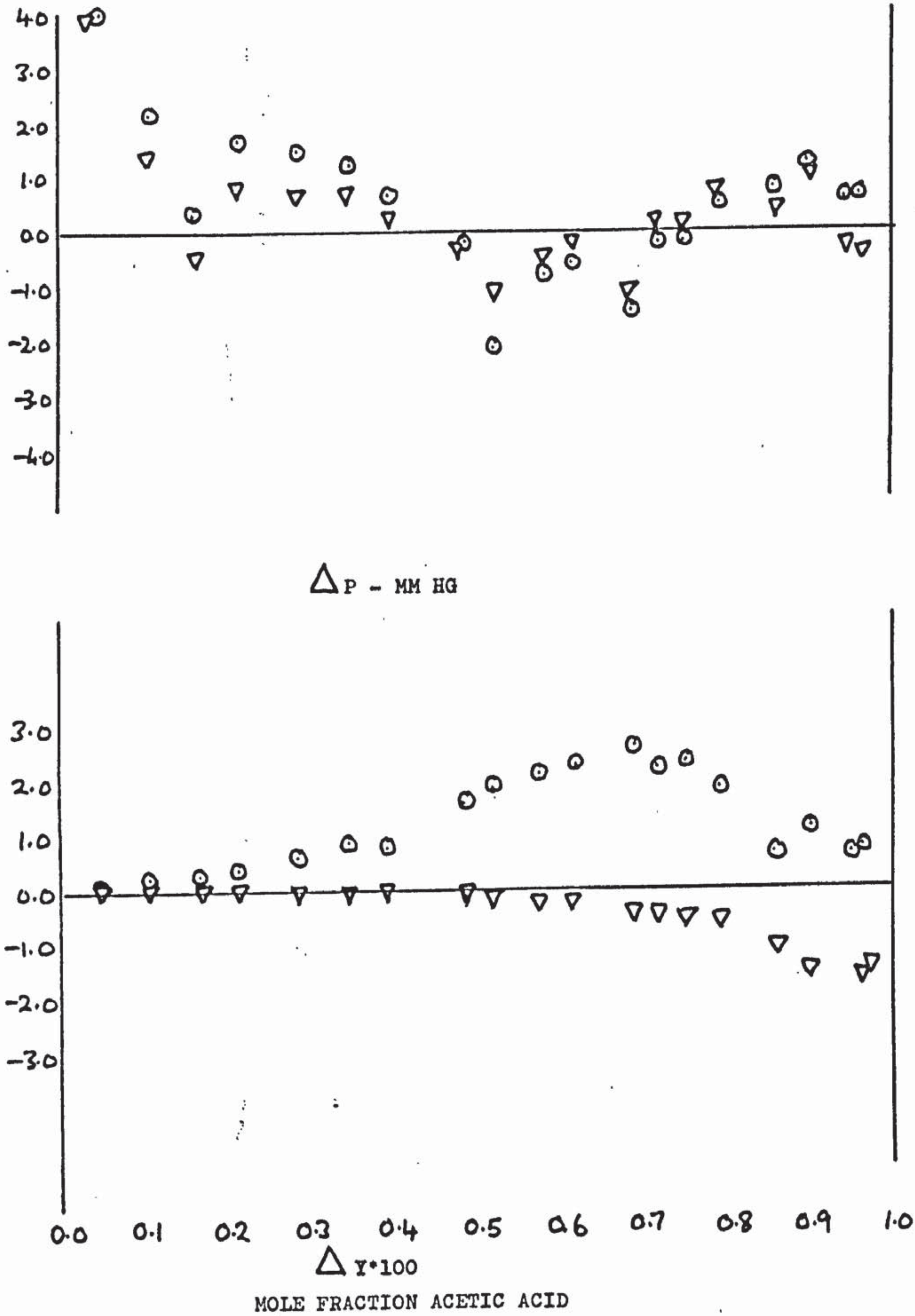


FIG. 51 DEVIATION PLOTS FOR SYSTEM ACETIC ACID - METHANOL (R17), WILSON EQN

⊙ VAPOUR PHASE CORRECTION ONLY, ▽ LIQUID PHASE MODEL

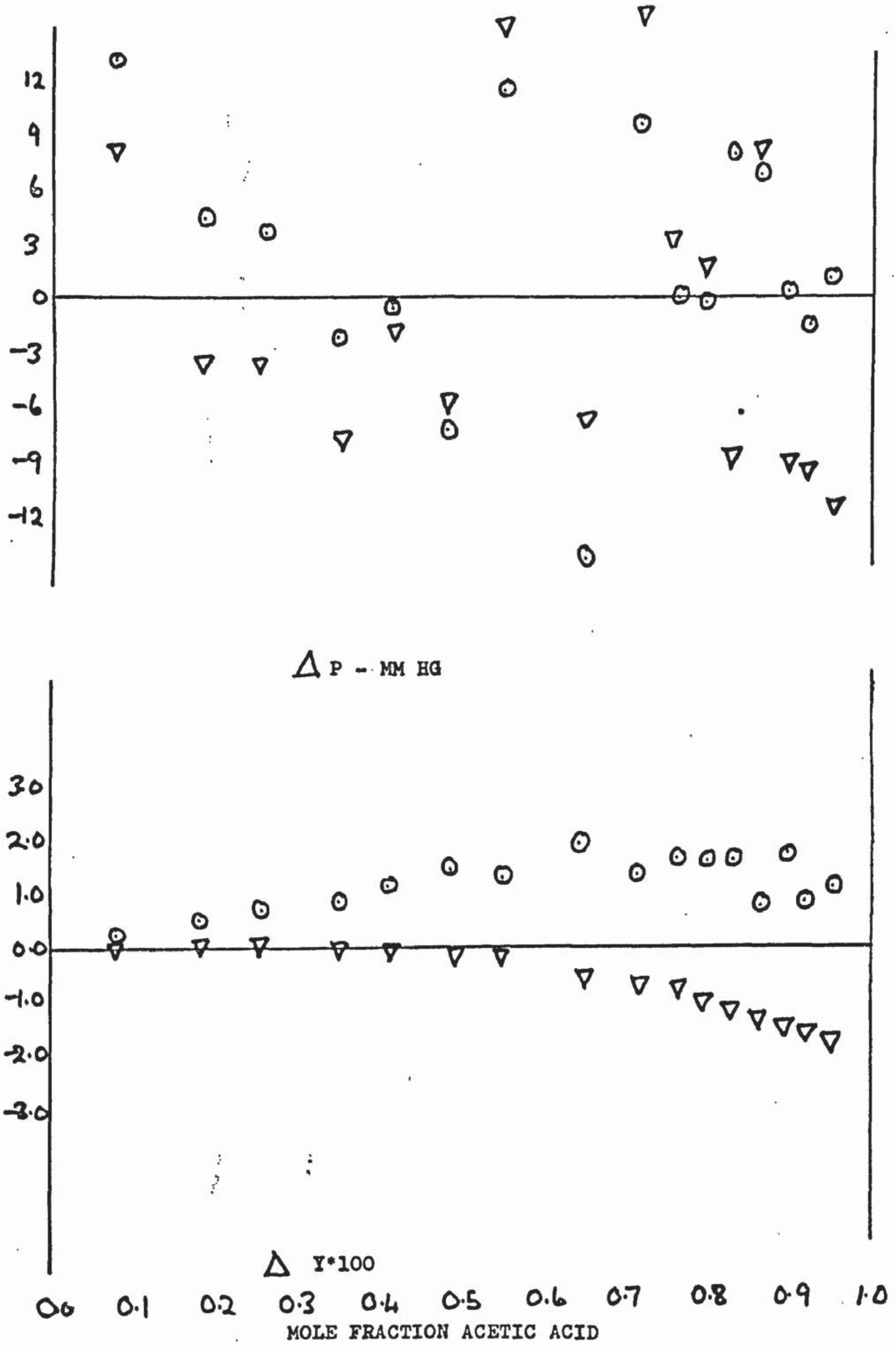
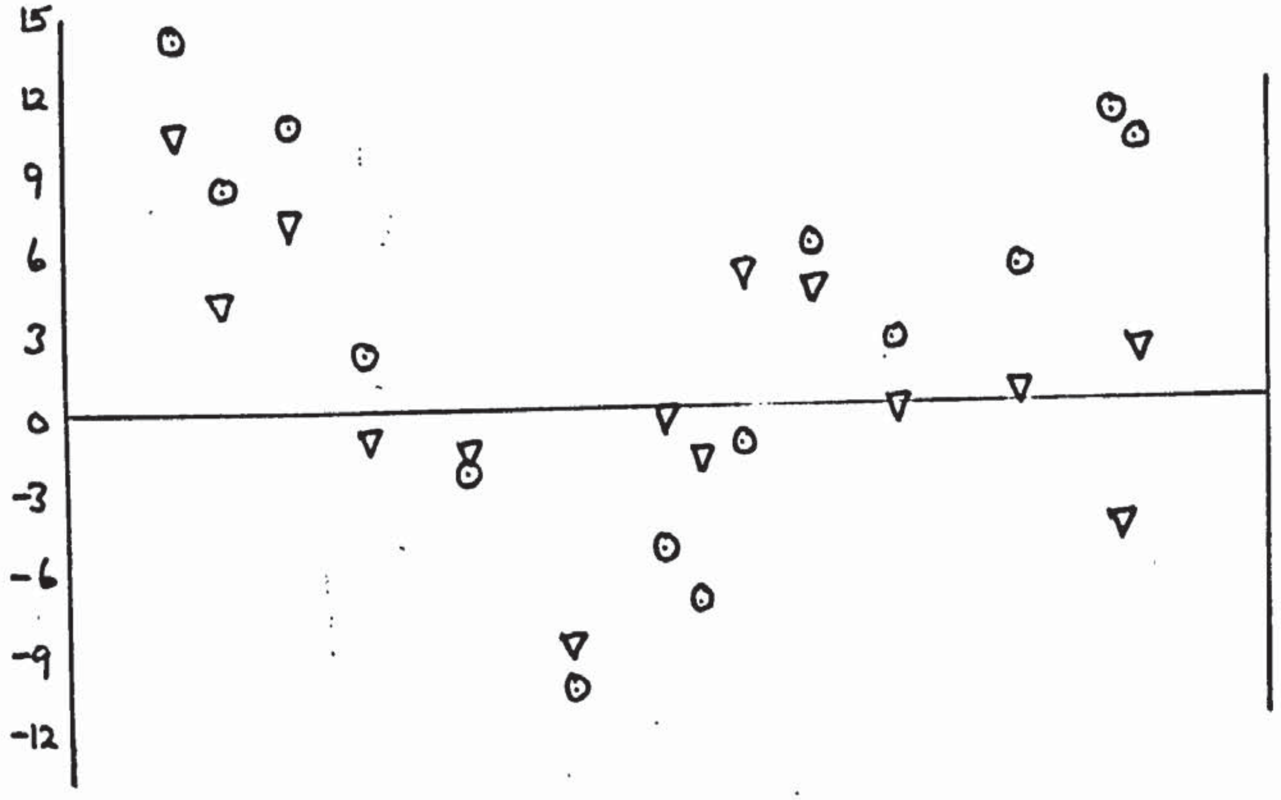
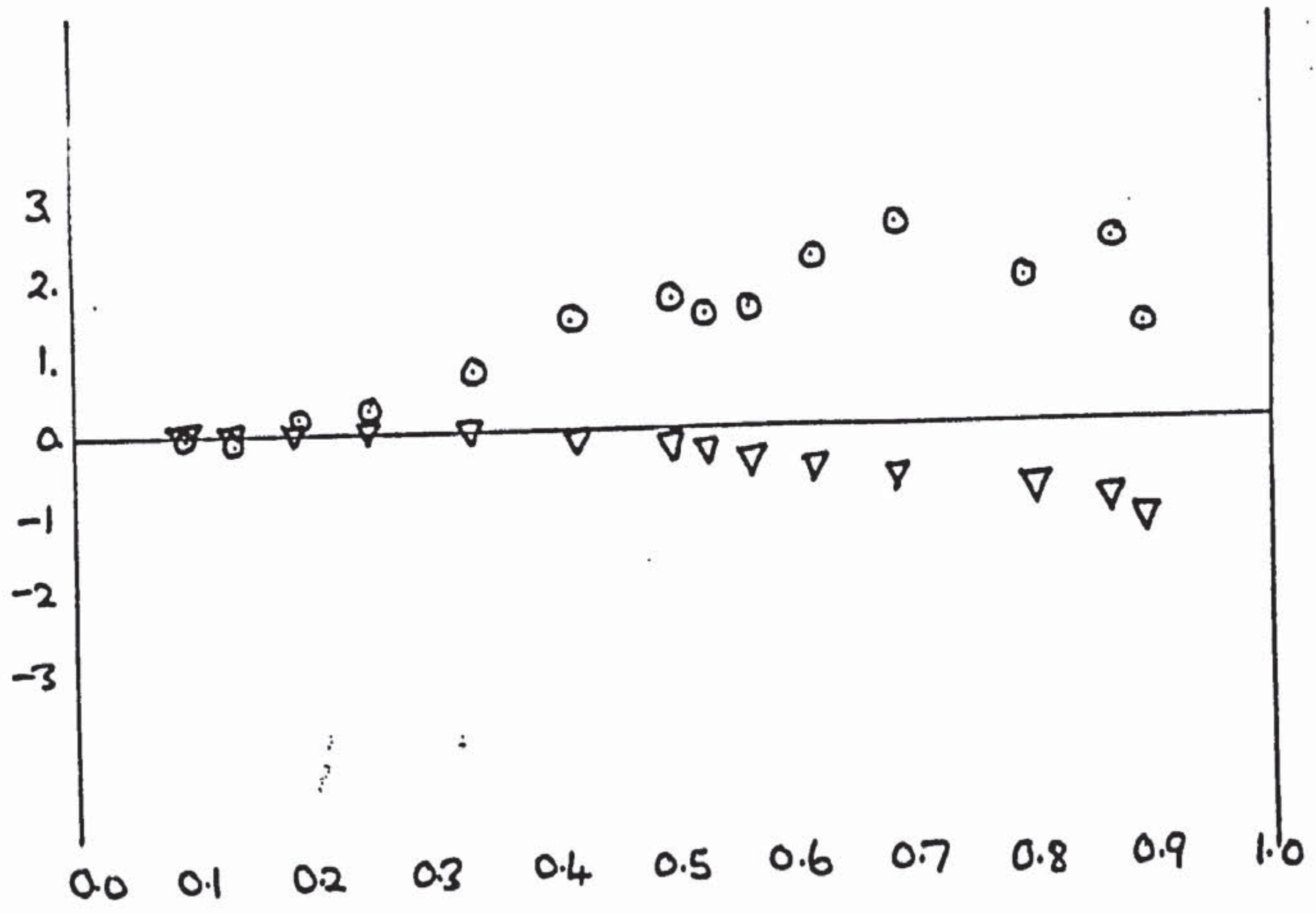


FIG. 52 SYSTEM ACETIC ACID-ETHANOL (R17), USING WILSON EQUATION

⊙ VAPOUR CORRECTION ONLY, ▽ LIQUID PHASE MODEL



Δ P - MM HG



Δ Y*100

MOLE FRACTION ACETIC ACID

FIG. 53 DEVIATION PLOTS FOR ACETIC ACID N-BUTANOL, 2 APPROACHES WILSON EQN

⊙ VAPOUR PHASE CORRECTION ONLY, ▽ LIQUID PHASE MODEL

FIG. 54 SYSTEM ACETIC ACID - TOLUENE AT 30°C (M10)
ACTIVITY COEFFICIENTS

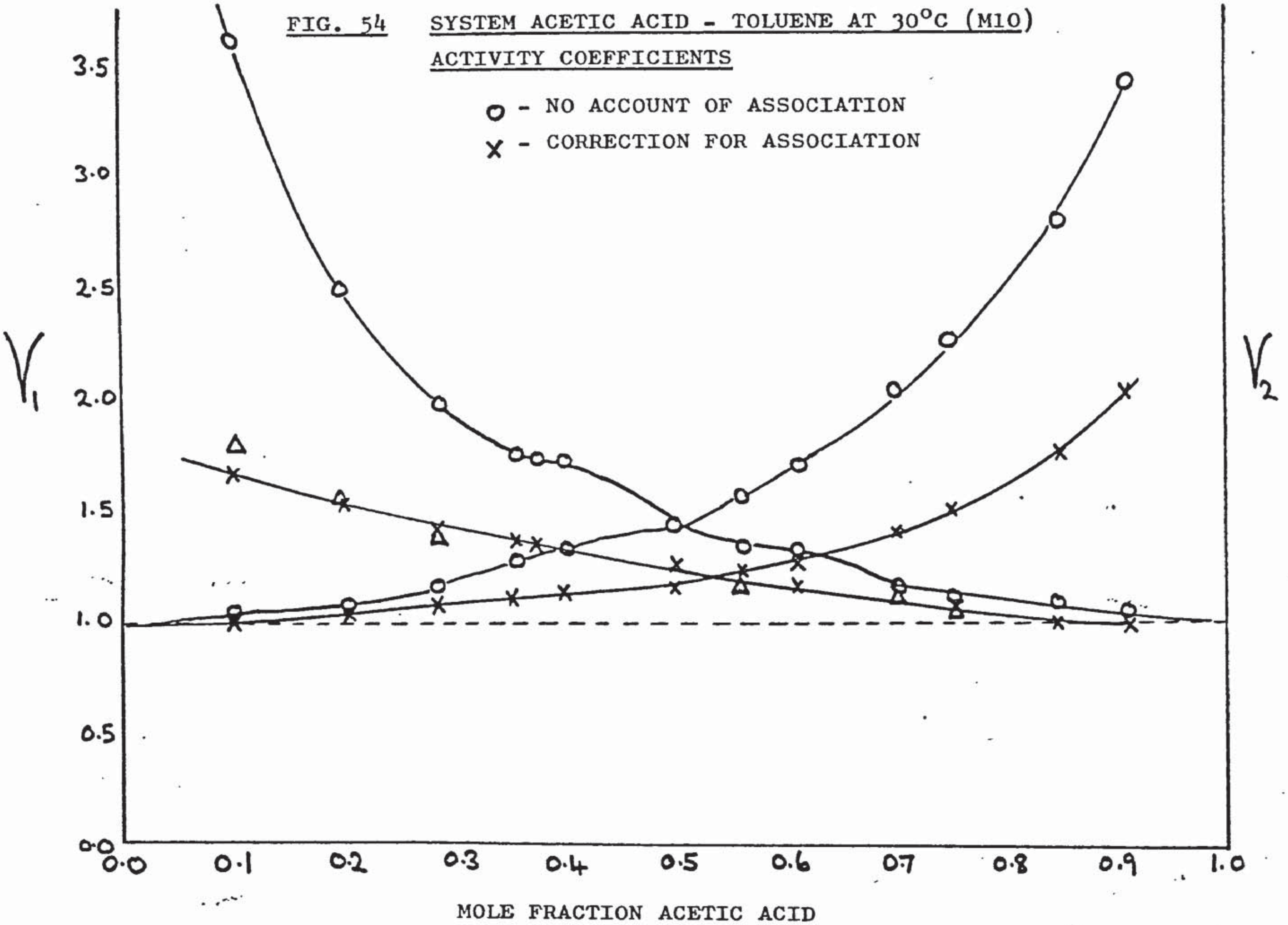


FIG. 55 SYSTEM ACETIC ACID - TOLUENE AT 30°C (M10)

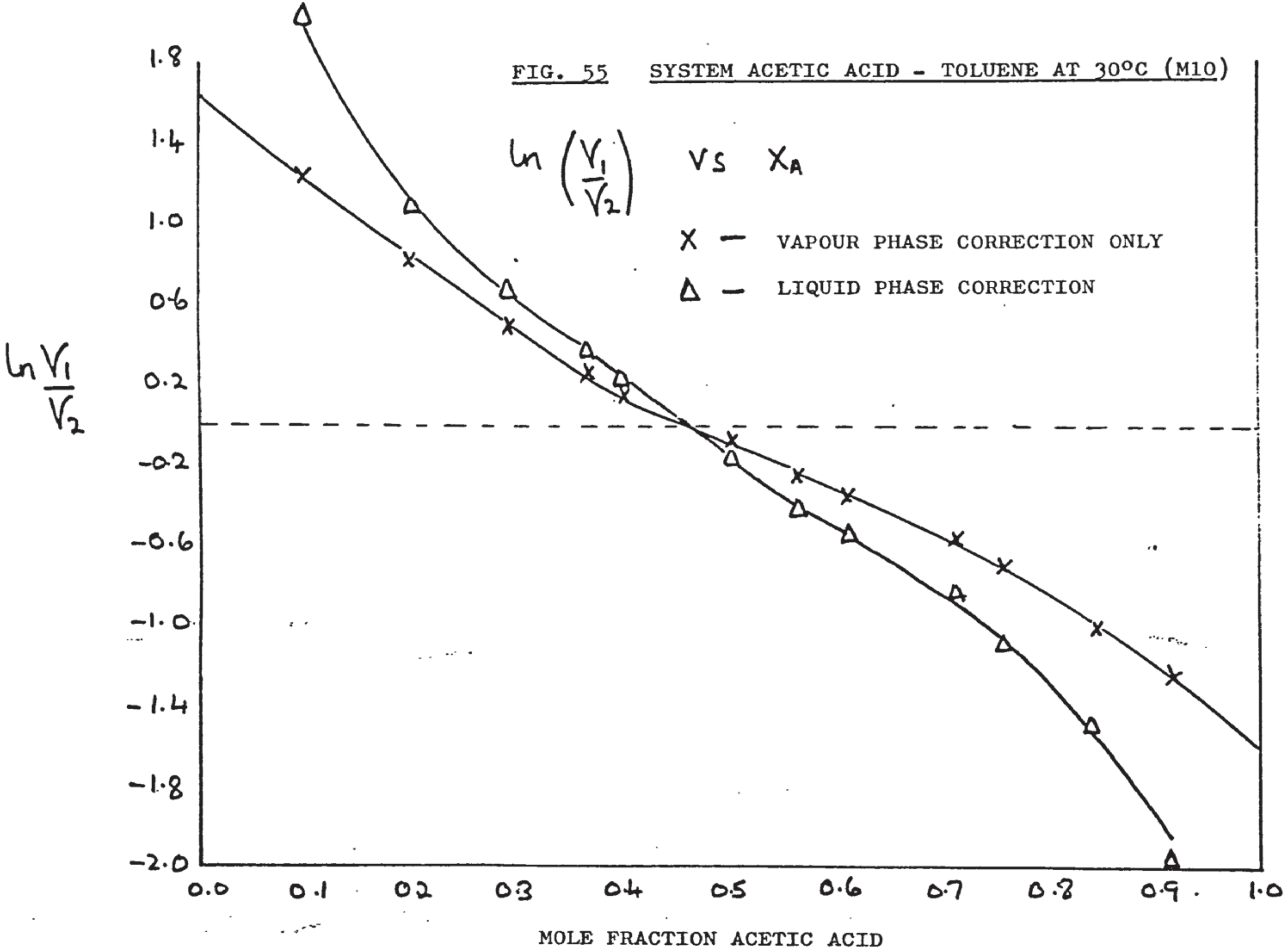
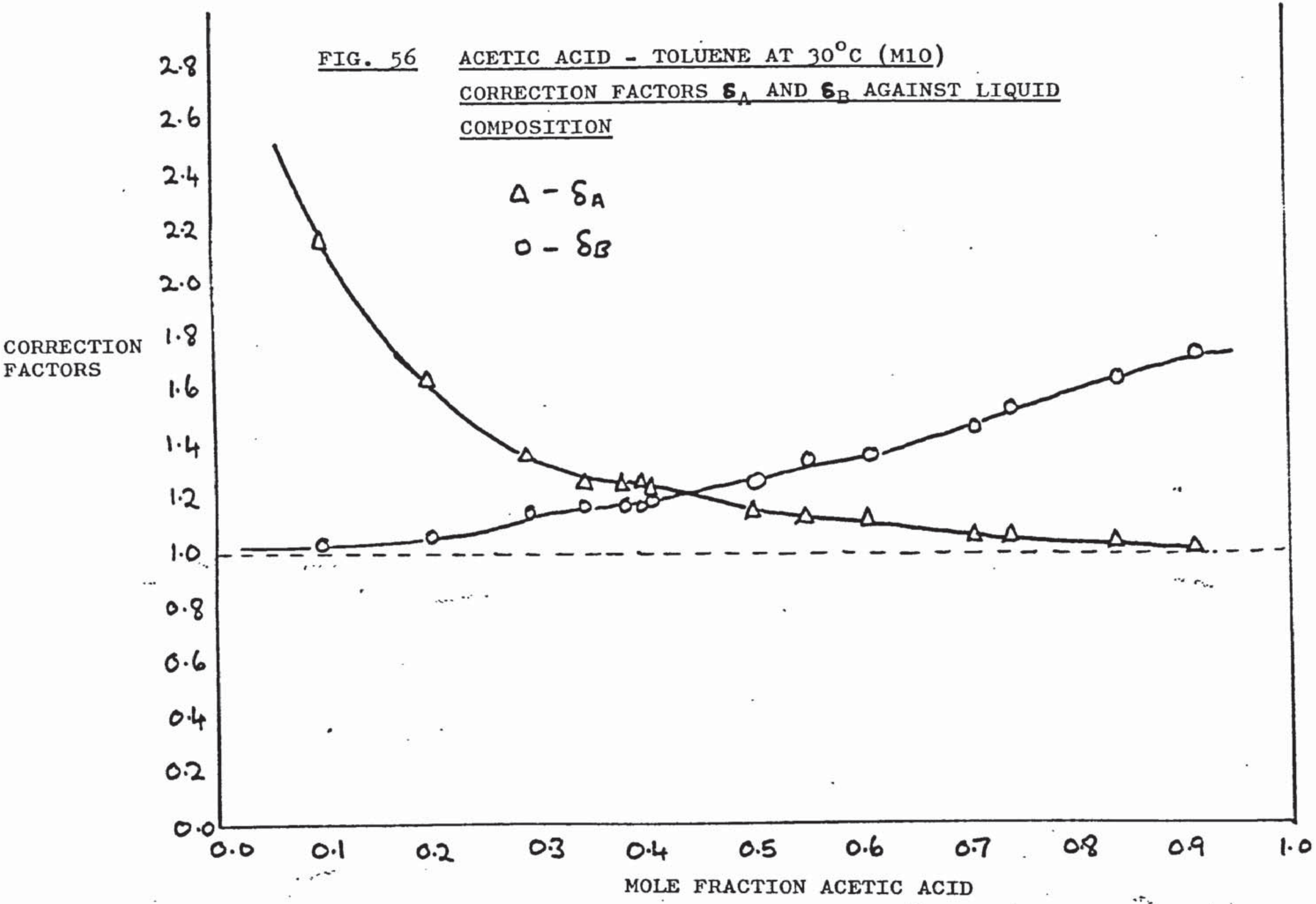


FIG. 56 ACETIC ACID - TOLUENE AT 30°C (M10) CORRECTION FACTORS δ_A AND δ_B AGAINST LIQUID COMPOSITION



performance of the two approaches may be assessed.

The results for the systems of acetic acid and esters are similar to hydrocarbon systems with only the data in system acetic acid-cyclohexyl acetate appearing to be inconsistent. The curves obtained on plotting k_m against x are once again similar but unique to this class of compounds. Results of the Barker fit and the curves for k_m against x are shown in figs. 58 to 61.

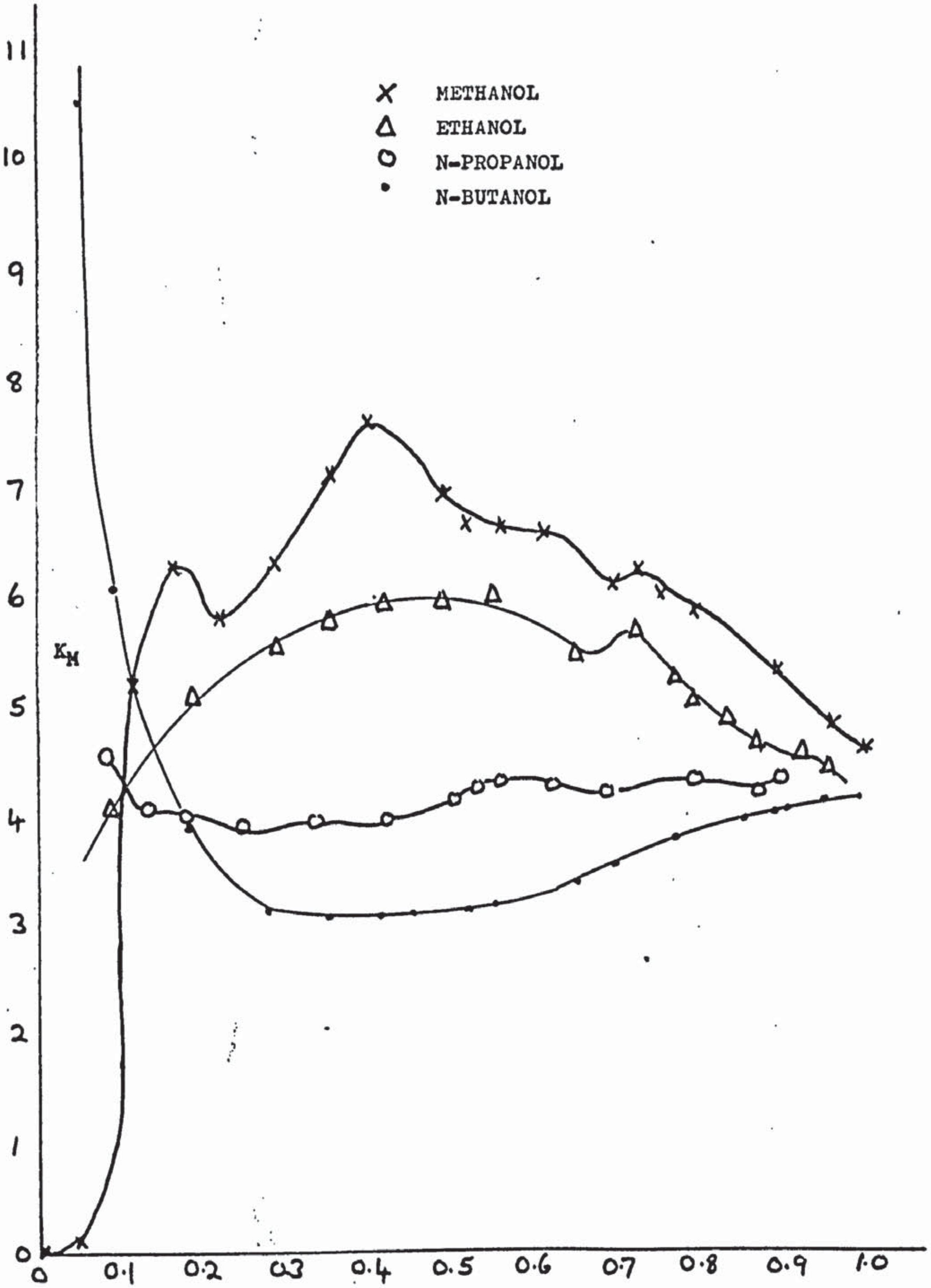
The results for other miscellaneous systems such as acetic acid acetone and acetic acid diethyl ether provide similar conclusions. In all cases the new approach offers a substantial improvement with the curves of k_m against x showing similar shapes for each group of compounds. Results are presented in Appendix A3 and illustrated in figs. 62 to 65.

In the majority of cases the Wilson equation appears to give superior results to both the 2 and 3 parameter NRTL equations.

The fact that the variation of k_m with x is dependent upon the class of compound may make it possible to derive a generalised correlation which in

FIG. 57

EQUILIBRIUM CONSTANT , K_M V X_A FOR ACETIC ACID N-ALCOHOLS



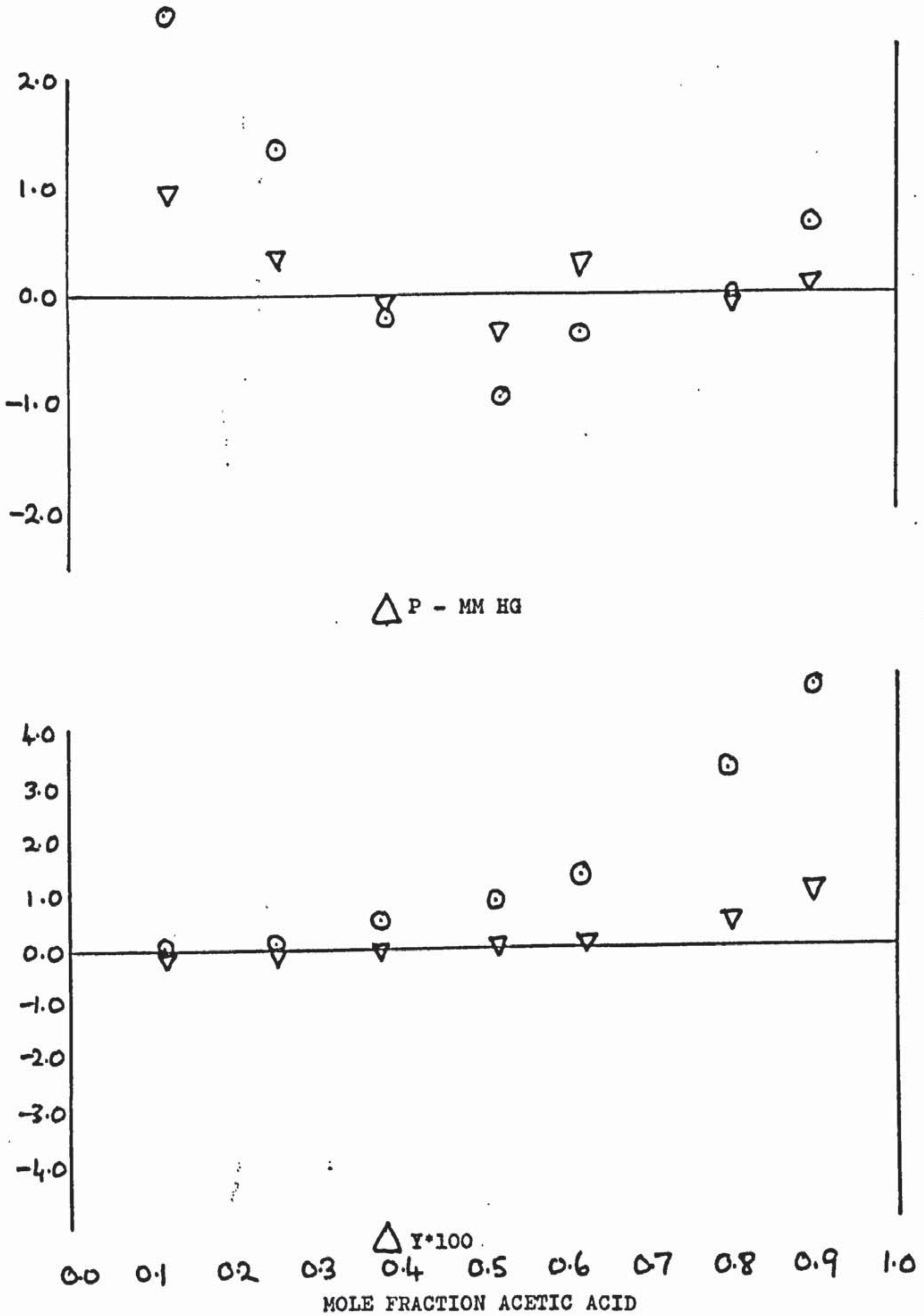


FIG. 58 SYSTEM ACETIC ACID - ETHYL ACETATE AT 30 CENT (M16), WILSON EQN
⊙ VAPOUR PHASE CORRECTION, ▽ LIQUID PHASE MODELS

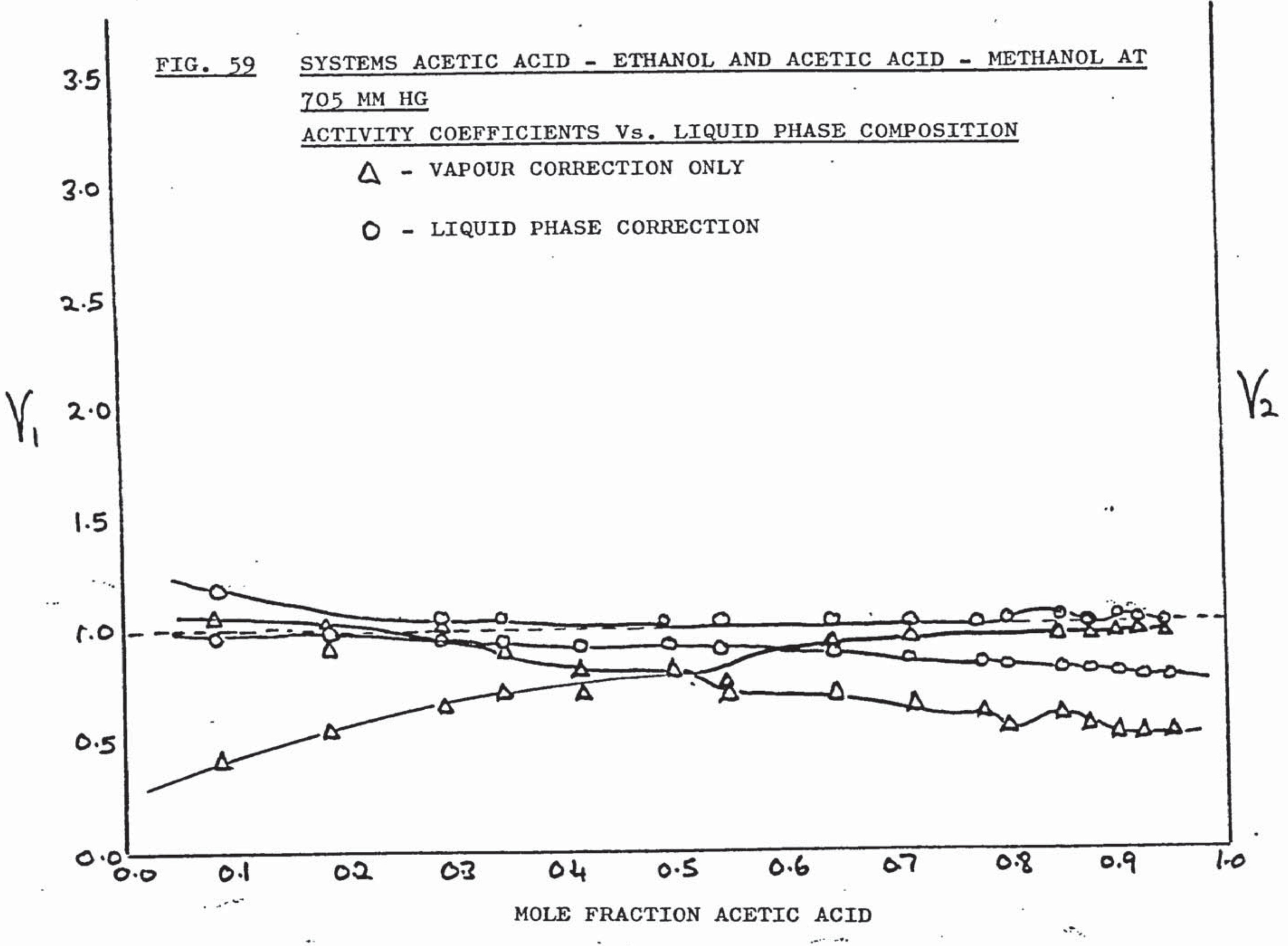


FIG. 59 SYSTEMS ACETIC ACID - ETHANOL AND ACETIC ACID - METHANOL AT 705 MM HG

ACTIVITY COEFFICIENTS Vs. LIQUID PHASE COMPOSITION turn would lead to a substantial reduction in computional effort. It would also account for the fact that the Liszi correlation for k_m against x is not successful when applied to systems other than the carbon tetrachloride-acetic acid system from which it was derived. It was also found that the correlations were not particularly affected by varying k_A implying that it is the variation of k with composition that is important. This would explain why improvements obtained by fitting with a concentration independent k are only marginal.

It is also apparent from inspection of the results for the various systems that in general the deviation between y^{exp} and y^{calc} increases with increasing mole fraction of acetic acid. One possibility is that the data is inconsistent in these regions but since the trend is apparent for nearly all the systems this is unlikely. One possible explanation is that at higher concentrations, higher polymers of acetic acid are present in the liquid phase as have been found in the vapour phase. However, Freedman in his study of pure acetic acid liquid (F7) reported only dimers and there appears to be no other experimental evidence to either support or refute this view.

FIG. 60 SYSTEM ACETIC ACID - ETHANOL AT 705 MM HG (R17) CORRECTION FACTORS δ_A AND δ_B AGAINST LIQUID COMPOSITION

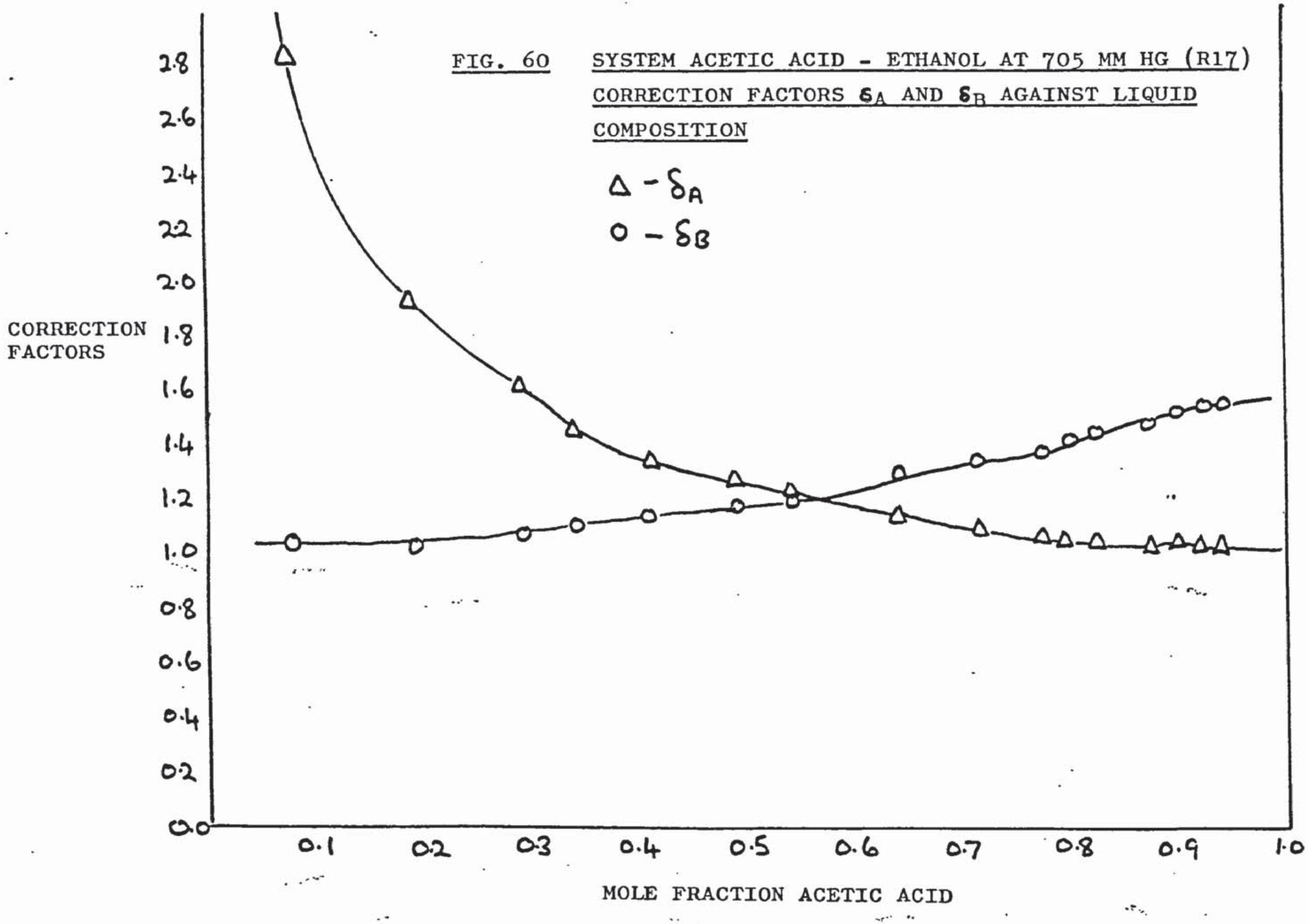
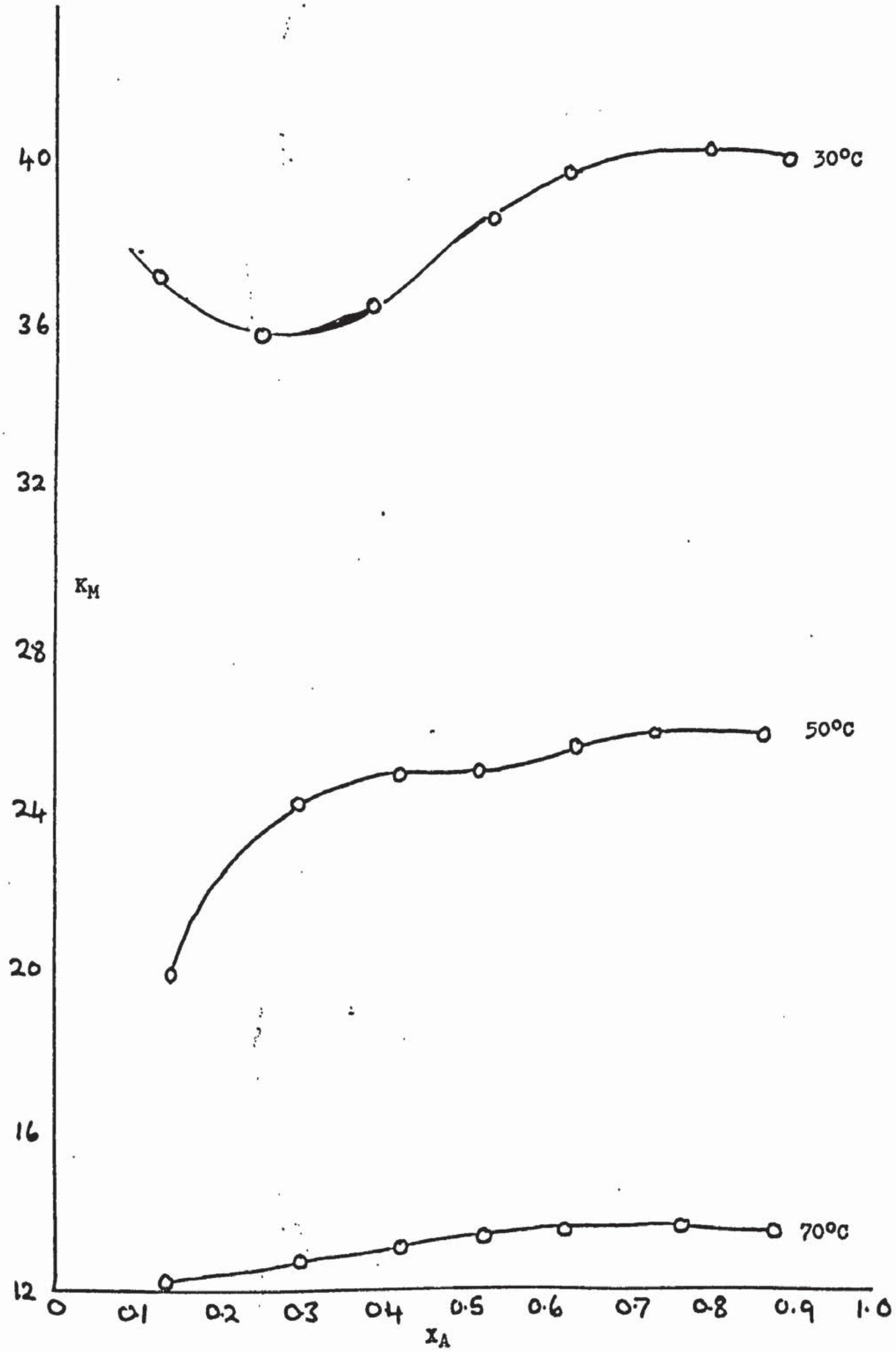


FIG. 61: EQUILIBRIUM CONSTANT, K_M V X_A FOR ACETIC ACID ETHYL ACETATE



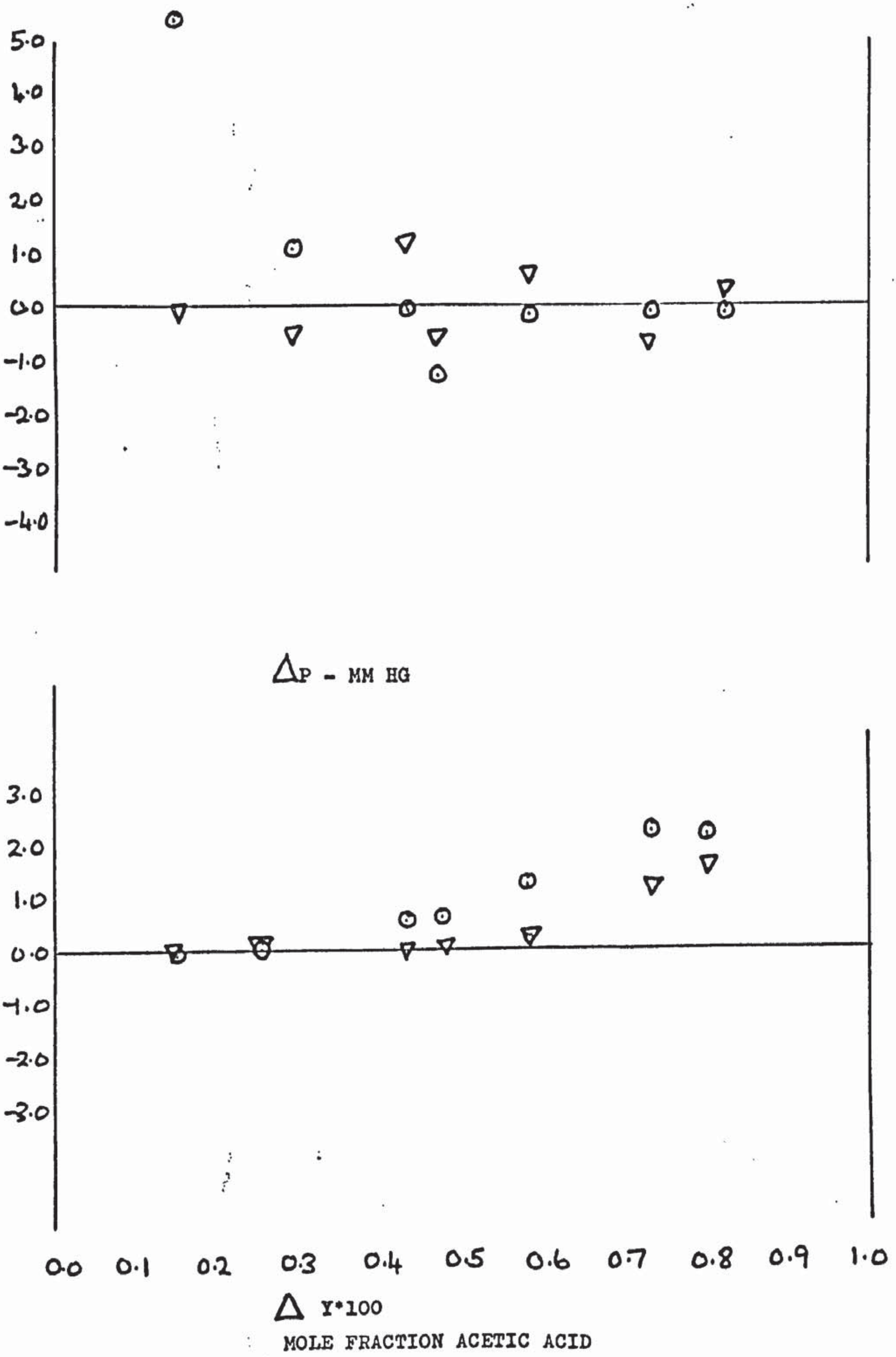


FIG. 62 SYSTEM ACETIC ACID-ACETONE AT 50°C (M17), 2 APPROACHES WILSON EQN

⊙ VAPOUR PHASE CORRECTION ONLY, ▽ LIQUID PHASE MODEL

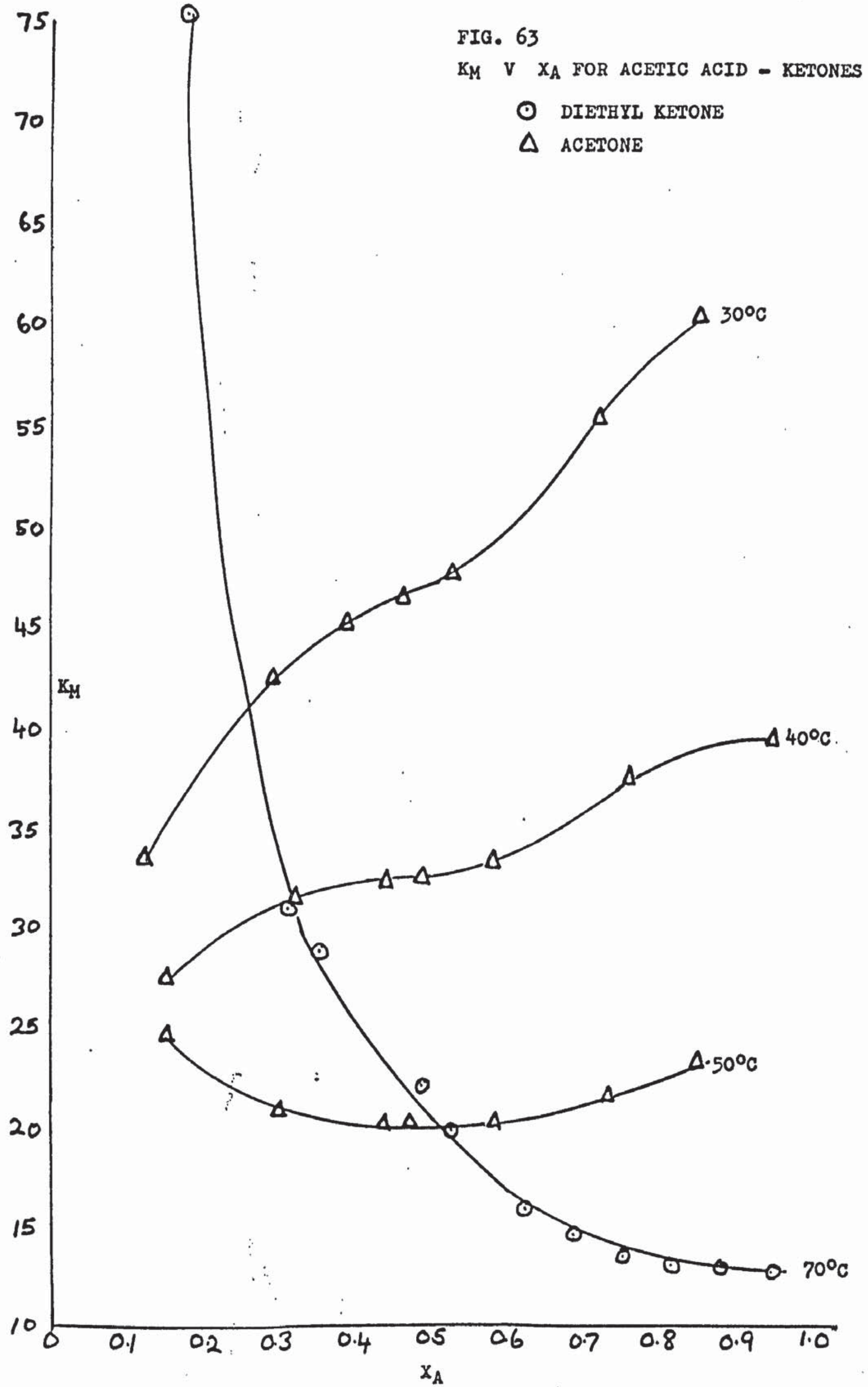
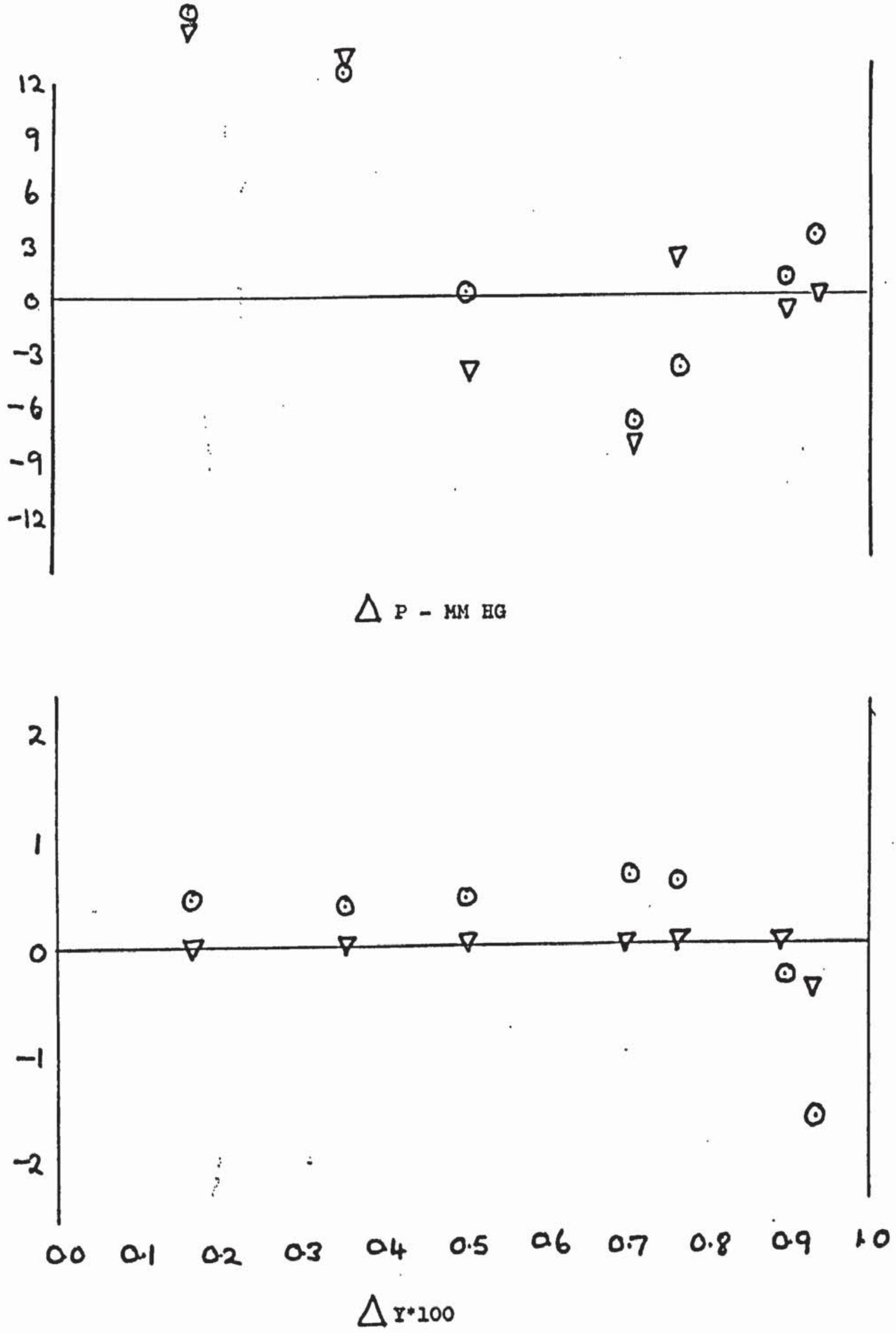


FIG. 63
K_M V X_A FOR ACETIC ACID - KETONES
⊙ DIETHYL KETONE
△ ACETONE
30°C
40°C
50°C
70°C
K_M
X_A
75
70
65
60
55
50
45
40
35
30
25
20
15
10
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

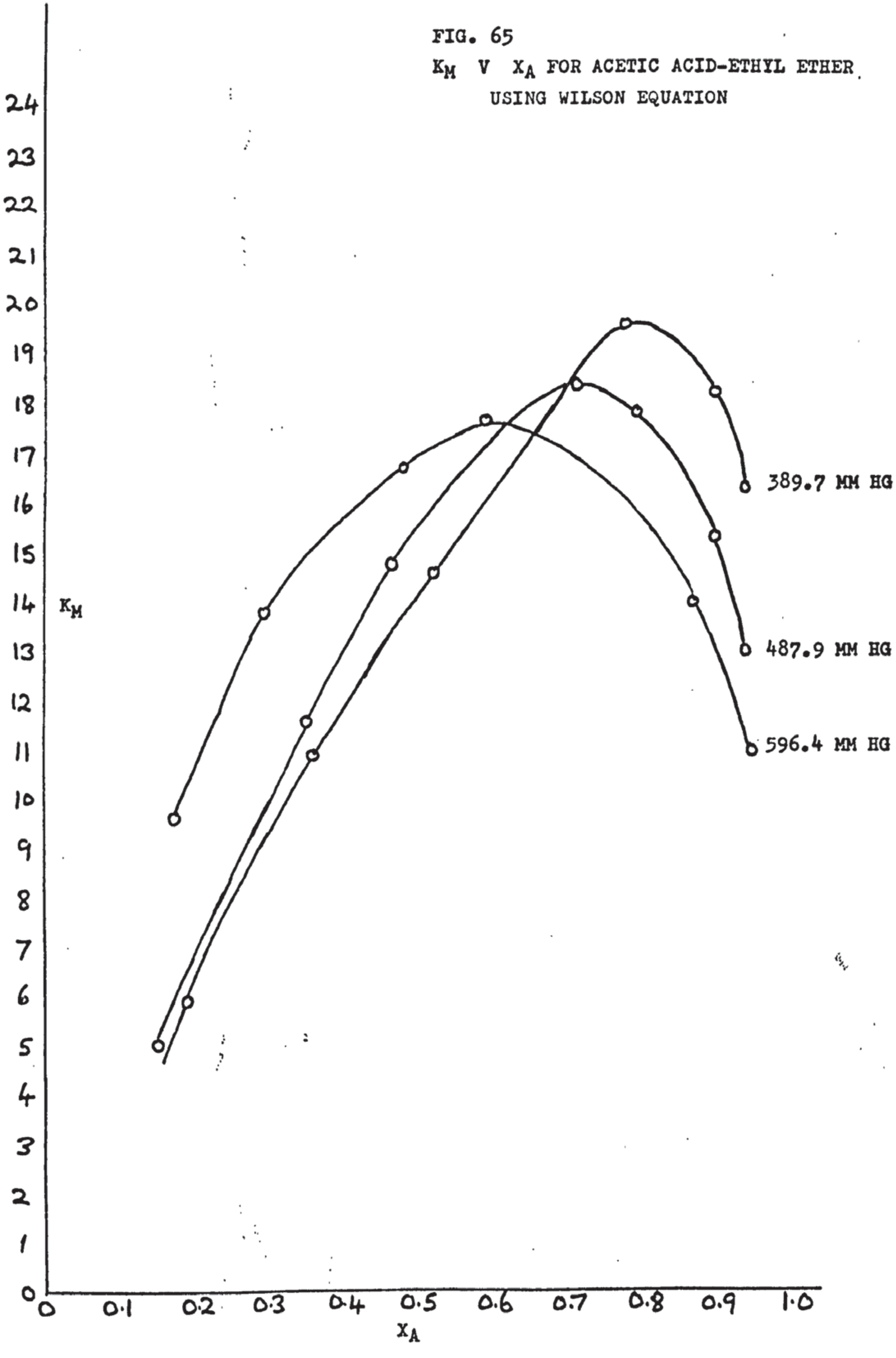


MOLE FRACTION ACETIC ACID

FIG. 64 SYSTEM ACETIC ACID - ETHYL ETHER AT 389.7 MM HG (M15), WILSON EQN
⊙ VAPOUR PHASE CORRECTION ONLY, ▽ LIQUID PHASE MODEL

FIG. 65

K_M V X_A FOR ACETIC ACID-ETHYL ETHER USING WILSON EQUATION



7.5 Comparison of various models used in reduction of V.L.E. data.

Inspection of tables 1 to 2 in Appendix A4. show the results of fitting the Wilson, the 3 parameter NRTL and UNIQUAC equations to approximately 160 systems including some containing acetic acid. For 96 of the systems the Wilson equation is marginally the best with the UNIQUAC the best in another twelve. The remainder are the best represented by the NRTL equation. It was found that the 2 parameter NRTL equation using a fixed value of α chosen according to the rules of Renon and Prausnitz (R11) gives nearly as good results as the three parameter equation and would seem to be adequate for most purposes.

The UNIQUAC equation for some systems is comparable to the Wilson equation, while in others it gives an extremly poor fit. Reasons for this are not clear.

7.6 Prediction of liquid-liquid equilibrium in system acetic acid-toluene-water.

From figs. 66 to 70 it can be seen that the two

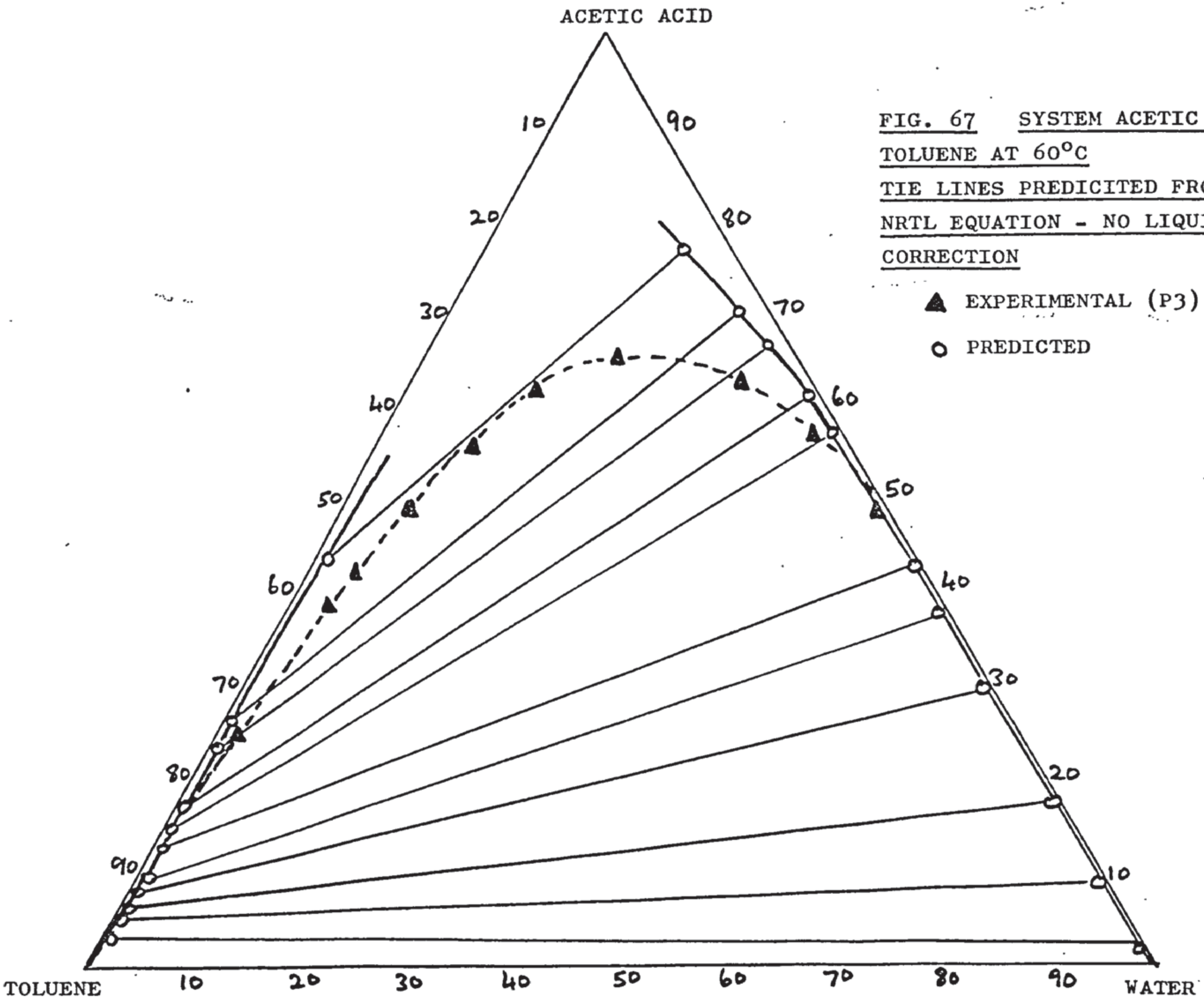


FIG. 67 SYSTEM ACETIC ACID-WATER-TOLUENE AT 60°C
TIE LINES PREDICITED FROM 3 PARAMETER NRTL EQUATION - NO LIQUID PHASE CORRECTION

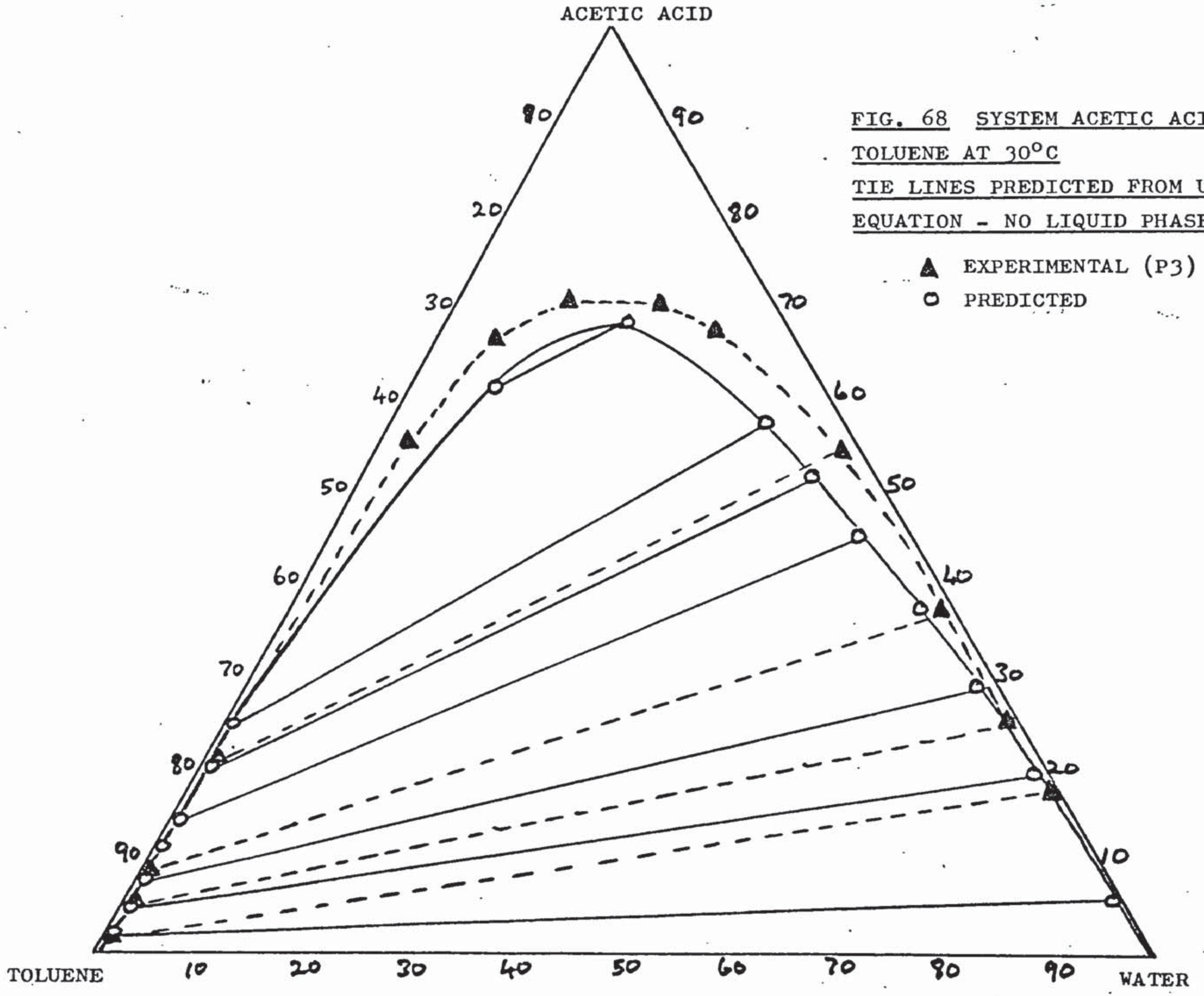


FIG. 68 SYSTEM ACETIC ACID-WATER-TOLUENE AT 30°C
TIE LINES PREDICTED FROM UNIQUAC EQUATION - NO LIQUID PHASE CORRECTION

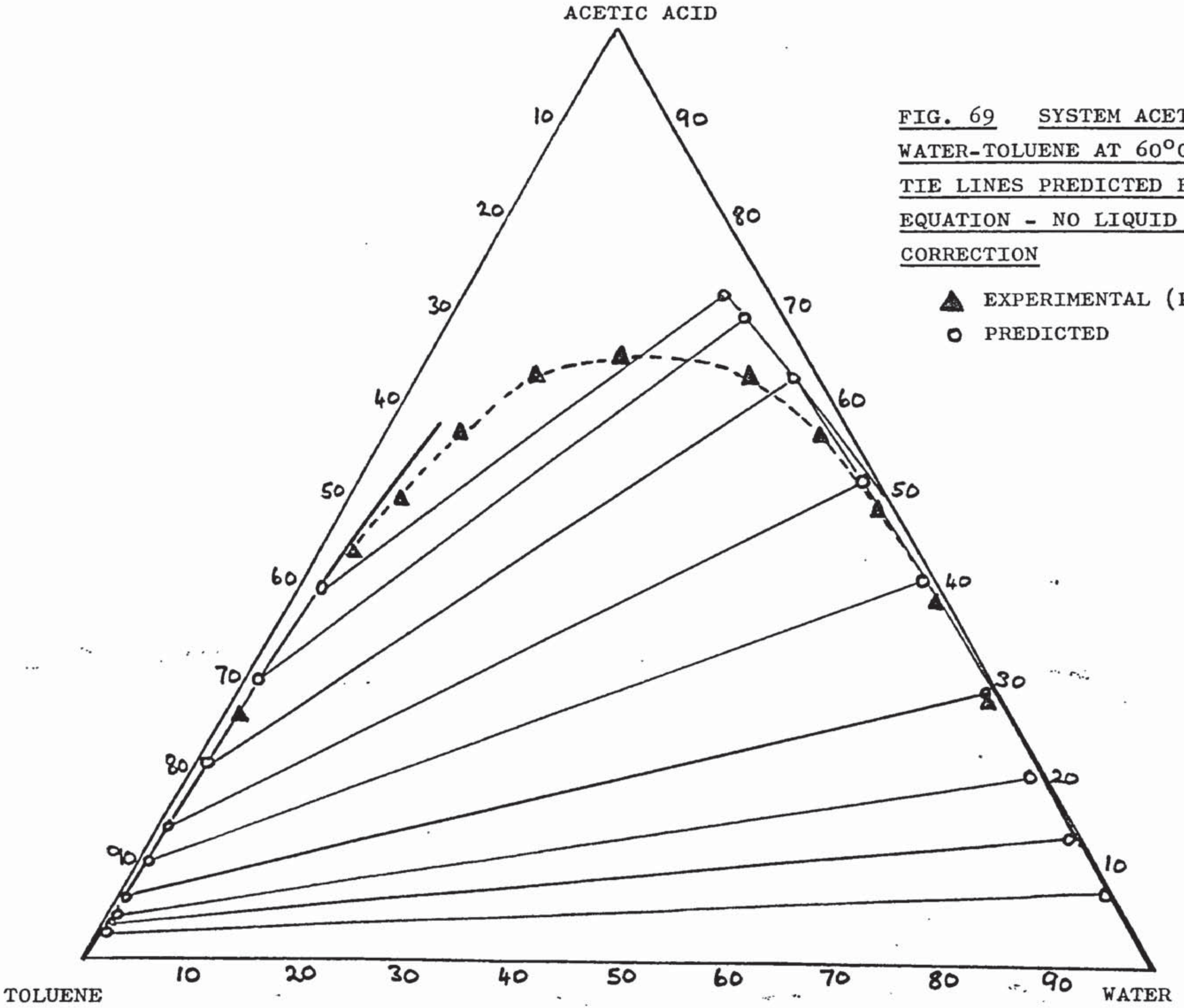


FIG. 69 SYSTEM ACETIC ACID-WATER-TOLUENE AT 60°C TIE LINES PREDICTED FROM UNIQUAC EQUATION - NO LIQUID PHASE CORRECTION

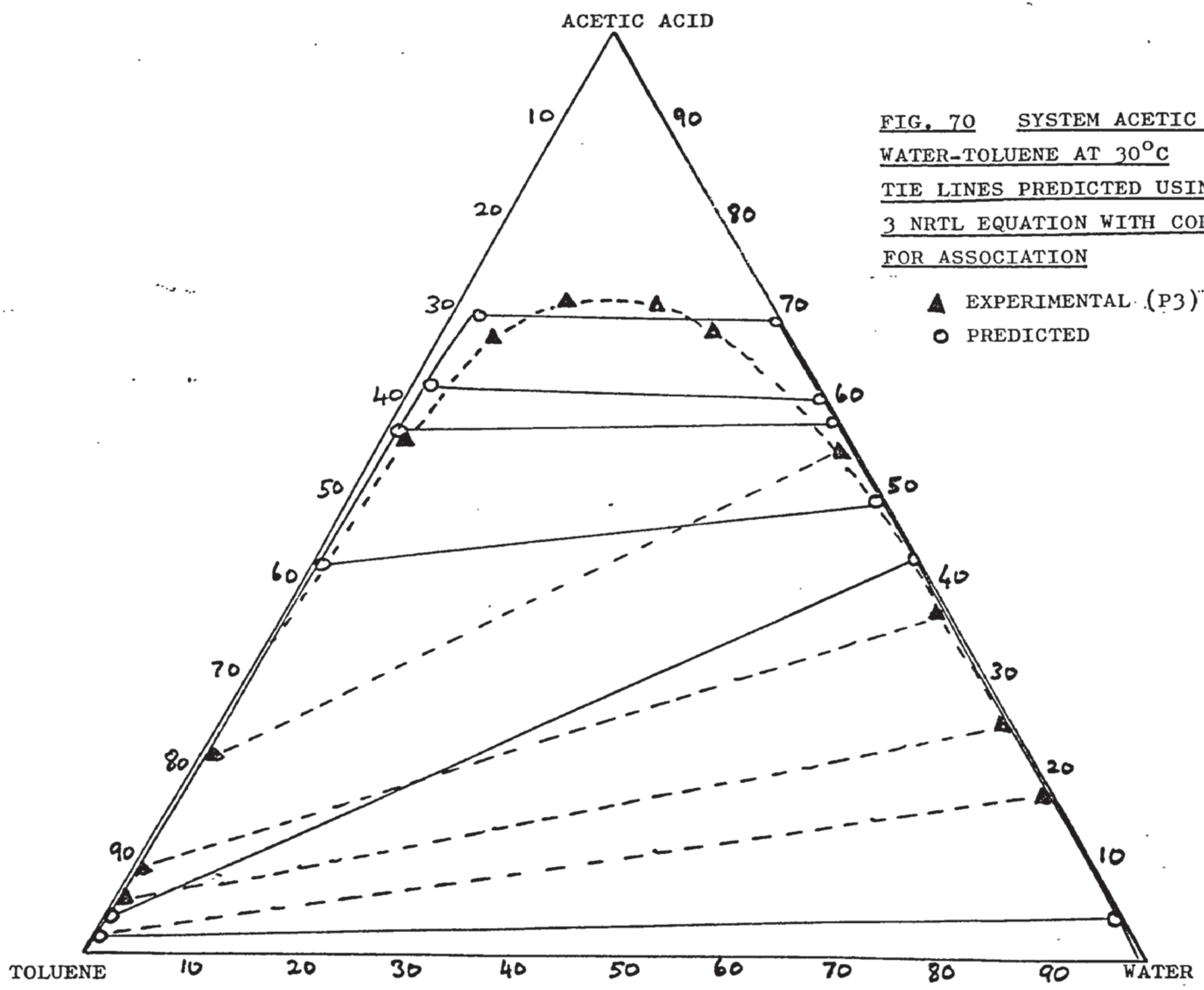


FIG. 70 SYSTEM ACETIC ACID-WATER-TOLUENE AT 30°C TIE LINES PREDICTED USING 3 NRTL EQUATION WITH CORRECTIONS FOR ASSOCIATION

phase envelope and the tie lines for the ternary liquid-liquid system acetic acid-toluene-water predicted using the NRTL equation at various temperatures are in rough agreement with experimental data (W6) (S2) (P3). However when the model using a concentration dependent k is included the results are virtually identical. This may be because the results are heavily dependent on the parameters for toluene-water and are not much affected by association in acetic acid and water. In support of this is the fact that when an attempt was made to fit the NRTL equation to tie line data by adjusting the parameters it was only possible to obtain good results when the water-toluene and toluene-water parameters were allowed to vary. When computation was attempted with these two parameters kept fixed, since they are defined by the mutual solubilities, it was found that no adjustment of the parameters for the other two systems could give a good fit.

8. Conclusions and recommendations.

8.1 Analysis of experimental work.

Vapour liquid equilibrium at a constant pressure of 760 mm Hg has been determined for the systems ethyl acetate-n-butyl acetate, ethyl acetate-n-butanol and n-butanol-n-butyl acetate. The presence of an azeotrope in the last system has been confirmed and it has been shown that the level of random error in the analytical technique has a marked effect on the correlation parameters obtained during data reduction using the Wilson and the NRTL equations.

This leads to an immediate conclusion that a small quantity of accurate data is better than a large amount of data of lower precision. It has been shown that statistical methods are not guaranteed to yield parameters which correctly model the system behaviour and the failure of the various consistency tests employed to detect any systematic errors in the system n-butanol-n-butyl acetate suggest that only gross error may be detectable by such tests and that there must be

Some doubt as to the usefulness of consistency tests in general. This work has shown that satisfaction of the various criteria proposed in different tests does not necessarily give an indication of the absolute accuracy of such data.

Furthermore it is evident from this work that nothing is lost by using the Gibbs-Duhem equation in the Barker method in conjuction with experimental techniques which eliminate the need for analysis, provided that the effects of association are properly accounted for. That this is an advantage should be realised from the fact that the greatest contribution to random error in the data comes from the level of reliability and accuracy of the analytical technique.

It may also be concluded that despite the limitations of the consistency tests the Cathala still produces data equal in value to that obtained on other flow and circulatory stills and may therefore be used with as much confidence as these other devices in the determination of V.L.E. data in general and, further it can be used in reactive systems.

The results of the consistency tests when applied to the system n-Butyl acetate-n-Butanol indicate the possibility of association effects. A marked deviation appears in the plot of ΔY against x although the results appear to be in approximate agreement with those of other workers (B19) (S9).

8.2 Modelling of acetic acid association.

In this work three possible approaches to modelling systems containing acetic acid have been explored by carrying out Barker fits on the various data sets set out in Appendix A3. In virtually all cases the results obtained show that only the model derived in this work, which uses a concentration-dependent liquid-phase association constant, can adequately represent the equilibrium data. In the previous chapter results for the various systems have been considered in detail but it is possible to draw a number of general conclusions based on the trends observed in the body of data considered.

Firstly it appears that for acetic acid-hydrocarbon systems, at least, that parameters obtained for the Wilson and NRTL equations, during the Barker fits on the data using a concentration dependent k, give superior estimates of the heat of mixing when substituted into the appropriate forms of the equations (see eqn. A1.35) This is demonstrated in figs. 34 to 38 where the results obtained from both approaches are compared with the experimental results of Liszi.

Examination of figs. 30 to 50 in which the value of the concentration dependent constant, k_m is plotted against x, the liquid phase mole fraction indicates similar trends for the various classes of compounds considered. This raises the possibility that it may be possible to develop a polynomial expression for the variation of k_m with temperature and liquid mole fraction with constants that are unique to each class of compounds such as the hydrocarbons, ketones etc. This would sharply reduce the amount of computation required making the approach more attractive for general use.

In general a marginally better fit of the pressures is obtained compared with the standard approach. This is not surprising since normally it is possible to fit most data to within the experimental error, and by and large a good fit was initially obtained on the pressure, This latter fact taken with the significant deviations between the experimental and measured vapour compositions strengthens the supposition that the models used for the fits are inadequate when no account is taken of association. It is also true that the results obtained when applying the model to isobaric data are not so good as in the isothermal cases.

On examining the results it is apparent that in virtually all cases that at high acid concentrations a systematic deviation occurs which is quite large for some systems, in particular those which contain another associating component such as alcohols. Reasons for this are not clear but it does appear to be possibly due to inadequacy of the model (as has been noted previously). It may be that at richer acetic acid concentrations there is a tendency for higher polymers to form although there is no experimental evidence to support this for the liquid phase, or it may be due to deficiencies in the data-reduction procedure. There is however reason to doubt this latter supposition since if this was so the deviation would tend to appear at the low concentration end of the data set just as often as at the high concentration end.

An additional possibility could be erroneous values for the saturated vapour pressure of acetic acid. Although a good fit to the extended Antoine equation was achieved there was no check on the accuracy of the experimental data. It may be necessary to redetermine the vapour pressure of acetic acid.

Most of the data sets considered appear to be consistent when association has been taken into account. Among the exceptions to this are the results of Othmer (O8) for the system acetic acid-benzene, those of Volpicelli and Zizza (V8) for acetic acid-toluene, although as has been pointed out earlier it appears that the results presented in their paper are a mixture of derived and experimental values, and the data of Bagga and Raju (B2) for the systems acetic acid-p-xylene and acetic acid-ethylbenzene. Furthermore the acetic acid-p-xylene data quoted by Marek (M6) also appears inconsistent. The other acetic-acid-hydrocarbon system which appears marginally inconsistent is that due to Schicktanz (S16) for octane. Other data sets, which may be inconsistent are acetic acid-chloroform (K5), acetic acid-water of Riveng (R14) and Brown and Ewald (B16) and acetic acid-cyclohexyl acetate (B12). The data of Amer Azega (A3) for acetic acid-alcohols also give poor results. In this case data exists for the same systems by a different worker (R17) which gives much better results and therefore the quality of the data is in doubt rather than the ability of the model to represent data for systems of this kind.

Examination of the performance of the three models employed: Viz: the Wilson and 2 and 3 parameter NRTL equations yields the conclusion that if association has been properly accounted for then there is no discernable advantage in any one of them and it is best to use the simplest. Although it has not been done in this work, it is possible that using the Wilson or NRTL equations with only one adjustable parameter as described by Eckert (P6) and Bruin (B18) would yield just as good results.

8.3 Multicomponent V.L.E. for ethyl acetate-ethanol-n-butanol-n-butyl acetate.

It is impossible to come to any positive conclusion as to the quality of the data for the quarternary and four ternary systems involving the above components since it was impossible to obtain fits to the Wilson equation for systems involving n-butanol which gave non-random trends.

8.4 Prediction of liquid-liquid equilibrium in the system acetic acid-toluene-water.

The prediction of tie-lines and the two phase envelope for this system was accomplished using the three parameter NRTL equation. Parameters for the toluene-water binary were obtained by fitting the NRTL equation to mutual solubility data and for the other two binaries by reduction of V.L.E. data at the appropriate temperatures. The results obtained were in approximate agreement with experimental data. No improvement was obtained when the concentration dependent correction factors were introduced both during the initial reduction on the two V.L.E. binaries to give parameters needed for the prediction procedure and during the prediction itself. It seems that results are dependent on the quality of the mutual solubility data and the parameters obtained therefrom and any improvements that may be obtained from correcting for association are masked by this. However it is difficult to draw any firm conclusion from this section of work since the prediction technique used depends on nested iteration loops which it was found were critically sensitive to the choice of convergence criteria. Moreover the use of a concentration dependent value of k adds an extra iteration loop which correspondingly makes the results more difficult to compute and more uncertain. The UNIQUAC equation was also used but gave very poor results initially and failed to give convergence when used with the new model, even though good fits appeared to have been obtained for the consistent binaries. This point will be returned to in the next section.

8.5 Comparison of Wilson, NRTL and UNIQUAC equations.

The results obtained during the data fits on systems listed in Appendix A4 indicate that the Wilson equation is marginally better than the NRTL equation and substantially better than the UNIQUAC equation for most cases. Notable exceptions are systems containing water or alcohols where the more complex NRTL equation is superior. It is therefore concluded that unless it is suspected that association or solvation take place or the system is partly immisible then the Wilson equation is the most satisfactory equation. It also appears that the two parameter form of the NRTL equation is adequate for most cases but for reasons unknown the UNIQUAC is very unreliable both for the representation of V.L.E.

data and liquid-liquid equilibrium data as has been pointed out earlier.

8.6 Recommendations for future work.

The unsatisfactory nature of the data for the system ethyl acetate-n-butanol and the appearance of significant non random trends for n-butanol-n-butyl acetate, coupled with the rather high level of random error occasioned by the proximity of the refractive indices for the two components, renders the redetermination of the data for these two systems desirable. It is felt that the feed system to the Cathala still should be modified to ensure steady flow since during the experimental work it was found that extreme care was needed to obtain steady flow conditions. It was also felt that part of the scatter in the result was ~~due to~~ caused by fluctuations in the feed system. In addition to establish whether the inconsistency observed in the system n-butanol-n-butyl acetate was because of malfunction of the still or to chemical effects, an alternative method of analysis should be employed such as density measurements.

The modelling of acetic acid systems using a concentration dependant k opens many avenues for further work. In particular there is a need to investigate the origins of the non-random trend that occurs in virtually all data sets. A possible approach would be to try to extend the model to account for higher polymers. The difficulty would arise of finding a suitable pure component equilibrium constant for higher reactions should no values be available in the literature. Values for dimerisation and tetramerisation have been reported by Ritter and Simons for pure acetic acid vapour and as a first approximation it is suggested that the ratio between the two in the vapour phase is taken to be the same in the liquid phase. It has been mentioned earlier that the results are relatively insensitive to the values of the pure component constant k_o, depending rather on the variation of k with composition. Thus provided the ratio between k_o (dimer) and k_o (tetramer) is of the right order of magnitude, some indication may be obtained as to whether this is the reason for the trend. It will require however a considerable amount of work to extend the approach to higher polymers and it is open to question whether the extra effort entailed is worthwhile for general use even though in a few cases the deviations are quite marked. It is also felt that there is scope for reduction in the computational effort. One approach is to try to fit the values of k_m obtained during the data reduction procedure to a suitable polynomial in x, the liquid mole fraction and to see whether particular classes of systems can be characterised by suitable coefficients. If this could be achieved then it would lead to a substantial reduction in computer time and make the approach more attractive for incorporation in design procedures etc. As has been mentioned earlier similar trends are apparent in the plots of k_m against x for groups such as acetic acid-hydrocarbons.

A most important piece of further work is to apply the new model to multicomponent vapour liquid equilibrium, since most practical systems encountered are liable to contain more than two components. This would require little extra work to incorporate the procedure in the bubble point programmes of Prausnitz in place of conventional activity coefficient equations.

It would also be of interest to test the approach on systems containing the higher carboxylic acids such as proprionic and butyric acids. Freedman (F7) gives values for k_o for several of these and provided suitable data can be found little modification to the programmes is required. In addition the approach could be further extended to account for association in systems containing alcohols such as the n-butanol-n-butyl acetate systems on which data has been gathered during this work. This may lead to better results for acetic acid-alcohol systems since, as has been mentioned previously it is felt that the less sucessful fits obtained on these types is at least partially due to the complex behaviour of the alcohols.

It has been noted that when used in conjunction with correction factors the 3 parameter NRTL equation offers no improvement over the 2 parameter version and hence it may well be possible to use the one parameter versions of the Wilson and NRTL equations as suggested by Bruin and others (B18) (T7). This would greatly simplify the data reduction process and is a point well worth pursuing. In conjunction with this attention should be paid to the least squares method used to fit the data. The modified Rosenbrock method used, while being very reliable is slow. Other methods tried have included those of Marquardt (M11) and the Spiral Algorithm of Jones (J7) but these have tended to be erratic although considerably better in some cases. Further investigation in this area would be worthwhile. Another area in which further work is required is in the prediction of the heat of mixing in acetic acid systems using the new approach. As has been noted previously the predictions obtained from parameters obtained with the association model appear to give a better prediction of the heat of mixing - at least in acetic acid - hydrocarbon systems - when they are substituted into the differentiated forms of the Wilson and NRTL equations. It would be of interest to try this with other systems and clarify this point.

The problems associated with the computation of the two phase envelope and tie lines in ternary component liquid systems have been mentioned. The method used based on that described by Null (N8) is not satisfactory, both tending not to converge and to giving erroneous values. In particular the incorporation of concentration dependent correction factors necessitates the inclusion of additional iterative loops in the procedure which makes it very slow to converge if at all. For this reason it was impossible to draw any positive conclusion as to the effect of the introduction of the approach of this work into the procedure. It is recommended that alternative methods are explored, in particular the method of 'minimization of free energy' described by Dluzniewski and Adler. Another possibility is to use a least squares fit on to the tie line data. This was tried during this work but was not very satisfactory since the results appeared to be sensitive only to variations in the parameters for toluene-water and water-toluene. It would be of interest to see whether data reduction using the new approach would overcome this.

Finally, it was found during this work that the UNIQUAC model of Abrams and Prausnitz (A2) performed extremely badly compared to the Wilson and NRTL equations for a substantial number of systems, especially when used to predict liquid-liquid equilibrium. Possible reasons for this may be that the actual numerical method i.e. Rosenbrocks was unsatisfactory, or the model is not very good or the equation is sensitive to the values of r_i and q_i, the parameters which must be calculated from X ray diffraction data. Although Abrams and Prausnitz claim that it is not sensitive to values of the co-ordination number, Z, it would be worthwhile investigating the sensitivity of the results to r_i and q_i.

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LIST OF SYMBOLS.

a. ALPHABETIC.

SYMBOL.	MEANING.	FORTRAN NAME(S)
a	Van der Waals constant.	-
b	"	-
B_{ii}	Second virial coefficient.	B(I,I)
E(f)	Error bound for function f.	EG(F)
f_i	Fugacity, component i.	-
f(a,b)	Consistency test function between pts A & B.	F(A,B)
G,g	Gibbs free energy.	GEEPL, GECALC
H,h	Enthalpy.	HEPL, HCALC.
K_d, K_t	Equilibrium constant for dimer and tetamer.	KDIM, KTET.
n_i	No of moles, component, i.	-
P, p	Pressure.	PEPL, PCALC, PF.
Psi.	Saturated vapour pressure component, i.	PSAT (I,J).
P_f	Probability (binonial)	-
P_c	Critical pressure.	PCRIT (I,I).
q	Heat added to system.	-
q_i	Parameter for UNIQUAC equation.	QUA(I)
R	Gas constant.	R, GC.
r_i	Parameter for UNIQUAC equation.	RAD(I).
S	Entropy.	-

LIST OF SYMBOLS (CONTINUED).

a. ALPHABETIC.

SYMBOL.	MEANING.	FORTRAN NAME(S)
S^2_{pf}, S_{pf}	Variance and std deviation of p_f.	SPFSQ, SPF.
S_x, S_y, S_T, S_p	Std deviations of experiment x, y, P, T.	SX, SY, SP, ST.
T	Temperature.	Temp.
T_c, T_R	Critical temperature, Reduced temperature.	TCRIT (I,T).
U	Internal energy.	-
V	**Volume.**	-
V_i v_i	Liquid molar volumes.	MLIQV (I,J).
V_c	Critical volume.	VCRIT (I,I).
W	Work done by system.	-
x_i	Mole fraction component, i.	X(I), XA(I).
Z	Compressibility factor.	-

b. GREEK.

SYMBOL.	MEANING.	FORTRAN NAME(S)
$\delta_A, \delta_B, \delta_A$.	Correction factors for association.	DELTA (I,J).
η	Association factor for normal system.	ETA
ξ_i	True mole fractions in acetic acid liquid.	-
$Ø_i$	Fugacity coefficient, component i.	PHI, PHISØ,FUGC.

LIST OF SYMBOLS.(CONTINUED).

b. GREEK.

SYMBOL.	MEANING.	FORTRAN NAME(S)
η_i	True mole fractions in acetic acid vapour.	-
γ_i	Activity coefficient component, i.	G, ACT, GAMMA.
γ_i^{∞}	Infinite dilution activity coefficient.	GINFEX, GINFC.
μ_i	Chemical potential component, i.	-
μ, μ_R	Dipole and reduced dipole moment.	MU(I), RD.
W_i, W_H	Acentric factor, component, i and homomorph.	OMEGA, OMEGAH.

APPENDIX A1 - MANUAL OF COMPUTER PROGRAMMES

1. General Considerations

1.1. CONTROL CARDS

The programmes are written in CDC FORTRAN and are all stored on file at the University of Manchester Regional Computer Centre (UMRCC). The hardware consists of a CDC 7600 computer with an I.C.L. 1906A computer as a "front end". The 7600 is a very fast computer and as such is used primarily for 'number crunching'. There is a limited permanent filestore associated with it, but, use of this is severely restricted to certain users. The majority of files are stored on the 1906A machine whose main function is to handle input and output and to supply the CDC 7600 with temporary files and attached data in machine code for processing, together with manipulation of files. Though the 1906A can perform work in its own right, the system used is the one that has just been described. The University of Aston has a link with Manchester via Birmingham University but jobs may only be submitted on cards. The jobs may either be input as complete jobs with the programme + data submitted or as data only with the programme on file or with both cards and data on file. Most work to date has been carried out using the second option. Similarly editing instructions may only be submitted on cards as will be described later.

The control cards required for the various options are as follows:

For a job with programme and data on cards the layout is as follows

```
JØB  :EAXXX, JF4JØB, CP76 (Tn, Pn000)
FTN.
LDSET (MAP = B/ZZZZMP, PRESET = ZERØ)
LGØ.
####S
↑
DATA
↓
****
```

Note that the MASTER and FINISH cards required if a job is to be submitted to the University of Aston computer are omitted when using the Manchester system.

For a job which requires the use of a programme on file on the 1906A with the data to be input on cards the layout is as follows

```
JØB :EAXXX, JF4JØB, CP76 (Tn, Pn000)
ATTACH (SOURCE, JF4FILE, ST = S6A)
FTN (I = SØURCE, SL = 0)
LDSET (MAP = B/ZZZZMP, PRESET = ZERØ)
LGØ (PL = n000)
####S
↑
DATA
↓
****
```

If both data and programme exist on file then the layout becomes

```
JØB  :EAXXX,JF4JØB, CP76 (Tn, Pn000)
ATTACH (SØURCE, JF4FILE, ST = S6A)
ATTACH (DATA, JF4DATA, ST = S6A)
FTN (I = SØURCE, SL = 0)
LDSET (MAP = B/ZZZZMP, PRESET = ZERØ)
LGØ (DATA, PL = n000)
####S
****
```

Other combinations are possible and will be described later.

Points to note when using the preceding job layouts are as follows. Firstly all filenames and jobnames must be prefixed by the code JF4 which is a registered user name with the UMRCC. Job names can total up to 6 aplhanumeric characters leaving three after the mandatory JF4 for the choice of the user. An example is shown in the above examples i.e. JF4JOB. File names may consist of up to nine characters after JF4 to give a total of twelve. In the examples JF4FILE is a filename for a file containing a programme to be compiled while JF4DATA is a file containing data only.

The parameters EAXXX and CP76 are the University of Aston user No. and a specification for the computer to be used for processing respectively. CP76 refers to the CDC 7600 while CP19 requests the 1906A.

The job time may be controlled by means of the parameter Tn where n is the number of octal seconds of central processor time required. For instance T40 requests 40 octal seconds (32 real time seconds) which is adequate for all but very time consuming jobs. The turn round time may be varied according to the value of n in the Pn000. n may take any value from 0 to 5, the highest priority P5000 giving a turn round of less than half an hour with P1000 taking anything up to a week. There are, however, penalties associated with the use of a higher priority. Each succeeding increase in priority increases the unit cost factor by 2 and higher priorities have lower limits on the value of n in the Tn parameter (i.e. T4 at P5000 is the upper limit). P2000 is suitable for most jobs with P3000 used if a fast turnround is required.

Other adjustable parameters are the PL = n000 command which specifies the number of lines of output required. The default value is 1000 in which case the command LGO (PL = n000) reduces to LGO.. A listing of the compiled file may be obtained by setting R = 0 in place of SL = 0 in the FTN request. If SL = 0 is retained then only the compilation error messages together with the line of the file which they refer to will be printed out.

The command PRESET = ZERO may be replaced by PRESET = NGINF in which case all variables and arrays must be initialised. This latter form can be helpful in error diagnostics.

1.2 LIST OF FILES

The files may be divided into six groups. The first group involves a least squares data reduction by various non-linear methods to a variety of models. The files in this group are as follows

1. JF4LSQMKK
2. JF4LSQMKC
3. JF4LSQMKJ
4. JF4LSQSOL
5. JF4LSQMKR
6. JF4LSQFIT
7. JF4LSQSPI
8. JF4LSQMARQFT
9. JF4LSQMKH
10. JF4REACTC

The second group contains the various consistency tests which have been merged into one file

11. JF4ERRAN

The third group are for the prediction of liquid-liquid equilibrium by an iterative method

12. JF4LIQLIQ
13. JF4LAQLAQ

The fourth group consists of a file containing a least squares fit on liquid-liquid equilibrium data by means of a non linear method

14. JF4LFT

The fifth group consists of programmes to predict multi-component vapour liquid equilibrium using a variety of models

15. JF4BUB
16. JF4BUBLT

17. JF4BABLT

18. JF4BIBLT

Finally there is a file enabling vapour pressure data to be fitted to a variety of polynomials of the Antoine type.

19. JF4VAPFIT

The contents of these files will be described in greater detail later.

1.3 EDITS AND COMMANDS

This section is intended as a brief resumé of commands available under the George 3 operating system. For fuller details the relevant manuals should be consulted.

To obtain a numbered listing of a particular file the following instruction is issued

```
LF  JF4FILENAME, * LP, NU
```

while to obtain a listing of the EAXXX filestore the command LD is sufficient.

A typical editing job may be as follows

```
 JOB  :EAXXX,JF4EDT
 ED  JF4FILENAME (n1) - generation number can be
 ↑                      omitted if necessary
 |
 |  editing instructions
 |
 ↓
 E
LF  JF4FILENAME (n2)
ER  JF4FILENAME (n1)
LD
EJ
****
```

The Runjob command can also be issued in this context for further details see UMRCC manual.

2. COMMON SUBROUTINES

All the programmes to be described contain a number of common subroutines. In order to avoid duplication these will be described separately prior to the description of the main programmes.

2.1. Least squares fitting subroutines

2.1.1 SUBROUTINE ROSEN

The main method used is the Davies, Swann and Company modification of Rosenbrocks direct search method. This is used to minimise an error function of the form

$$\phi = \sum_{i=1}^{N} \left[\frac{X_{iCALC} - X_{iEXPL}}{X_{iEXPL}} \right]^2 \qquad (A1.1)$$

where Xi is a variable such as pressure or vapour composition. This accomplished by adjusting the parameters of some empirical or semi empirical equation which is used to determine X_{iCALC} until a minimum value of ϕ is obtained.

The basis of the method is to search in the n mutually ortho-normal directions. The original Rosenbrock method (R16) started from a given point by making perturbations along each search direction in turn. If this perturbation results in a function value no greater than the current best value, the trial is termed a success, this trial point replaces the current point and the step length is multiplied by a factor, α and the next search direction considered. If the perturbation results in an increased function value, the trial is termed a failure, the current point remains unchanged, the step length multiplied by β and again the next search direction considered.

When perturbations have been made in all n directions, each direction corresponding to one adjustable parameter, the first direction is again explored and so on. This repeated cycling around the direction vectors is continued until a success followed by a failure has occurred along every direction.

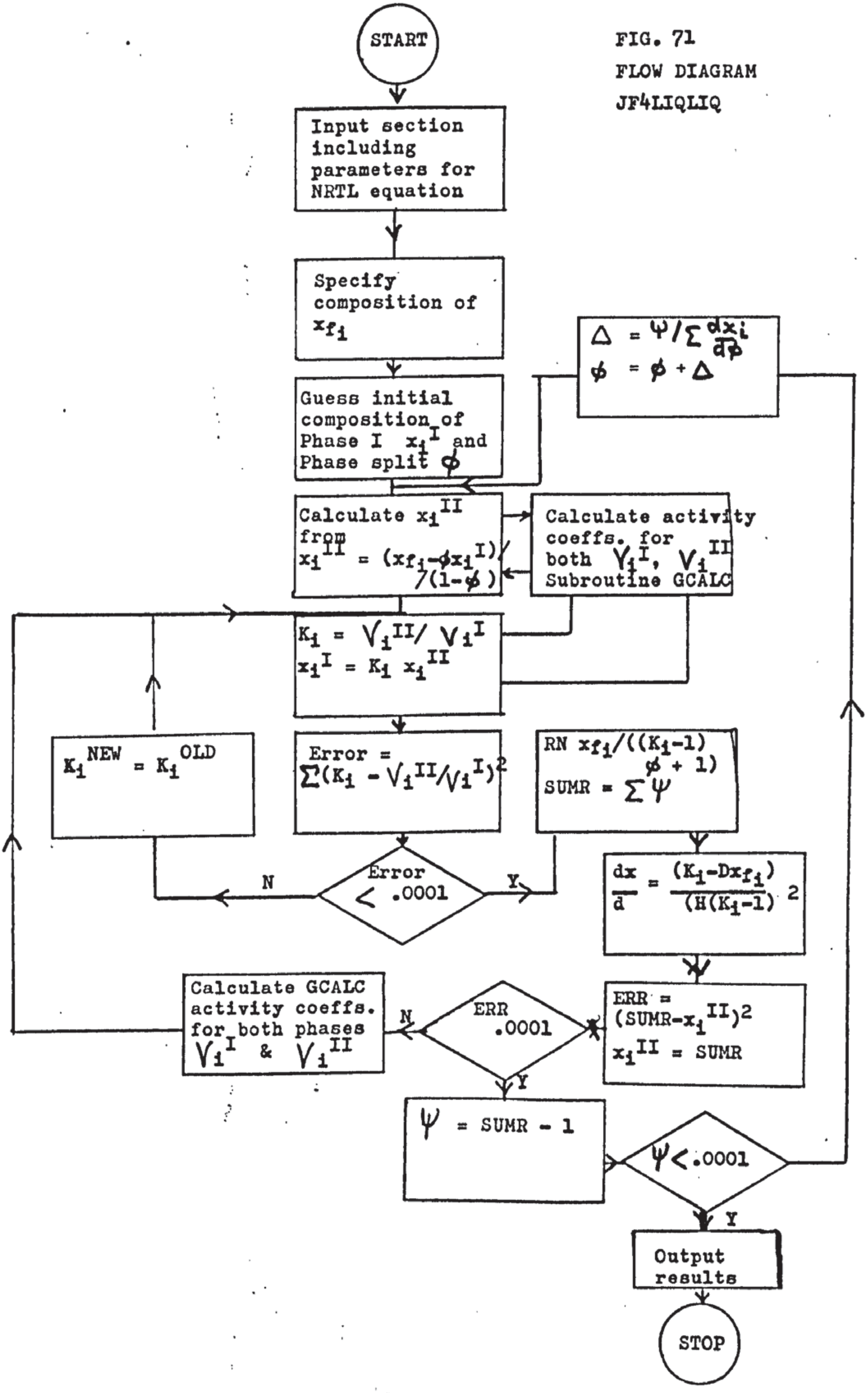
At this point a stage has been completed, and new direction vectors are computed such that the first lies in the direction of total progress made during the previous stage. The others are computed to be as nearly orthogonal to each other using the Gram-Schmidt procedure (B9) and the whole process repeated until convergence is obtained. Originally Rosenbrock set the values of α at 3.0 and β at - 0.5 which he found to be the most reasonable during testing of his method.

Swann (S17) has described a modification of Rosenbrock's method which has, in general, proved superior to it. The search proceeds in the same n orthogonal directions but a single quadratic interpolation is performed along each stage to locate the minimum. However, with this procedure it is possible that there will be zero progress in some directions which will cause the Gram-Schmidt process to fail. This was overcome by performing the orthogonalization on only those directions in which progress has been made. Convergence is assumed when the step lengths fall below a certain preset value.

This last method was programmed as SUBROUTINE ROSEN with the orthogonalization procedure as SUBROUTINE VECTOR. This employed a variation on the Gram-Schmidt process due to Palmer (P1).

This method was used for the great majority of the work.

FIG. 71
FLOW DIAGRAM
JF4LIQLIQ



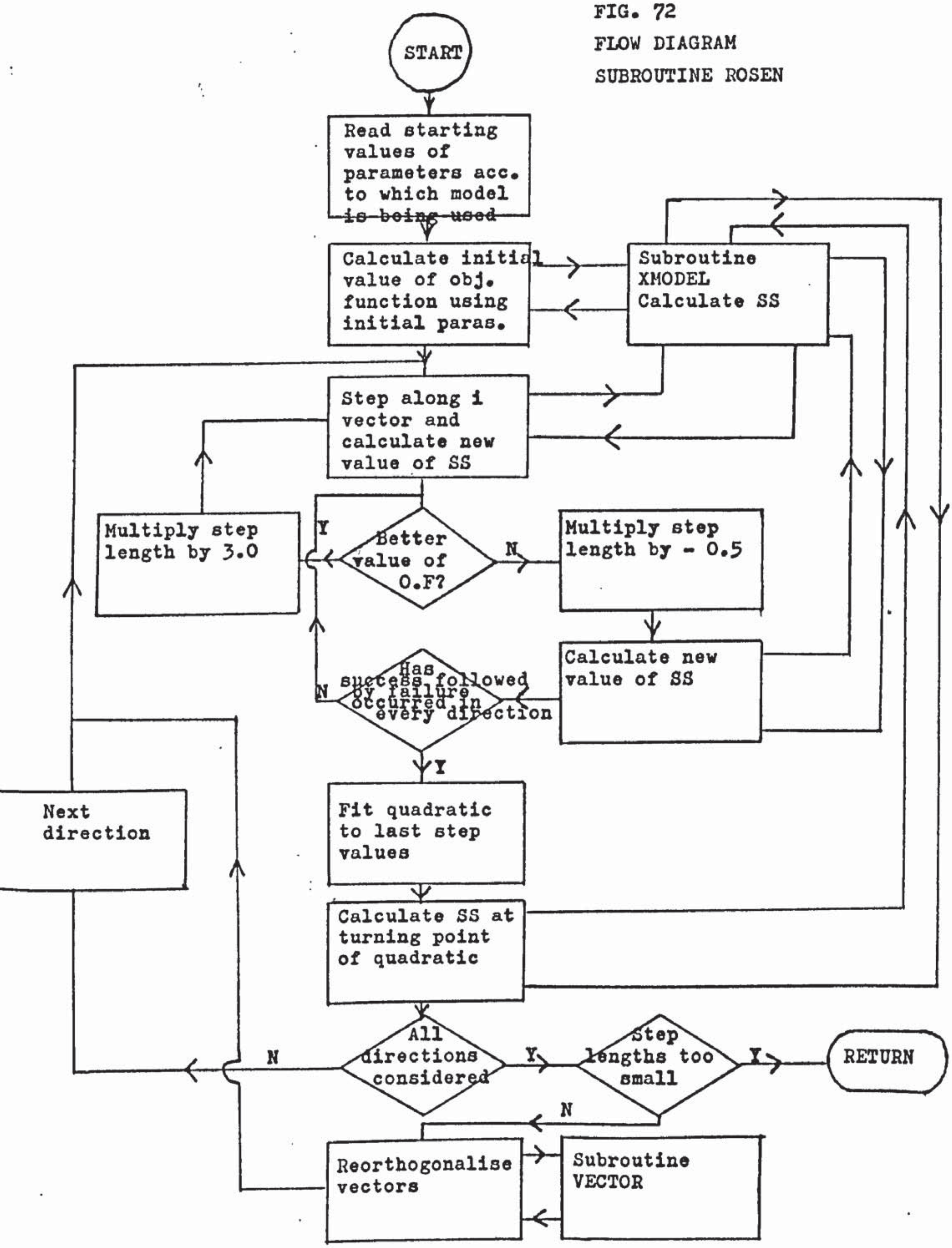
Other methods used were a version of the Spiral algorithm due to Jones (J7) and Marquardts (M11) search procedure. The former was programmed as SUBROUTINE SPIRAL and the latter SUBROUTINE MARQ but will not be described further.

A flow diagram is shown in Fig.72. The only inputs required to be read in are the initial guessed values of the variables and the number of them. The input will be discussed further in connection with the main programmes. The remainder of the input is transferred through the COMMON blocks.

2.1.2. List of variables

FORTRAN NAME	Description
X(I), Z(I)	Variable values
PW(I)	Best values of variables found to date
N	Number of variables
FUNC, F3, F2, F4, F1	Objective function values (sum of squares)
YSTAR	Best value of objective function found to date
MODEL	Model to be fitted
NERR	Number of function evaluations allowed
BETA	Failure multiplier for step length
ALPHA	Success multiplier for step length
NFUNC	Counter for function evaluations
ERROR	Convergence criterion for step length
E(I)	Step lengths in each orthogonal direction
D(I)	Distance of progress in each orthogonal direction
V(I,J)	Orthogonal vector matrix
A	Parameter to ensure success followed by failure
IFUNC	Stage counter
S, S1 STEP	Interpolated step lengths

FIG. 72
FLOW DIAGRAM
SUBROUTINE ROSEN



2.2. Physical property subroutines

SUBROUTINES VIRIAL, PHIMIX, LIQP, PCLCA

Two versions of subroutine VIRIAL were employed. The purpose of both was to calculate both the pure and mixed second virial coefficients. The first one used Prausnitz's extension of Pitzer and Curls (P4) correlation and has been extensively described by Prausnitz et al (P6). For this reason it will not be discussed further here. The second employed a new correlation developed by Tsonopoulos (T12) which has been found to be superior to earlier work.

For non polar gases a similar correlation to that of Pitzer and Curl was used based upon the three parameter theory of corresponding states.

$$\frac{P_{ci}\ B_{ii}}{RT_{ci}} = f^{o}(T_R) + W_i f^{(1)}(T_R) \qquad \text{(A1.2)}$$

where W_i is the acentric factor

and T_R is the reduced temperature T/T_{ci}

$$f^{o}(T_R) = f_{PC}{}^{(o)}(T_R) - 0.000607/T_R{}^{8} \qquad \text{(A1.3)}$$

where $f^{o}{}_{PC}(T_R)$ is the Pitzer and Curl correlation given by

$$f^{o}{}_{PC}(T_R) = 0.1445 - 0.330/T_R - 0.1385/T_R{}^{2} - 0.0121/T_R{}^{3} \qquad \text{(A1.4)}$$

$$f^{1}(T_R) = 0.0637 + 0.331/T_R{}^{2} - 0.423/T_R{}^{3} - 0.008/T_R{}^{8} \qquad \text{(A1.5)}$$

The acentric factor is defined as (P6)

$$W_i = -\log_{10}\left(\frac{P^{o}}{P_c}\right)_{T_R = 0.7} - 1.000 \qquad \text{(A1.6)}$$

For polar gases eqn (A1.3) is modified by the addition of terms which depend on whether the compound forms hydrogen bonds or not. For non hydrogen bonding compounds the term is given by

$$f^{(2)}(T_R) = a/T_R^{\,6} \qquad (A1.7)$$

Unfortunately, a is dependant on the class of compound under consideration. For ketones Tsonopoulos gives a as a linear function of μ_R, the reduced dipole moment

$$\text{i.e. } a = -\ 0.00020483\ (\mu_R) \qquad (A1.8)$$

where

$$\mu_R = \frac{10^5 \mu^2 P_c}{T_c^{\,2}} \qquad (A1.9)$$

and μ is the dipole moment in Debyes.

For ethers the relationship is

$$\ln\ (-a) = -\ 12.63147 + 2.09681\ \ln\ (\mu_R) \qquad (A1.10)$$

For hydrogen bonding compounds $f^{(2)}\ (T_R)$ is modified thus

$$f^{(2)}(T_R) = \frac{a}{T_R^{\,6}} - \frac{b}{T_R^{\,8}} \qquad (A1.11)$$

For alkanols $a = 0.0878$ while

$$b = 0.00908 + 0.0006957\mu_R \qquad (A1.12)$$

To calculate the value of the cross coefficient the mixing rules to be discussed later in connection with subroutine PCLCA are used for the mixed critical temperature T_{cij}, critical pressure P_{cij} and acentric factor W_{ij}. The mixed values for and b are given by the arithmetic means of the pure values.

A flow diagram for this subroutine is given in Fig. 73.

LIST OF VARIABLES

FORTRAN NAMES	Description
MU	Dipole moment
RD	Reduced dipole moment
PCRIT	Critical pressure
TCRIT	Critical temperature

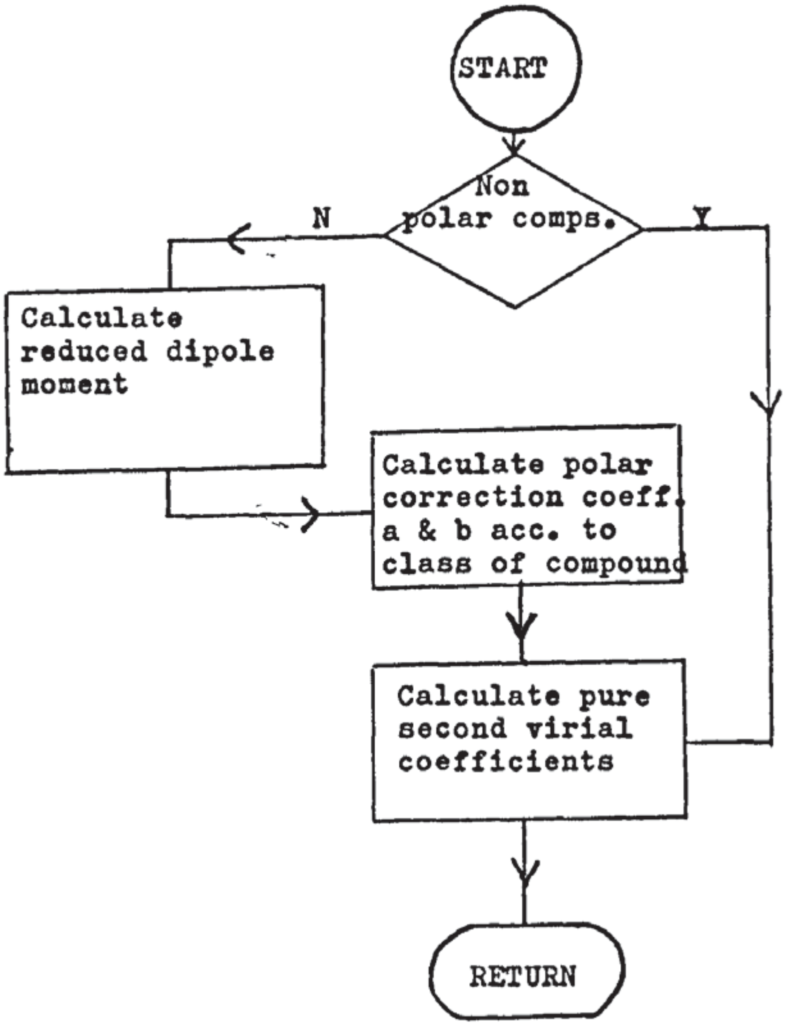


FIG. 73
FLOW DIAGRAM
SUBROUTINE VIRIAL

NCLASS (I)	Variable denoting which class system belongs to
A (I,J)	Correction term, a
BA (I,J)	Correction term, b

Subroutine PHIMIX is used to calculate the vapour phase correction factor, ϕ_1. It is identical with the subroutine described in the monograph of Prausnitz et al (P6) and will therefore not be described here.

Subroutine LIQP is similar to subroutine RSTATE described by Prausnitz et al (P6). However only components that are at a temperature less than the critical are treated. The corrections for supercritical components have been omitted.

The subroutine calculates the reference-state properties of the pure liquids at the temperature in question, i.e. the quantity

$$P_{si}\ \phi_{si}(P_{si})\ \exp\left[\frac{1}{RT}\int_{P_{si}}^{P} \upsilon_i^{L}\,dP\right] \qquad (A1.13)$$

To calculate the vapour pressure an extended Antoine type equation is used

$$\ln P = C_1 + \frac{C_2}{C_3+T} + C_4T + C_5T^2 + C_6\ \ln T \qquad (A1.14)$$

To calculate $\phi_{si}(P_{si})$ the virial coefficient is used if $T_R < 0.56$

$$\text{i.e.}\quad \phi_{si}(P_{si}) = \text{EXP}\left[\frac{B_{ii}\ P_{si}}{RT}\right] \qquad (A1.15)$$

or if $T_R > 0.56$ a generalised correlation is used due to Lyckman (P6) of the form

$$\phi_{si}(P_{si}) = \text{EXP}\ (\phi_o(T_R) + W_i\phi_1(T_R)) \qquad (A1.16)$$

$$\text{where } \phi_o\ (T_R) = 0.57335015/T_R^{\,3} - 3.076574T_R^{\,2} + 6.6085595/T_R - 3.5021358 \qquad (A1.17)$$

$$\begin{aligned}\text{and } \phi_1\ (T_R) = {} & 0.012089114/T_R^{\,12} - 0.015172164/T_R^{\,11} - 0.068603516/T_R^{\,10} \\ & + 0.024364816/T_R^{\,9} + 0.14936906/T_R^{\,8} + 0.18927037/T_R^{\,7} \\ & - 0.12147436/T_R^{\,6} - 0.10665730/T_R^{\,5} - 1.1662283/T_R^{\,4} \\ & + 0.12666184/T_R^{\,3} + 0.3166137/T_R^{\,2} + 4.3538729/T_R \\ & - 3.7694018 \end{aligned} \qquad (A1.18)$$

The liquid molar volume is calculated from the quadratic in temperature of the form

$$v_1^L(T) = a + bT + cT^2 \qquad (A1.19)$$

The coefficients a, b, and c are obtained from subroutine PCLCA. A flow diagram is shown in Fig. 74.

LIST OF VARIABLES

FORTRAN NAME	Description
MLIQV (I,J)	Molar liquid volumes
VPUNIT (I)	Parameter determining vapour pressure units
PSAT (I,J)	Vapour pressure
PHIS	$\phi_{is}\ (P_{si})$
B (I,I)	Second virial coefficient
TR	Reduced temperature T_R
CONSTB (I,J)	Molar volume constants
CONSTA (I,J)	Antoine constants
GC	Gas constant
TF	Temperature at ref. properties are to be calculated
OMEGA (I)	Acentric factor W_1

Other variables that appear are either dummy variables or occur in the main programme where they are described.

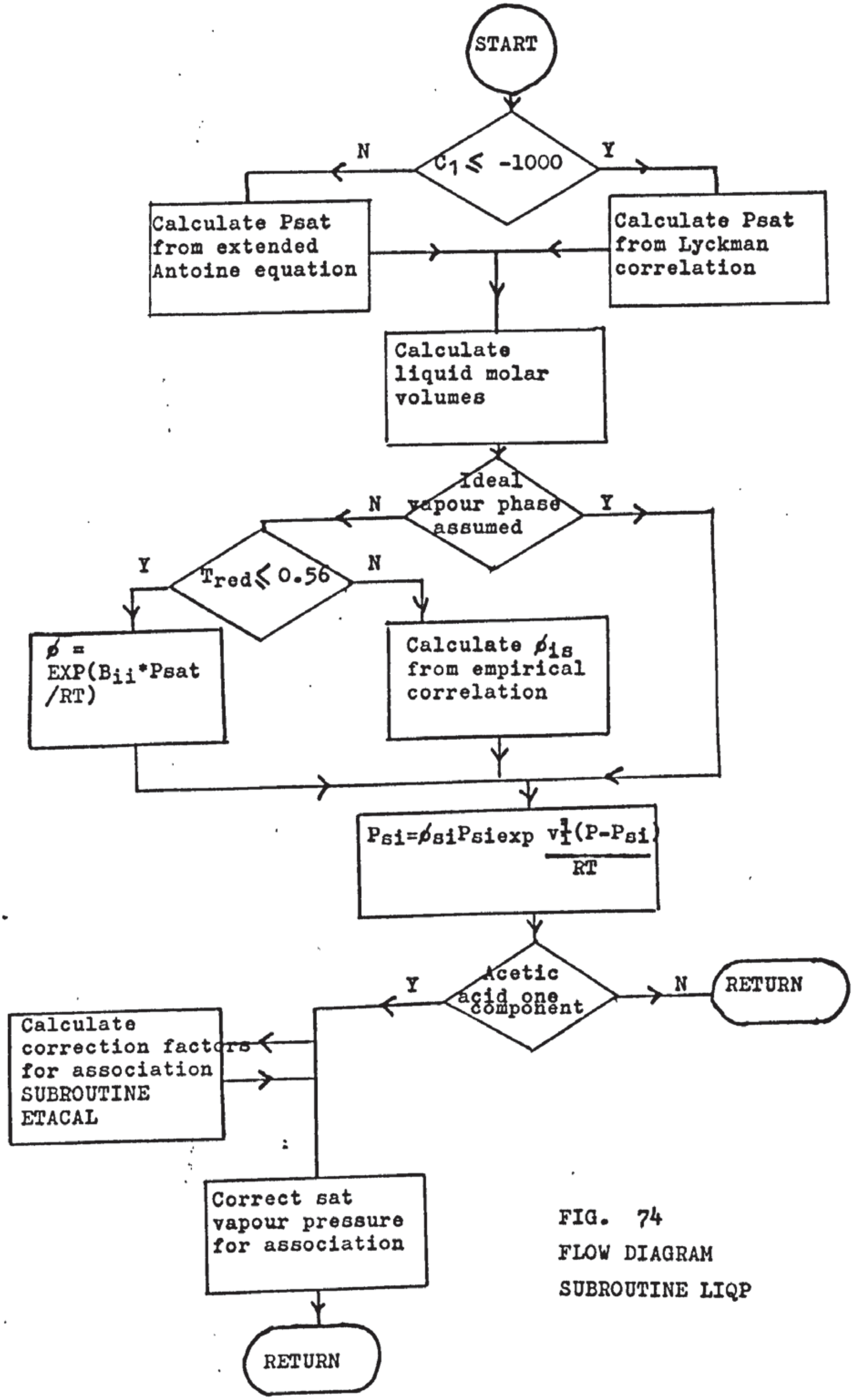


FIG. 74
FLOW DIAGRAM
SUBROUTINE LIQP

Subroutine PCLCA calculates the constants of the molar volume equation and the critical constants of the mixtures according to the following mixing rules

$$T_{cij} = (T_{ci}\ T_{cj})^{\frac{1}{2}} \tag{A1.20}$$

$$P_{cij} = \frac{4\ T_{cij}\ (P_{ci}\ V_{ci}/T_{ci} + P_{cj}\ V_{cj}/T_{cj})}{(V_{ci}{}^{1/3} + V_{cj}{}^{1/3})^3} \tag{A1.21}$$

$$W_{ij} = 0.5\ (W_i + W_j) \tag{A1.22}$$

A flow diagram is shown in Fig.75.

LIST OF VARIABLES

FORTRAN NAME	Description
MU (I)	Dipole moment
OMEGAH (I)	Homomorph acentric factor
T1(I), T2(I), T3(I)	Temperatures
V1(I), V2(I), V3(I)	Molar volumes at temps. T1, T2, T3
CONSTB (I,J)	Molar volume constants
TCRIT (I,J)	Critical temperature
PCRIT (I,J)	Critical pressure
VCRIT (I,J)	Critical volume
OMEGA (I)	Acentric factor

Subroutinr PCLCB is identical.

2.3 Objective function and activity coefficient subroutines

SUBROUTINES XMODEL, GCALC, ACTCO, ACTEXP

All these subroutines calculate activity coefficients using the various models discussed in chapters 2 and 3. In the versions of XMODEL used with the least squares fitting subroutines the activity coefficients are used to calculate variables to be compared with experimental variables such as pressure. A full list of possible objective functions is given in connection

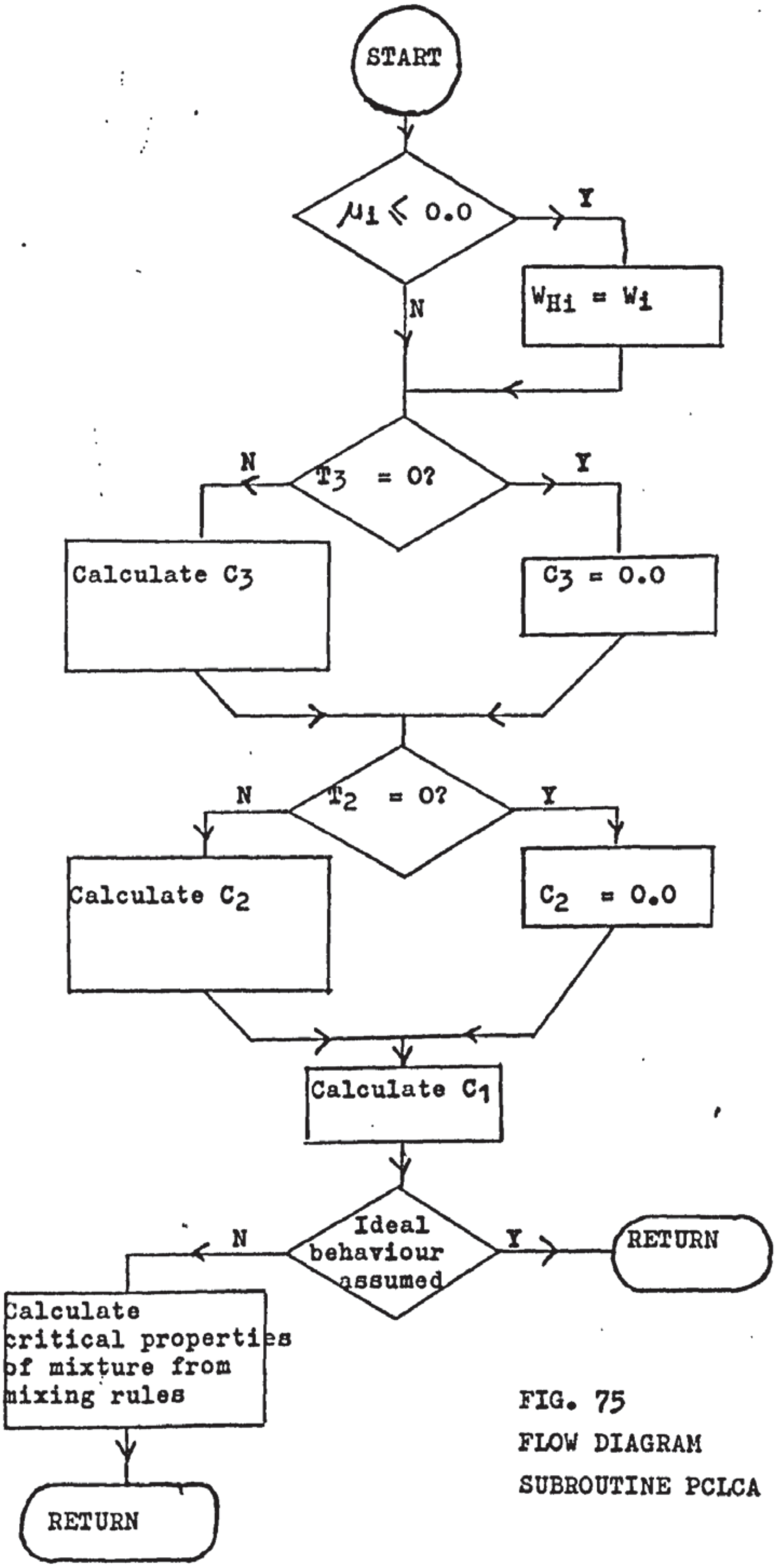


FIG. 75
FLOW DIAGRAM
SUBROUTINE PCLCA

with the main least squares programme JF4LSQMKA. XMODEL calculates the heat of mixing, excess free energy of mixing and the activity coefficients at infinite dilution according to the various models.

The versions of XMODEL used in conjunction with the error analysis programme calculates only activity coefficients and heat of mixing according to supplied parameters. Other versions calculate activity coefficients only. A flow diagram is shown in Fig. 82 for the main version.

LIST OF VARIABLES

FORTRAN NAME	Description
TAU (I)	Adjustable parameters for activity coefficient models.
MODEL	Parameter specifying model to be employed.
CONSTC	Conststant K in Modified Orye equation.
SUMSQ	Objective function.
NFUNC	Function evaluation counter
JDEC	Parameter specifying objective function to be used.
R	Gas constant
PHI (I)	ϕ_i
VOL (I,J) Q (I,J)	Parameters for Bruin modified NRTL equation
ACT (I,J)	Liquid phase activity coefficients
IDEAL	Parameter specifying whether vapour ideal or not
X(J)	Liquid mole fraction more volatile component
RAD, QUA	Uniquac parameters r_i, and q_i
RKA, RKB, RKC, RKD	Redlich Kister parameters A, B, C, D.
NCOMP	No. of components present
NOPARA	No. of parameters used
N	No. of data points considered

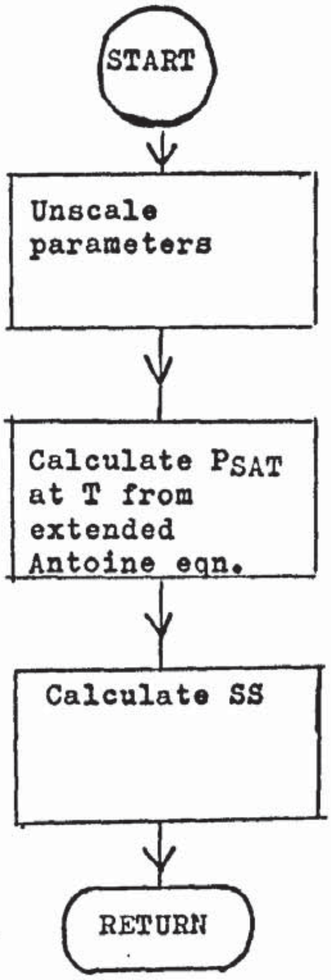


FIG. 76
FLOW DIAGRAM
SUBROUTINE XMODEL/VAPFIT

DELTA (I,J)	Liquid phase association factor
PCALC (J)	Calculated pressure
PEPL (J), PF	Experimental pressure
YCALC (J)	Calculated vapour composition
YEPL (J), Y(J)	Vapour composition, more volatile component
MLIQV (I,J)	Liquid molar volume
HCALC (J)	Heat of mixing-calculated
HEPL (J)	Experimental heat of mixing
GECALC (J)	Calculated g^E
GEEPL (J)	Experimental g^E
GINFC (I)	Calculated V_i^∞
GINFEX (I)	Experimental V_i^∞

Other variables are dummy variables used solely in the subroutine.

Subroutine GCALC calculates activity coefficients for a given set of parameters for the UNIQUAC and NRTL equations. It is used in conjunction in the JF4LIQLIO, the programme which calculates liquid-liquid equilibrium and differs only from XMODEL in that the FORTRAN name for the activity coefficient is GAMMA instead of ACT. It will therefore not be described any further.

Subroutine ACTCO is used in conjunction with the multi component vapour-liquid equilibrium programme BUBLT of PRAUSNITZ (P6). It is identical to the one he describes but in addition contains the UNIQUAC and NRTL equations. This too will not be described any further as it has been extensively described in the monograph of Prausnitz et al (P6).

Subroutine ACTEXP calculates experimental activity coefficients from the relation

$$V_i = \frac{Y_i \phi_i P}{x_i P_{si} \phi_{si}(P_{si}) \exp\left[\frac{1}{RT}\int_{P_{si}}^{P} \upsilon_i^L \, dP\right]} \qquad (A1.23)$$

```
                                                              COMMENTS
JOB :EAXXX,JF4KIL,CP76(T40,P2000)
ATTACH(SOURCE,JF4LSQMKA,ST=S6A)
FTN(I=SOURCE,SL=0)
LDSET(MAP=B/ZZZZMP,PRESET=ZERO)                               STANDARD HEADER CARDS
LGO(PL=5000)
####S
1                                                             JDEC (WHICH OBJ. FUNCTION)
4                                                             NDSETS (HOW MANY DATA SETS)
00000000000000001                                             IDEC (ASSOCIATION MODEL TO BE USED)
00                                                            MA (I) (WHICH MODELS)
46211                                                         VPUNIT (I) (VAPOUR PRESS. UNITS)
0                                                             SWITCH
SYSTEM ETHYL ACETATE - N-BUTYL ACETATE                        NO PTS, NO COMPS, ISOTHERMAL,IDEAL?
DATA OBTAINED ON CATHALA STILL - ANALYSIS BY REFRACTIVE INDEX TITLE
1
112                                                           TEMP, CONC AND PRESS UNITS
   4.9        17.5          122.4
               ↑                                              X, Y, PRESS AND TEMP
               ↓                                              DATA (N POINTS)
  96.1        99.1          78.6
 760.
  523.3      37.8     286.0       0.373     0.278     1.78     0.5    CRITICAL PROPS. & W_H & ETA
  573.1      30.1     397.8       0.455     0.400     1.68     0.4
  293.15    298.15      0.0      97.9      98.89      0.0             MOLAR VOLS AND TEMPS
  298.15    389.25      0.0     131.58    147.5       0.0
  -2.2317474 -1871.4222-71.9206  0.02680875 0-0.000027455  0.49952   VAPOUR PRESSURE DATA
  11.2375060 -3229.2711-58.9833  0.0049529 80-0.000002542 -0.55286
     0.2       0.2       0.2        0.2        0.2  5                 WILSON  )
****                                                                  NRTL    )  STARTING PARAMETERS
                                                                      UNIQUAC)
```

FIG. 77 INPUT DATA LAYOUT FOR JF4LSQMKA

All the variables in this routine are defined in connection with the main programme JF4LSQMKA.

2.4 Housekeeping routines

SUBROUTINE UNITS

This subroutine converts all experimental data into units of mole fractions, atmospheres and degrees K, thus enabling data to be read in in a variety of units such as mm mercury, degrees Centigrade, providing the parameters TUNIT, CUNIT and PUNIT are correctly expressed. The values these variables may take are discussed in connection with the input to the main programme.

LIST OF VARIABLES

FORTRAN NAME	Description
TUNIT	Temperature unit parameter
PUNIT	Pressure unit parameter
CUNIT	Concentration unit parameter
MOL WT(I)	Molecular Weight of component i

2.5 Conclusion

Other subroutines that have been written are specific only to the main programmes with which they are used and therefore are described in the section dealing with those programmes.

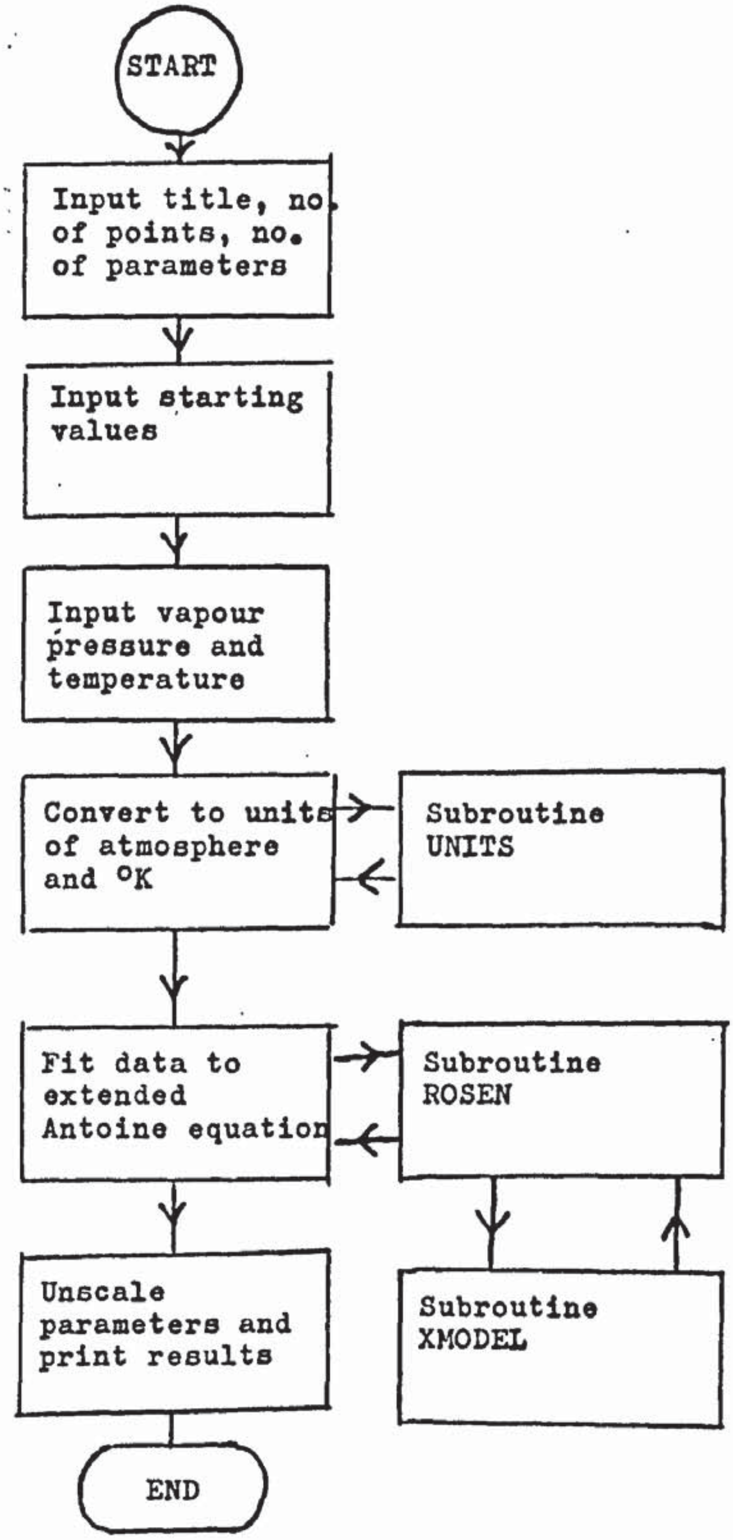


FIG. 78

FLOW DIAGRAM

JF4VAPFIT

3. Main Programmes

3.1. Fitting programmes JF4LSQMKA and JF4LSQMKB

3.1.1. General Description of programme

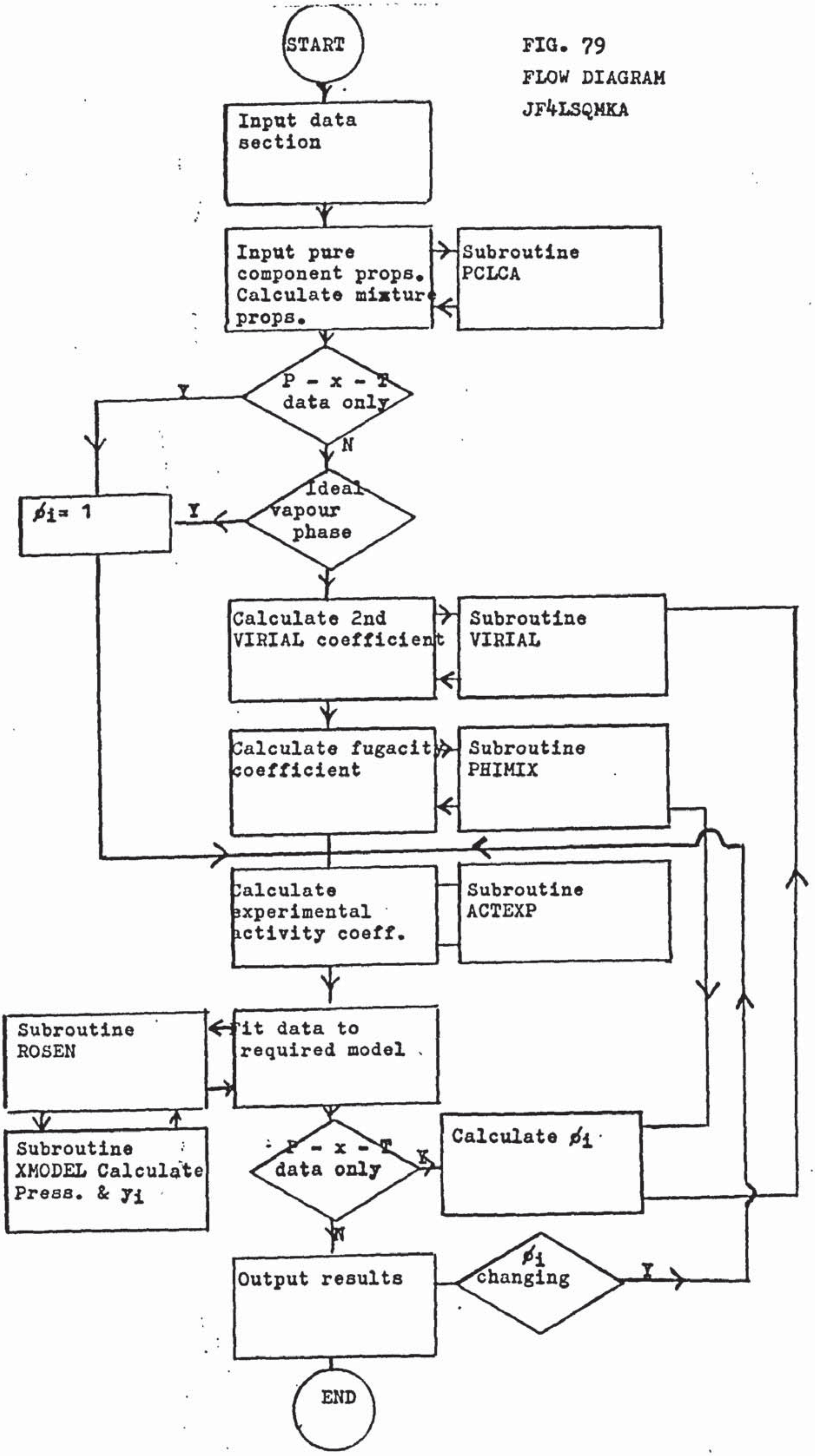
The programme begins with the data input section which will be described in detail in section 3.1. After this subroutine UNITS is called to ensure that all the data has consistent units of atmospheres, degrees K and mole fractions. This is followed by an initialisation section and by an ordering procedure which arranges the data in ascending order of liquid phase mole fraction.

The next section is also an input section in which the necessary pure component property data is read in including vapour pressure parameters and critical properties. Subroutine PCLCA is then called to calculate the critical properties of the mixture according to the mixing rules outlined on page 240 and to calculate the constants of the molar volume quadratic equation. Following this the vapour phase fugacity coefficient, ϕ_i is calculated using subroutines VIRIAL and PHIMIX and the reference state properties of the pure liquids.

The experimental activity coefficients are calculated using subroutine ACTEXP and the programme then proceeds to fit the data to a given model using subroutine ROSEN. When this has been done the programme outputs the results and moves on to consider the next model. When all the required models have been fitted the programme stops.

If however the experimental vapour compositions are not part of the input data then an iterative procedure must be adopted in which initially the vapour phase is assumed to be ideal, the model fitted and the calculated vapour compositions are used in subroutines VIRIAL and PHIMIX to calculate ϕ_i.

FIG. 79
FLOW DIAGRAM
JF4LSQMKA



The iteration loop is terminated when successive values of ϕ_i are changing with less than a specified tolerance. As before the programme then proceeds to the next model or the end as the case may be. A flow diagram for this programme is shown in Fig. 79.

3.1.2. Details of input required

CARD 1 Reads in the value of JDEC, FORMAT I1. This variable specifies the value of the objective function (O.F.) to be used in the minimisation procedure.

If JDEC = 1 $$\text{O.F.} = \sum_{j=1}^{N}\left[\frac{\text{Pcalj} - \text{Pexptlj}}{\text{Pexptlj}}\right]^2$$

If JDEC = 2 $$\text{O.F.} = \sum_{j=1}^{N}\left[\frac{\text{Ycalj} - \text{Yexptl}}{\text{Yexptl}}\right]^2$$

If JDEC = 3 $$\text{O.F.} = \sum_{j=1}^{N}\left[h^{m}_{\text{calcj}} - h^{m}_{\text{exptlj}}\right]^2$$

If JDEC = 4 $$\text{O.F.} = \sum_{j=1}^{N}\left[V^{\infty}_{\text{iexptl}} - V^{\infty}_{\text{icalc}}\right]^2$$

If JDEC = 5 $$\text{O.F.} = \sum_{j=1}^{N}\left[g^{E}_{\text{calcj}} - g^{E}_{\text{exptlj}}\right]^2$$

CARD 2 Reads in NDSETS the number of data sets to be fitted. Also format I1.

CARD 3 Reads in IDEC, Format I1, This may either be zero if correction for liquid phase association is to be made or 1 if it is to be ignored.

CARD 4 Reads in the vector MA(I) containing 18 elements, Format 18I1. If MA(I) equals 0 then a particular

```
                                                                                            COMMENTS

JOB :EAXXX,JF4LMA,CP76(T40,P3000)
FTN(I=SOURCE,R=0)                                                                           STANDARD HEADER CARDS
LDSET(MAP=B/ZZZZMP,PRESET=ZERO)
LGO(PL=3000)
####S
3                                                                                           NO. OF COMPONENTS
1                                                                                           MODEL AND NO. OF PARAMETERS
13
SYSTEM WATER - TOLUENE - ACETIC ACID  NRTL AT 30 MOL WT  60.0                               TITLE
PREDICTED TERNARY DIAGRAM - LIQ PHASE REACTION NOT TAKEN INTO A/C
WATER                                                                                       COMPONENT NAMES
TOLUENE
ACETIC                                                                                      |
   18.0     92.0    60.0                                                                     MOL. WTS.
 4388.756    1502.802      0.198       0.0          0.0          0.0
 1893.43      875.7        0.67051    -3.231        2.776        0.0015                      NRTL PARAMETERS
  826.51      563.08       0.57364    -1.917        1.678       -0.00103
333.15
0
****
```

FIG. 80   INPUT DATA LAYOUT FOR JF4LIQLIQ model is not fitted, if it equals 1 then the model is considered.

MA(1) - Wilson equation
MA(2) - Two parameter NRTL equation
MA(3) - Bruin modified NRTL equation
MA(4) - Three parameter NRTL equation
MA(5) - Six parameter NRTL equation
MA(6) - Enthalpic Wilson equation
MA(7) - Orye equation
MA(8) - Two parameter modified Orye equation
MA(9) - Three parameter modified Orye equation
MA(10) - Van Laar equation
MA(11) - Two parameter Redlich-Kister equation
MA(12) - Three parameter Redlich-Kister equation
MA(13) - Four parameter Redlich-Kister equation
MA(14) - Two parameter UNIQUAC equation
MA(15) - Four parameter UNIQUAC equation
MA(16) - Four suffix Margules equation
MA(17) - Five suffix Margules equation
MA(18) - Van Ness modified Margules equation

CARD 5 This card is omitted if infinite dilution activity coefficients, heat of mixing or free energy date are being fitted Reads in VPUNIT(1) and VPUNIT(2), FORMAT 2I1. These determine the units with which the vapour pressures are calculated.

If VPUNIT(I) = 0 Temperature is in degrees K and the vapour pressure has units of atmospheres.

If VPUNIT(I) = 1 Temperature is in degrees C and vapour pressure is in atmospheres.

If VPUNIT(I) = 2 Temperature is in degrees C and vapour pressure in mm of mercury.

Subroutine LIQP automatically ensures consistent units, i.e. atmospheres and degrees K.

CARD 6 Reads in SWITCH, format I1. This is used to ensure that the more volatile component is component 1

If SWITCH = 0 Take no action

If SWITCH = 1 Reverse the order

CARD 7 Reads in No. of data points (N), Number of components (NCOMP), a parameter specifying whether data is isothermal or not (ISO) and a parameter specifying whether an ideal vapour phase is to be assumed, (IDEAL). Format I2, 3I1

If ISO = 0 data is isothermal

If ISO = 1 data is isobaric

If ISO = 2 data is neither

If IDEAL = 0 ideal vapour phase assumed

If IDEAL = 1 non ideal vapour phase

CARDS 8 & 9 Title of system under consideration and data source. Format 8A10.

CARD 10 This card is omitted if JDEC is greater than 2.

Read in TUNIT, CUNIT, PUNIT. These are parameters specifying units of input data.

If TUNIT = 0 the temperatures have been input in °F

If TUNIT = 1 the temperatures have been input in °C

If TUNIT = 2 the temperatures are in °K

If PUNIT = 0 the pressures are in lbs/in^2

If PUNIT = 1 the pressures are in atmospheres

If PUNIT = 2 the pressures are in mm mercury

If CUNIT = 0 The compositions are in weight %

If CUNIT = 1 The compositions are in mole%

If CUNIT = 2 The compositions are in mole fractions

The next set of input depends on the value of JDEC. If JDEC equals 3 then N values of liquid phase composition with the corresponding values of the heat of mixing are input. On the other hand if JDEC equals 5 then N values of liquid phase composition are read in together with excess free energy data. The format is 2F10.3.

If JDEC equals 4 then a pair of infinite dilution activity coefficients is to be read in.

If JDEC is less than 2 then it is vapour liquid equilibrium data which is to be read in. If it is isothermal data then N values of liquid composition, X(J) vapour composition, Y(J) and experimental pressure, PEPL(J) are read in with the temperature TF on the N + 1th card. If it is isobaric the liquid and vapour compositions and the experimental temperatures, TEMP(J), are read with the pressure PF on the N + 1th card. All the preceding input statements are read in on a format of 2F11.6, F11.3.

Finally if the data is neither isothermal nor isobaric then it is read in a liquid composition, vapour composition, pressure and temperature with a format 2F11.6, 2F11.3.

The next card depends on whether the input composition data is in weight %. If it is then the molecular weights of the pure component must be read in, format 2F10.3. If JDEC is greater than 2 it is omitted.

CARDS N + 11 & N + 12 These contain the critical properties of each component with the more volatile on the first card

The properties are in order critical temperature (TCRIT), critical pressure (PCRIT), critical volume (VCRIT), acentric factor (OMEGA), acentric factor of homomorph (OMEGAH), dipole moment (MU) and association factor (ETA). The format is 7F9.3.

The next two cards contain the pure component molar volume data. First come three temperatures T1, T2, T3 and then the corresponding molar volumes at these temperatures V1,V2 and V3. These are read in format 6F9.3.

The last of the pure component data is the vapour pressure equation parameters, one card for each component. CONSTA (I,1) corresponds to C1 with CONSTA (I,2) for C2 and so on.

Lastly come the starting values for the minimisation routine together with the number of parameters required for each model. The format for this is 3F10.3, I1. Each model requires a set of starting values except the 3 and 6 parameter NRTL and 4 parameter UNIQUAC which utilise the 2 parameter equation parametersas starting points. With the UNIQUAC model an additional card has to be included to read in the values of r_i (RAD(I)) and q_i (QUA(I)) and the co-ordination number (ZNO). The format is 5F10.3.

A sample of the data input is shown in Fig.80 while a typical output is shown in Fig.77.

JF4LSQMKA and JF4LSQMKB are identical except that while the former employs Prausnitz's version of VIRIAL the latter utilises that of Tsonopoulos. This requires an additional card after JDEC and NDSETS which specifies to which class the compounds belong.

The programme has been tested on approximately 150 systems and the results are presented in Appendix A4. The pure component properties used are listed in Appendix A5.

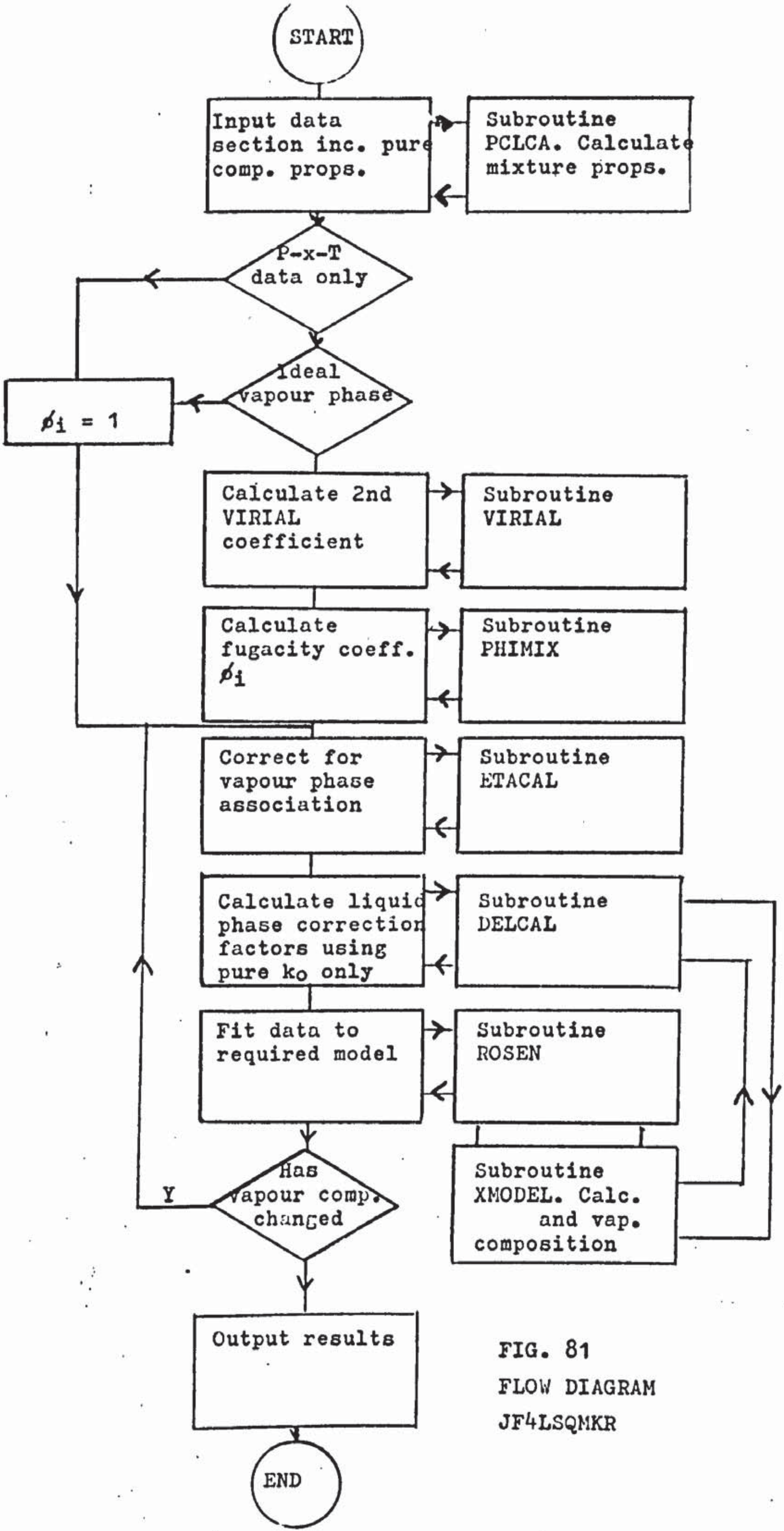


FIG. 81
FLOW DIAGRAM
JF4LSQMKR

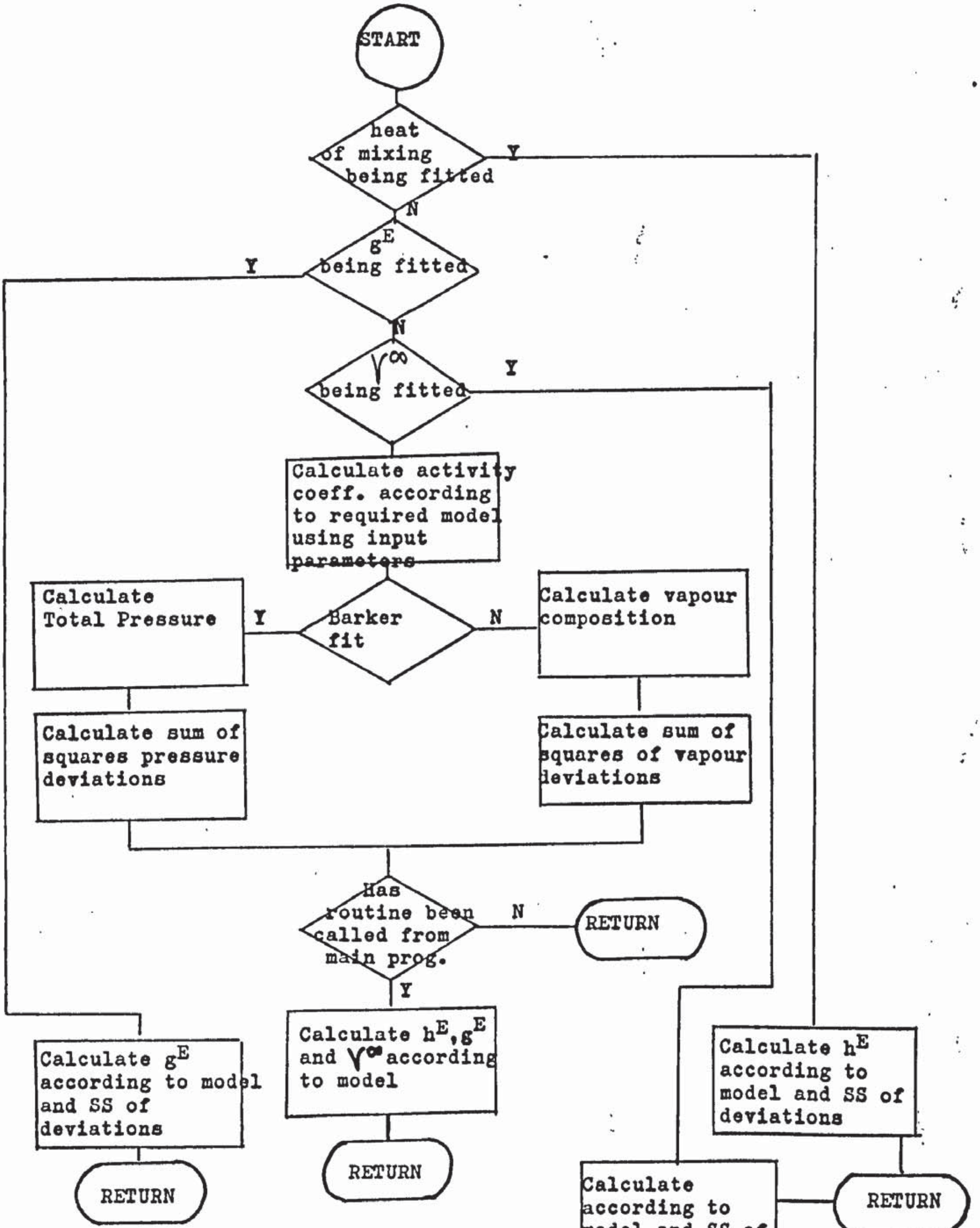


FIG. 82 FLOW DIAGRAM SUBROUTINE XMODEL

3.2 Fitting programme incorporating association model JF4LSQFIT

3.2.1 General description of programme

The programme is derived from JF4LSQMKA and is identical except for the additional subroutines ETACAL and DELCAL which calculate respectively the vapour phase and liquid phase association factors. There is also an extra iteration loop since the vapour phase association factor must be determined using the calculated values of vapour composition.

The input section is identical with that of JF4LSQMKA except that the vapour phase association factors ETA are set at - 1000.0

The programme proceeds as before but subroutine ETACAL is called after VIRIAL and PHIMIX have been called and the vapour phase association factors Z_A and Z_B are calculated as described in the next section. Initially the experimental values of Y are used. Subroutine DELCAL is then called and the liquid phase association factors δ_A and δ_B are calculated initially using a concentration independent k . The programme then calls subroutine ROSEN and fits the data by the Barker method using one of the activity coefficient models. On this first iteration loop a variable NSET prevents subroutine DELCAL being called from subroutine XMODEL after the activity coefficient has been calculated.

After a value of y has been calculated subroutine ETACAL is again called and new vapour phase association factors are calculated using the calculated values of y in place of the experimental values. The data is then refitted and this time the value of NSET has been altered so that when the activity coefficients are calculated in XMODEL, subroutine DELCAL is called and values of the liquid phase association factors

ε_A and ε_B recalculated according to the theory outlined in Appendix A2..

The iteration proceeds until the calculated values of y change by less than a specified amount at which point the iteration is terminated and the results output.

A flow diagram for the main programme is shown in Figs. 82 and 83. The specialiased subroutines used in this programme are now described in more detail.

3.2.2. Subroutine ETACAL

There are two versions of this subroutine depending on the mode of association assumed. The first version was initially used when acetic acid data was fitted using vapour phase corrections only and assumes the formation of both dimers and tetramers.

The equilibrium constants of the polymerization reactions have been given by Ritter and Simons (R13).

For the dimer

$$\ln K_d = \ln \frac{P_t}{P_m^2} = -23.98925 + \frac{7285.38}{T} \qquad \text{(A1.24)}$$

For the tetramer

$$\ln K_t = \ln \frac{P_t}{P_m^4} = -54.07022 + \frac{13548.41}{T} \qquad \text{(A1.25)}$$

with K_d and K_t in $(\mathrm{mm\ H_g})^{-1}$ and $(\mathrm{mm\ H_g})^{-3}$

P_t is the total pressure and P_m is the partial pressure of acetic acid monomer.

Carli et at (C1) have derived the following relation from stochiometric considerations

$$y_1 P = P_{1m} + (2-y_1)K_d P_{1m}^2 + (4-3y_1)K_t P_{1m}^4 \qquad \text{(A1.26)}$$

which can be solved for P_{1m}, the true partial pressure of the monomer acid in the vapour phase. The correction factors are then defined, where P_2 is the partial pressure of the other component,

$$\alpha_1 = \frac{P_{1m}}{y_1 P} \quad \text{and} \quad \alpha_2 = \frac{P_2}{y_2 P}$$

The correction factors are then applied by multiplying the fugacity coefficients as shown by S_A and S_B

$$\phi_1{}^1 = \alpha_1\phi_1 \quad \text{and} \quad \phi_2{}^1 = \alpha_2\phi_2 \qquad (A1.27)$$

A similar procedure holds for the pure acetic acid whose vapour pressure is given by

$$P_1{}^o = P_{1m}{}^o + K_d P_{1m}{}^{o2} + K_t P_{1m}{}^{o4} \qquad (A1.28)$$

which again can be solved by the Newton-Raphson method to give the correction factor

$$\alpha_1{}^o = \frac{P_{1m}{}^o}{P_1{}^o} \quad \text{and} \quad \alpha_2{}^o = 1.0 \qquad (A1.29)$$

The correction factors are then applied as before

$$\phi_{s1}{}'(P_{s1}) = \alpha_1{}^o\phi_{s1}(P_{s1}) \text{ and } \phi_{s2}(P_{s2}) = \alpha_2{}^o\phi_{s2}(P_{s2}) \qquad (A1.30)$$

A flow diagram is shown in Fig.83.

LIST OF VARIABLES

FORTRAN NAME	Description
CONV	Convergence criterion
KDIM	Dimerisation constant
KTET	Tetramisation constant
PM	Partial pressure of monomer
FP	Equation (A1.26)
DFP	Differential or equation (A1.26)

PID	Partial pressure of dimer
PIT	Partial pressure of tetramer
P2	Partial pressure of second component
ALF(I)	Correction factor
PA	System total pressure
Z1	yP in eqn. A1.26
Z2	(2-y) in eqn. A1.26
Z3	(4-3y) in eqn. A1.26
PB	= Z1, or $P_{SAT}(1)$
PC	(1-y)P, or $P_{SAT}(2)$

The second version of ETACAL assumes that dimerisation is the only reaction of importance. In this case the last terms of equations (A1.26) and (A1.25) drop out reducing both to quadratics which have been solved in Appendix A2 algebraically. In this case no iteration procedure is necessary, the necessary coefficients being calculated directly. A flow diagram is shown in Fig.84.

LIST OF VARIABLES

FORTRAN NAMES	Description
YCACL(J)	Calculated value of vapour composition
IAB	Iteration counter
ZA(1,J)	Z_A correction factor - equation
ZB(2,J)	Z_B correction factor - equation
ZB(J)	Z_A^1 correction factor - equation

Other variables are the same as the first version of ETACAL.

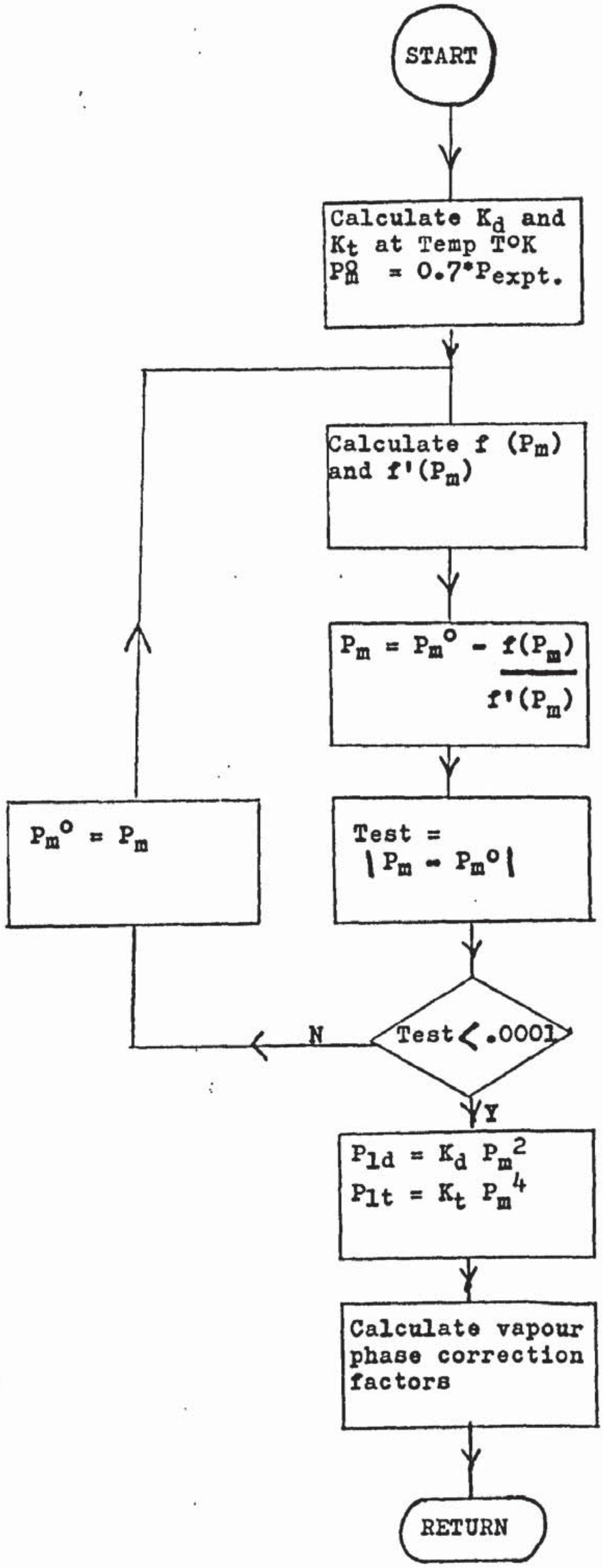
The factors Z_A and Z_B are related to the correction factors in the first version as follows

$$Z_A = \frac{\alpha_1}{\alpha_1^{\circ}} \quad \text{and} \quad Z_B = \frac{\alpha_2}{\alpha_2^{\circ}} \qquad (A1.30)$$

FIG. 83

FLOW DIAGRAM

SUBROUTINE ETACAL (a)



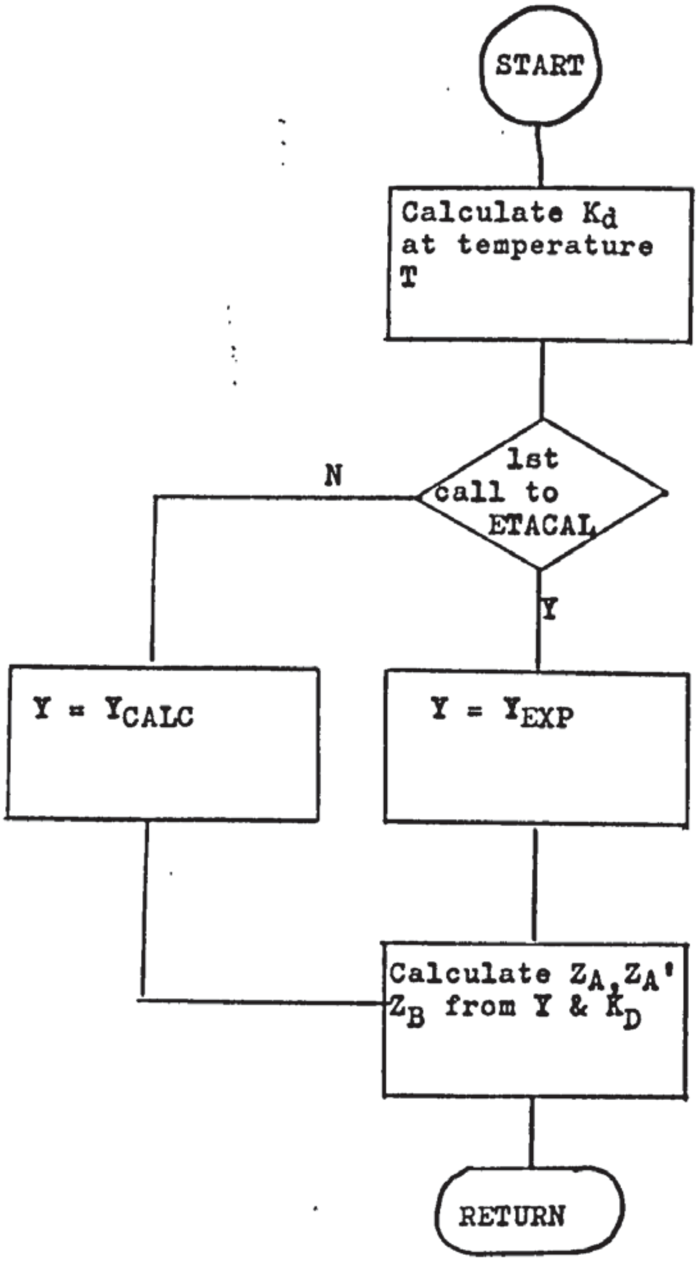


FIG. 84

FLOW DIAGRAM

SUBROUTINE ETACAL (b)

(FOR LIQUID PHASE MODEL VERSION)

3.2.3 Subroutine DELCAL

Initially when this subroutine is called, the correction factors δ_A and δ_B are calculated using a pure component equilibrium constant K_A. This related to the temperature as given in chapter 5 by

$$\ln K_A = \frac{3131}{T} - 6.5197 \qquad (A1.31)$$

This is achieved by the variable NSET which is set equal to zero on the first iteration and at one thereafter.

The calculation of the association constant for the mixture, k_m is given by equation (5.30) in chapter 5.

i.e. $$k_m = K_A \, \beta \, \gamma_A \qquad (5.30)$$

where $$\beta = \frac{Z_A}{Z_A^1} : \frac{\phi_A}{\phi_A^1} \cdot \frac{\delta_A^1}{\delta_A} \qquad (5.31)$$

where Z_A, Z_A^1, δ_A, δ_A^1 are defined by equations (5.6), 5.16), (5.7) and (5.17) and γ_A is obtained from one of the models such as the Wilson equation in subroutine XMODEL. Since both β and γ_A are composition dependent and since β contains, k_m, implicitly in the factors δ_A and δ_A^1 an iterative procedure must be adopted.

The method of successive approximations was found to be satisfactory in which successive values of are calculated until convergence has been achieved. The correction factors δ_A and δ_B are then calculated. A flow diagram is shown in Figs.86. The correction factors are passed to subroutine XMODEL where they are used to correct the activity coefficients

i.e. $$\gamma_A^1 = \delta_A \gamma_A \qquad (A1.32)$$

and $$\gamma_B^1 = \delta_B \gamma_B \qquad (A1.33)$$

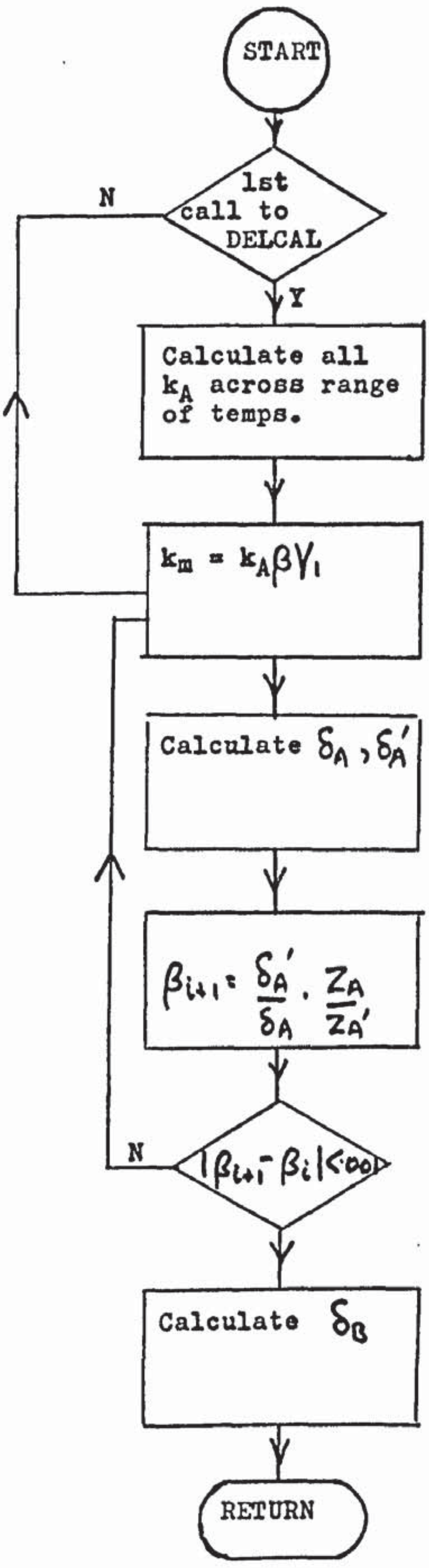


FIG. 85
FLOW DIAGRAM
SUBROUTINE DELCAL

LIST OF VARIABLES

FORTRAN NAME	Description
KO(J)	Pure component equilibrium constant, $_A$
K1M(J)	Mixture equilibrium constant,
BETA(J)	β
DELTA(1,J)	δ_A
DELTA (2,J)	δ_B
DTA(J)	δ'_A

This programme was tested on approximately sixty systems containing acetic acid. The results are shown in Appendix A3. The layout of the input is exactly as shown in Fig. for programme JF4LSQMKA and so further illustration is not necessary.

3.3. Fitting programme for mutual solubilities JF4LSQSOL

3.3.1. General description of the programme

Once again this programme is generally similar to JF4LSQMKA from which it was derived. However since its purpose is to calculate the parameters in one of the Gibbs-Duhem models from mutual solubility data the data input and general structure of the programme are considerably simplified.

The mutual solubility data is read in as detailed in the input section later on. Once again subroutine ROSEN is used to adjust the parameters of the activity coefficient equations until the objective function shown below has been minimised

$$\text{i.e.}\quad \text{Sumsq} = \left[(x_1\gamma_1)^{I} - (x_1\gamma_1)^{II}\right]^2 + \left[(x_2\gamma_2)^{I} - (x_2\gamma_2)^{II}\right]^2 \qquad \text{(A1.34)}$$

where the superscripts I and II refer to the two phases

3.3.2. Description of Input required

CARD 1 Reads the value of SOLUB, Format I1. This must be set equal to 1 to fit mutual solubility data.

CARD 2 Reads in the value of NDSETS which specifies the number of sets of mutual solubility data to be fitted. Format I1.

CARD 3 Reads in the value of IDEC which must be set equal to 1 for reduction of mutual solubility data. Format I1.

CARD 4 Reads in the vector MA which specifies which model is to be employed. The full details are given in the description of the input for JF4LSQMKA. In this case only the first 13 models are included. Format 13I1. The Wilson equation cannot be used since it does not predict partial miscibility.

CARD 5 Contains the mutual solubility data, the temperature at which it is determined and the number of data points. This is read into subroutine SLBLTY which has at this point been called. The input is the mole fraction of the more volatile component in the first phase, X(1) and in the second phase, X(2), the temperature, TF and the number of data points, N. Format 2F12.7, F10.3, F1.

CARDS 6 and 7 These two cards read in the title and other details. Format 8A10.

CARD 8 Reads in MODEL, the number of the first model to be employed, i.e. MODEL = 2 ensures the programme starts with the two parameter NRTL equation.

CARDS 9 onwards. These are read in through subroutine ROSEN and contain the starting values needed in the search

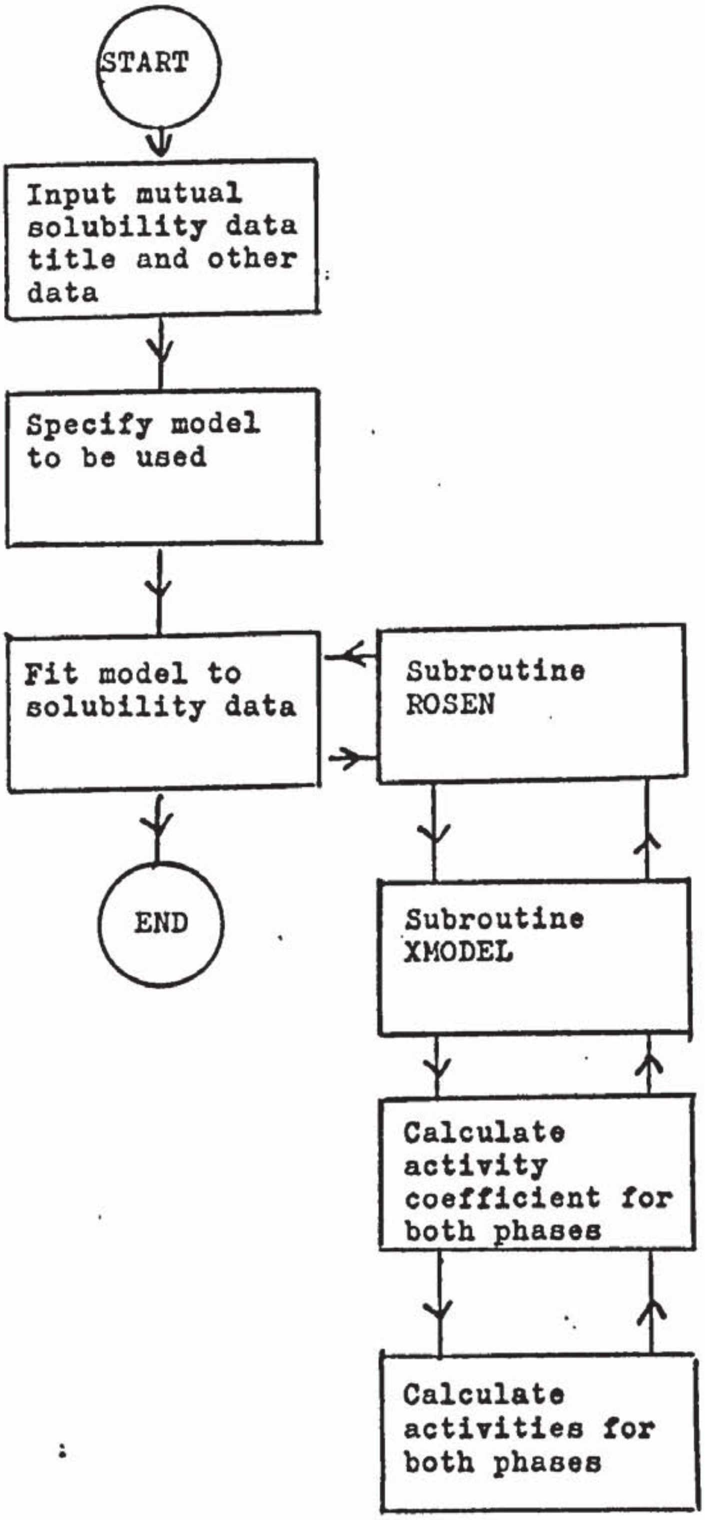


FIG. 86
FLOW DIAGRAM
JF4LSQSOL

procedure together with the number of parameters to be employed. Format 3F10.3, I1. It must be noted also that if the UNIQUAC equation is to be employed then the value of r_1 (RAD(1)), r_2(RAD(2)), q_1(QUA(1)), q_2(QUA(2)) and the co-ordination number (ZNO) must be read in. The values are given in Appendix A5 for various compounds.

A sample of the data input is shown in Fig. 90 and a flow diagram of the complete programme is given in Fig. 86 All the variables in the programme are identical with those described for JF4LSQMKA.

3.4. Error analysis programme JF4ERRAN

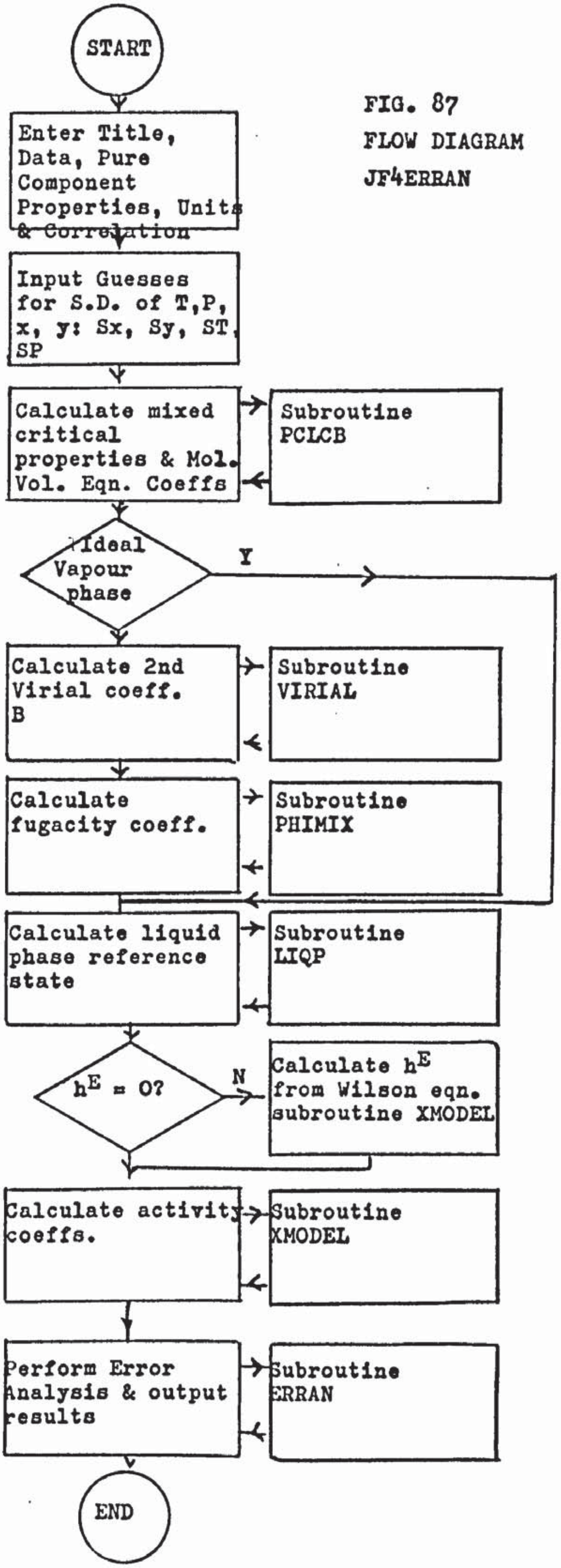
3.4.1. General description of the programme

This programme incorporates the consistency tests of Ulrichson, and Stevenson (U1) and Samuels, Ulrichson and Stevenson (S4) discussed in chapter 4. This programme employs many of the subroutines used in connection with the fitting programmes.

The programme reads in the experimental data, the pure component properties and the standard deviations of the experimental variables. It then performs the tests as has been described in chapter 4 and outputs the calculated quantities from which a judgement of thermodynamic consistency is made by the user.

The use of the tests requires either that heat of mixing data is available or that an estimate is made. The programme contains provision for reading this data or if necessary an estimate is made using the Wilson equation. Orye (O3) reports that this equation gives a reasonable if rough estimate

FIG. 87
FLOW DIAGRAM
JF4ERRAN



```
JOB :EAXXX,JF4WIA,CP76(T40,P4000)                                                       COMMENTS
ATTACH(SOURCE,JF4ERRAN,ST=S6A)
FTN(I=SOURCE,SL=0)                                                                      STANDARD HEADER CARDS
LDSET(MAP=B/ZZZZMP,PRESET=ZERO)
LGO(PL=5000)
####S
111                                                                                     MODEL, ENTHALPY MODEL, HPRED
46211                                                                                   NO PNTS, NCOMPS, ISOTHERMAL, IDEAL
00                                                                                      VAPOUR PRESSURE UNITS
SYSTEM N-BUTANOL - N-BUTYL ACETATE AT CONST PRESSURE 760 MM HG                          TITLE
DATA OBTAINED ON CATHALA - ANALYSIS BY G.L.C.
1                                                                                       NO ASSOCIATION
112                                                                                     TEMP, CONC, PRESS UNITS
   0.001      0.001       0.00013   0.1                                                 STD DEVS, X, Y, PRESS & TEMP
   1.4         4.6          125.7

                                                                                        X, Y, PRESS AND TEMP DATA


  99.3        99.99         117.7
 760.0
  562.9       43.6     223.3       0.667     0.252      1.65      0.45
  573.1       30.1     397.8       0.455     0.4        1.68      0.4                   CRITICAL PROPERTIES
  307.75     389.25     0.0      92.81     101.7        0.0
  298.15     389.25     0.0     131.58     147.5        0.0                             MOLAR VOL. DATA
  -2.8269242 -2943.1148-82.5656  0.02365567 0-0.000029487  1.27729
  11.2375060 -3229.2711-58.9833  0.004952980-0.000002542 -0.55286                       VAPOUR PRESSURE PARAMETERS
  698.82       -91.44         0.0            0.0           0.0          0.0             EQUATION PARAMETERS
     0.2        0.2         0.2         0.2         0.2  5
****
```

FIG. 88   INPUT DATA LAYOUT FOR JF4ERRAN of the heat of mixing. It may be shown using the thermodynamic relationship

$$-\frac{h^E}{T^2} = \left[\frac{\partial g^E/T}{\partial T} \right]_{P,x}$$

(A1.35)

$$h^E = \sum_{i=1}^{n} x_i \sum_{j=1}^{n} \left[\frac{x_j \Lambda_{ij} (\lambda_{ij} - \lambda_{ii})}{\sum x_j \Lambda_{ij}} \right]$$

This approach assumes that the interaction parameters are independent of temperature. The NRTL and UNIQUAC models can also be used in this programme.

The programme calculates the f(a,b) values of the Ulrichson test and also the 68% confidence limits for f(a,b) using eqns. (422) and (4.25) with estimates of the standard deviation of the experimental measurements. It also performs a chi-square test to assess whether there is any non-random trend in the f(a,b) data. The programme then goes on to calculate the sum of the f(a,b) values and the individual variances of the f(a,b) values in the manner of Samuels et al (S4), to determine whether small systematic errors across the composition range exist. Finally the programme uses the estimated standard deviations to establish confidence regions for the activity coefficients using equation (4.28).

Vapour phase non idealities etc. are calculated in the same manner as for JF4LSQMKA. A flow diagram is shown in Figs.87 and 89.

3.4.2. Details of input required

CARD 1 Reads MODEL, a variable which denotes which model is to be used to calculate the activity coefficients, HMODEL which specifies which model is to be used to calculate the heat of mixing, and HPRED which indicates whether the heat of mixing is to be calculated or input.

If $\left.\begin{matrix}\text{MODEL}\\ \text{HMODEL}\end{matrix}\right\} = 1$	Wilson equation is used
If $\left.\begin{matrix}\text{MODEL}\\ \text{HMODEL}\end{matrix}\right\} = 2$	NRTL equation is used
If MODEL = 3	Van Laar equation is used
If $\left.\begin{matrix}\text{MODEL}\\ \text{HMODEL}\end{matrix}\right\} = 4$	UNIQUAC equation is used

The Van Laar equation cannot be used to predict the heat of mixing.

If HPRED = 0	then experimental heat of mixing data is to be read in
If HPRED = 1	then the heat of mixing data is to be calculated

The input format for this card is 3I1.

CARD 2 Inputs the number of data points, N, the number of components in the system, NCOMP, a parameter specifying whether the data is isothermal or not, ISO and IDEAL to denote whether the vapour phase is to be assumed ideal or not. The format is I2, 3I1.

CARD 3 Reads in parameters VPUNIT(I) (up to 4) which convey to the programme what units the vapour pressure will be calculated from the parameters that are input later in the programme. They ensure that the vapour pressures will be converted to atmospheres. They take the same values as described in connection with JF4LSQMKA. Format 4I1.

CARDS 4 and 5 Read in the title of the system under consideration and other details. Format 8A10.

CARD 6 Reads in the value of IDEC a parameter which determines whether a liquid phase association correction factor should be applied or not. Format I1.

If IDEC = 0	the correction is applied
If IDEC = 1	no correction used.

The next card depends on whether the UNIQUAC equation is to be used. If it is then the values of RAD, QUA, and ZNO must be input as described in previous sections. Format 2F10.3. If not the card is omitted.

CARD 7 Reads in the values of TUNIT, CUNIT and PUNIT which determine the units of the input data as described in the input section of programme JF4LSQMKA. Format 3I1.

CARD 8 Reads in the estimates of the standard deviations of experimental variables, SX(x_1), SY(y_1), SP (Pressure), and ST (Temperature.) Format 4F10.5.

CARDS 9 onwards Read in the experimental data according to the value of ISO. This is exactly the same again as the input section as JF4LSQMKA and will not be repeated. The Format is 2F11.6, F10.3 or 2F11.6, 2F10.3.

The next input depends on whether the heat of mixing data is to be input or calculated. If it is to be read in then it is input here with a format of F10.3.

The following six cards input the critical properties, molar volume data and vapour pressure parameters as has been

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OFF IN
ORIGINAL

described in connection with JF4LSQMKA. Since the input is identical it will not be described again.

The last cards read in the values of the correlation parameters needed to calculate the activity coefficients and the heat of mixing. If different models are to be used to calculate the two different things then two lots of parameters must be read in. It should be noted the parameters read in must be the interaction energies in cals/mole and not the dimensionless forms. Provision is made for up to six parameters.

A sample of the input data is shown in Fig. 88.

3.4.3. Subroutine ERRAN

This subroutine contains the consistency test and statistical tests. A flow diagram is shown in fig.89.

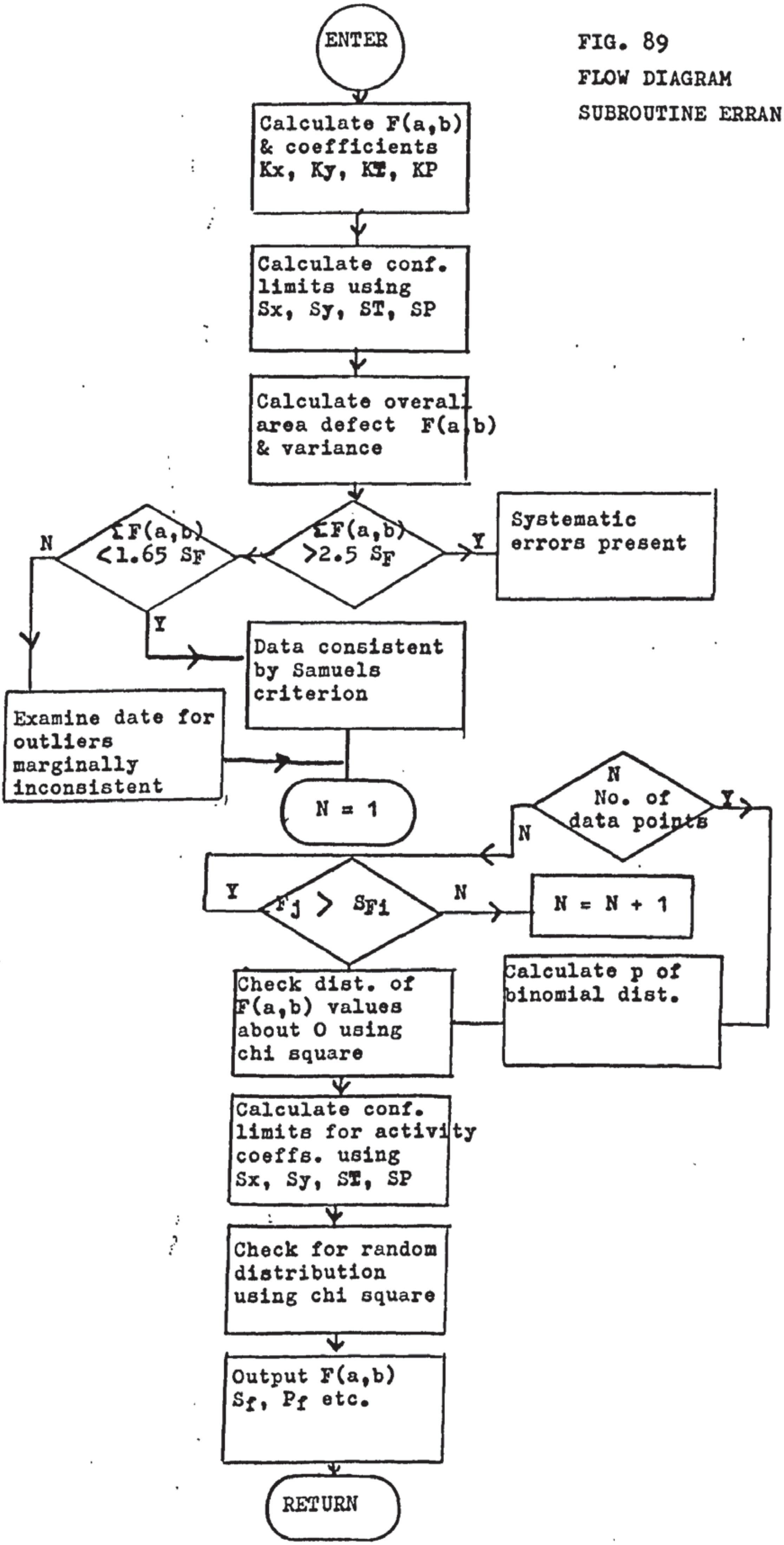
LIST OF VARIABLES

FORTRAN NAME	Description
VARX	Variance of x_i measurements
VARY	Variance of y_i measurements
VARP	Variance of pressure measurements
VART	Variance of temperature measurements
KX	K_x defined by equation chapter 4.
KY	K_y defined by equation chapter 4
KT	K_T defined by equation chapter 4
KP	K_p defined by equation chapter 4
R	Gas constant
FUNC	Statement function giving slope of vapour pressure curve with respect toT
F(J)	$F(a, b)$ values for Ulrichson test

FIG. 89

FLOW DIAGRAM

SUBROUTINE ERRAN



SFSQ	Variance of F(α,b) values
SF	Standard deviation of F(α,b) values
SUMF	$\sum F(\alpha,b)$
SUMVAR	$\sum S_f^2$
SGSQ	Variance of activity coefficients
NN(I)	Counters
SPFSQ	Variance of binomial test
SPF	Standard deviation of binomialtest
CHISQ	Value of Chisquare test
PF	Proportion of given number of data points lying within a particular region

The programme was used to assess the results of data obtained using a modified Cathala still. Some results are illustrated in Figs.20

3.5 Prediction of liquid-liquid equilibrium JF4LIQLIQ

3.5.1. Theory of the method

The equations to be solved for two liquid phases are

$$(V_i x_i)^{I} = (V_i x_i)^{II} \qquad (i = 1,\ 2,\ 3) \qquad \text{(A1.36)}$$

$$\sum_{i=1}^{3} x_i^{I} = 1.0 \qquad \text{(A1.37)}$$

$$\sum_{i=1}^{3} x_i^{II} = 1.0 \qquad \text{(A1.38)}$$

The above assumes a ternary system and the superscripts refer to the phases. The absence of a solution to the above equations indicates a single liquid phase.

The solution of the above equations proceeds by assuming that the feed of composition x_i^{F} splits into two liquid phases

```
                                                                   COMMENTS
JOB :EAXXX,JF4LSQSBL,CP76(T10,P4000)                               STANDARD HEADER CARDS
ATTACH(SOURCE,JF4LSQSCL,ST=S6A)
FTN(I=SOURCE,R=0)
LDSET(MAP=B/ZZZZMP,PRESET=ZERO)
LGO.
####S
1                                                                  MUTUAL SOLUBILITY DATA TO BE FIT
2                                                                  NO. OF DATA SETS
0                                                                  IDEC
0000100000000                                                      SPECIFIES MODEL (UNIQUAC IN THIS CASE)
   0.99974540.0050902   303.15     2                               MUTUAL SOLUBILITY DATA AND TEMPERATURE
TOLUENE/WATER MUTUAL SOLUBILITY DATA AT 30 CENT                    TITLE
DATA OF SALEM AND JEFFRIES
5                                                                  FIRST MODEL TO BE EMPLOYED
  5000.0     3000.0         0.0  2                                 STARTING VALUES
     3.87        0.92         2.93        1.4         10.0         UNIQUAC PARAMETERS
****
```

FIG. 90   INPUT DATA LAYOUT FOR JF4LSQSOL of composition x_i^{I} and x_i^{II}, with the fraction of the total feed (mole basis) going into phase I. Thus a material balance gives

$$x_i^{F} = \phi x_i^{I} + (1 - \phi)\, x_i^{II} \tag{A1.39}$$

Equation (A1.36)can be rearranged to give

$$x_i^{I} = \frac{\gamma_i^{II}}{\gamma_i^{I}}\, x_i^{II} = K_i x_i^{II} \tag{A1.40}$$

$$\text{where} \quad K_i = \frac{\gamma_i^{II}}{\gamma_i^{I}} \tag{A1.41}$$

Substituting for x_i^{I} in equation (A1.39) using equation (A1.40) gives

$$x_i^{F} = K_i \phi x_i^{II} + (1 - \phi) x_i^{II} \tag{A1.42}$$

$$\text{or} \qquad x_i^{II} = \frac{x_i^{F}}{1 + (K_i - 1)\phi} \tag{A1.43}$$

Thus, if two liquid phases exist, a set of solutionsto equation (A1.42) must be found for which $x_i^{II} = 1.0$. If equation (A1.42) holds, then the material balance of equation (A1.37) will ensure $x_i^{I} = 1.0$.

To solve the quations an initial set of values are assumed for x_i^{I} and an initial value of ϕ. Then x_i^{II} values are calculated by equation (A1.43). The γ_i^{I} and γ_i^{II} values are calculated from the compositions thus obtained using either the NRTL or UNIQUAC equations. New values of x_i^{II} and x_i^{I} are then calculated from equations (A1.43) and (A1.40) respectively. If equation (A1.37) is not satisfied, ϕ is adjusted and equations (A1.40) and (A1.43) are used again for x_i^{II} and x_i^{I} respectively until equation (A1.37) is satisfied.

Some modification of the Newton-Raphson technique has been used by Null to modify the value of ϕ after each iteration.

If $\Psi = \sum x_i^{II} - 1.0$ (A1.44)

then $$\frac{d\Psi}{d\phi} = \sum \frac{dx_i^{II}}{d\phi} \qquad \text{(A1.45)}$$

The values of $dx_i^{II}/d\phi$ are obtained by differentiating equation (A1.42), neglecting the dependence of K_i on composition.

$$\frac{dx_i^{II}}{d\phi} \simeq \frac{(K_i - 1)x_i^F}{1+(K_i - 1)\phi^{\,2}} \qquad \text{(A1.46)}$$

The Newton-Raphson technique gives successive estimates of ϕ by

$$\phi_{new} = \phi_{old} - \frac{\Psi}{d\Psi/dO} \qquad \text{(A1.47)}$$

This procedure has been incorporated in the programme.

3.5.2. General description of programme

The first part of the programme is the input section to be described later. The solution of the equations begins by fixing a feed x_i^F and defining an initial guess of ϕ. Also defined are initial guesses for x_i^I. The value of, ϕ, is tested to make sure it does not give negative answers when used to calculate x_i^{II}. If it does it is reduced until satisfactory. Having established the two preliminary liquid phase compositions, the activity coefficients are calculated by subroutine GCALC and these are to obtain a K_i value by equation (A1.41). An iteration loop is now begun in which new values of x_i^I are calculated from K_i and

and x_i^{II} and are used to recalculate K_i. The loop is terminated when K_i is no longer changing. Another iteration loop is now begun in which the values of x_i^{II} are calculated from equation (A1.43) using the value of K_i until x_i^{II} no longer changes. ψ is then calculated and if significantly different from 0.,ϕ

When ψ reaches 0. the mole fractions are converted into wt fractions using subroutine WTFRAC and the results output. The programme proceeds with a new value of the feed to repeat the process. If the process does not converge it is assumed that there is no solution and only a single phase exists. A flow diagram is given in Fig. 71.

3.5.3. Description of Input required

CARD 1 Reads in NCOMP, the number of components in the system. Format I1.

CARD 2 Reads in MODEL which specifies which activity coefficient model is to be used and NOPARA denotes the number of parameters therein. Format 2I1.

If MODEL = 1	NRTL equation to be used
If MODEL = 2	UNIQUAC equation to be used

CARDS 3 & 4 Read in the system title and other details. Format 8A10.

CARDS 5, 6 & 7 Read in component names one to a card. Format A10.

CARD 8 Contains molecular wts of each of the components. Format 10F8.2.

CARDS 9, 10 & 11 Read in the interaction parameters for the three components for use in the activity coefficient models.

CARDS 12, 13 & 14 Read in vapour pressure parameters if liquid phase model is to be used.

The last cards to be read are the UNIQUAC parameters r and q as detailed earlier. A sample of the input is shown in Fig. 80.

LIST OF VARIABLES

FORTRAN NAME	Description
R	Gas constant
XF(I)	Feed composition x_i^F
PHI	ϕ
X(I,1)	x_i^I
X(I,2)	x_i^{II}
K(I)	K_i
G(I,J)	Activity coefficients
DXDPHI	$dx_i^{II}/d\phi$
PSI	Ψ
SUMR	$\sum x_i^{II} - 1$
XWT(I,1)	x_i^I on weight fraction basis
XWT(I,2)	x_i^{II} on weight fraction basis
XFWT(I)	x_i^F on weight fraction basis

If the liquid phase model is taken into account a fictitious vapour phase is calculated and subroutines DELCAL and ETACAL applied as in connection with programme JF4LSQFIT.

3.6. Vapour pressure fitting programme JF4VAPFIT

3.6.1. General description of the programme

The general equation to be fitted is given by

$$\ln P = C_1 + \frac{C_2}{C_3+T} + C_4T + C_5T^2 + C_6 \ln T \qquad (A1.48)$$

where T is in ^{o}K and P_{si} is in atmospheres.

The fitting is carried out using subroutine ROSEN which minimises an objective function of the form.

$$O.F = \sum_{i=1}^{n}\left[\frac{Pexptl - Pcalc}{Pexptl}\right]^2 \qquad (A.49)$$

where Pcalc is found from equation (A1.48). The subroutine XMODEL in this programme contains only the objective function and equation (A1.49).

The coefficients are multiplied by scale factors to make them all approximately of the same order of magnitude.

A flow diagram is shown in Fig.78.

3.6.2. Input required

CARD 1 Reads NDSETS, the number of sets of vapour pressure data to be fitted. Format I2.

CARDS 2 & 3 Reads the title and other details. Format 8A10.

CARD 4 Reads number of data points (NPTS), the number of parameters required (NOPARA), the units of temperature (TUNIT) and the units of pressure (PUNIT). Format I2, 3I1.

CARD 5 Reads factors (PI.(I). Each parameter in the vapour equation has a factor PI multiplied by it. If PI is 1.0 parameter is used. If it is 0.0 parameter is not used. In this way equation may be reducted to simpler form of any combination. Format 6 F4.1.

CARD 6 Reads in starting values for parameters C(I).
Format 6F9.3.

CARDS 7 onwards Read in experimental vapour pressure
data and corresponding temperatures. Format 2F10.4.

A sample of input for this programme is shown in Fig.

The programme has been tested on approximately 20 components, results are given in Appendix A7.

3.7 Other programmes

3.7.1 JF4BUBLT

This is a version of programme BUBLT of Prausnitz et al (P6). The only difference is that the NRTL and UNIQUAC models have been added to the activity coefficient subroutine and a variable MODEL added to the input to specify which one is to be used. Since in other respects it is identical it will not be described further.

It was used to predict quaternary and ternary vapour liquid equilibrium in systems of ethanol-n-butanol-ethyl acetate-n-butyl acetate and the results are shown in Figs.22 and 23.

APPENDIX A2

Detailed derivation of correction factors $\delta_A{}^1$ and $Z_A{}^1$

Considering the pure acetic acid vapour phase. The equilibrium constant, K_A is given by

$$K_A = \frac{\eta_{2A}}{PAO\,\eta_{1A}{}^2} \qquad (A21)$$

where η_{2A} and η_{1A} are true mole fractions of the dimer and monomer acetic acid respectively in the vapour phase and PAO is the vapour pressure of pure acetic acid.

Since $\eta_{1A} + \eta_{2A} = 1$. equation (A2.1) can be written

$$K_A{}' = \frac{\eta_{2A}}{(1 - \eta_{2A})^2\ PAO} \qquad (A2.2)$$

or $K_A PAO - (2K_A PAO + 1)\eta_{2A} + K\ PAO\,\eta_{2A}{}^2 \qquad (A2.3)$

Solving the quadratic for η_{2A} yields

$$\eta_{2A} = \frac{2K_A PAO + 1 - \sqrt{4K_A PAO + 1}}{2K_A\ PAO} \qquad (A2.4)$$

Similarly for the liquid phase where ξ_{1A} and ξ_{2A} are the mole fractions of the monomer and dimer in the pure acetic acid liquid phase.

$$k_A = \frac{\xi_{2A}}{\xi_{1A}{}^2} \qquad (A2.5)$$

giving $$\xi_{2A} = \frac{2k_A + 1 - \sqrt{4k_A + 1}}{2k_A} \qquad (A2.6)$$

The equilibrium relationship for the dimer may be written as

$$PAO\,\eta_{2A}\ \phi_{2A} = P_{20}\,\xi_{2A}\ V_{2A} \qquad (A2.7)$$

where P_{20} is the vapour pressure of the dimer, ϕ_{2A} is the fugacity coefficient of the dimer and V_{2A} the activity coefficient.

Equation may be rearranged to give an expression for the vapour pressure of the dimer in terms of the overall acetic acid vapour pressure

$$P_{20} = PAO \left[\frac{\eta_{2A}}{\xi_{2A}}\right] \frac{\phi_{2A}}{V_{2A}} \qquad (A2.8)$$

or substituting for η_{2A} and ξ_{2A} using (C1.4) and (A2.6)

$$P_{20} = PAO \left[\frac{(2K_A PAO + 1 - \sqrt{4K_A PAO + 1})\, k_A}{(2k_A + 1 - \sqrt{4k_A + 1})\, K_A PAO}\right] \frac{\phi_{2A}}{V_{2A}} \qquad (A2.9)$$

For the mixture of acetic acid with the non-associating component the equilibrium relationship for the vapour phase is given by

$$K = \frac{\eta_2}{P\eta_1^2} \qquad (A2.10)$$

where P is the total pressure of the system and η_1 and η_2 are the true mole fractions of monomer and dimer in the mixture. They are related to the overall mole fraction of acetic acid in the vapour phase, Y_A by the following stochiometric relationship

$$Y_A = \frac{\eta_1 + 2\eta_2}{1 + \eta_2} \qquad (A2.11)$$

which, on solving for η_1 and squaring gives

$$\eta_1^2 = \left[Y_A(1 + \eta_2) - 2\eta_2\right]^2 \qquad (A2.12)$$

From equation (A2.10) $\eta_1^2 = \dfrac{\eta_2}{KP}$ (A2.13)

Substituting for η_1^2 and rearranging gives a quadratic in η_2

$$\eta_2^2 (KPY_A^2 + 4KP + 4KPY_A) - \eta_2(4KPY_A - 2KPY_A^2 + 1) + KPY_A^2 \quad (A2.14)$$

Solving for η_2 yields.

$$\eta_2 = \frac{(4KPY_A + 1 - 2KPY_A^2) - \sqrt{1 + 8KPY_A - 4KPY_A^2}}{2(KPY_A^2 + 4KP - 4KPY_A)} \quad (A2.15)$$

In an analogous manner utilising the relations

$$k = \frac{\xi_2}{\xi_1^2} \quad (A2.16)$$

and $$x_A = \frac{\xi_1 + 2\xi_2}{1 + \xi_2} \quad (A2.17)$$

where ξ_2 and ξ_1 are the true mole fractions of dimer and monomer in the liquid phase and x_A is the nominal mole fraction of acetic acid, the following expression for ξ_2 is obtained

$$\xi_2 = \frac{(4kx_A + 1 - 2kx_A^2) - \sqrt{1 + 8kx_A - 4kx_A^2}}{2(kx_A^2 + 4k - 4kx_A)} \quad (A2.18)$$

Dividing (A2.15) by Y_A and (A2.18) by x_A gives

$$\eta_2 = Y_A \left[\frac{(4KP + 1/Y_A - 2KPY_A) - \sqrt{1/Y_A^2 + 8KP/Y_A - 4KP}}{2(KPY_A^2 + 4KP - 4KPY_A)} \right] \quad (A2.19)$$

and $$\xi_2 = x_A \left[\frac{(4k + 1/x_A - 2kx_A) - \sqrt{1/x_A^2 + 8k/x_A - 4k}}{2(kxA^2 + 4k - 4kx_A)} \right] \quad (A2.20)$$

For the mixture of acetic acid and non-associating component the equilibrium relationship may be written

$$P \eta_2 \phi_2 = P_{20} \xi_2 V_2 \quad (A2.21)$$

Substituting for η_2, ξ_2 and P_{20} using (A2.15), (A2.18) and (A2.9) gives

$$PY_A \, Z_A^{\ 1} \, \phi_A^{\ 1} = PAO \, x_A \, \delta_A^{\ 1} \, V_A^{\ 1}$$

where $V_A^{\ 1} = \dfrac{V_2}{V_{2A}}$ and $\phi_A^{\ 1} = \dfrac{\phi_2}{\phi_{2A}}$ (A2.22)

$$\text{and } Z_A^{\ 1} = \frac{Y_A \left[(4KP + {}^{1}/_{Y_A} - 2KPY_A) - \sqrt{{}^{1}/_{Y_A}{}^{2} + {}^{8KP}/_{Y_A} - 4KP} \right] \left[K_A \, PAO \right]}{(KPY_A^{\ 2} + 4KP - 4KPY_A)\,(2K_A PAO + 1 - \sqrt{4K_A PAO + 1})} \tag{A2.23}$$

$$\delta_A^{\ 1} = \frac{x_A \left[(4k + {}^{1}/_{x_A} - 2kx_A) - \sqrt{{}^{1}/_{x_A}{}^{2} + {}^{8k}/_{x_A} - 4k} \right] \left[k_A \right]}{(kx_A^{\ 2} + 4k - 4kx_A)\,(2k_A + 1 - \sqrt{4k_A + 1})} \tag{A2.24}$$

APPENDIX A3

Results of data reduction using concentration dependent correction factors on systems containing acetic acid.

1. Acetic Acid - Toluene
   - a. Isothermal - 30°C (M10)
   - b. " - 50°C (M16)
   - c. " - 69.94°C (Z1)
   - d. " - 70°C (M16)
   - e. " - 80.05°C (Z1)
   - f. Pressure range 742-750 mm Hg (H3)

2. Acetic Acid - Benzene
   - a. Isothermal - 20°C (W1)
   - b. " - 30°C (M16)
   - c. " - 49.99°C (Z1)
   - d. " - 50.0°C (M16)
   - e. " - 70.0°C (M16)
   - f. Isobaric - 758 mm (05)
   - g. " - 760 mm (G1)

3. Acetic Acid - n - Heptane
   - a. Isothermal - 20°C (W1)
   - b. " - 20°C (M10)
   - c. " - 30°C (M10)
   - d. " - 40°C (M10)

4. Acetic Acid - Ethybenzene
   - a. Isobaric - 725 mm (B2)

5. Acetic acid - P - xylene
    a. Isobaric - 725 mm (B1)
    b. " - 760 mm (M5)

6. Acetic acid - n-Octane
    a. Isobaric - 760 mm (S10)
    b. " - 760 mm (Z2)

7. Acetic acid - n-Decane
    a. Isobaric - 760 mm (Z2)

8. Acetic acid - Trichloroethylene
    a. Isobaric - 250 mm (F4)
    b. " - 350 mm (F4)
    c. " - 500 mm (F4)
    d. " - 650 mm (F4)
    e. " - 750 mm (F4)

9. Acetic acid - Methylene Chloride
    a. Isobaric - 760 mm (D8)

10. Acetic acid - Carbon Tetrachloride
    a. Isothermal - 20°C (L7)

11. Acetic acid - Chloroform
    a. Isobaric - 760 mm (K5)

12. Acetic acid - Water
    a. Isothermal - 69.7°C (A5)
    b. " - 70°C (H1)
    c. " - 79.9°C (A5)

Acetic acid - Water cont'd

d. Isothermal - 89.9°C (A5)
e. Isobaric - 50.0 mm (K1)
f. " - 70.0 mm (F1)
g. " - 200.0 mm (I1)
h. " - 760.0 mm (I1)
i. " - 760.0 mm (G1)
j. " - 760.0 mm (S8)
k. " - 760.0 mm (B16)
l. " - 760.0 mm (R14)

13. Acetic acid - Methanol

a. Pressure range - 704 - 711.1 mm (R17)

14. Acetic acid - Ethanol

a. Pressure range - 689 - 708 mm (R17)

15. Acetic acid - n-Propanol

a. Pressure range - 701 - 707 mm (R17)
b. Isobaric - 760 mm (A3)

16. Acetic acid - Iso Propanol

a. Isobaric - 760 mm (A3)

17. Acetic acid - n-Butanol

a. Pr3ssure range - 693 - 712 mm (R17)

18. Acetic acid - 2-Butanol

a. Isobaric - 760 mm (A3)

19. Acetic acid - Iso-butanol

a. Isobaric - 760 mm (A3)

20. Acetic acid - Tert-butanol
    a. Isobaric - 760 mm (A3)

21. Acetic acid - Ethylacetate
    a. Isothermal - 30°C (M16)
    b. " - 50°C (M16)
    c. " - 70°C (M16)

22. Acetic acid - n-Butyl Acetate
    a. Isobaric - 760 mm (I2)

23. Acetic acid - Cyclo-hexyl acetate
    a. Isobaric - 760 mm (O4)

24. Acetic acid - Vinyl acetate
    a. Isobaric - 760 mm (S14)

25. Acetic acid - Acetone
    a. Isothermal - 30°C (M17)
    b. " - 40°C (M17)
    c. " - 50°C (M17)
    d. Isobaric - 760 mm (L4)

26. Acetic acid - Diethylketone
    a. Isothermal - 70°C (H1)

27. Acetic acid - Ethyl ether
    a. Isobaric - 389.7 mm (M17)
    b. " - 487.9 mm (M17)
    c. " - 596.4 mm (M17)

28. Acetic acid - Pyridine
    a. Isothermal - 80.05°C (Z1)

29. Acetic acid - Acetic ankydride
    a. Isobaric - 100 mm (J8)

30. Acetic acid - Acetaldehyde
    a. Isobaric - 760 mm (F8)

31. Acetic acid - Dimethylacetamide
    a. Isobaric - 760 mm (Cl)

```
SYSTEM  ACETIC ACID-TOLUENE AT CONSTANT TEMPERATURE 30 DEG.
DATA OF MARKUZIN N.P. AND PAVLOVA L.M. RUSSIAN J. APPL. CHEM
. 1971,VOL 44 NO 3

                    TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 -  523.78 WILSON PARAMETER 21 -    14.72

  LIQUID     VAPOUR     VAPOUR     DELTA   EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100   PRESS    PRESS    MM HG
            EXPTL      CALC
  .10320    .15100    .15097     .003   38.100   38.786   -.686
  .19640    .22600    .22597     .003   38.900   39.040   -.140
  .28810    .28800    .28800     .000   39.600   39.248    .352
  .35550    .32600    .32601    -.001   39.700   39.196    .504
  .36880    .33900    .33901    -.001   39.700   39.315    .385
  .37090    .34100    .34101    -.001   39.700   39.333    .367
  .40000    .35500    .35501    -.001   39.600   39.214    .386
  .50000    .41100    .41095     .005   38.900   38.813    .087
  .56370    .44300    .44286     .014   38.200   38.258   -.058
  .61170    .47900    .47879     .021   37.700   38.046   -.346
  .61510    .47600    .47579     .021   37.600   37.862   -.262
  .70440    .53500    .53463     .037   36.500   36.832   -.332
  .75580    .56600    .56545     .055   35.400   35.608   -.208
  .84110    .63700    .63601     .099   32.900   32.784    .116
  .91930    .75300    .75115     .185   28.900   28.651    .249

     SUM OF SQUARES                         -     .11966272E-02
     STANDARD ERROR OF ESTIMATE             -     .95941776E-02
     AVERAGE PRESSURE DEVIATION MM HG       -     .79294323E+00
     AVERAGE VAPOUR DEVIATION*100           -     .2976E-01
     NUMBER OF FUNCTION EVALUATIONS         -     263

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT     A          B       COEFF 1    COEFF 2
  .10320    39.1700   2.1824    1.0380    3.65596    1.04307
  .19640    44.6231   1.6046    1.0847    2.48814    1.10505
  .28810    44.8848   1.3824    1.1361    1.99243    1.18487
  .35550    45.0958   1.2780    1.1780    1.74927    1.25904
  .36880    43.9900   1.2758    1.1862    1.72900    1.27502
  .37090    43.8293   1.2754    1.1875    1.72572    1.27760
  .40000    44.1661   1.2383    1.2072    1.64003    1.31637
  .50000    43.6210   1.1587    1.2799    1.43030    1.47866
  .56370    43.9045   1.1155    1.3319    1.32084    1.61342
  .61170    42.4195   1.1087    1.3731    1.27465    1.73472
  .61510    43.1538   1.0985    1.3767    1.26031    1.74488
  .70440    42.1273   1.0761    1.4628    1.17508    2.04126
  .75580    42.8748   1.0528    1.5190    1.12146    2.26718
  .84110    43.7072   1.0263    1.6228    1.05686    2.77228
  .91930    43.5293   1.0193    1.7308    1.02775    3.45492
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SYSTEM ACETIC ACID-TOLUENE AT 50 CENT
DATA OF MEEHAN


                    TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 - 1411.75 WILSON PARAMETER 21 - -807.82

  LIQUID     VAPOUR     VAPOUR     DELTA   EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100   PRESS    PRESS    MM HG
            EXPTL       CALC
  .09520    .08010    .08008    .002   93.800   92.375   1.425
  .19220    .17900    .17893    .007   95.200   94.857    .343
  .28950    .27310    .27301    .009   96.400   96.991   -.591
  .41760    .37600    .37592    .008   97.400   97.779   -.379
  .53310    .46530    .46511    .019   96.500   96.479    .021
  .63360    .55250    .55194    .056   93.300   93.568   -.268
  .75400    .65750    .65606    .144   87.200   86.806    .394
  .85010    .76850    .76569    .281   79.100   78.947    .153

    SUM OF SQUARES                        -    .32907326E-03
    STANDARD ERROR OF ESTIMATE            -    .74057777E-02
    AVERAGE PRESSURE DEVIATION MM HG      -    .47950607E+00
    AVERAGE VAPOUR DEVIATION*100          -    .6585E-01
    NUMBER OF FUNCTION EVALUATIONS        -    457

  LIQUID  EQUILIBRIUM DELTA     DELTA    ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT    A         B      COEFF 1    COEFF 2
  .09520    48.1609  1.5448   1.0357   2.44762    1.05139
  .19220    24.8639  1.5518   1.0758   2.03892    1.12593
  .28950    18.4663  1.5154   1.1218   1.78326    1.21515
  .41760    16.3148  1.4138   1.1948   1.53240    1.35256
  .53310    16.0269  1.3256   1.2742   1.38024    1.49521
  .63360    16.2365  1.2615   1.3554   1.28742    1.63528
  .75400    17.4975  1.1782   1.4732   1.18687    1.82972
  .85010    18.5892  1.1274   1.5850   1.12995    2.00856
```

```
SYSTEM ACETIC ACID-TØLUENE AT 69,94 C
DATA ØF ZAWIDSKI (1900)


                    THREE PARAMETER NRTL EQUATIØN

   NRTL PARAMETER 12 -  641,24 NRTL PARAMETER 21 -  503,71
                  NRTL PARAMETER ALPHA -     1,35515

  LIQUID     VAPØUR     VAPØUR    DELTA  EXPTL     CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC    Y*100  PRESS     PRESS    MM HG
            EXPTL      CALC
  ,00660    ,00890     ,00889     ,001 206,200 199,633   6,567
  ,02430    ,05640     ,05633     ,007 207,400 204,329   3,071
  ,03500    ,07510     ,07505     ,005 211,100 206,100   5,000
  ,06100    ,11260     ,11252     ,008 210,700 208,716   1,984
  ,06200    ,11470     ,11462     ,008 210,700 208,902   1,798
  ,10040    ,16300     ,16297     ,003 214,600 212,845   1,755
  ,10420    ,16830     ,16829     ,001 215,500 213,422   2,078
  ,12020    ,18490     ,18490    -,000 216,600 214,702   1,898
  ,13880    ,20270     ,20270    -,000 216,600 215,801    ,799
  ,20700    ,26450     ,26462    -,012 220,600 220,547    ,053
  ,24990    ,29870     ,29892    -,022 222,700 222,975   -,275
  ,31730    ,34710     ,34741    -,031 224,300 225,495  -1,195
  ,32310    ,35060     ,35093    -,033 224,600 225,667  -1,067
  ,34230    ,36200     ,36236    -,036 225,100 226,020   -,920
  ,40460    ,40090     ,40130    -,040 225,800 226,852  -1,052
  ,44890    ,42640     ,42676    -,036 225,000 226,343  -1,343
  ,50950    ,46030     ,46061    -,031 224,000 225,071  -1,071
  ,53800    ,47540     ,47568    -,028 223,400 224,092   -,692
  ,59500    ,50740     ,50750    -,010 221,300 221,526   -,226
  ,64240    ,53410     ,53402     ,008 218,900 218,578    ,322
  ,71770    ,58120     ,58061     ,059 213,500 212,561    ,939
  ,79080    ,63440     ,63297     ,143 204,900 203,921    ,979
  ,85160    ,69240     ,68987     ,253 195,600 194,919    ,681
  ,92400    ,79260     ,78737     ,523 175,300 175,947   -,647

    SUM ØF SQUARES                          -    ,24364654E-02
    STANDARD ERRØR ØF ESTIMATE              -    ,10771358E-01
    AVERAGE PRESSURE DEVIATIØN MM HG        -    ,76895533E+00
    AVERAGE VAPØUR DEVIATIØN*100            -    ,5405E-01
    NUMBER ØF FUNCTIØN EVALUATIØNS          -   1133

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY    ACTIVITY
MØLE FRAC   CØNSTANT     A          B       CØEFF 1     CØEFF 2
  ,00660    119,4576   2,2782    1,0015     6,03835     1,00161
  ,02430     15,9221   2,7959    1,0041     6,92715     1,00528
  ,03500     17,1224   2,4864    1,0073     5,93294     1,00961
  ,06100     18,8380   2,0316    1,0163     4,46355     1,02284
  ,06200     18,6015   2,0295    1,0166     4,44569     1,02334
  ,10040     17,2521   1,7694    1,0307     3,49931     1,04686
  ,10420     16,8654   1,7613    1,0320     3,46186     1,04929
  ,12020     16,5107   1,6889    1,0383     3,19180     1,06058
  ,13880     16,2680   1,6145    1,0460     2,93507     1,07461
  ,20700     14,5591   1,4643    1,0753     2,36866     1,13180
  ,24990     13,8259   1,4003    1,0953     2,13816     1,17267
  ,31730     13,1704   1,3175    1,1296     1,86953     1,24480
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SYSTEM ACETIC ACID-TØLUENE AT 69,94 C
DATA ØF ZAWIDSKI (1900)

                         THREE pARAMETER NRTL EQUATIØN

  LIQUID  EQUILIBRIUM DELTA       DELTA      ACTIVITY    ACTIVITY
MØLE FRAC   CØNSTANT    A           B         CØEFF 1     CØEFF 2
  .32310    13,1406   1,3108      1,1327      1,84987     1,25150
  .34230    13,0889   1,2884      1,1434      1,78657     1,27432
  .40460    12,8547   1,2308      1,1795      1,62317     1,35452
  .44890    12,8870   1,1914      1,2076      1,52345     1,41892
  .50950    12,9441   1,1467      1,2488      1,41233     1,51885
  .53800    13,0098   1,1274      1,2695      1,36525     1,57183
  .59500    13,1129   1,0950      1,3134      1,28715     1,69229
  .64240    13,2306   1,0713      1,3529      1,22962     1,81205
  .71770    13,3401   1,0432      1,4211      1,15482     2,05655
  .79080    13,4598   1,0223      1,4953      1,09413     2,40161
  .85160    13,3303   1,0166      1,5627      1,05963     2,83790
  .92400    13,2879   1,0108      1,6528      1,02528     3,74236
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SYSTEM ACETIC ACID-TOLUENE AT 70 CENT
DATA OF MEEHAN


                    TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 =  710,85 WILSON PARAMETER 21 = -100,68

 LIQUID     VAPOUR     VAPOUR     DELTA   EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC    Y*100   PRESS    PRESS    MM HG
           EXPTL      CALC
 ,08760    ,14830    ,14813       ,017 215,100 210,741   4,359
 ,18450    ,24750    ,24719       ,031 219,400 216,739   2,661
 ,28650    ,32040    ,32012       ,028 222,500 220,429   2,071
 ,41470    ,40120    ,40089       ,031 224,100 223,808    ,292
 ,53740    ,47320    ,47275       ,045 223,600 224,796  -1,196
 ,64500    ,53540    ,53448       ,092 219,100 221,160  -2,060
 ,76930    ,61720    ,61505       ,215 207,400 208,430  -1,030
 ,86790    ,70740    ,70298       ,442 188,300 186,533   1,767

    SUM OF SQUARES                           =     ,87587537E-03
    STANDARD ERROR OF ESTIMATE               =     ,12082186E-01
    AVERAGE PRESSURE DEVIATION MM HG         =     ,90132851F+00
    AVERAGE VAPOUR DEVIATION*100             =     ,1126E+00
    NUMBER OF FUNCTION EVALUATIONS           =     303

 LIQUID  EQUILIBRIUM DELTA      DELTA    ACTIVITY   ACTIVITY
MOLE FRAC  CONSTANT    A          B      COEFF 1    COEFF 2
 ,08760    14,5871   1,9666    1,0244    3,76950    1,03049
 ,18450    15,1093   1,5015    1,0654    2,53193    1,09354
 ,28650    14,7043   1,3026    1,1155    1,95031    1,18766
 ,41470    13,5255   1,1951    1,1874    1,57530    1,35426
 ,53740    12,6109   1,1419    1,2678    1,36207    1,58349
 ,64500    12,3335   1,1021    1,3514    1,22574    1,86793
 ,76930    12,5547   1,0571    1,4682    1,10731    2,34583
 ,86790    13,2241   1,0174    1,5814    1,03349    2,90354
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SYSTEM ACETIC ACID-TØLUENE AT 80.05
DATA ØF ZAWIDSKI (1900)


                     TWØ PARAMETER WILSØN EQUATIØN

WILSØN PARAMETER 12 =  639.22 WILSØN PARAMETER 21 =  169.95

  LIQUID     VAPØUR     VAPØUR    DELTA   EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC   Y*100   PRESS    PRESS    MM HG
            EXPTL      CALC
   .02770     .06811     .06798      .013 302.200 293.823   8.377
   .06211     .12244     .12222      .022 308.400 299.862   8.538
   .09547     .16451     .16430      .021 313.700 304.516   9.184
   .12748     .20002     .19986      .016 317.500 308.366   9.134
   .16533     .23629     .23622      .007 321.700 312.323   9.377
   .20300     .26894     .26892      .002 324.200 315.647   8.553
   .32770     .36118     .36141     -.023 331.700 325.669   6.031
   .40789     .41004     .41034     -.030 333.300 329.955   3.345
   .40840     .40982     .41014     -.032 333.600 329.991   3.609
   .41920     .41544     .41573     -.029 333.000 330.047   2.953
   .48597     .45290     .45313     -.023 332.100 332.012    .088
   .55005     .48458     .48470     -.012 331.000 332.417  -1.417
   .58650     .52245     .52227      .018 326.800 334.694  -7.894
   .68876     .56043     .55975      .068 320.500 326.376  -5.876
   .75129     .60153     .60009      .144 312.100 319.040  -6.940
   .92844     .79207     .78479      .728 260.500 260.160    .340
   .94551     .82782     .81911      .871 250.100 248.815   1.285
   .97602     .91399     .90190     1.209 229.300 227.137   2.163
   .97963     .92520     .91250     1.270 225.300 222.966   2.334
   .98043     .93082     .91793     1.289 224.400 222.654   1.746
   .98355     .93739     .92419     1.320 222.600 219.843   2.757
   .99490     .97997     .96466     1.631 210.400 207.402   2.998

     SUM ØF SQUARES                           =     .74660953E-02
     STANDARD ERRØR ØF ESTIMATE               =     .19321096E-01
     AVERAGE PRESSURE DEVIATIØN MM HG         =     .15763944E+01
     AVERAGE VAPØUR DEVIATIØN*100             =     .3945E+00
     NUMBER ØF FUNCTIØN EVALUATIØNS           =     187

  LIQUID  EQUILIBRIUM DELTA      DELTA    ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT    A          B      CØEFF 1    CØEFF 2
   .02770      6.8216  2.9230    1.0031    6.67767    1.00373
   .06211     12.2048  2.0805    1.0144    4.52365    1.01730
   .09547     13.7161  1.7473    1.0269    3.62616    1.03398
   .12748     14.1209  1.5682    1.0397    3.11582    1.05266
   .16533     14.1660  1.4314    1.0559    2.70563    1.07820
   .20300     13.9765  1.3397    1.0728    2.41331    1.10743
   .32770     12.5193  1.1899    1.1341    1.84918    1.23503
   .40789     11.7329  1.1400    1.1787    1.62605    1.34933
   .40840     11.7383  1.1394    1.1790    1.62428    1.35019
   .41920     11.7031  1.1318    1.1855    1.59582    1.36822
   .48597     11.1692  1.1050    1.2268    1.46029    1.49394
   .55005     10.8255  1.0826    1.2704    1.35117    1.64506
   .58650     10.0909  1.0969    1.2941    1.32825    1.74388
   .68876     10.3198  1.0486    1.3791    1.17772    2.12229
   .75129     10.1903  1.0374    1.4360    1.12133    2.43966
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SYSTEM ACETIC ACID-TOLUENE AT 80.05
DATA OF ZAWIDSKI (1900)


                   TWO PARAMETER WILSON EQUATION

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY    ACTIVITY
MOLE FRAC   CONSTANT     A          B       COEFF 1     COEFF 2
  .92844    10.2027   1.0116     1.6338     1.01923     4.04882
  .94551    10.1958   1.0109     1.6561     1.01545     4.29723
  .97602     9.9199   1.0217     1.6947     1.02259     4.79980
  .97963     9.9733   1.0193     1.7004     1.01995     4.86824
  .98043     9.9120   1.0219     1.7008     1.02255     4.88130
  .98355     9.9358   1.0209     1.7055     1.02128     4.94126
  .99490     9.9650   1.0195     1.7220     1.01953     5.16761
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SYSTEM  ACETIC ACID-TØLUENE - NØN-ISØTHERMAL,NØN-ISØBARIC
DATA ØF HAUGHTØN - CØMPØNENT 1 TØLUENE


                  THREE PARAMETER NRTL EQUATIØN

   NRTL PARAMETER 12 - 1087,02 NRTL PARAMETER 21 - 1097,35
                  NRTL PARAMETER ALPHA -    1,04445

  LIQUID      VAPØUR      VAPØUR     DELTA  EXPTL     CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC  Y*100  PRESS     PRESS     MM HG
            EXPTL       CALC
  ,04800     ,13300     ,13226     ,074 755,000 728,971 26,029
  ,07800     ,18100     ,17998     ,102 753,000 734,009 18,991
  ,11500     ,23600     ,23468     ,132 750,000 740,459  9,541
  ,21900     ,31900     ,31723     ,177 749,000 755,668 -6,668
  ,25500     ,35000     ,34809     ,191 760,000 760,279-10,279
  ,31300     ,36900     ,36702     ,198 750,000 755,755 -5,755
  ,42900     ,43500     ,43224     ,276 742,000 752,398-10,398
  ,47500     ,45500     ,45196     ,304 742,000 752,267-10,267
  ,52700     ,48100     ,47800     ,300 746,000 747,517 -1,517
  ,57200     ,49800     ,49483     ,317 747,000 743,065  3,935
  ,62900     ,52300     ,51932     ,368 743,000 734,060  8,940
  ,80600     ,64000     ,63434     ,566 742,000 730,265 11,735
  ,90200     ,74700     ,73927     ,773 750,000 748,655  1,345
  ,94700     ,83700     ,82611    1,089 750,000 766,480-16,480
  ,97000     ,87100     ,85870    1,230 750,000 747,922  2,078
  ,99200     ,92900     ,91433    1,467 750,000 721,531 28,469

    SUM ØF SQUARES                          -      ,50616204E-02
    STANDARD ERRØR ØF ESTIMATE              -      ,19732091E-01
    AVERAGE PRESSURE DEVIATIØN MM HG        -      ,15913220E+01
    AVERAGE VAPØUR DEVIATIØN*100            -      ,4728E+00
    NUMBER ØF FUNCTIØN EVALUATIØNS          -       974

  LIQUID  EQUILIBRIUM DELTA       DELTA     ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT    A           B       CØEFF 1    CØEFF 2
  ,04800    15,6158  1,6025     1,0110    5,72381    1,02246
  ,07800    11,4496  1,5343     1,0192    4,45031    1,04527
  ,11500     8,0174  1,5401     1,0291    3,69296    1,07688
  ,21900     6,2633  1,3823     1,0655    2,42474    1,18425
  ,25500     5,7689  1,3621     1,0790    2,23773    1,22386
  ,31300     6,1582  1,2535     1,1073    1,90001    1,29638
  ,42900     6,2152  1,1422     1,1683    1,55481    1,45625
  ,47500     6,4334  1,0935     1,1968    1,44200    1,53138
  ,52700     6,4145  1,0675     1,2294    1,36338    1,62442
  ,57200     6,6163  1,0319     1,2614    1,28461    1,71971
  ,62900     6,8105   ,9967     1,3045    1,20280    1,86386
  ,80600     6,3237   ,9682     1,4513    1,05961    2,69560
  ,90200     5,3969  1,0005     1,5348    1,03617    3,98492
  ,94700     4,8660  1,0117     1,5734    1,02481    5,36469
  ,97000     4,7939  1,0053     1,5987    1,00997    6,57563
  ,99200     4,5584  1,0075     1,6187    1,00786    8,29979
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SYSTEM ACETIC ACID - BENZENE AT 20 DEG CENT
DATA ØF WERNER,JNL.FUR.PRAK.CHEM.,NØ 4,VØL 29,1965,PG 28


                         TWØ PARAMETER WILSØN EQUATIØN

WILSØN PARAMETER 12 =  516.84 WILSØN PARAMETER 21 =  -53.32

  LIQUID     VAPØUR     VAPØUR    DELTA   EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC   Y*100   PRESS    PRESS    MM HG
           EXPTL      CALC
  .03000    .01600    .01602    -.002   74.900   73.920     .980
  .06500    .02900    .02904    -.004   74.300   73.109    1.191
  .08100    .03500    .03505    -.005   74.000   72.766    1.234
  .12000    .04600    .04606    -.006   73.400   71.880    1.520
  .19100    .06600    .06607    -.007   71.800   70.392    1.408
  .19800    .06800    .06806    -.006   71.400   70.237    1.163
  .27800    .09100    .09106    -.006   69.800   68.707    1.093
  .32900    .10200    .10204    -.004   68.400   67.572     .828
  .36200    .11200    .11203    -.003   67.600   66.909     .691
  .39300    .12000    .12000     .000   66.400   66.157     .243
  .51400    .15700    .15688     .012   62.600   62.917    -.317
  .51500    .15700    .15688     .012   62.500   62.865    -.365
  .57800    .17400    .17379     .021   60.200   60.487    -.287
  .65000    .20500    .20460     .040   56.700   57.177    -.477
  .66700    .21300    .21256     .044   56.000   56.284    -.284
  .71200    .23500    .23436     .064   53.000   53.351    -.351
  .73000    .25000    .24924     .076   51.500   52.103    -.603
  .74900    .26700    .26615     .085   50.200   50.500    -.300
  .77700    .27400    .27296     .104   48.000   47.998     .002
  .78400    .28600    .28487     .113   47.200   47.451    -.251
  .82400    .32900    .32743     .157   43.300   43.390    -.090
  .83400    .33600    .33432     .168   42.200   42.116     .084
  .84500    .35200    .35013     .187   40.700   40.746    -.046
  .85400    .36000    .35803     .197   40.000   39.628     .372
  .86400    .36900    .36685     .215   38.400   38.048     .352
  .87600    .39200    .38958     .242   36.900   36.474     .426

    SUM ØF SQUARES                              =    .30319681E-02
    STANDARD ERRØR ØF ESTIMATE                  =    .11239751E-01
    AVERAGE PRESSURE DEVIATIØN MM HG            =    .91572556E+00
    AVERAGE VAPØUR DEVIATIØN*100                =    .6841E-01
    NUMBER ØF FUNCTIØN EVALUATIØNS              =    302

  LIQUID   EQUILIBRIUM DELTA     DELTA    ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT     A         B      CØEFF 1    CØEFF 2
  .03000    62.7061   3.4239    1.0091    6.81591    1.00982
  .06500    75.0194   2.3592    1.0243    4.45890    1.02767
  .08100    75.1031   2.1558    1.0315    3.98213    1.03680
  .12000    79.4937   1.7887    1.0504    3.13154    1.06215
  .19100    77.7965   1.4928    1.0871    2.38802    1.11760
  .19800    77.6568   1.4725    1.0909    2.33581    1.12379
  .27800    71.5489   1.3370    1.1361    1.93880    1.20364
  .32900    71.4800   1.2553    1.1679    1.72879    1.26543
  .36200    68.8524   1.2334    1.1890    1.64657    1.30967
  .39300    68.2171   1.2032    1.2100    1.56234    1.35538
  .51400    63.0995   1.1423    1.2995    1.35016    1.57371
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SYSTEM ACETIC ACID - BENZENE AT 20 DEG CENT
DATA OF WERNER,JNL.FUR.PRAK.CHEM.,NO 4,VOL 29,1965,PG 28

                       TWO PARAMETER WILSON EQUATION

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT     A          B       COEFF 1    COEFF 2
  .51500    63.3072   1.1399     1.3004     1.34638    1.57592
  .57800    63.6012   1.1000     1.3540     1.24787    1.72259
  .65000    61.4606   1.0841     1.4202     1.18263    1.92299
  .66700    60.8748   1.0823     1.4368     1.17104    1.97641
  .71200    61.1735   1.0644     1.4838     1.12915    2.13228
  .73000    60.0178   1.0684     1.5027     1.12545    2.19953
  .74900    61.4153   1.0518     1.5248     1.10019    2.27666
  .77700    62.1971   1.0387     1.5579     1.07637    2.39750
  .78400    60.6317   1.0496     1.5653     1.08526    2.42770
  .82400    59.4017   1.0517     1.6142     1.07532    2.62068
  .83400    60.4913   1.0410     1.6279     1.06188    2.67432
  .84500    60.3450   1.0405     1.6423     1.05861    2.73377
  .85400    60.6492   1.0367     1.6545     1.06272    2.78446
  .86400    62.5332   1.0206     1.6695     1.03427    2.84436
  .87600    61.5345   1.0268     1.6865     1.03822    2.91488
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SYSTEM ACETIC ACID - BENZENE AT 30 CENT
DATA OF MEEHAN


                    TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 -  542.86 WILSON PARAMETER 21 - -109.26

  LIQUID     VAPOUR     VAPOUR     DELTA  EXPTL     CALC     DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100  PRESS     PRESS     MM HG
            EXPTL      CALC
  .09730    .05530     .05539    -.009 116.800 115.192   1.608
  .22250    .08750     .08764    -.014 109.700 110.575   -.875
  .34780    .11610     .11617    -.007 103.500 105.739  -2.239
  .48670    .15210     .15206     .004  98.500  99.644  -1.144
  .61690    .20170     .20148     .022  93.000  91.912   1.088
  .71850    .25620     .25552     .068  84.300  82.437   1.863
  .82800    .35700     .35485     .215  66.200  65.898    .302
  .90460    .48560     .48095     .465  47.000  47.892   -.892

    SUM OF SQUARES                           -     .18628789E-02
    STANDARD ERROR OF ESTIMATE               -     .17620437E-01
    AVERAGE PRESSURE DEVIATION MM HG         -     .14042792E+01
    AVERAGE VAPOUR DEVIATION*100             -     .1005E+00
    NUMBER OF FUNCTION EVALUATIONS           -     277

  LIQUID  EQUILIBRIUM DELTA     DELTA    ACTIVITY  ACTIVITY
MOLE FRAC   CONSTANT    A         B      COEFF 1   COEFF 2
  .09730    34.9138  2.3396    1.0346    4.04279   1.04208
  .22250    46.5271  1.5008    1.0992    2.22554   1.13970
  .34780    49.1613  1.2387    1.1745    1.62336   1.27908
  .48670    47.7299  1.1212    1.2718    1.32078   1.49473
  .61690    43.8159  1.0900    1.3788    1.19236   1.77504
  .71850    42.4389  1.0681    1.4779    1.12055   2.06909
  .82800    43.4990  1.0307    1.6058    1.04920   2.49195
  .90460    48.2209   .9733    1.7147     .97858   2.88195
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SYSTEM ACETIC ACID - BENZENE AT 49.99 CENT
DATA OF ZADWISKI,Z.PHYS.CHEM,1900,PG 153


                        TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 =   459.06 WILSON PARAMETER 21 =    60.03

  LIQUID      VAPOUR      VAPOUR     DELTA   EXPTL     CALC     DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC  Y*100   PRESS     PRESS     MM HG
             EXPTL       CALC
  .02254      .01924      .01928     -.004 265.900 263.542   2.358
  .05821      .03699      .03707     -.009 265.200 260.875   4.325
  .06609      .04156      .04166     -.009 264.400 260.365   4.035
  .12853      .06918      .06932     -.014 261.400 255.968   5.432
  .17554      .08764      .08780     -.016 259.000 252.723   6.277
  .26028      .12228      .12237     -.009 250.200 246.890   3.310
  .31166      .13502      .13503     -.001 245.200 242.462   2.738
  .42495      .16981      .16962      .018 236.000 233.200   2.800
  .48465      .19132      .19091      .041 228.000 227.387    .613
  .50808      .20553      .20499      .054 224.300 225.361  -1.061
  .71503      .29801      .29578      .223 189.500 192.264  -2.764
  .73922      .30962      .30706      .257 184.000 186.061  -2.061
  .77783      .34881      .34552      .329 175.300 176.741  -1.441
  .90793      .55143      .54234      .909 126.000 125.046    .954
  .98878      .89336      .87085     2.251  68.000  66.017   1.983
  .99617      .95787      .93239     2.547  59.200  57.464   1.736

    SUM OF SQUARES                              =      .42408655E-02
    STANDARD ERROR OF ESTIMATE                  =      .17404567E-01
    AVERAGE PRESSURE DEVIATION MM HG            =      .14325752E+01
    AVERAGE VAPOUR DEVIATION*100                =      .4182E+00
    NUMBER OF FUNCTION EVALUATIONS              =      380

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY    ACTIVITY
MOLE FRAC    CONSTANT     A          B       COEFF 1     COEFF 2
  .02254      8.3774   4.1950     1.0026     8.07178     1.00288
  .05821     20.5708   2.5703     1.0157     4.73567     1.01792
  .06609     20.8302   2.4516     1.0187     4.47483     1.02151
  .12853     23.9196   1.8336     1.0454     3.11452     1.05646
  .17554     24.4130   1.6194     1.0674     2.61306     1.08868
  .26028     23.5043   1.4234     1.1102     2.10682     1.15996
  .31166     24.6132   1.3088     1.1399     1.84539     1.21436
  .42495     24.2255   1.1869     1.2106     1.51930     1.36456
  .48465     23.8339   1.1477     1.2520     1.40414     1.46544
  .50808     22.8990   1.1519     1.2680     1.38610     1.50876
  .71503     22.9989   1.0558     1.4479     1.12852     2.07832
  .73922     23.4512   1.0400     1.4736     1.10024     2.17420
  .77783     22.3089   1.0541     1.5124     1.09875     2.33779
  .90793     20.9825   1.0631     1.6680     1.07117     3.09751
  .98878     22.4031   1.0286     1.7919     1.02873     3.81859
  .99617     23.4230   1.0082     1.8074     1.00826     3.90438
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SYSTEM ACETIC ACID - BENZENE AT 50 CENT
DATA OF MEEHAN


                    TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 -  608.68 WILSON PARAMETER 21 - -106.91

  LIQUID      VAPOUR      VAPOUR     DELTA   EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC  Y*100   PRESS    PRESS     MM HG
            EXPTL       CALC
  .10290     .05950     .05964     -.014 269.000 259.840   9.160
  .23460     .10890     .10915     -.025 252.500 251.407   1.093
  .36600     .14820     .14828     -.008 238.900 241.509  -2.609
  .51720     .19750     .19728      .022 225.800 227.393  -1.593
  .65100     .25740     .25653      .087 209.000 208.006    .994
  .76080     .33170     .32935      .235 182.400 181.191   1.209
  .85290     .43650     .43102      .548 144.800 145.209   -.409
  .93840     .63540     .62293     1.247  96.000  96.274   -.274

    SUM OF SQUARES                            -     .14300339E-02
    STANDARD ERROR OF ESTIMATE                -     .15438231E-01
    AVERAGE PRESSURE DEVIATION MM HG          -     .91785610E+00
    AVERAGE VAPOUR DEVIATION*100              -     .2733E+00
    NUMBER OF FUNCTION EVALUATIONS            -     268

  LIQUID  EQUILIBRIUM DELTA       DELTA      ACTIVITY    ACTIVITY
MOLE FRAC   CONSTANT    A           B        COEFF 1     COEFF 2
  .10290    23.6902   1.9951     1.0342     3.57448     1.04355
  .23460    24.8170   1.4427     1.0974     2.16980     1.14711
  .36600    24.6699   1.2353     1.1728     1.61978     1.29997
  .51720    23.4076   1.1335     1.2756     1.32004     1.55259
  .65100    22.1978   1.0928     1.3850     1.18142     1.87115
  .76080    22.1003   1.0610     1.4934     1.09997     2.23048
  .85290    23.2102   1.0210     1.6030     1.03487     2.63078
  .93840    25.0914    .9779     1.7239      .98020     3.11357
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SYSTEM ACETIC ACID - BENZENE AT 70 CENT
DATA ØF MEEHAN


                  THREE PARAMETER NRTL EQUATIØN

   NRTL PARAMETER 12 =  489.20 NRTL PARAMETER 21 =10476.10
                  NRTL PARAMETER ALPHA =      .34967

  LIQUID     VAPØUR     VAPØUR     DELTA  EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC   Y*100  PRESS    PRESS    MM HG
             EXPTL       CALC
  .10040    .05920    .05935    -.015 557.000 550.898  6.102
  .24010    .12750    .12783    -.033 530.100 530.235  -.135
  .36640    .17760    .17752     .008 501.000 505.729 -4.729
  .50680    .23140    .23048     .092 468.400 473.853 -5.453
  .65720    .29820    .29584     .236 432.200 429.250  2.950
  .73820    .35040    .34623     .417 397.200 393.299  3.901
  .86130    .49000    .47888    1.112 304.000 305.109 -1.109
  .94110    .68160    .65871    2.279 211.700 212.322  -.622

    SUM ØF SQUARES                           =     .50965639E-03
    STANDARD ERRØR ØF ESTIMATE               =     .10096102E-01
    AVERAGE PRESSURE DEVIATIØN MM HG         =     .92823430E+00
    AVERAGE VAPØUR DEVIATIØN*100             =     .5240E+00
    NUMBER ØF FUNCTIØN EVALUATIØNS           =    2755

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY  ACTIVITY
MØLE FRAC  CØNSTANT     A          B       CØEFF 1   CØEFF 2
  .10040   12.1119  2.0053    1.0277    3.29661   1.10260
  .24010   12.0178  1.4995    1.0878    2.15547   1.19896
  .36640   12.4824  1.2844    1.1559    1.67656   1.32869
  .50680   12.6975  1.1569    1.2462    1.37499   1.54099
  .65720   12.6075  1.0873    1.3631    1.18973   1.89246
  .73820   12.6338  1.0616    1.4375    1.12136   2.16536
  .86130   13.1353  1.0211    1.5730    1.03805   2.76404
  .94110   14.0051   .9864    1.6806     .98945   3.33679
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SYSTEM BENZENE - ACETIC ACID AT 758 MM,HG(ACETIC ACID COMPON
DATA OF OTHMER,IND,ENG,CHEM,JULY 1928,PG 745


                    THREE PARAMETER NRTL EQUATION

  NRTL PARAMETER 12 -  870,01 NRTL PARAMETER 21 - 2802,93
                   NRTL PARAMETER ALPHA -     ,85605

  LIQUID     VAPOUR     VAPOUR     DELTA  EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100  PRESS    PRESS     MM HG
            EXPTL      CALC
  ,02954    ,02267     ,02278    -,011 758,000 743,725 14,275
  ,07141    ,04105     ,04125    -,020 758,000 759,037 -1,037
  ,33611    ,13071     ,13098    -,027 758,000 762,434 -4,434
  ,52734    ,19574     ,19543     ,031 758,000 750,281  7,719
  ,73367    ,28407     ,28143     ,264 758,000 750,429  7,571
  ,87847    ,46921     ,45983     ,938 758,000 778,705-20,705
  ,95257    ,64520     ,62412    2,108 758,000 743,479 14,521
  ,98406    ,89990     ,86174    3,817 758,000 758,397  -,397

  . SUM OF SQUARES                          -     ,17076292E-02
    STANDARD ERROR OF ESTIMATE              -     ,18480417E-01
    AVERAGE PRESSURE DEVIATION MM HG        -     ,16653672E+01
    AVERAGE VAPOUR DEVIATION*100            -     ,9020E+00
    NUMBER OF FUNCTION EVALUATIONS          -    750

  LIQUID  EQUILIBRIUM DELTA     DELTA    ACTIVITY  ACTIVITY
MOLE FRAC  CONSTANT     A         B      COEFF 1   COEFF 2
 ,02954   106,1553   1,2447   1,0101   5,53059   1,04134
 ,07141    23,3254   1,5970   1,0213   3,42581   1,09011
 ,33611    16,0132   1,0358   1,1448   1,43413   1,32338
 ,52734    15,7393    ,8804   1,2693   1,10243   1,58938
 ,73367    14,5219    ,7973   1,4416    ,88964   2,22337
 ,87847     9,8036    ,8490   1,5686    ,87691   3,37151
 ,95257     7,9683    ,8509   1,6391    ,86593   4,67827
 ,98406     5,0392    ,9722   1,6226    ,97286   5,38364
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SYSTEM BENZENE - ACETIC ACID AT 760 MM HG(ACETIC ACID CØMPØN
DATA ØF GARNER,ELLIS & PEARCE


                    THREE PARAMETER NRTL EQUATIØN

   NRTL PARAMETER 12 -  487,64 NRTL PARAMETER 21 -  862,74
                    NRTL PARAMETER ALPHA -    1,31011

   LIQUID     VAPØUR     VAPØUR     DELTA  EXPTL    CALC    DELTA P
 MØLE FRAC MØLE FRAC MØLE FRAC  Y*100  PRESS    PRESS    MM HG
             EXPTL       CALC
   ,25000     ,14700     ,14732    -,032 760,000 757,383  2,617
   ,34700     ,18500     ,18540    -,040 760,000 763,246 -3,246
   ,45000     ,22500     ,22536    -,036 760,000 761,346 -1,346
   ,54200     ,27500     ,27528    -,028 760,000 760,836  -,836
   ,63000     ,31000     ,30996     ,004 760,000 752,230  7,770
   ,70700     ,37200     ,37134     ,066 760,000 762,743 -2,743
   ,78000     ,43800     ,43645     ,155 760,000 762,551 -2,551
   ,97000     ,84800     ,83649    1,161 760,000 758,477  1,523

     SUM ØF SQUARES                           -      ,16728583E-03
     STANDARD ERRØR ØF ESTIMATE               -      ,57842169E-02
     AVERAGE PRESSURE DEVIATIØN MM HG         -      ,55161835E+00
     AVERAGE VAPØUR DEVIATIØN*100             -      ,1890E+00
     NUMBER ØF FUNCTIØN EVALUATIØNS           -     1337

   LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
 MØLE FRAC   CØNSTANT    A          B       CØEFF 1    CØEFF 2
   ,25000     9,0496   1,4604    1,0869    2,15774    1,20789
   ,34700     8,6491   1,3251    1,1346    1,75647    1,31958
   ,45000     8,5655   1,2160    1,1934    1,49339    1,45962
   ,54200     7,9622   1,1739    1,2502    1,36855    1,60944
   ,63000     8,2382   1,0969    1,3167    1,22569    1,80003
   ,70700     7,5996   1,0768    1,3750    1,16381    2,00975
   ,78000     7,1119   1,0569    1,4363    1,11039    2,27789
   ,97000     4,6676   1,0343    1,5951    1,03562    3,58483
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SYSTEM ACETIC ACID - N-HEPTANE AT 20 DEG CENT
DATA ØF WERNER,JNL,FUR PRAK,CHEM,,NØ 4,VØL 29,PG 29,1965


                     TWØ PARAMETER WILSØN EQUATIØN

WILSØN PARAMETER 12 -  910,91 WILSØN PARAMETER 21 -  557,29

  LIQUID      VAPØUR      VAPØUR     DELTA   EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC   Y*100   PRESS    PRESS     MM HG
            EXPTL       CALC
  ,08400     ,18100     ,18086     ,014   38,400   38,065     ,336
  ,09400     ,20700     ,20683     ,017   38,700   38,576     ,124
  ,13500     ,24400     ,24386     ,014   39,400   39,153     ,247
  ,16300     ,25800     ,25788     ,012   39,800   39,341     ,459
  ,19400     ,28200     ,28189     ,011   40,100   39,762     ,338
  ,21400     ,28200     ,28192     ,008   40,300   39,694     ,606
  ,27900     ,30800     ,30793     ,007   40,900   40,191     ,709
  ,37300     ,33100     ,33095     ,005   41,100   40,599     ,501
  ,41900     ,34000     ,33995     ,005   41,100   40,793     ,307
  ,49900     ,35000     ,34994     ,006   41,000   41,058    -,058
  ,55800     ,34500     ,34497     ,003   41,200   41,109     ,091
  ,62600     ,35200     ,35195     ,005   41,200   41,422    -,222
  ,69600     ,34700     ,34697     ,003   41,200   41,407    -,207
  ,77800     ,35000     ,34995     ,005   41,000   41,197    -,197
  ,80900     ,35200     ,35191     ,009   40,600   40,792    -,192
  ,82500     ,36400     ,36390     ,010   40,500   40,780    -,280
  ,84500     ,36200     ,36186     ,014   40,300   40,219     ,081
  ,86600     ,38000     ,37978     ,022   39,700   39,751    -,051
  ,87500     ,37900     ,37874     ,026   39,300   39,209     ,091
  ,87900     ,38400     ,38365     ,035   38,600   38,880    -,280
  ,90600     ,39800     ,39749     ,051   36,900   36,894     ,006
  ,92800     ,43900     ,43818     ,082   35,500   35,146     ,354

     SUM ØF SQUARES                          -     ,13769277E-02
     STANDARD ERRØR ØF ESTIMATE              -     ,82973721E-02
     AVERAGE PRESSURE DEVIATIØN MM HG        -     ,66264783E+00
     AVERAGE VAPØUR DEVIATIØN*100            -     ,1643E-01
     NUMBER ØF FUNCTIØN EVALUATIØNS          -     252

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT    A           B       CØEFF 1    CØEFF 2
  ,08400     88,2186   1,9814    1,0336    6,88860    1,04309
  ,09400     80,2396   1,9707    1,0379    6,69393    1,04977
  ,13500     82,3898   1,6769    1,0581    5,19415    1,08307
  ,16300     84,4940   1,5342    1,0728    4,47402    1,10968
  ,19400     80,9289   1,4572    1,0891    3,98467    1,14239
  ,21400     83,7661   1,3789    1,1004    3,62200    1,16629
  ,27900     79,2018   1,2744    1,1379    2,95644    1,25601
  ,37300     74,3764   1,1776    1,1976    2,31899    1,43105
  ,41900     71,9775   1,1480    1,2293    2,09949    1,54207
  ,49900     69,0384   1,1056    1,2893    1,79313    1,79102
  ,55800     69,4754   1,0661    1,3386    1,59320    2,03838
  ,62500     67,0682   1,0510    1,3985    1.44051    2,41435
  ,69600     68,0672   1,0175    1,4700    1,28198    2,99079
  ,77800     68,0286    ,9958    1,5623    1,15013    4,06275
  ,80900     68,7151    ,9849    1,6008    1,10427    4,66698
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SYSTEM ACETIC ACID - N-HEPTANE AT 20 DEG CENT
DATA OF WERNER,JNL.FUR PRAK.CHEM.,NO 4,VOL 29,PG 29,1966


                      TWO PARAMETER WILSON EQUATION

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY    ACTIVITY
MOLE FRAC   CONSTANT     A          B       COEFF 1     COEFF 2
  .82500    66.1580    .9998     1.6198     1.10471     5.03939
  .84500    67.5257    .9871     1.6469     1.07192     5.59438
  .86600    64.9118   1.0026     1.6738     1.07030     6.29316
  .87500    66.2196    .9922     1.6872     1.05181     6.64727
  .87900    66.5386    .9895     1.6931     1.04580     6.81515
  .90600    67.8654    .9776     1.7331     1.01393     8.16695
  .92800    63.0279   1.0104     1.7630     1.03404     9.62847
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SYSTEM ACETIC ACID - N-HEPTANE AT 20 CENT
DATA OF MARKUZIN & PAVLOVA,RUSSIAN JNL.APPL.CHEM,1971,VOL 44


                     TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 -  893.15 WILSON PARAMETER 21 -  617.38

  LIQUID      VAPOUR      VAPOUR     DELTA   EXPTL     CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC  Y*100   PRESS     PRESS    MM HG
             EXPTL        CALC
  .08620     .18200      .18151      .049   38.400   38.043    .357
  .16800     .26200      .26126      .074   40.300   39.392    .908
  .22210     .29700      .29611      .069   40.700   39.904    .796
  .35430     .34700      .34585      .115   41.200   40.603    .597
  .38010     .35300      .35182      .118   41.200   40.672    .528
  .39310     .38800      .38655      .145   40.500   41.236   -.736
  .45940     .36700      .36575      .125   41.300   40.903    .397
  .60000     .38000      .37867      .133   40.900   41.073   -.173
  .61720     .38200      .38065      .135   40.900   41.135   -.235
  .71640     .38400      .38263      .137   40.800   41.188   -.388
  .86530     .39300      .39151      .149   39.500   39.515   -.015
  .92210     .42300      .42109      .191   35.800   35.702    .098
  .96300     .52400      .52091      .309   28.700   28.718   -.018

     SUM OF SQUARES                            -     .19228488E-02
     STANDARD ERROR OF ESTIMATE                -     .13221363E-01
     AVERAGE PRESSURE DEVIATION MM HG          -     .99786017E+00
     AVERAGE VAPOUR DEVIATION*100              -     .1360E+00
     NUMBER OF FUNCTION EVALUATIONS            -     222

  LIQUID  EQUILIBRIUM DELTA       DELTA      ACTIVITY    ACTIVITY
MOLE FRAC   CONSTANT     A           B        COEFF 1     COEFF 2
  .08620    76.7641   2.0818     1.0340     6.72949     1.04252
  .16800    75.1725   1.5971     1.0745     4.40781     1.10858
  .22210    73.0225   1.4461     1.1037     3.61926     1.16603
  .35430    67.8298   1.2516     1.1837     2.51626     1.36688
  .38010    67.0393   1.2272     1.2009     2.37105     1.41908
  .39310    66.2638   1.2738     1.2081     2.41317     1.44542
  .45940    64.5612   1.1709     1.2572     2.01350     1.61656
  .60000    62.2927   1.0995     1.3733     1.56831     2.18331
  .61720    61.7955   1.0954     1.3890     1.52976     2.28232
  .71640    61.4005   1.0612     1.4686     1.32061     3.08554
  .86530    63.3200   1.0144     1.6716     1.09091     6.14104
  .92210    66.0434    .9889     1.7562     1.01923     9.26932
  .96300    64.9238    .9947     1.8202     1.00298    13.84465
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SYSTEM ACETIC ACID - N-HEPTANE AT 30 CENT
DATA OF MARKUZIN & PAVLOVA,RUSSIAN JNL.APPL.CHEM,1971,VOL 44


                     THREE PARAMETER NRTL EQUATION

   NRTL PARAMETER 12 = 1241.54 NRTL PARAMETER 21 =   612.73
                     NRTL PARAMETER ALPHA =      .64406

   LIQUID      VAPOUR      VAPOUR     DELTA   EXPTL     CALC    DELTA P
 MOLE FRAC MOLE FRAC MOLE FRAC   Y*100   PRESS     PRESS    MM HG
              EXPTL       CALC
   .10000     .20800     .20722      .078   64.400    63.894    .506
   .15100     .26100     .25996      .104   66.100    65.638    .462
   .22030     .30800     .30671      .129   67.800    67.318    .482
   .24210     .32100     .31963      .137   68.200    67.796    .404
   .32460     .35200     .35041      .159   68.600    68.623   -.023
   .37050     .36400     .36232      .168   68.600    68.812   -.212
   .38160     .36600     .36430      .170   68.600    68.820   -.220
   .44890     .37800     .37620      .180   68.500    68.805   -.305
   .55000     .39200     .39004      .196   68.100    68.420   -.320
   .60000     .39200     .39004      .196   67.900    67.906   -.006
   .63500     .39300     .39102      .198   67.600    67.512    .088
   .70000     .40300     .40091      .209   67.100    67.107   -.007
   .80150     .41000     .40779      .221   66.100    65.947    .153
   .86760     .42300     .42058      .242   64.600    64.545    .055
   .92500     .45800     .45497      .303   60.100    60.158   -.058

     SUM OF SQUARES                              =      .26693435E-03
     STANDARD ERROR OF ESTIMATE                  =      .47164106E-02
     AVERAGE PRESSURE DEVIATION MM HG            =      .44671347E+00
     AVERAGE VAPOUR DEVIATION*100                =      .1792E+00
     NUMBER OF FUNCTION EVALUATIONS              =    1025

  LIQUID   EQUILIBRIUM DELTA       DELTA      ACTIVITY   ACTIVITY
 MOLE FRAC   CONSTANT     A          B        COEFF 1    COEFF 2
  .10000     61.1155   1.8336     1.0393     6.12368    1.05826
  .15100     54.5322   1.6311     1.0632     4.72098    1.10504
  .22030     48.5647   1.4783     1.0985     3.63467    1.18473
  .24210     46.8116   1.4489     1.1101     3.40497    1.21367
  .32460     43.9765   1.3353     1.1580     2.70066    1.34316
  .37050     43.1910   1.2843     1.1870     2.41735    1.43055
  .38160     43.1323   1.2720     1.1943     2.35531    1.45366
  .44890     42.7366   1.2098     1.2410     2.04263    1.61272
  .55000     42.6663   1.1381     1.3196     1.70147    1.93672
  .60000     43.5718   1.1007     1.3633     1.55726    2.15614
  .63500     44.1122   1.0788     1.3968     1.47038    2.34472
  .70000     43.6590   1.0599     1.4595     1.35052    2.80855
  .80150     44.1946   1.0280     1.5737     1.18329    4.13375
  .86760     44.0380   1.0191     1.6582     1.10216    5.98689
  .92500     43.7929   1.0160     1.7396     1.04866    9.47658
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SYSTEM ACETIC ACID - N-HEPTANE AT 40 CENT
DATA OF MARKUZIN & PAVLOVA,RUSSIAN JNL.APPL.CHEM.,1971,VOL 4
4

                      THREE PARAMETER NRTL EQUATION

  NRTL PARAMETER 12 - 1219.41 NRTL PARAMETER 21 -  577.25
                    NRTL PARAMETER ALPHA -      .64905

  LIQUID     VAPOUR     VAPOUR     DELTA   EXPTL     CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100   PRESS     PRESS    MM HG
           EXPTL       CALC
  .01730     .06100     .06041     .059  94.800   94.513     .287
  .15000     .27100     .26801     .299 105.100  104.149     .951
  .24820     .34200     .33766     .434 107.700  107.619     .081
  .30410     .35600     .35140     .460 108.300  107.954     .346
  .36320     .38200     .37677     .523 108.700  108.985    -.285
  .40490     .38900     .38360     .540 108.700  108.910    -.210
  .49860     .40300     .39717     .583 108.100  108.346    -.246
  .52720     .40500     .39905     .595 107.700  107.920    -.220
  .62540     .42100     .41450     .650 107.000  107.203    -.203
  .70810     .42100     .41442     .658 105.800  105.429     .371
  .78990     .42900     .42197     .703 104.000  103.647     .353
  .83010     .43800     .43051     .749 102.100  102.264    -.164
  .89420     .45900     .46029     .871  97.300   97.478    -.178
  .97430     .64500     .62437    2.063  67.600   67.552     .048

    SUM OF SQUARES                           -      .15567190E-03
    STANDARD ERROR OF ESTIMATE               -      .37619132E-02
    AVERAGE PRESSURE DEVIATION MM HG         -      .40383580E+00
    AVERAGE VAPOUR DEVIATION*100             -      .6562E+00
    NUMBER OF FUNCTION EVALUATIONS           -      443

  LIQUID   EQUILIBRIUM DELTA      DELTA    ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT     A          B      COEFF 1    COEFF 2
  .01730    31.2987   3.7654    1.0034   15.49442    1.00398
  .15000    36.2025   1.6757    1.0592    4.69043    1.09643
  .24820    31.7978   1.4617    1.1084    3.32289    1.20780
  .30410    31.9196   1.3545    1.1402    2.79095    1.28998
  .36320    30.2128   1.3036    1.1754    2.44975    1.39237
  .40490    30.3000   1.2560    1.2026    2.22341    1.47799
  .49860    30.5360   1.1710    1.2695    1.84183    1.72117
  .52720    30.8668   1.1464    1.2919    1.74383    1.81436
  .62540    30.5479   1.1002    1.3744    1.50220    2.23722
  .70810    31.7064   1.0518    1.4553    1.31858    2.81342
  .78990    32.1064   1.0251    1.5451    1.18534    3.81161
  .83010    32.1747   1.0168    1.5935    1.13189    4.62414
  .89420    32.6264   1.0021    1.6783    1.05536    6.92245
  .97430    32.3591   1.0010    1.7969    1.00525   15.12950
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SYSTEM ACETIC ACID-ETHYLBENZENE DATA OF HAGGA AND RAJU
JNL CHEM ENG DATA,VOL 15,NO 4,1970,P 531


                    THREE PARAMETER NRTL EQUATION

  NRTL PARAMETER 12 =  815.98 NRTL PARAMETER 21 = 8262.17
                    NRTL PARAMETER ALPHA =      .36241

  LIQUID     VAPOUR     VAPOUR     DELTA   EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100   PRESS    PRESS    MM HG
            EXPTL       CALC
  .05000     .17500     .17297      .203 725.000 724.716     .284
  .06000     .20000     .19767      .233 725.000 724.545     .455
  .07500     .22500     .22243      .257 725.000 723.872   1.128
  .09000     .27000     .26709      .291 725.000 715.704   9.296
  .14500     .35500     .35108      .392 725.000 723.600   1.400
  .17500     .38500     .38082      .418 725.000 720.168   4.832
  .29000     .50500     .49951      .549 725.000 723.045   1.955
  .55000     .69500     .68703      .797 725.000 740.797-15.797
  .72000     .76500     .75584      .916 725.000 738.359-13.359
  .82000     .80500     .79468     1.032 725.000 729.321  -4.321
  .90700     .87000     .85737     1.263 725.000 721.934   3.066
  .96000     .92000     .90522     1.478 725.000 707.821  17.179
  .98000     .95000     .93366     1.634 725.000 704.907  20.093

    SUM OF SQUARES                              =     .24200521E-02
    STANDARD ERROR OF ESTIMATE                  =     .15556517E-01
    AVERAGE PRESSURE DEVIATION MM HG            =     .11247857E+01
    AVERAGE VAPOUR DEVIATION*100                =     .7280E+00
    NUMBER OF FUNCTION EVALUATIONS              =    1379

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT     A          B       COEFF 1    COEFF 2
  .05000    64.2904    .8136     1.0172    4.14757    1.14384
  .06000    33.3083    .9885     1.0187    3.92190    1.16144
  .07500    19.1927   1.1264     1.0216    3.51153    1.18409
  .09000    10.6354   1.3180     1.0229    3.50939    1.20033
  .14500     6.3258   1.3697     1.0370    2.78807    1.25681
  .17500     6.0193   1.3265     1.0473    2.50583    1.28605
  .29000     5.0832   1.2384     1.0912    1.97146    1.40500
  .55000     4.1269   1.1623     1.2201    1.44616    1.87484
  .72000     4.1519   1.1081     1.3392    1.22048    2.54945
  .82000     4.3361   1.0683     1.4285    1.11565    3.25352
  .90700     4.3361   1.0515     1.5146    1.06471    4.19874
  .96000     4.3706   1.0370     1.5745    1.03950    5.02535
  .98000     4.3548   1.0296     1.5976    1.03024    5.39973
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      SYSTEM ACETIC ACID-P-XYLENE  DATA OF BAGGA AND RAJU
        JNL CHEM ENG DATA,VOL 15,NO 4,1970, P 531


                      THREE PARAMETER NRTL EQUATION

     NRTL PARAMETER 12 -  382.44 NRTL PARAMETER 21 -*********
                      NRTL PARAMETER ALPHA -      .02449

     LIQUID     VAPOUR     VAPOUR     DELTA  EXPTL    CALC    DELTA P
   MOLE FRAC MOLE FRAC MOLE FRAC   Y*100  PRESS    PRESS    MM HG
               EXPTL       CALC
     .00400     .00800     .00800    -.000 725.000 416.233308.767
     .04500     .07000     .07013    -.013 725.000 705.018 19.982
     .07500     .10500     .10538    -.038 725.000 730.301  -5.301
     .13000     .14500     .14581    -.081 725.000 734.766  -9.766
     .16300     .16600     .16710    -.110 725.000 733.968  -8.968
     .25500     .21500     .21690    -.190 725.000 736.124-11.124
     .49000     .28000     .28326    -.326 725.000 706.562 18.438
     .64000     .35500     .36021    -.521 725.000 694.812 30.188
     .68000     .41500     .42203    -.703 725.000 723.414  1.586
     .76000     .48000     .48922    -.922 725.000 721.510  3.490
     .81500     .56000     .57224   -1.224 725.000 739.145-14.145
     .89000     .68000     .69759   -1.759 725.000 734.002 -9.002
     .99000     .84000     .86503   -2.503 725.000 656.193 68.807

      SUM OF SQUARES                              -     .19471223E+00
      STANDARD ERROR OF ESTIMATE                  -     .13953933E+00
      AVERAGE PRESSURE DEVIATION MM HG            -     .75283011E+01
      AVERAGE VAPOUR DEVIATION*100                -     .6455E+00
      NUMBER OF FUNCTION EVALUATIONS              -    2946

     LIQUID   EQUILIBRIUM DELTA      DELTA      ACTIVITY    ACTIVITY
   MOLE FRAC    CONSTANT    A          B         COEFF 1     COEFF 2
     .00400   *********   .0000     1.0020     4.87358     1.25692
     .04500    265.4966   .5071     1.0187     3.01193     2.17200
     .07500     30.7151  1.0240     1.0243     2.50710     2.29287
     .13000     14.7623  1.1147     1.0413     1.86847     2.41303
     .16300     13.2621  1.0749     1.0540     1.65346     2.47371
     .25500     12.5687   .9405     1.0960     1.27251     2.66130
     .49000     15.8072   .6885     1.2425      .78612     3.35879
     .64000     14.9624   .6496     1.3570      .69343     4.06103
     .68000     12.9070   .6750     1.3844      .71058     4.31845
     .76000     12.3823   .6625     1.4578      .68181     4.91434
     .81500     11.2211   .6707     1.5082      .68222     5.44165
     .89000      9.8690   .6858     1.5829      .68992     6.26913
     .99000      9.6297   .6579     1.7111      .65789     7.93544
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SYSTEM ACETIC ACID P-XYLENE AT 760 MM,HG,
DATA OF OTHMER(QUOTED  BY MAREK)


                    THREE PARAMETER NRTL EQUATION

   NRTL PARAMETER 12 -  751,01 NRTL PARAMETER 21 -  497,25
                  NRTL PARAMETER ALPHA -      ,87566

  LIQUID     VAPOUR     VAPOUR     DELTA   EXPTL     CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100   PRESS     PRESS    MM HG
            EXPTL      CALC
  ,10000    ,42100     ,41430      ,670 760,000 779,246-19,246
  ,20000    ,52500     ,51914      ,586 760,000 753,648  6,352
  ,30000    ,60500     ,60058      ,442 760,000 753,065  6,935
  ,40000    ,66400     ,66095      ,305 760,000 759,940   ,060
  ,50000    ,70100     ,69907      ,193 760,000 760,161  -,161
  ,60000    ,73200     ,73102      ,098 760,000 760,878  -,878
  ,70000    ,76400     ,76406     -,006 760,000 759,702   ,298
  ,80000    ,80700     ,80836     -,136 760,000 761,062 -1,062
  ,85000    ,83200     ,83405     -,205 760,000 760,441  -,441
  ,90000    ,86500     ,86798     -,298 760,000 758,635  1,365
  ,95000    ,91600     ,92023     -,423 760,000 759,823   ,177

    SUM OF SQUARES                           -     ,80150950E-03
    STANDARD ERROR OF ESTIMATE               -     ,10009430E-01
    AVERAGE PRESSURE DEVIATION MM HG         -     ,55911646E+00
    AVERAGE VAPOUR DEVIATION*100             -     ,3055E+00
    NUMBER OF FUNCTION EVALUATIONS           -   3132

  LIQUID   EQUILIBRIUM DELTA       DELTA      ACTIVITY    ACTIVITY
MOLE FRAC   CONSTANT     A           B        COEFF 1     COEFF 2
  ,10000      2,5865  1,8053     1,0140      4,07425     1,02556
  ,20000      4,0799  1,4098     1,0498      2,68283     1,09528
  ,30000      4,1162  1,2871     1,0897      2,12918     1,19242
  ,40000      4,0808  1,2106     1,1359      1,78220     1,32469
  ,50000      4,1764  1,1460     1,1908      1,52838     1,50689
  ,60000      4,3065  1,0928     1,2548      1,33839     1,76367
  ,70000      4,3787  1,0598     1,3279      1,20558     2,14353
  ,80000      4,3688  1,0427     1,4111      1,11457     2,75122
  ,85000      4,3920  1,0326     1,4583      1,07569     3,21134
  ,90000      4,3631  1,0294     1,5080      1,05014     3,84648
  ,95000      4,2769  1,0277     1,5601      1,03335     4,75552
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SYSTEM ACETIC ACID - N-ØCTANE AT CØNST.PRESS.760 MM HG
DATA ØF SCHICKTANZ,J.RES.BUR.STAND,VØL 18,PG 123,(1937)


                 THREE PARAMETER NRTL EQUATIØN

  NRTL PARAMETER 12 = 1450.33 NRTL PARAMETER 21 =   964.20
                 NRTL PARAMETER ALPHA =      .62439

  LIQUID      VAPØUR      VAPØUR     DELTA   EXPTL     CALC    DELTA P
MØLE FRAC  MØLE FRAC  MØLE FRAC    Y*100   PRESS     PRESS    MM HG
             EXPTL        CALC
  .05000     .17800     .17434       .366 760.000 744.059  15.941
  .10000     .31700     .31044       .666 760.000 750.723   9.277
  .20000     .48200     .47163      1.037 760.000 758.119   1.881
  .30000     .56200     .54999      1.201 760.000 760.133   -.133
  .40000     .62100     .60781      1.319 760.000 763.770  -3.770
  .50000     .65800     .64414      1.386 760.000 764.949  -4.949
  .60000     .67300     .65884      1.416 760.000 763.117  -3.117
  .70000     .67900     .66461      1.439 760.000 759.819    .181
  .80000     .68600     .67123      1.477 760.000 756.253   3.747
  .90000     .72700     .70984      1.716 760.000 758.817   1.183
  .95000     .79480     .77254      2.226 760.000 761.669  -1.669

     SUM ØF SQUARES                           =     .71054557E-03
     STANDARD ERRØR ØF ESTIMATE               =     .94243406E-02
     AVERAGE PRESSURE DEVIATIØN MM HG         =     .66907140E+00
     AVERAGE VAPØUR DEVIATIØN*100             =     .1294E+01
     NUMBER ØF FUNCTIØN EVALUATIØNS           =   1194

  LIQUID   EQUILIBRIUM DELTA       DELTA       ACTIVITY    ACTIVITY
MØLE FRAC   CØNSTANT     A           B         CØEFF 1     CØEFF 2
  .05000     36.8839   1.0533     1.0152     4.99282     1.02176
  .10000     19.4600   1.0716     1.0315     4.13077     1.05619
  .20000     10.2476   1.1169     1.0664     3.11428     1.15695
  .30000      7.5793   1.1261     1.1067     2.47789     1.30008
  .40000      6.1220   1.1430     1.1516     2.10141     1.49134
  .50000      5.4670   1.1386     1.2044     1.81323     1.75551
  .60000      5.3681   1.1032     1.2687     1.55495     2.14851
  .70000      5.4493   1.0637     1.3449     1.34365     2.79602
  .80000      5.5164   1.0353     1.4332     1.18206     4.05108
  .90000      5.2495   1.0344     1.5295     1.08200     7.19155
  .95000      4.9116   1.0331     1.5780     1.04696    10.92700
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SYSTEM ACETIC ACID - N-ØCTANE AT 760 MM HG
DATA ØF ZIEBØRAK & BRZØWNITØWSKI,BULL.ACID.PØL.SCI.,VØL 6,NØ
3,1958,PG 169

                    THREE PARAMETER NRTL EQUATIØN

   NRTL PARAMETER 12 - 1548.16 NRTL PARAMETER 21 - 1040.07
                    NRTL PARAMETER ALPHA -      .67164

  LIQUID      VAPØUR      VAPØUR     DELTA   EXPTL     CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC  Y*100   PRESS     PRESS     MM HG
             EXPTL       CALC
  .03900     .23000     .22518      .482 760.000 741.608 18.392
  .13600     .45400     .44429      .971 760.000 755.366  4.634
  .26500     .57100     .55865     1.235 760.000 762.902 -2.902
  .42000     .63500     .62128     1.372 760.000 765.445 -5.445
  .59500     .67000     .66120     1.480 760.000 762.146 -2.146
  .68700     .68700     .67176     1.524 760.000 757.405  2.596
  .77400     .70400     .68785     1.615 760.000 758.052  1.948
  .83800     .71800     .70105     1.695 760.000 758.612  1.388
  .87500     .73200     .71417     1.783 760.000 760.931  -.931
  .95400     .80800     .78442     2.358 760.000 764.584 -4.584
  .98100     .89000     .85967     3.033 760.000 755.037  4.963

     SUM ØF SQUARES                          -     .29678560E-03
     STANDARD ERRØR ØF ESTIMATE              -     .99924071E-02
     AVERAGE PRESSURE DEVIATIØN MM HG        -     .76802082E+00
     AVERAGE VAPØUR DEVIATIØN*100            -     .1595E+01
     NUMBER ØF FUNCTIØN EVALUATIØNS          -   1258

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT    A           B       CØEFF 1    CØEFF 2
  .03900     13.9194  1.5980     1.0028     8.03886    1.01253
  .13600      8.9652  1.3234     1.0380     4.31012    1.08706
  .26500      6.2287  1.2614     1.0853     2.84274    1.24521
  .42000      5.4109  1.1841     1.1578     2.03660    1.52718
  .59500      5.3285  1.1023     1.2648     1.54521    2.06177
  .68700      5.4597  1.0611     1.3347     1.35817    2.56190
  .77400      5.4498  1.0387     1.4081     1.22383    3.39155
  .83800      5.4063  1.0287     1.4680     1.14204    4.53695
  .87500      5.3276  1.0267     1.5043     1.10293    5.65970
  .95400      4.9610  1.0224     1.5840     1.03643   11.29286
  .98100      4.5323  1.0293     1.6044     1.03201   15.71612
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SYSTEM ACETIC ACID-N-DECANE AT 760 MM HG
DATA ØF ZIEBØRAK & BRZØSTØWSKI,BULL.ACAD.PØL.SER.SCI.CHI.,19
57,5,309

                    TWØ PARAMETER WILSØN EQUATIØN

WILSØN PARAMETER 12 = 1567.50 WILSØN PARAMETER 21 = 1809.50

  LIQUID     VAPØUR      VAPØUR     DELTA   EXPTL     CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC   Y*100   PRESS     PRESS    MM HG
            EXPTL       CALC
  .69000    .91300     .87766     3.534 760.000 751.108  8.892
  .76200    .91500     .87957     3.543 760.000 753.563  6.437
  .82100    .91300     .87780     3.520 760.000 753.746  6.254
  .89700    .92700     .89065     3.635 760.000 762.868 -2.868
  .91700    .92900     .89248     3.652 760.000 763.859 -3.859
  .91900    .93000     .89338     3.662 760.000 764.404 -4.404
  .96900    .94900     .91054     3.846 760.000 767.015 -7.015
  .97500    .95500     .91589     3.911 760.000 766.936 -6.936
  .98800    .96900     .92828     4.072 760.000 758.488  1.512
  .99400    .98200     .93953     4.247 760.000 749.296 10.704

     SUM ØF SQUARES                           =     .72075156E-03
     STANDARD ERRØR ØF ESTIMATE               =     .94917830E-02
     AVERAGE PRESSURE DEVIATIØN MM HG         =     .77474518E+00
     AVERAGE VAPØUR DEVIATIØN*100             =     .3762E+01
     NUMBER ØF FUNCTIØN EVALUATIØNS           =     318

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT     A          H       CØEFF 1    CØEFF 2
  .69000      4.8673   1.0115    1.3284    1.40476    2.98665
  .76200      4.7074   1.0095    1.3846    1.27948    3.97319
  .82100      4.6585   1.0042    1.4367    1.18687    5.38549
  .89700      4.4152   1.0189    1.5062    1.10808    9.49618
  .91700      4.3929   1.0195    1.5269    1.08635   11.75355
  .91900      4.3818   1.0203    1.5288    1.08509   12.03358
  .96900      4.2198   1.0332    1.5802    1.04981   28.06087
  .97500      4.1805   1.0360    1.5860    1.04793   32.92231
  .98800      4.1176   1.0392    1.5993    1.04278   51.27769
  .99400      4.0935   1.0360    1.6057    1.03700   67.21257
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SYSTEM ACETIC ACID - TRICHLOROETHYLENE AT 250 MM.HG.
DATA OF FRANCESCONI,R., & CONJUTTI,A.,CHEM.ENG.SCI.,1971,VOL
 26,PP 1341-1356

                   THREE PARAMETER NRTL EQUATION

  NRTL PARAMETER 12 -  402,29 NRTL PARAMETER 21 -  504,88
                   NRTL PARAMETER ALPHA -    1,46790

  LIQUID      VAPOUR     VAPOUR    DELTA  EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC  Y*100  PRESS    PRESS    MM HG
             EXPTL       CALC
  ,15400     .09100     .09203    -.103 250.000 245.144  4.856
  ,22900     .13700     .13853    -,153 250,000 250,714  -,714
  .29100     .16800     .16996    -,196 250,000 251,634 -1,634
  ,44300     ,22700     ,22980    -,280 250,000 251,441 -1,441
  ,77700     ,42800     ,43332    -.532 250,000 249.513   ,487
  .83000     ,49500     .50112    -,612 250,000 250.135  -,135
  ,91300     ,63700     ,64445    -,745 250,000 247,722  2,278
  ,94300     ,72700     ,73512    -,812 250,000 249,261   ,739
  .96100     .80900     ,81774    -,874 250,000 253,724 -3,724

    SUM OF SQUARES                          -     ,77909306E-03
    STANDARD ERROR OF ESTIMATE              -     .11395124E-01
    AVERAGE PRESSURE DEVIATION MM HG        -     .87937972E+00
    AVERAGE VAPOUR DEVIATION*100            -     ,4785E+00
    NUMBER OF FUNCTION EVALUATIONS          -     750

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT    A          B       COEFF 1    COEFF 2
  ,15400    25,5985   1,5941    1,0577    2,71414    1,09610
  ,22900    19,5237   1,5258    1,0908    2,29391    1,16366
  ,29100    17,7246   1,4537    1,1218    2,02730    1,22850
  ,44300    17,1684   1,2634    1,2130    1,55352    1,42714
  .77700    14,7770   1,0792    1,4869    1,13172    2,25815
  .83000    13,6129   1,0773    1,5393    1,11032    2,60587
  ,91300    11,8821   1,0607    1,6284    1,07046    3,04693
  ,94300    10,8290   1,0586    1,6688    1,06297    3,29847
  .96100     9,8622   1,0646    1,6734    1,06669    3,46918
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SYSTEM ACETIC ACID - TRICHLOROETHYLENE AT 350 MM.HG.
DATA OF FRANCESCONI,R. & CONJUTTI,A.,CHEM.ENG.SCI.,1971,VOL
26,PP 1341-1356

                    THREE PARAMETER NRTL EQUATION

  NRTL PARAMETER 12 -  470,59 NRTL PARAMETER 21 -  592,76
                    NRTL PARAMETER ALPHA -    1,47485

  LIQUID     VAPOUR     VAPOUR     DELTA  EXPTL    CALC   DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC  Y*100  PRESS    PRESS    MM HG
           EXPTL      CALC
 ,22400    ,14200     .14395     -,195 350,000 349,928     ,072
 ,43700    ,22900     ,23210     -,310 350,000 349,340     ,660
 ,53400    ,27800     ,28184     -,384 350,000 351,064  -1,064
 ,62800    ,32200     ,32646     -,446 350,000 346,958   3,042
 ,71000    ,39500     ,40033     -,533 350,000 356,540  -6,540
 ,80900    ,45900     ,46492     -,592 350.000 345.114   4,886
 ,87800    ,57700     ,58434     -,734 350,000 350,485   -,485
 ,91000    ,63800     ,64584     -,784 350.000 348.831   1,169
 ,94200    ,73400     ,74259     -,859 350.000 352.142  -2,142

   SUM OF SQUARES                          -      ,68292654E-03
   STANDARD ERROR OF ESTIMATE              -      ,10668697E-01
   AVERAGE PRESSURE DEVIATION MM HG        -      ,78691207E+00
   AVERAGE VAPOUR DEVIATION*100            -      ,5375E+00
   NUMBER OF FUNCTION EVALUATIONS          -      681

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MOLE FRAC  CONSTANT     A          B       COEFF 1    COEFF 2
 ,22400     14,9525  1,5282    1,0839    2,30879    1,16263
 ,43700     13,8791  1,2397    1,2023    1,53331    1,41731
 ,53400     13,3120  1,1715    1,2676    1,37223    1,57251
 ,62800     13,2701  1,1077    1,3409    1,24139    1,76868
 ,71000     12,0441  1,0888    1,4076    1,17862    1,99107
 ,80900     12,0522  1,0319    1,6070    1,07597    2,39851
 ,87800     10,2226  1,0488    1,5718    1,06990    2,81061
 ,91000      9,6331  1,0449    1,6050    1,05715    3,06993
 ,94200      8,6341  1,0510    1.6342    1,05652    3,37633
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SYSTEM ACETIC ACID - TRICHLOROETHYLENE AT 500 MM.HG.
DATA OF FRANCESCONI,R. & CONJUTTI,A.,CHEM.ENG.SCI.,1971,VOL
26,PP 1341-1356

                THREE PARAMETER NRTL EQUATION

   NRTL PARAMETER 12 -  426,37 NRTL PARAMETER 21 -  682,90
                NRTL PARAMETER ALPHA -    1,31911

  LIQUID     VAPOUR     VAPOUR     DELTA  EXPTL    CALC   DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100  PRESS    PRESS    MM HG
            EXPTL      CALC
  ,25700    ,17700     ,18001    -,301 500,000 496,758  3,242
  ,30700    ,20500     ,20846    -,346 500,000 501,425 -1,425
  ,37300    ,23000     ,23399    -,399 500,000 501,122 -1,122
  ,57100    ,32000     ,32585    -,585 500,000 502,490 -2,490
  ,67800    ,38500     ,39216    -,716 500,000 499,722   ,278
  ,77400    ,45200     ,46004    -,804 500,000 496,210  3,790
  ,83200    ,51700     ,52538    -,838 500,000 501,181 -1,181
  ,90500    ,64900     ,65902   -1,002 500,000 500,935  -,935

    SUM OF SQUARES                        -      ,14684536E-03
    STANDARD ERROR OF ESTIMATE            -      ,54193240E-02
    AVERAGE PRESSURE DEVIATION MM HG      -      ,52563047E+00
    AVERAGE VAPOUR DEVIATION*100          -      ,6239E+00
    NUMBER OF FUNCTION EVALUATIONS        -      876

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT    A          B       COEFF 1    COEFF 2
  ,25700    10,2637  1,5064    1,0929     2,23983    1,20229
  ,30700     9,4995  1,4587    1,1160     2,03665    1,25832
  ,37300     9,5032  1,3659    1,1516     1,78633    1,34267
  ,57100     9,2408  1,1935    1,2782     1,36780    1,67423
  ,67800     8,8105  1,1471    1,3600     1,24948    1,93773
  ,77400     8,6818  1,0917    1,4464     1,14500    2,27631
  ,83200     8,3778  1,0589    1,5026     1,08966    2,55107
  ,90500     7,2299  1,0623    1,5700     1,07324    3,00019
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SYSTEM ACETIC ACID - TRICHLOROETHYLENE AT 650 MM.HG
DATA OF FRANCESCONI,R.,& CONJUTTI,A.,CHEM.ENG.SCI.,1971,VOL
26,PP 1341-1356

                    THREE PARAMETER NRTL EQUATION

  NRTL PARAMETER 12 -  521.03 NRTL PARAMETER 21 -  658.76
                 NRTL PARAMETER ALPHA -    1.43158

  LIQUID     VAPOUR     VAPOUR    DELTA  EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC  Y*100  PRESS    PRESS    MM HG
            EXPTL      CALC
  .21600    .15300    .15601   -.301 650.000 646.079  3.921
  .27000    .18000    .18350   -.350 650.000 652.164 -2.164
  .49000    .28000    .28598   -.598 650.000 653.042 -3.042
  .81100    .50400    .51499 -1.099 650.000 645.262  4.738
  .86000    .57400    .58626 -1.226 650.000 649.758   .242
  .89900    .65200    .66583 -1.383 650.000 655.317 -5.317
  .92900    .71400    .72868 -1.468 650.000 651.454 -1.454
  .94500    .75200    .76741 -1.541 650.000 646.156  3.844

   SUM OF SQUARES            ,                -    .22954216E-03
   STANDARD ERROR OF ESTIMATE                 -    .67755761E-02
   AVERAGE PRESSURE DEVIATION MM HG           -    .67769994E+00
   AVERAGE VAPOUR DEVIATION*100               -    .9956E+00
   NUMBER OF FUNCTION EVALUATIONS             -    674

  LIQUID  EQUILIBRIUM DELTA     DELTA    ACTIVITY  ACTIVITY
MOLE FRAC  CONSTANT    A         B       COEFF 1   COEFF 2
  .21600    9.2756   1.5096   1.0718   2.33485   1.14943
  .27000    8.8004   1.4247   1.0958   2.04731   1.20304
  .49000    8.3403   1.1904   1.2175   1.43543   1.48334
  .81100    7.0427   1.0636   1.4658   1.11066   2.37387
  .86000    6.5041   1.0631   1.5090   1.09174   2.65655
  .89900    5.8758   1.0754   1.5409   1.09187   2.94194
  .92900    6.5468   1.0730   1.5686   1.08176   3.22188
  .94500    5.3245   1.0769   1.5823   1.08232   3.39504
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SYSTEM ACETIC ACID - TRICHLOROETHYLENE AT 750 MM HG
DATA OF FRANCESCONI,R.,& COJUTTI,A.,CHEM.ENG.SCI,1971,VOL 26
,PP 1341-1356

                    THREE PARAMETER NRTL EQUATION

   NRTL PARAMETER 12 -  290.69 NRTL PARAMETER 21 - 2036.26
                    NRTL PARAMETER ALPHA -     .89330

  LIQUID     VAPOUR     VAPOUR    DELTA  EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC  Y*100  PRESS    PRESS    MM HG
            EXPTL      CALC
  .18500    .13800    .14105    -.305 750.000 748.119  1.881
  .21800    .15800    .16158    -.358 750.000 750.543  -.543
  .36000    .22900    .23576    -.676 750.000 754.685 -4.685
  .45300    .26800    .27685    -.885 750.000 748.846  1.154
  .51900    .30600    .31715   -1.115 750.000 749.941   .059
  .57900    .34000    .35326   -1.326 750.000 752.036 -2.036
  .64100    .37700    .39288   -1.588 750.000 746.893  3.107
  .78400    .48900    .51328   -2.428 750.000 745.217  4.783
  .91200    .70000    .74721   -4.721 750.000 755.812 -5.812

    SUM OF SQUARES                         -    .17345605E-03
    STANDARD ERROR OF ESTIMATE             -    .53767409E-02
    AVERAGE PRESSURE DEVIATION MM HG       -    .59860885E+00
    AVERAGE VAPOUR DEVIATION*100           -    .1489E+01
    NUMBER OF FUNCTION EVALUATIONS         -    585

  LIQUID  EQUILIBRIUM DELTA      DELTA    ACTIVITY  ACTIVITY
MOLE FRAC   CONSTANT    A          B       COEFF 1   COEFF 2
  .18500     6.8543  1.6890    1.0533    2.51576   1.20073
  .21800     6.1985  1.6611    1.0649    2.32355   1.23329
  .36000     5.7838  1.4510    1.1286    1.75264   1.38478
  .45300     6.0662  1.3243    1.1811    1.51590   1.50389
  .51900     5.9513  1.2748    1.2205    1.41613   1.59929
  .57900     5.9845  1.2231    1.2606    1.32733   1.70042
  .64100     5.9797  1.1825    1.3054    1.25665   1.82028
  .78400     5.9592  1.0855    1.4251    1.11125   2.18388
  .91200     4.7734  1.0857    1.5315    1.09019   2.61838
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SYSTEM ACETIC ACID - METHYLENE CHLØRIDE AT 760 MM HG
DATA ØF DØBRØSERDØV & SHAKHANØV,ZHUR.PRIKL.KHIM,44(2),PP 445
-447 -1971

                 THREE PARAMETER NRTL EQUATIØN

  NRTL PARAMETER 12 =    69.76 NRTL PARAMETER 21 =  469.94
                 NRTL PARAMETER ALPHA =    3.23560

  LIQUID     VAPØUR     VAPØUR     DELTA   EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC   Y*100   PRESS    PRESS    MM HG
            EXPTL      CALC
  .07650    .00630     .00619      .011 760.000 758.104   1.896
  .10100    .00820     .00806      .014 760.000 757.063   2.937
  .21900    .01770     .01741      .029 760.000 761.814  -1.814
  .27600    .02290     .02253      .037 760.000 763.206  -3.206
  .38100    .03480     .03426      .055 760.000 763.780  -3.780
  .50900    .05660     .05578      .082 760.000 757.623   2.377
  .58200    .07530     .07427      .103 760.000 757.441   2.559
  .66500    .11350     .11218      .132 760.000 766.301  -6.301
  .78400    .19430     .19283      .147 760.000 744.447  15.553
  .86490    .31900     .31815      .085 760.000 764.148  -4.148
  .91690    .47200     .47348     -.148 760.000 766.761  -6.761

    SUM ØF SQUARES                              =     .68695225E-03
    STANDARD ERRØR ØF ESTIMATE                  =     .92665544E-02
    AVERAGE PRESSURE DEVIATIØN MM HG            =     .70171189E+00
    AVERAGE VAPØUR DEVIATIØN*100                =     .7663E-01
    NUMBER ØF FUNCTIØN EVALUATIØNS              =    2303

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT     A          B       CØEFF 1    CØEFF 2
  .07650    29.9195   2.3086    1.0248    3.01889    1.04124
  .10100    27.1057   2.1555    1.0344    2.66303    1.05679
  .21900    23.8552   1.6511    1.0887    1.82043    1.13465
  .27600    23.4642   1.5030    1.1188    1.62053    1.17468
  .38100    22.4185   1.3226    1.1800    1.39030    1.25452
  .50900    20.0878   1.2023    1.2644    1.23965    1.36580
  .58200    18.4857   1.1536    1.3179    1.17964    1.43828
  .66500    15.2004   1.1422    1.3797    1.15891    1.52583
  .78400    12.1631   1.0971    1.4812    1.10398    1.67524
  .86490     9.6393   1.0443    1.5513    1.04690    1.78673
  .91690     7.5912   1.0268    1.6893    1.02777    1.85394
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SYSTEM  ACETIC ACID-CARBON TETRACHLORIDE AT CONSTANT TEMPERA
DATA OF LISZI - ACTA.CHIM.ACAD.SCI.HUNG,64,1970 (EXPERIMENTA
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                    TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 -  576.96 WILSON PARAMETER 21 - -170.61

  LIQUID     VAPOUR     VAPOUR    DELTA  EXPTL    CALC   DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100  PRESS    PRESS    MM HG
             EXPTL      CALC
  .16900    .03570    .03576    -.006  82.500  76.723  5.777
  .51420    .13100    .13125    -.025  66.000  65.728    .272
  .55010    .14200    .14228    -.028  64.800  64.266    .534
  .71780    .20170    .20207    -.037  53.000  54.014 -1.014
  .80470    .26210    .26256    -.046  46.200  46.208  -.008
  .85500    .32970    .33021    -.051  39.400  40.048  -.648
  .91880    .42190    .42231    -.041  30.000  29.314    .686

    SUM OF SQUARES                          -     .61478712E-02
    STANDARD ERROR OF ESTIMATE              -     .36065285E-01
    AVERAGE PRESSURE DEVIATION MM HG        -     .20146480E+01
    AVERAGE VAPOUR DEVIATION*100            -     .3337E-01
    NUMBER OF FUNCTION EVALUATIONS          -     227

  LIQUID  EQUILIBRIUM DELTA      DELTA    ACTIVITY  ACTIVITY
MOLE FRAC   CONSTANT    A          B      COEFF 1   COEFF 2
  .16900   107.1373  1.3571    1.0776   2.05411   1.09353
  .51420    73.0958  1.0666    1.3028   1.26141   1.51277
  .55010    71.5959  1.0556    1.3324   1.21303   1.58415
  .71780    75.1806   .9648    1.4964   1.02325   2.04591
  .80470    72.2673   .9627    1.5972    .99141   2.39919
  .85500    69.7810   .9706    1.6617    .98685   2.65670
  .91880    76.1914   .9249    1.7576    .92987   3.06951
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SYSTEM ACETIC ACID - CHLOROFORM AT 760 MM.HG.
DATA OF KENNY


                    TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 - 1292.13 WILSON PARAMETER 21 --1144.00

  LIQUID      VAPOUR      VAPOUR     DELTA   EXPTL     CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC  Y*100   PRESS     PRESS    MM HG
               EXPTL       CALC
  .07739     .01479     .01005      .474 760.000 741.933 18.067
  .13765     .02472     .02515     -.043 760.000 754.708  5.292
  .14484     .02367     .02408     -.042 760.000 757.330  2.670
  .18565     .03323     .03378     -.055 760.000 763.014 -3.014
  .19775     .03538     .03595     -.057 760.000 766.199 -6.199
  .27415     .05738     .05815     -.077 760.000 783.001-23.001
  .39211     .09516     .09603     -.088 760.000 817.003-57.003
  .52458     .15545     .15628     -.083 760.000 818.982-58.982
  .64463     .23098     .23159     -.061 760.000 789.621-29.621
  .65549     .23478     .23537     -.059 760.000 778.676-18.676
  .74169     .33099     .33131     -.032 760.000 757.892  2.108
  .89089     .47955     .47976     -.020 760.000 602.822157.178
  .89089     .41275     .41371     -.096 760.000 529.231230.769

    SUM OF SQUARES                          -     .15037410E+00
    STANDARD ERROR OF ESTIMATE              -     .11692037E+00
    AVERAGE PRESSURE DEVIATION MM HG        -     .62001876E+01
    AVERAGE VAPOUR DEVIATION*100            -     .9136E-01
    NUMBER OF FUNCTION EVALUATIONS          -     314

  LIQUID   EQUILIBRIUM DELTA       DELTA     ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT     A           B       COEFF 1    COEFF 2
  .07739       .0013  4.4700     1.0000     1.63202     .98201
  .13765       .7377  3.7156     1.0103     1.77431     .96376
  .14484      1.4375  3.3174     1.0179     1.62604     .96716
  .18565      2.6336  2.6916     1.0370     1.50388     .96244
  .19775      3.1611  2.5023     1.0441     1.44632     .96214
  .27415      5.2067  1.8659     1.0849     1.28147     .95423
  .39211      8.7826  1.2784     1.1599     1.03944     .95123
  .52458     11.1068   .9913     1.2532      .89648     .95484
  .64463     11.9427   .8574     1.3494      .81815     .96767
  .65549     12.2046   .8441     1.3598      .80820     .96954
  .74169     10.9542   .8192     1.4317      .80164     .98281
  .89089     10.3504   .7804     1.5883      .77787    1.01883
  .89089     11.6884   .7750     1.5991      .77248    1.01429
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SYSTEM ACETIC ACID - WATER AT 69,7 DEG CENT
DATA OF ARICH & TAGLIAVANI,RIC, SCI,,DEC 1958


                 TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 = -344,15 WILSON PARAMETER 21 =  498,82

  LIQUID     VAPOUR     VAPOUR    DELTA   EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100   PRESS    PRESS    MM HG
            EXPTL      CALC
  ,05000    ,04200     ,04205    -,005 228,800 226,946   1,854
  ,10000    ,08100     ,08111    -,011 226,700 224,950   1,750
  ,20000    ,15230     ,15262    -,032 221,000 219,883   1,117
  ,30000    ,22500     ,22560    -,060 214,300 213,752    ,548
  ,40000    ,30890     ,30989    -,099 206,700 207,300   -,600
  ,50000    ,40050     ,40204    -,154 199,200 200,236  -1,036
  ,60000    ,49780     ,49996    -,216 191,200 192,068   -,868
  ,70000    ,60050     ,60333    -,283 182,000 182,246   -,246
  ,80000    ,71230     ,71573    -,343 170,500 170,142    ,358
  ,90000    ,83750     ,84123    -,373 165,700 154,747    ,953
  ,95000    ,90830     ,91198    -,368 146,800 145,620   1,180

    SUM OF SQUARES                             -     ,32173094E-03
    STANDARD ERROR OF ESTIMATE                 -     ,59789633E-02
    AVERAGE PRESSURE DEVIATION MM HG           -     ,48805308E+00
    AVERAGE VAPOUR DEVIATION*100               -     ,1766E+00
    NUMBER OF FUNCTION EVALUATIONS             -     357

  LIQUID   EQUILIBRIUM DELTA     DELTA    ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT    A          B      COEFF 1    COEFF 2
  ,05000     6,6019   2,9236    1,0079    2,94953    1,00820
  ,10000     8,0254   2,3063    1,0239    2,30731    1,02489
  ,20000     9,6851   1,7368    1,0654    1,72212    1,06806
  ,30000    10,5762   1,4694    1,1151    1,45327    1,11874
  ,40000    10,8386   1,3285    1,1714    1,31472    1,17476
  ,50000    10,9973   1,2373    1,2357    1,22710    1,23708
  ,60000    11,2237   1,1702    1,3099    1,16351    1,30723
  ,70000    11,5694   1,1170    1,3961    1,11321    1,38717
  ,80000    12,0262   1,0740    1,4972    1,07236    1,47936
  ,90000    12,6440   1,0374    1,6173    1,03702    1,58751
  ,95000    12,9944   1,0220    1,6859    1,02187    1,64886
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SYSTEM ACETIC ACID - WATER AT 70 CENT.
DATA OF HADDAD & EDMISTER,JNL CHEM ENG DATA,VOL 17,NO 3,1972


                    TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 - -487.74 WILSON PARAMETER 21 -  543.60

  LIQUID     VAPOUR     VAPOUR     DELTA  EXPTL     CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC  Y*100  PRESS     PRESS     MM HG
             EXPTL      CALC
  .08719     .06411     .06420     -.008 228.600 227.397   1.203
  .18572     .13760     .13784     -.024 223.600 222.455   1.145
  .29549     .22291     .22346     -.054 215.900 216.167   -.267
  .40638     .31646     .31746     -.100 208.500 209.262   -.762
  .51064     .40061     .40205     -.144 200.300 200.324   -.024
  .59547     .48924     .49124     -.200 193.100 194.002   -.902
  .66497     .55658     .55904     -.246 187.400 187.306    .094
  .75389     .65434     .65745     -.311 179.100 178.376    .724
  .84701     .76101     .76464     -.363 168.300 166.322   1.978
  .90393     .84675     .85063     -.388 158.900 158.425    .475
  .96014     .94089     .94422     -.333 143.100 144.579 -1.479
  .97607     .99535     .99893     -.358 139.600 144.946 -5.346

    SUM OF SQUARES                           -      .18276572E-02
    STANDARD ERROR OF ESTIMATE               -      .13519087E-01
    AVERAGE PRESSURE DEVIATION MM HG         -      .73324111E+00
    AVERAGE VAPOUR DEVIATION*100             -      .2109E+00
    NUMBER OF FUNCTION EVALUATIONS           -      376

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT     A          B       COEFF 1    COEFF 2
  .08719     9.4923   2.2714    1.0210    2.26744    1.02111
  .18572    10.0016   1.7527    1.0598    1.74711    1.06010
  .29549    10.4629   1.4779    1.1125    1.47261    1.11299
  .40638    10.6691   1.3260    1.1747    1.32179    1.17495
  .51064    11.3799   1.2087    1.2445    1.20564    1.24397
  .59547    11.2587   1.1668    1.3065    1.16463    1.30494
  .66497    11.5057   1.1275    1.3647    1.12599    1.36192
  .75389    11.6446   1.0952    1.4477    1.09436    1.44261
  .84701    12.0384   1.0620    1.5494    1.06172    1.54112
  .90393    12.0465   1.0552    1.6180    1.05508    1.60735
  .96014    12.6499   1.0299    1.6975    1.02987    1.68392
  .97607    11.9522   1.0548    1.7145    1.05482    1.70003
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SYSTEM ACETIC ACID - WATER AT 79,9 DEG CENT
DATA OF ARICH & TAGLIAVANI,RIC,SCI,,DEC 1958


                    TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 = -412,88 WILSON PARAMETER 21 =  582,27

  LIQUID      VAPOUR      VAPOUR     DELTA   EXPTL     CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC  Y*100   PRESS     PRESS     MM HG
             EXPTL        CALC
  ,05000     ,04150     ,04158    -,008 349,900 346,411    3,489
  ,10000     ,08050     ,08068    -,018 345,800 343,229    2,571
  ,20000     ,15050     ,15095    -,045 336,900 335,250    1,650
  ,30000     ,22150     ,22228    -,078 326,600 325,686     ,914
  ,40000     ,30350     ,30473    -,123 315,000 315,618    -,618
  ,50000     ,39300     ,39481    -,181 302,800 304,262  -1,462
  ,60000     ,49000     ,49247    -,247 289,400 291,138  -1,738
  ,70000     ,59280     ,59591    -,311 274,800 275,565    -,765
  ,80000     ,70650     ,71021    -,371 257,800 257,389     ,411
  ,90000     ,83150     ,83538    -,388 236,500 234,353    2,147
  ,95000     ,90600     ,90974    -,374 223,100 221,102    1,998

     SUM OF  SQUARES                          =     ,42266574E-03
     STANDARD ERROR OF ESTIMATE               =     ,68529454E-02
     AVERAGE PRESSURE DEVIATION MM HG         =     ,54829790E+00
     AVERAGE VAPOUR DEVIATION*100             =     ,1949E+00
     NUMBER OF FUNCTION EVALUATIONS           =     682

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY    ACTIVITY
MOLE FRAC   CONSTANT    A          B       COEFF 1     COEFF 2
  ,05000      4,8267   2,7979    1,0066    2,88918     1,00704
  ,10000      6,0449   2,2430    1,0214    2,28816     1,02276
  ,20000      7,4643   1,7048    1,0609    1,71338     1,06508
  ,30000      8,1842   1,4497    1,1087    1,44691     1,11553
  ,40000      8,3745   1,3157    1,1628    1,30986     1,17155
  ,50000      8,5199   1,2266    1,2250    1,22100     1,23426
  ,60000      8,6891   1,1621    1,2966    1,15793     1,30482
  ,70000      8,9444   1,1112    1,3799    1,10861     1,38524
  ,80000      9,2103   1,0736    1,4770    1,07242     1,47733
  ,90000      9,6311   1,0402    1,5927    1,03994     1,58553
  ,95000      9,8104   1,0289    1,6581    1,02886     1,64620
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SYSTEM ACETIC ACID - WATER AT 89,9 DEG CENT
DATA OF ARICH & TAGLIAVANI,RIC,SCI,,DEC 1958


                    THREE PARAMETER NRTL EQUATION

    NRTL PARAMETER 12 -     -1,24 NRTL PARAMETER 21 - 3123,02
                    NRTL PARAMETER ALPHA -     1,21038

  LIQUID     VAPOUR     VAPOUR     DELTA   EXPTL     CALC     DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100   PRESS     PRESS     MM HG
            EXPTL       CALC
  ,05000     ,04100     ,04106    -,006 518,300 517,653    ,647
  ,10000     ,08000     ,08016    -,016 512,300 512,454   -,154
  ,20000     ,14900     ,14947    -,047 498,900 498,819    ,081
  ,30000     ,21650     ,21736    -,086 483,400 482,394  1,006
  ,40000     ,29650     ,29796    -,146 466,900 466,269    ,631
  ,50000     ,38600     ,38823    -,223 448,100 448,885   -,785
  ,60000     ,48200     ,48505    -,305 426,000 428,153 -2,153
  ,70000     ,58600     ,58995    -,395 402,700 404,458 -1,758
  ,80000     ,69950     ,70423    -,473 376,200 376,257   -,057
  ,90000     ,82530     ,83044    -,514 345,000 341,865  3,148
  ,95000     ,90100     ,90581    -,481 322,400 319,426  2,974

     SUM OF SQUARES                           -      ,22372284E-03
     STANDARD ERROR OF ESTIMATE               -      ,52882280E-02
     AVERAGE PRESSURE DEVIATION MM HG         -      ,39490678E+00
     AVERAGE VAPOUR DEVIATION*100             -      ,2446E+00
     NUMBER OF FUNCTION EVALUATIONS           -    4501

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT     A          B       COEFF 1    COEFF 2
  ,05000     3,1343   2,7357    1,0051    2,83236    1,02427
  ,10000     4,0406   2,2581    1,0177    2,27527    1,03924
  ,20000     5,4941   1,7098    1,0553    1,71114    1,07877
  ,30000     6,3688   1,4374    1,1020    1,43708    1,12681
  ,40000     6,5743   1,3047    1,1543    1,30427    1,18032
  ,50000     6,6643   1,2208    1,2139    1,22038    1,24125
  ,60000     6,8372   1,1557    1,2832    1,15540    1,31197
  ,70000     7,0182   1,1076    1,3634    1,10741    1,39376
  ,80000     7,2506   1,0696    1,4574    1,06955    1,48948
  ,90000     7,5609   1,0383    1,5688    1,03832    1,60298
  ,95000     7,7866   1,0227    1,6332    1,02267    1,66849
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SYSTEM ACETIC ACID - WATER AT 50 MM HG
DATA ØF KUSHNER,ZH,FIZ,KHIM,VØL 40,(12),P,3010(1966)


                   TWØ PARAMETER WILSØN EQUATIØN

WILSØN PARAMETER 12 =  -66,26 WILSØN PARAMETER 21 =   243,63

  LIQUID     VAPØUR     VAPØUR     DELTA    EXPTL     CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC    Y*100    PRESS     PRESS     MM HG
            EXPTL      CALC
  ,09600    ,07200     ,07204    -,004    50,000    52,635  -2,635
  ,27100    ,21600     ,21619    -,019    50,000    51,185  -1,185
  ,36400    ,30600     ,30641    -,041    50,000    50,589    -,589
  ,40000    ,33200     ,33247    -,047    50,000    50,742    -,742
  ,43100    ,37100     ,37167    -,067    50,000    47,515    2,485
  ,45200    ,38500     ,38571    -,071    50,000    48,159    1,841
  ,52100    ,47800     ,47909    -,109    50,000    49,177     ,823
  ,64700    ,61000     ,61166    -,166    50,000    51,037  -1,037
  ,75000    ,70700     ,70920    -,220    50,000    50,867    -,867
  ,90000    ,87500     ,87820    -,320    50,000    50,645    -,645

    SUM ØF SQUARES                         =      ,86928001E-02
    STANDARD ERRØR ØF ESTIMATE             =      ,32963616E-01
    AVERAGE PRESSURE DEVIATIØN MM HG       =      ,25698336E+01
    AVERAGE VAPØUR DEVIATIØN*100           =      ,1064E+00
    NUMBER ØF FUNCTIØN EVALUATIØNS         =      272

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT    A          B       CØEFF 1    CØEFF 2
  ,09600    24,1390  2,3541     1,0315     2,15656    1,03133
  ,27100    23,5582  1,6171     1,1161     1,51820    1,10926
  ,36400    22,8373  1,4764     1,1698     1,40731    1,15428
  ,40000    23,9670  1,3930     1,1938     1,33486    1,17367
  ,43100    21,6887  1,4606     1,2117     1,40753    1,18884
  ,45200    22,6543  1,3995     1,2273     1,35210    1,20091
  ,52100    20,9950  1,3789     1,2749     1,34364    1,23689
  ,64700    22,2061  1,2335     1,3813     1,21660    1,31395
  ,75000    23,6066  1,1427     1,4853     1,13511    1,38733
  ,90000    24,3264  1,0651     1,6676     1,06398    1,51137
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SYSTEM ACETIC ACID - WATER AT 70 MM HG
DATA OF ITO,JNL CHEM ENG DATA,VOL 3,PG 315,1963


                      TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 --1261.83 WILSON PARAMETER 21 - 1859,82

  LIQUID      VAPOUR      VAPOUR     DELTA   EXPTL     CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC  Y*100   PRESS     PRESS    MM HG
            EXPTL       CALC
 ,04100     ,02700     ,02702    -,002   70,000   69,570    ,430
 ,10400     ,07500     ,07506    -,006   70,000   70.172   -,172
 ,16900     ,12200     ,12213    -,013   70,000   69,864    ,136
 ,25600     ,18900     ,18927    -,027   70,000   69,791    ,209
 ,33700     ,25800     ,25848    -,048   70,000   69,521    ,479
 ,43400     ,34700     ,34783    -,083   70,000   69,804    ,196
 ,46600     ,37800     ,37898    -,098   70,000   69,893    ,107
 ,52900     ,43900     ,44028    -,128   70,000   70,409   -,409
 ,64000     ,54700     ,54895    -,195   70,000   70,039   -,039
 ,74600     ,65300     ,65571    -,271   70,000   69,923    ,077
 ,84800     ,76300     ,76655    -,355   70,000   70,097   -,097
 ,92800     ,86000     ,86436    -,436   70,000   70,098   -,098
 ,95650     ,90350     ,90821    -,471   70,000   70,130   -,130
 ,99400     ,96450     ,96973    -,523   70,000   68,976   1,024

    SUM OF SQUARES                             -    ,37072447E-03
    STANDARD ERROR OF ESTIMATE                 -    ,55582107E-02
    AVERAGE PRESSURE DEVIATION MM HG           -    ,36781651E+00
    AVERAGE VAPOUR DEVIATION*100               -    ,1897E+00
    NUMBER OF FUNCTION EVALUATIONS             -    500

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY    ACTIVITY
MOLE FRAC    CONSTANT    A          B       COEFF 1     COEFF 2
 ,04100     29,5349   2,7456    1,0111     2,72841     1,01091
 ,10400     24,6504   2,0960    1,0350     2,10815     1,03403
 ,16900     25,1855   1,7296    1,0646     1,75804     1,06206
 ,25600     25,4785   1,4677    1,1092     1,51135     1,10326
 ,33700     25,0979   1,3340    1,1553     1,38714     1,14505
 ,43400     24,7413   1,2237    1,2173     1,28420     1,20143
 ,46600     24,5628   1,1973    1,2394     1,25911     1,22194
 ,52900     24,4942   1,1451    1,2861     1,20777     1,26705
 ,64000     24,0236   1,0899    1,3783     1,14752     1,36534
 ,74600     23,4441   1,0554    1,4807     1,10057     1,50678
 ,84800     22,4782   1,0392    1,5949     1,06543     1,75242
 ,92800     21,5267   1,0314    1,6977     1,04035     2,15455
 ,95650     21,0777   1,0272    1,7374     1,03107     2,40529
 ,99400     20,3810   1,0282    1,7921     1,02829     2,90287
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SYSTEM ACETIC ACID - WATER AT 200 MM HG
DATA OF ITO,JNL CHEM ENG DATA,VOL 9(3),PG 315,(1963)


                   TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 - -1214.50 WILSON PARAMETER 21 - 1543.52

  LIQUID     VAPOUR     VAPOUR    DELTA   EXPTL     CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100   PRESS     PRESS    MM HG
            EXPTL      CALC
  .04500    .03100    .03103    -.003 200.000 197.095   2.905
  .09900    .07100    .07109    -.009 200.000 199.212    .788
  .15800    .11200    .11220    -.020 200.000 198.270   1.730
  .25800    .18400    .18450    -.050 200.000 197.648   2.352
  .35800    .26600    .26702    -.102 200.000 196.639   3.361
  .44000    .33800    .33957    -.157 200.000 199.324    .676
  .45700    .35300    .35470    -.170 200.000 199.834    .166
  .53300    .42700    .42944    -.244 200.000 200.757   -.757
  .61100    .50100    .50428    -.328 200.000 201.582  -1.582
  .72000    .60900    .61372    -.472 200.000 201.343  -1.343
  .83200    .72800    .73450    -.650 200.000 200.110   -.110
  .85200    .75400    .76091    -.691 200.000 200.405   -.405
  .92200    .84700    .85541    -.841 200.000 199.783    .217
  .95000    .88900    .89815    -.915 200.000 198.950   1.050
  .98900    .96150    .97180   -1.030 200.000 199.109    .891

    SUM OF SQUARES                          -      .90926497E-03
    STANDARD ERROR OF ESTIMATE              -      .83632206E-02
    AVERAGE PRESSURE DEVIATION MM HG        -      .61116953E+00
    AVERAGE VAPOUR DEVIATION*100            -      .3787E+00
    NUMBER OF FUNCTION EVALUATIONS          -      500

  LIQUID  EQUILIBRIUM DELTA     DELTA     ACTIVITY    ACTIVITY
MOLE FRAC   CONSTANT    A         B       COEFF 1     COEFF 2
  .04500    14.0521   2.5516    1.0096    2.67168     1.00959
  .09900    12.9995   2.0357    1.0278    2.13832     1.02762
  .15800    13.3999   1.7147    1.0520    1.80413     1.05166
  .25800    13.6264   1.4299    1.0991    1.50673     1.09886
  .35800    13.0484   1.2989    1.1522    1.36715     1.15314
  .44000    12.8167   1.2144    1.2016    1.27574     1.20598
  .45700    12.7933   1.1990    1.2126    1.25866     1.21811
  .53300    12.2856   1.1597    1.2635    1.21206     1.27641
  .61100    12.0665   1.1186    1.3222    1.16181     1.34955
  .72000    11.6865   1.0813    1.4152    1.11037     1.48278
  .83200    11.2954   1.0546    1.5273    1.06857     1.68633
  .85200    11.1473   1.0529    1.5489    1.06436     1.73375
  .92200    10.7621   1.0416    1.6307    1.04548     1.94353
  .95000    10.5057   1.0438    1.6651    1.04551     2.04944
  .98900    10.1451   1.0377    1.7156    1.03777     2.23462
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SYSTEM ACETIC ACID - WATER AT 760 MM HG
DATA ØF ITØ,JNL,CHEM ENG DATA, VØL 8(3),PG 315 (1963)

                    THREE PARAMETER NRTL EQUATIØN

  NRTL PARAMETER 12 - -117,21 NRTL PARAMETER 21 - 1053,46
                    NRTL PARAMETER ALPHA -    1,81729

  LIQUID     VAPØUR     VAPØUR     DELTA   EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC     Y*100   PRESS    PRESS    MM HG
             EXPTL       CALC
  ,01500     ,01100     ,01102     -,002 760,000 747,331 12,669
  ,02400     ,08600     ,04902     3,698 760,000 772,475-12,475
  ,05500     ,04000     ,04005     -,005 760,000 758,748  1,252
  ,07700     ,05600     ,05609     -,009 760,000 762,144 -2,144
  ,22200     ,04900     ,04905     -,005 760,000 737,793 22,207
  ,30400     ,20800     ,20933     -,133 760,000 767,011 -7,011
  ,37600     ,26500     ,26714     -,214 760,000 766,150 -6,150
  ,47800     ,35100     ,35471     -,371 760,000 763,493 -3,493
  ,58700     ,45500     ,46108     -,608 760,000 762,448 -2,448
  ,69700     ,56700     ,57629     -,929 760,000 754,917  5,083
  ,80100     ,70200     ,71563    -1,363 760,000 766,472 -6,472
  ,89900     ,81200     ,82954    -1,754 760,000 751,738  8,262
  ,90100     ,81700     ,83456    -1,756 760,000 754,652  5,348
  ,90400     ,83100     ,84930    -1,830 760,000 760,595  -,595
  ,94600     ,87700     ,89698    -1,998 760,000 748,859 11,141
  ,97800     ,94100     ,96328    -2,228 760,000 760,544  -,544

    SUM ØF SQUARES                          -     ,20947893E-02
    STANDARD ERRØR ØF ESTIMATE              -     ,12694000E-01
    AVERAGE PRESSURE DEVIATIØN MM HG        -     ,96482131E+00
    AVERAGE VAPØUR DEVIATIØN*100            -     ,1056E+01
    NUMBER ØF FUNCTIØN EVALUATIØNS          -    1452

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MØLE FRAC  CØNSTANT    A          B        CØEFF 1    CØEFF 2
  ,01500    78,4523  1,4677    1,0040     3,20836    1,00694
  ,02400      ,0021  3,0742    1,0000     5,67251    1,00630
  ,05500     9,3554  1,9066    1,0108     2,50557    1,03068
 1,07700     5,9193  1,9746    1,0144     2,29785    1,04314
  ,22200    33,2846   ,7339    1,0948      ,70037    1,15716
  ,30400     4,2002  1,4767    1,0920     1,40186    1,15633
  ,37600     4,2534  1,3770    1,1257     1,31500    1,18875
  ,47800     4,3774  1,2653    1,1806     1,22350    1,23606
  ,58700     4,4234  1,1832    1,2479     1,15871    1,28915
  ,69700     4,4501  1,1243    1,3269     1,11208    1,34816
  ,80100     4,2832  1,0907    1,4100     1,08579    1,40847
  ,89900     4,4043  1,0450    1,5080     1,04386    1,48050
  ,90100     4,4164  1,0404    1,5105     1,03924    1,48274
  ,90400     4,2693  1,0546    1,5096     1,05350    1,48086
  ,94600     4,3594  1,0335    1,5581     1,03319    1,51680
  ,97800     4,2161  1,0300    1,5907     1,02997    1,54066
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SYSTEM ACETIC ACID = WATER AT 760 MM HG
DATA ØF GARNER,ELLIS & PEARCE

                    THREE PARAMETER NRTL EQUATIØN

  NRTL PARAMETER 12 =  -52,61 NRTL PARAMETER 21 =  878,03
                NRTL PARAMETER ALPHA =    2,47342

  LIQUID      VAPØUR     VAPØUR     DELTA   EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC   Y*100   PRESS    PRESS    MM HG
              EXPTL      CALC
  ,08270     ,06630     ,06645     -,016 760,000 759,812    ,188
  ,19700     ,13600     ,13645     -,045 760,000 759,989    ,011
  ,29200     ,20100     ,20207     -,107 760,000 760,286   -,286
  ,38700     ,27800     ,28012     -,212 760,000 761,163  -1,163
  ,52000     ,39500     ,39940     -,440 760,000 758,494   1,506
  ,61000     ,48500     ,49159     -,659 760,000 760,928   -,928
  ,66000     ,53300     ,54089     -,789 760,000 759,802    ,198
  ,73900     ,61600     ,62636    -1,036 760,000 758,252   1,748
  ,77900     ,66100     ,67270    -1,170 760,000 758,886   1,114
  ,85600     ,76000     ,77507    -1,507 760,000 760,033   -,033
  ,91500     ,84300     ,86099    -1,799 760,000 760,740   -,740
  ,96500     ,93000     ,95120    -2,120 760,000 768,879  -8,879

    SUM ØF SQUARES                          =      ,15290468E-03
    STANDARD ERRØR ØF ESTIMATE              =      ,41218211E-02
    AVERAGE PRESSURE DEVIATIØN MM HG        =      ,25312660E+00
    AVERAGE VAPØUR DEVIATIØN*100            =      ,8248E+00
    NUMBER ØF FUNCTIØN EVALUATIØNS          =    1886

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MØLE FRAC    CØNSTANT    A          B       CØEFF 1    CØEFF 2
  ,08270      3,6507   2,1858     1,0126    2,40564    1,03743
  ,19700      4,3509   1,6635     1,0499    1,64362    1,09184
  ,29200      4,5808   1,4513     1,0892    1,41999    1,13634
  ,38700      4,5226   1,3356     1,1334    1,30946    1,18151
  ,52000      4,5007   1,2236     1,2066    1,20763    1,25141
  ,61000      4,4436   1,1715     1,2636    1,16127    1,30385
  ,66000      4,4986   1,1388     1,2999    1,13128    1,33685
  ,73900      4,5248   1,0988     1,3618    1,09459    1,39254
  ,77900      4,5478   1,0781     1,3962    1,07514    1,42346
  ,85600      4,4535   1,0561     1,4656    1,05487    1,48493
  ,91500      4,3754   1,0406     1,5243    1,04009    1,53684
  ,96500      4,2003   1,0359     1,5749    1,03585    1,58144
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SYSTEM ACETIC ACID - WATER AT 760 MM HG,
DATA ØF SEBASTIANI & LACQUANTI,CHEM ENG SCI,1967,VØL 22,PP 1
155-1162

                    TWØ PARAMETER WILSØN EQUATIØN

WILSØN PARAMETER 12 -  541,37 WILSØN PARAMETER 21 -  234,87

  LIQUID     VAPØUR     VAPØUR    DELTA   EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC  Y*100  PRESS    PRESS    MM HG
           EXPTL       CALC
  ,13500    ,09300     ,09325    -,026 760,000 752,792  7,208
  ,16800    ,11300     ,11333    -,033 760,000 753,131  6,869
  ,24500    ,18300     ,18395    -,095 760,000 764,534 -4,534
  ,32500    ,23000     ,23152    -,152 760,000 760,637  -,637
  ,35900    ,25000     ,25180    -,180 760,000 759,171   ,829
  ,42750    ,32200     ,32504    -,304 760,000 763,880 -3,880
  ,42800    ,32000     ,32300    -,300 760,000 762,733 -2,733
  ,48000    ,36500     ,36888    -,388 760,000 762,900 -2,900
  ,56000    ,44400     ,44966    -,566 760,000 768,090 -8,090
  ,60500    ,48500     ,49174    -,674 760,000 763,948 -3,948
  ,69500    ,58000     ,58949    -,949 760,000 761,299 -1,299
  ,71750    ,61600     ,62669   -1,069 760,000 767,797 -7,797
  ,72500    ,58300     ,59245    -,945 760,000 742,661 17,339
  ,74300    ,62500     ,63589   -1,089 760,000 754,818  5,182
  ,75000    ,63500     ,64618   -1,118 760,000 757,232  2,768
  ,77000    ,64500     ,65642   -1,142 760,000 748,540 11,460
  ,81000    ,69800     ,71125   -1,325 760,000 750,237  9,763
  ,82500    ,71800     ,73194   -1,394 760,000 751,007  8,993
  ,85500    ,77300     ,78891   -1,591 760,000 763,861 -3,861
  ,87300    ,79200     ,80854   -1,654 760,000 760,471  -,471
  ,87500    ,81750     ,83503   -1,753 760,000 777,952-17,952
  ,89750    ,82750     ,84531   -1,781 760,000 762,533 -2,533
  ,90500    ,85000     ,86868   -1,868 760,000 771,922-11,922

    SUM ØF SQUARES                          -    ,24651816E-02
    STANDARD ERRØR ØF ESTIMATE              -    ,10834648E-01
    AVERAGE PRESSURE DEVIATIØN MM HG        -    ,81790278E+00
    AVERAGE VAPØUR DEVIATIØN*100            -    ,8867E+00
    NUMBER ØF FUNCTIØN EVALUATIØNS          -    225

 LIQUID   EQUILIBRIUM DELTA     DELTA    ACTIVITY   ACTIVITY
MØLE FRAC  CØNSTANT    A         B       CØEFF 1    CØEFF 2
 ,13500     5,2736   1,7508   1,0312    1,87464    1,05562
 ,16800     5,0708   1,6628   1,0420    1,71812    1,07337
 ,24500     3,7574   1,6345   1,0648    1,61495    1,10865
 ,32500     4,2626   1,4410   1,1018    1,40138    1,15340
 ,35900     4,4870   1,3721   1,1194    1,33175    1,17251
 ,42750     4,0381   1,3508   1,1495    1,31209    1,20244
 ,42800     4,0977   1,3434   1,1504    1,30491    1,20336
 ,48000     4,1513   1,2909   1,1791    1,25742    1,22941
 ,56000     4,1469   1,2299   1,2266    1,20510    1,26829
 ,60500     4,2166   1,1967   1,2568    1,17576    1,29197
 ,69500     4,2192   1,1488   1,3212    1,13702    1,33868
 ,71750     4,0699   1,1532   1,3356    1,14302    1,34759
 ,72500     4,6681   1,0929   1,3530    1,08377    1,36349
 ,74300     4,3348   1,1160   1,3614    1,10784    1,36716
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SYSTEM ACETIC ACID - WATER AT 760 MM HG,
DATA OF SEBASTIANI & LACQUANTI,CHEM ENG SCI,1967,VOL 22,PP 1
155-1162

                   TWO PARAMETER WILSON EQUATION

  LIQUID   EQUILIBRIUM DELTA     DELTA     ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT    A          B       COEFF 1    COEFF 2
  ,75000     4,3237   1.1126    1,3669     1,10494    1,37064
  ,77000     4,5024   1.0877    1,3875     1,08130    1,38558
  ,81000     4,4057   1.0812    1,4209     1,07687    1,40695
  ,82500     4,3803   1.0776    1,4342     1,07398    1,41528
  ,85500     4,1965   1.0805    1,4582     1,07794    1,42809
  ,87300     4,2403   1.0697    1,4770     1,06783    1,44034
  ,87500     4,0205   1.0869    1,4729     1,08500    1,43464
  ,89750     4,2108   1.0624    1,5011     1,06115    1,45463
  ,90500     4,0939   1.0688    1,5056     1,06778    1,45551
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SYSTEM ACETIC ACID WATER AT 760 MM HG
DATA ØF BRØWN & EWALD,AUST,J.SCI,RES,,A3,PG 3061,1960


                    TWØ PARAMETER WILSØN EQUATIØN

WILSØN PARAMETER 12 =  711,02 WILSØN PARAMETER 21 =  193,73

  LIQUID      VAPØUR     VAPØUR     DELTA   EXPTL      CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC   Y*100   PRESS      PRESS    MM HG
            EXPTL        CALC
  ,01090     ,00790     ,00791     -,001 760,000 744,267 15,733
  ,03240     ,02390     ,02394     -,004 760,000 747,903 12,097
  ,07900     ,05750     ,05766     -,016 760,000 754,312  5,688
  ,17490     ,12170     ,12228     -,058 760,000 762,913 -2,913
  ,26120     ,17830     ,17947     -,117 760,000 763,321 -3,321
  ,35370     ,24760     ,24975     -,215 760,000 763,175 -3,175
  ,46410     ,34090     ,34479     -,389 760,000 760,794  -,794
  ,58020     ,45040     ,45692     -,652 760,000 757,767  2,233
  ,66220     ,54270     ,55185     -,915 760,000 761,136 -1,136
  ,70830     ,59290     ,60367    -1,077 760,000 759,215   ,785
  ,78020     ,67270     ,68613    -1,343 760,000 757,473  2,527
  ,85030     ,76180     ,77856    -1,676 760,000 757,640  2,360
  ,91880     ,85540     ,87565    -2,025 760,000 759,963   ,037
  ,95260     ,90210     ,92416    -2,206 760,000 758,956  1,044
  ,99450     ,98880    1,00000    -1,120 760,000 777,611-17,611
  ,99660     ,99310    1,00000     -,690 760,000 778,405-18,405
  ,99980     ,99980    1,00000     -,020 760,000 779,660-19,660
  ,99980     ,99960    1,00000     -,040 760,000 779,521-19,521
  ,99980     ,99970    1,00000     -,030 760,000 779,597-19,597

    SUM ØF SQUARES                          -      ,39420417E-02
    STANDARD ERRØR ØF ESTIMATE              -      ,15227764E-01
    AVERAGE PRESSURE DEVIATIØN MM HG        -      ,10293366E+01
    AVERAGE VAPØUR DEVIATIØN*100            -      ,6629E+00
    NUMBER ØF FUNCTIØN EVALUATIØNS          -      253

  LIQUID   EQUILIBRIUM DELTA       DELTA     ACTIVITY    ACTIVITY
MØLE FRAC    CØNSTANT    A           B       CØEFF 1     CØEFF 2
  ,01090     39,8533   1,9896     1,0020    3,29182     1,00248
  ,03240     13,2942   1,9967     1,0058    2,84812     1,00955
  ,07900      6,1095   1,9443     1,0152    2,28138     1,03011
  ,17490      4,2940   1,7271     1,0418    1,72772     1,07947
  ,26120      4,2442   1,5406     1,0742    1,48093     1,12426
  ,35370      4,2446   1,4041     1,1149    1,34106     1,16874
  ,46410      4,2842   1,2874     1,1718    1,24043     1,21878
  ,58020      4,3345   1,1978     1,2422    1,16949     1,27055
  ,66220      4,2440   1,1598     1,2972    1,14186     1,30591
  ,70830      4,2462   1,1378     1,3319    1,12472     1,32763
  ,78020      4,3036   1,0995     1,3921    1,09243     1,36390
  ,85030      4,2383   1,0796     1,4547    1,07639     1,39958
  ,91880      4,2013   1,0564     1,5234    1,05554     1,43706
  ,95260      4,1947   1,0449     1,5605    1,04465     1,45719
  ,99450      3,9930   1,0430     1,6027    1,04297     1,47511
  ,99660      3,9848   1,0427     1,6049    1,04271     1,47607
  ,99980      3,9847   1,0401     1,6088    1,04009     1,47768
  ,99980      3,9811   1,0409     1,6087    1,04086     1,47767
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SYSTEM ACETIC ACID WATER AT 760 MM HG
DATA OF BROWN & EWALD.AUST.J.SCI.RES.,A3,PG 3061,1950

                      TWO PARAMETER WILSON EQUATION

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY  ACTIVITY
MOLE FRAC   CONSTANT    A          B       COEFF 1   COEFF 2
  .99980     3.9812  1.0408    1.6087    1.04076   1.47765
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SYSTEM ACETIC ACID - WATER AT 760 MM HG
DATA OF RIVENG,GER.CHIM.ETAT,38(1953)


                     THREE PARAMETER NRTL EQUATION

   NRTL PARAMETER 12 - -265.60 NRTL PARAMETER 21 -  144.34
                    NRTL PARAMETER ALPHA -     -.86780

  LIQUID      VAPOUR     VAPOUR    DELTA   EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100   PRESS    PRESS    MM HG
             EXPTL       CALC
  .04060     .02750     .02760    -.010 760.000 739.085 20.915
  .19700     .13400     .13494    -.094 760.000 747.837 12.163
  .35100     .24900     .25253    -.353 760.000 758.254  1.746
  .49000     .37000     .37814    -.814 760.000 765.694 -5.694
  .60600     .46700     .48017   -1.317 760.000 763.063 -3.063
  .70300     .56300     .58249   -1.949 760.000 762.080 -2.080
  .79400     .66200     .68974   -2.774 760.000 757.873  2.127
  .87500     .76000     .79776   -3.776 760.000 754.460  5.540
  .94700     .86700     .91862   -5.162 760.000 762.580 -2.580
  .99450     .96800    1.03580   -6.780 760.000 793.953-33.953

     SUM OF SQUARES                         -     .31669776E-02
     STANDARD ERROR OF ESTIMATE             -     .21270293E-01
     AVERAGE PRESSURE DEVIATION MM HG       -     .12963048E+01
     AVERAGE VAPOUR DEVIATION*100           -     .2303E+01
     NUMBER OF FUNCTION EVALUATIONS         -     752

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT    A          B       COEFF 1    COEFF 2
  .04060     1.9370   2.7207    1.0025    2.54819    1.00243
  .19700     3.9124   1.7083    1.0479    1.61687    1.04628
  .35100     4.2487   1.3924    1.1137    1.33418    1.10672
  .49000     4.2704   1.2514    1.1862    1.21344    1.16855
  .60600     4.5635   1.1426    1.2626    1.11905    1.22892
  .70300     4.6269   1.0857    1.3347    1.07154    1.28027
  .79400     4.6140   1.0491    1.4109    1.04181    1.32886
  .87500     4.5270   1.0287    1.4864    1.02579    1.37096
  .94700     4.2411   1.0327    1.5556    1.03217    1.40226
  .99450     3.8007   1.0585    1.5954    1.05848    1.41315
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SYSTEM ACETIC ACID - METHANØL
DATA ØF RIUS ET AL,CHEM ENG SCI,VØL 10,PP 105-111,1959,& ERR
ATA PG 288 FF

                    TWØ PARAMETER WILSØN EQUATIØN

WILSØN PARAMETER 12 - -301,63 WILSØN PARAMETER 21 - -236,68

  LIQUID      VAPØUR      VAPØUR     DELTA   EXPTL     CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC   Y*100   PRESS     PRESS    MM HG
              EXPTL       CALC
  ,00500      ,00100      ,00040      ,060 708,800 832,665*******
  ,04100      ,00400      ,00386      ,014 708,800 668,471  40,329
  ,11800      ,01100      ,01116     -,016 704,700 689,815  14,885
  ,16100      ,01700      ,01723     -,023 704,700 709,632  -4,932
  ,21500      ,02900      ,02940     -,040 708,800 700,189   8,611
  ,28700      ,04900      ,04964     -,064 708,800 702,316   6,484
  ,34300      ,06600      ,06684     -,084 708,800 702,629   6,171
  ,39900      ,08900      ,09008     -,108 705,900 702,705   3,195
  ,48300      ,14700      ,14881     -,181 705,900 707,368  -1,468
  ,50800      ,16900      ,17112     -,212 711,100 722,325-11,225
  ,57300      ,22400      ,22687     -,287 709,300 715,169  -5,869
  ,61300      ,26500      ,26852     -,352 711,100 714,335  -3,235
  ,69400      ,37000      ,37511     -,511 705,900 717,674-11,774
  ,72000      ,39700      ,40263     -,563 705,900 703,825   2,075
  ,75000      ,44400      ,45059     -,659 709,800 708,301   1,499
  ,79200      ,50900      ,51688     -,788 709,800 702,878   6,922
  ,86300      ,64700      ,65779    -1,079 711,100 706,804   4,296
  ,89300      ,69700      ,70871    -1,171 709,800 696,423  13,377
  ,94200      ,83500      ,84989    -1,489 709,800 713,944  -4,144
  ,96300      ,89100      ,90715    -1,615 709,800 716,228  -6,428

      SUM ØF SQUARES                           -      ,35835609E-01
      STANDARD ERRØR ØF ESTIMATE               -      ,44619135E-01
      AVERAGE PRESSURE DEVIATIØN MM HG         -      ,19812695E+01
      AVERAGE VAPØUR DEVIATIØN*100             -      ,4658E+00
      NUMBER ØF FUNCTIØN EVALUATIØNS           -      323

  LIQUID   EQUILIBRIUM DELTA      DELTA      ACTIVITY    ACTIVITY
MØLE FRAC   CØNSTANT     A          B        CØEFF 1     CØEFF 2
  ,00500         ,0005  4,3098     1,0000     1,47619      ,99996
 ',04100         ,0120  4,5535     1,0000     1,70997      ,99748
  ,11800        5,2552  2,6135     1,0256     1,20561     1,00582
  ,16100        6,3009  2,2103     1,0428     1,12605     1,00715
  ,21600        5,8323  2,0482     1,0625     1,16279     1,00157
  ,28700        6,3131  1,7736     1,0957     1,13997      ,99268
  ,34300        7,1937  1,5634     1,1269     1,09062      ,98505
  ,39900        7,6461  1,4232     1,1591     1,06555      ,97416
  ,48300        6,9174  1,3449     1,2049     1,09903      ,94947
  ,50800        6,7321  1,3161     1,2195     1,09995      ,94205
  ,57300        6,6996  1,2406     1,2628     1,09000      ,92352
  ,61300        6,5607  1,2058     1,2903     1,08716      ,91143
  ,69400        6,1978  1,1456     1,3496     1,07743      ,88698
  ,72000        6,2514  1,1232     1,3719     1,06783      ,87998
  ,75000        6,0399  1,1085     1,3953     1,06560      ,87091
  ,79200        5,8734  1,0852     1,4313     1,05666      ,85917
  ,86300        5,3845  1,0688     1,4929     1,04718      ,83949
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SYSTEM ACETIC ACID - METHANØL
DATA ØF RIUS ET AL,CHEM ENG SCI,VØL 10,PP 105-111,1959,& ERR
ATA PG 288 FF

                    TWØ PARAMETER WILSØN EQUATIØN

  LIQUID  EQUILIBRIUM DELTA      DELTA   ACTIVITY  ACTIVITY
MØLE FRAC  CØNSTANT     A          B     CØFFF 1   CØEFF 2
  .89300     5.3887  1.0351    1.5248   1.02832    .83381
  .94200     4.7863  1.0364    1.5655   1.03450    .81967
  .96300     4.6178  1.0319    1.5853   1.03115    .81479
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SYSTEM ACETIC ACID - ETHANØL
DATA ØF RIUS.ET AL.CHEM ENG SCI,VØL 10,PP 105-111,1959 & ERR
ATA PG 288 FF

                    THREE PARAMETER NRTL EQUATIØN

   NRTL PARAMETER 12 = -252.04 NRTL PARAMETER 21 = -197.59
                  NRTL PARAMETER ALPHA =    2.58652

  LIQUID     VAPØUR     VAPØUR     DELTA   EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC    Y*100   PRESS    PRESS    MM HG
            EXPTL      CALC
  .07600     .01000     .01016     -.016 706.000 693.722 12.278
  .18400     .03400     .03451     -.051 700.800 698.522  2.278
  .27200     .06600     .06695     -.095 697.900 696.070  1.830
  .34100     .10000     .10144     -.144 706.400 709.414 -4.014
  .41300     .14600     .14814     -.214 707.200 708.810 -1.610
  .48400     .20700     .20987     -.287 690.600 699.445 -8.845
  .54000     .25000     .25380     -.380 706.000 694.285 11.715
  .65300     .40300     .40944     -.644 705.500 720.748-15.248
  .71800     .47400     .48153     -.753 689.700 676.737 12.963
  .76700     .56300     .57297     -.997 710.000 707.923  2.077
  .79300     .60700     .61788    -1.088 708.100 706.073  2.027
  .83400     .68800     .70062    -1.262 707.500 714.380 -6.880
  .86700     .72600     .73933    -1.333 700.800 688.557 12.243
  .89700     .80300     .81843    -1.543 706.000 710.481 -4.481
  .92700     .85600     .87259    -1.659 707.500 711.907 -4.407
  .94500     .89300     .91060    -1.760 708.100 715.113 -7.013

    SUM ØF SQUARES                          =     .22109024E-02
    STANDARD ERRØR ØF ESTIMATE              =     .13041067E-01
    AVERAGE PRESSURE DEVIATIØN MM HG        =     .10570069E+01
    AVERAGE VAPØUR DEVIATIØN*100            =     .7640E+00
    NUMBER ØF FUNCTIØN EVALUATIØNS          =    1324

  LIQUID  EQUILIBRIUM DELTA      DELTA    ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT    A          B      CØEFF 1    CØEFF 2
  .07600     3.3740  2.8185     1.0105    1.15805     .99880
  .18400     5.3020  1.9349     1.0486    1.06746     .99481
  .27200     5.7378  1.6344     1.0864    1.05587     .98631
  .34100     5.9178  1.4705     1.1198    1.04276     .97854
  .41300     5.8751  1.3627     1.1572    1.04337     .96827
  .48400     5.7410  1.2889     1.1971    1.04915     .95596
  .54000     5.8547  1.2218     1.2332    1.03588     .94628
  .65300     5.2371  1.1580     1.3055    1.05029     .91560
  .71800     5.4755  1.1070     1.3600    1.03479     .89497
  .76700     5.0650  1.0934     1.3954    1.04269     .87319
  .79300     4.9959  1.0826     1.4175    1.04199     .86069
  .83400     4.8062  1.0689     1.4522    1.04204     .83845
  .86700     4.9359  1.0492     1.4878    1.03163     .81933
  .89700     4.5936  1.0551     1.5109    1.04421     .79710
  .92700     4.5742  1.0382     1.5429    1.03258     .77640
  .94500     4.4703  1.0387     1.5602    1.03550     .76130
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SYSTEM ACETIC ACID - N-PROPANOL
DATA OF RIUS ET AL,CHEM ENG SCI,VOL 10,PP 105-111,1959,& ERR
ATA PG 288-FF

                    TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 -  -80.39 WILSON PARAMETER 21 - -454.83

 LIQUID     VAPOUR     VAPOUR     DELTA  EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100  PRESS    PRESS    MM HG
           EXPTL      CALC
 .09200    .02400    .02436    -.036 703.700 693.271 10.429
 .13200    .04000    .04068    -.058 704.200 700.554  3.646
 .17700    .06000    .06086    -.086 702.900 696.367  6.533
 .24300    .10000    .10137    -.137 702.900 704.074 -1.174
 .33100    .16900    .17128    -.228 701.800 704.091 -2.291
 .41400    .25500    .25845    -.345 704.200 713.246 -9.046
 .50000    .34900    .35377    -.477 701.800 702.740  -.940
 .51200    .36200    .36704    -.504 706.800 708.740 -1.940
 .56300    .42200    .42788    -.588 701.800 696.559  5.241
 .62300    .50700    .51443    -.743 706.800 702.021  4.779
 .68800    .60300    .61210    -.910 706.800 706.887  -.087
 .79500    .74400    .75580   -1.180 708.200 708.094   .106
 .86800    .84600    .85998   -1.398 706.800 712.650 -5.850
 .87400    .84100    .85466   -1.366 704.200 702.306  1.894

   SUM OF SQUARES                              -    .69787716E-03
   STANDARD ERROR OF ESTIMATE                  -    .76260363E-02
   AVERAGE PRESSURE DEVIATION MM HG            -    .54732672E+00
   AVERAGE VAPOUR DEVIATION*100                -    .5754E+00
   NUMBER OF FUNCTION EVALUATIONS              -    322

 LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MOLE FRAC  CONSTANT    A           B       COEFF 1    COEFF 2
 .09200     4.5915   2.0781    1.0167    1.02959    1.00771
 .13200     4.0147   1.9476    1.0269    1.03640    1.00863
 .17700     4.0630   1.7832    1.0416    1.02251    1.00918
 .24300     3.9542   1.6219    1.0652    1.02729    1.00510
 .33100     3.9918   1.4572    1.1024    1.03477     .99355
 .41400     3.9745   1.3460    1.1419    1.04624     .97588
 .50000     4.1997   1.2399    1.1911    1.03998     .95549
 .51200     4.2488   1.2213    1.1987    1.03430     .95245
 .56300     4.3779   1.1744    1.2317    1.03115     .93881
 .62300     4.2820   1.1400    1.2701    1.04247     .91915
 .68800     4.2200   1.1164    1.3159    1.04923     .89771
 .79500     4.3187   1.0644    1.4055    1.03778     .86544
 .86800     4.2229   1.0563    1.4716    1.04565     .84200
 .87400     4.3900   1.0401    1.4819    1.03059     .84268
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SYSTEM ACETIC ACID - N-PRØPANØL AT CØNST,PRESS, 760 MM HG
DATA ØF AMER AMEZAGA,ANAL,REAL,SØC,ESP,FIS,QUIM,VØL 69,PG 58
7,NØ 5,MAY 1973

                    THREE PARAMETER NRTL EQUATIØN

   NRTL PARAMETER 12 = -716,12 NRTL PARAMETER 21 =   324,09
                    NRTL PARAMETER ALPHA =       ,83540

  LIQUID      VAPØUR      VAPØUR     DELTA  EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC -MØLE FRAC   Y*100   PRESS    PRESS    MM HG
              EXPTL        CALC
  ,02700      ,00700      ,00382      ,318 760,000 742,651 17,349
  ,10800      ,03500      ,03458      ,042 760,000 739,529 20,471
  ,16700      ,06500      ,06593     -,093 760,000 752,651  7,349
  ,21700      ,09900      ,10040     -,140 760,000 746,432 13,568
  ,24800      ,12200      ,12368     -,168 760,000 756,733  3,267
  ,26000      ,13300      ,13482     -,182 760,000 760,988  -,988
  ,28700      ,15800      ,16013     -,213 760,000 767,338 -7,338
  ,28900      ,16100      ,16319     -,219 760,000 761,567 -1,567
  ,31600      ,18300      ,18544     -,244 760,000 769,031 -9,031
  ,35500      ,22200      ,22497     -,297 760,000 765,772 -5,772
  ,42000      ,29600      ,30002     -,402 760,000 764,644 -4,644
  ,47500      ,35400      ,35877     -,477 760,000 768,380 -8,380
  ,55700      ,45200      ,45834     -,634 760,000 762,219 -2,219
  ,63200      ,54700      ,55502     -,802 760,000 759,959   ,041
  ,68800      ,60700      ,61629     -,929 760,000 748,642 11,358
  ,75200      ,69200      ,70295    -1,095 760,000 754,698  5,302
  ,84000      ,80300      ,81646    -1,346 760,000 758,596  1,404
  ,84100      ,79700      ,81027    -1,327 760,000 754,287  5,713
  ,88600      ,86600      ,88087    -1,487 760,000 767,109 -7,109

     SUM ØF SQUARES                          =      ,25622698E-02
     STANDARD ERRØR ØF ESTIMATE              =      ,12654717E-01
     AVERAGE PRESSURE DEVIATIØN MM HG        =      ,98384403E+00
     AVERAGE VAPØUR DEVIATIØN*100            =      ,5480E+00
     NUMBER ØF FUNCTIØN EVALUATIØNS          =    1223

  LIQUID   EQUILIBRIUM DELTA        DELTA       ACTIVITY    ACTIVITY
MØLE FRAC    CØNSTANT     A           B         CØEFF 1     CØEFF 2
  ,02700        ,0002   3,1511     1,0000       ,68325      ,99710
  ,10800        ,0086   3,0774     1,0001      1,10999      ,96362
  ,16700       1,1509   2,3687     1,0197      1,10874      ,94482
  ,21700       1,8021   2,0300     1,0391      1,12303      ,92676
  ,24800       2,2797   1,8323     1,0538      1,10489      ,91725
  ,26000       2,3834   1,7816     1,0590      1,10709      ,91298
  ,28700       2,6345   1,6745     1,0714      1,10644      ,90385
  ,28900       2,5743   1,6861     1,0715      1,11844      ,90224
  ,31600       2,9902   1,5597     1,0866      1,09167      ,89535
  ,35500       3,2687   1,4595     1,1062      1,09091      ,88303
  ,42000       3,5494   1,3424     1,1401      1,09365      ,86408
  ,47500       3,9678   1,2350     1,1741      1,06303      ,85350
  ,55700       4,1775   1,1538     1,2261      1,05336      ,83872
  ,63200       4,2263   1,1082     1,2754      1,04921      ,82964
  ,68800       4,3409   1,0769     1,3181      1,03922      ,82673
  ,75200       4,2857   1,0577     1,3678      1,03665      ,82613
  ,84000       4,1944   1,0446     1,4437      1,03707      ,83086
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SYSTEM ACETIC ACID - N-PROPANOL AT CONST.PRESS. 760 MM HG
DATA OF AMER AMEZAGA,ANAL.REAL.SOC.ESP.FIS.QUIM,VOL 69,PG 58
7,NO 5,MAY 1973

                  THREE PARAMETER NRTL EQUATION

  LIQUID   EQUILIBRIUM DELTA     DELTA    ACTIVITY  ACTIVITY
MOLE FRAC   CONSTANT     A         B      COEFF 1   COEFF 2
  .84100      4.2925  1.0345    1.4471    1.02715    .83252
  .88600      4.1112  1.0416    1.4865    1.03809    .83628
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SYSTEM ACETIC ACID - ISØ-PRØPANØL AT CØNST PRESS 760 MM HG,
DATA ØF AMER AMEZAGA,ANAL,REAL,SØC,ESP,FIS,QUIM,VØL 69,PG 68
7,NØ 6,MAY 1973

                    THREE PARAMETER NRTL EQUATIØN

   NRTL PARAMETER 12 - -781,08 NRTL PARAMETER 21 -  307,04
                  NRTL PARAMETER ALPHA -     ,83255

  LIQUID     VAPØUR     VAPØUR     DELTA  EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC  Y*100  PRESS    PRESS    MM HG
            EXPTL      CALC
  ,04600     ,00700     ,00333       ,367 760,000 764,502 -4,502
  ,09500     ,02100     ,01358       ,742 760,000 748,613 11,387
  ,12400     ,02700     ,02374       ,326 760,000 750,125  9,876
  ,21100     ,06100     ,06088       ,012 760,000 750,232  9,768
  ,27700     ,09800     ,09763       ,037 760,000 752,895  7,105
  ,30700     ,11800     ,11742       ,058 760,000 765,841 -5,841
  ,35800     ,15700     ,15605       ,095 760,000 762,573 -2,573
  ,41400     ,20400     ,20254       ,146 760,000 759,786    ,214
  ,47400     ,27600     ,27365       ,235 760,000 772,492-12,492
  ,55600     ,35100     ,34745       ,355 760,000 767,856 -7,856
  ,60800     ,41100     ,40654       ,446 760,000 763,534 -3,534
  ,67400     ,50200     ,49625       ,575 760,000 759,152    ,848
  ,76400     ,63800     ,63008       ,792 760,000 762,132 -2,132
  ,81200     ,70100     ,69209       ,891 760,000 752,916  7,084
  ,86100     ,77900     ,76892     1,008 760,000 751,941  8,059
  ,90700     ,84000     ,82887     1,113 760,000 743,053 16,947
  ,97700     ,94900     ,93609     1,291 760,000 739,493 20,507

    SUM ØF SQUARES                              -      ,25840251E-02
    STANDARD ERRØR ØF ESTIMATE                  -      ,13585773E-01
    AVERAGE PRESSURE DEVIATIØN MM HG            -      ,10905767E+01
    AVERAGE VAPØUR DEVIATIØN*100                -      ,4993E+00
    NUMBER ØF FUNCTIØN EVALUATIØNS              -    1484

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY  ACTIVITY
MØLE FRAC   CØNSTANT    A          B       CØEFF 1   CØEFF 2
  ,04600      ,0002  3,6154    1,0000      ,59016     ,98859
  ,09500      ,0004  3,5637    1,0000      ,88744     ,95891
  ,12400      ,0022  3,5156    1,0000    1,07189     ,93677
  ,21100     1,4256  2,4502    1,0330    1,16253     ,89104
  ,27700     2,5858  1,9277    1,0672    1,14251     ,86128
  ,30700     3,0980  1,7485    1,0840    1,12160     ,84951
  ,35800     3,6781  1,5592    1,1118    1,11465     ,82870
  ,41400     4,2375  1,4007    1,1446    1,09658     ,80933
  ,47400     4,2592  1,3176    1,1770    1,10939     ,78986
  ,55600     5,0265  1,1585    1,2352    1,04544     ,77577
  ,60800     5,1440  1,1080    1,2717    1,03106     ,76824
  ,67400     4,9698  1,0808    1,3176    1,03460     ,76025
  ,76400     4,6971  1,0536    1,3861    1,03343     ,75685
  ,81200     4,6682  1,0372    1,4285    1,02555     ,75889
  ,86100     4,4672  1,0371    1,4709    1,03128     ,76149
  ,90700     4,4439  1,0249    1,5176    1,02250     ,76815
  ,97700     4,2269  1,0268    1,5899    1,02565     ,78006
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SYSTEM ACETIC ACID - N-BUTANØL
DATA ØF RIUS ET AL,CHEM ENG SCI,VØL 10,PP 105-111,1959 & ERR
ATA PG 288 FF

                    THREE PARAMETER NRTL EQUATIØN

    NRTL PARAMETER 12 -  191.20 NRTL PARAMETER 21 - -665.30
                  NRTL PARAMETER ALPHA -     .04798

   LIQUID     VAPØUR      VAPØUR     DELTA  EXPTL    CALC   DELTA P
 MØLE FRAC MØLE FRAC MØLE FRAC    Y*100  PRESS    PRESS   MM HG
              EXPTL        CALC
   .04600     .02000      .02024    -.024 706.400 693.632 12.768
   .08000     .04000      .04047    -.047 706.400 698.563  7.837
   .17600     .11100      .11225    -.125 705.600 697.954  7.646
   .26900     .21000      .21233    -.233 707.900 708.757  -.857
   .34300     .29800      .30126    -.326 707.900 707.542   .358
   .41000     .38600      .39023    -.423 707.900 708.836  -.936
   .45500     .44500      .44988    -.488 707.300 709.776 -2.476
   .51500     .52600      .53085    -.585 707.300 709.564 -2.264
   .54100     .56100      .56727    -.627 706.800 710.634 -3.834
   .64500     .68900      .69709    -.809 707.000 708.942 -1.942
   .69600     .74100      .74993    -.893 707.000 705.959  1.041
   .74600     .79100      .80092    -.992 706.700 702.932  3.768
   .76600     .81200      .82233   -1.033 707.000 704.175  2.825
   .83900     .87600      .88770   -1.170 706.800 703.790  3.010
   .88300     .91500      .92768   -1.268 706.900 707.396  -.496
   .89500     .92200      .93438   -1.238 700.700 700.496   .204
   .94000     .96100      .97445   -1.345 702.200 708.564 -6.364
   .98200     .99100     1.00000    -.900 702.200 712.738-10.538

     SUM ØF SQUARES                          -     .10027372E-02
     STANDARD ERRØR ØF ESTIMATE              -     .81761327E-02
     AVERAGE PRESSURE DEVIATIØN MM HG        -     .57674933E+00
     AVERAGE VAPØUR DEVIATIØN*100            -     .6959E+00
     NUMBER ØF FUNCTIØN EVALUATIØNS          -    1350

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
 MØLE FRAC  CØNSTANT    A          B        CØEFF 1    CØEFF 2
  .04600   10.6528  1.6819     1.0088      .95840   1.00757
  .08000    6.1861  1.6774     1.0156      .99322   1.01174
  .17600    3.9531  1.5327     1.0408     1.00353   1.02189
  .26900    3.1785  1.4491     1.0698     1.03613   1.02466
  .34300    3.0685  1.3715     1.0987     1.04408   1.02389
  .41000    3.0325  1.3132     1.1284     1.05250   1.01957
  .45500    3.0889  1.2705     1.1513     1.05105   1.01552
  .51500    3.1466  1.2265     1.1840     1.05449   1.00716
  .54100    3.1662  1.2105     1.1990     1.05687   1.00250
  .64500    3.3603  1.1476     1.2677     1.05706    .97990
  .69600    3.5432  1.1130     1.3077     1.04752    .96715
  .74600    3.6624  1.0933     1.3488     1.04770    .95135
  .76600    3.6960  1.0872     1.3658     1.04843    .94432
  .83900    3.9040  1.0608     1.4351     1.04251    .91761
  .88300    3.9681  1.0551     1.4793     1.04546    .89861
  .89500    4.0902  1.0429     1.4951     1.03514    .89506
  .94000    4.1278  1.0413     1.5442     1.03871    .87366
  .98200    4.2137  1.0368     1.5954     1.03656    .86357
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SYSTEM ACETIC ACID - 2-BUTANØL AT CØNST,PRESS 760,MM HG
DATA ØF AMER AMEZAGA,ANAL,REAL,SØC,ESP,FIS,QUIM,VØL 69,PG 58
7,NØ 5,MAY 1973

                    THREE PARAMETER NRTL EQUATIØN

  NRTL PARAMETER 12 - -737,86 NRTL PARAMETER 21 -    48,11
                    NRTL PARAMETER ALPHA -     3,30921

  LIQUID     VAPØUR     VAPØUR     DELTA   EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC    Y*100   PRESS    PRESS    MM HG
             EXPTL      CALC
  ,09300     ,02800     ,01289    1,511 760,000 797,534-37,534
  ,13600     ,05000     ,05083    -,083 760,000 741,192 18,808
  ,17200     ,07200     ,07321    -,121 760,000 734,545 25,455
  ,19300     ,08800     ,08946    -,146 760,000 736,916 23,084
  ,26800     ,14800     ,15042    -,242 760,000 740,960 19,040
  ,31500     ,19500     ,19816    -,316 760,000 753,562  6,438
  ,35300     ,23600     ,23982    -,382 760,000 764,261 -4,261
  ,45200     ,34600     ,35171    -,571 760,000 780,917-20,917
  ,53100     ,44500     ,45258    -,758 760,000 794,870-34,870
  ,60600     ,54200     ,55158    -,958 760,000 805,052-45,052
  ,68800     ,63600     ,64752   -1,152 760,000 805,167-45,167
  ,77300     ,75100     ,76550   -1,450 760,000 807,589-47,589
  ,82500     ,80100     ,81679   -1,579 760,000 797,767-37,767
  ,85600     ,38400     ,38962    -,562 760,000 495,099264,901
  ,87600     ,85700     ,87438   -1,738 760,000 790,513-30,513
  ,89500     ,88000     ,89803   -1,803 760,000 789,288-29,288
  ,92500     ,91300     ,93202   -1,902 760,000 784,775-24,775
  ,94900     ,93300     ,95253   -1,953 760,000 776,543-16,543

    SUM ØF SQUARES                               -     ,14824870E+00
    STANDARD ERRØR ØF ESTIMATE                   -     ,99414520E-01
    AVERAGE PRESSURE DEVIATIØN MM HG             -     ,62302369E+01
    AVERAGE VAPØUR DEVIATIØN*100                 -     ,9570E+00
    NUMBER ØF FUNCTIØN EVALUATIØNS               -    1292

  LIQUID  EQUILIBRIUM DELTA       DELTA     ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT    A           B        CØEFF 1    CØEFF 2
  ,09300      ,0001  3,0361     1,0000      ,47758     ,59047
  ,13600      ,2977  2,8037     1,0048     1,09430     ,53181
  ,17200     2,4139  1,9705     1,0316     1,09655     ,51467
  ,19300     3,3010  1,7470     1,0434     1,10676     ,50724
  ,26800     5,2979  1,3428     1,0826     1,09341     ,49294
  ,31500     5,5216  1,2460     1,1051     1,09328     ,49021
  ,35300     5,5121  1,1952     1,1235     1,09006     ,49038
  ,45200     5,3199  1,1113     1,1749     1,07022     ,49768
  ,53100     4,9450  1,0841     1,2184     1,06455     ,50850
  ,60600     4,6315  1,0688     1,2636     1,05952     ,52234
  ,68800     4,5443  1,0415     1,3216     1,03782     ,54257
  ,77300     4,1685  1,0528     1,3830     1,05159     ,56468
  ,82500     4,2372  1,0344     1,4308     1,03390     ,58325
  ,85600    18,5932   ,5576     1,5922      ,55744     ,64848
  ,87600     4,1965  1,0304     1,4788     1,03025     ,60208
  ,89500     4,1608  1,0312     1,4971     1,03111     ,60939
  ,92500     4,1370  1,0305     1,5281     1,03048     ,62179
  ,94900     4,2045  1,0214     1,5567     1,02137     ,63354
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SYSTEM ACETIC ACID - ISØ-BUTANØL  AT CØNST,PRESS,760 MM,HG
DATA ØF AMER AMEZAGA,ANAL,REAL,SØC,ESP,FIS,QUIM,VØL 69,PG 58
7,NØ 5,MAY 1973

                    TWØ PARAMETER WILSØN EQUATIØN

WILSØN PARAMETER 12 = ·258,92 WILSØN PARAMETER 21 = -846,58

  LIQUID     VAPØUR     VAPØUR     DELTA   EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC    Y*100   PRESS    PRESS    MM HG
            EXPTL      CALC
  ,01300    ,00400     ,00403    -,003 760,000 737,858 22,142
  ,04500    ,01600     ,01627    -,027 760,000 737,157 22,843
  ,09300    ,04100     ,04169    -,069 760,000 744,808 15,192
  ,11400    ,05700     ,05794    -,094 760,000 750,737  9,263
  ,18400    ,10300     ,10471    -,171 760,000 751,170  8,830
  ,25000    ,17300     ,17585    -,285 760,000 767,922 -7,922
  ,31100    ,23100     ,23482    -,382 760,000 770,035-10,035
  ,38900    ,32500     ,33054    -,554 760,000 768,903 -8,903
  ,42200    ,36300     ,36926    -,626 760,000 766,276 -6,276
  ,45400    ,40800     ,41515    -,715 760,000 766,243 -6,243
  ,54900    ,51500     ,52445    -,945 760,000 753,272  6,728
  ,66500    ,66300     ,66683   -1,283 760,000 744,845 15,155
  ,73600    ,72900     ,74382   -1,482 760,000 742,450 17,550
  ,76800    ,75700     ,77257   -1,557 760,000 746,054 13,946
  ,79000    ,79000     ,80641   -1,641 760,000 747,449 12,551
  ,80300    ,80000     ,81680   -1,680 760,000 744,676 15,324
  ,82000    ,82100     ,83834   -1,734 760,000 748,937 11,063
  ,83700    ,84200     ,85992   -1,792 760,000 753,084  6,916
  ,88500    ,88900     ,90842   -1,942 760,000 756,901  3,099
  ,90900    ,91900     ,93946   -2,046 760,000 764,550 -4,550
  ,91100    ,91300     ,93309   -2,009 760,000 759,453   ,547
  ,93000    ,92700     ,94766   -2,066 760,000 758,802  1,198
  ,93600    ,93900     ,96017   -2,117 760,000 764,294 -4,294
  ,98900    ,98900    1,00000   -1,100 760,000 774,593-14,593

     SUM ØF SQUARES                           =      ,57671707E-02
     STANDARD ERRØR ØF ESTIMATE               =      ,16190865E-01
     AVERAGE PRESSURE DEVIATIØN MM HG         =      ,13440917E+01
     AVERAGE VAPØUR DEVIATIØN*100             =      ,1097E+01
     NUMBER ØF FUNCTIØN EVALUATIØNS           =      242

  LIQUID  EQUILIBRIUM DELTA     DELTA     ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT    A         B       CØEFF 1    CØEFF 2
  ,01300       ,0566  2,8749    1,0000    1,06448     ,99976
  ,04500       ,6290  2,7214    1,0011    1,09947     ,99840
  ,09300       ,8580  2,5002    1,0058    1,13833     ,99454
  ,11400       ,7149  2,4851    1,0072    1,18725     ,99069
  ,18400      1,5450  2,0294    1,0277    1,11759     ,98680
  ,25000      1,5813  1,8719    1,0457    1,15580     ,97414
  ,31100      2,0503  1,6502    1,0727    1,11483     ,96594
  ,38900      2,3136  1,4980    1,1076    1,11471     ,94804
  ,42200      2,4831  1,4329    1,1252    1,10482     ,94048
  ,45400      2,5251  1,3980    1,1409    1,11248     ,93078
  ,54900      3,0169  1,2552    1,2006    1,08118     ,90553
  ,66500      3,3828  1,1572    1,2819    1,06981     ,86749
  ,73600      3,6385  1,1060    1,3403    1,05471     ,84384
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SYSTEM ACETIC ACID - ISO-BUTANOL AT CONST.PRESS.760 MM.HG
DATA OF AMER AMEZAGA,ANAL.REAL.SOC.ESP.FIS.QUIM,VOL 69,PG 58
7,NO 5,MAY 1973

TWO PARAMETER WILSON EQUATION

LIQUID MOLE FRAC	EQUILIBRIUM CONSTANT	DELTA A	DELTA B	ACTIVITY COEFF 1	ACTIVITY COEFF 2
.75800	3.6588	1.0980	1.3583	1.05541	.83560
.79000	3.7707	1.0780	1.3878	1.04669	.82496
.80300	3.8183	1.0724	1.4003	1.04509	.82032
.82000	3.8408	1.0657	1.4160	1.04314	.81424
.83700	3.8487	1.0617	1.4317	1.04330	.80781
.88500	3.9407	1.0477	1.4805	1.03881	.79041
.90900	3.8878	1.0528	1.5034	1.04718	.77999
.91100	4.0110	1.0379	1.5093	1.03259	.78163
.93000	4.0628	1.0333	1.5312	1.03003	.77492
.93600	3.9797	1.0427	1.5351	1.03998	.77102
.98900	4.0385	1.0354	1.5977	1.03528	.75207

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SYSTEM ACETIC ACID - TERT,BUTANOL AT CONST PRESS 760 MM HG
DATA OF AMER AMEZAGA,ANAL,REAL,SOC,ESP,FIS,QUIM,VOL 69,PG 58
7,NO 5 MAY 1973

                    THREE PARAMETER NRTL EQUATION

  NRTL PARAMETER 12 =-1155,03 NRTL PARAMETER 21 =  460,10
                    NRTL PARAMETER ALPHA =      ,32992

  LIQUID      VAPOUR      VAPOUR     DELTA   EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC  Y*100   PRESS    PRESS    MM HG
              EXPTL       CALC
  ,10300      ,01800      ,01378       ,422 760,000 710,310 49,690
  ,15400      ,03100      ,03152      -,052 760,000 717,319 42,681
  ,20200      ,05400      ,06498      -,098 760,000 721,431 38,669
  ,24400      ,07800      ,07937      -,137 760,000 744,642 15,358
  ,27100      ,09200      ,09359      -,159 760,000 747,874 12,126
  ,31600      ,12900      ,13116      -,216 760,000 762,980 -2,980
  ,35900      ,16400      ,16668      -,268 760,000 765,794 -5,794
  ,39200      ,19300      ,19611      -,311 760,000 770,560-10,560
  ,43300      ,23400      ,23771      -,371 760,000 774,307-14,307
  ,46100      ,26900      ,27320      -,420 760,000 784,920-24,920
  ,49900      ,31100      ,31585      -,485 760,000 782,018-22,018
  ,53600      ,35400      ,35945      -,545 760,000 785,802-25,802
  ,60000      ,42300      ,42956      -,656 760,000 768,228 -8,228
  ,63300      ,46800      ,47537      -,737 760,000 763,641 -3,641
  ,68900      ,53000      ,53849      -,849 760,000 745,936 14,064
  ,72700      ,59000      ,59968      -,968 760,000 746,891 13,109
  ,79900      ,69800      ,70993     -1,193 760,000 747,417 12,683
  ,84400      ,75600      ,76924     -1,324 760,000 742,415 17,685
  ,88400      ,82500      ,83993     -1,493 760,000 752,261  7,749
  ,91600      ,86200      ,87775     -1,575 760,000 748,800 11,200
  ,94000      ,90400      ,92080     -1,680 760,000 757,226  2,774
  ,94500      ,89900      ,91566     -1,666 760,000 748,537 11,463

    SUM OF SQUARES                              =      ,16606598E-01
    STANDARD ERROR OF ESTIMATE                  =      ,29474876E-01
    AVERAGE PRESSURE DEVIATION MM HG            =      ,23092704E+01
    AVERAGE VAPOUR DEVIATION*100                =      ,7102E+00
    NUMBER OF FUNCTION EVALUATIONS              =     1422

  LIQUID   EQUILIBRIUM DELTA      DELTA      ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT     A          B        COEFF 1    COEFF 2,
  ,10300        ,0007  3,5599    1,0000      ,84439     ,96518
  ,15400        ,1058  3,3799    1,0024     1,04954     ,93226
  ,20200        ,5186  2,9347    1,0157     1,12468     ,90516
  ,24400       1,0163  2,5064    1,0343     1,12498     ,88449
  ,27100       1,4572  2,2446    1,0498     1,10026     ,87256
  ,31600       1,8133  2,0073    1,0705     1,11975     ,84715
  ,35900       2,2854  1,7918    1,0947     1,10908     ,82480
  ,39200       2,6605  1,6491    1,1147     1,09396     ,80835
  ,43300       3,0369  1,5152    1,1395     1,08292     ,78758
  ,46100       3,1899  1,4469    1,1559     1,08145     ,77337
  ,49900       3,4869  1,3586    1,1808     1,07047     ,75513
  ,53600       3,7903  1,2769    1,2066     1,05166     ,73910
  ,60000       4,2892  1,1700    1,2546     1,02488     ,71229
  ,63300       4,3535  1,1409    1,2782     1,02540     ,69817
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SYSTEM ACETIC ACID - TERT.BUTANOL AT CONST PRESS 760 MM HG
DATA OF AMER AMEZAGA,ANAL.REAL.SOC.ESP.FIS.QUIM,VOL 69,PG 58
7,NO 5 MAY 1973

                    THREE PARAMETER NRTL EQUATION

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY  ACTIVITY
MOLE FRAC   CONSTANT     A          B       COEFF 1   COEFF 2
  .68900     4.6710   1.0803     1.3245    1.00583    .67783
  .72700     4.5882   1.0678     1.3532    1.01327    .66336
  .79900     4.5086   1.0438     1.4132    1.01699    .63981
  .84400     4.5388   1.0270     1.4559    1.01184    .62773
  .88400     4.3414   1.0327     1.4908    1.02464    .61632
  .91600     4.4005   1.0191     1.5261    1.01507    .61046
  .94000     4.2784   1.0239     1.5489    1.02186    .60490
  .94500     4.3861   1.0147     1.5577    1.01308    .60498
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SYSTEM ACETIC ACID - ETHYL ACETATE AT 30 CENT
DATA OF MEEHAN


                     TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 - -409.53 WILSON PARAMETER 21 - 1014.78

  LIQUID     VAPOUR     VAPOUR     DELTA   EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100   PRESS    PRESS    MM HG
            EXPTL      CALC
  .12590    .01840     .01850     -.010 108.300 107.500     .800
  .25310    .04640     .04662     -.022  98.000  97.989     .011
  .38480    .09140     .09161     -.021  85.800  86.423    -.623
  .53170    .17120     .17111      .009  70.900  71.507    -.607
  .60670    .23100     .23058      .042  63.600  63.370     .230
  .80120    .50190     .49898      .292  42.000  41.806     .194
  .89250    .70210     .69681      .529  32.600  32.665    -.065

    SUM OF SQUARES                              -     .21903491E-03
    STANDARD ERROR OF ESTIMATE                  -     .66186843E-02
    AVERAGE PRESSURE DEVIATION MM HG            -     .47936042E+00
    AVERAGE VAPOUR DEVIATION*100                -     .1320E+00
    NUMBER OF FUNCTION EVALUATIONS              -     347

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT     A         B       COEFF 1    COEFF 2
  .12590    36.9532   2.0693    1.0480    1.54637    1.04395
  .25310    35.8552   1.6025    1.1128    1.26830    1.09357
  .38480    36.4256   1.3686    1.1932    1.15035    1.13964
  .53170    38.4307   1.2053    1.3018    1.08218    1.17516
  .60670    39.0736   1.1536    1.3660    1.06929    1.18224
  .80120    40.1663   1.0744    1.5690    1.06335    1.16001
  .89250    39.9913   1.0624    1.6875    1.06583    1.16088
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SYSTEM ACETIC ACID - ETHYL ACETATE AT 50 CENT
DATA OF MEEHAN


                    TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 - -242.91 WILSON PARAMETER 21 -  385.19

  LIQUID     VAPOUR      VAPOUR     DELTA   EXPTL     CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100   PRESS     PRESS    MM HG
             EXPTL       CALC
  .13850     .02640     .02664     -.024 252.200 250.980   1.220
  .29130     .06850     .06903     -.053 224.900 224.931   -.031
  .41150     .11620     .11670     -.050 201.200 200.969    .231
  .50540     .17040     .17064     -.024 180.700 180.468    .232
  .63370     .27410     .27327      .083 150.000 149.605    .395
  .73010     .39800     .39536      .264 124.600 125.222   -.622
  .86840     .64980     .64219      .761  89.600  89.462    .138

     SUM OF SQUARES                              -     .60647525E-04
     STANDARD ERROR OF ESTIMATE                  -     .34827439E-02
     AVERAGE PRESSURE DEVIATION MM HG            -     .23682567E+00
     AVERAGE VAPOUR DEVIATION*100                -     .1799E+00
     NUMBER OF FUNCTION EVALUATIONS              -     246

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT     A          B       COEFF 1    COEFF 2
  .13850    19.9909   1.9126    1.0481    1.54231    1.04446
  .29130    20.0923   1.4594    1.1244    1.23693    1.10519
  .41150    20.7265   1.2818    1.1976    1.12909    1.15260
  .50540    20.8052   1.2017    1.2629    1.08977    1.18577
  .63370    21.5107   1.1152    1.3681    1.04955    1.22242
  .73010    21.4165   1.0839    1.4596    1.04544    1.23718
  .86840    21.8429   1.0470    1.6187    1.03680    1.23323
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SYSTEM ACETIC ACID - ETHYL ACETATE AT 70 CENT
DATA OF MEEHAN


                    THREE PARAMETER NRTL EQUATION

  NRTL PARAMETER 12 - -448.57 NRTL PARAMETER 21 -  770.62
                  NRTL PARAMETER ALPHA -     .77665

  LIQUID     VAPOUR     VAPOUR     DELTA  EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC  Y*100  PRESS    PRESS    MM HG
            EXPTL       CALC
  .13570    .03210     .03312    -.102 539.300 530.899   8.401
  .29270    .08240     .08452    -.212 481.600 482.244   -.644
  .41900    .13670     .13860    -.190 432.200 431.926    .274
  .52190    .19710     .19765    -.055 384.300 384.958   -.658
  .62080    .27490     .27253     .237 336.600 336.123    .477
  .76530    .45510     .44163    1.347 255.600 258.058 -2.458
  .86790    .64360     .61396    2.964 203.400 201.241  2.159

    SUM OF SQUARES                          -     .45496322E-03
    STANDARD ERROR OF ESTIMATE              -     .10664933E-01
    AVERAGE PRESSURE DEVIATION MM HG        -     .69388613E+00
    AVERAGE VAPOUR DEVIATION*100            -     .7295E+00
    NUMBER OF FUNCTION EVALUATIONS          -     760

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
 MOLE FRAC   CONSTANT    A          B        COEFF 1    COEFF 2
  .13570    12.5063   1.7937    1.0418    1.63385    1.04910
  .29270    11.5453   1.4258    1.1134    1.28991    1.12154
  .41900    12.2568   1.2411    1.1869    1.15144    1.17865
  .52190    12.9999   1.1363    1.2578    1.07876    1.22363
  .62080    13.6177   1.0658    1.3362    1.03173    1.26658
  .76530    14.2833   1.0008    1.4725     .98885    1.33282
  .86790    14.4443    .9793    1.5884     .97566    1.38533
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SYSTEM ACETIC ACID - N-BUTYL ACETATE
DATA ØF JAPANESE


                        THREE PARAMETER NRTL EQUATIØN

  NRTL PARAMETER 12 = -128,89 NRTL PARAMETER 21 = 9059,87
                    NRTL PARAMETER ALPHA =      ,41033

  LIQUID      VAPØUR      VAPØUR     DELTA   EXPTL     CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC  Y*100   PRESS     PRESS    MM HG
             EXPTL       CALC
  ,03796     ,04353     ,04370    -,016 760,000 758,442  1,558
  ,14893     ,18167     ,18193    -,026 760,000 761,958 -1,958
  ,19287     ,18968     ,18999    -,031 760,000 744,156 15,844
  ,19762     ,22414     ,22428    -,014 760,000 762,951 -2,951
  ,28797     ,36608     ,36583     ,025 760,000 759,523   ,477
  ,34754     ,44124     ,44032     ,092 760,000 769,970 -9,970
  ,49115     ,58134     ,57906     ,228 760,000 764,231 -4,231
  ,55486     ,63626     ,63333     ,293 760,000 759,204   ,796
  ,56413     ,65639     ,65307     ,332 760,000 766,833 -6,833
  ,57632     ,67859     ,67504     ,355 760,000 770,923-10,923
  ,61936     ,70517     ,70131     ,386 760,000 762,474 -2,474
  ,65819     ,73801     ,73350     ,451 760,000 762,853 -2,853
  ,73399     ,78440     ,77916     ,525 760,000 750,883  9,117
  ,83461     ,88168     ,87480     ,688 760,000 757,822  2,178
  ,89928     ,89054     ,88352     ,702 760,000 729,750 30,250
  ,90910     ,92943     ,92173     ,770 760,000 750,731  9,269

    SUM ØF SQUARES                          =     ,28622695E-02
    STANDARD ERRØR ØF ESTIMATE              =     ,14838281E-01
    AVERAGE PRESSURE DEVIATIØN MM HG        =     ,10290943E+01
    AVERAGE VAPØUR DEVIATIØN*100            =     ,3083E+00
    NUMBER ØF FUNCTIØN EVALUATIØNS          =    1843

  LIQUID  EQUILIBRIUM DELTA      DELTA      ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT    A          B        CØEFF 1    CØEFF 2
  ,03796    15,7139  1,4879    1,0079     1,89901    1,07953
  ,14893     2,3495  1,7560    1,0249     1,59441    1,12065
  ,19287     4,2020  1,4068    1,0477     1,27829    1,14522
  ,19762     2,9668  1,5457    1,0429     1,40545    1,14009
  ,28797     2,1294  1,5710    1,0666     1,44975    1,15703
  ,34754     2,2436  1,4805    1,0895     1,38288    1,17623
  ,49115     2,7607  1,2883    1,1640     1,23575    1,23141
  ,55486     2,9866  1,2257    1,2034     1,18736    1,25865
  ,56413     2,9032  1,2325    1,2069     1,19554    1,26038
  ,57632     2,8023  1,2450    1,2117     1,20966    1,26211
  ,61936     3,0270  1,1985    1,2433     1,17102    1,28358
  ,65819     3,1633  1,1665    1,2720     1,14499    1,30270
  ,73399     3,5432  1,1026    1,3364     1,09029    1,34492
  ,83461     3,5598  1,0916    1,4211     1,08696    1,39271
  ,89928     4,1808  1,0217    1,5021     1,02011    1,44621
  ,90910     3,8092  1,0617    1,5009     1,06035    1,44010
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SYSTEM ACETIC ACID - CYCLØHEXYL ACETATE AT 760 MM HG
DATA ØF ØTHMER,IND.ENG.CHEM,35,614 (1943)


                    THREE PARAMETER NRTL EQUATIØN

   NRTL PARAMETER 12 =-1800.34 NRTL PARAMETER 21 = 3544.28
              NRTL PARAMETER ALPHA =      .20091

  LIQUID      VAPØUR      VAPØUR     DELTA   EXPTL     CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC    Y*100   PRESS     PRESS    MM HG
            EXPTL       CALC
   .02000     .36500     .20606   15.894 760.000 748.725 11.275
   .05000     .47000     .38949    8.051 760.000 775.796-15.796
   .10000     .55900     .53012    2.888 760.000 757.132  2.868
   .20000     .65500     .66042    -.542 760.000 749.959 10.041
   .30000     .73100     .74129   -1.029 760.000 738.610 21.390
   .40000     .79600     .81103   -1.503 760.000 742.534 17.466
   .50000     .85300     .87288   -1.988 760.000 751.110  8.890
   .60000     .90000     .92475   -2.475 760.000 760.290  -.290
   .70000     .93700     .96598   -2.898 760.000 770.339-10.339
   .80000     .96400     .99651   -3.251 760.000 777.760-17.760
   .90000     .98300    1.00000   -1.700 760.000 782.715-22.715

     SUM ØF SQUARES                          =      .39225419E-02
     STANDARD ERRØR ØF ESTIMATE              =      .22143119E-01
     AVERAGE PRESSURE DEVIATIØN MM HG        =      .18653504E+01
     AVERAGE VAPØUR DEVIATIØN*100            =      .38381E+01
     NUMBER ØF FUNCTIØN EVALUATIØNS          =    2606

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT     A          B       CØEFF 1    CØEFF 2
   .02000      .0006   1.8861    1.0000    4.11898    1.00161
   .05000      .0018   1.9454    1.0000    3.42168    1.00913
   .10000      .0048   2.0370    1.0000    2.69836    1.03086
   .20000      .1914   2.0123    1.0068    1.93590    1.09079
   .30000      .3796   1.9201    1.0251    1.62992    1.14725
   .40000      .6728   1.7470    1.0613    1.45491    1.18814
   .50000     1.0391   1.5769    1.1132    1.35042    1.20347
   .60000     1.4707   1.4327    1.1792    1.28326    1.19006
   .70000     2.0222   1.2956    1.2617    1.21400    1.15665
   .80000     2.6600   1.1831    1.3601    1.14881    1.10722
   .90000     3.3702   1.0930    1.4764    1.08496    1.04919
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SYSTEM ACETIC ACID - VINYL ACETATE AT 760 MM HG
DATA ØF CZECHS,CØLL,CZECH,CHEM,CØMM,28,1963,PG 2236


                    TWØ PARAMETER WILSØN EQUATIØN

WILSØN PARAMETER 12 - 1730,44 WILSØN PARAMETER 21 - -852,85

  LIQUID     VAPØUR     VAPØUR     DELTA  EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC    Y*100  PRESS    PRESS    MM HG
             EXPTL      CALC
  ,19800     ,07800     ,07777     ,023 760,000 740,501 19,499
  ,32400     ,13500     ,13497     ,003 760,000 764,129 -4,129
  ,43100     ,17800     ,17847    -,047 760,000 755,336  4,664
  ,45100     ,18900     ,18960    -,060 760,000 768,763 -8,763
  ,55900     ,25100     ,25271    -,171 760,000 770,730-10,730
  ,56800     ,25800     ,25983    -,183 760,000 776,631-16,631
  ,68100     ,34500     ,34914    -,414 760,000 757,444  2,556
  ,75600     ,42900     ,43602    -,702 760,000 751,270  8,730
  ,83000     ,53900     ,55025   -1,125 760,000 763,551 -3,551
  ,83500     ,54100     ,55260   -1,160 760,000 745,956 14,044
  ,87800     ,62900     ,64469   -1,569 760,000 755,716  4,284
  ,89600     ,66900     ,68690   -1,790 760,000 753,475  6,525
  ,94100     ,78400     ,80863   -2,453 760,000 756,175  3,825
  ,97800     ,90400     ,93609   -3,209 760,000 767,967 -7,967

    SUM ØF SQUARES                           -    ,22838958E-02
    STANDARD ERRØR ØF ESTIMATE               -    ,13795820E-01
    AVERAGE PRESSURE DEVIATIØN MM HG         -    ,10892704E+01
    AVERAGE VAPØUR DEVIATIØN*100             -    ,9222E+00
    NUMBER ØF FUNCTIØN EVALUATIØNS           -    562

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MØLF FRAC   CØNSTANT     A          B       CØEFF 1    CØEFF 2
  ,19800      6,3201   1,9037    1,0571    2,10069    1,11448
  ,32400      5,7127   1,6471    1,1104    1,68327    1,20261
  ,43100      6,2639   1,4355    1,1698    1,43693    1,28401
  ,45100      6,3914   1,3891    1,1822    1,38853    1,41020
  ,55900      6,6557   1,2461    1,2527    1,24091    1,38689
  ,56800      6,6837   1,2311    1,2591    1,22601    1,39475
  ,68100      6,6093   1,1422    1,3435    1,13833    1,49147
  ,75600      6,2688   1,1039    1,4037    1,10163    1,55928
  ,83000      6,0282   1,0434    1,4706    1,04236    1,63679
  ,83500      5,9102   1,0606    1,4737    1,05952    1,63843
  ,87800      5,5772   1,0379    1,5124    1,03739    1,68402
  ,89600      5,3513   1,0413    1,5273    1,04093    1,70082
  ,94100      4,8585   1,0374    1,5662    1,03730    1,74663
  ,97800      4,3872   1,0363    1,5962    1,03630    1,78376
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SYSTEM ACETIC ACID - ACETØNE AT CØNSTAN TEMPERATURE 30 CENT
DATA ØF MEEHAN AND MURPHY CHEM ENG SCIENCE,1965,VØL 20,PP 75
7-769

                    TWØ PARAMETER WILSØN EQUATIØN

WILSØN PARAMETER 12 -  300,42 WILSØN PARAMETER 21 - -639,39

  LIQUID     VAPØUR     VAPØUR    DELTA  EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC   Y*100  PRESS    PRESS    MM HG
            EXPTL      CALC
  ,12640     ,00450     ,00449     ,001 243,500 248,122 -4,622
  ,27580     ,01700     ,01696     ,004 203,900 207,271 -3,371
  ,38640     ,03440     ,03418     ,022 176,000 175,089    ,911
  ,45940     ,05270     ,05220     ,050 155,200 154,285    ,915
  ,51870     ,07180     ,07095     ,085 139,200 137,881   1,319
  ,70680     ,16980     ,16660     ,330  88,000  88,003   -,003
  ,84900     ,34400     ,33546     ,854  51,800  52,084   -,284

    SUM ØF SQUARES                          -     ,81481964E-03
    STANDARD ERRØR ØF ESTIMATE              -     ,12765733E-01
    AVERAGE PRESSURE DEVIATIØN MM HG        -     ,87950316E+00
    AVERAGE VAPØUR DEVIATIØN*100            -     ,1921E+00
    NUMBER ØF FUNCTIØN EVALUATIØNS          -     421

  LIQUID   EQUILIBRIUM DELTA      DELTA      ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT     A          B        CØEFF 1    CØEFF 2
  ,12640    37,0161   2,0647    1,0482    1,04897    1,02147
  ,27580    42,3880   1,4414    1,1281     ,98638    1,02179
  ,38640    45,2600   1,2393    1,1984     ,97686    1,01276
  ,45940    46,1772   1,1592    1,2504     ,97798    1,00553
  ,51870    47,3189   1,1040    1,2967     ,97296    1,00021
  ,70680    55,2594    ,9485    1,4749     ,91232     ,99312
  ,84900    60,2585    ,8830    1,6476     ,87505    1,00076
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SYSTEM ACETIC ACID = ACETØNE AT CØNSTANT TEMPERATURE 40 CENT
DATA ØF MEEHAN AND MURPHY,CHEM ENG.SCIENCE,1965,VØL 20 PP 75
7-769

                  THREE PARAMETER NRTL EQUATIØN

  NRTL PARAMETER 12 = -685.41 NRTL PARAMETER 21 =  864.46
                  NRTL PARAMETER ALPHA =      .69220

  LIQUID      VAPØUR     VAPØUR    DELTA  EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC  Y*100  PRESS    PRESS    MM HG
            EXPTL       CALC
  .15550     .00720     .00717     .003 362.100 362.706  -.606
  .32220     .02680     .02672     .008 292.900 293.797  -.897
  .43840     .05450     .05397     .053 242.700 243.004  -.304
  .48430     .07000     .06916     .084 224.700 223.732   .968
  .57930     .11150     .10961     .189 187.000 185.154  1.846
  .76250     .25750     .25061     .689 112.200 114.146 -1.946
  .94340     .67230     .64873    2.357  49.400  48.638   .762

    SUM ØF SQUARES                         =    .66834005E-03
    STANDARD ERRØR ØF ESTIMATE             =    .12926137E-01
    AVERAGE PRESSURE DEVIATIØN MM HG       =    .87348055E+00
    AVERAGE VAPØUR DEVIATIØN*100           =    .4834E+00
    NUMBER ØF FUNCTIØN EVALUATIØNS         =   1341

  LIQUID  EQUILIBRIUM DELTA      DELTA    ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT    A          B      CØEFF 1    CØEFF 2
  .15550    27.1243  1.8642    1.0590    1.04283    1.02558
  .32220    30.5933  1.3518    1.1503     .99825    1.02287
  .43840    31.8505  1.1960    1.2267     .99873    1.01221
  .48430    32.0638  1.1658    1.2601    1.00096    1.00785
  .57930    33.3794  1.0780    1.3370     .98964    1.00132
  .76250    38.0151   .9546    1.5215     .93359    1.00414
  .94340    38.8613   .9215    1.7605     .92055    1.03135
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SYSTEM ACETIC ACID - ACETONE AT CONSTANT TEMPERATURE 50 CENT
DATA OF MEEHAN AND MURPHY,CHEM ENG SCIENCE,1965,VOL 20 PP 75
7-769

                    THREE PARAMETER NRTL EQUATION

  NRTL PARAMETER 12 --1331,86 NRTL PARAMETER 21 - 1762,91
                    NRTL PARAMETER ALPHA -      ,23442

  LIQUID     VAPOUR     VAPOUR    DELTA   FXPTL     CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC  Y*100   PRESS     PRESS    MM HG
            EXPTL      CALC
  ,15610    ,00820     ,00814     ,006 533,400 533,435   -,035
  ,29970    ,02610     ,02597     ,013 455,900 456,598   -,698
  ,43710    ,06110     ,06017     ,093 370,700 369,534   1,166
  ,46910    ,07200     ,07071     ,129 348,000 348,769   -,769
  ,58450    ,13580     ,13225     ,355 277,100 276,462    ,648
  ,73470    ,27900     ,26882    1,018 186,600 187,399   -,799
  ,82930    ,42350     ,40558    1,792 135,200 134,858    ,342

    SUM OF SQUARES                          -      ,47301633E-04
    STANDARD ERROR OF FSTIMATE              -      ,34388091E-02
    AVERAGE PRESSURE DEVIATION MM HG        -      ,29685639E+00
    AVERAGE VAPOUR DEVIATION*100            -      ,4865E+00
    NUMBER OF FUNCTION EVALUATIONS          -    2989

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY  ACTIVITY
MOLE FRAC   CONSTANT    A          B        COEFF 1   COEFF 2
  ,15610    24,1942   1,6957    1,0581    1,03740   1,04431
  ,29970    20,5046   1,4327    1,1295    1,02096   1,06525
  ,43710    20,1203   1,2739    1,2137    1,03091   1,06282
  ,46910    20,7718   1,2294    1,2367    1,02049   1,06038
  ,58450    20,3034   1,1671    1,3237    1,04653   1,04174
  ,73470    21,6408   1,0777    1,4648    1,03382   1,01213
  ,82930    23,3961   1,0208    1,5745    1,00421    ,99448
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SYSTEM ACETIC ACID - ACETONE AT 760 MM HG
DATA OF LONGEST


                    THREE PARAMETER NRTL EQUATION

   NRTL PARAMETER 12 - -137.55 NRTL PARAMETER 21 -  399.45
                NRTL PARAMETER ALPHA -    2.53271

   LIQUID     VAPOUR     VAPOUR     DELTA  EXPTL    CALC    DELTA P
 MOLE FRAC MOLE FRAC MOLE FRAC  Y*100  PRESS    PRESS    MM HG
            EXPTL      CALC
   .09650    .00190     .00185      .005 760.000 756.324   3.676
   .11200    .00300     .00292      .008 760.000 757.228   2.772
   .17500    .00730     .00711      .019 760.000 757.709   2.291
   .27800    .01600     .01556      .044 760.000 746.110  13.890
   .35140    .02680     .02598      .082 760.000 752.048   7.952
   .37230    .03070     .02973      .097 760.000 752.424   7.576
   .43140    .04680     .04517      .163 760.000 763.176  -3.176
   .52520    .06780     .08423      .357 760.000 784.847-24.847
   .64030    .15210     .14493      .717 760.000 774.171-14.171
   .75190    .26300     .24869     1.431 760.000 751.635   8.365
   .83770    .43220     .40498     2.722 760.000 750.076   9.924
   .94940    .80140     .73474     6.666 760.000 731.814  28.186

     SUM OF SQUARES                          -     .36896388E-02
     STANDARD ERROR OF ESTIMATE              -     .20247466E-01
     AVERAGE PRESSURE DEVIATION MM HG        -     .15239761E+01
     AVERAGE VAPOUR DEVIATION*100            -     .1026E+01
     NUMBER OF FUNCTION EVALUATIONS          -     750

   LIQUID   EQUILIBRIUM DELTA      DELTA      ACTIVITY   ACTIVITY
 MOLE FRAC   CONSTANT     A          B        COEFF 1    COEFF 2
   .09650   403.1150   .5337     1.0451     .54262    1.05506
   .11200   218.0778   .6634     1.0512     .66380    1.06318
   .17500    90.2526   .8106     1.0796     .78145    1.09868
   .27800    54.9580   .8251     1.1329     .78518    1.15727
   .35140    40.6169   .8426     1.1735     .80587    1.19693
   .37230    37.6126   .8476     1.1856     .81236    1.20808
   .43140    28.9167   .8796     1.2195     .84903    1.23815
   .52520    19.7628   .9251     1.2760     .90293    1.28546
   .64030    15.6197   .9115     1.3594     .89948    1.35295
   .75190    11.8224   .9195     1.4467     .91412    1.42204
   .83770     8.5690   .9506     1.5107     .94843    1.47259
   .94940     5.5648   .9780     1.5930     .97478    1.53986
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SYSTEM ACETIC ACID - DIETHYLKETØNE AT 70 CENT
DATA ØF HADDAD & EDMISTER,J.CHEM.ENG.DAT.,17(3),1972,PG 276


                  THREE PARAMETER NRTL EQUATIØN

   NRTL PARAMETER 12 = -224.63 NRTL PARAMETER 21 =*********
                  NRTL PARAMETER ALPHA =     .03701

  LIQUID      VAPØUR      VAPØUR    DELTA   EXPTL     CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC  Y*100   PRESS     PRESS    MM HG
            EXPTL       CALC
  .02550     .00920     .00906       .014 259.500 232.577 26.923
  .06380     .02560     .02525       .035 245.700 243.988  1.712
  .09960     .04560     .04500       .060 245.200 244.173  1.027
  .11770     .05610     .05537       .073 242.100 243.124 -1.024
  .18040     .09590     .09471       .119 232.200 237.610 -5.410
  .31240     .18750     .18545       .205 216.600 221.957 -5.367
  .35310     .21750     .21521       .229 211.300 216.302 -5.002
  .43710     .29050     .28778       .272 203.500 205.446 -1.946
  .50080     .34510     .34207       .303 194.200 195.455 -1.255
  .61760     .48900     .48551       .349 178.100 180.405 -2.305
  .67660     .54980     .54630       .350 173.800 172.716  1.084
  .74780     .64650     .64310       .340 166.900 165.331  1.569
  .81050     .72930     .72601       .329 160.100 158.094  2.006
  .87560     .80080     .79753       .327 152.900 148.542  4.358
  .95560     .93170     .92887       .283 144.600 143.059  1.541

     SUM ØF SQUARES                           =     .14073600E-01
     STANDARD ERRØR ØF ESTIMATE               =     .34246249E-01
     AVERAGE PRESSURE DEVIATIØN MM HG         =     .28187943E+01
     AVERAGE VAPØUR DEVIATIØN*100             =     .2192E+00
     NUMBER ØF FUNCTIØN EVALUATIØNS           =    3843

  LIQUID   EQUILIBRIUM DELTA        DELTA      ACTIVITY    ACTIVITY
MØLE FRAC   CØNSTANT     A            B        CØEFF 1     CØEFF 2
  .02550   3618.0538   .3007      1.0120      1.94881     1.54025
  .06380     38.1151  1.5444      1.0209      1.67938     1.66387
  .09960     15.4998  1.8435      1.0295      1.63253     1.70710
  .11770     13.1387  1.8487      1.0351      1.58187     1.72354
  .18040     10.5686  1.7340      1.0583      1.44201     1.77006
  .31240     10.7906  1.4338      1.1221      1.23751     1.86242
  .35310     11.2449  1.3560      1.1454      1.18835     1.87647
  .43710     11.6242  1.2570      1.1962      1.13586     1.92091
  .50080     12.3918  1.1727      1.2410      1.08235     1.95596
  .61760     12.2938  1.1146      1.3285      1.06311     2.00823
  .67660     12.6800  1.0780      1.3804      1.04209     2.03589
  .74780     12.5212  1.0633      1.4464      1.04159     2.06440
  .81050     12.6589  1.0452      1.5123      1.03308     2.09116
  .87560     13.3521  1.0123      1.5915      1.00722     2.12386
  .95560     12.8054  1.0247      1.6923      1.02401     2.15373
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SYSTEM ACETIC ACID - ETHYL ETHER AT CONSTANT PRESSURE 389,7
DATA OF MEEHAN AND MURPHY,CHEM ENG SCIENCE,1965,VOL 20 PP 75
7-769

                    THREE PARAMETER NRTL EQUATION

  NRTL PARAMETER 12 - -234,73 NRTL PARAMETER 21 -  262,83
                    NRTL PARAMETER ALPHA -     ,47000

  LIQUID     VAPOUR     VAPOUR     DELTA  EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100  PRESS    PRESS    MM HG
            EXPTL      CALC
  ,16390    ,01130     ,01169    -,039 389.700 380.519  9,181
  ,35430    ,02660     ,02743    -,083 389,700 411,991-22,291
  ,51240    ,06160     ,06277    -,117 389,700 426,392-36,692
  ,70690    ,11330     ,11470    -,140 389,700 411,552-21,852
  ,76690    ,14300     ,14424    -,124 389,700 395,504 -5,804
  ,89970    ,30250     ,30128     ,122 389,700 355,894 33,806
  ,93300    ,39430     ,39042     ,388 389,700 345,030 44,670

    SUM OF SQUARES                         -    ,36722940E-01
    STANDARD ERROR OF ESTIMATE             -    ,95816152E-01
    AVERAGE PRESSURE DEVIATION MM HG       -    ,77501064E+01
    AVERAGE VAPOUR DEVIATION*100           -    ,1449E+00
    NUMBER OF FUNCTION EVALUATIONS         -     85

  LIQUID  EQUILIBRIUM DELTA     DELTA    ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT    A         B      COEFF 1    COEFF 2
  ,16390    21,1766  2,7680    1,0602    2,66973    1,05866
  ,35430    28,4852  1,6686    1,1685    1,63577    1,16108
  ,51240    27,2383  1,3723    1,2767    1,35793    1,26093
  ,70690    23,3462  1,1765    1,4405    1,17248    1,41017
  ,76690    22,4471  1,1160    1,5008    1,11369    1,46518
  ,89970    17,1153  1,0003    1,6417     ,99993    1,59545
  ,93300    15,2902   ,9553    1,6772     ,95521    1,62957
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SYSTEM ACETIC ACID - ETHYL ETHER AT CONSTANT PRESSURE 487.9
DATA OF MEEHAN AND MURPHY,CHEM ENG SCIENCE,1965,VOL 20,PP 76
7-769

                    THREE PARAMETER NRTL EQUATION

   NRTL PARAMETER 12 -  981.77 NRTL PARAMETER 21 - -532.57
                  NRTL PARAMETER ALPHA -     .47000

  LIQUID     VAPOUR     VAPOUR     DELTA  EXPTL     CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100  PRESS     PRESS     MM HG
            EXPTL      CALC
  .15190    .01050     .01092    -.042 487.900 467.181 20.719
  .34530    .02520     .02612    -.092 487.900 481.032  6.868
  .49650    .04720     .04849    -.129 487.900 487.777   .123
  .68810    .10610     .10764    -.154 487.900 491.268 -3.368
  .78420    .16190     .16301    -.111 487.900 487.526   .374
  .89460    .31250     .31044     .206 487.900 491.556 -3.666
  .93740    .43900     .43228     .672 487.900 483.171  4.729

    SUM OF SQUARES                         -     .21998975E-02
    STANDARD ERROR OF ESTIMATE             -     .23451532E-01
    AVERAGE PRESSURE DEVIATION MM HG       -     .17609364E+01
    AVERAGE VAPOUR DEVIATION*100           -     .2007E+00
    NUMBER OF FUNCTION EVALUATIONS         -      86

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MOLE FRAC   CONSTANT    A          B       COEFF 1    COEFF 2
  .15190    17.0301  2.8387    1.0522    2.64733    1.04640
  .34530    26.9174  1.6036    1.1618    1.60852    1.13213
  .49650    27.3969  1.2979    1.2648    1.34458    1.21147
  .68810    22.7704  1.1243    1.4209    1.16955    1.37457
  .78420    19.6962  1.0648    1.5124    1.09473    1.52678
  .89460    14.5586   .9960    1.6223    1.00549    1.83548
  .93740    12.3191   .9817    1.6637     .95525    2.01799
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SYSTEM ACETIC ACID - ETHYL ETHER AT CØNSTANT PRESSURE 596,4
DATA ØF MEEHAN AND MURPHY,CHEM ENG SCIENCE,1966,VØL 20 PP 76
7-769

                    THREE PARAMETER NRTL EQUATIØN

  NRTL PARAMETER 12 -  391,33 NRTL PARAMETER 21 -    20,26
                    NRTL PARAMETER ALPHA -    4,28788

  LIQUID     VAPØUR     VAPØUR    DELTA  EXPTL    CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC  Y*100  PRESS    PRESS    MM HG
            EXPTL      CALC
  ,16980    ,01070    ,01095    -,025 596,400 577,037 19,363
  ,31900    ,02260    ,02310    -,050 596,400 583,216 13,184
  ,47270    ,04390    ,04463    -,073 596,400 600,926 -4,526
  ,58410    ,06840    ,06926    -,086 596,400 603,560 -7,160
  ,79910    ,18550    ,18587    -,037 596,400 594,088  2,312
  ,86830    ,28410    ,28322     ,088 596,400 597,123  -,723
  ,94140    ,47790    ,47286     ,504 596,400 596,440  -,040

    SUM ØF SQUARES                         -     ,17610496E-02
    STANDARD ERRØR ØF ESTIMATE             -     ,20982430E-01
    AVERAGE PRESSURE DEVIATIØN MM HG       -     ,17217507E+01
    AVERAGE VAPØUR DEVIATIØN*100           -     ,1233E+00
    NUMBER ØF FUNCTIØN EVALUATIØNS         -   1798

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT    A          B       CØEFF 1    CØEFF 2
  ,16980    27,1202  2,0564    1,0659    2,18634    1,06709
  ,31900    28,2153  1,5185    1,1469    1,60078    1,15154
  ,47270    25,5840  1,2819    1,2454    1,34183    1,25706
  ,58410    23,2491  1,1760    1,3286    1,22498    1,34951
  ,79910    16,0794  1,0590    1,5162    1,08915    1,59730
  ,86830    12,9990  1,0249    1,5805    1,04609    1,73768
  ,94140    10,1896   ,9422    1,6606     ,94996    2,06403
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SYSTEM ACETIC ACID - PYRIDINE AT 80.05 CENT
DATA ØF ZAWIDSKI,Z.PHYS.CHEM,1900,PG 153


                       TWØ PARAMETER WILSØN EQUATIØN

WILSØN PARAMETER 12 =-2138.06 WILSØN PARAMETER 21 =  -36.54

  LIQUID      VAPØUR     VAPØUR     DELTA   EXPTL     CALC    DELTA P
MØLE FRAC MØLE FRAC MØLE FRAC  Y*100   PRESS     PRESS    MM HG
             EXPTL       CALC
  .29053     .03179     .03168      .011 153.600 166.952 -3.352
  .38341     .08421     .08398      .023 123.500 127.480 -3.980
  .45434     .19473     .18613      .861 104.100 106.127 -2.027
  .49679     .30416     .27184     3.232  94.600  95.820 -1.220
  .55605     .47129     .42162     4.967  86.400  86.123  1.277
  .62534     .65202     .63950     1.253  81.600  80.555  1.045
  .66396     .74751     .74286      .465  87.000  84.056  2.944
  .67212     .76171     .75856      .315  88.900  85.290  3.610
  .75678     .91588     .91942     -.353 104.000 101.546  2.454
  .82917     .97508     .98268     -.760 128.200 127.257   .943
  .88047     .99049    1.00000     -.951 153.200 153.621  -.421
  .91044     .99369    1.00000     -.631 169.600 170.782 -1.182
  .94465     .99666    1.00000     -.334 186.400 188.620 -2.220
  .96727     .99749    1.00000     -.251 196.700 199.466 -2.766

    SUM ØF SQUARES                              =     .62427979E-02
    STANDARD ERRØR ØF ESTIMATE                  =     .22808620E-01
    AVERAGE PRESSURE DEVIATIØN MM HG            =     .18220011E+01
    AVERAGE VAPØUR DEVIATIØN*100                =     .1029E+01
    NUMBER ØF FUNCTIØN EVALUATIØNS              =     196

  LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT    A          B       CØEFF 1    CØEFF 2
  .29053       .7944  2.8922    1.0395     .21240     .94364
  .38341       .2573  3.3056    1.0291     .29459     .84601
  .45434       .0025  3.7614    1.0005     .39396     .73170
  .49679       .0011  3.7649    1.0003     .43731     .66589
  .55605       .0012  3.7644    1.0004     .51032     .56045
  .62534       .0088  3.7401    1.0034     .61852     .42114
  .66396       .0243  3.6903    1.0103     .68892     .34014
  .67212       .0327  3.6641    1.0140     .70256     .32351
  .75678       .2543  3.1415    1.1012     .81744     .16158
  .82917       .7504  2.5303    1.2326     .90283     .05265
  .88047      1.5378  2.0604    1.3564     .96286     .01149
  .91044      2.4159  1.7717    1.4427     .99331     .00253
  .94465      4.2940  1.4335    1.5546    1.01608     .00013
  .96727      6.4007  1.2244    1.6323    1.02550     .00000
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SYSTEM ACETIC ACID - ACETIC ANHYDRIDE AT 100 MM HG
DATA ØF JØNES,J.CHEM.ENG.DATA.,7(1),P13,1962


                     THREE PARAMETER NRTL EQUATIØN

     NRTL PARAMETER 12 = -828.92 NRTL PARAMETER 21 = 1312.34
                     NRTL PARAMETER ALPHA =      .25394

   LIQUID       VAPØUR       VAPØUR      DELTA   EXPTL     CALC    DELTA P
 MØLE FRAC  MØLE FRAC  MØLE FRAC   Y*100   PRESS     PRESS    MM HG
               EXPTL        CALC
   .10000      .19900      .19769       .131 100.000 100.728   -.728
   .20000      .36000      .35838       .162 100.000  99.673    .327
   .30000      .49500      .49339       .161 100.000  99.638    .362
   .40000      .61000      .60879       .121 100.000 100.109   -.109
   .50000      .70300      .70234       .066 100.000 100.250   -.250
   .60000      .78000      .78005      -.005 100.000 100.095   -.095
   .70000      .84500      .84582      -.082 100.000  99.916    .084
   .80000      .90200      .90363      -.163 100.000  99.819    .181
   .90000      .95300      .95548      -.248 100.000  99.921    .079
   .95000      .97800      .98097      -.297 100.000 100.202   -.202
   .97500      .98900      .99216      -.316 100.000 100.251   -.251

     SUM ØF SQUARES                              =     .10003793E-03
     STANDARD ERRØR ØF ESTIMATE                  =     .35362044E-02
     AVERAGE PRESSURE DEVIATIØN MM HG            =     .26840457E+00
     AVERAGE VAPØUR DEVIATIØN*100                =     .1592E+00
     NUMBER ØF FUNCTIØN EVALUATIØNS              =    4500

   LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
 MØLE FRAC    CØNSTANT     A         B       CØEFF 1    CØEFF 2
   .10000     16.0245   1.6407    1.0299    1.88701    1.03676
   .20000     12.2532   1.4660    1.0693    1.55225    1.09144
   .30000     10.9732   1.3671    1.1160    1.38248    1.15550
   .40000     10.6338   1.2909    1.1708    1.27705    1.22517
   .50000     10.9649   1.2191    1.2356    1.19734    1.29865
   .60000     11.6430   1.1577    1.3117    1.13826    1.37412
   .70000     12.5880   1.1043    1.4011    1.09120    1.45104
   .80000     13.6623   1.0630    1.5063    1.05653    1.52918
   .90000     14.8234   1.0333    1.6307    1.03154    1.60961
   .95000     15.4046   1.0226    1.7015    1.02215    1.65136
   .97500     15.7419   1.0171    1.7397    1.01695    1.67302
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SYSTEM ACETIC ACID = ACETALDEHYDE AT 760 MM HG
DATA ØF FRIED ET AL,CØLL.CZECH.CHEM.CØMM.,VØL 28,PG 3171,196
3

                         THREE PARAMETER NRTL EQUATIØN

   NRTL PARAMETER 12 =-2465.14 NRTL PARAMETER 21 = 2179.47
                      NRTL PARAMETER ALPHA =     .00945

   LIQUID      VAPØUR      VAPØUR     DELTA  EXPTL     CALC    DELTA P
 MØLE FRAC MØLE FRAC MØLE FRAC   Y*100  PRESS     PRESS     MM HG
              EXPTL       CALC
   .42500      .01700      .01634      .066 760.000 762.818 -2.818
   .53600      .03600      .03478      .122 760.000 748.758 11.242
   .64200      .07400      .07165      .235 760.000 749.116 10.884
   .71600      .12700      .12331      .369 760.000 787.182-27.182
   .78200      .15700      .15258      .442 760.000 735.105 24.895
   .87500      .33300      .32618      .682 760.000 767.959 -7.959
   .87500      .35700      .35038      .662 760.000 775.867-15.867
   .90000      .43200      .42509      .691 760.000 782.876-22.876
   .92300      .50400      .49736      .664 760.000 757.109  2.891
   .94000      .56700      .56068      .632 760.000 740.802 19.198
   .95400      .66900      .66367      .533 760.000 766.506 -6.506
   .96900      .72200      .71749      .451 760.000 727.113 32.887
   .97800      .79800      .79491      .309 760.000 737.448 22.552

     SUM ØF SQUARES                           =     .77202507E-02
     STANDARD ERRØR ØF ESTIMATE               =     .27785339E-01
     AVERAGE PRESSURE DEVIATIØN MM HG         =     .27158212E+01
     AVERAGE VAPØUR DEVIATIØN*100             =     .4506E+00
     NUMBER ØF FUNCTIØN EVALUATIØNS           =   2696

   LIQUID  EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
 MØLE FRAC   CØNSTANT    A          B       CØEFF 1    CØEFF 2
   .42500    24.3012   1.5215    1.2107    1.24982    1.07966
   .53600    19.0666   1.4601    1.2829    1.28158    1.07627
   .64200    14.5804   1.3897    1.3575    1.29518    1.06665
   .71600    11.8061   1.3197    1.4121    1.26470    1.05943
   .78200    12.7369   1.1694    1.4823    1.14124    1.06249
   .87500     8.8893   1.0864    1.5556    1.07831    1.05661
   .87500     7.9652   1.1369    1.5452    1.12848    1.04958
   .90000     7.3734   1.0929    1.5663    1.08786    1.05077
   .92300     6.7714   1.0779    1.5843    1.07499    1.04890
   .94000     6.3835   1.0582    1.5980    1.05645    1.04888
   .95400     5.6772   1.0448    1.6010    1.04381    1.04736
   .96900     5.4363   1.0363    1.6139    1.03584    1.04640
   .97800     4.9640   1.0390    1.6131    1.03876    1.04322
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SYSTEM  ACETIC ACID-DIMETHYLACETAMIDE AT CONSTANT PRESSURE 7
DATA OF CARLI ET.AL. - CHEM.ENG.SCI.VOL 27,PAGES 993-1001,19
72

                     TWO PARAMETER WILSON EQUATION

WILSON PARAMETER 12 =-2263.81 WILSON PARAMETER 21 = 1064.39

  LIQUID      VAPOUR     VAPOUR     DELTA   EXPTL    CALC    DELTA P
MOLE FRAC MOLE FRAC MOLE FRAC   Y*100   PRESS    PRESS     MM HG
             EXPTL       CALC
  .05000     .03000     .02959      .041 760.000 727.806 32.194
  .14500     .09200     .09080      .120 760.000 737.916 22.084
  .22500     .19000     .18710      .290 760.000 749.634 10.366
  .28700     .28700     .28210      .490 760.000 758.263  1.737
  .32500     .35500     .34857      .643 760.000 761.163 -1.163
  .39200     .49200     .48219      .981 760.000 770.329-10.329
  .48000     .67500     .66065     1.435 760.000 771.945-11.945
  .51500     .73700     .72155     1.545 760.000 763.323 -3.323
  .57500     .82000     .80274     1.726 760.000 762.782 -2.782
  .60000     .85700     .83967     1.733 760.000 758.792  1.208
  .64000     .91500     .89715     1.785 760.000 764.718 -4.718
  .67500     .93800     .92049     1.751 760.000 760.843  -.843
  .73200     .97300     .96742     1.558 760.000 757.910  2.090
  .77500     .97500     .95984     1.616 760.000 749.625 10.375
  .80200     .99100     .97728     1.372 760.000 754.516  5.484
  .81700     .98800     .97563     1.237 760.000 749.896 10.104
  .84000.    .99300     .98137     1.163 760.000 751.072  8.928
  .87500     .99600     .98562     1.038 760.000 751.179  8.821
  .90200     .99700     .98743      .957 760.000 751.296  8.704
  .93700     .99800     .99071      .729 760.000 753.040  6.960

    SUM OF SQUARES                          =     .42492975E-02
    STANDARD ERROR OF ESTIMATE              =     .15364637E-01
    AVERAGE PRESSURE DEVIATION MM HG        =     .10799698E+01
    AVERAGE VAPOUR DEVIATION*100            =     .1105E+01
    NUMBER OF FUNCTION EVALUATIONS          =     297

  LIQUID   EQUILIBRIUM DELTA      DELTA      ACTIVITY    ACTIVITY
MOLE FRAC   CONSTANT     A          B        COEFF 1     COEFF 2
  .05000      9.2137   1.2315    1.0093      .32223     1.00623
  .14500      7.4586    .9567    1.0391      .31071     1.01122
  .22500      4.5193    .9840    1.0612      .38108      .99184
  .28700      3.7424    .9754    1.0814      .42925      .96725
  .32500      3.4133    .9732    1.0946      .46031      .94833
  .39200      2.9090    .9830    1.1183      .52141      .90749
  .48000      2.3037   1.0352    1.1487      .61597      .84137
  .51500      2.0084   1.0856    1.1580      .66438      .80966
  .57500      2.0493   1.0763    1.1899      .70125      .75067
  .60000      1.7530   1.1459    1.1921      .75085      .71601
  .64000      1.4673   1.2313    1.1995      .81966      .66308
  .67500      1.5056   1.2345    1.2206      .84214      .59627
  .73200      1.2821   1.3440    1.2377      .92654      .46811
  .77500      1.7837   1.2144    1.2986      .89354      .38443
  .80200      1.5856   1.2930    1.3040      .96114      .29961
  .81700      1.5396   1.3245    1.3108      .97373      .25153
  .84000      1.6690   1.3047    1.3368      .98447      .19127
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SYSTEM  ACETIC ACID-DIMETHYLACETAMIDE AT CØNSTANT PRESSURE 7
DATA ØF CARLI ET.AL. - CHEM.ENG.SCI,VØL 27,PAGES 993-1001,19
72

                      TWØ PARAMETER WILSØN EQUATIØN

  LIQUID   EQUILIBRIUM DELTA      DELTA     ACTIVITY   ACTIVITY
MØLE FRAC   CØNSTANT     A          B       CØEFF 1    CØEFF 2
  .87500     1.9781   1.2531    1.3854     .99341     .10822
  .90200     2.3629   1.1907    1.4321     .99217     .05864
  .93700     2.6773   1.1723    1.4822    1.03053     .01219
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APPENDIX A4

Parameters for Wilson, NRTL and UNIQUAC equations obtained from data reduction.

A4.1 WILSON PARAMETERS

SYSTEM	Temp. or Press.	$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
1. ACETONE-TOLUENE (K9)	35°C	744.43	-343.16	0.72731	0.44854
2. " " "	45°C	838.85	-422.63	1.1626	0.97692
3. " " "	55°C	858.84	-434.99	1.1717	1.0738
4. ACETONE-BENZENE (K9)	30°C	639.32	-251.51	1.1907	0.33619
5. " " "	40°C	486.33	-150.83	0.65034	1.0359
6. " " "	50°C	776.21	-331.46	1.0402	0.50259
7. ETHYL ACETATE-BENZENE (L5)	50°C	1106.22	-286.70	2.1262	0.95061
8. " " " "	60°C	1400.52	-313.15	2.2815	0.74046
9. " " " "	70°C	1183.24	-238.11	2.6064	0.77064
10. ETHYL ACETATE-TOLUENE (L5)	50°C	29.55	611.19	7.4221	2.0364
11. " " "	60°C	94.03	470.87	7.2798	1.6744
12. " " "	70°C	104.67	429.39	7.6574	1.9346
13. CYCLOHEXANE-N-PROPANOL (S15)	55°C	494.07	1625.89	1.5941	1.3928
14. " " "	65°C	553.70	1417.39	0.86161	0.59175

	Temp. or Press.	$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
15. CYCLOHEXANE-N-BUTANOL (S15)	50°C	305.30	1930.68	1.2195	0.87301
16. " " "	70°C	463.53	1458.08	1.0117	0.83966
17. METHANOL-CYCLOHEXANE (S16)	50°C	2827.18	1157.77	2.8474	3.0219
18. " " "	55°C	2475.76	1258.25	2.8460	1.5992
19. BENZENE-N-HEPTANE (H13)	720 MM	-74.39	1242.95	2.3580	1.1867
20. ETHANOL-CYCLOHEXANE (S16)	760 MM	1949.58	725.53	2.5036	1.1377
21. METHANOL-BENZENE (S14)	45°C	1579.49	427.47	1.0969	0.60301
22. " " (S13)	230 MM	1649.44	452.84	0.89804	0.36985
23. " " "	340 MM	1574.54	487.15	1.2821	0.38232
24. " " "	521 MM	1524.71	489.99	1.4624	0.65812
25. " " "	740 MM	1517.37	454.64	1.4079	0.64989
26. BENZENE-N-HEPTANE (H13)	740 MM	-74.81	1251.10	2.3601	1.2348
27. " " "	760 MM	875.85	-426.50	0.1000	0.60826
28. METHYETHYL KETONE-TOLUENE (K9)	75°C	1975.59	+641.82	3.1005	3.4484

SYSTEM	Temp. or Press.	$\lambda_{12} - \lambda_{11}$	$\lambda_{21} - \lambda_{22}$	$\frac{\Sigma 100 \Delta Y}{N}$	$\frac{\Sigma \Delta P/P}{N}$
29. METHANOL-N-HEXANE	760 MM	3000.09	1034.57	2.6259	1.7617
30. CARBON TETRACHLORIDE-METHANOL (S6)	$35^\circ C$	2372.77	395.87	1.5873	1.6254
31. " " "	$55^\circ C$	2105.44	387.70	2.5274	1.9906
32. BENZENE-2-BUTANOL (E1)	$60^\circ C$	156.32	1256.66	2.3605	1.0184
33. " " "	$70^\circ C$	-1.62	1182.55	1.1348	0.26833
34. " " "	$80^\circ C$	67.48	911.64	1.5933	0.31336
35. BENZENE-TERT-BUTANOL (E1)	$60^\circ C$	620.30	517.09	2.3294	0.58535
36. " " "	$70^\circ C$	549.98	517.98	1.9014	0.31881
37. " "	$75^\circ C$	492.09	610.52	2.8664	0.60151
38. BENZENE-ISO-BUTANOL (E1)	$60^\circ C$	119.42	1246.37	1.7660	0.71067
39. " " "	$70^\circ C$	216.18	1054.04	1.6941	1.6617
40. " " "	$80^\circ C$	148.20	967.03	1.0857	0.51257
41. DIPROPYL ETHER-ETHYLBENZENE (L6)	$50^\circ C$	-465.59	949.0	3.3301	1.4888
42 " " "	$60^\circ C$	-411.65	770.98	2.5723	1.1119

SYSTEM	Temp. or Press.	$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
43. DIPROPYL ETHER-ETHYLBENZENE (L6)	70°C	-391.58	794.48	2.8617	1.4651
44. BENZENE-METHYL ETHYL KETONE (K9)	40°C	-281.90	584.64	0.51930	0.39335
45. " " "	50°C	-276.75	625.41	0.67192	0.40797
46. " " "	60°C	-214.79	590.21	1.1215	0.74623
47. METHYL ETHYL KETONE-ETHYLBENZENE (K9)	55°C	-638.88	1172.42	4.1149	5.8339
48. " " "	65°C	265.54	1911.19	1.3952	1.0081
49. " " "	75°C	555.90	-246.14	0.81467	0.7007
50. BENZENE-DIPROPYL ETHER (L6)	50°C	15.11	88.09	0.48014	0.28435
51. " " "	60°C	-94.22	389.87	0.58623	0.29152
52. " " "	70°C	277.03	-124.69	1.2490	0.60421
53. DIPROPYL ETHER-TOLUENE (L6)	50°C	381.72	-248.52	1.6406	0.66993
54. METHYL ETHYL KETONE-TOLUENE (K9)	65°C	625.16	-307.30	0.33138	0.13314
55. " " "	55°C	565.35	-301.20	0.29015	0.20043
56. PYRIDINE-TETRACHLORETHYLENE (F8)	60°C	557.49	56.44	0.66249	0.15899

SYSTEM	Temp. or Press.	$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	$\frac{\sum 100\Delta y}{N}$	$\frac{\sum \Delta P/P}{N}$
57. PYRIDINE-TETRACHLORETHYLENE (F8)	80°C	659.28	4.81	1.0561	0.41321
58. " " "	100°C	531.40	97.30	0.90988	0.36627
59. DI-ISO PROPYL ETHER-ETHYLBENZENE (L6)	70°C	-130.65	321.04	2.5971	0.94832
60. ETHYL ACETATE-ETHYLBENZENE (L5)	60°C	-14.60	268.38	1.2504	1.1231
61. " " "	70°C	20.25	211.05	1.5415	0.93654
62. BENZENE-DI-ISOPROPYL ETHER (L6)	50°C	131.53	236.38	1.3395	0.54752
63. " " "	60°C	477.04	-267.48	1.0859	0.47925
64. " " "	70°C	805.27	-505.71	3.9729	2.9840
65. DI-ISOPROPYL ETHER-TOLUENE (L6)	50°C	-208.19	426.94	2.2575	0.80811
66. " " "	60°C	-240.98	473.32	2.2003	0.51649
67. " " "	70°C	-45.04	242.25	2.4209	0.50567
68. DI-ISOPROPYL ETHER-ETHYLBENZENE (L6)	50°C	-172.62	382.60	3.3795	1.7253
69. " " "	60°C	-321.72	618.50	2.2954	1.0833
70. " " "	70°C	-133.29	324.58	2.1462	1.1621

SYSTEM	Temp. or Press.	$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
71. ETHANOL-ETHYL ACETATE (D4)	760 MM	1009.37	-209.35	1.5728	0.58436
72. ETHANOL-N-BUTYL ACETATE (D4)	760 MM	674.28	227.85	4.1403	2.9354
73. ETHANOL-N-BUTANOL (D4)	760 MM	1148.07	-854.11	3.1459	2.1331
74. ETHYL ACETATE-N-BUTANOL	760 MM	128.83	318.43	1.8043	1.1271
75. ETHYL ACETATE-N-BUTYL ACETATE	760 MM	-189.98	500.24	0.52817	0.44381
76. N-BUTANOL-N-BUTYL ACETATE	760 MM	698.82	-91.44	1.5191	0.70328
77. METHANOL-WATER (D1)	760 MM	136.97	637.25	0.80309	1.9693
78. ETHANOL-WATER (D1)	760 MM	450.18	988.75	0.91264	2.4471
79. METHANOL-WATER (M14)	35°C	240.69	341.98	2.5029	2.1733
80. " " "	50°C	47.27	466.89	1.3900	0.96012
81. ACETIC ACID-N-HEPTANE (M10)	20°C	1792.66	771.28	1.1112	0.75881
82. " " "	30°C	1745.38	922.90	0.90451	0.33479
83. " " "	40°C	1760.53	801.71	1.1065	0.39091
84. ACETIC ACID-PYRIDINE (Z1)	80.05°C	-725.45	-565.52	1.7382	1.8239

SYSTEM	Temp. or Press	$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	$\frac{\Sigma 100\Delta Y}{N}$	$\frac{\Sigma \Delta P/P}{N}$
85. ACETIC ACID-BENZENE (Z1)	49.99°C	1191.09	112.82	1.1239	2.1716
86. " " (M21)	760 MM	1552.10	74.97	1.5364	1.3565
87. ACETIC ACID-ETHYL ACETATE (G1)	760 MM	-56.62	5433.0	7.3131	1.0256
88. ACETIC ACID-BENZENE (O5)	758 MM	1319.47	137.91	3.7874	2.8552
89. ACETIC ACID-CHLOROFORM (K5)	760 MM	-650.43	18522.73	5.4759	4.371
90. ACETIC ACID-TRICHLOROETHYLENE (F4)	500 MM	1560.81	100.95	1.6484	0.94504
91. " " " "	750 MM	2591.37	-113.77	1.6019	1.0200
92. " " " "	650 MM	1183.48	306.22	2.1507	6.3542
93. " " " "	350 MM	1156.38	210.98	1.1302	1.5465
94. " " " "	250 MM	1258.71	179.29	1.9902	1.7480
95. ACETIC ACID-ACETONE (M16)	50°C	-543.14	38047.15	0.84313	0.56732
96. " " "	40°C	-53.49	53.49	0.68265	0.9718
97. " " "	30°C	-540.10	25667.17	1.6751	0.38272
98. ACETIC ACID-ETHYL ETHER (M16)	389.7 MM	335.44	229.92	0.63255	2.1006

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SYSTEM	Temp. or Press.	$\lambda_{12} - \lambda_{11}$	$\lambda_{21} - \lambda_{22}$	$\frac{\sum 100 \Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
99. ACETIC ACID-ETHYL ETHER (M16)	487.9 MM	688.65	-147.93	0.57632	2.9697
100. " " "	596.4 MM	1208.91	-437.00	0.8414	2.3854
101 . ACETIC ACID-ETHYLBENZENE (B2)	725 MM	1685.19	430.75	7.0769	2.3209
102. ACETIC ACID-BENZENE (M16)	30°C	1238.35	-3.84	0.58303	1.8818
103. " " "	50°C	1355.47	4.20	0.61662	1.3559
104. " " "	70°C	1586.43	9.29	1.2327	1.6100
105. ACETIC ACID-ETHYL ACETATE (M16)	30°C	1520.20	-716.68	1.5677	0.7255
106. " " " "	50°C	1566.99	-733.81	1.0073	0.3385
107. " " " "	70°C	1881.79	-796.09	0.63172	3.9837
108. ACETIC ACID-ACETONE (M16)	760 MM	1926.26	-580.36	1.0869	1.3897
109. ACETIC ACID-METHANOL (R17)	709 MM	-335.55	244.33	1.2940	2.3331
110. ACETIC ACID-ETHANOL "	706 MM	-518.37	643.87	1.1682	0.7726
111. ACETIC ACID-N-PROPANOL "	705 MM	724.74	-514.17	1.2321	0.9503
112. ACETIC ACID-N-BUTANOL "	707 MM	-149.76	530.26	0.96995	0.8928

SYSTEM	Temp. or Press.	$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	$\frac{\Sigma 100\Delta Y}{N}$	$\frac{\Sigma \Delta P/P}{N}$
113. ACETIC ACID-N-PROPANOL (A3)	760 MM	504.71	-555.77	2.7142	2.3523
114. ACETIC ACID-ISO-BUTANOL (A3)	760 MM	-288.81	959.89	0.90306	0.79245
115. ACETIC ACID-ISO-PROPANOL (A3)	760 MM	1138.51	-1052.30	3.2504	2.5404
116. ACETIC ACID-2-BUTANOL (A3)	760 MM	2313.59	-2212.43	6.9601	1.6003
117. ACETIC ACID-TERT-BUTANOL (A3)	760 MM	-836.09	919.67	4.5756	3.2470
118. ACETIC ACID-P-XYLENE (B2)	725 MM	3685.06	-97.29	6.3076	2.5074
119. " " (M5)	760 MM	1890.06	291.82	3.2821	0.4082
120. ACETIC ACID-OCTANE (S10)	760 MM	1581.21	1895.96	2.3046	1.8544
121. ACETIC ACID-DIMETHYLACETAMIDE (C1)	760 MM	-1449.13	549.02	5.1669	4.8523
122. ACETIC ACID-WATER (R14)	760 MM	6853.5	300.0	2.7667	3.5066
123. " " (B16)	760 MM	6853.5	300.0	4.9710	7.3645
124. " " (K1)	50 MM	7483.4	200.1	7.0271	6.2922
125. ACETIC ACID-TOLUNEN (M16)	$50^{\circ}C$	1298.1	-104.67	1.7122	0.44785
126. " " "	$30^{\circ}C$	1342.25	-48.19	1.2018	0.69801

SYSTEM	Temp. or Press.	$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
127. ACETIC ACID-TOLUENE (M16)	70°C	1392.17	24.16	1.47262	0.61633
128. " " (Z1)	80.05°C	1300.97	247.29	2.0745	1.7400
129. " " (H3)	745 MM	1487.34	292.48	1.8245	2.7914
130. " " (V8)	50 MM	-48.31	15890.45	7.2332	8.8546
131. " " (Z1)	69.94°C	1448.76	4.58	1.4363	1.0841
132. ACETIC ACID-N-DECANR (Z2)	760 MM	6853.50	300.0	9.0928	9.2937
133. ACETIC ACID-DIETHYL ETHER (B12)	760 MM	208.78	439.15	3.7996	3.8441
134. ACETIC ACID-N-OCTANE (Z2)	760 MM	1870.59	1139.37	2.6287	1.3949
135. ACETIC ACID-METHYLENE CHLORIDE (D8)	760 MM	1159.81	-111.34	0.54022	1.4920
136. ACETIC ACID-DIETHYL KETONE (H1)	70°C	6853.50	300.0	10.655	1.5738
137. ACETIC ACID-BENZENE (W1)	20°C	1252.18	42.76	0.65674	1.2012
138. ACETIC ACID-N-HEPTANE (W1)	20°C	1683.26	958.54	1.8147	0.95339
139. ACETIC ACID-CYCLOHEXYL ACETATE (O4)	760 MM	1458.23	-149.05	6.5771	3.0022
140. ACETIC ACID-N-BUTYL ACETATE (A11)	760 MM	2821.67	-1884.04	3.9807	1.4492
141. ACETIC ACID-ACETIC ANHYDRIDE (J8)	100 MM	644.40	9.49	1.8197	0.67791

A4.2 NRTL PARAMETERS

SYSTEM	Temp. or Press.	$g_{12}-g_{11}$	$g_{21}-g_{22}$	α	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
1. ACETONE-TOLUENE (K9)	35°C	-126.40	524.94	0.19943	0.72201	0.42386
2. " " "	45°C	-303.63	746.50	0.19932	1.1151	0.91158
3. " " "	55°C	-332.98	788.03	0.19926	1.1038	1.0070
4. ACETONE-BENZENE (K9)	30°C	-324.90	738.45	0.20059	1.2260	0.37989
5. " " "	40°C	-101.32	435.21	0.20132	0.65444	1.0349
6. " " "	50°C	-462.46	950.94	0.20023	1.0667	0.52576
7. ETHYL ACETATE-BENZENE (L5)	50°C	-762.27	1484.02	0.20118	2.3262	1.0659
8. " " "	60°C	-887.45	1808.61	0.20078	2.7247	0.97106
9. " " "	70°C	-818.04	1676.97	0.20066	2.8973	0.90452
10. ETHYL ACETATE-TOLUENE (L5)	50°C	862.15	-234.20	0.30254	7.5210	2.0947
11. " " "	60°C	850.51	-278.62	0.20116	7.3427	1.7076
12. " " "	70°C	717.72	-187.59	0.20297	7.7183	1.9716
13. CYCLOHEZANE-N-PROPANOL (S15)	55°C	1378.71	142.96	0.20731	2.3204	2.5448
14. " " "	65°C	1339.28	205.97	0.23793	1.6542	1.6129

SYSTEM	Temp. or Press.	$g_{12}-g_{11}$	$g_{21}-g_{22}$	α	$\frac{\sum 100\Delta y}{N}$	$\frac{\sum \Delta P/P}{N}$
15. CYCLOHEXANE-N-BUTANOL (S15)	50°C	1808.15	-183.40	0.20901	2.3566	2.1119
16. " " "	70°C	1672.37	-168.76	0.20563	1.7499	1.6448
17. METHANOL-CYCLOHEXANE (S16)	50°C	910.28	2209.14	0.36616	5.6773	6.6983
18. " " "	55°C	627.71	1775.02	0.28061	7.0899	9.6058
19. BENZENE-N-HEPTANE (H13)	720 MM	1936.38	-906.41	0.20013	2.9735	1.5390
20. EHTANOL-CYCLOHEXANE (S16)	760 MM	988.71	1617.42	0.46636	2.5431	1.0891
21. METHANOL-BENZENE (S14)	45°C	853.65	1204.46	0.49869	0.95794	0.82323
22. " " "	230 MM	779.65	1276.60	0.47506	1.0624	0.7921
23. " " "	340 MM	814.08	1213.74	0.47397	1.3222	0.57491
24. " " "	521 MM	829.08	1154.23	0.47136	1.4970	0.61739
25. " " "	740 MM	820.57	1122.0	0.4761	1.4917	0.7633
26. BENZENE-N-HEPTANE (S13)	740 MM	1907.62	-885.2	0.20428	2.8635	1.5464
27. " " "	760 MM	-335.28	817.48	0.2603	1.0066	0.6131
28. METHYL ETHYL KETONE-TOLUENE (K9)	75°C	-1321.04	3633.17	0.20168	0.86312	0.59502

SYSTEM	Temp. or Press.	$g_{12}-g_{11}$	$g_{21}-g_{22}$	α	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
29. METHANOL-N-HEXANE (R1)	760°C	1789.71	2171.67	0.44590	3.1906	3.1631
30. CARBON TETRACHLORIDE-METHANOL (S6)	35°C	982.80	1758.61	0.46111	1.5016	1.4612
31. " " " "	55°C	1044.80	1467.86	0.48700	3.1203	2.3763
32. BENZENE-2-BUTANOL (E1)	60°C	1110.20	168.68	0.42438	2.6663	0.98339
33. " " "	70°C	1077.29	22.96	0.47536	1.2808	0.30417
34. " " "	80°C	860.12	60.76	0.47320	1.6223	0.31982
35. BENZENE-TERT-BUTANOL (E1)	60°C	754.90	502.66	0.65445	2.3469	0.57050
36. " " "	70°C	740.49	311.05	0.47868	1.9728	0.33849
37. " " "	75°C	820.64	528.54	0.84784	2.5701	0.40907
38. BENZENE-ISO-BUTANOL (E1)	60°C	1134.64	255.23	0.60617	1.8672	0.77038
39. " " "	70°C	985.94	172.26	0.39797	1.8411	1.7134
40. " " "	80°C	888.53	155.91	0.43321	1.0564	0.47470
41. DIPROPYL ETHER-ETHYLBENZENE (L6)	50°C	1155.79	-712.06	0.20407	3.4465	1.6450
42. " " " "	60°C	1015.78	-648.82	0.20274	1.9419	1.1595

SYSTEM	Temp. or Press.	$g_{12}-g_{11}$	$g_{21}-g_{22}$	α	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
43. DIPROPYL ETHER-ETHYLBENZENE (L6)	70°C	1064.79	-644.52	0.20235	2.9239	1.5597
44. BENZENE-METHYL ETHYL KETONE (K9)	40°C	916.36	-580.19	0.20165	0.57112	0.42610
45. " " "	50°C	983.22	-604.53	0.20210	0.75755	0.44884
46. " " "	60°C	933.05	-536.94	0.20342	1.2288	0.77569
47. METHYL ETHYL KETONE-ETHYLBENZENE (L6)	55°C	1644.59	-967.32	0.19783	4.3271	5.8162
48. " " " "	65°C	2130.95	-423.62	0.20879	1.4711	1.1971
49. " " " "	75°C	-268.82	597.43	0.20009	0.8221	0.70208
50. BENZENE-DIPROPYL ETHER (L6)	50°C	658.02	-524.33	0.19747	0.48944	0.28265
51. " " " "	60°C	1037.95	-729.03	0.20172	0.60675	0.33767
52. " " " "	70°C	332.12	-174.87	0.20325	1.2643	0.60087
53. DIPROPYL ETHER-TOLUENE (K9)	50°C	-643.97	821.28	0.19996	1.6069	0.65887
54. METHYL ETHYL KETONE-TOLUENE (K9)	65°C	-455.96	813.54	0.20022	0.34892	0.15353
55. " " "	55°C	-395.79	695.58	0.19975	0.28327	0.18306
56. PYRIDINE-TETRACHLORETHYLENE (F)	60°C	81.18	495.46	0.20227	0.70728	0.17654

SYSTEM	Temp. or Press.	$g_{12}-g_{11}$	$g_{21}-g_{22}$	α	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
57. PYRIDINE-TETRACHLORETHYLENE (F8)	80°C	-25.46	657.71	0.2026	1.1125	0.45211
58. " " "	100°C	204.65	389.04	0.24131	0.94266	0.39988
59. DI-ISO PROPYL ETHER-ETHYLBENZENE (L6)	70°C	400.53	-201.25	0.20112	2.5932	0.94926
60. ETHYL ACETATE-ETHYLBENZENE (L5)	60°C	553.86	-279.09	0.29620	1.2269	1.1016
61. " " "	70°C	467.59	-222.23	0.29743	1.5237	0.93816
62. BENZENE-DI-ISO PROPYL ETHER (L6)	50°C	873.91	-465.73	0.20099	1.3749	0.56122
63. " " "	60°C	-31.22	238.99	0.21108	1.0843	0.4816
64. " " "	70°C	-441.84	763.39	0.20407	3.9382	2.9755
65. DI-ISO PROPYL ETHER-TOLUENE (L6)	50°C	546.21	-313.76	0.2018	2.2531	0.8309
66. " " "	60°C	596.45	-343.53	0.20174	2.1953	0.53647
67. " " "	70°C	170.28	119.14	3.31609	2.3821	0.45199
68. DI-ISO PROPYL ETHER-ETHYLBENZENE (L6)	50°C	476.56	-258.12	0.20308	3.3741	1.7306
69. " " " "	60°C	843.24	-522.20	0.20203	2.3206	1.1533
70. " " " "	70°C					

SYSTEM	Temp or Press.	$g_{12}-g_{11}$	$g_{21}-g_{22}$	α	$\frac{\sum 100\Delta y}{N}$	$\sum \Delta P/P$
71. ETHANOL-ETHYL ACETATE (D4)	760 MM	171.56	583.63	0.32102	1.6356	0.6439
72. ETHANOL-N-BUTYL ACETATE (D4)	760 MM	1253.08	-302.31	0.31724	4.2788	2.8123
73. ETHANOL-N-BUTANOL (D4)	760 MM	-633.98	1032.01	0.30441	3.0684	2.1013
74. ETHYL ACETATE-N-BUTANOL	760 MM	227.18	254.01	0.85668	1.8401	1.1491
75. ETHYL ACETATE-N-BUTYL ACETATE	760 MM	837.16	-526.15	0.3000	0.50879	0.45151
76. N-BUTANOL-N-BUTYL ACETATE	760 MM	129.70	457.63	0.31240	1.5499	0.70739
77. METHANOL-WATER (D1)	760 MM	-590.03	1364.31	0.19988	0.84444	1.9066
78. ETHANOL-WATER (D1)	760 MM	-497.96	1872.45	0.19990	1.0707	2.1976
79. METHANOL-WATER (M14)	35°C	-556.36	1202.65	0.2003	2.5240	2.1325
80. " " "	50°C	-416.94	976.91	0.19941	1.3460	0.83777
81. ACETIC ACID-N-HEPTANE (M10)	20°C	1357.6	1188.84	0.46049	1.0687	0.88945
82. " " "	30°C	1427.5	1231.31	0.46527	0.96437	0.64123
83. " " "	40°C	1382.74	1291.68	0.47632	1.2875	0.53679
84. ACETIC ACID-PYRIDINE (Z1)	80.05°C	-321.99	-991.50	0.43378	1.3446	1.4190

SYSTEM	Temp. or Press.	$g_{12}-g_{11}$	$g_{21}-g_{22}$	α	$\frac{\sum 100\Delta y}{N}$	$\frac{\sum \Delta P/P}{N}$
85. ACETIC ACID-BENZENE (Z1)	49.99°C	427.75	933.86	0.53439	1.1575	2.0664
86. " " (M21)	760 MM	672.09	1174.07	0.64898	1.018	1.2652
87. ACETIC ACID-ETHYL ACETATE (G1)	760 MM	6483.5	347.14	0.46736	7.4364	5.7916
88. ACETIC ACID-BENZENE (O5)	758 MM	420.89	1181.50	0.55728	3.6691	2.9637
89. ACETIC ACID-CHLOROFORM (K5)	760 MM	-389.55	444.15	1.0432	4.0744	4.3588
90. ACETIC ACID-TRICHLOROETHYLENE (F4)	500 MM	565.23	1147.92	0.5696	1.4696	0.88337
91. " " "	750 MM	505.12	1679.65	0.5756	1.2829	0.90255
92. " " "	650 MM	594.55	969.91	0.5248	2.1365	1.8356
93. " " "	350 MM	507.37	951.83	0.54109	1.2184	1.6088
94. " " "	250 MM	649.37	921.74	0.62873	1.6824	1.4019
95. ACETIC ACID-ACETONE (M16)	50°C	-542.77	1122.58	0.47088	1.0137	0.55915
96. " " "	40°C	-526.07	884.37	0.47026	0.7523	0.49775
97. " " "	30°C	-505.72	810.90	0.46305	0.75281	0.5147
98. ACETIC ACID-ETHYL ETHER (M16)	389.7 MM	564.82	-23.15	0.5015	0.63889	2.3116

SYSTEM	Temp. or Press.	$g_{12}-g_{11}$	$g_{21}-g_{22}$	α	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
99. ACETIC ACID-ETHYL ETHER (M16)	487.9 MM	280.74	604.82	1.27907	0.64154	2.5443
100. " " "	596.4 MM	58.88	643.86	0.50588	0.79666	2.7824
101. ACETIC ACID-ETHYLBENZENE (B2)	725 MM	1634.39	1435.11	0.62634	5.9272	0.56100
102. ACETIC ACID BENZENE (M16)	30°C	292.89	876.43	0.46193	0.63262	1.8224
103. " " "	50°C	317.07	976.65	0.47149	0.66607	1.4021
104. " " "	70°C	348.60	1169.50	0.4842	1.3027	1.858
105. ACETIC ACID-ETHYL ACETATE (M16)	30°C	-325.93	942.79	0.47295	1.5903	1.1225
106. " " "	50°C	-324.91	1007.03	0.47132	1.0705	0.5730
107. " " "	70°C	-340.26	1180.55	0.4717	0.71593	0.80244
108. ACETIC ACID-ACETONE (M16)	760 MM	-275.54	1243.45	0.52030	1.1064	2.1403
109. ACETIC ACID-METHANOL (R17)	709 MM	-10.73	-81.39	0.38281	1.2866	2.3383
110. ACETIC ACID-ETHANOL (R17)	706 MM	-117.50	44.42	0.47264	1.1147	0.77687
111. ACETIC ACID-N-PROPANOL (R17)	705 MM	-523.81	764.08	0.48638	1.4357	0.93759
112. ACETIC ACID-N-BUTANOL (R17)	707 MM	644.45	-341.52	0.48156	1.0692	0.93733

SYSTEM	Temp. or Press.	$g_{12}-g_{11}$	$g_{21}-g_{22}$	α	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
113. ACETIC ACID-N-PROPANOL (A3)	760 MM	-550.30	536.84	0.57805	2.8277	2.1743
114. ACETIC ACID-ISO-BUTANOL (A3)	760 MM	1080.19	-597.75	0.47617	0.95038	0.77262
115. ACETIC ACID-ISO-PROPANOL (A3)	760 MM	-211.35	640.52	5.59472	2.6676	1.6210
116. ACETIC ACID-2-BUTANOL (A3)	760 MM	-525.87	1298.10	6.26701	3.3213	1.71617
117. ACETIC ACID-TERT BUTANOL (A3)	760 MM	-789.02	636.18	0.51222	2.5372	2.053
118. ACETIC ACID-P-XYLENE (B2)	725 MM	1286.52	2683.33	0.5454	5.3925	2.6194
119. " " (M5)	760 MM	1077.78	1297.68	0.53718	3.6380	0.41614
120. ACETIC ACID-N-OCTANE (S10)	760 MM	1936.87	769.66	0.41801	2.8387	1.4285
121. ACETIC ACID-DIMETHYLACETAMIDE (C1)	760 MM	-731.92	-885.45	-0.1498	2.9060	2.3685
122. ACETIC ACID-WATER (R14)	760 MM	-188.20	996.27	0.5045	1.5038	1.1536
123. " " (B16)	760 MM	-29.99	919.35	0.47628	2.3405	7.5612
124. " " (K1)	50 MM	171.37	490.66	0.39721	2.6569	2.8916
125. " " (I1)	70 MM	496.54	314.04	0.89775	1.4425	1.6912
126. " " "	200 MM	508.27	393.21	0.98809	1.3187	1.6108

	SYSTEM	Temp. or Press.	$g_{12}-g_{11}$	$g_{21}-g_{22}$	α	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
127.	ACETIC ACID-WATER (A5)	69.7°C	-376.06	1158.27	0.20208	1.5474	1.1561
128.	" " "	89.9°C	-461.74	1339.87	0.20217	1.4255	1.3365
129.	" " "	79.9°C	-336.34	1102.2	0.20275	1.4805	1.3019
130.	ACETIC ACID-CARBONTETRACHLORIDE (L7)	20°C	286.48	859.58	0.50716	1.2969	2.4997
131.	ETHYL ACETATE-N-BUTANOL (M3)	725 MM	266.33	665.93	0.57623	6.3259	2.8750
132.	ACETIC ACID-TOLUENE (M16)	50°C	391.95	771.96	0.46481	1.7924	0.42627
133.	" " "	30°C	572.10	786.82	0.55362	1.0611	0.71935
134.	" " "	70°C	498.03	91350	0.49002	1.5941	0.71534
135.	" " "	80.05°C	686.16	1058.85	0.58454	1.8532	1.4967
136.	" " "	745 MM	1089.45	1058.73	0.6353	2.0454	2.1023
137.	" " "	50 MM	1980.94	-678.4	0.34603	7.0188	.82964
138.	" " "	69.94°C	483.17	985.89	0.50637	1.5793	1.1266
139.	ACETIC ACID-N-DECANE (Z2)	760 MM	3460.98	1208.48	0.47154	3.6552	0.76132
140.	ACETIC ACID-DIETHYL ETHER (B12)	760 MM	708.88	-236.54	0.46791	3.7086	3.9462

SYSTEM	Temp. or Press.	$g_{12}-g_{11}$	$g_{21}-g_{22}$	α	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
141. ACETIC ACID TRIETHYLAMINE (H15)	760 MM	1174.22	-1886.74	0.52891	1.4523	2.3975
142. " " (D9)	760 MM	1021.82	-1861.98	0.96014	2.2344	2.3590
143. ACETIC ACID-N-OCTANE (B12)	760 MM	1812.53	1288.43	0.49067	2.1607	1.3131
144. ACETIC ACID-METHYLENE CHLORIDE (D8)	760 MM	-39.17	1007.10	0.47650	0.56685	1.6821
145. ACETIC ACID-DIETHYLKETONE (H1)	70°C	-710.51	481.497	0.20208	1.0402	4.0388
146. ACETIC ACID-BENZENE (W1)	20°C	347.36	916.40	0.48473	0.70929	1.4038
147. ACETIC ACID-N-HEPTANE (W1)	20°C	1338.25	1235.94	0.45946	1.6462	1.1718
148. ACETIC ACID-CYCLOHEXYL ACETATE (04)	760 MM	505.39	872.66	0.58502	6.2068	2.8108
149. ACETIC ACID-N-BUTYL ACETATE (H11)	760 MM	117.83	832.31	0.50141	4.1061	1.4001
150. ACETIC ACID-ACETIC ANHYDRIDE (J8)	100 MM	388.08	335.87	0.80669	1.7297	0.62758

A4.3 UNIQUAC PARAMETERS

SYSTEM	Temp. or Press.	$U_{12}-U_{11}$	$U_{21}-U_{22}$	$\frac{\sum 100\Delta y}{N}$	$\frac{\sum \Delta P/P}{N}$
1. ETHANOL-CYCLOHEXANE (S16)	760 MM	-125.932	1096.955	2.8731	1.4325
2. METHANOL-BENZENE (S14)	45°C	-85.503	1216.463	1.6317	1.4049
3. " " "	230 MM	-58.929	1098.449	1.5105	2.2481
4. " " "	340 MM	-64.113	1190.259	1.1808	1.1346
5. " " "	521 MM	-58.623	1164.197	0.95727	1.8140
6. " " "	740 MM	-51.772	1054.531	1.1407	2.5281
7. ETHANOL-ETHYL ACETATE (D4)	760 MM	-183.772	618.64	1.6557	0.65112
8. ETHANOL-N-BUTYL ACETATE (D4)	760 MM	86.595	234.091	4.1703	2.8262
9. ETHYL ACETATE-N-BUTANOL	760 MM	60.798	74.550	1.8288	1.1376
10. ETHYL ACETATE-N-BUTYL ACETATE	760 MM	368.328	-262.19	0.52912	0.44461
11. N-BUTANOL-N-BUTYL ACETATE	760 MM	-181.151	399.264	1.5434	0.71142
12. METHANOL-WATER (M14)	760 MM	-319.15	500.0	1.3732	2.4718
13. ETHANOL-WATER (M14)	760 MM	-319.15	500.0	1.5722	1.9827
14. BENZENE-2-BUTANOL (E1)	60°C	466.366	-86.697	2.7146	0.95373

SYSTEM	Temp. or Press.	$u_{12}-u_{11}$	$u_{21}-u_{22}$	$\frac{\sum 100\Delta y}{N}$	$\frac{\sum \Delta P/P}{N}$
15. BENZENE-2-BUTANOL (E1)	70°C	566.172	-206.985	1.2389	0.28089
16. " " "	80°C	394.903	-123.210	1.6163	0.31916
17. BENZENE-TERT-BUTANOL (E1)	60°C	150.967	127.354	2.5929	0.74963
18. " " "	70°C	152.308	107.495	2.1652	0.3929
19. " " "	75°C	242.204	32.54	2.975	0.71294
20. BENZENE-ISO-BUTANOL (E1)	60°C	543.229	-154.956	1.7914	0.82112
21. " " "	70°C	369.607	-33.476	1.8636	1.7256
22. " " "	80°C	328.561	-33.818	1.0855	0.48455
23. ACETIC ACID-N-HEPTANE (M10)	20°C	31.502	647.346	1.7058	2.1057
24. " " "	30°C	0.046	711.01	2.0069	2.0784
25. " " "	40°C	24.538	667.059	1.7912	2.7804
26. METHANOL-N-HEXANE (B1)	760 MM	15.213	1864.451	4.9858	5.6399
27. ACETIC ACID-BENZENE (M21)	760 MM	-333.35	1059.016	1.7715	1.0865
28. ACETIC ACID-TRICHLORDETHYLENE (F4)	500 MM	-177.955	870.848	1.7979	1.2309

SYSTEM	Temp. or Press.	$u_{12}-u_{11}$	$u_{21}-u_{22}$	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
29. ACETIC ACID-TRICHLORDETHYLENE (F4)	650 MM	-44.541	616.456	2.3673	2.1808
30. " " "	350 MM	-69.576	602.078	1.2648	1.8783
31. " " "	250 MM	-105.244	688.324	2.1889	2.1538
32. ACETIC ACID-ACETONE (M16)	50°C	-110.231	128.005	0.66712	3.5194
33. " " "	40°C	38.400	-42.486	0.64464	1.9470
34. " " "	30°C	38.406	-42.490	0.81961	1.7855
35. ACETIC ACID-ETHYL ETHER (M16)	389.7 MM	122.044	74.875	0.6312	2.2592
36. " " "	487.9 MM	-128.058	401.452	0.57804	3.0764
37. " " "	596.4.MM	-275.314	701.136	0.82911	2.6067
38. ACETIC ACID-BENZENE (M16)	30°C	-158.396	661.570	0.65127	0.17810
39. " " "	50°C	-268.731	829.496	0.62987	1.441
40. " " "	70°C	-300.574	965.389	1.2646	1.7361
41. ACETIC ACID-P-XYLENE (B2)	760 MM	-239.746	1006.299	3.4844	1.2731
42. ACETIC ACID-N-OCTANE (S10)	760 MM	66.494	651.092	3.5615	1.8813

SYSTEM	Temp. or Press.	$U_{12}-U_{11}$	$U_{21}-U_{22}$	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
43. ACETIC ACID-WATER (B14)	760 MM	44.679	200.057	2.3214	0.74953
44. " " (K1)	50 MM	343.377	-81.713	2.8010	2.9118
45. " " (I1)	70 MM	763.657	-309.736	1.3348	1.5876
46. " " "	200 MM	725.826	-291.959	1.3219	1.6166
47. " " (A5)	69.7°C	192.66	-11.847	1.4588	1.0797
48. " " "	89.9°C	54.635	133.723	1.3759	1.2580
49. " " "	79.9°C	323.37	-115.245	1.3503	1.2028
50. ACETIC ACID-TOLUENE (M16)	50°C	-261.754	762.649	1.7331	0.45057
51. " " "	30°C	-212.133	715.284	1.3578	0.76447
52. " " "	70°C	-255.752	823.01	1.5969	0.70956
53. " " (Z1)	80.05°C	-199.580	757.45	2.1473	1.9607
54. " " (H1)	745 MM	-279.922	991.996	1.5458	2.8474
55. " " (V8)	50 MM	103.809	-101.629	5.8391	10.412
56. " " (Z1)	69.94°C	-273.756	873.755	1.5601	1.1862

SYSTEM	Temp. or Press.	$u_{12}-u_{11}$	$u_{21}-u_{22}$	$\frac{\sum 100\Delta y}{N}$	$\frac{\sum \Delta P/P}{N}$
57. ACETIC ACID-N-DECANE (Z2)	760 MM	1070.43	-230.699	4.4671	1.0915
58. ACETIC ACID-DIETHYL ETHER (B12)	760 MM	308.744	-127.383	3.7217	3.9332
59. ACETIC ACID-N-OCTANE (Z2)	760 MM	43.94	707.451	3.9133	3.0062
60. ACETIC ACID-METHYLENE CHLORIDE (P8)	760 MM	112.638	384.955	0.53236	1.7948
61. ACETIC ACID-DIETHYLKETONE (H1)	70°C	-139.766	712.624	5.3844	1.5795
62. ACETIC ACID-BENZENE (W1)	20°C	-129.253	637.200	0.74913	1.6280
63. ACETIC ACID-N-HEPTANE (W1)	20°C	-8.912	709.652	1.5662	1.5581
64. ACETIC ACID-CYCLOHEXYL ACETATE (O4)	760 MM	-291.59	978.883	7.4745	3.8073
65. ACETIC ACID-N-BUTYL ACETATE (A11)	760 MM	-330.796	902.58	4.0458	1.5740
66. ACETIC ACID-ACETIC ANHYDRIDE (J8)	100 MM	-120.073	440.797	1.8725	0.74463

APPENDIX A5

TABLE A5.1 PURE COMPONENT PROPERTIES

COMPONENT	UNIQUAC PARAMETERS r	q	CRITICAL TEMP. °K	CRITICAL PRESS ATMS	CRITICAL VOLUME CC/GM MOLE	ACENTRIC FACTOR W	ACENTRIC FACTOR HOMOMORPH WH	DIPOLE MOMENT DEBYE	ASSOC. FACTOR
1. ACETIC ACID	2.02	1.40	594.76	57.2	171.0	0.439	0.439	1.75	0.0
2. ACETONE	2.57	2.34	508.7	46.6	213.5	0.309	0.187	2.880	0.0
3. BENZENE	3.19	2.40	562.0	48.6	260.1	0.211	0.211	0.0	0.0
4. N-BUTANOL	3.492	3.116	562.9	43.6	223.3	0.667	0.252	1.65	0.45
5. 2-BUTANOL	3.45	3.05	535.95	41.39	259.73	0.578	0.578	1.66	0.0
6. ISO-BUTANOL	3.45	3.05	549.85	42.390	261.23	0.586	0.586	1.64	0.0
7. TERT-BUTANOL	3.45	3.05	506.15	39.2	255.73	0.614	0.0	1.67	0.0
8. N-BUTYL ACETATE	4.84	4.196	573.1	30.1	397.8	0.455	0.400	1.680	0.400
9. CARBON TETRACHLORIDE	1.431	2.41	283.15	44.9	262.0	0.193	0.193	0.0	0.0
10. CHLOROFORM	2.87	2.41	536.6	54.0	276.0	0.214	0.187	1.020	0.28
11. CYCLOHEXANE	4.046	3.25	553.2	40.0	311.2	0.210	0.210	0.0	0.0
12. DI-ETHYL ETHER	3.395	3.20	466.95	36.2	284.0	0.283	0.252	1.160	0.0
13. DI-ISOPROPYL ETHER	4.74	4.096	500.05	28.4	0.0	0.340	0.0	1.13	0.0
14. DIMETHYLACETAMIDE			658.16	40.2	306.7	0.371	0.371	3.81	0.0
15. DIPROPYL ETHER	4.74	4.096	528.127	28.938	388.88	0.376	0.128	1.210	0.234

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TABLE A5.2 LIQUID MOLAR VOLUMES AT VARIOUS TEMPERATURES

	T_1 (°K)	T_2 (°K)	T_3 (°K)	V_1 (CC/GM MOLE)	V_2 (CC/GM MOLE)	V_3 (CC/GM MOLE)
1. ACETONE	228.15	273.15	323.15	67.38	71.483	76.826
2. TOLUENE	303.15	353.15	400.0	107.415	113.717	120.879
3. BENZENE	273.15	323.15	373.15	86.783	92.263	98.537
4. ETHYL ACETATE	293.15	409.45	0.0	122.445	138.426	0.0
5. CYCLOHEXANE	288.15	306.30	352.35	107.47	109.841	116.63
6. N -PROPANOL	293.15	343.15	393.15	74.785	78.962	84.515
7. N-BUTANOL	307.75	389.25	0.0	92.81	101.70	0.0
8. METHANOL	273.15	373.15	473.15	39.556	44.874	57.939
9.N-HEPTANE	273.15	323.15	373.15	143.045	152.303	163.619
10. ETHANOL	273.15	323.15	373.15	57.141	60.356	64.371
11. METHYL ETHYL KETONE	288.15	303.15	0.0	89.001	90.747	0.0
12. N-HEXANE	273.15	323.15	373.15	127.301	136.388	148.211
13. CARBON-TETRACHLORIDE	273.15	373.15	473.15	39.556	44.874	57.939
14. 2-BUTANOL	273.15	298.15	307.75	89.873	91.995	92.812
15. TERT-BUTANOL	313.15	373.15	413.15	96.864	106.280	114.915
16. ISO-BUTANOL	293.15	333.15	393.15	92.407	96.359	103.664

TABLE A5.2 continued

	T_1 (^oK)	T_2 (^oK)	T_3 (^oK)	V_1 (CC/GM MOLE)	V_2 (CC/GM MOLE)	V_3 (CC/GM MOLE)
17. DIPROPYL ETHER	288.15	303.15	0.0	135.904	138.56	0.0
18. ETHYLBENZENE	293.15	409.45	0.0	122.445	138.426	0.0
19. PYRIDINE	293.15	0.0	0.0	80.55	0.0	0.0
20. TETRACHLOROETHYLENE	333.16	353.16	0.0	84.04	85.85	0.0
21. DI-ISOPROPYL ETHER	293.15	342.15	0.0	140.294	146.827	0.0
22. N-BUTYL ACETATE	298.15	389.25	0.0	131.58	147.510	0.0
23. WATER	277.15	373.15	0.0	18.06	18.844	0.0
24. ACETIC ACID	343.16	303.16	0.0	60.201	57.001	0.0
25. CHLOROFORM	209.85	273.15	303.15	72.661	78.218	81.185
26. TRICHLOROETHYLENE	359.16	362.56	377.96	61.481	61.753	62.895
27. ETHYL ETHER	273.15	303.15	0.0	100.679	105.599	0.0
28. P-XYLENE	352.85	373.15	0.0	131.09	134.18	0.0
29. N-OCTANE	273.15	393.15	0.0	158.97	185.182	0.0
30. N-DECANE	253.15	333.15	423.15	192.18	208.99	233.56
31. METHYLENE CHLORIDE	293.15	0.0	0.0	63.578	0.0	0.0
32. CYCLO-HEXYL ACETATE	293.15	0.0	0.0	144.355	0.0	0.0
33. DIETHYL KETONE	293.15	0.0	0.0	105.551	0.0	0.0

TABLE A5.3

CONSTANTS FOR EXTENDED ANTOINE EQUATION

(TEMPERATURE IN °K)

$$\mathrm{LN}\ P\ (\mathrm{ATM}) = C1 + \frac{C2}{C3+T} + C4T + C5T^2 + C6\ \mathrm{LN}T$$

COMPONENT	N-VALERIC ACID	P-XYLENE	BENZENE	CARBON TETRACHLORIDE	METHANOL	N-HEPTANE
C_1	-92.3300280	-125.0746511	-181.4980334	-114.4587210	-138.1141270	-259.0937357
C_2	-388.6936	-136.4260	1356.9578	-1402.4668	465.6287	2394.8215
C_3	-180.1673	682.9106	1278.0651	-40.3325	385.5231	34214.3802
C_4	0.015767582	-0.002514263	-0.098544226	-0.083630133	-0.018978468	-0.177742418
C_5	-0.000024071	-0.000029652	0.00040697	0.000042500	-0.00002227	0.000091829
C_6	14.94564	21.80365	35.86096	24.41867	25.14546	51.91759
TEMPERATURE RANGE °C	42.2 - 184.4	58.4 - 139.30	11.0 - 142.5	-50.0 - 141.7	11.9 - 112.5	26.0 - 165.7
ΔP AVE MM HG	0.445145	0.768088	2.16295	0.448199	0.79818	3.3642

COMPONENT	ETHANOL	N-BUTYL ACETATE	N-BUTANOL	ACETIC ACID	TOLUENE	WATER
C_1	-228.8515206	-7.8627688	-2.8269242	-156.4916416	-144.0840519	-292.9366624
C_2	-3128.0278	-3886.3618	-2943.1148	1077.5339	-8547.4742	-11623.5836
C_3	811.4467	0.1562	-82.5656	77.2293	375.9085	776.9732
C_4	-0.129801335	0.023565518	0.023655670	-0.00617468	-0.099361942	-0.244124749
C_5	0.000050713	-0.000031017	-0.000039487	-0.000036648	0.000040695	0.000136191
C_6	46.21066	2.19155	1.27729	27.17252	31.50849	63.35345
TEMPERATURE RANGE °C	-31.3 - 78.6	52.6 - 125.8	15.1 - 139.8	10.0 - 140.1	35.5 - 178.0	10.0 - 120.1
ΔP AVE MM HG	6.388254	1.961449	2.061781	2.346	1.713	0.82006

COMPONENT	ETHYL ACETATE	CHLOROFORM	N-OCTANE	DIETHYL-ETHER	ACETONE	TRICHLORO-ETHYLENE
C_1	-2.2317474	-209.5836	-337.8023308	-133.8979297	-456.79997	-301.3131159
C_2	-1871.4222	-43061.9000	16067.9471	-19414.213	6858.6066	27097.326
C_3	-71.9206	688.1534	983.2278	281.8819	46.8097	31737.7544
C_4	0.026808750	-0.313319578	-0.241008115	-0.248396791	-0.308002292	-0.242870156
C_5	0.000027455	0.000199218	0.000138773	0.000159850	0.000171219	0.000155666
C_6	0.49952	57.54059	66.8322	39.81736	91.49684	60.42351
TEMPERATURE RANGE °C	0.0 - 136.6	-58.0 - 61.3	0.0 - 130.0	-74.3 - 122.0	-59.4 - 113.0	-43.8 - 86.7
Δ P AVE MM HG	0.89126	1.6853	4.1771	2.3588	5.3711	0.28154

COMPONENT	ISO-BUTANOL	TERT-BUTANOL	SEC-BUTANOL	N-PROPANOL	ISO PROPANOL
C_1	-294.5159756	-3915505441	-335.8517151	-166.3531124	-237.1009026
C_2	-16936.9127	26459.8725	-3971.2682	-348.4762	14721.6404
C_3	31204.1231	32465.2372	32713.3774	-36.1392	32065.4792
C_4	-0.223389573	-0.276961546	-0.239966296	-0.02534639	-0.108911672
C_5	0.000117818	0.000136299	-0.00124043	0.000029886	0.000034737
C_6	62.80022	78.89508	69.13812	30.58179	45.17645
TEMPERATURE RANGE °C	-9.0 - 108.0	-20.4 - 82.9	7.2 - 147.5	-15.0 - 111.3	-26.1 - 122.7
Δ P AVE MM HG	2.1506	2.1791	0.65313	5.1021	0.92949

APPENDIX A.6

EXPERIMENTAL RESULTS

Table A6.1 System Ethyl Acetate (1)-n-Butanol at 760 mm Hg

Analysis by Refractive Index

Run No.	x Mole frac.	y Mole frac.	Temperature ^{o}C	V_1	V_2
1	0.070	0.235	111.6	1.331	1.059
2	0.121	0.355	107.3	1.295	1.103
3	0.147	0.415	105.1	1.318	1.119
4	0.150	0.420	105.0	1.310	1.117
5	0.175	0.490	103.7	1.355	1.063
6	0.217	0.550	100.8	1.324	1.104
7	0.221	0.532	99.4	1.306	1.219
8	0.225	0.550	100.1	1.301	1.147
9	0.310	0.680	96.0	1.306	1.078
10	0.334	0.696	95.0	1.276	1.104
11	0.375	0.725	93.1	1.252	1.156
12	0.380	0.740	93.6	1.240	1.075
13	0.399	0.747	92.2	1.241	1.143
14.	0.414	0.762	91.6	1.241	1.131
15	0.460	0.798	91.2	1.183	1.059
16	0.490	0.815	90.4	1.161	1.062
17	0.501	0.812	90.1	1.141	1.117
18	0.520	0.835	90.6	1.114	0.998
19	0.565	0.840	87.5	1.130	1.219
20	0.585	0.845	87.7	1.091	1.228
21	0.600	0.855	87.2	1.092	1.218
22	0.615	0.867	86.0	1.120	1.223
23	0.635	0.865	85.4	1.102	1.344

Table A6.1 continued

Run No.	x Mole frac.	y Mole frac.	Temperature ^{o}C	V_1	V_2
24	0.640	0.870	85.7	1.090	1.295
25	0.645	0.880	85.8	1.091	1.207
26	0.675	0.881	84.7	1.079	1.372
27	0.695	0.895	84.0	1.087	1.331
28	0.700	0.905	83.5	1.108	1.252
29	0.764	0.917	82.6	1.058	1.448
30	0.793	0.926	81.7	1.058	1.537
31	0.800	0.920	81.0	1.065	1.771
32	0.820	0.954	81.2	1.071	1.121
33	0.855	0.955	80.8	1.041	1.387
34	0.860	0.950	80.5	1.039	1.618
35	0.890	0.974	79.8	1.052	1.106
36	0.900	0.968	79.7	1.037	1.504
37	0.930	0.990	78.5	1.066	0.710
38	0.950	0.985	78.0	1.055	1.526
39	0.920	0.994	78.1	1.040	1.013

Table A6.2 System n-Butanol (1)-n-Butyl Acetate (2) at 760 mm Hg

Analysis by refractive index

Run No.	x Mole frac.	y Mole frac.	Temperature °C	V_1	V_2
1	0.021	0.058	125.7	2.186	1.012
2	0.031	0.061	125.3	1.619	1.024
3	0.035	0.066	125.4	1.652	1.026
4	0.037	0.084	125.5	1.807	1.006
5	0.039	0.076	125.2	1.598	1.018
6	0.046	0.108	125.1	1.895	1.001
7	0.050	0.114	124.6	1.852	1.004
8	0.051	0.099	124.0	1.741	1.076
9	0.055	0.115	124.8	1.693	1.006
10	0.061	0.131	125.4	1.746	0.997
11	0.062	0.130	124.7	1.706	1.000
12	0.070	0.126	123.8	1.414	1.022
13	0.074	0.141	124.2	1.676	1.002
14	0.092	0.166	122.7	1.513	1.062
15	0.109	0.191	122.4	1.495	1.070
16	0.129	0.221	121.2	1.567	1.071
17	0.138	0.227	121.1	1.515	1.080
18	0.180	0.275	120.5	1.466	1.084
19	0.191	0.289	120.1	1.499	1.070
20	0.191	0.291	120.2	1.438	1.079
21	0.197	0.298	120.0	1.433	1.080
22	0.202	0.303	120.0	1.404	1.092
23	0.220	0.326	119.8	1.430	1.073

Table A6.2 continued

Run No.	x Mole frac.	y Mole frac.	Temperature °C	V_1	V_2
24	0.242	0.355	119.3	1.425	1.074
25	0.247	0.358	119.3	1.411	1.078
26	0.263	0.379	119.2	1.409	1.070
27	0.269	0.381	119.0	1.388	1.077
28	0.280	0.396	118.9	1.394	1.073
29	0.285	0.401	118.7	1.390	1.073
30	0.286	0.397	118.7	1.381	1.089
31	0.304	0.412	118.6	1.352	1.092
32	0.318	0.426	118.4	1.206	1.049
33	0.320	0.429	118.45	1.337	1.085
34	0.347	0.445	118.3	1.291	1.108
35	0.362	0.465	118.2	1.300	1.098
36	0.408	0.501	117.7	1.255	1.113
37	0.418	0.506	117.7	1.249	1.126
38	0.432	0.518	117.6	1.238	1.130
39	0.455	0.525	117.5	1.193	1.163
40	0.489	0.559	117.4	1.197	1.164
41	0.491	0.560	117.4	1.189	1.161
42	0.512	0.568	117.3	1.161	1.194
43	0.521	0.577	117.3	1.159	1.191
44	0.547	0.598	117.3	1.177	1.163
45	0.559	0.605	117.3	1.139	1.209
46	0.564	0.604	117.3	1.126	1.229
47	0.568	0.608	117.3	1.126	1.229
48	0.569	0.612	117.3	1.128	1.225
49	0.583	0.624	117.3	1.126	1.221
50	0.607	0.636	117.25	1.089	1.287

Table A6.2 continued

Run No.	x Mole frac.	y Mole frac.	Temperature °C	V_1	V_2
51	0.615	0.647	117.25	1.109	1.245
52	0.628	0.657	117.25	1.090	1.275
53	0.630	2.655	117.25	1.063	1.295
54	0.640	0.667	117.25	1.084	1.242
55	0.640	0.660	117.25	1.029	1.383
56	0.641	0.655	117.25	1.035	1.361
57	0.650	0.677	117.2	1.088	1.234
58	0.681	0.698	117.2	1.064	1.281
59	0.714	0.722	117.2	1.076	1.225
60	0.716	0.718	117.2	1.037	1.360
61	0.726	0.726	117.2	1.069	1.316
62	0.739	0.735	117.2	1.036	1.410
63	0.745	0.736	117.2	1.047	1.319
64	0.760	0.748	117.2	1.024	1.418
65	0.774	0.755	117.25	1.042	1.346
66	0.777	0.763	117.25	1.036	1.408
67	0.782	0.768	117.2	1.052	1.320
68	0.786	0.776	117.3	1.047	1.362
69	0.792	0.779	117.3	1.096	1.185
70	0.801	0.793	117.3	1.031	1.409
71	0.805	0.792	117.3	1.035	1.445
72	0.820	0.811	117.3	1.037	1.418
73	0.821	0.810	117.3	1.037	1.436
74	0.824	0.812	117.3	1.033	1.442
75	0.837	0.811	117.4	1.014	1.563
76	0.842	0.829	117.4	1.032	1.461

Table A6.2 continued

Run No.	x Mole frac.	y Mole frac.	Temperature ^{o}C	V_1	V_2
77	0.845	0.823	117.4	1.019	1.539
78	0.875	0.867	117.5	1.014	1.614
79	0.885	0.868	117.3	1.022	1.541
80	0.937	0.911	117.6	1.005	1.885
81	0.950	0.935	117.6	1.017	1.733
82	0.972	0.975	117.7	1.031	1.185

Table A6.3 System n-Butanol-n-Butyl Acetate at 760 mm Hg

Analysis by Gas Liquid Chromatography

Run No.	x Mole frac.	y Mole frac.	Temperature °C	V_1	V_2
1	0.014	0.046	125.7	2.600	1.018
2	0.034	0.071	125.5	1.663	1.017
3	0.03	0.059	125.3	1.566	1.026
4	0.032	0.081	125.4	2.028	1.010
5	0.038	0.098	125.2	2.060	0.994
6	0.027	0.069	125.1	2.063	1.025
7	0.049	0.104	124.0	1.829	1.070
8	0.059	0.125	124.7	1.724	1.003
9	0.055	0.125	124.8	1.841	0.994
10	0.054	0.119	124.6	1.790	1.003
11	0.068	0.138	124.4	1.650	0.997
12	0.069	0.173	124.2	2.056	0.965
13	0.073	0.174	123.8	1.952	0.966
14.	0.096	0.169	122.7	1.540	1.058
15	0.114	0.199	122.4	1.558	1.059
16	0.134	0.218	121.2	1.546	1.075
17	0.177	0.274	120.5	1.461	1.086
18	0.136	0.225	121.1	1.523	1.080
19	0.182	0.269	120.1	1.395	1.100
20	0.187	0.271	120.2	1.373	1.107
21	0.196	0.297	120.0	1.436	1.080
22	0.206	0.304	120.0	1.409	1.090
23	0.218	0.379	119.8	1.663	0.989

Table A6.3 continued

Run No.	x Mole frac.	y Mole frac.	Temperature ^oC	V_1	V_2
24	0.238	0.349	119.3	1.425	1.079
25	0.251	0.364	119.3	1.411	1.074
26	0.247	0.351	119.2	1.390	1.095
27	0.268	0.384	119.0	1.404	1.070
28	0.276	0.404	118.9	1.443	1.053
29	0.279	0.383	118.7	1.358	1.098
30	0.287	0.397	118.7	1.366	1.083
31	0.292	0.398	118.6	1.359	1.099
32	0.296	0.408	118.45	1.375	1.087
33	0.331	0.424	118.4	1.200	1.053
34	0.349	0.451	118.3	1.301	1.099
35	0.362	0.459	118.2	1.283	1.110
36	0.404	0.504	117.7	1.285	1.106
37	0.416	0.490	117.7	1.237	1.142
38	0.427	0.515	117.6	1.245	1.127
39	0.450	0.526	117.5	1.209	1.150
40	0.473	0.552	117.4	1.223	1.146
41	0.487	0.561	117.4	1.201	1.150
42	0.514	0.570	117.3	1.161	1.193
43	0.533	0.584	117.3	1.150	1.204
44	0.541	0.584	117.3	1.130	1.222
45	0.558	0.604	117.3	1.137	1.212
46	0.568	0.611	117.3	1.131	1.219
47	0.571	0.604	117.3	1.113	1.250
48	0.580	0.615	117.3	1.114	1.241
49	0.587	0.627	117.3	1.124	1.223

Table A6.3 continued

Run No.	x Mole frac.	y Mole frac.	Temperature ^oC	V_1	V_2
50	0.611	0.644	117.25	1.112	1.242
51	0.616	0.647	117.25	1.108	1.248
52	0.635	0.650	117.25	1.079	1.301
53	0.640	0.661	117.25	1.074	1.264
54	0.642	0.662	117.25	1.074	1.269
55	0.659	0.668	117.25	1.056	1.310
56	0.669	0.677	117.25	1.056	1.314
57	0.683	0.690	117.2	1.052	1.315
58	0.696	0.708	117.2	1.055	1.287
59	0.648	0.668	117.2	1.074	1.268
60	0.712	0.719	117.2	1.054	1.314
61	0.721	0.722	117.2	1.043	1.341
62	0.731	0.721	117.2	1.026	1.394
63	0.741	0.742	117.2	1.046	1.373
64	0.764	0.758	117.2	1.038	1.377
65	0.755	0.749	117.25	1.034	1.379
66	0.761	0.744	117.2	1.019	1.441
67	0.774	0.761	117.25	1.033	1.420
68	0.749	0.744	117.3	1.047	1.373
69	0.779	0.775	117.3	1.046	1.368
70	0.797	0.784	117.3	1.034	1.440
71	0.799	0.782	117.3	1.030	1.460
72	0.820	0.802	117.3	1.025	1.485
73	0.825	0.794	117.3	1.008	1.589
74	0.831	0.809	117.3	1.023	1.530
75	0.838	0.811	117.4	1.012	1.572

Table A6.3 continued

Run No.	x Mole frac.	y Mole frac.	Temperature ^{o}C	V_1	V_2
76	0.842	0.822	117.4	1.021	1.518
77	0.863	0.839	117.4	1.012	1.577
78	0.867	0.846	117.5	1.018	1.557
79	0.883	0.869	117.3	1.018	1.557
80	0.931	0.902	117.6	1.002	1.895
81	0.952	0.931	117.6	1.010	1.916
82	0.993	1.000	117.7	1.035	1.000

Table A6.4 System Ethyl Acetate-n-Butyl Acetate at 760 mm Hg

Analysis by Refractive Index

Run No.	x Mole frac.	y Mole frac.	Temperature ^{o}C	V_1	V_2
1	0.024	0.104	124.9	1.245	1.004
2	0.039	0.146	123.3	1.115	1.017
3	0.042	0.154	122.9	1.102	1.023
4	0.049	0.175	122.4	1.085	1.019
5	0.050	0.176	122.3	1.072	1.022
6	0.053	0.183	122.1	1.057	1.022
7	0.065	0.224	121.0	1.082	1.015
8	0.075	0.251	120.2	1.070	1.014
9	0.100	0.327	118.1	1.098	0.996
10	0.109	0.344	117.2	1.083	1.007
11	0.113	0.356	116.8	1.091	1.005
12	0.143	0.425	114.6	1.085	0.992
13	0.153	0.450	113.6	1.100	0.989
14	0.160	0.460	113.0	1.091	0.998
15	0.185	0.506	111.2	1.085	0.994
16	0.200	0.531	110.1	1.083	0.995
17	0.210	0.547	109.2	1.087	1.001
18	0.225	0.569	108.3	1.079	0.999
19	0.235	0.580	107.5	1.075	1.011
20	0.245	0.595	107.1	1.069	1.001
21	0.259	0.611	106.2	1.062	1.008
22	0.272	0.628	105.3	1.064	1.010
23	0.282	0.639	104.6	1.063	1.016
24	0.307	0.669	103.05	1.065	1.015

Table A6.4 continued

Run No.	x Mole frac.	y Mole frac.	Temperature ^oC	V_1	V_2
25	0.315	0.675	102.8	1.054	1.017
26	0.325	0.687	102.4	1.051	1.007
27	0.336	0.700	101.7	1.055	1.004
28	0.381	0.740	99.1	1.055	1.017
29	0.428	0.777	96.8	1.050	1.023
30	0.436	0.783	96.5	1.055	0.995
31	0.441	0.788	96.2	1.036	1.051
32	0.493	0.822	93.9	1.044	1.014
33	0.558	0.854	91.3	1.035	1.046
34	0.571	0.861	90.8	1.051	1.022
35	0.602	0.874	89.7	1.042	1.031
36	0.658	0.898	87.8	1.021	1.066
37	0.690	0.908	86.7	1.017	1.110
38	0.707	0.912	86.1	1.015	1.148
39	0.713	0.916	86.0	1.014	1.123
40	0.803	0.950	83.5	1.007	1.068
41	0.822	0.952	83.0	1.000	1.156
42	0.858	0.960	82.0	0.997	1.254
43	0.895	0.969	80.9	0.998	1.370
44	0.914	0.970	80.4	0.993	1.650
45	0.945	0.987	79.7	0.998	1.137
46	0.961	0.991	78.6	1.021	1.170

Table A6.5 System Ethyl Acetate-n-Butyl Acetate at 760 mm Hg

Analysis by Gas liquid chromatography

Run No.	x Mole frac.	y Mole frac.	Temperature ^oC	V_1	V_2
1	0.016	0.046	124.9	0.826	1.061
2	0.032	0.101	123.3	0.940	1.063
3	0.05	0.152	122.9	0.913	1.034
4	0.051	0.198	122.4	1.183	0.996
5	0.056	0.204	122.3	1.107	0.991
6	0.061	0.219	122.1	1.127	1.017
7	0.064	0.232	121.0	1.109	0.972
8	0.076	0.239	120.2	1.005	1.031
9	0.099	0.304	118.1	1.031	1.029
10	0.111	0.319	117.2	0.986	1.048
11	0.117	0.383	116.8	1.134	0.967
12	0.139	0.421	114.6	1.106	0.994
13	0.156	0.450	113.6	1.079	0.993
14	0.166	0.464	113.0	1.061	0.997
15	0.184	0.509	111.2	1.098	0.987
16	0.198	0.519	110.1	1.069	1.018
17	0.210	0.567	109.2	1.126	0.957
18	0.231	0.579	108.3	1.070	0.983
19	0.237	0.579	107.5	1.064	1.016
20	0.240	0.598	107.1	1.096	0.987
21	0.261	0.620	106.2	1.070	0.987
22	0.275	0.625	105.3	1.047	1.022
23	0.288	0.640	104.6	1.043	1.022
24	0.311	0.680	103.05	1.069	0.987

Table A6.5 continued

Run No.	x Mole frac.	y Mole frac.	Temperature °C	V_1	V_2
25	0.320	0.691	102.8	1.062	0.974
26	0.323	0.685	102.4	1.055	1.010
27	0.335	0.684	101.7	1.034	1.056
28	0.382	0.731	99.1	1.040	1.054
29	0.421	0.761	96.8	1.046	1.081
30	0.436	0.791	96.5	1.067	0.990
31	0.441	0.784	96.2	1.044	1.045
32	0.504	0.826	93.9	1.027	1.013
33	0.563	0.868	91.3	1.050	0.967
34	0.577	0.869	90.8	1.044	1.013
35	0.613	0.871	89.7	1.014	1.130
36	0.661	0.897	87.8	1.015	1.086
37	0.694	0.902	86.7	1.010	1.136
38	0.711	0.913	86.1	1.010	1.151
39	0.719	0.909	86.0	0.997	1.242
40	0.804	0.964	83.5	1.020	0.773
41	0.825	0.960	83.0	1.005	0.980
42	0.861	0.956	82.0	0.989	1.409
43	0.900	0.963	80.9	0.986	1.717
44	0.918	0.964	80.4	0.983	2.077
45	0.951	0.971	79.7	0.975	2.860
46	0.967	0.997	78.6	1.021	0.461

Table A6.6 Calibration Data for Refractive Index Composition

1. System Ethyl Acetate-n-Butanol

Mole Fraction Ethyl Acetate	N_D^{25}
0.0	1.39825
0.1	1.39613
0.2	1.39381
0.3	1.39171
0.4	1.38918
0.5	1.38685
0.6	1.38426
0.7	1.38130
0.8	1.37789
0.9	1.37427
1.0	1.37057

2. System Ethyl Acetate-n-Butyl Acetate

Mole Fraction Athyl Acetate	N_D^{25}
0.0	1.39191
0.1	1.39045
0.2	1.38860
0.3	1.38690
0.4	1.38514
0.5	1.38311
0.6	1.38056
0.7	1.37804
0.8	1.37548
0.9	1.37293
1.0	1.37057

3. System-n-Butanol-n-Butyl Acetate

Mole Fraction n-Butanol	N_D^{25}
0.0	1.39191
0.1	1.39265
0.2	1.39335
0.3	1.39419
0.4	1.39487
0.5	1.39552
0.6	1.39611
0.7	1.39670
0.8	1.39727
0.9	1.39776
1.0	1.39825

Table A6.7 Refractive Indices and Boiling Points

Ethyl Acetate

N_D^{25}	B.Pt (°C)
1.36900 (M3)	77.15 (T11)
1.36970 (T11)	77.11 (T11)
1.37012 (T11)	77.15 (T11)
1.37008 (T11)	77.3 This work
1.37057 This work	

n-Butanol

N_D^{25}	B.Pt (°C)
1.39728 (T11)	117.5 (S9)
1.39800 (M3)	117.8 (T11)
1.39920 (T11)	117.8 (T11)
1.39825 This work	117.8 This work

n-Butyl Acetate

N_D^{25}	B.Pt (°C)
1.39176 (T11)	126.1 (S9)
1.39265 (S9)	126.09 (T11)
1.39191 This work	126.52 (T11)
	126.1 This work

APPENDIX A.7

Miscellaneous experimental results.

A7.1. Tie lines in acetic acid-toluene-water system.

A7.2. Comparison of models for acetic acid-toluene data using vapour phase correction only.

A7.3. Results of data reduction and consistency test on experimental data.

A7.1

Table 1 Tie lines in acetic acid-toluene-water system computed using NRTL equation

System temperature 30°C

Compositions in wt% basis

WATER	TOLUENE	ACETIC ACID	WATER	TOLUENE	ACETIC ACID
18.49	4.31	77.21	0.89	55.31	43.80
21.60	3.42	74.99	0.74	62.35	36.92
35.71	2.45	61.84	1.66	93.47	6.36
36.50	2.37	61.13	1.60	93.81	6.03
40.94	1.85	57.21	1.46	94.91	4.94
42.20	1.70	56.09	1.44	95.13	4.73
44.61	1.47	53.95	1.43	95.42	4.44
47.13	0.82	52.04	0.42	88.95	10.63
48.41	0.76	50.83	0.42	88.57	11.01
50.44	0.68	48.87	0.42	89.02	10.56
52.23	1.06	46.71	1.12	97.07	2.82
54.98	0.55	44.47	0.41	90.06	9.52
56.05	0.53	43.42	0.41	90.39	9.20
58.5	0.47	41.02	0.41	90.67	8.91
62.27	0.64	37.09	0.09	98.13	1.76
68.32	0.50	31.18	0.05	99.25	0.70
76.23	0.29	23.47	0.11	98.70	1.18
93.20	1.74	6.63	0.03	99.9	0.07

Table 2 Tie lines in acetic acid-toluene-water system computed using NRTL equation

System temperature 60°C

Compositions on wt% basis

PHASE 1 (WATER)			PHASE 2 (TOLUENE)		
WATER	TOLUENE	ACETIC ACID	WATER	TOLUENE	ACETIC ACID
18.09	5.25	76.66	1.04	54.83	44.13
26.28	3.03	70.68	0.704	73.67	25.63
25.51	2.89	69.59	0.71	70.55	28.74
31.22	2.44	66.33	0.63	76.20	23.17
37.63	1.68	60.69	0.52	87.99	11.49
41.81	1.50	56.68	0.531	84.07	15.40
48.20	1.14	50.66	0.531	86.31	13.16
57.90	0.75	41.35	0.70	74.02	25.27
60.12	0.93	38.95	0.50	90.79	8.70
61.43	0.60	37.93	0.50	88.25	11.23
63.19	0.63	36.18	0.50	89.76	9.74
69.22	0.49	30.3	0.50	90.02	9.47
71.19	0.45	28.36	0.50	90.19	9.31
81.46	0.31	18.22	0.48	92.2	7.31
83.28	0.29	16.42	0.48	92.56	6.97
87.07	0.25	12.68	0.47	93.44	6.09
90.96	0.20	8.83	0.46	94.33	5.20
99.68	0.04	0.27	0.33	95.90	7.45

Table 3 Tie lines in acetic acid-toluene-water system computed using UNIQUAC equation

System temperature 60°C

Compositions on wt% basis

PHASE 1 (WATER)			PHASE 2 (TOLUENE)		
WATER	TOLUENE	ACETIC ACID	WATER	TOLUENE	ACETIC ACID
26.08	3.25	70.66	2.22	69.77	30.01
34.78	2.10	63.11	0.11	78.3	21.58
36.85	1.93	61.22	0.10	79.93	19.96
39.94	1.64	58.41	0.09	81.56	18.34
42.25	1.51	56.23	0.80	83.13	16.78
44.73	1.39	53.87	0.71	84.67	15.25
46.90	1.31	51.79	0.06	86.08	13.85
49.80	1.19	49.0	0.06	87.58	12.36
50.32	1.16	48.51	0.05	87.68	12.26
58.09	0.74	41.16	0.05	89.11	10.84
61.42	0.68	37.90	0.04	90.55	9.41
65.04	0.63	36.32	0.04	91.96	7.99
69.06	0.59	30.36	0.03	93.34	6.61
73.55	0.54	25.91	0.03	94.72	5.24
78.65	0.49	20.85	0.02	96.07	0.39
84.53	0.45	15.01	0.02	97.40	2.57
91.41	0.41	8.17	0.02	98.7	1.27

Table 4 Tie lines in acetic acid-toluene-water system computed using UNIQUAC equation

System temperature 30°C

Compositions on wt% basis

PHASE 1 (WATER)			PHASE 2 (TOLUENE)		
WATER	TOLUENE	ACETIC ACID	WATER	TOLUENE	ACETIC ACID
16.60	15.81	67.58	7.57	31.22	61.2
34.42	8.18	57.39	0.69	74.78	25.12
36.94	5.42	57.64	0.43	75.67	23.90
37.98	7.48	54.56	0.60	76.82	22.58
41.70	6.87	51.41	0.51	79.48	20.00
45.72	6.33	47.94	0.44	82.06	17.50
48.39	6.06	45.55	0.39	83.80	15.80
49.73	5.93	44.34	0.37	84.59	15.04
52.07	5.53	42.40	0.38	85.06	14.56
55.52	5.23	39.24	0.34	86.77	12.89
57.82	4.91	37.27	0.33	87.41	12.26
59.71	3.13	37.16	0.21	87.64	12.14
69.92	4.67	32.41	0.28	89.90	9.82
64.05	3.09	32.86	0.18	90.04	9.78
66.40	4.63	30.97	0.27	90.61	9.12
68.40	2.79	28.8	0.16	91.47	8.37
68.61	4.39	27.0	0.24	92.1	7.61
72.2	3.98	23.82	0.23	92.88	6.89
78.56	3.76	17.68	0.20	95.04	4.76
79.72	2.39	17.88	0.12	95.13	4.75
92.67	2.04	5.30	0.09	98.58	1.32
98.49	1.17	0.34	7.77	91.36	0.86

Table 5 Tie lines in acetic acid-toluene-water system computed using NRTL equation and concentration dependent correction factors.

PHASE 1 (WATER)			PHASE 2 (TOLUENE)		
WATER	TOLUENE	ACETIC ACID	WATER	TOLUENE	ACETIC ACID
30.53	2.29	67.17	1.69	28.8	69.50
33.46	1.87	64.66	1.67	31.37	66.95
38.95	1.1	59.93	0.65	37.33	62.0
41.14	0.9	57.90	0.3	42.6	57.07
49.94	0.56	49.49	0.10	57.27	42.62
53.14	0.48	46.37	0.04	71.1	28.85
54.48	0.53	44.97	0.01	97.13	2.85
55.81	5.17	43.67	0.01	98.5	1.48
96.14	1.39	3.72	0.01	98.69	1.30

A7.2

Acetic acid-toluene, comparison of models

Table 1 Wilson, 2 & 3 NRTL and UNIQUAC using vapour phase correction only.

DATA & MODEL	$PAR_{12}-PAR_{11}$	$PAR_{21}-PAR_{22}$	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
Meehan's at 70 (M16)-Wilson	1392.17	24.16	1.4762	0.61633
-2NRTL (= 0.47)	498.03	884.58	1.5836	0.68572
-3NRTL (= 0.49002)	498.03	913.50	1.5941	0.71534
-UNIQUAC	-255.752	823.01	1.5969	0.70956
Zawidski at 69.94 (Z1)-Wilson	1448.75	4.58	1.4363	1.0841
" -2NRTL (= 0.47)	483.17	931.81	1.5375	1.2048
" -3NRTL (= 0.50637)	483.17	985.89	1.5793	1.1266
" -UNIQUAC	-273.756	873.755	1.5601	1.1862

Table 2 3 Parameter NRTL equation using vapour phase correction only

DATA	$g_{12}-g_{11}$	$g_{21}-g_{22}$		$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
Zawidski at 80.05 (Z1)	686.16	1058.85	0.58454	1.8532	1.4967
Meehan at 50.0 (M16)	392.21	87.92	0.4246	1.4035	0.64473
Markuzin & Pavlova at 30 (M10)	461.83	303.82	1.21206	0.54496	0.4418

Table 3 Wilson equation fitted to Meehan's data at 50°C

MODEL USED	$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	$\frac{\sum 100\Delta Y}{N}$	$\frac{\sum \Delta P/P}{N}$
Vapour correction only	1298.10	-104.67	1.7122	0.44785
$k = k_A$	583.14	-93.48	1.3660	0.65803
$k \neq k_A$	562.83	-137.18	0.059577	0.47965

Table 4 Wilson equation fitted to data of Markuzin and Pavlova at 30°C

MODEL USED	$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	$\sum\frac{100\Delta Y}{N}$	$\sum\frac{\Delta P/P}{N}$
Vapour correction only	1342.25	-48.19	1.2018	0.69801
$k = k_A$	609.87	-34.86	0.8252	0.5954
$k \neq k_A$	671.92	-152.76	0.02938	1.0721

Table 5 NRTL parameters for acetic acid-toluene and acetic acid-water

SYSTEM	$g_{12}-g_{11}$	$g_{21}-g_{22}$	α	$\sum\frac{100\Delta Y}{N}$	$\sum\frac{\Delta P/P}{N}$
ACETIC ACID-TOLUENE [a] (L.E.M.F.)	423.92	351.72	-1.0	2.3971	4.3397
ACETIC ACID-TOLUENE [b] (L.E.M.F.)	423.92	769.02	0.31335	2.3782	4.1658
ACETIC ACID-TOLUENE ($k \neq k_A$)	630.88	-30.52	0.38528	0.9566	5.0385
ACETIC ACID-TOLUENE	563.08	826.51	0.57364	2.4980	4.2269
ACETIC ACID-TOLUENE ($k = k_A$)	631.86	5.84	0.5238	2.3295	4.5302
ACETIC ACID-WATER	875.7	1099.34	0.79110	4.1758	1.8125
ACETIC ACID-WATER ($k = k_A$)	1360.73	-578.87	0.16832	4.5483	2.5259
ACETIC ACID-WATER [a] (L.E.M.F.)	440.54	317.91	-1.0	5.7836	3.1622
ACETIC ACID-WATER [b] (L.E.M.F.)	440.54	304.12	-1.09893	5.7421	3.0841

Data sources as for six parameter NRTL equation

a. 2 parameter fit used

b. 3 parameter fit used

Table 6 6 parameter NRTL equation

SYSTEM	C_1	C_2	α°	D_1	D_2	α^T	$\sum\frac{100\Delta Y}{N}$	$\sum\frac{\Delta P/P}{N}$
ACETIC ACID-TOLUENE (L.E.M.F.)	319.88	883.33	0.4202	3.841	-3.305	-0.00084	2.9761	5.3126
ACETIC ACID-TOLUENE	563.08	826.51	0.57364	1.678	-1.917	-0.00103	2.4262	4.0946
ACETIC ACID-TOLUENE ($k = k_A$)	621.66	107.54	0.30112	14.17	-13.25	-0.002528	2.3888	4.1568
ACETIC ACID-WATER	875.7	1893.43	0.67057	2.776	-3.231	0.001523	3.4909	1.2237
ACETIC ACID-WATER ($k = k_A$)	1301.135	-673.91	0.16147	-6.779	6.842	0.001646	4.7545	2.1107
ACETIC ACID-WATER (L.E.M.F.)	185.41	200.04	-6.76601	1.279	0.8848	0.0316	2.9511	2.8741

Acetic Acid-Toluene data	Zawidski (Z1), Haughton (H3), Meehan (M16), Markuzin and Pavlova (M10)
Acetic Acid-Water data	ITO (I1), Arich and Tagliavani (A5), Sebastiani and Lacquanti (S8)
L.E.M.F.	Modification of NRTL equation due to Marina. $\alpha = -1$ used as starting point.

Table 7 Wilson parameters for acetic acid-toluene data

SYSTEM	$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	$\sum\frac{100\Delta Y}{N}$	$\sum\frac{\Delta P/P}{N}$
ACETIC ACID-TOLUENE ($k \neq k_A$)	509.3	92.69	0.9309	4.9747
ACETIC ACID-TOLUENE	1184.91	151.72	2.4113	4.4128
ACETIC ACID-TOLUENE ($k = k_A$)	481.88	242.78	2.1431	4.3377

Acetic-toluene data as for six parameter NRTL equation

A7.3

Table 1 4 Suffix Margules parameters

SYSTEM	A	B	D	$\frac{\sum \Delta Y * 100}{N}$	$\frac{\sum \Delta P/P}{N}$
ETHYL ACETATE-N-BUTANOL (REF.IND.)	0.62686	0.60085	0.22250	1.8285	0.95732
ETHYL ACETATE-N-BUTYL ACETATE (REF.IND.)	0.14958	0.29531	0.26967	0.64402	0.40612
N-BUTANOL-N-BUTYL ACETATE "	0.75276	0.42326	-0.38184	2.6512	0.64894
ETHYL ACETATE-N-BUTYL ACETATE (G.L.C.)	0.12708	0.24164	0.15626	1.1746	0.61056
N-BUTANOL-N-BUTYL ACETATE "	0.75728	0.39350	-0.43947	2.7084	0.71359
METHANOL-WATER * (35°C)	0.77930	0.24927	-0.37091	2.9323	2.5203
METHANOL-WATER * (50°C)	0.67823	0.26615	-0.57964	1.2765	0.53343

* DATA OF McGLASHAN AND WILLIAMSON (M14)

Table 2 Van Laar parameters

SYSTEM (ALL AT 760 MM HG)	A_{12}	A_{21}	$\sum \frac{\Delta Y * 100}{N}$	$\sum \frac{\Delta P/P}{N}$
ETHYL ACETATE-N-BUTANOL (REF.IND.)	0.54069	0.58447	1.8259	1.553
ETHYL ACETATE-N-BUTYL ACETATE (REF.IND.)	0.10806	0.28078	0.53405	0.44742
N-BUTANOL-N-BUTYL ACETATE "	0.73485	0.66239	1.5267	0.70708
ETHYL ACETATE-N-BUTYL ACETATE (G.L.C.)	0.10865	0.22720	1.1206	0.60255
N.-BUTANOL-N-BUTYL ACETATE "	0.75053	0.65260	1.5559	0.76347
ETHANOL-ETHYL ACETATE * "	1.06973	0.89373	1.6500	0.63055
ETHANOL-N-BUTYL ACETATE * "	0.57638	1.39450	4.1728	2.7134
ETHANOL-N-BUTANOL * "	0.91608	0.07399	2.6200	1.6849

* DATA OF DAVIES (D4)

Table 3 3 parameter NRTL equation

SYSTEM (at 760 mm Hg)	$g_{12}-g_{11}$	$g_{21}-g_{22}$		$\frac{\Sigma 100 \Delta Y}{N}$	$\frac{\Sigma \Delta P/P}{N}$
Ethyl Acetate-n-Butyl Acetate (R.I.)	837.16	-526.15	0.3	0.5088	0.45151
Ethyl Acetate-n-Butyl Acetate (G.L.C.)	700.54	-451.94	0.30068	1.1122	0.60552
n-Butanol-n-Butyl Acetate (R.I.)	129.7	457.63	0.31240	1.5499	0.70739
n-Butanol-n-Butyl Acetate (G.L.C.)	87.89	507.37	0.30684	1.5799	0.76309

Table 4 UNIQUAC parameters

SYSTEM (at 760 mm Hg)	$U_{12}-U_{11}$	$U_{21}-U_{22}$	$\frac{\Sigma 100 \Delta Y}{N}$	$\frac{\Sigma \Delta P/P}{N}$
Ethyl Acetate-n-Butyl Acetate (R.I.)	368.328	-262.19	0.52912	0.44461
Ethyl Acetate-n-Butyl Acetate (G.L.C.)	239.358	-174.302	1.1187	0.60291
n-Butanol-n-Butyl Acetate (R.I.)	-181.151	399.264	1.5434	0.71142
n-Butanol-n-Butyl Acetate (G.L.C.)	-197.286	423.565	1.5791	0.76605

Table 5 5 Suffix Margules parameters

SYSTEM	A	B	λ_{12}	λ_{21}	$\frac{\sum \Delta Y*100}{N}$	$\frac{\sum \Delta P/P}{N}$
ETHYL ACETATE-N-BUTANOL (R.I.)	0.35987	0.82831	-0.82232	1.23671	1.7785	0.79948
ETHYL ACETATE-N-BUTYL ACETATE (R.I.)	0.17622	0.24608	0.39814	0.02174	0.63104	0.36537
N-BUTANOL-N-BUTYL ACETATE "	0.60565	1.12323	-0.85295	2.41116	1.58500	0.44923
ETHYL ACETATE-N-BUTYL ACETATE (G.L.C.)	0.13819	0.20300	0.19506	-0.0208	1.1462	0.61242
N-BUTANOL-N-BUTYL ACETATE "	0.62588	1.09764	-0.78607	2.30499	1.5859	0.49953
METHANOL-WATER * (35°C)	0.96919	0.26170	0.90428	-0.79545	2.2271	1.9177
METHANOL-WATER * (50°C)	0.74074	0.28145	-0.19972	-0.62451	1.0244	0.30822

* DATA OF McGLASHAN AND WILLIAMSON

Table 6 Results of Samuels Consistency Test

SYSTEM	$\sum F_j$	$\sigma_{F_j}^2$	σ_{F_j}
ETHYL ACETATE-N-BUTANOL (R.I.)	0.00762	0.0302	0.17893
ETHYL ACETATE-N-BUTYL ACETATE (R.I.)	0.01969	0.00121	0.03475
ETHYL ACETATE-N-BUTYL ACETATE (G.L.C.)	0.06546	0.00135	0.03669
N-BUTANOL-N-BUTYL ACETATE (R.I.)	0.00829	0.00161	0.04012
N-BUTANOL-N-BUTYL ACETATE (G.L.C.)	-0.00027	0.0760	0.27568

R.I. - Refractive Index

G.L.C. - Gas-liquid chromatography

Comparison between correlations on refractive index and G.L.C. data

Table 7 Wilson parameters

SYSTEM (at 760 mm Hg)	$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	$\frac{\Sigma 100\Delta Y}{N}$	$\frac{\Sigma \Delta P/P}{N}$
Ethyl Acetate-n-Butyl Acetate (R.I.)	-189.98	500.24	0.52817	0.44381
Ethyl Acetate-n-Butyl Acetate (G.L.C.)	-122.59	355.94	1.1201	0.60251
n-Butanol-n-Butyl Acetate (R.L.)	698.82	-91.44	1.5191	0.70328
n-Butanol-n-Butyl Acetate (G.L.C.)	732.98	-118.62	1.5493	0.75931

R.I. - refractive index

G.L.C. - Gas liquid chromatography

Table 8 2 parameter NRTL equation (=0.3)

SYSTEM (at 760 mm Hg)	$g_{12}-g_{11}$	$g_{21}-g_{22}$	$\frac{\Sigma 100\Delta Y}{N}$	$\frac{\Sigma \Delta P/P}{N}$
Ethyl Acetate-n-Butyl Acetate (R.I.)	837.16	-526.15	0.5088	0.45151
Ethyl Acetate-n-Butyl Acetate (G.L.C.)	700.54	-452.2	1.1122	0.60555
n-Butanol-n-Butyl Acetate (R.I)	129.70	455.52	1.5363	0.71013
n-Butanol-n-Butyl Acetate (G.L.C.)	87.89	505.99	1.5720	0.76494