VAPOUR-LIQUID EQUILIBRIA AT LOW CONCENTRATION OF ONE COMPONENT

by

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SUMMARY

This thesis details experimental work performed on the development of a total pressure apparatus to acquire isothermal vapour-liquid equilibrium data for binary mixtures. The method has been demonstrated to be capable of producing up to 30 data points from one experimental run and provide data at very low concentrations of one component ($< 10^{-4}$ mole fraction).

A literature survey is presented critically reviewing existing methods, particularly total pressure techniques. The survey also reviews theoretical models and correlations for predicting the non-ideal behaviour of mixtures. The theoretical basis of the correlations based on the "local mole-fraction" concept and their adaptability to "infinite dilution" prediction are discussed.

The performance of the present apparatus has been tested using the binary mixtures; methanol-water, ethanol-water over the temperature range 25°C to 65°C. Data obtained has been compared with literature values, when available, and the behaviour of the mixtures approaching infinite dilution shown to correspond to that expected from Henry's Law. A computer program has been developed to analyse the raw data.

The data from both systems has been fitted to some of the more commonly used correlations for predicting x-y behaviour.

The difficulties met in fitting the data by the use of optimisation techniques are discussed.

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1.0 INTRODUCTION:

In recent years industrial demands have increased for high purity products and for the removal of solvent and other organics from waste-water. These processes often involve mass transfer where one or more components is in low concentration. These concentrations may be down to parts per million. In order to study the mass transfer operation, the phase equilibrium data for the systems involved must be obtained.

In the past vapour-liquid equilibrium data has been largely obtained by methods involving the use of analysis. This has resulted in large errors in the activity coefficients at low concentrations of one component, it is rare therefore to have data below 0.05 mole fraction of either component in a binary. Activity coefficients at low concentrations have been obtained by fitting the data by the usual equations (e.g. the Wilson and the N.R.T.L. equations, see below), and then extrapolating. It is well known that each equation will yield differing activity coefficient values when extrapolated to infinite dilution in this way.

It is necessary therefore, to make measurements at lower concentrations than hitherto has been customary. Data at low concentrations are also of general interest in relation to the theory of vapour-liquid equilibrium. Any explanation for the imperfect behaviour of a mixture must take into account two effects. An athermal effect as molecules attempt to achieve the optimum packing configuration and a thermal effect from the forces acting between molecules. At low concentrations, statistically the situation can be attained where a molecule of the component in low concentration will be surrounded by molecules of the other components. This provides a basis of a study of the forces involved.

Techniques so far employed at these levels are retention-time measurements in gas-liquid chromatography and a technique based on the use of radio-carbon tagging of the solute (1). In this thesis is described experimental work on the application of a new total pressure method to the problem of measurements at low concentrations.

The method is tested using the systems methanol-water and ethanol-water at four differing temperatures. The results are discussed in relation to the accuracy of the method and to the limited data of other workers.

2.0 EXPERIMENTAL TECHNIQUES SURVEY

2.1 Introduction

Experimental methods for the determination of vapour-liquid equilibrium data have been developed since the early 1900's. Zadwiski (2.) laid the foundations by working on positive and negative deviations from Raoult's Law. The early data so obtained while valuable as a beginning, unfortunately was not checked for thermodynamic consistency and later workers have shown these earlier methods to be unreliable.

Direct determination normally involves the separation of samples of liquid and vapour in true equilibrium and the analysis of the two phases when separated. The determinations can be carried out isothermally or isobarically, though the former is normally preferable as isobaric data is inconvenient for theoretical analysis since the excess functions based on such results are complicated functions of temperature and composition.

At present, no still has been constructed which will yield completely thermodynamically consistent data for every system. In practice however, adequate precision for distillation calculations can usually be achieved by judicial selection of the still whose errors will be a minimum with respect to the nature of the system (relative volatility, heat of vapourisation etc).

The methods for direct determination of equilibrium data will be classified into the following groups for this survey.

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

The majority of recent techniques fall into the last two groups, consequently this review will concentrate on these two. Jenkins (3) in 1963 critically reviewed techniques within these groups at that period and an excellent review of the earlier methods of groups 1 - 4 is given in Hala, Pick, Fried and Vilim (4). The discussion of groups 1 - 4 will be limited, in general, to outlining the principle and associated problems of the method.

2.2 Distillation Method

In this, the oldest of the methods, a large charge is placed in a boiling flask which has arrangements for removing liquid and vapour samples. There are a large number of serious disadvantages with this type of still such as the removal of the liquid and vapour samples which will alter the composition of the mixture, hence the need for the large charge.

The technique has largely been abandoned in present times though Ramalho, Tiller, James and Bunch (5) have proposed a related technique. A simple distillation is performed with continuous determination of the concentration of either the vapour or liquid stream, the other being found by a material balance.

2.3. Circulation Method

This is the most widely used method. In this method vapours from a boiling mixture pass to a condenser where they are totally condensed and returned through a condensate receiver and a non-return device to the boiling vessel. It has been proved (6) that the steady state does correspond to phase equilibrium, though this is only true if the vapour condensing in the receiver is continuously in equilibrium with the boiling liquid in the distilling flask i.e. superheating and partial condensation do not occur.

Circulation stills can be classified into two types:-

(1) Stills with vapour phase circulation
(2) Stills with circulation of both liquid and vapour phases

The first satisfactory equilibrium still with vapour phase circulation was that of Othmer (7) and his modified stills (8, 9) are still commonly used. At reduced pressures (0.5 → 20mmHg) Jones (10, 11) or a modified Jones still (12) gives reliable results and avoids erratic boiling. The stills are especially useful when large density differences in the system components are present, conventional circulation stills often giving spurious and false results.

The attractive feature of these stills is the excellent mixing and intimate contact of vapour bubbles with surrounding liquid in the equilibrium chamber. There are however, several drawbacks such as the often imprecise measurement of the boiling temperature and difficulties encountered in exactly balancing heat losses to maintain adiabatic operation of the equilibrium chamber. In addition, vertical temperature gradients in the latter, such as may arise from uneven heating, can produce erroneous results.

Some of these drawbacks are largely eliminated in stills with circulation of both liquid and vapour phases, such as proposed by Gillespie (13) and his subsequent modifications (14, 15, 16). The Cottrell pump feature of these stills permits very precise temperature measurement, although it provides less satisfactory mixing and vapour-liquid contact than stills with circulation in the vapour phase only . An additional drawback, not completely eliminated, is partial condensation of the vapour, particularly in the region of the thermocouple.

Most circulation stills are fairly satisfactory up to 760mmHg but at higher pressures adequate control of the system is always a problem. As the pressure rises the vapour phase pressure approaches the partial pressure and the enthalpy of vapourisation is reduced, encouraging liquid entrainment in the recirculating vapour and flash evaporation of the condensate as it returns to the reboiler.

The majority of circulation stills require a charge of 250 - 750 cm^3 though stills can be reduced in size (17) to give still charges of approximately 30 cm^3 and a vapour condensate of

1.0 - 3.0 cm^3. Packer (18) has modified a 30 cm^3 circulation still to sample a small volume of the circulating vapour phase by gas chromatography. There is no condensate receiver, the condensate returning direct to the still by means of a capillary tube.

The most satisfactory circulation still is probably that of Raal, Code and Best (19) who have attempted to combine the good mixing characteristics of the vapour phase circulation stills with a novel adaption of the Cottrell pump. The still is shown in Figure 1, where the liquid and vapour paths are outlined. Liquid heated in the lower portion of B by the main heater forms vapour bubbles so that the small annular space between A and B acts as a Cottrell pump, propelling a mixture of vapour and liquid onto the jacketed thermocouple while maintaining the inner chamber at the temperature of the boiling liquid.

2.4. Flow Methods

The dynamic flow method, in contrast to the circulation method, has the feed entering the equilibrium chamber as a steady stream of constant composition which can be either in the liquid or in the vapour phase or a combination of the two. The arrangement shortens the time required to attain steady state. The principal disadvantage with flow stills is the demanding control needed in their operation. These stills are mainly used for systems of limited miscibility in the liquid phase and with heat sensitive materials because of the low residence period in the reboiler.

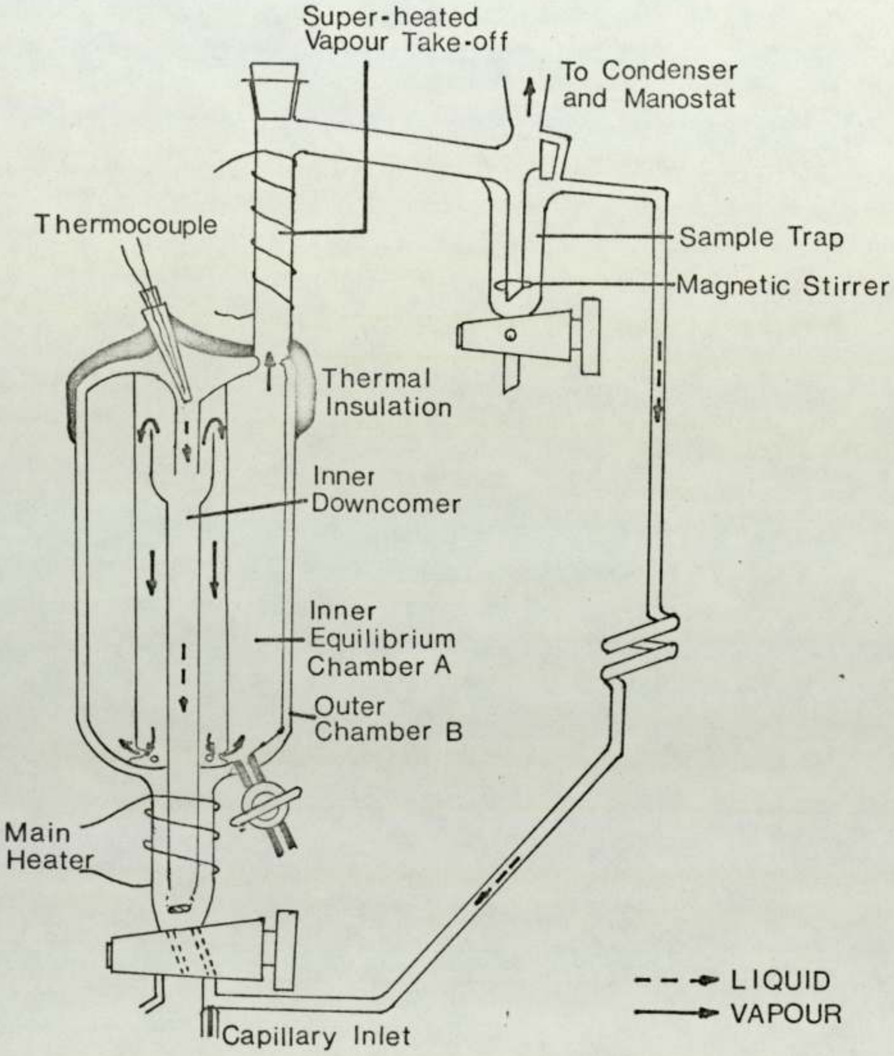


Figure **1**

Equilibrium Still of Raal, Code & Best

The first modern still on the flow principle was the Colburn (20) still. Cathala (21) later described a still in which two feeds are used. One is the superheated vapour, the second is preheated liquid. The vapour is introduced below the mixing chamber which contains two sintered glass discs to give good contact between the two phases. The liquid feed enters between these two discs. Jenkins, Davies and Gibson-Robinson (17) have recently employed the Cathala still to investigate the effect of random error.on the results. The samples were analysed using both gas-liquid chromatography and refractive index.

Vilim, Hala, Pick and Fried (4) have described a simpler and more effective still for achieving the same purposes, In this the binary or multicomponent feed is partially vapourised in a heated tube and the mixture of liquid and vapour impinges on a thermometer pocket and is then separated into vapour and liquid in equilibrium. These are respectively condensed and cooled and samples taken for analysis.

2.5 Static Methods

In the static method, the vapour and liquid phases are maintained in contact in an evacuated chamber, immersed in a constant temperature bath, and agitated until equilibrium between the phases is reached. The pressure is measured and samples of the vapour and liquid phases are withdrawn for analysis.

The advent of chromatographic analytical techniques making possible analysis from a small sample of the vapour phase, has resulted in an increasing usage of this method at medium to high pressures. This method can be of value when only relatively small quantities of the components are available, when there are large density differences and when the system exhibits limited miscibility. The method is often quite difficult in practice requiring considerable care and experience in operation, and at low pressures the amount of vapour required for analysis is such that the equilibrium is often disturbed.

Of the recent techniques using chromatographic analysis Wichterle and Hala (22) have described a still using small quantities and having a very small vapour sample which although allows rapid operation does not yield results as accurate as the classical methods. Wichterle and Boublikoua (23) later produced a technique suitable for direct measurement of the dependence of partial pressures on concentration with rapidity of measurement. This was achieved by removal of the need to wait for phase equilibrium to be established because the ratio of concentrations of the two components in the gaseous phase does not vary with time. This assumption that rates of vapourisation of components (which do not differ sizeably) are approximately equal, was experimentally verified by analysing the vapour phase at different times after injection of the liquid phase.

The technique however, is difficult practically especially in erradicating condensation in the sampling circuit which is at the same temperature as the equilibrium cell. Maffiolo and Vidal (24) have improved this technique, by reducing the risk of condensation, as long as the temperature at which the equilibrium is achieved is lower than the ambient temperature, and improving the arrangement for obtaining a reproducible volume

2.6 Total Pressure

A consequence of the serious drawbacks outlined in the use of stills has been the increasing popularity of total pressure techniques in recent times. Total pressure techniques normally involve the direct determination in a static cell of the temperature, total pressure and composition of the liquid phase, the vapour phase being determined by calculation. Mackay and Salvador (25) 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. Errors in the computed vapour composition arise from erroneous gradients in the pressure-liquid composition curve rather than from absolute pressure errors. They concluded that generally, computed vapour compositions were more accurate than measured compositions, particularly in systems of high relative volatility. An exception to this rule is with data in azeotropic regions.

Methods for computing vapour compositions (the required apparatus will be described afterwards) can be separated into two types, direct and indirect. The direct method involves calculation of vapour compositions by integration of the co-existence equation, a first-order differential equation derived from the Gibbs-Duhem equation, or by the step-wise integration procedure of Ho, Boshko and Lu (26). This latter method does not work for azeotropic systems.

The indirect method involves first the calculation by some appropriate means of the liquid phase activity coefficients and subsequent calculation of vapour compositions therefrom. These methods usually involve ascertaining which of selected equations giving a solution to the Gibbs-Duhem equation lead to the best fit to the experimental vapour pressure data, and of the determination of the parametric values producing the best fit. The indirect method avoids the use of numerical integration but the accuracy is dependent on the analytical form used to express the liquid activity coefficients. Errors in y arise from errors in the gradient of the P, x curve encouraging the use of low-order polynomials in the P.x. correlation.

A variation on this method is the use of end-point (Van Laar) calculation on data where one component is near infinite dilution. Treybal (27) gives examples of this method and Ellis and Jonah (28) have described a rigorous method of calculating the parameters

Hala et al have provided a detailed review of direct calculation methods. Recently Nagata and Ohta (29) reported a precise procedure using Forsythe orthogonal polynomials to correlate the total pressure data in terms of liquid mole fraction. An accurate fit for the strongly non-ideal system chloroform-ethanol was obtained, however the polynomials are very sensitive to any experimental errors reducing the accuracy of the method for obtaining vapour compositions.

Early calculational indirect procedures such as those of Levy (30), Carlson and Colburn(31), Christian (32), Redlich, Kister and Turnquist (33) and Prengle and Palm (34) have been reviewed by Hala et al. The majority of the earlier procedures were either poorly adapted to digital computation or assume ideality of the vapour phase. An exception was the procedure of Prengle and Palm, however if one takes their final results for the activity and fugacity coefficients and substituting them in equation (2.1).

$$P = x_1 \gamma_1 P_1^{\circ} \phi_1 + x_2 \gamma_2 P_2^{\circ} \phi_2 \qquad (2.1)$$

the values of the total pressure thus calculated deviate considerably from their own experimental values.

The most commonly used indirect method is that of Barker (35) who starts from the assumption that the excess free energy can be represented as a polynomial function of composition

$$G^E = x_1 \mu_1^E + x_2 \mu_2^E \qquad (2.2)$$

$$= RT\, x_1 x_2 \left[A + B\,(x_1 - x_2) + c\,(x_1 - x_2)^2 + \ldots\ldots \right]$$

This is equivalent to assuming that the Margules equations relate the activity coefficients to composition. Using equations (2.1) and (2.2) the total pressure of the mixture can be related to the unknown constants A, B, C. Although the relationship is non-linear, it is necessary initially to estimate or assume the unknown constants and vapour phase compositions. The equations are then linearised in the constants by taking only the first terms of a Taylor series, and solving for A, B, C. The new values are used to compute new estimates of vapour phase composition and the whole process repeated. In practice the method converges rapidly, two or three iterations usually being sufficient.

Diaz Pera (36) has recently reported that methods using a function similar to Barkers for G^E do not hold in general, for complex systems having dipole moments or hydrogen bonding. This obviously is to be expected from the limitations of the Margules Diaz Pera suggests that 'in complex systems an equation of the form originally proposed by Van Ness should be used

$$G^E = \frac{x_1 x_2}{\sum_{j=1} Bj \; (x_1 - x_2)^{j-1}} \qquad (2.3)$$

To overcome the main deficiency of Barkers method, Tao (37) presented an indirect method in which the necessity for the 'a priori' assumption of a particular functional form for the excess free energy has been removed. Tao's procedure involves calculation of the activity coefficients essentially by integration of an equation resembling the co-existence equation. The procedure though indirect, retains the rigor usually associated with the direct method.

Mixon, Gumowski and Carpenter (38) produced a technique retaining the same degree of rigor but unlike Tao's, which appeared specific to binary systems, was comparatively easy to generalise to tenary and higher order systems. Basically their technique was to write an expression for the solution vapour pressure in terms of the excess free energy and it's composition derivatives. The expression is 'inverted' to give the excess free energy function that produces the observed vapour pressure behaviour and activity coefficients are then deduced from the excess free energy function.

Ramalho and Delmas (39, 40) and in 1968 produced a method especially adaptable to digital computation. The technique employs two fundamental equations (2.1) and (2.4).

$$x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_2} = 0 \qquad (2.4)$$

with the Redlich-Kister expansion with two coefficients (B^R, C^R). By obtaining $d\gamma_1/dx_1 = f(B^R, C^R)$ and substitution, two equations can be formed with the unknowns $\gamma_1, \gamma_2, d\gamma_1/dx_1$. An iteration is then performed to evaluate B^R and C^R at two concentrations, x = 0.9 and 0.1, (i.e. obtaining local constants) and the same calculation repeated for other concentrations. An increase in the number of coefficients in the Redlich-Kister expansion in an attempt to obtain a better fit usually results in difficulty in obtaining convergence.

Ramalho and Delmas demonstrated the technique to be superior to that of Prengle and Palm though it contains several drawbacks. Convergence is not always obtained and the results are sometimes physically impossible e.g. $y > 1.0$, especially when $\gamma^{\infty} > 10$

One reason for these failures can be attributed to the poor fit accorded by the Redlich-Kister expansion. Minh and Ruel (41) modified the method by replacing this expansion with a simple empirical correlation.

$$\gamma_1 = 1 + B_1 x_2 + B_2 x_2^2 + B_3 x_2^3$$

This has the apparent advantage of greater flexibility, more directness, and no derivative of experimental data need be taken. Whether any improvement in the fit is obtained must be in doubt for most systems, though the authors showed it superior for the system cyclohexane-I-butanol.

Ramalho and Bui (42) extended the technique of Ramalho and Delmas to cover tenary systems by replacing the two constant Redlich-Kister expansion with the three constant form. They introduced a least squares technique to obtain optimum values of the three constants in order to cover the full composition range, and compared their work with that of McDermott and Ellis (43), claiming improvements in data attainment time and accuracy. Minh and Ruel (44) have extended this method to cover constant pressure data.

Davidson and Smith (45) have presented a method suitable for computer solution that does not require that the data be fitted with a thermodynamically constant polynomial. This characteristic is necessary for highly non-ideal solutions and they demonstrate this on amine-water data.

Ba Tai, Ramalho and Kaliaguine (46) have recently developed a technique incorporating the Wilson equation for isothermal data for binary and tenary systems, and for heats of mixing for tenary systems from binary data. The technique has the improvements accorded by the suitability of the Wilson equation and does not utilise the assumption that the energy parameters are independent of temperature.

Jambon and Clechet (47) have compared the indirect and direct methods and shown the superior fit accorded by the direct method. They also outlined the dangers that arise from an unwise selection of the function for representing the activity coefficients.

Experimentally two forms of apparatus have been used, a static method using a form of isoteniscope and a circulating still technique using an ebulliometer.

Holtzlander and Riggle (48) and Rose and Williams (49) both used a modified form of the Smith-Menzies isoteniscope. The comparisons of the liquid phase in both cases were by chemical analysis. Ljurglin and Van Ness (50) employed a glass cell which was almost completely filled with liquid. A miniature pressure transducer was used to measure the pressure in order to keep the cell light and portable, allowing successive weighings of it to find the composition of the solution formed. As the vapour phase was small, the composition of the liquid phase was not significantly affected by vapourisation, thus avoiding analysis.

Hermsen and Prausnitz (51) used an apparatus (see Figure 2) consisting of two identical isoteniscope assemblies, each having a metallic vapour pressure cell, sampling bulb and null manometer. Measurements of the liquid phase were by refractive index, samples having been withdrawn with a hypodermic syringe. Jose, Phillipe and Clechet (52) have employed this technique with modifications to control the temperature to 0.001°C and improvement in the degassing procedure.

The ebulliometer was used by Redlich and Kister (53) and Prengle and Palm (34), the method having been initially developed by Swietoslawski (54). This is in effect a circulating still where the condensed vapour is returned immediately 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 (55) 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 provides to a limited accuracy both isothermal and isobaric vapour-liquid equilibrium data without the analysis of either phase. The liquid composition is adjusted gravimetrically and assumed constant during operation. The technique assumes vapour phase ideality.

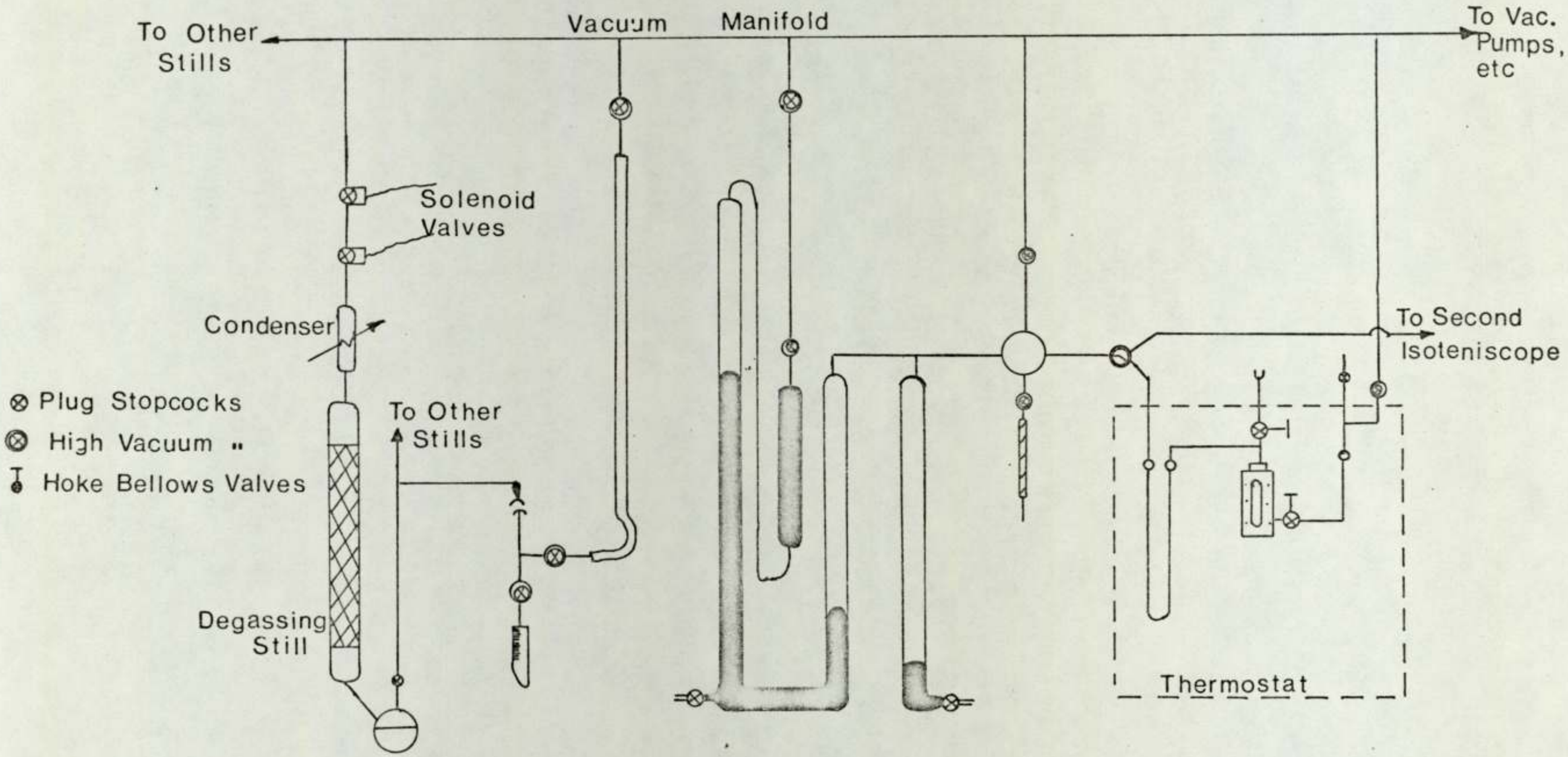


Figure 2
Total Pressure Apparatus of Hermsen & Prausnitz

The ebulliometric method in general, has the disadvantage that it can produce spurious results when the mixture consists of widely differing boiling points. This characteristic is probably due to the difficulty in obtaining real equilibrium.

Very recently (1972) Gibbs and Van Ness (56) have described a technique (see Figure 3) where liquid solutions of known composition are prepared in a test cell by volumetric metering of degassed liquids from accurate piston injectors. The initial injector volume reading is determined by use of a break-point torque wrench. The technique enables isothermal data over the full composition range to be measured in one day. The vapour-liquid relationship is obtained by solution of the coexistence equation.

2.7 Other Methods

Kojima, Kato and Coworkers have presented several methods based on the dew and bubble point technique culminating in an apparatus for obtaining isobaric vapour-liquid equilibria without analysis of either phase.

The dew and bubble point technique is an indirect static method, For a mixture of a given composition, the "dew-point", is the condition at which an infinetely small amount of liquid is in equilibrium with the vapour and the "bubble-point" that at which an infinitely small bubble of vapour is in equilibrium with the liquid. If the dew and bubble point curves, as shown in Figure 4, can be

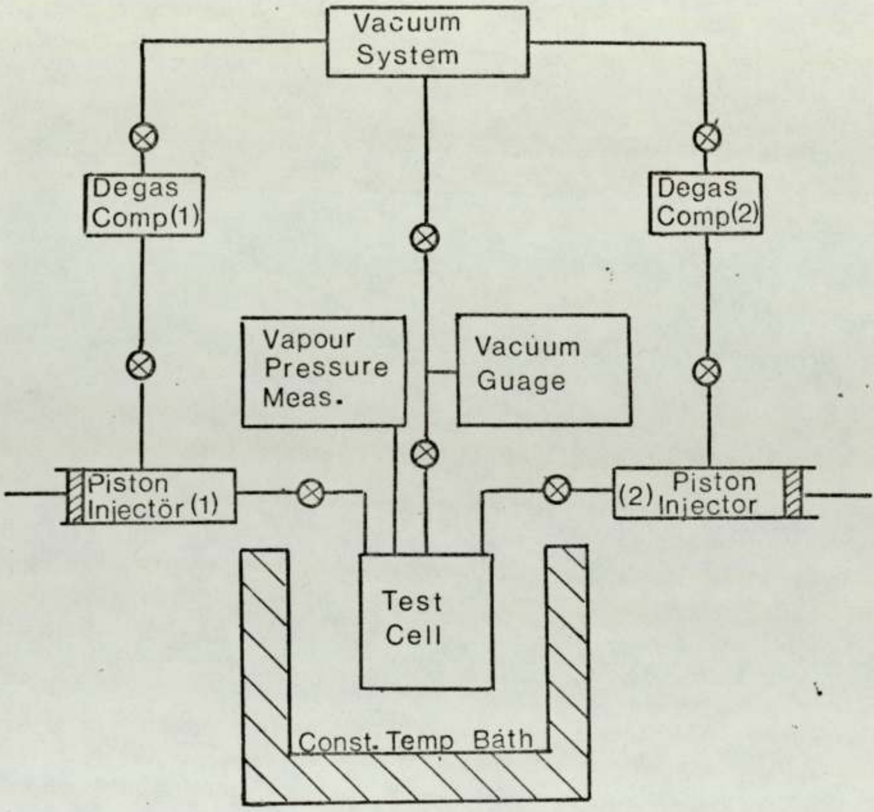


Figure 3
Schematic Diagram of Equipment of Gibbs & Van Ness

then lines drawn at constant pressure P_1 will cut them and the intersections will give the composition of liquid and vapour in equilibrium at P_1

For measurements of isobaric dew points, Kojima et al (57) proposed a novel apparatus in which however, it was necessary to ahalyse the sample and it was also difficult to measure the dew point at the precise composition desired. In addition the bubble points needed determination by separate measurements or by theoretical estimations.

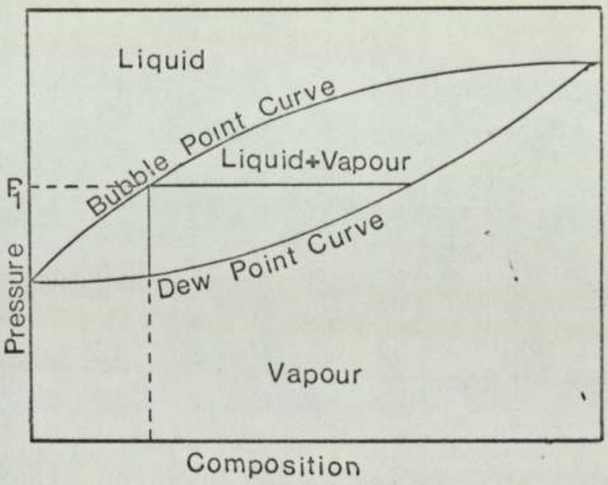


Figure 4

For measurement of isobaric bubble points several authors (54, 58, 59) proposed ebulliometers. However, in general in a batch-type ebulliometer it is necessary to correct for the difference between the liquid composition at steady state and the feed composition. The dew points must be determined separately.

Kato, Konishi and Hirata (60) initially proposed a flow-type apparatus for measurement of isobaric dew and bubble points.

The apparatus unfortunately was not easy to operate at the accurate composition desired and for a multicomponent system appeared complex. They later produced a new apparatus (61) shown in Figure 5. The principal parts 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 B after condensation. The internal construction of both stills is almost similar to that of the flow-type ebulliometer. The boiling vapour-liquid mixture rises through the Cottrell tube and flushes to the thermometer well. Using the capillary connecting tube, C, the liquid flows from B to D. To obtain the dew and bubble points without analysis, a prepared solution is charged from feeder, F, and the liquid is boiled in the dew point still, D, and bubble point still, B. It can be shown that, when steady state has been attained, the temperatures in stills, B and D, should equal the bubble point and dew point at the feed compositions respectively.

Kato, Sato, Konishi and Hirata (62) proposed a further technique for tenary systems based on the following two relations:-

(i) The bubble point of the equilibrium liquid composition should be equal to the dew point of the equilibrium vapour composition.

(ii) The condensation point of the equilibrium liquid composition should be the bubble point of the equilibrium vapour composition.

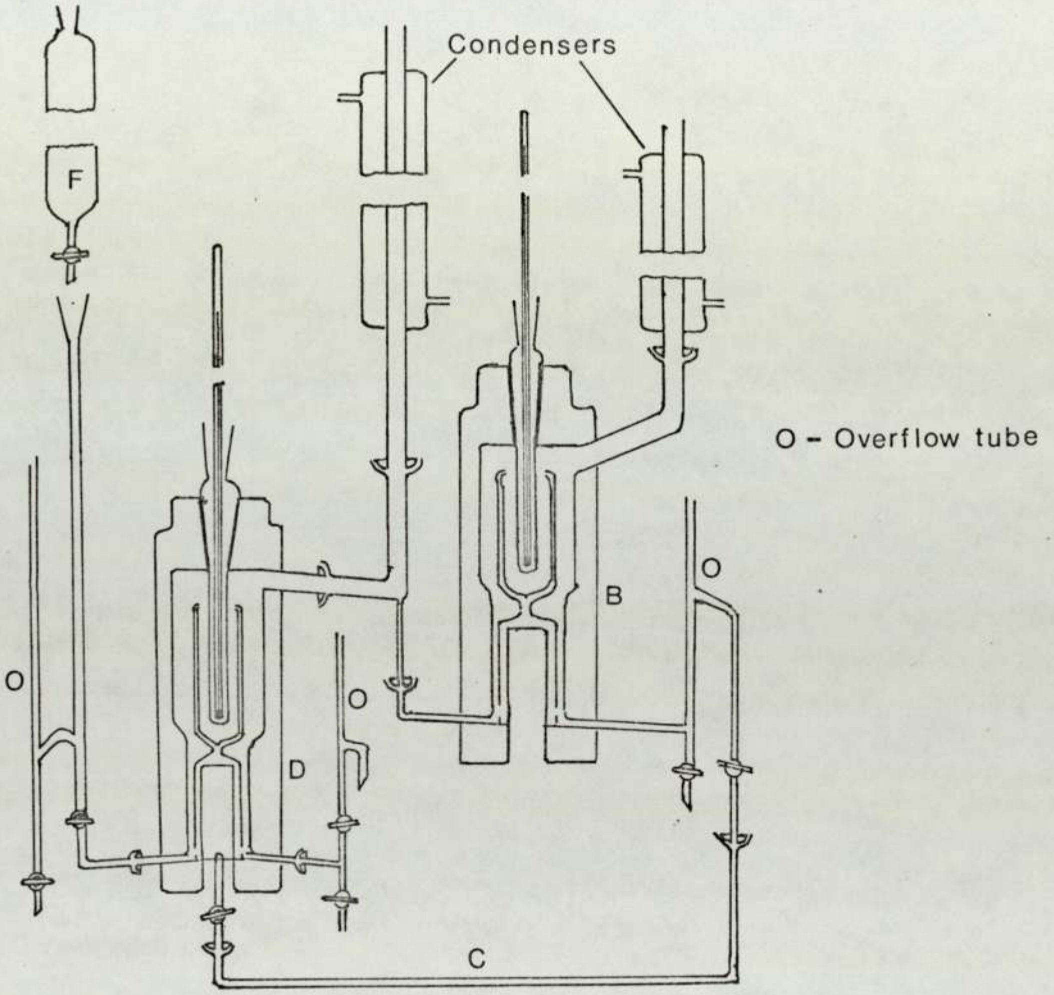


Figure 5
Apparatus of Kato, Konishi & Hirata

The condensation point means the bubble point temperature at the equilibrium vapour composition.

The authors presented a circulation type apparatus consisting of three stills for the measurements.

Kato, Konishi, Hirata and Katayama (63) have presented a calculational technique based on those of Hirata (64) and Clark (65) whereby the dew point and bubble point curves may be expressed by two or three straight lines similar to the x - y relations of equilibrium vapour and liquid compositions. This reduces the number of data points required using the dew and bubble point method, only four data points being required to obtain the dew or bubble point curve over the whole composition range.

Dalager (1) has presented a novel technique for determining vapour-liquid equilibrium data for binary systems adopted principally for use at concentrations of one of the components in the parts per million range. The method is based on the use of radio-active tracers, as the component in low concentration is added partly in an isotopic form. This use of isotopic tracers makes it possible to measure very small amounts of the component in question. He used a modified Thornton (66) equilibrium still to obtain equilibrium. His method, using only one isotopic tracer, was reasonably successful at low concentrations though a fair scatter was apparent at very low concentrations. One must query however if he achieved true equilibrium at these concentrations. The method is unsuitable for high concentrations of the labelled component.

2.8 Summary of the Methods

This review of the more recent and important methods illustrates the vast range of methods, and hence the problems associated with vapour-liquid equilibrium data acquisition. The worker must judicially select the apparatus by considering principally the properties of the system to be investigated.

The difficulties inherent in all methods which directly sample one or both of the phases is that the equilibrium must be affected by the sampling and the change in the sample before and during measurement. This is especially critical in the vapour phase.

The elimination of the need to sample either phase is therefore a pre-requisite to developing a method suitable for all systems. This brings the additional advantage that by not affecting the equilibrium, measurements can be taken more rapidly.

3.0 THEORETICAL SURVEY

In this chapter a survey of the literature related to the theory of vapour-liquid equilibrium is presented. As with the techniques survey the quantity of work is large, therefore after a brief account of the classical background and properties of the liquid state the survey will concentrate on the more recent relationships, especially those based on the 'local mole fraction' concept.

A review is given at the end of the chapter in which certain anomalies in the literature are discussed together with the possibility of attributing any physical significance to the models.

3.1 Classical Background

In classical thermodynamics, a system is in equilibrium where there is no tendency for a change in state to occur. From the second law for reversible processes, there is no change in the surroundings and since a reversible process is one through a series of equilibrium states the change in entropy (dS) must be zero. Hence

$$dS = 0 \qquad 3.1$$

Combining first and second law analyses on the system gives

$$TdS - (dU + W) = 0, \quad dT = 0, \quad dP = 0 \qquad 3.2$$

If non-mechanical work is neglected, this becomes for the internal energy U

$$dU = TdS - PdV \qquad 3.3$$

This form of the equation implies that the system is characterised by the two independent variables or degrees of freedom S and V. In order to form the equation with T and P as the independent variables the Gibbs free energy or Gibbs function, G, is defined by

$$G = U + PV - TS \qquad 3.4$$

Differentiating at dT = 0, dP = 0 gives

$$dG = dU + PdV - TdS \qquad 3.5$$

Comparing this with 3.3 shows that at equilibrium

$$dG_{(T,P)} = 0 \qquad 3.6$$

The chemical potential of a species i, μi, in a mixture is defined with the system at constant pressure and temperature by

$$\mu i = \left(\frac{\partial G}{\partial ni}\right)_{TPnj,\ j \neq i} \qquad 3.7$$

This also happens to be the definition of the partial molar Gibbs function, $\bar{G}_i$

For phases in equilibrium the appropriate equilibrium criteria are dP = 0, dT = 0, dG = 0. If the reversible transfer of a small quantity of species i from one phase to the other is considered then the equality

$$\mu i_{(\text{phase } 1)} = \mu i_{(\text{phase } 2)} \qquad 3.8$$

is seen to hold as well

Gibbs-Duhem Equation

From the definition of the chemical potential in terms of the internal energy, it can be shown that

$$dU = TdS - PdV + \sum \mu i \, dni \qquad 3.9$$

Integrating equation 3.9 at constant temperature, pressure and composition, from zero mass to a state of finite mass gives

$$U = TS - PV + \sum_i \mu_i \, n_i \qquad 3.10$$

Differentiating 3.10 so as to give a general expression for dU

$$dU = TdS + SdT - PdV - VdP + \sum \mu i \, dni + \sum n_i d\mu i \qquad 3.11$$

comparing 3.11 and 3.7

$$SdT - VdP + \sum_i n_i \, d\mu_i = 0 \qquad 3.12$$

This is a fundamental equation of thermodynamics known as the Gibbs-Duhem equation.

Fugacity and Activity

From 3.4 it follows that

$$d\mu_i = -S_i\,dT + V_i\,dP \qquad 3.13$$

for a pure ideal gas from 3.13

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = V_i \qquad 3.14$$

Substituting in the ideal gas equation

$$V_i = \frac{RT}{P} \qquad 3.15$$

and integrating (dT = 0) from an initial state denoted ^{o}

$$\mu_i - \mu_i^o = RT \ln P/P^o \qquad 3.16$$

For a non-ideal gas, G.M. Lewis introduced "fugacity" so that

$$\mu_i - \mu_i^o = RT \ln f_i/f_i^o \qquad 3.17$$

While either μ_i^o or f_i^o is arbitary, bothmay not be chosen independently; when one is chosen the other is fixed.

For a pure, ideal gas, the fugacity is equal to the pressure, and for a component i in a mixture of ideal gases it is equal to it's partial pressure $y_i P$. Since all systems, pure or mixed, approach ideal-gas behaviour at very low pressures, the definition of fugacity is completed by the limit

$$\frac{f_i}{y_i P} \longrightarrow 1 \text{ as } P \longrightarrow 0 \qquad 3.18$$

For general use a function called the "activity coefficient" was defined. The activity at same temperature, pressure and composition is defined as the ratio of the fugacity at these conditions to the fugacity in the standard state.

$$a_i(T,P x) = \frac{F(T, P, x)}{F^o(T^o, P^o, x^o)} \qquad 3.19$$

The activity coefficient γ i is the ratio of activity of i to some convenient measure of the concentration of i usually the mole fraction

$$\gamma_i = {}^{ai}/x \qquad 3.20$$

There are two conventions for defining activity coefficients. In the symmetrical convention the activity coefficient is defined with reference to an ideal solution

$$\gamma_i \longrightarrow 1 \quad \text{as} \quad x_i \longrightarrow 1 \qquad 3.21$$

The unsymmetrical convention defines the activity coefficient with reference to an ideal dilute solution

$$\begin{matrix} \gamma_1 \longrightarrow 1 & \text{as} \quad x_1 \longrightarrow 1 & \text{solvent} \\ \gamma_2 \longrightarrow 1 & \text{as} \quad x_2 \longrightarrow 0 & \text{solvent} \end{matrix} \qquad 3.22$$

From equations 3.17, 3.19 and 3.20 can be derived

$$fi = \gamma_1 x_1 \exp \left(\frac{\mu i - \mu i^o}{RT} \right) \qquad 3.23$$

Introduction of a fugacity coefficient ϕ_i

$$\phi_i = fi/_{Pi} \qquad 3.24$$

and evaluation of the exponential term leads to the general expression

$$\gamma_i \, x_i \, \phi'_{i(Pi)} \, Pi' \ \exp \left(\frac{1}{RT} \int_{Pi'}^{P} V_i^L \, dP \right) = \phi_i \, (Pi) Y_i \, P$$

3.25

where $Q_i'(Pi)$ is the fugacity coefficient of the pure gas component i at the pressure Pi' corresponding to the saturated vapour pressure of i at the temperature of the mixture.

In practice, several assumptions can often be made to this expression. If the assumption is made of an ideal vapour phase (often valid at low to moderate pressures) then $Q_i' = 1$, $Q_i = 1$ and neglecting the exponential term

$$\gamma i \, xi \ P_i' = y_i P \qquad 3.26$$

The further assumption of an ideal liquid solution leads to Raoults Law

$$xi \, P_i' = yi \, P \qquad 3.27$$

for an ideal vapour phase, if the liquid phase reference state for component i is taken as that at infinite dilution, one obtains

$$\gamma i \, x_i \exp \left(\frac{\mu i - \mu i^{o}}{RT} \right) = yi \, P \qquad 3.28$$

The constant exponential part is termed the Henry's Law constant, Hi. At low concentrations, $\gamma_i \longrightarrow 1$ and

$$x_i \, Hi = Yi \, P \qquad 3.29$$

From equations 3.07 and 3.17 and

$$G^E = Gi\ (\text{real}) - \overline{Gi}\ (\text{ideal}) \qquad 3.30$$

the partial excess Gibbs free energy can be related to the activity coefficient by the basic thermodynamic relationship

$$\overline{Gi}^E = RT \ln \gamma_1 \qquad 3.31$$

and further

$$G_i^E = RT \sum_i x_i \ln \gamma_i \qquad 3.32$$

3.2 Activity Coefficients from Excess Functions

Many empirical equations have been prepared for expressing the composition dependence of the excess Gibbs energy. Two of the earliest relationships were the Van Laar (67) equations

$$\ln \gamma_1 = \frac{A}{\left(1 + \dfrac{A \; x1}{B \; x2}\right)^2} \qquad 3.33$$

and the Margules (68) equations

$$\ln \gamma_1 = \frac{A'}{RT} \cdot x_2^2 \qquad 3.34$$

$$\ln \gamma_2 = \frac{A'}{RT} \cdot x_1^2$$

A, B, $A^{/}$ are empirical constants having units of energy characteristic of components 1 and 2, and are dependent on temperature but not on composition. The constants can be negative or positive, and they are frequently found in simple systems to be nearly constant over a small temperature range.

The Margules equations are derived from the simplest non-trivial expression for G^E obeying the boundary conditions.

$$G^E = 0 \qquad x_1 = 0$$
$$G^E = 0 \qquad x_2 = 0 \qquad 3.35$$

$$\text{i.e.} \quad G^E = Ax_1 x_2 \qquad 3.36$$

Wohl (69) showed that many of the empirical equations in common usage can be derived from a generalised treatment by expressing G^E as a polynomial expansion in the effective volume fractions, Z_1 and Z_2 i.e.

$$\frac{G^E}{RT\,(x_1q_1 + x_2q_2)} = 2\,q_{12}\,z_1\,z_2 + 3q_{112}\,Z_1^2\,Z_2 + 3q_{122}\,Z_1Z_2^2$$
$$+ 4\cdot q_{112}\,z_1^3\,z_2 + 4q_{1222}\,z_1\,z_2^3 + 6\,q_{1122}\,z_1^2\,z_2^2 + \ldots$$

where
$$Z_1 \equiv \frac{x_1\,q_1}{x_1\,q_1 + x_2\,q_2}$$
$$3.37$$
and
$$Z_2 \equiv \frac{x_2\,q_2}{x_1\,q_1 + x_2\,q_2}$$

The parameters, q's, are effective volumes, or cross-sections of the molecules. The parameters, a's, are interaction parameters, a_{12} being a constant characterstic of the interaction between molecule 1 and molecule 2.

Van Laar's equations can be obtained by truncating after the first term, so that

$$A's \equiv 2q_1 \; q_{12}$$

$$b's \equiv 2q_2 \; q_{12}$$

Adler, Friend and Pigford (70) have extensively tested the Margules - Wohl expansion for tenary systems, obtaining reasonable fits, average absolute errors in y for 24 systems being less than 0.03. However the 3-suffix form employs seven constants and the 4-suffix form, which was required for higher non-ideality resulting from one component being polar, employs ten constants.

When a series expansion is used to express the excess Gibbs energy function, equations commonly known as the Redlich-Kister (71) expansion are formed.

$$G^E = x_1 x_2 \left(A + B \left(x_1 - x_2 \right) + c \left(x_1 - x_2 \right)^2 + D \left(x_1 - x_2 \right)^3 + \ldots \right) \qquad 3.38$$

Where A,B,C,D are temperature-dependent parameters obtained from experimental data.

The corresponding activity coefficients are given by

$$RT \; \mathrm{In} \, \gamma_1 = q^{(1)} x_2^{\,2} + b^{(1)} x_2^{\,3} + c^{(1)} x_2^{\,4} + d^{(1)} x_2^{\,5} + \qquad 3.39$$

$$RT \ln \gamma_2 = a^{(2)} x_1^{\ 2} + b^{(2)} x_1^{\ 3} + c^{(2)} x_1^{\ 4} + d^{(2)} x_1^{\ 5} +$$

where $a^{(1)} = A + 3B + 5C + 7D$ $\qquad a^{(2)} = A - 3B + 5C - 7D$

$b^{(1)} = -4\ (B + 4C + 9D)$ $\qquad b^{(2)} = 4\ (B - 4C + 9D)$

$c^{(1)} = 12\ (C + 5D)$ $\qquad c^{(2)} = 12(C - 5D)$

$d^{(1)} = -32D$ $\qquad d^{(2)} = 32D$

The number of parameters is usually two or three, very extensive and accurate data are needed to warrant the use of further empirical constants.

3.3 Properties of the Liquid State

The major difficulty in representing the relationship between the excess Gibbs free energy and composition is the lack of knowledge on the liquid state of matter. The present day knowledge will be now briefly outlined with it's relevance to theories to be discussed later in the thesis.

Liquid can be considered to lie somewhere between the states of dense gases and disordered solids. The distinguishing feature between solids and liquids lies in the molecular arrangement. In solids, order governs until melting occurs. On melting this long-range order breaks down to leave short-range order only, extending over the order of a few molecular diameters.

This short-range order can be illustrated by introducing the concept of a Radial Distribution function. This function specifies the number of atoms or molecules to be found at any distance r, from the arbitary chosen molecule.

One way to represent the structure of a liquid is to plot the number density of the molecule ρ (r) for any distance r. This is simply the number of molecules per unit volume at distance r and is obtained by dividing the number in a spherical shell by the volume of the shell (for symmetrical molecules).

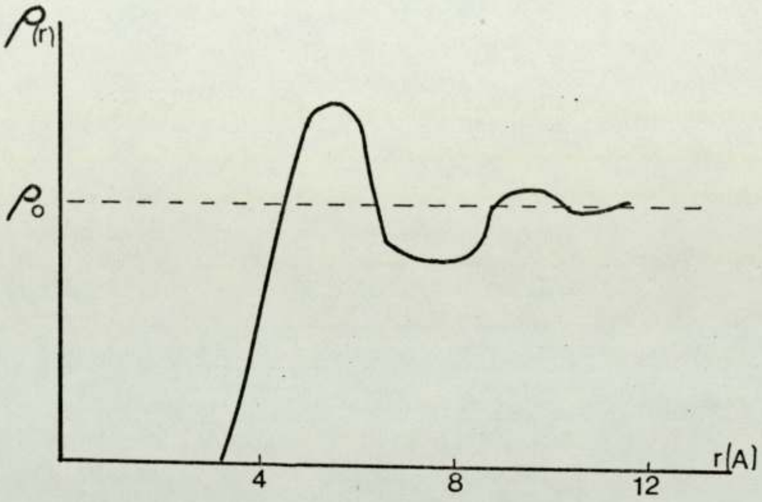


Figure 6

A raising of the temperature reduces the distance of the order. At large distance ρ (r) approaches the mean-diameter density for the liquid as a whole ρo. At small distances, the short-range order is revealed in the peaks and hollows of the full curve.

When relating to the internal forces acting, one can make the assumption that the force F(r) exerted on one molecule by another acts along the line joining them. At large distances the force is attractive (negative) but changes to repulsion (positive) at short distances which increases very rapidly with a further decrease in r. The same situation occurs if one considers energy ϕ (r) instead of forces, and these are shown in Figures 7(a) and 7(b).

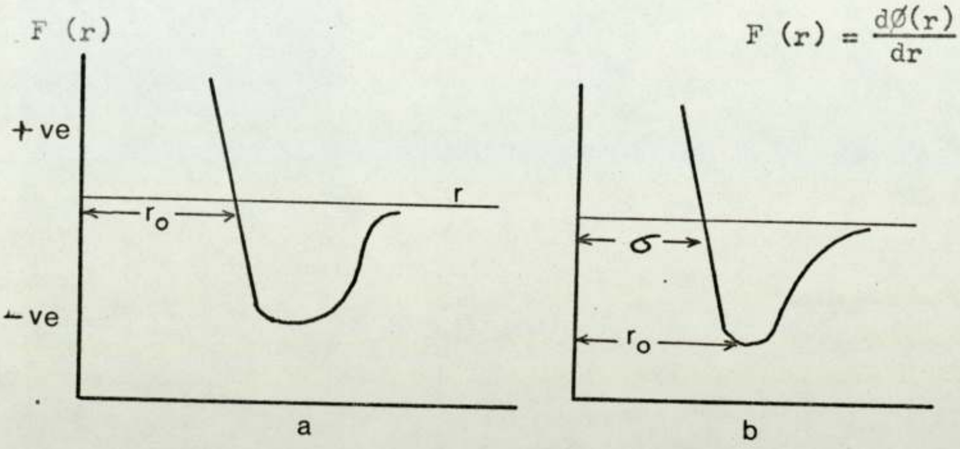


Figure 7

The distance ro, which represents the distance r when the force changes from repulsion to attraction, is of the order of an Angstrom unit or so, and would be the equilibrium distance between a pair of isolated undisturbed molecules.

There are three possible approaches when considering the effect on energy of the surrounding molecules. The one of most interest in this field is the radial distribution function approach, i.e. find ρ (r), as this is analagous to one adopted in the local mole fraction based activity coefficient-composition relationships (Section 3.4).

One can attempt to calculate ρ (r) by solving complex mathematical procedures. A more interesting approach is to perform simple experiments with solid balls, as performed recently by Scott and Bernal. Scott (72) looked at ρ (r) values and found some close relationships between some of his results and corresponding values of inert gases.

Bernal (73) looked primarily at co-ordination numbers. The importance of these co-ordination numbers is that the potential energy of the liquid is determined largely by the nearest neighbours of a central molecule. The number of neighbours lying just beyond the limit for near contact was not revealed by Bernal's experiments but Scotts' experiments showed that the number which lie between 1.0σ and 1.2σ is 9.3 ± 0.8. Bernal's experiments show that the greater specific volume of a liquid compared with the solid, is to be attributed largely to a decrease in co-ordination number, from 12 in the solid to a value in the region of 8 to 10. in the liquid, while the most probable nearest-neighbour distance is little changed. The conclusion to be drawn from the experiments would appear to be that while strictly the structure of liquids is determined by thermodynamical criteria yet, nevertheless, this is to a large extent equivalent to a structure determined by geometrical factors.

3.4 Equations based on Local Mole Fraction Concept

A new approach to relating the excess Gibbs function to composition, was provided by Wilson (74) when he introduced the local mole fraction (L.M.F)concept. Molecules in a liquid mixture do not, in general, distribute themselves in a random manner but exhibit a tendency to segregate. This results in the local mole fraction i.e. immediate surroundings of a certain molecule, having a different value to the overall mole fraction.

In a binary mixture there are four local mole fractions, however only two are independent thus

$$x_{ij} + x_{jj} = 1 \qquad 3.40$$

$$x_{ji} + x_{ii} = 1 \qquad 3.41$$

where x_{ij} = local mole fraction of molecule i around a central molecule j

Wilson related the local mole fractions to overall mole fractions by assuming a relationship of the Boltzmann type

$$\frac{x_{ji}}{x_{ki}} = \frac{x_j e^{-Gji/RT}}{x_k e^{-Gki/RT}} \qquad 3.42$$

where G_{ji} = energy term relating forces between molecules of species i and j (NB $G_{ji} = G_{ij}$)

By substituting local volume fractions for overall volume fractions in the equation of Flory-Huggins (3.43)

$$\bar{G}^{m} / RT = \sum x_i \, \mathrm{In}\, \varepsilon_i \qquad 3.43$$

$$\varepsilon_i = \frac{x_i V_i e^{-G_{ii}/RT}}{\sum_j x_j v_j e^{-G_{ij}/RT}} \qquad 3.44$$

where $\bar{G}^{m}$ = free energy of mixing

ε_i = local volume fraction of component i about central molecule of same type

Vi = Motor volume of component i

the relationship for the excess Gibbs energy is derived

$$\frac{\overline{G}^{E}}{RT} = - \sum_{i} x_i \; \mathrm{In} \; \sum_{j} x_j \, ({}^{Vj}/{}_{Vi}) \; e^{-\;(Gij\,-\,Gii)\,/\,RT} \tag{3.45}$$

If

$$\Lambda_{ji} = 1 - {}^{Vj}/{}_{Vi} \; e^{-\;(Gji\,-\,Sii)/RT} \tag{3.46}$$

then for a binary mixture the activity coefficient relationship becomes

$$\mathrm{In}\; \gamma_1 = -\mathrm{In}\;(x_1 + \Lambda_{12}\, x_2\,) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}\, x_2} - \frac{\Lambda_{21}}{\Lambda_{21}\, x_1 + x_2} \right] \tag{3.47}$$

$$\mathrm{In}\; \gamma_2 = -\;\mathrm{In}\;(x_2 + \Lambda_{21} x_1\,) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right]$$

The multicomponent form is

$$\ln \gamma_k = 1 - \ln\left[\sum_{j=1}^{n} x_j \Lambda_{kj}\right] - \sum_{i=1}^{n} \left[\frac{x_i \Lambda_{ik}}{\sum_{i=1}^{n} x_j \Lambda_{ij}} \right] \tag{3.48}$$

The Wilson equations have several important advantages over the earlier models. Often a reasonable approximation is to assume that the characteristic energies are independent of temperature. Several authors (75, 76) have shown the temperature dependence to be a linear function with normally only a slight gradient. For normal accuracy the assumption is valid for an approximate 20°C temperature interval.

The superiority of the Wilson equation over the Margules and Van Laar equations becomes most noted for highly assymetric systems such as solutions of polar or associating components in non-polar solvents.

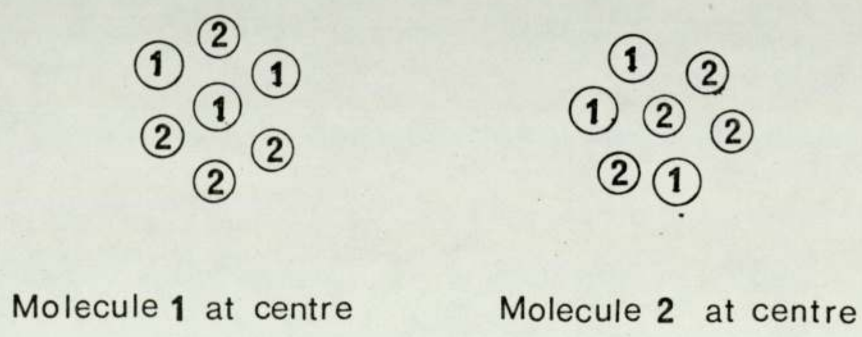
The principal advantage of the Wilson equation is that it is readily extended to multicomponent mixtures from only data of the corresponding binaries. Many workers have demonstrated this facility, Weatherford and Van Winkle (77) having successfully correlated a quinary system. They correlated the relatively ideal hydrocarbon quinary of hexane, methylcyclopentane, cyclohexane, benzene and toluene and found that the Wilson equation predicted temperatures consistently high by 0.50C.

One major shortcoming of the Wilson equation is that it is not applicable to partially miscible liquid mixtures. When the correlation is substituted into the equations of thermodynamic stability for a binary system, no parameters Λ_{12} and Λ_{21}

can be found which indicate the existence of two stable liquid phases. To overcome this Wilson proposed that the right-hand side of equation 3.45 be multiplied by a third constant C. However, for $C \neq 1$ Wilson's equation cannot be generalised for a multicomponent solution unless the binary constants Cij are the same for all binary ij pairs. Wilson and Scatchard (78) showed that a good fit for the liquid-liquid system n-butyl-glycol-water was obtained with C = 1.465.

Renon and Prausnitz (79) combined the local mole fraction concept with Scott's (80) two liquid theory of mixtures in deriving the NRTL (Non-Random Two-Liquid) equation. Scott's theory assumes that for a binary mixture there are two types of cells, as shown in Figure 8.

Figure 8



The residual Gibbs energy for a cell containing molecule ① at it's centre is $G^{(1)}$ and

$$G^{(1)} = x_{11}\, G_{11} + x_{21}\, G_{21} \qquad 3.49$$

Similarly for $G^{(2)}$

Thus the molar excess Gibbs energy for a binary solution is the sum of two changes in residual Gibbs energy

(a) transferring x_1 molecules from a cell of pure (1) to a cell of the solution.

(b) similarly for 2.

From these the NRTL equation for the excess Gibbs energy becomes

$$\frac{G^E}{RT} = x_1 x_2 \left(\frac{\tau_{21}\, G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12}\, G_{12}}{x_2 + x_1 G_{12}} \right) \qquad 3.50$$

where $\tau_{12} = - \dfrac{(G_{12} - G_{22})}{RT}$ $\qquad \tau_{21} = - \dfrac{(G_{12} - G_{11})}{RT}$

$$G_{12} = \exp\,(-\alpha_{12}\,\tau_{12}) \qquad G_{21} = \exp\left(-\alpha_{12}\,\tau_{21}\right)$$

The parameter α_{12} is related to the non-randomness in the mixture, when α_{12} is zero the mixture is completely random and equation 3.50 reduces to the two suffix Margules equation. When compared with Guggenheims (81) quasichemical theory α_{12} can be shown to be approximately equivalent to $2/z$ where z is the co-ordination number.

The subsequent activity coefficient relationships are

$$\mathrm{In}\,\gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right]$$

3.51

$$\mathrm{In}\,\gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]$$

The NRTL equation unlike the Wilson equation, is applicable to partially miscible systems provided α_{12} does not exceed 0.426. The equation is equivalent to the Wilson equation in correlating strongly non-ideal mixtures and is readily extended to multicomponent systems using only parameters obtained from data on the corresponding binary systems.

It is normally preferable with binaries to optimise the value of α_{12}, however for lower accuracy Renon and Prausnitz recommended values, between 0.2 and 0.47, depending on the chemical nature of the system. Mertl (82) has proved that polycomponent thermodynamic quantities depend on the values of the NRTL parameters more markedly than the binary values. He also showed that the values of the parameters of the NRTL equation with the minimised α_{ij} are extraordinarily sensitive to the character of the experimental data, so that when predicting polycomponent equilibria with no experimental check he recommends the use of the 2-parameter NRTL equation.

Similar behaviour of the Wilson equation has been observed by Oyre and Prausnitz (86) and Hudson and Van Winkle (82). Renon and Prausnitz later showed that Wilson's constant C could be derived on the basis of well-defined assumptions by introducing the concept of local composition into Scott's two-liquid theory of mixtures. The special case C = 1 corresponds to a co-ordination number of 2 which is unreasonably low for typical liquids.

Asselineau and Renon (84) modified the NRTL equation to extend it's validity to large temperature intervals. For this purpose it was found sufficient to represent the parameters as linear functions of temperature.

$$\begin{aligned} G_{21} - G_{11} &= C_1 + D_1 \ (T - 273.15) \\ G_{12} - G_{22} &= C_2 + D_2 \ (T - 273.15) \\ \alpha_{12} &= C_3 + D_3 \ (T - 273.15) \end{aligned} \qquad 3.52$$

This modification allows the representation of the excess molar enthalpy or integral heat of mixing (h^E) with concentration

$$h^E = \frac{x_1 x_2 \exp(-\alpha_{12}\tau_{21})}{x_1 + x_2 \exp(-\alpha_{12}\tau_{21})} \left[\left(1 - \frac{\alpha_{12}\tau_{21} x_1}{x_1 + x_2 \exp(-\alpha_{12}\tau_{21})} \right) (C_1 - 273\text{-}15 D_1)\right.$$

$$\left. + \frac{\tau_{12}^2 x_1 D_3 RT^2}{x_1 + x_2 \exp(-\alpha_{12}\tau_{21})} \right] + \frac{x_1 x_2 \exp(-\alpha_{12}\tau_{12})}{x_2 + x_1 \exp(-\alpha_{12}\tau_{12})} \left[\left(1 - \frac{\alpha_{12}\tau_{12} x_2}{x_2 + x_1 \exp(\alpha_{12}\tau_{12})} \right) \right.$$

$$\left. (C_2 - 273.15 D_2) + \frac{\tau_{12}^2 x_2 D_3 RT^2}{x_2 + x_1 \exp(\alpha_{12}\tau_{12})} \right] \qquad 3.53$$

Tassios (85) reduced the number of unknown parameters for the Wilson equation to one for a binary system by substitution of the interchange energy, Gii. He substituted the opposite of the energy of vapourisation of pure i, at the same pressure and temperature of the solution, namely Hildebrand's cohesive energy though with it's basis being one mole instead of one cc. The equation contains the same shortcomings as the two parameter form and is still extendable to multicomponent systems, there being only three unknowns for a tenary system.

Tassio's applied his equation to the system acetone - chloroform-methanol comparing his results with those of Orye (86) and showed a distinct improvement of the Van-Laar equations. The accuracy of the one parameter equation is generally significantly poorer than the two parameter form.

Wong and Eckert (87) have modified this approach to retain the physical interpretation of the Wilson parameters; they interpreted λ_{ij} as the configurational energy per pair interaction.

Schreiber and Eckert (88) have extensively investigated the one parameter Wilson equation with the interpretation of Wong and Eckert. They found that the equation gives a good representation of a binary system provided deviations from Raoults Law are not excessive. For highly non-ideal systems the single parameter equation was significantly less satisfactory.

Bruin and Prausnitz (89) in a similar manner to Tassio's produced a form of the NRTL equation containing only one unknown parameter. They also modified the original approach by firstly substituting local volume fractions for local mole fractions and then introducing a physically reasonable approximation. Renon's assumption that the molecules of the two species were of the same size was removed and from the two cell theory Bruin derived

$$G^{(1)} = Z\, q_{12}\, \Phi_{11}\, G_{11} + Z\, q_{12}\, \Phi_{21}\, G_{12} \qquad 3.54$$

where q_{12} is a measure of the number of sites available

Φ = local volume fraction.

The resulting equation for γ_1 is

$$\ln \gamma_1 = q_{12}\, \Phi_{21}^{\,2}\, \tau_{21} + q_{21}\, {}^{x_2}/_{x_1} \Phi_{12}\, (1 - \Phi_{12})\, \tau_{12} \qquad 3.55$$

where $\tau_{12} = \alpha_{12}^{-1}\, q_{21}\, (G_{12} - G_{22}) / RT$

$\tau_{21} = \alpha_{12}^{-1}\, q_{12}\, (G_{12} - G_{11}) / RT$

$$\Phi_{12} = \frac{V_1\, x_1 \exp(-\alpha_{12}\, \tau_{12} / q_{21})}{V_2\, x_2 + V_1\, x_1 \exp(-\alpha_{12}\, \tau_{12} / q_{12})} \qquad 3.56$$

$$\Phi_{21} = \frac{V_2\, x_2 \exp(-\alpha_{12}\, \tau_{21} / q_{12})}{V_1\, x_1 + V_2\, x_2 \exp(-\alpha_{12}\, \tau_{21} / q_{21})} \qquad 3.57$$

Bruin introduced size factors into three differing points in the analysis, and with each addition obtained improved accuracy, often equivalent to the two-parameter form when all three additions were made. The equation proved satisfactory for aqueous as well as non-aqueous systems (the molar volume of water is much smaller than that of most organic liquids).

Morisue (90) has demonstrated by showing that Q when plotted against (λji - λii) does not exceed - 0.15, that the correlation is incapable of dealing with systems exhibiting large negative deviations from Raoult's Law.

Andiappan and McLean (91) have recently replaced the interchange energy between two different types of molecules by defining two types of local energy parameters derived from Scotts two liquid concept and introducing them into the quasichemical approximation. They obtained for the excess Gibbs energy

$$G^E/RT = \frac{Z_{12}}{2} \left[x_1 \mathrm{In}\, A_{12} + x_2 \mathrm{In}\, A_{21} \right] \qquad 3.58$$

where $$A_{ij} = \frac{\beta_{ij} + x_i - x_j}{x_i \left(\beta_{ij} + 1\right)}$$

$$\beta_{ij} = \left[1 + 4\, x_i\, x_j \left(\eta^2_{ij} - 1\right) \right]^{1/2}$$

$$\eta_{ij} = \exp\left(W_{ij} / Z_{ij}\, RT\right)$$

$$Z_{ij} = Z_{ji} \quad ; \quad n_{ij} \neq n_{ji}$$

The binary constant Z_{12} is a measure of the co-ordination number and W is the interchange energy.

The activity coefficients are given by

$$\ln \gamma_1 = Z_{12}/2 \left[\ln A_{12} + x_2 \left[(x_2 - x_1)\xi + \psi \right] \right]$$

3.59

$$\ln \gamma_2 = Z_{21}/2 \left[\ln A_{21} + x_1 \left[(x_1 - x_2)\xi - \psi \right] \right]$$

where ξ_{ij} = potential energy of the i - j pair

$$\xi = \xi_{12} + \xi_{21}$$

$$\xi_{ij} = \frac{\beta ij - 1}{\beta ij \, (\beta ij + x_i - x_j)}$$

$$\psi = \psi_{12} - \psi_{21}$$

$$\psi = 2xi \,/\, (\beta ij + x_i - x_j)$$

3.5 Theoretical Review

This section will review the correlations cited in the previous chapter on the basis of any physical interpretation of the models, their accuracy and the calculational techniques employed for the associated parameters. Numerous reviews have been published but the authors have frequently been in disagreement over the more recent 'L.M.F.' correlations.

The superiority in data-fitting of the L.M.F. correlations over the earlier models is well documented. For certain systems, normally with $\gamma^{\infty} < 2.0$, a series expansion such as the Redlich-Kister expansion can be fitted very accurately, though in general this necessitates the use of a large number of parameters making the equations unwieldy and impractical in use.

Reports on the Wilson and NRTL equations often fail to recognise that the accuracy depends on the methods and principles adopted in calculating the parameters by a best-fit technique. Why this is so is shown for the Wilson equation by Figues (9) and (10) on which the error function of Hudson and Van Winkle (83) has been plotted against the parameter pairs Λ_{ij}. The systems are chosen to represent the difference between a fairly ideal system (2-2-4 Tri-methylpentane-Toluene) and a highly non-ideal system (Ethanol-n-heptane). It can be observed that a large range of parameter pairs are possible which can produce a required fit, even for a small error function. This range increases with a decrease in non-ideality. The values obtained are thus depend-

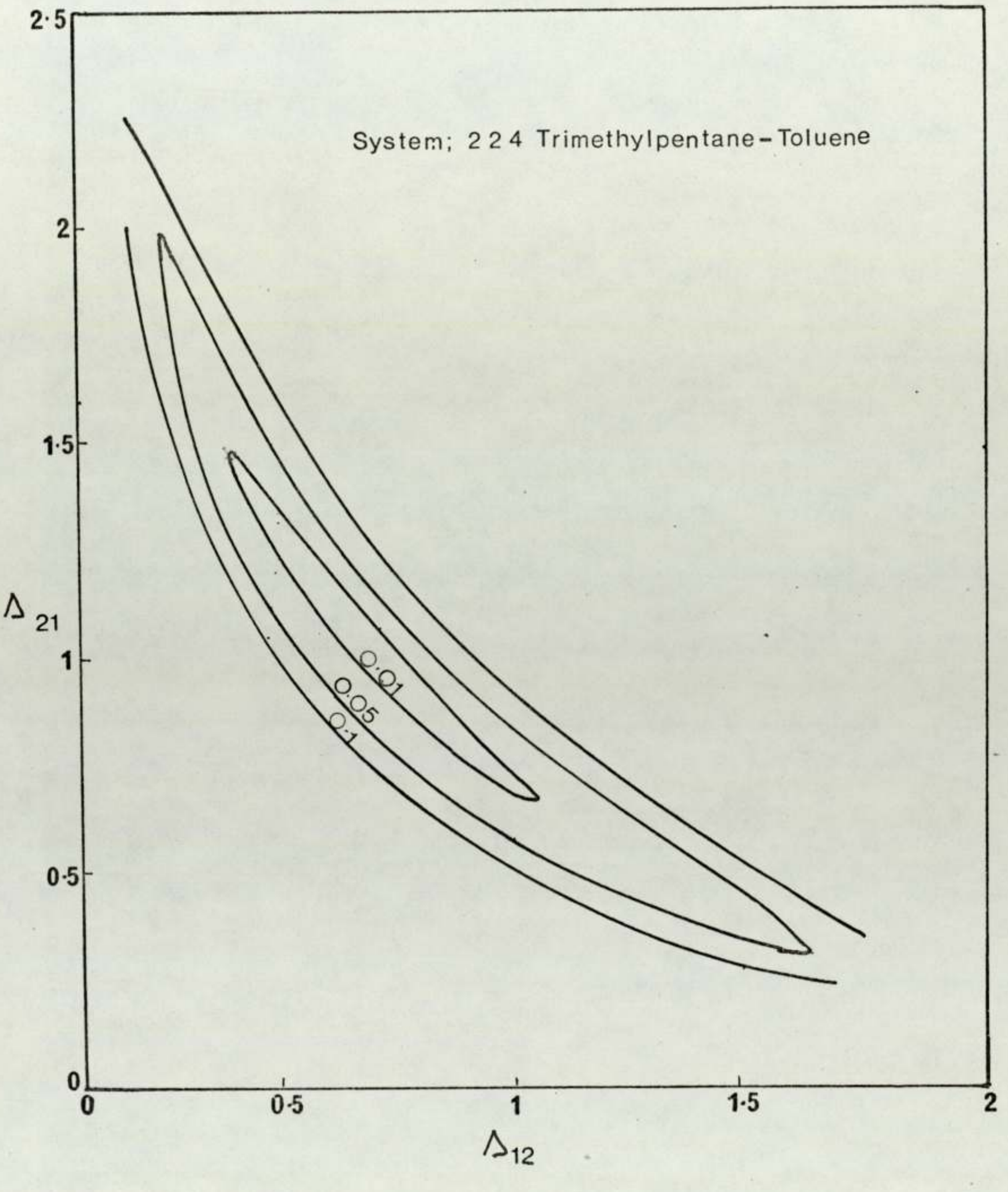

System; 2 2 4 Trimethylpentane-Toluene
2·5
2
1·5
1
0·5
0
0
0·5
1
1·5
2
Δ_{21}
Δ_{12}
0·01
0·05
0·1

Figure 9

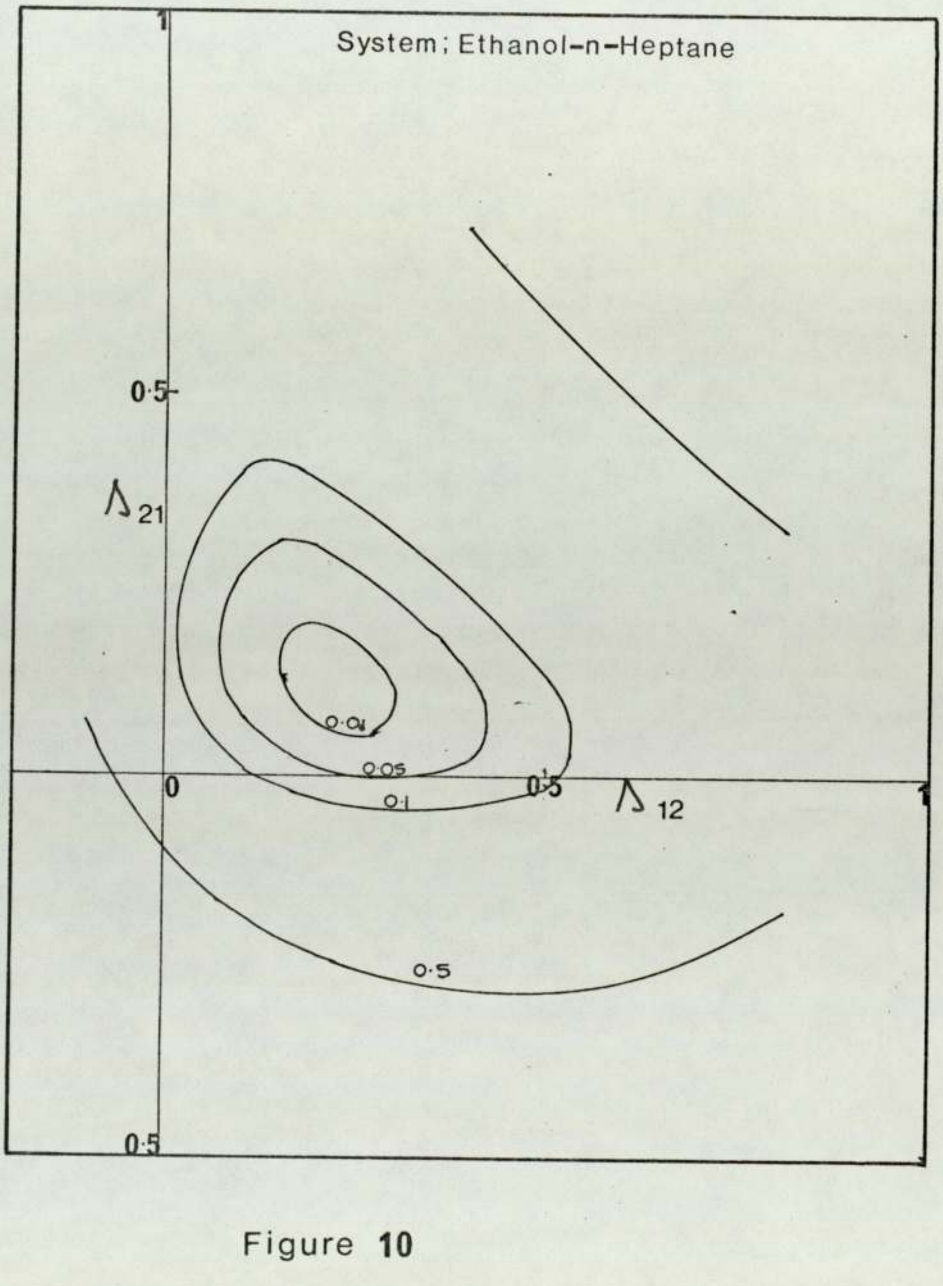

System; Ethanol-n-Heptane
1
0·5
Λ_{21}
0
0·5
Λ_{12}
1
0·5
0·01
0·05
0·1
0·5

Figure **10**

ent on the error function and the method adopted and/or the initial values chosen. Hudson and Van Winkle have compared fits obtained using error functions given below.

$$\sum_{i=1.}^{k}\left[\frac{P_{exp} - P_{calcd}}{P_{exp}}\right]^{2} \qquad 3.60$$

$$\frac{\sum_{i=1}^{k}(\gamma_{1exp} - \gamma_{1calc})_i^{2}}{\sum_{i=1.}^{k}(\gamma_{1exp} - 1.0)} + \frac{\sum_{i=1}^{k}(\gamma_{2exp} - \gamma_{2calc})_i^{2}}{\sum_{i=1.}^{k}(\gamma_{2exp} - 1.0)} \qquad 3.61$$

$$Q = (G^{E}_{exp} - G^{E}_{calc})^{2} \qquad 3.62$$

They concluded that the Q error function produced the best fit, and the activity error the least accurate fit.

The NRTL equation behaves in a very similar manner to the Wilson equation.

A more detailed and concise insight into the accuracy of the Wilson and NRTL equations has been undertaken by using parameters calculated at one composition only. Figures 11 and 12, for the 2.2-4 Trimethylpentane-Toluene data shows the fits obtained when the parameters are calculated from the two activity coefficients at the mid-point ($x_1 = x_2 = 0.5$). The figures show a decrease in accuracy away from the mid-point with a characteristic change in error either side of the mid-point. This behaviour corroborates the statement of Hudson and Van Winkle that

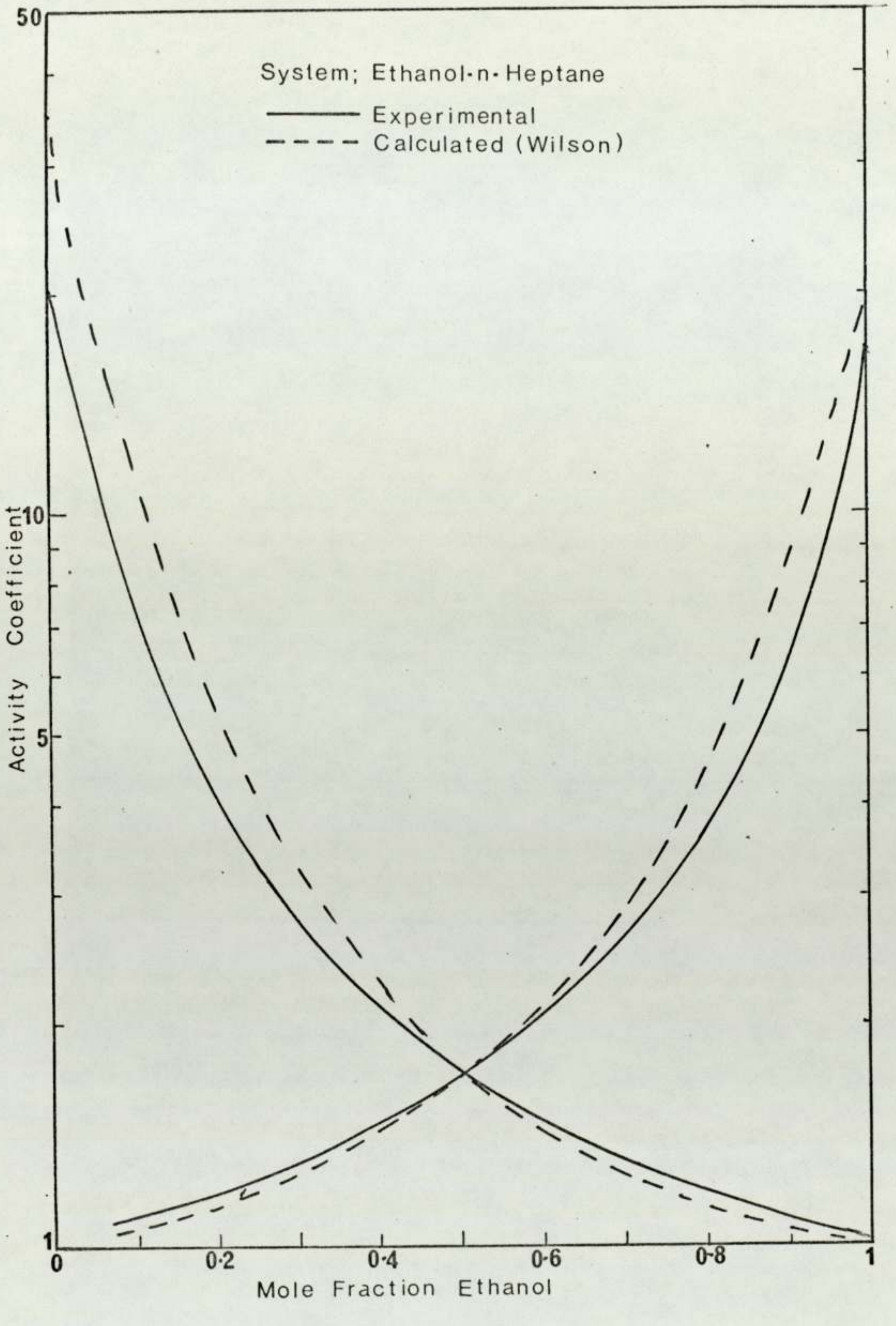

System; Ethanol-n-Heptane
Experimental
Calculated (Wilson)
50
10
5
1
Activity Coefficient
0
0·2
0·4
0·6
0·8
1
Mole Fraction Ethanol

Figure 11

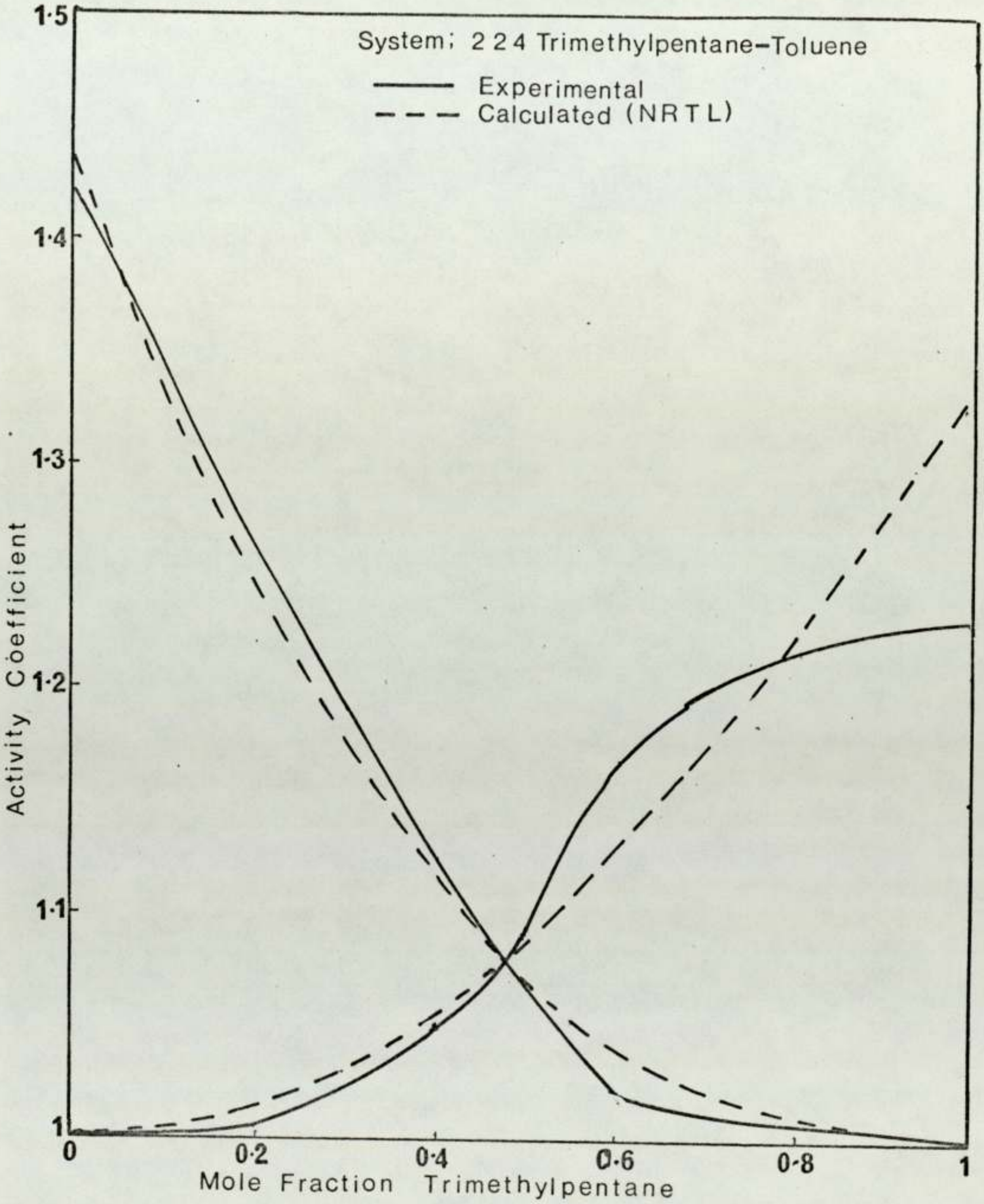

System; 224 Trimethylpentane–Toluene
Experimental
Calculated (NRTL)
Activity Coefficient
1·5
1·4
1·3
1·2
1·1
1
0
0·2
0·4
0·6
0·8
1
Mole Fraction Trimethylpentane

Figure 12

data is required at both ends of the composition range (0.1, 0.9) in addition to near the mid-point.

This characteristic change in error sign noted above could result for the NRTL equation, from the assumption of equally-sized molecules. For unequal size molecules the number of interactions depends on the co-ordination number of the central molecule which is dependent on the composition, size ratio of molecules and structure.

To ascertain the predominant effects over differing portions of the composition range with the NRTL equation, the size parameter, α , was examined. For a binary with differing size molecules the co-ordination number (proportional to $^1/\alpha$) should behave in a manner indicated in Figure 13.

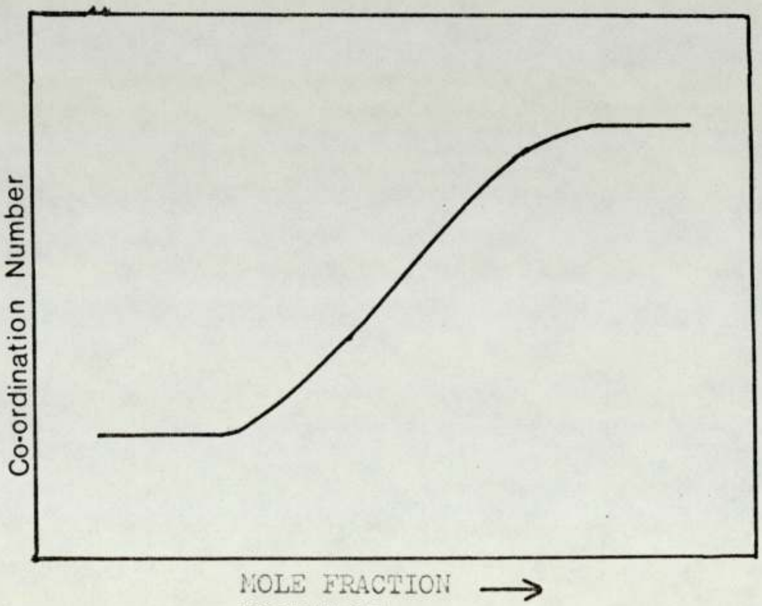


FIGURE 13.

For A $>>$ B, as more molecules B are introduced the number of neighbours to A will increase until the theoretical limit based on size considerations or packing structure. For systems containing highly differing molecule sizes, the energy parameters were calculated at the mid-point using both the value of α suggested by Renon and the value obtained by optimisation. The value of α was then calculated to give the experimental activity coefficient maintaining the energy parameters constant. Figure 14 shows typical results. The theoretical trends are only temporarily followed with always failure to obtain any values of α capable of giving any real or sensible activity coefficients near the end-points. Similar results were obtained when the energy parameters were calculated at the composition relating to the size ratio i.e. equal neighbours from a volume basis.

The observations noted above when compared with results obtained with systems containing molecules of similar size, indicate that around the mid-range, the athermal effect is of major influence but nearer the end-points, related to the packing structure and size ratio, thermal forces predominate. The NRTL equation does not adequately describe the thermal behaviour.

The effect of the α value on the data fit is difficult to generalise. A change of α on mid-composition data will only slightly affect the accuracy of fit although it considerably changes the energy parameter values. A change of the α value near the end-point will have a considerable effect on the fit.

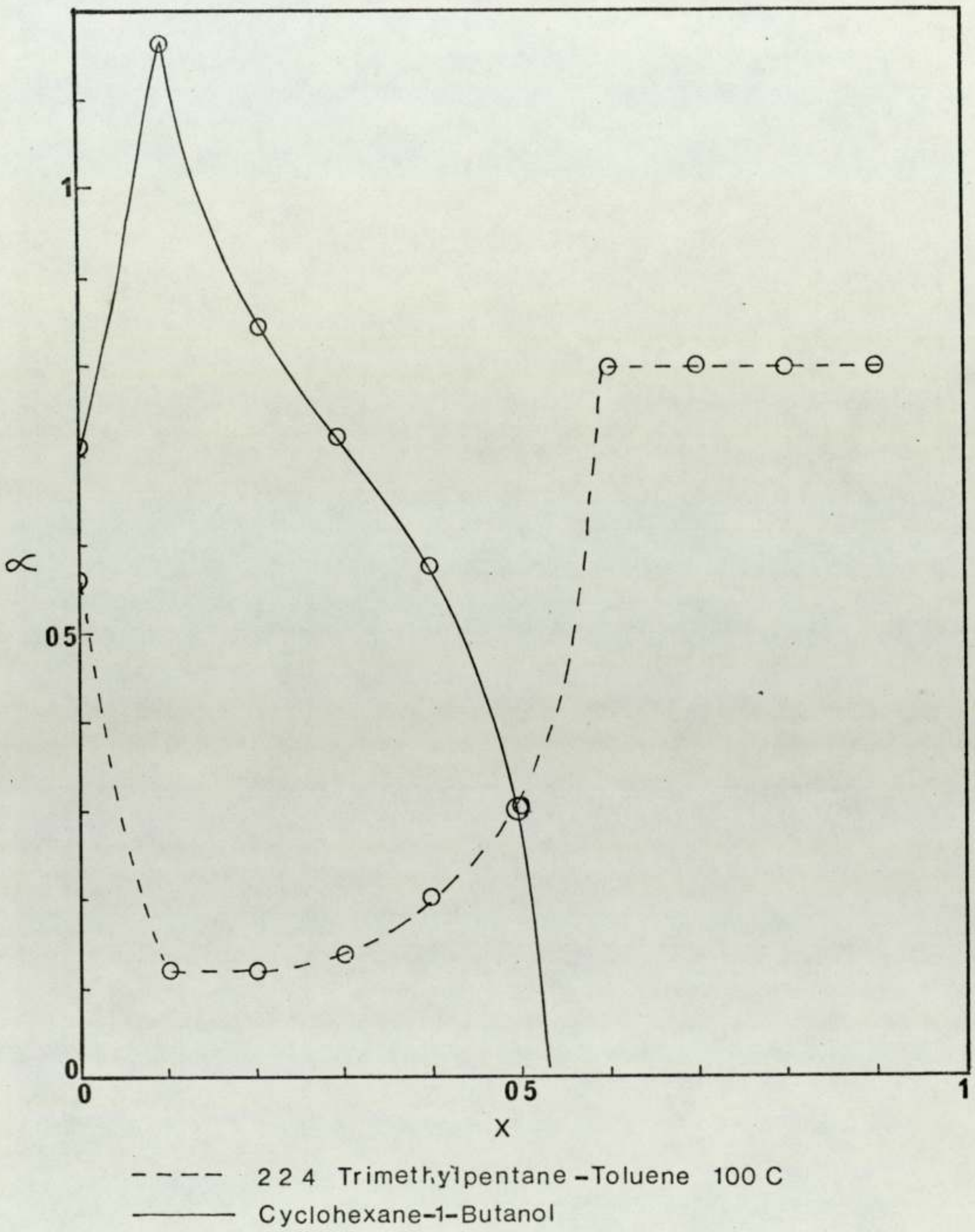

1
05
0
α
0
05
1
X
---- 224 Trimethylpentane-Toluene 100 C
—— Cyclohexane-1-Butanol

Figure 14

The work of Bruin and Prausnitz (89) indicates that λ_{ij} compensates for the error resulting from the equal-sized molecules assumption when the parameters are minimised. Bruin employed the size modifications which were very successful for his one-parameter form of the NRTL equation in the two parameter equation and found no improvement in fit. Investigation of the C-parameter in the Wilson three-parameter equation was not considered to be of any benefit due to the similarity with α shown by Renon and Prausnitz (92).

The application of all the correlations near infinite dilution is an excellent test of the relationship as well as being of great interest in this work. Many authors have assumed without adequate investigation that the parameters can be obtained by solution of the simultaneous equations obtained using the activity coefficients at infinite dilution. The Wilson and NRTL equations reduce to simple forms at these values.

Wilson equation:-

$$\text{at } x_1 = 0 \qquad \text{In}\, \gamma_1 = \text{In}\,(\Lambda 12) + 1 - \Lambda_{21} \qquad 3.4$$

$$\text{at } x_2 = 0 \qquad \text{In}\, \gamma_2 = \text{In}\,(\Lambda_{21}) + 1 - \Lambda_{12} \qquad 3.5$$

NRTL equation :-

$$\text{at } x_1 = 0 \qquad \text{In}\, \gamma_1 = \tau_{21} + \tau_{12} \quad G_{12} \qquad 3.6$$

$$\text{at } x_2 = 0 \qquad \text{In}\, \gamma_2 = \tau_{12} + \tau_{21} \quad G_{21} \qquad 3.7$$

The general behaviour of the most important correlations is illustrated on Figure 15. The parameters were obtained from data

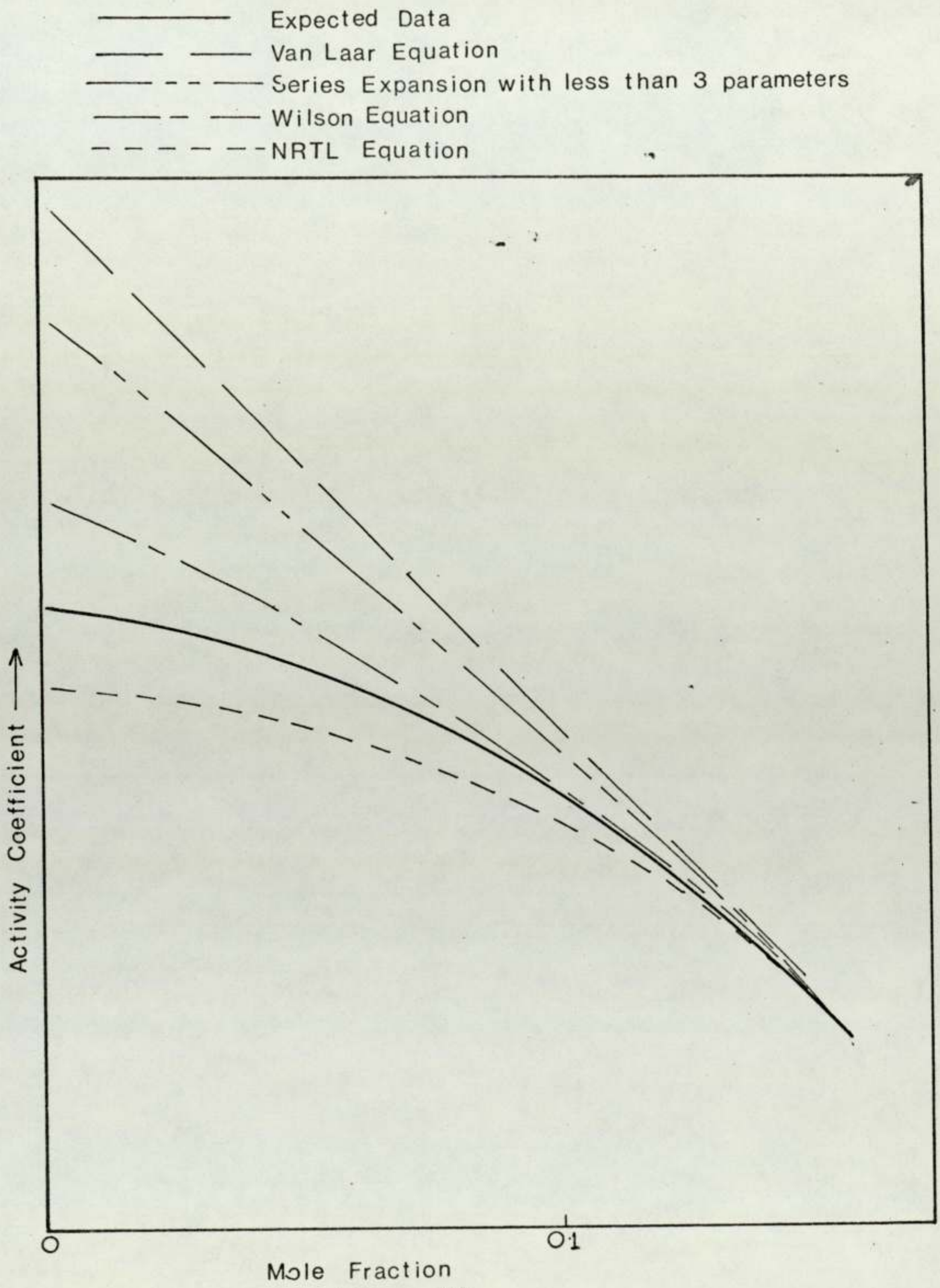

Expected Data
Van Laar Equation
Series Expansion with less than 3 parameters
Wilson Equation
NRTL Equation
Activity Coefficient ⟶
0
0·1
Mole Fraction

Figure 15

between 0.1 and 0.9 mole fraction. The Wilson and NRTL equations are in general approximately + 10% and -10% in error respectively for fairly non-ideal mixtures. The figure can however alter significantly depending on the experimental error and non-linear regression technique adopted as referred to earlier.

The accuracies associated with employing infinite dilution values to obtain parameters for the Wilson and NRTL equations to cover the full composition range is illustrated by Figure 16. The error function at infinite dilution has been plotted against the energy parameter pairs in an identical manner to Figures 9 and 10. Comparison shows that a parameter pair at the mid-point will impart a larger error near infinite dilution and vice-versa. Several authors have noted that the fit is often insensitive to an error of ± 10% in the infinite dilution activity coefficient. The insensitivity however reduces with increase in ideality and will reduce the acceptable error at infinite dilution to within 1% - 2%.

Data in the region of low concentrations ($x < 10^{-2}$) is very scarce and must be regarded with a high degree of uncertainty. Tsonopoulos and Prausnitz (93) have recently investigated aromatic solutes and solvents in dilute aqueous solutions. They extrapolated data of mole fraction between 10^{-2} and 10^{-3} to 10^{-6} for their limits.

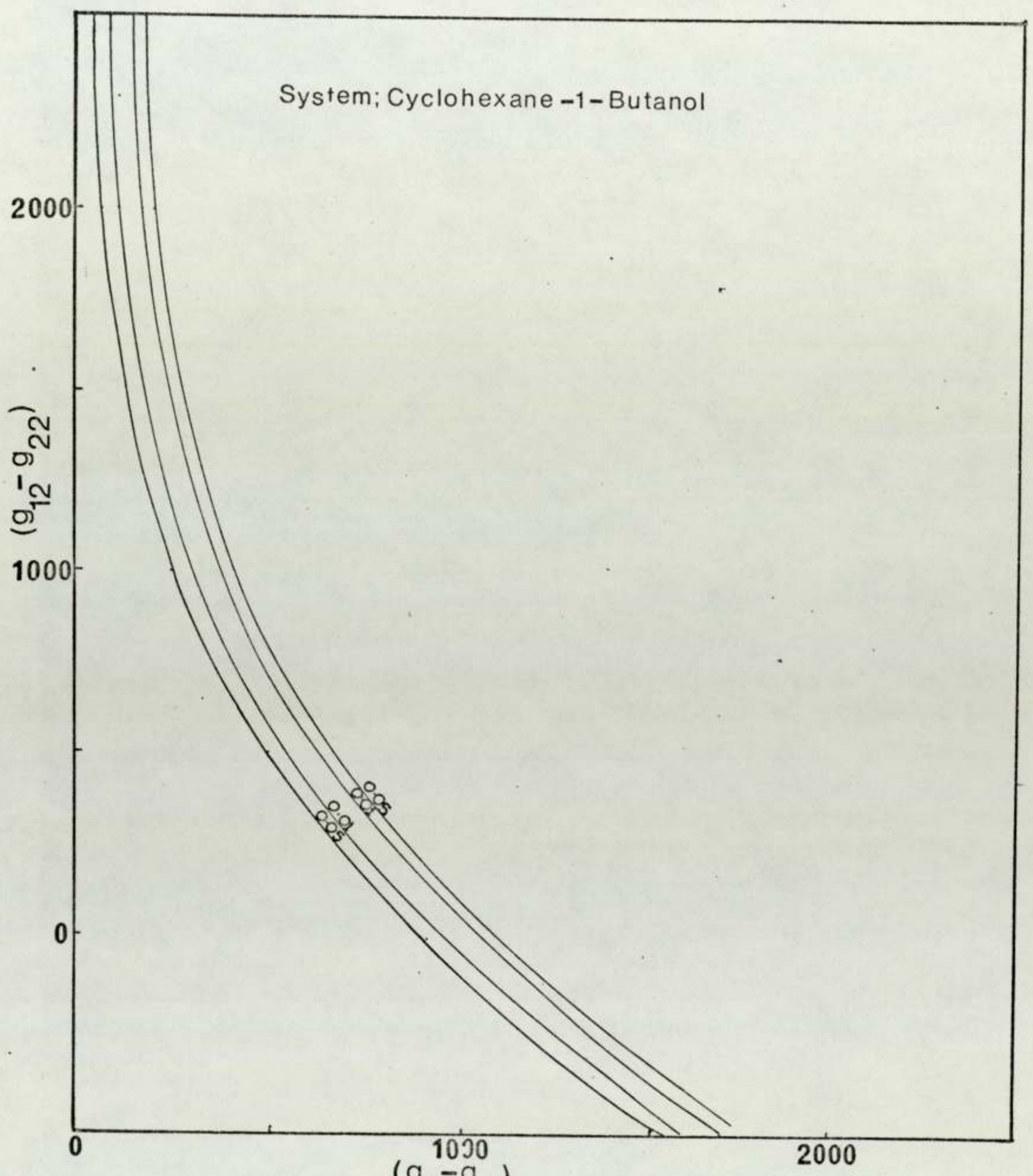

System; Cyclohexane -1- Butanol
2000
1000
0
$(g_{12}-g_{22})$
0
1000
2000
$(g_{21}-g_{11})$
0.005
0.01
0.02
0.05

Figure 16

4.0 AN OUTLINE OF THE METHOD

The proposed method is basically a total pressure method, with the need for analysis of either phase eliminated. The method produces isothermal data for binary systems over the full composition range but is primarily developed for data acquisition at very low concentrations of one component.

For a binary system, A-B, work is carried out over two concentration ranges, low A in B ($x < 0.01$) and vice-versa. An equilibrium cell of approximately 100 mls capacity is constructed so that a known quantity of A is introduced into it and B is then added in successive amounts. The cell is of a known volume and the volume of the liquid phase is carefully measured after each addition. The cell is maintained at a constant temperature and the total pressure of the mixture measured.

4.1 Theory related to the method

Two calculational procedures have been developed for use with the apparatus, one based on certain assumptions related to ideality in the phases and one based on an adaption of the Gibbs phase rule.

4.1.1. Method A

In this procedure only one run(ideally) is performed for A in B, and it is assumed that the virial coefficients for A and B are known or can be computed. The method contains two iterative procedures within the calculation. The calculation is performed using the computer program 'DATACALC' which is detailed in Appendix.3. An Anotated flow diagram is shown in figure 17.

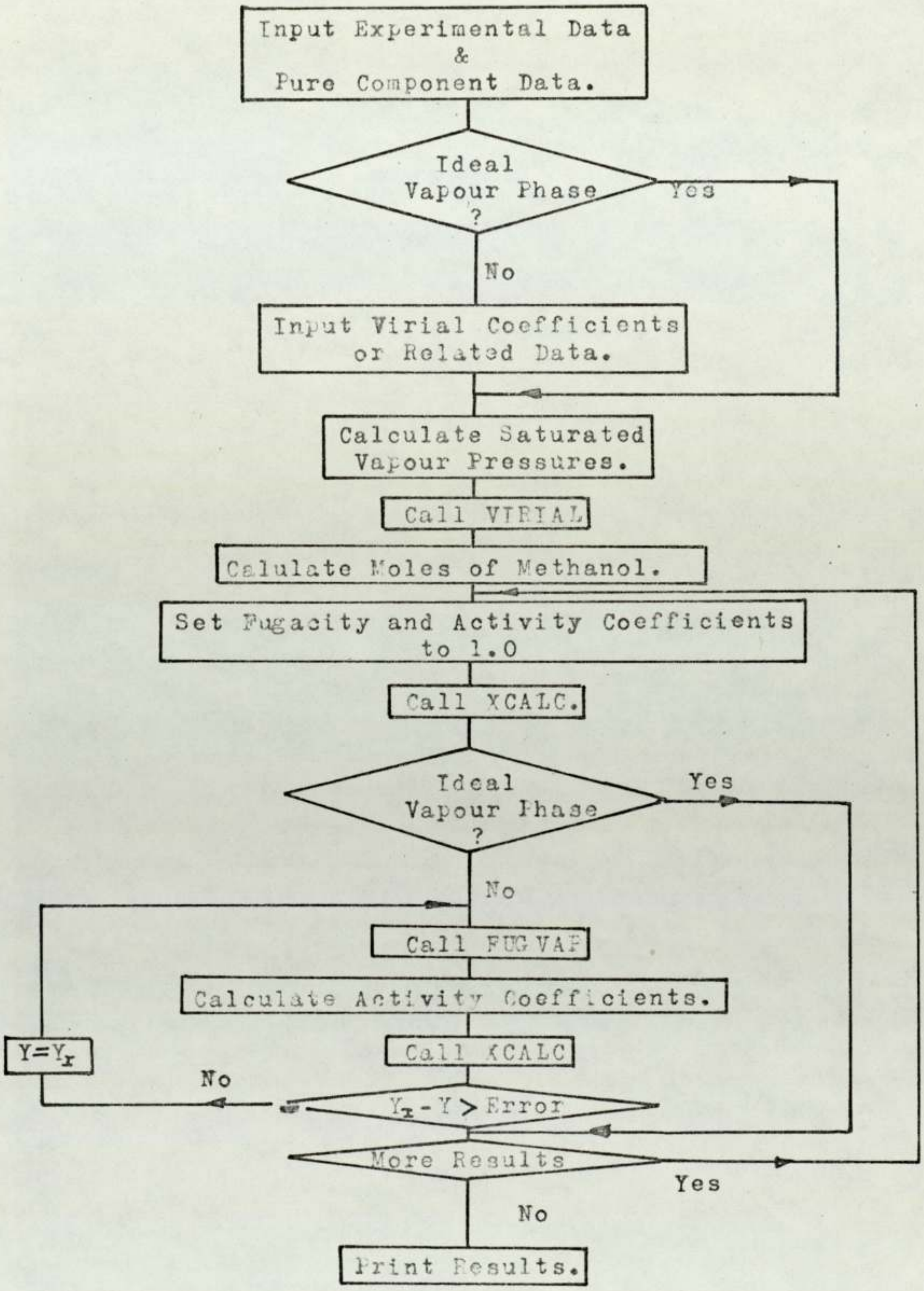
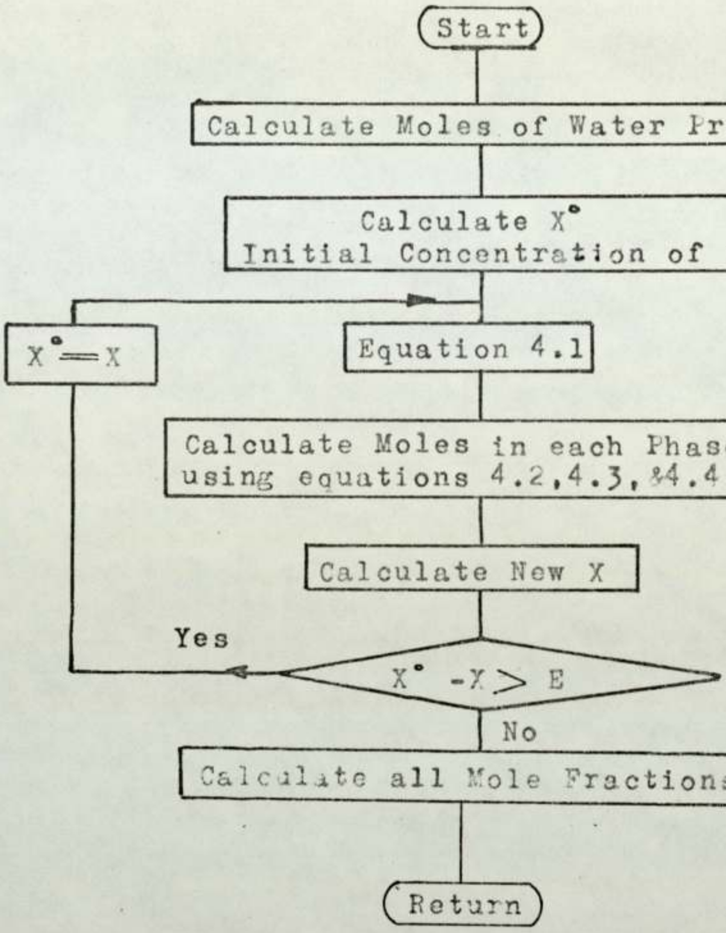


Figure 17
Flowchart for Method A



Subroutine XCALC

The inner iteration, which is the subroutine 'XCALC', calculates the compositions from values of the activity and fugacity coefficients. It is assumed initially that all the mixture is in the liquid phase. From this assumption the partial pressure of B (P_B) above the liquid may be calculated from

$$P_B = P_B^{\circ} x_B \gamma_B \phi_B \qquad (4.1)$$

where P_B^o is the saturated vapour pressure of B at the system temperature.

From the total pressure, P, in the cell, P_A can be calculated by difference, i.e.

$$P_A = P - P_B \qquad (4.2)$$

Application of a truncated form of the virial equation of state yields the number of mols of both A and B in the vapour phase, i.e. for B

$$\frac{P_B \; V_B}{RT} = 1 + \frac{B_B}{V_B} \qquad (4.3)$$

where V_B is the second virial coefficient for B, and

$$V_B = V/n_B^v$$

where V is the vapour phase volume (calculated from total cell volume - liquid phase volume)

n_B^V is the number of mols of B in the vapour phase.

The number of mols of each component in the liquid phase, n_B^L, is calculated for B from

$$n_B^L = N_B - n_B^v \qquad (4.4)$$

where N_B is the total number of mols of B introduced into the cell.

From the n^L values, new estimates of the mole fraction are calculated

$$X_B = \frac{n^L_B}{n_B^L + n_A^L} \qquad (4.5)$$

This new value is assigned to the initial value and the procedure repeated until successive values are within the required error.

When the virial coefficients are unknown, an ideal vapour phase may be assumed and the ideal gas law applied,

$$P\,V = n\,R\,T \qquad (4.6)$$

In the calculation, initially ideality of B is assumed, the γ_B and ϕ_B values being placed equal to 1.0. This reduces equation (4.1) to Raoult's Law. With these values, the vapour phase composition of B is calculated from 'XCALC'. This then allows a value for the fugacity coefficient of B to be computed (using subroutine 'FUGVAP') and hence, the activity coefficient of B via

$$\gamma_B = P_B y_B \Big/ P_B^{\circ} \phi_B x_B \qquad (4.7)$$

Subroutine 'XCALC' is then recalled and a new value of y_B computed. The two y_B values are compared and, if the difference is greater than the required error, new ϕ_B and γ_B values are calculated using the new y_B value and the procedure repeated.

If data is available from a B in A run, this can be utilised to handle the non-ideality of B in equation (4.1).

4.1.2. Method B.

In this method, two runs are performed at the same temperature but with different initial charges of component 1. From the two sets of data it is possible to obtain two fillings that have the same total pressure but have different volumes of each phase present. The calculation of the mole fraction of each component in the liquid and vapour phases is then performed based on a simple application of the phase rule. The Gibbs phase rule states that for a isothermally univariant system, the intensive properties of the liquid and vapour must be the same in the two experiments, i.e. concentration and density.

There are four unknowns - x, y, ρ_L, ρ_g therefore it is necessary to obtain four simultaneous equations. For each run depicted in figure 18, internal material balances made on the cell yield

For run 1 (denoted')

for component 1 $N_1' = y_1 \rho_g V_g' + x_1 \rho_L V_L'$ (B.1)

component 2 $N_2' = (1-y_1) \rho_g V_g' + (1-x_1) \rho_L V_L'$ (B.2)

Run 2 (denoted ")

component 1 $N_1'' = y_1 \rho_g V_g'' + x_1 \rho_L V_L''$ (B.3)

component 2 $N_2'' = (1-y_1) \rho_g V_g'' + (1-x_1) \rho_L V_L''$ (B.4)

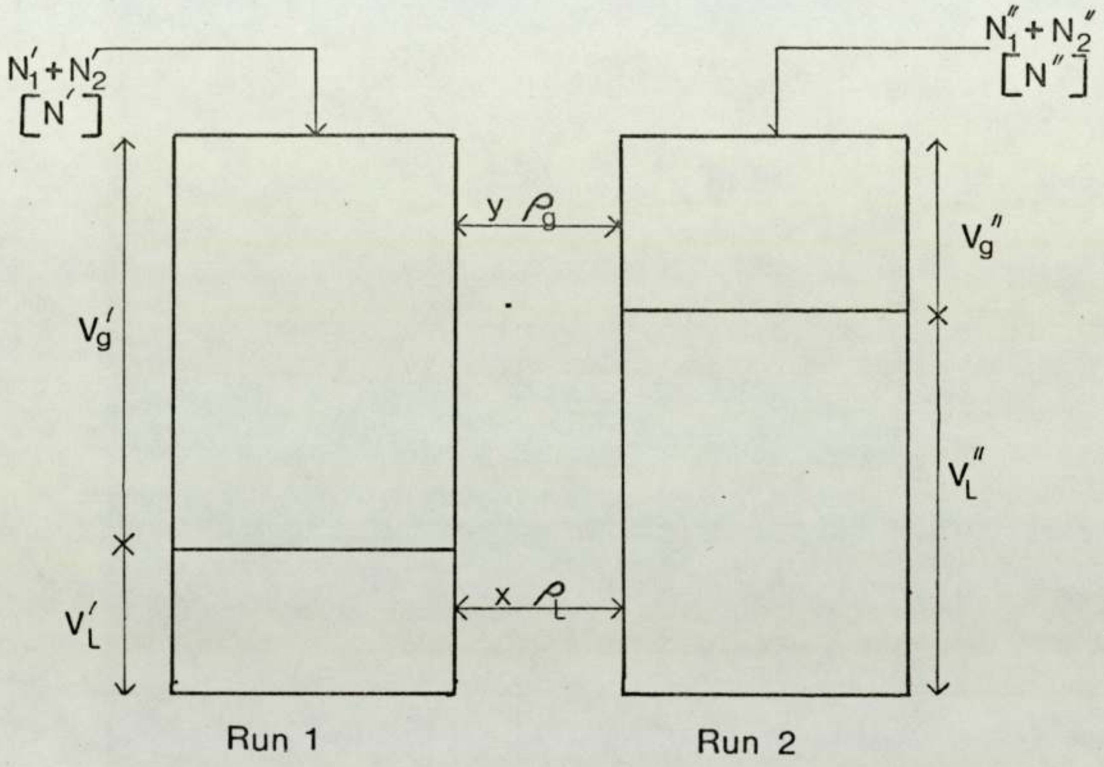


Figure 18

The equation for y can be solved by removing x and by (B.3) - (B.1) and (B.4) - (B.2) and then dividing the resulting intermediate equations.

$$y = \frac{N_1'' V_L' - N_1' V_L''}{N'' V_L' - N' V_L''} \qquad (B.5)$$

where $N' = N_1' + N_2'$ = total moles charged to cell.
Similarily for N'' .

The corresponding equation for X is:

$$X = \frac{N_1'' V' - N_1' V''}{N'' V'' - N' V''} \qquad (B.6)$$

Equations for the densities of the co-existing phases are obtained from overall material balances.

Run 1. $N' = V_g' \rho_g + V_L' \rho_L$ (B.7)

Run 2. $N'' = V_g'' \rho_g + V_L'' \rho_L$ (B.8)

Elimination of ρ_L gives:

$$\rho_g = \frac{N' V_L'' - V_L' N''}{V_g' V_L'' - V_g'' V_L'} \qquad (B.9)$$

Solving for ρ_L gives

$$\rho_L = \frac{N' V_g'' - N'' V_g'}{V_L' V_g'' - V_L'' V_g'} \qquad (B.10)$$

It should be noted that the bounds of equations (B.5) and (B.6) are the dew and bubble points, one must take the limits of these equations as V_L'' and V_g' approach zero, respectively.

Methods based on this simple application of the phase rule have been presented by Hill (94) in 1923 and Rodewald et al (95). Hill determined binary liquid-liquid behaviour at room temperature and pressure and Rodewald adopted the procedure for use with dew and bubble isotherms of the system Helium-Nitrogen.

The sensitivity of both methods to experimental errors will be detailed in the discussion chapter. Method A is generally more accurate than method B as the latter is sensitive to the phase volumes, the least accurate of the measurements.

4.2. Practical Considerations

The apparatus requirements will be considered as four sections of differing functions.

(1) Degassing Section
(2) Temperature Measurement and Control Section
(3) Pressure Measurement and Control Section
(4) Equilibrium Cell and General Glassware Section

4.2.1. Degassing Section

The removal of all air and gases from the mixture components is an essential pre-requisite to ensure that the cell pressure is a function of the mixture vapour composition only. Failure to completely degas the components is often the cause of the largest experimental error present in total pressure techniques and is severely critical in this method where pressure differences may be of the order of only 10 mm Hg.

Techniques are listed in the literature which in general involve boiling under vacuum followed by condensing and/or freezing of the vapour phase. Initial testing showed that a simple version of this procedure was adequate for the organics under investigation but not for water, probably because of the small size of the water molecules.

4.2.2. Temperature Control and Measurement

Control of the cell temperature is required to 0.001°C because of the temperature dependence of the partial pressures of the components. Control to this degree will generally allow pressure measurement to within 0.01 mmHg up to 70°C to 80°C. The control is achieved by immersion of the critical apparatus in a suitably designed thermostatted water bath.

Temperature measurement was achieved using a platinum resistance thermometer.

4.2.3. Pressure Measurement and Control

High precision pressure measurement and control are required as the absolute pressure may only be of the order of 10 mm Hg and differences in pressure are of greater interest than absolute pressure. Two techniques have been developed for this function leading to two alternative methods and apparatus.

The one method, which will be referred to as 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 second method, to be referred to as the 'simple' method, does not employ any electronics. A schematic diagram is incorporated in Figure 19, for the methanol-water system. The equilibrium cell and water burette are arranged to function as a U-tube manometer. A reference bulb 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 capillary tube, preventing back mixing or diffusion of the cell mixture into the burette.

The drawback of the simple method is that the composition of the more volatile component is limited to a very small value (approx. 10^{-5} mole fraction for methanol-water) and to a limited range. This limitation is because the cell mixture pressure must be less than the small pressure head developed by

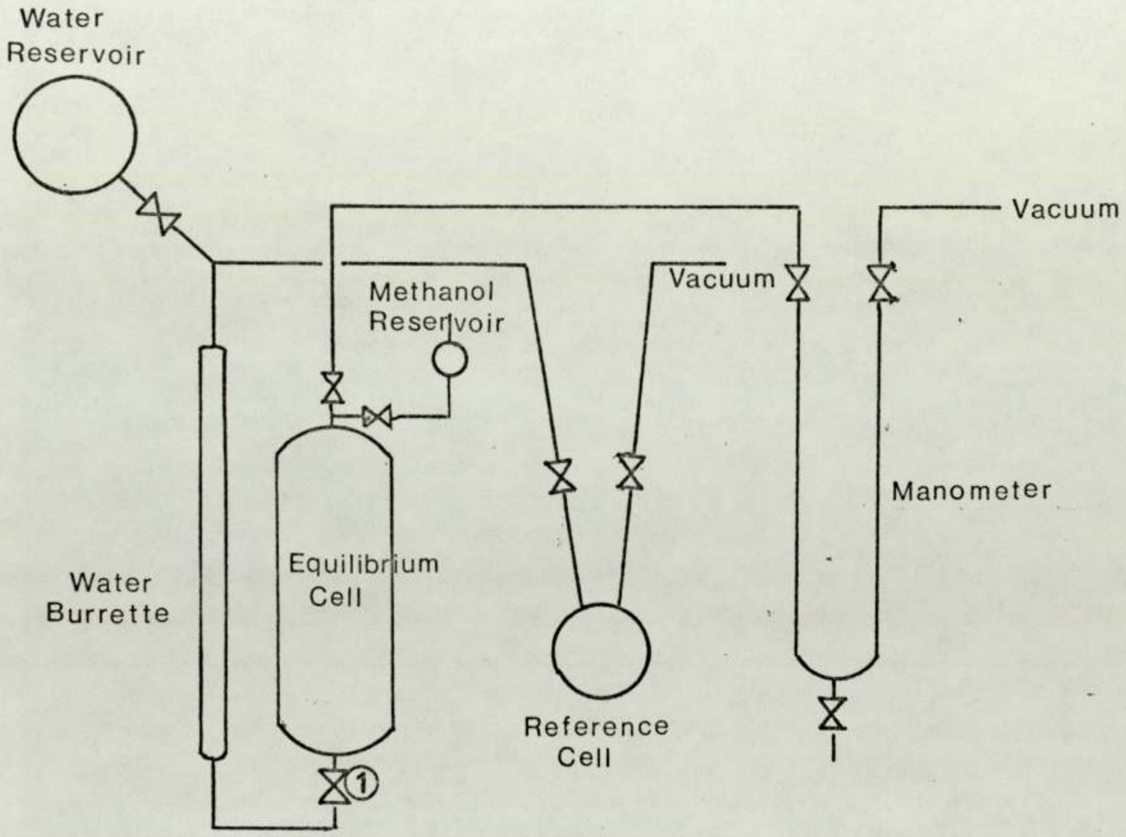


Figure 19

Outline of Simple Rig

the burette water. If this criteria is not met, a reverse flow will occur between the cell and burette. A second drawback is that the more volatile component must always be charged to the cell first.

4.2.4. Equilibrium Cell and General Glassware

The dimensions of the equilibrium cell are not critical, those adopted being determined by general convenience and the desire to avoid using too large quantities of material.

The construction of the general glassware is governed by the necessity for high purity and for connections and valves capable of maintaining a high vacuum.

4.3. Practical Work Plan

The practical work undertaken was primarily concerned with developing to an optimum level, and for industrial purposes, the apparatus and allied techniques for both methods. In the early stages the work was concentrated on the simple rig which was used to develop the apparatus and techniques common to both methods. During this period work on the main apparatus was centred on a comprehensive survey of transducer systems available on the market. This was followed by work to obtain an understanding of the criteria governing the selected system e.g. diaphragm characteristics.

After satisfactory testing of the simple method, the experience obtained was used to design and construct the main apparatus. Both methods were tested using the systems Methanol-water and Ethanol-water. These systems were chosen so that a comparison with the data of Dalager could be made and also because of their theoretical interest.

5.0 SIMPLE RIG: DETAILED DEVELOPMENT AND DESCRIPTION

For ease of description, this chapter will be described for operation with the system methanol-water.

5.01 General Glassware Considerations

The necessity for high purity in addition to high quality leak-proof connections and valves eliminated the use of grease. The valves incorporated in the glassware construction were 'Rotaflo' stopcocks. These are 'Fluon' glass stopcocks with adjustable seals with a claimed control to 10^{-5}torr. The assembly connections were from the range of 'Rotulex' flexible joints. These are ball and socket connections with a sealing ring of silicone rubber or viton encased in this p.t.f.e. capable of retaining a vacuum of 10^{-4}torr.

The glassware was constructed from Borosilicate glass with reinforced p.v.c. vacuum tubing. Glass to tubing connections were performed by expanding the tubing with an I.D. less than the glass O.D. by heating and then allowing to cool to form a tight seal. Small leaks were sealed using a proprietary spray-on vacuum sealant (Edwards High Vacuum 'Spray-seal').

5.1 Degassing of the Components

Degassing as previously stated is often the largest cause of error in the results. This is due to the difficulty in removing the last ten per cent of gas in the liquid and in the absence of a satisfactory test to show complete degassing. The measure of degassing relies on the experience of the operator.

A good estimate of the extent of degassing, especially with water, is given by the 'metallic clicking' of the liquid on the walls of the container. An additional test used initially in the work was to run the liquid into an evacuated closed cell and check that no air bubble appeared in the full cell.

The systems investigated required the development of two procedures, one for an organic liquid and one for water.

5.1.1. Degassing of Organic Liquids

Methods for the degassing of organic liquids such as methanol are well established in the literature. The basis of the method adopted is the boiling of the liquid under vacuum with condensation of the vapour. A schematic diagram is given in Figure 20.

The methanol flask is of 250 mls. capacity and the reservoir of 5 - 10 mls., this is sufficient for the small charge to the equilibrium cell. The valves are both of 3mm bore.

The procedure is initiated by placing the charge in the flask and evacuating the apparatus. This is continued for 20 - 30

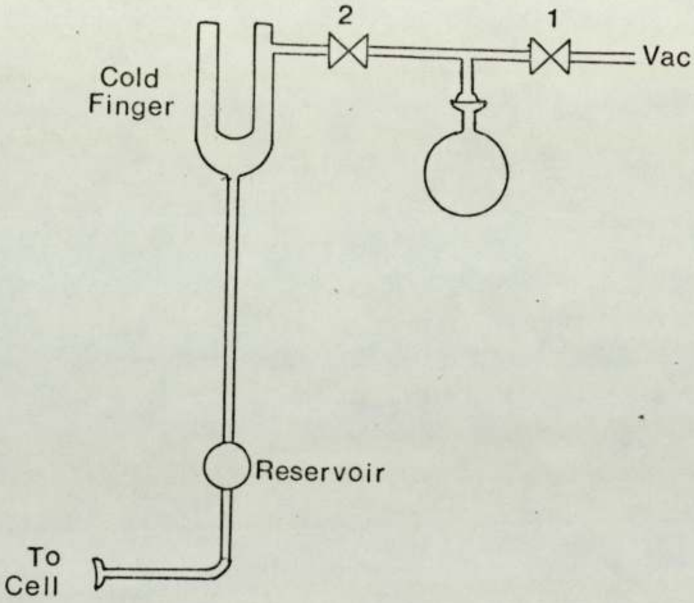


Figure 20

Diagram of Organics Degassing Apparatus

minutes with occasional heat applied to the flask, with valve 1 closed. This removes the substantial portion of air in the methanol.

After this period valve 2 is closed and a freezing mixture of ice and calcium chloride inserted into the 'cold finger'. Valve 1 is opened and by application of heat the methanol vapourised. The vapour condenses on the walls of the 'cold finger' and is collected in the reservoir. Valve 2 is opened to vacuum intermittently to remove any air collecting in the vicinity of the 'cold finger'. Any additional degassing can be performed whilst the methanol is in the reservoir.

5.1.2. Degassing of Water

The removal of air from water was found to be unsatisfactory using the apparatus described for organic liquids, even after several degassing periods totalling 2-3 hours. Complete removal was achieved by the addition of a further two stages. A line diagram of the apparatus is given in Figure 21 and the apparatus is shown mounted on the main rig on plate 1.

Stage 1 consists of a 500 ml. flask externally heated by an isomantle, and with a condenser. Valve 1 is an air inlet, normally used for ease of dismantling when a second fresh charge is required. Stage 2 is a boiler of approximately 750 mls. capacity with condenser and internal silica-sheathed immersion heater of 500 watts (Electrothermal 'Hot-Rod'). The heater arrangement works

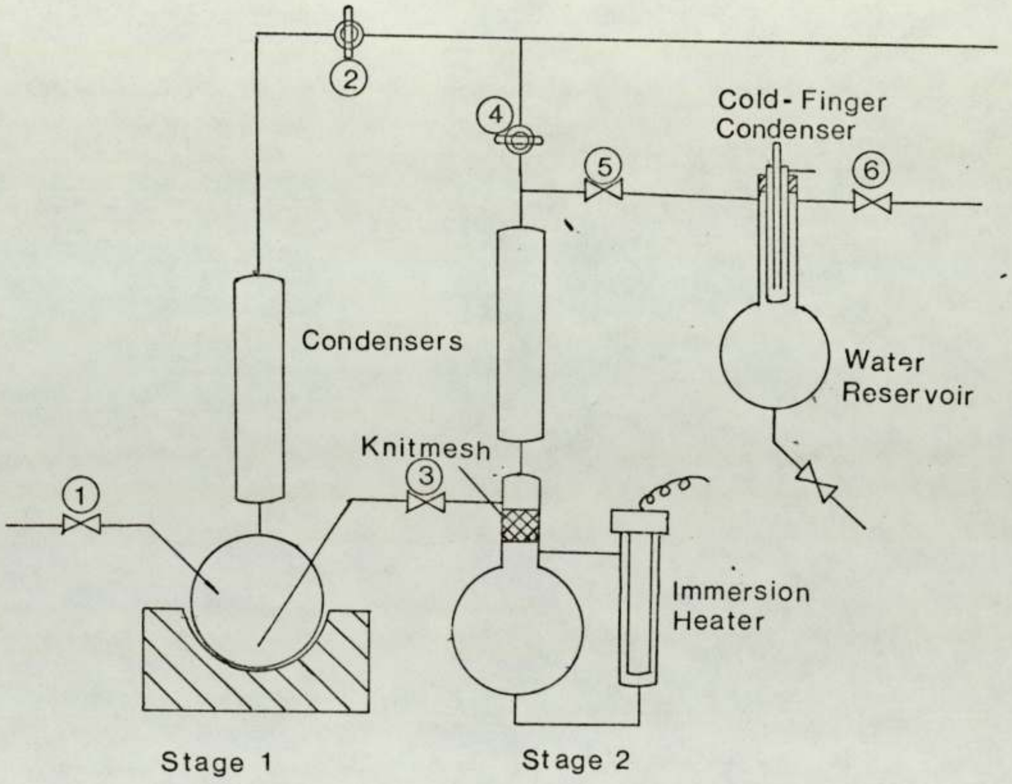
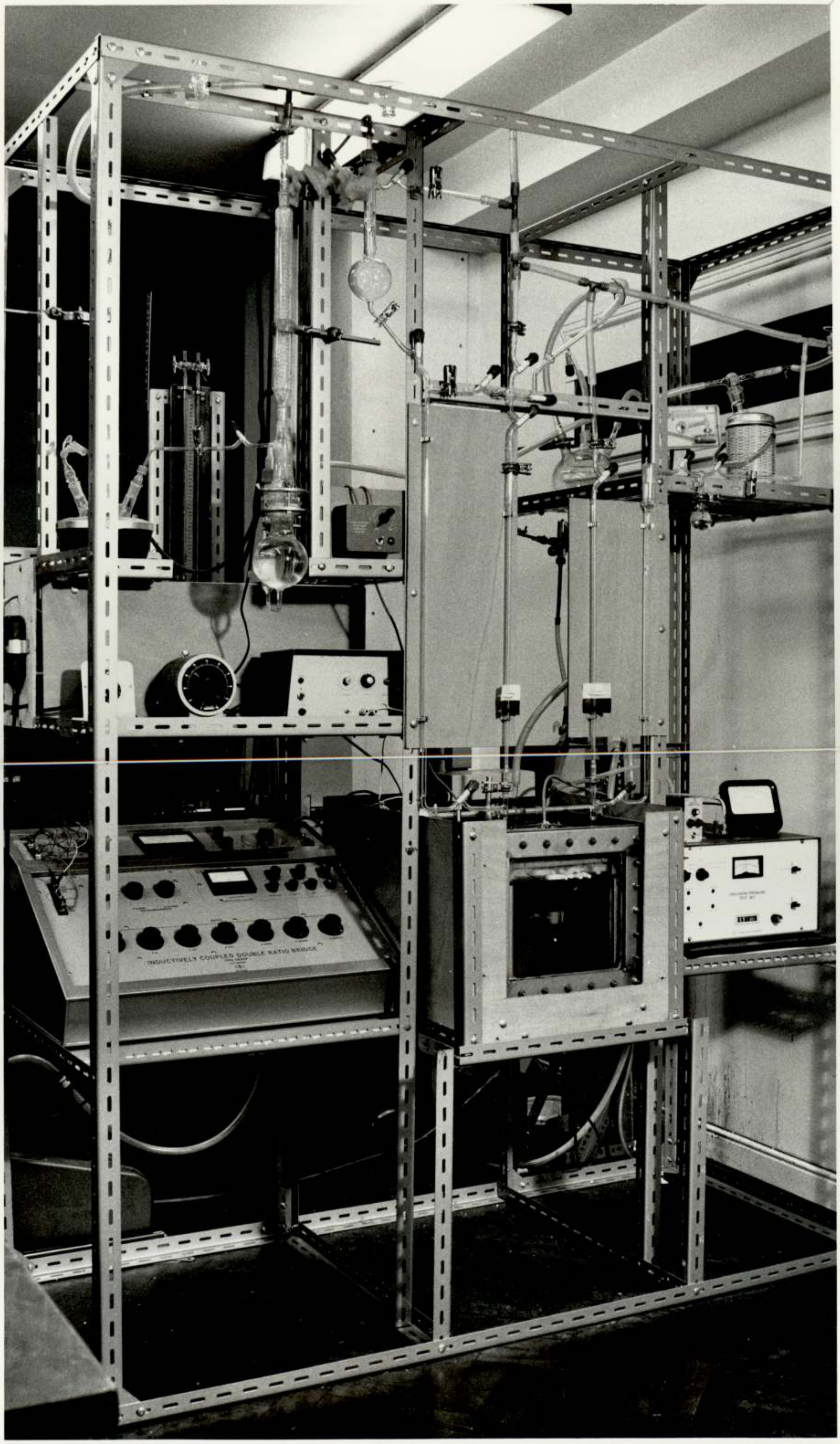


Figure **21**
Diagram of Water Degassing Apparatus

Plate 1
Main Rig


INDUCTIVELY COUPLED DOUBLE RATIO BRIDGE

on the 'thermosiphon' principle. Knitmesh is packed into the neck of the flask to act as a spray catcher. Stage 3, a 500 mls. long-neck flask, is the reservoir. A 'cold finger' condenser is positioned down the neck. Each individual section was connected to the vacuum system through a stopcock and could be separately isolated from the vacuum line.

The complete apparatus is initially evacuated (a vacuum of 5mmHg is adequate) and the Stage 1 flask charged with freshly distilled water. Boiling of the water, under reflux and with the isomantle on mark 7, is continued for 1-1½ hours. Valve 2 is maintained 5-10% open to purge off the air without excessive removal of water vapour. The completion of Stage 1 is signified by the establishment of a 'metallic clicking' of the water on the flask walls at regular intervals.

The water is transferred to the Stage 2 boiler by allowing a build-up of vapour pressure in Stage 1. For this, Stage 1 is isolated by closing Valve 2 and the condenser water disconnected. Degassing occurs at the inlet jet during the transfer by 'flashing - off'. On completion of the transfer, boiling under reflux and vacuum is continued for an additional period of 15 minutes, with the internal heater set near maximum.

Stage 2 is then isolated from the vacuum line by closing Valve 4 and the water vapour transferred to the reservoir by opening Valve 5 and discontinuing the reflux. The vapour liquifies on the 'cold finger' condenser and any air is removed by intermittent opening of Valve 6. This final condensation stage is to avoid any"carry-over"of grease.

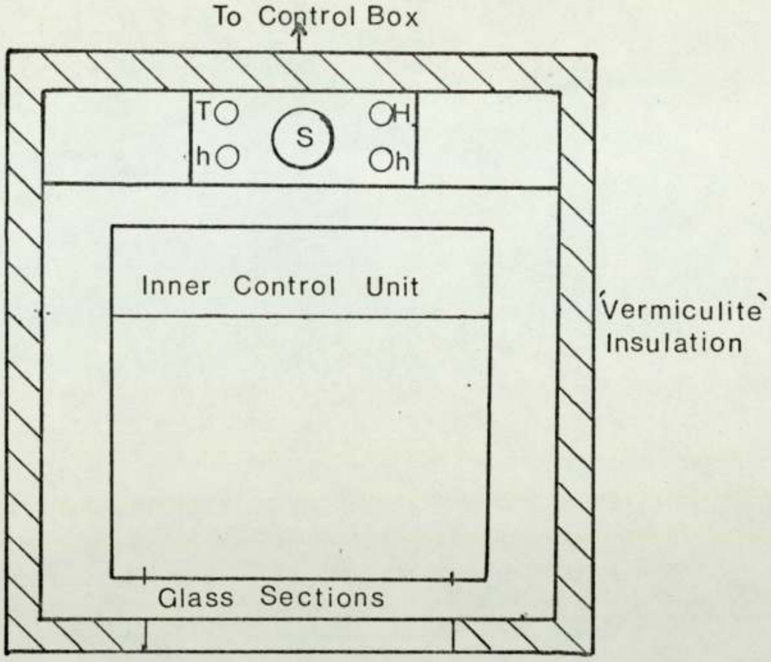
The degassed water is maintained in the reservoir until ready for use, any final degassing is achieved by vacuum induced boiling whilst in the reservoir.

5.2 Temperature Control

The thermostatically controlled water bath comprises of an inner and outer control compartment. The exterior compartment controls to within ± 0.02°C, with the inner compartment providing the necessary control to ± 0.001°C. The control bath for the main apparatus is shown in Figure 22.

The control unit for the inner compartment is a proportional control unit by Heto-therm. The outer compartment is governed by an externally situated proportional control unit connected to the detector and heater, h . The control unit was designed and constructed within the department. The other two heaters aid the initial water heat-up. This control section is compactly constructed to produce a well-stirred, intimate contact between the water, heater and detector. The detector was initially a copper/constantan thermistor but this has now been replaced by one using platinum wires because of tendencies to drift over long periods. Water is taken into the section via a weir arrangement and returned to the main section via exit holes at the bottom.

Plan



S – Stirrer
H – Main heater
h – 'Hot-Rod' heater
T – Thermistor

Side View

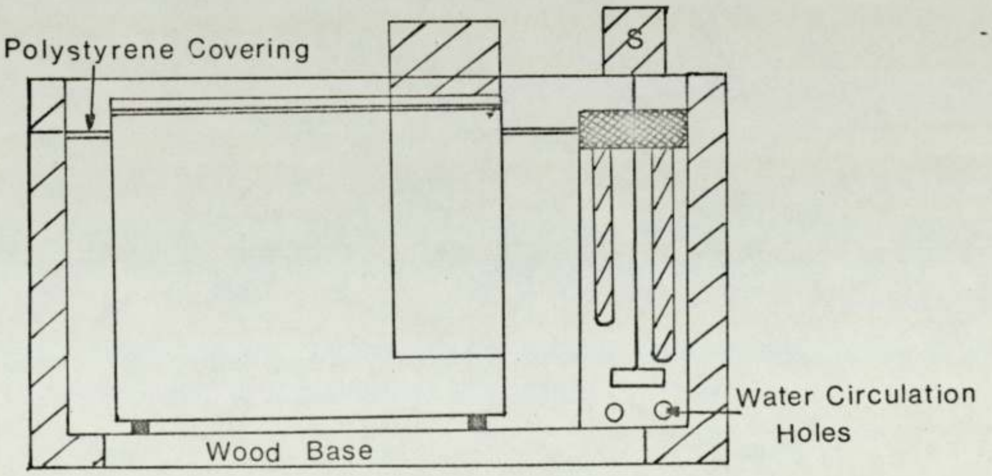


Figure 22

Thermostatic Control Bath

The outer compartment is surrounded by about 25 mm. thick insulation of 'Vermiculite' and is mounted on a wooden base. The bath is constructed of stainless steel with glass windows on the front of both compartments to permit the required measurements. The water surface is covered with polystyrene balls during operation to prevent heat loss through evaporation.

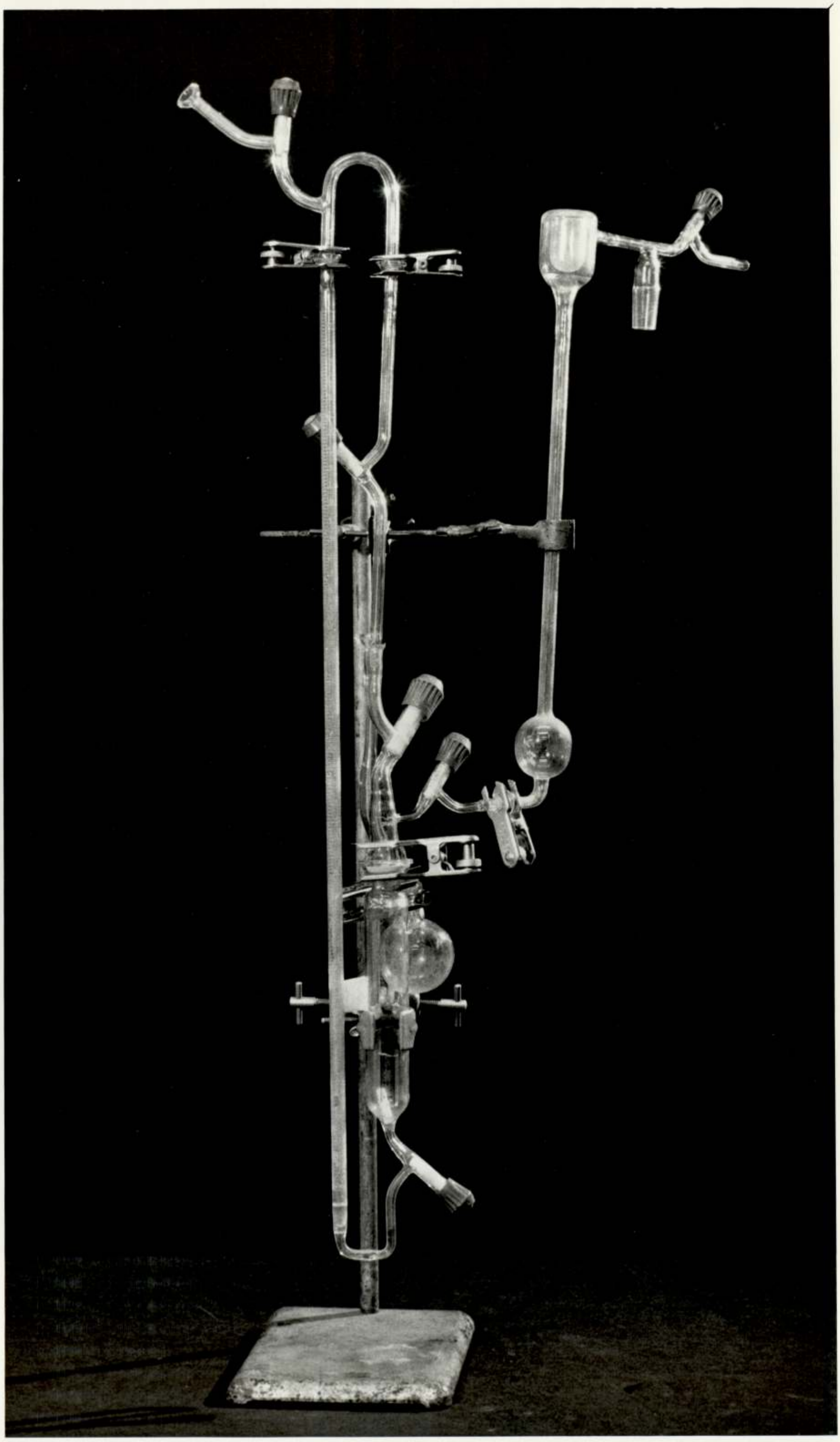
The bath has been tested satisfactorily at temperatures exceeding 70°C, though this was under ideal conditions, with no detectable temperature variance within the inner compartment. During operation, the outer compartment is maintained slightly below the controlled temperature to aid the performance of the inner unit.For operation at low and room temperatures a copper cooling coil can be incorporated in the exterior compartment if required.

The temperature was measured using a platinum resistance thermometer and a seven-dial inductively - coupled double-ratio bridge (see plate 1). The thermometer was calibrated by "The National Physics Laboratory"

5.3 Central Apparatus

This apparatus has previously been represented diagramatically on Figure 19 and is shown on plate 2 . The equilibrium cell was approximately 150mm. in length and 25mm. diameter. There are three connections to the cell, all constructed with the minimum deadspace practical. The bottom connection, to the class A water

Plate 2
Simple Rig



burette, formed the U-tube manometer arrangement. This link was constructed of capillary glass tubing to prevent any back diffusion from the cell mixture. Attached to the top of the water burette via a U-bend from the reservoir outlet was a reference bulb of approximately 50 mls. capacity. The reference bulb was sited adjacent to the cell to ensure the same temperature in both vessels. A second outlet and stopcock connected the bulb to the vacuum system.

The vacuum inlet to the cell was, in addition, the connection to the manometer employed to record the initial methanol addition. This connection should be as short as possible and constructed from glass to reduce adsorption errors (see Section 5.5). The connection was of reinforced p.v.c. tubing in this work. The manometric fluid, butyl phthalate, was added through stopcock 1 after evacuation of the manometer and then degassed in situ. The methanol inlet was situated at the top of the cell through a capillary stopcock from the reservoir.

The cell volume was calibrated against distance from an arbitary situated zero using degassed water. The calibration was performed with the equilibrium cell in the water bath and outside the water bath to eliminate any errors due to imperfections in the glass windows of the bath.

A magnetic stirrer was placed inside the cell to promote equilibrium of the cell mixture. The stirrer was motivated by an externally suspended magnet. The liquid level measurements in the cell and burette were taken with a high precision cathetometer with an accuracy to 0.01mm.

5.4 Vacuum System

The vacuum system, shown in Figure 23, can be considered in two halves, a 'high' vacuum side and a 'low' vacuum side. In the 'high' vacuum side an absolute pressure of less than 0.001mmHg was required to evacuate the equilibrium cell and manometer system. On the 'low' vacuum side, an absolute pressure of 2-3mmHg was considered sufficient for degassing of the components.

Each side of the system was served individually by an Edwards Rotary Vacuum Pump. The pumps could be joined in series if required by opening valve A. A cold trap was positioned immediately upstream of the pumps in each section to remove any condensables from the vapour entering the pumps. The traps normally contained 'liquid nitrogen', an alternative is a 'solid carbon dioxide/acetone' mixture.

The vacuum on the 'low' vacuum side was metered with a Macleod Gauge. Air inlets were positioned in both halves to allow rapid pressurisation if necessary.

5.5 Initial Preparation and Cleaning

The high degree of purity required and the supplementary effect of adsorption and/or desorption make the initial preparation and cleaning critical to the quality of the data.

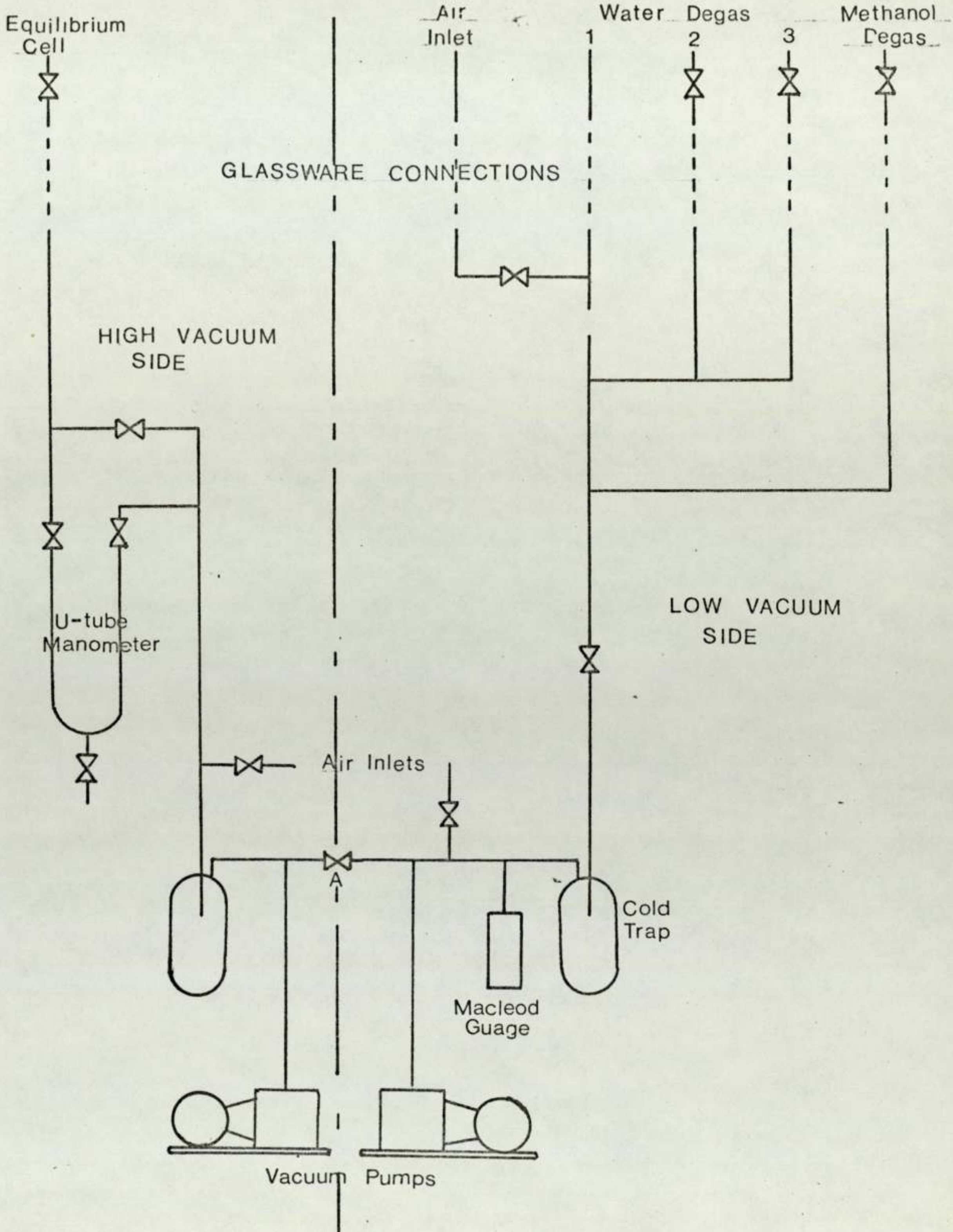


Figure 23
Vacuum System; Simple Rig

The possibility of adsorption being a major cause of error was realised from results obtained from initial runs performed on the apparatus. Results as high as 10 times greater than anticipated for the activity coefficients were obtained. A review of the relevant literature yielded no concise details on the quantitative or qualitative extent of adsorption of methanol or water on glass surfaces. Langmuir has stated that below the saturated vapour pressure no more than one monolayer should be formed but this is no longer considered the true case.

The data shown below of McHaffe and Lehner (96) for water on glass outlines the possible degree of adsorption.

TABLE: 1
Water adsorption on glass at 298°k.

Pressure mmHg	22.73	22.80	23.08	23.76
Number of layers present	51.8	56.1	88	184

The saturated vapour pressure of water at 298°k is 23.76. The data is plotted on Figure 24 and a tentative extrapolation yields that a mono-layer or less should be present at pressures less than 21.0mmHg. As, in this version of the technique, the maximum allowable initial pressure is much lower than this critical

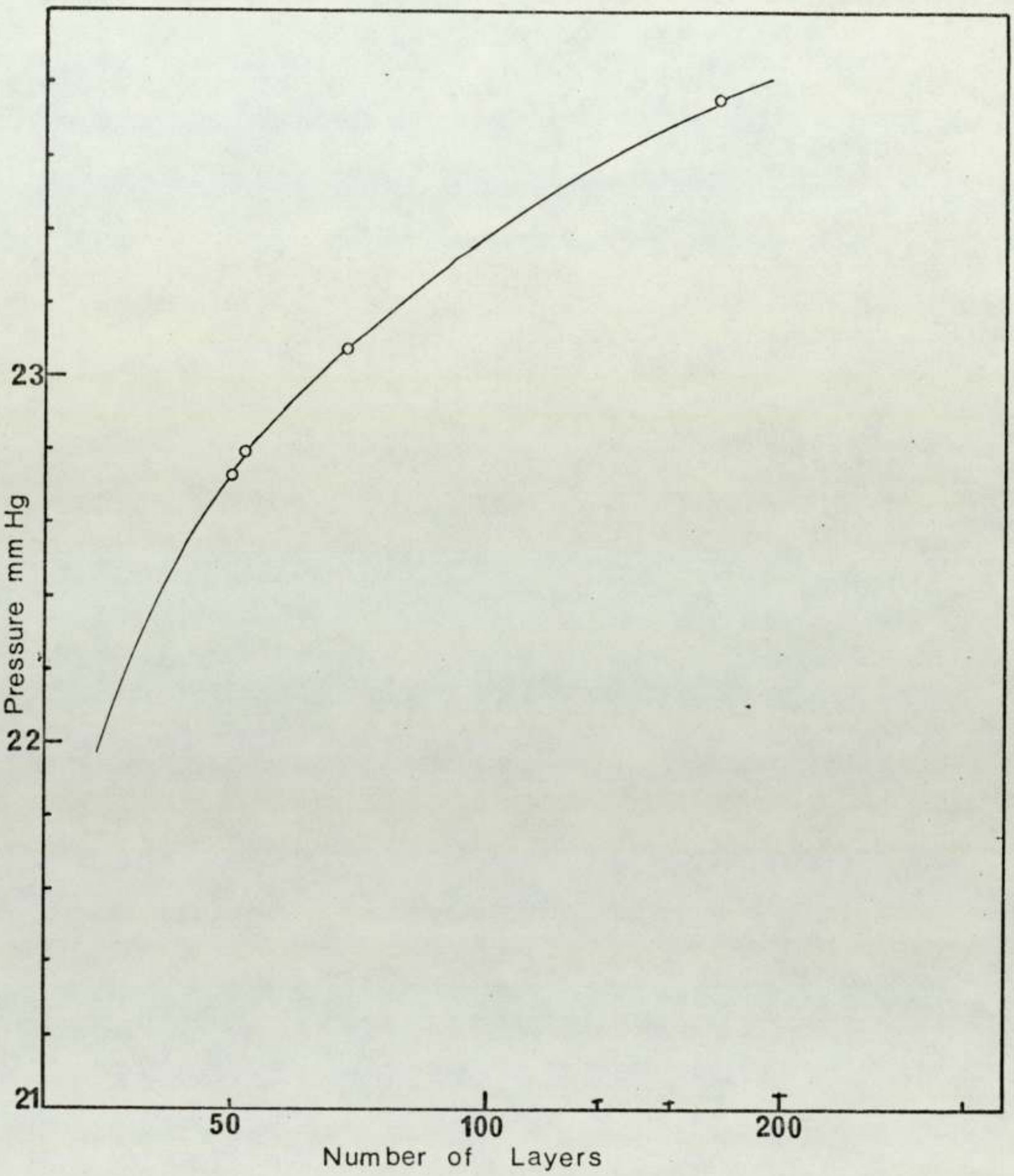


Figure 24
Adsorption Data

pressure, it was assumed that adsorption of methanol and ethanol on the glass surface was negligible.

Experiments were undertaken to substantiate the data shown but the accuracy required was found to be greater than that possible using the apparatus available. Qualitatively the experiments showed that adsorption on p.t.f.e. was considerably higher than on glass. P.T.F.E. surfaces were present on the stirrer and valves of the cell. Following the introduction of methanol vapour to a short length of previously evacuated p.t.f.e. tubing (ca 100mmHg) adsorption was still occuring after 30 minutes and that it's equilibrium pressure (approximately 25mmHg) would be attained after several short evacuations. This data showed the high error possible from the measurement of the initial methanol pressure as the cell to manometer connection was constructed of p.t.f.e. tubing. The data acquisition procedure attempts to allow for this effect, no immediate remedy being available with the present apparatus.

Improvements to eliminate adsorption are discussed in Section5.7 and further remedies attempted on the equilibrium cell of the main apparatus are discussed in Section 6.5.

The glass sections of the apparatus are cleaned using 'Decon' or boiling isopropanol vapour. Chromic acid is not considered suitable as it's etching effect on the glass surface could increase the number of sites available for adsorption.

The use of acetone is also unadvisable as it's complete removal requires high localised heating. Originally acetone was incorporated in the procedure with the glass dried at 70°C, however analysis using G-L chromatography showed traces still present.

The appropriate glassware is cleaned by immersion in the prescribed concentration of 'Decon' overnight followed by numerous flushings with copious amounts of freshly distilled water. The glass is finally dried in an oven at 70 - 80°C.

5.6 Data Acquisition Operation

The glassware is individually cleaned, as described in Section 5.5, before every run. The apparatus is constructed as previously illustrated with the utmost care taken to eliminate all traces of dust and grease. Each stopcock is adjusted, via an internal screw thread, until a continuous seal with the glass is visible. The cell and water burette must be parallel and vertical, a spirit level was used initially and a final check made with the cathetometer.

The cold traps are filled with liquid nitrogen to a level just below the downcomer tube. This level is stipulated to prevent water freezing in the downcomer tube, thus blocking the vacuum line. The apparatus is leak-tested until the vacuums indicated in Section 5.4 are attained. 'Sprayseal' is used to treat any small leaks at glass/tubing connections. This degassing procedure, especially in the vicinity of the equilibrium cell, includes the degassing of the p.t.f.e. valves by heating with an air blower while in situ. The cell and burette are considered adequately degassed when no pressure increase can be observed 1-hour after isolation from the vacuum pump.

On completion of this testing, the degassing of the two components is commenced. The required temperature in the thermostatted bath is attained and the unit checked for the required control.

On conclusion of the preliminary preparations the degassed water is run from the reservoir into both the burette and reference bulb. This is performed a little time before commencement of the actual run to allow the water to attain the operating temperature. If the burette water is at a higher temperature than the operating temperature, too much water will enter the cell initially, thus on cooling the cell mixture can be forced back into the burette. The level of water in the burette is recorded. This can be measured very accurately as degassed water on glass has a contact angle of approximately 90°.

A small methanol charge is then vapourised into the equilibrium cell and manometer system. This is allowed to reach equilibrium. The cell pressure is lowered to that required by opening the cell for short periods to the vacuum line and allowing equilibrium to be obtained. Depending on the materials connecting the cell and manometer, equilibrium can take 30 minutes to obtain.

The pressure which must be lower than the pressure head in the water burette is recorded.

The cell is closed from the manometer and the bottom valve opened. Water enters the cell until the pressures are equalised. The cell mixture is stirred until equilibrium is obtained. The time required varies between 5 - 30 minutes depending on the quantities present and the rate of stirring. Equilibrium is normally considered to have been reached when the burette water level remains constant. Stirring is performed by moving the internal agitator with an externally controlled magnet suspended in the bath. At equilibrium, measurements are taken of the liquid height in the cell and the burette water level using the cathetometer and the water reading recorded. The arbitary zero mark is also measured.

The bottom cell valve is then closed and additional water allowed into the burette from the reservoir. The above procedure is repeated, with the zero mark being read after each cell reading.

The run is concluded when the cell is completely filled with liquid or the pressure difference between the cell and burette is less than the experimental error.

The complete procedure required two days, one day being necessary to clean and prepare the apparatus. The period from start of the degassing of the components to the conclusion of the run was approximately 8 hours.

5.7 Results and Performance of Apparatus

The difficulty in assessing the performance of the apparatus at the time of the testing was the lack of data available for comparison. Runs were undertaken until modifications to the acquisition produced results which were considered realistic from the expected theory and Dalagers results.

When data from the main apparatus became available, these results were shown to be erroneous. The results for the methanol-water system at 25°C.are tabulated below.

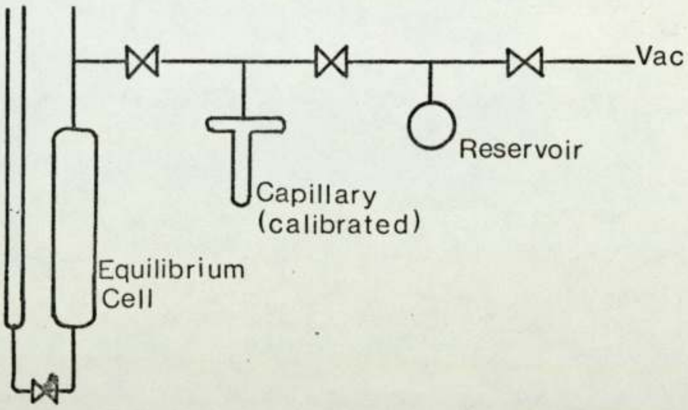
Table: 2

Mole Fraction Methanol		K-Value	Activity Coefficient
Liquid	Vapour		
0.000479	0.0221	46.1	9.00
0.000475	0.0221	46.5	9.09
0.000324	0.0113	34.9	6.75

Values predicted from Main apparatus K = 5.5

Activity Coefficient = 1.3.

The disagreement results from the problem discussed earlier in the measuring of the initial amount of methanol charged to the equilibrium cell. The obvious modification is to replace all the plastic tubing with glass. A better and more accurate alternative is shown overleaf.



The steps in the method are;

(a) Evacuate cell and methanol measurer

(b) Distil required amount of methanol into the calibrated capillary

(c) Admit water into equilibrium cell

(d) Allow all the methanol to evaporate into the cell

(e) Carry out the run with necessary additions of water

The other major difficulty with the apparatus was in the operation of the valves in general, and in particular, the valve situated at the bottom of the equilibrium cell. For manual operation this valve requires operation whilst situated within the water bath. For many reasons this is obviously undesirable. Attempts were made to construct a linkage exterior to the bath to operate this valve. These were unsuccessful because the 'rotaflo' valves were unsuitable. To sustain an airtight fit the valves require tightening to an extent which makes operation precarious with the fragile nature of the glassware. This difficulty can now be eliminated by replacing the valves with glass-body O-ring valves described in Section 6.4 Linkage to operate the valves in an open/shut mode is now straight-forward.

Testing of the modified apparatus has not been completed in the duration of this work.

One run using the apparatus will produce a maximum of approx. 6 data points, 3 being the normal. The number of data sets is limited because of the small pressure head produced between the water burette and equilibrium cell. This is satisfactory as it will be shown later that activity coefficients and K-valves are constant in the concentration region under investigation with this apparatus.

6.0 MAIN RIG: DETAILED DEVELOPMENT AND DESCRIPTION

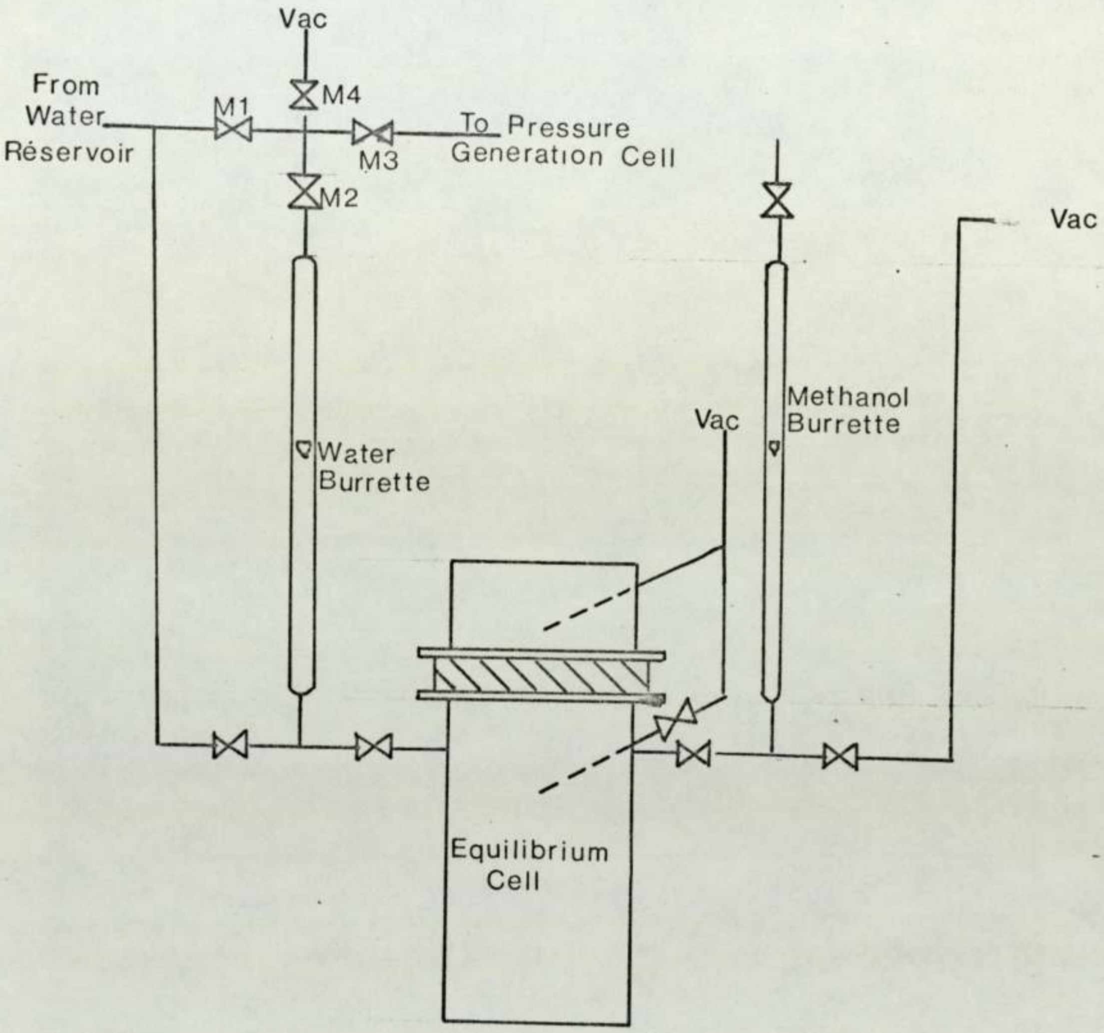
A substantial part of the peripheral apparatus of the simple rig is complementary to the main rig and thus will require no further detailing. These are the glassware and cleaning considerations, degassing of the components, temperature control bath and temperature measurement. The temperature control bath dimensions were altered to be compatible with the central apparatus.

An outline of the central section is shown in figure 25. The two degassed components are introduced via the two side connections to the cell. The diaphragm is positioned across the top of the cell.

6.1 Pressure Measurement and Control Development

The accuracy and control of the pressure apparatus is limited by the performance of the transducer system. As stated previously the cell pressure is transmitted to a transducer via a diaphragm situated on the top of the cell. The bourdon pressure gauge provides an equalising pressure to the opposite side of the diaphragm. Since the transducer is, in effect, being used as a null detector the assembly must have the attributes of both the required sensitivity and reproducibility of the null position.

An exhaustive review of all the commercially available transducer systems produced none with the required characteristics.



NOT TO SCALE

Figure 25

Central Apparatus – Main Rig.

The majority of commercial transducers are developed to detect the movement of two opposing plates from a central position.

The transducer obtained was a Linear Variable Differential Transducer (L.V.D.T.). This is shown on plate 3 and illustrated in figure 26. The L.V.D.T. is an electro-mechanical transducer which produces an electrical output proportional to the displacement of a separate moveable core. The transducer consists of three coils equally spaced on a cylindrical coil form. A rod-shaped magnetic core positioned axially inside this coil assembly provides a path for the magnetic flux linking the coils. When the primary coil (centre coil) is energised with alternating current (normally 5 volts r.m.s.), voltages are induced in the two outer coils. These two secondary coils are connected in series opposition so that the two voltages in the secondary circuit are opposite in phase, the net output of the transformer being the difference of the voltages. To cope with the required conditions of high temperature in a vacuum a specially designed case was developed.

Incorporated with the L.V.D.T. was a single channel carrier amplifier (Electro mechanisms type CAS 2500Z , see plate 3). This provided the 2500 H_z excitation to the transducer, signal amplification and gain control.

The arrangement of the transducer in the pressure system and the transducer mounting are shown in figure 27 (see also plate 3).

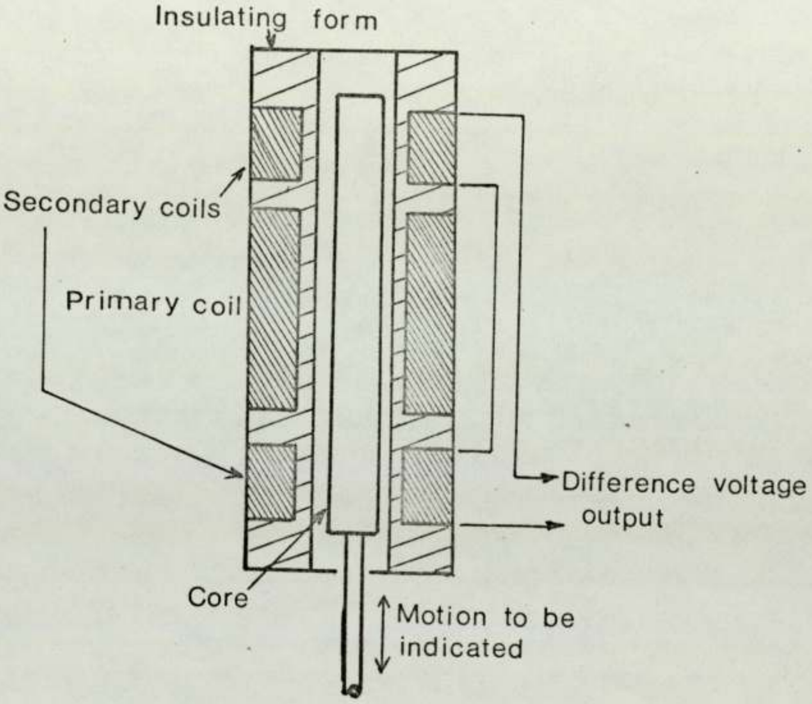


Figure 26

Operation of LVDT

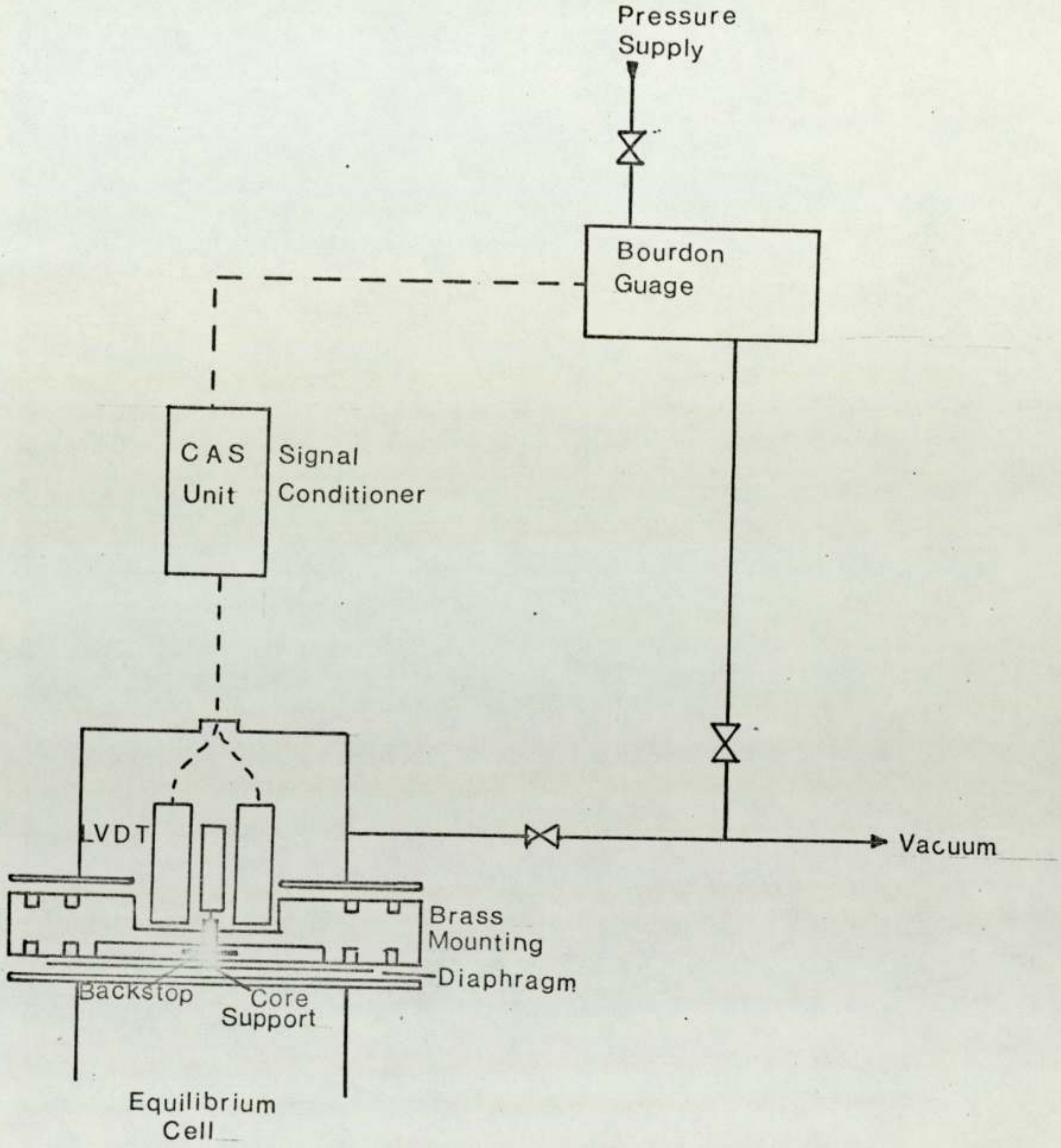
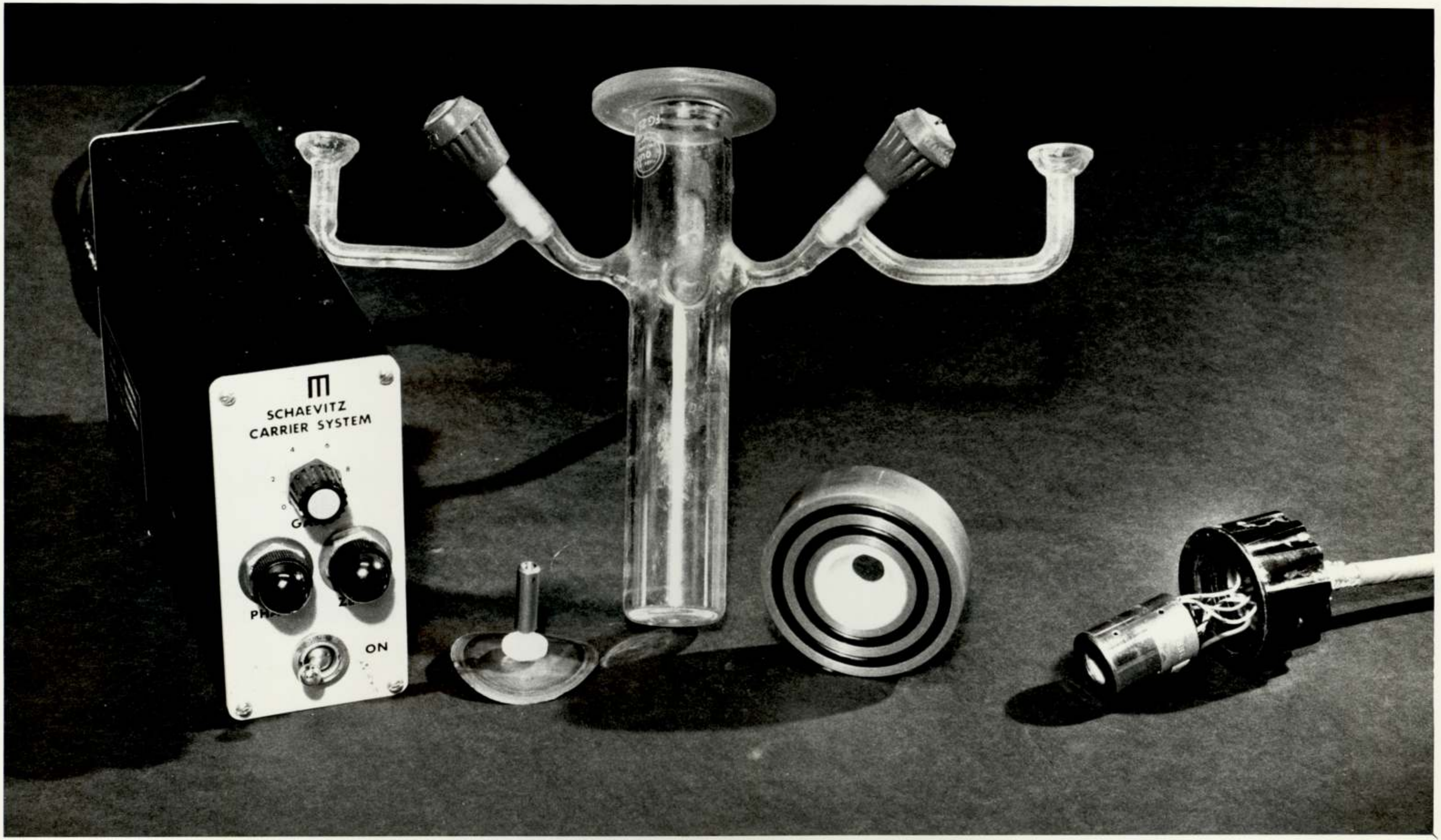


Figure 27
Pressure System & Transducer Mounting

Plate 3


SCHAEVITZ
CARRIER SYSTEM
0
2
4
6
8
GA
PHA
ZE
ON

The mounting block was made of brass with an inner central core of P.T.F.E. as a precaution against any electrical side effects. To overcome a troublesome difficulty in sealing, two O-rings are used in the mounting. The outer O-ring seals the cell from the atmosphere and the inner O-ring positioned on the diaphragm produces a seal between the diaphragm and glass cell. A moveable ring is incorporated on the P.T.F.E. core support to act as a backstop, i.e. to prevent any damage to the diaphragm by over-stretching the material.

The electrical connections through the top of the cell were made using a small brass plate. Into this plate were inserted gold connecting rods in a P.T.F.E. casing and the wires were soldered using gold connections either side of the rods. The plate was pinched between two flat rubber rings and connected to the cell by a screw connection. Complete sealing was finally obtained using a liberal coating of 'Sprayseal'.

The performance of the pressure apparatus is primarily dependent on the characteristics of the diaphragm. The diaphragm material must be resistant to any corrosive materials, sensitive enough to provide a detectable movement but sufficient rigidity to reproduce the null position.

From the earlier work of Jenkins (3) tantalum was the material initially selected.

A literature review yielded limited information on the dependence of the sensitivity of the diaphragm to the thickness of the material. The two correlations found were by Wildhack and Georke (97).

$$\frac{Fx}{PQ} = 2.25 \times 10^{5} \left({}^{t}/d \times 10^{3} \right) \qquad 6.1$$

where F = modulus of elasticity
P = pressure
x = deflection
D = diaphragm diameter
t = thickness

and (98)

$$x = \frac{3}{16} P \frac{(1 - k^{2})}{F t^{3}} R^{4} \left(1 - \left({}^{r}/_{R}\right)^{2}\right)^{2} \qquad 6.2$$

k = Poisson's Ratio
R = diaphragm radius
r = distance from centre of diaphragm

Cursory comparison shows a discrepancy between the two equations in the inverse power of the diaphragm thickness. Equation 6.1 quotes a power of 1.52 and equation 6.2 a power of 3.

From this information it was considered appropriate to undertake a series of comparative tests using initially diaphragms of thickness 0.025 , 0.05 and 0.01mm.

The apparatus used for these tests is shown in figure 28.

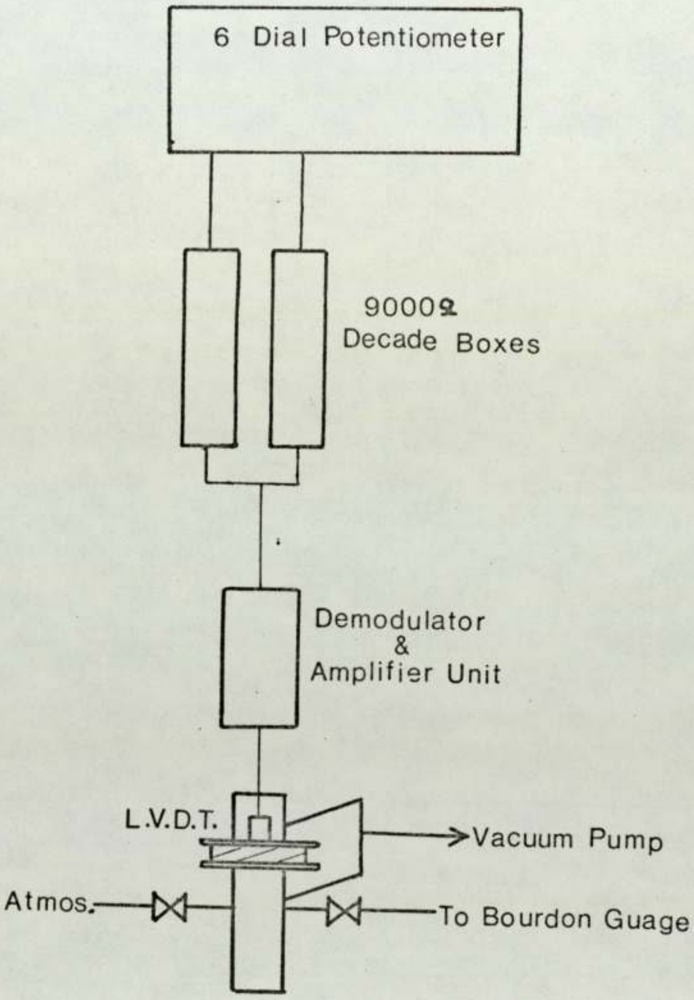


Figure 28

Diaphragm Testing Apparatus

The characteristics tested were sensitivity and ability to reproduce null. The L.V.D.T. was set to maximum gain for each diaphragm and the core positioned to give no voltage output when the bourdon gauge was reading zero pressure. The required output to drive the servo-mechanism of the bourdon gauge is 20 microvolts.

Results are given in Appendix 5 . Table 3 and figure 29 show the data obtained for diaphragm thickness against voltage output, hence sensitivity.

Table 3

Diaphragm thickness	Voltage output for pressure difference of 0.01mmHg microvolts
0.00254	180
0.00508	8
0.01016	0.33

(voltages taken by assuming straight line relationship initially).

The gradient corresponds to the sensitivity being proportional to $t^{4.0}$, a result markedly different from both the literature values. No logical reason can be suggested for this discrepancy.

Figure 30 shows the pressure voltage graph for the 0.005mm thick diaphragm. This curve is representative of the data obtained.

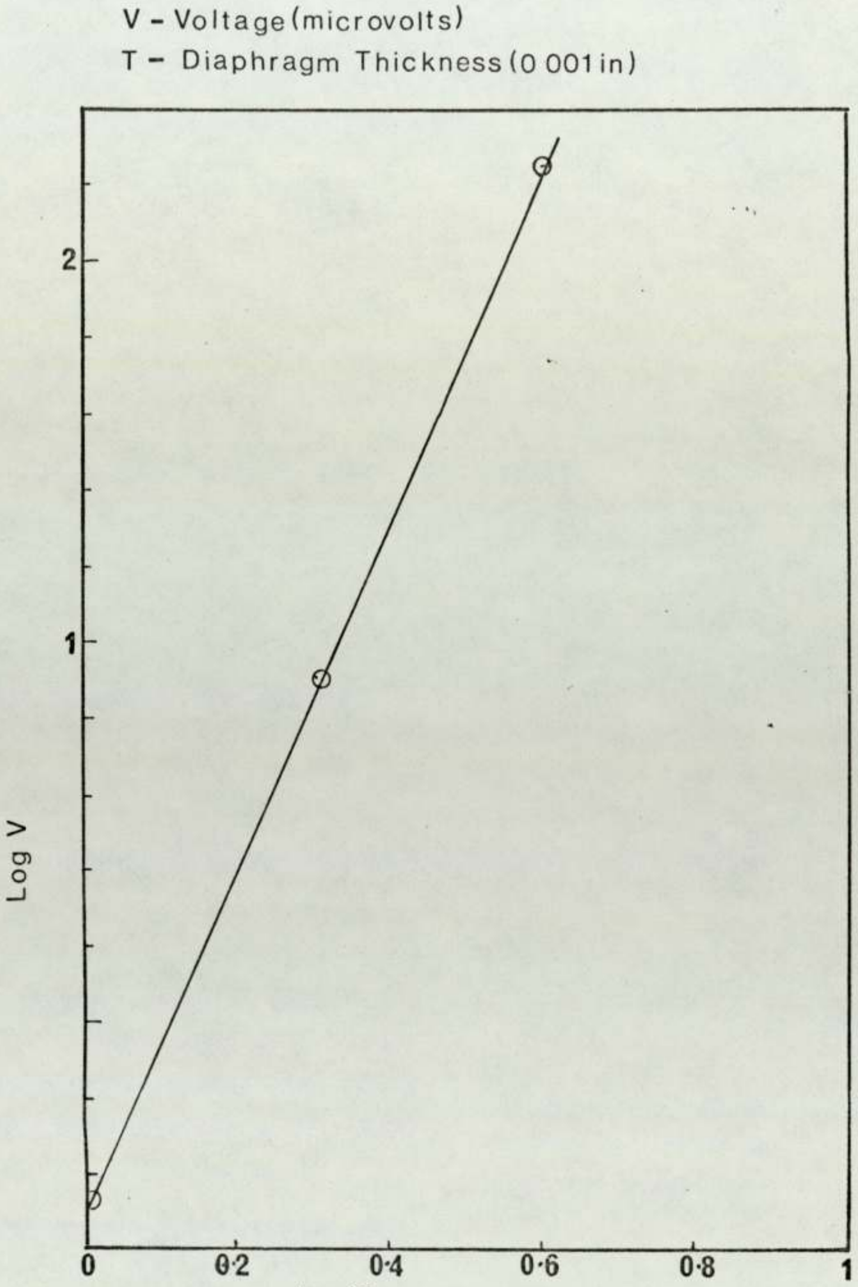
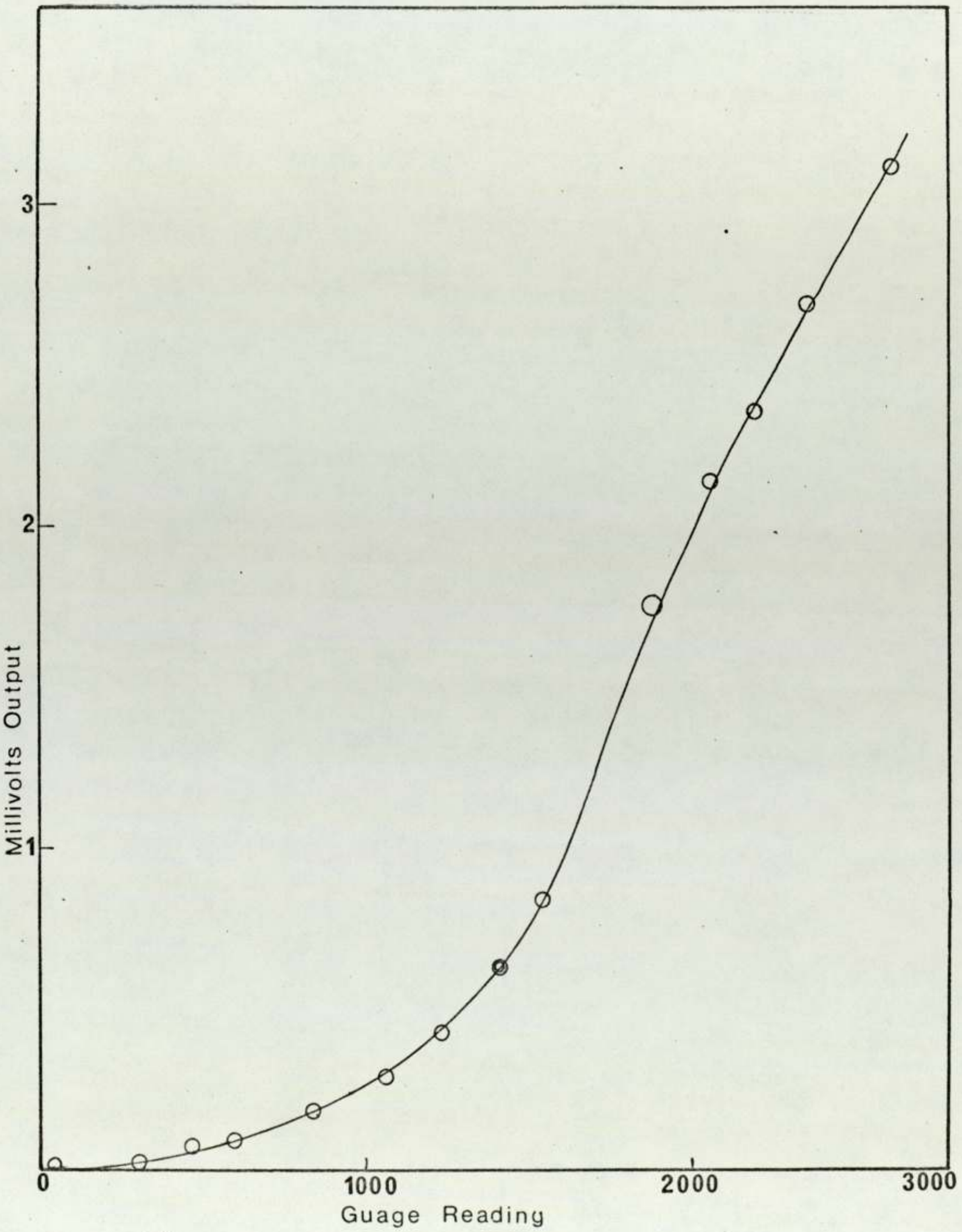


Figure 29

Results from Diaphragm Sensitivity Tests

Figure **30**

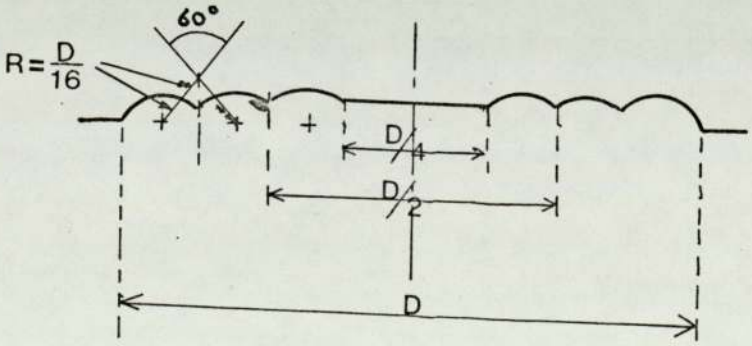
Results for 0·05mm Diaphragm



For later reference it should be noted how the sensitivity increases within the proximity of the central position.

The results indicated that a maximum thickness of 0.00254mm was allowable. Tests on reproducibility of zero however, demonstrated that this thickness would be unreliable, an error of 0.06mmHg being the most favourable result. To improve the reproducibility characteristics tests were undertaken using corrugated diaphragms of various designs. This improves the reproducibility properties but at a detriment to the sensitivity as the 'active' diameter is in effect, decreased.

The designs tested varied from one simple corrugation to that shown in figure 31 which is the design suggested by Wildhack and Georke.



The modifications were unproductive and therefore tantalum was discarded. An alternative material, an alloy of Copper/Berylium, was tested. This material was found to be more sensitive than tantalum in addition to having excellent reproducibility properties. Using the corrugation design of figure 31 (this was principally as an extra safeguard), a thickness of 0.005mm was suitable. Modifications to the L.V.D.T. mainly in the form of improved wiring connections, were also made to improve it's performance.

As illustrated in figure 27 the bourdon pressure gauge was being utilised to both provide and record the equalising pressure. The bourdon gauge on purchase is only capable of functioning in these two modes independently and therefore a re-adjustment of the internal circuitry of the instrument was undertaken. This is detailed in Appendix 4 . The work proved to be more drastic and troublesome than originally anticipated and together with delays in obtaining appropriate parts was threatening to prevent the acquisition of any data within the duration of the project. An alternative system was therefore sought.

It was noted earlier with reference to figure 30 that the voltage output from the L.V.D.T. increases markedly around it's central, stable position. This phenomenon was found to be more pronounced with the Cu-Be diaphragms due partly to it's greater sensitivity and partly to the increased ability to retain it's original state. Experiments showed that this peak could be reproduced within ± 0.02mmHg withadegree of confidence of approx. 95%. This technique was therefore temporarily adopted to obtain exploratory data from the main rig.

This pressure measurement technique is in effect a differential method as it measures a pressure difference from a datum. The datum is the saturated vapour pressure of the initial pure component which can be accurately ascertained from the temperature recordings. The diaphragms employed were of 0.0025mm thickness and corrugated to the design of figure 31 using a rapid press technique.

6.1.1. Alternative Pressure Measurement Technique

During the testing of the pressure apparatus and the actual experiments undertaken on the rig, difficulties continually arose because of instabilities created by enviromental effects on the electrical circuitry. The voltage output being critical in the range of 10^{-5}volts, proved sensitive to changes in noise levels and even positional effects within the laboratory. Extensive earthing and treating of connections could not fully curtail these effects. (It has since been noted by other workers that standard laboratory electrical equipment occasionally behaves uncharacteristically in the vicinity of the apparatus).

For future use, an alternative method was sought, which would eliminate the problems inherent in the L.V.D.T. method. A possible alternative tested has been to apply an optical approach by reflecting a beam of light from the top surface of the diaphragm. The technique can be described using figure 32.

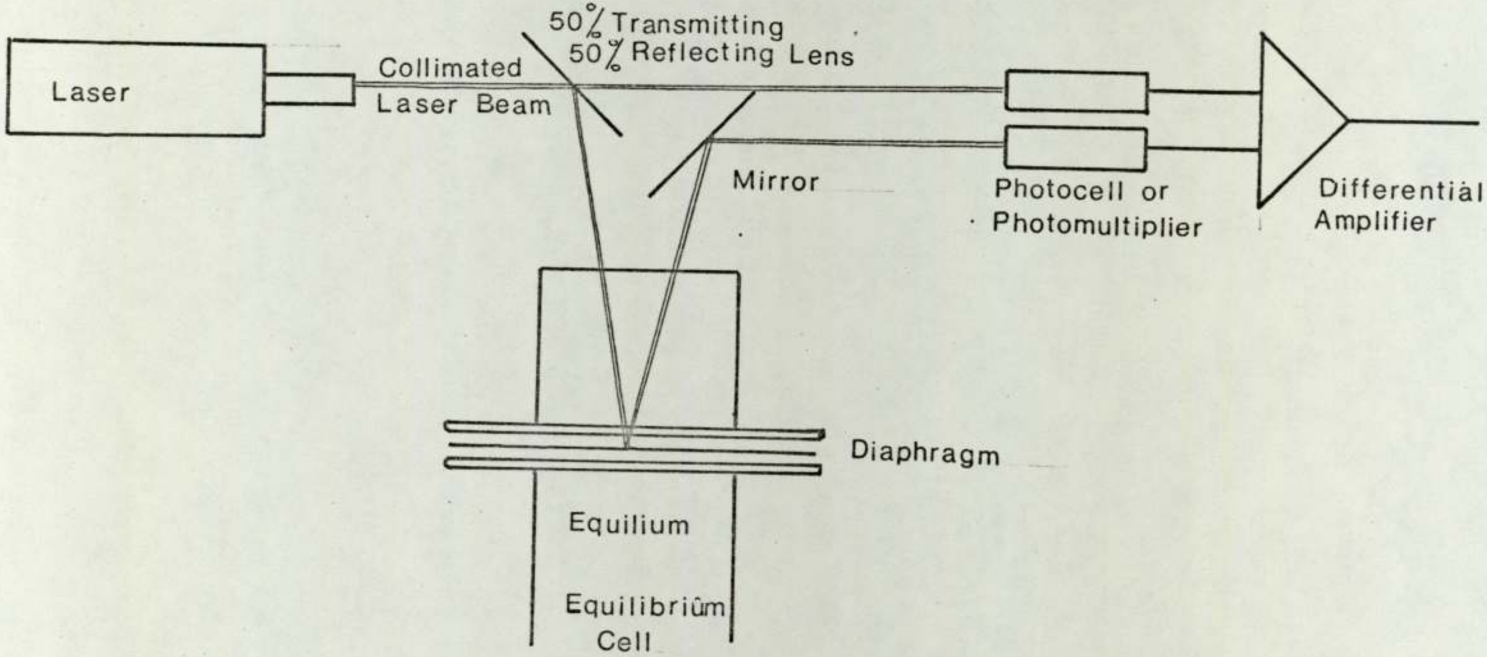


Figure 32

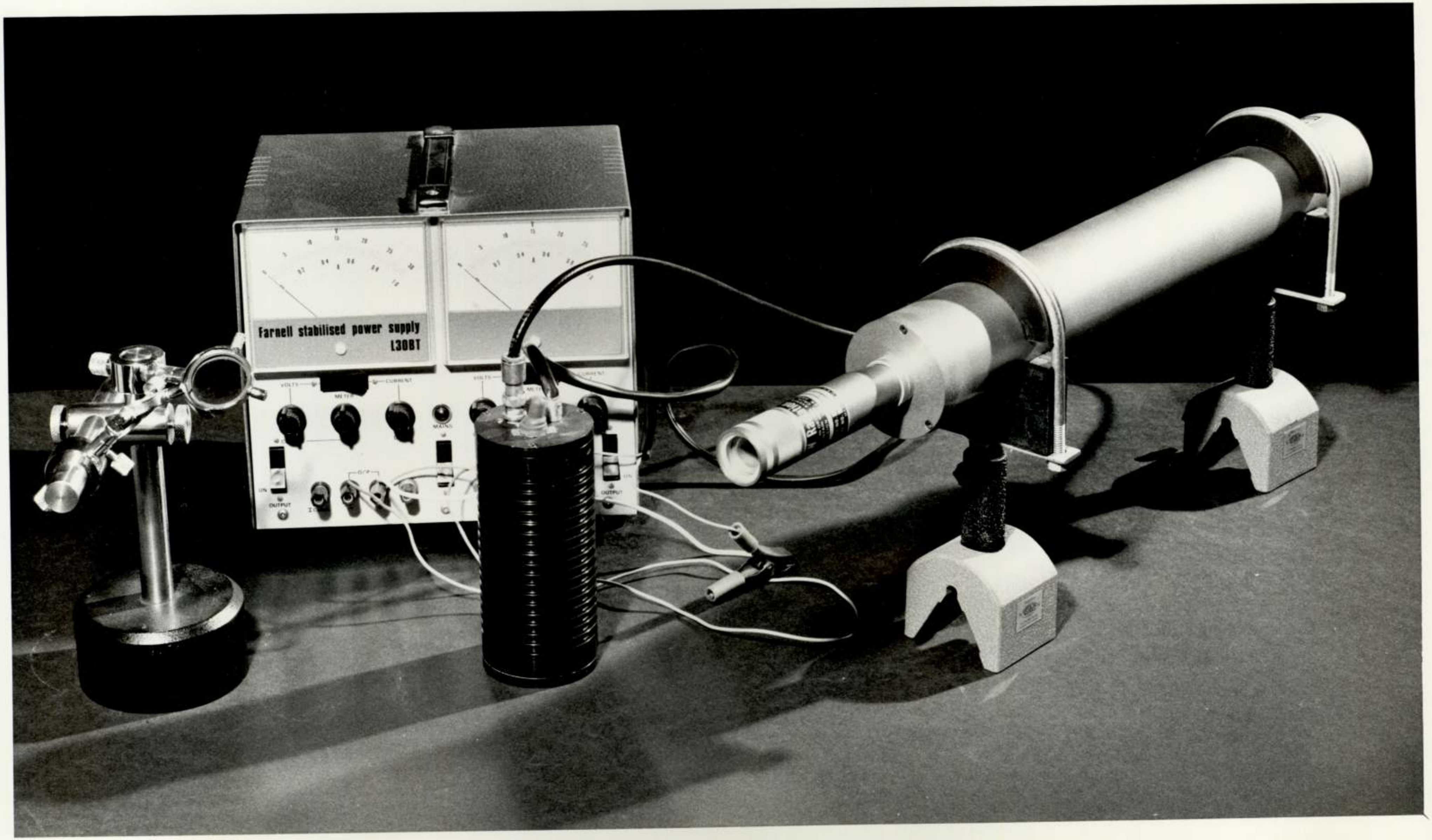
Outline of Alternative Pressure Measurement Apparatus

The beam of light from the laser passes initially to a 60% transmitting / 40% reflecting mirror. The transmitted section passes to the first photocell. The reflected half of the beam is directed onto the centre of the diaphragm and then onto a second photocell using mirrors. When the diaphragm position alters with change in the equilibrium cell pressure, the quantity of light directed onto the second photocell is reduced. There are two alternative ways of creating this effect. With a normal flat diaphragm as the cell pressure increases, the diaphragm becomes more convex to the light beam. This diffuses the beam over a wider area thus reducing the intensity of light on the photocell. Alternatively a corrugated diaphragm can be employed so that the active area of the diaphragm moves vertically. This directs the beam off the face of the photocell. The voltage difference created between the two photocells can be measured and/or transmitted to the bourdon gauge, an equalising pressure can then be applied.

This technique eliminates the troubles caused by having electrical connections through and around the equilibrium cell. The electronics can be housed together a suitable distance from the main apparatus.

The light souce in the test rig was a C - W Radiation helium neon laser (see plate 4). The photo-electric cells were of ordinary manufacture. Diaphragms of tantalum were initially tried, tantalum having a coefficient of reflectivity of 0.9 This material however was later rejected as imperfections in it's surface, probably resulting from the manufacturing process, prevented a clearly defined reflected beam being produced.

Plate 4


Farnell stabilised power supply
L30BT
VOLTS
METER
CURRENT
MAINS
ON
OUTPUT
O/P

Tests were conducted on diaphragms of copper/berylium with thicknesses of 0.025mm and 0.05mm. The results are shown graphically on Figure 33. The sensitivities achieved were a resistance change of approximately 24 ohms for the 0.025mm diaphragm and 1.1 ohms for the 0.05mm diaphragm. These were for a pressure change of 0.01mmHg and were calculated by averaging the resistance change over a pressure change from 0 to 5mmHg.

The shape of the curves is not purely a characteristic of sensitivity against pressure change because a circular beam is moving away from a circular surface. The quantity of light directed off the photocell for a certain diaphragm movement will increase over it's first half circle.

These results are greatly superior to those of the L.V.D.T. and the method eliminates the difficulties inherent with the L.V.D.T. approach. The electronic circuitry to drive the bourdon gauge servomotors is straightforward. The sensitivity can be further enhanced by increasing the angle of incidence and thus the angle of reflection.

6.2. Central Apparatus

The apparatus has been previously outlined in Figure 25. The two burettes were of 10ml. 'floating piston' manufacture. These have a small piston inserted within the burette on which is embossed a vernier scale. This vernier accords an accuracy one place greater than a normal burette. The piston also provides greater accuracy due to the elimination of liquid wetting on the walls of the burette. The burettes are bottom fed.

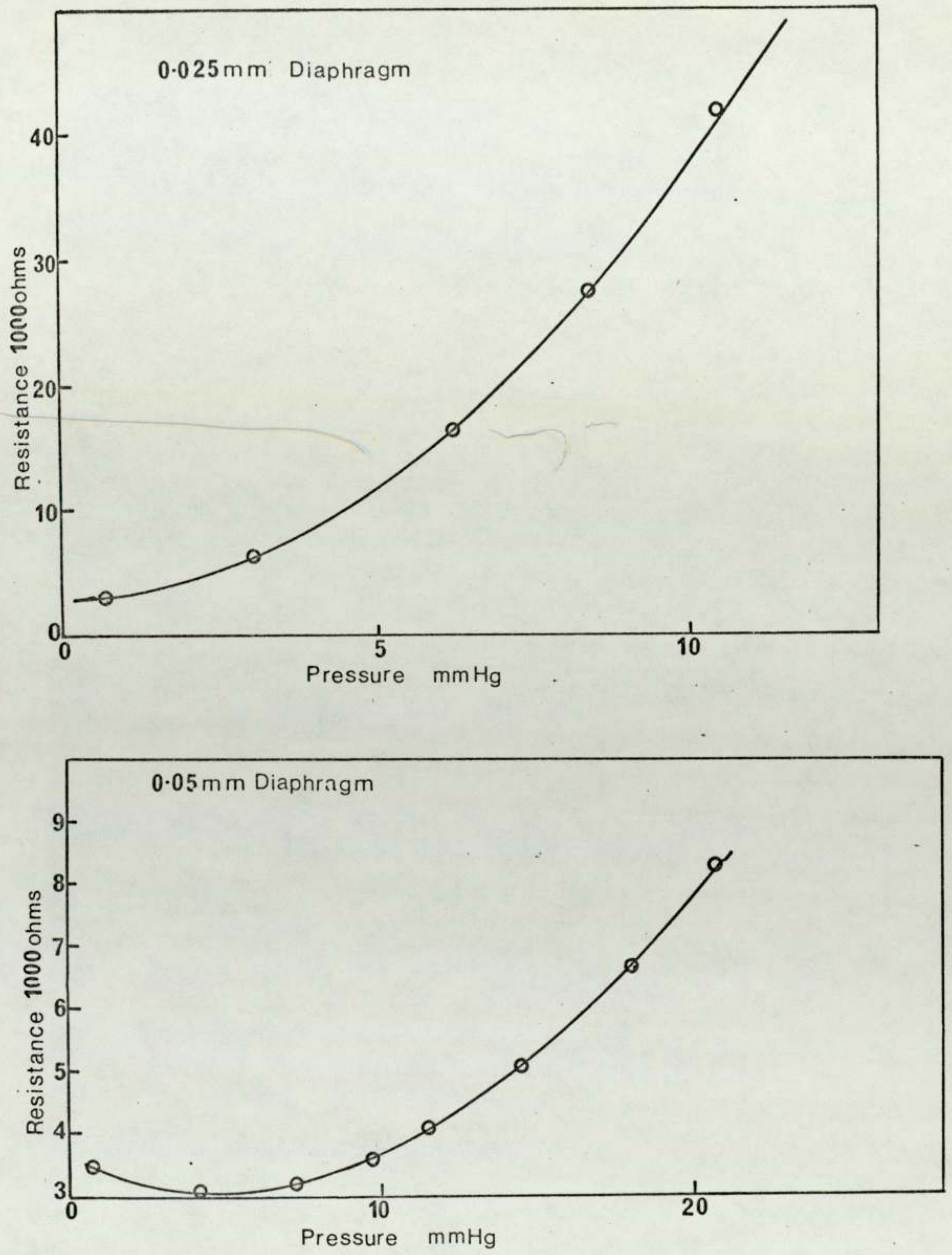


Figure 33
Results from Preliminary Testing of Optical Transducer

'Rotaflo' valves of 3mm bore were used in the central apparatus for all connections except for the equilibrium cell inlets which were of capillery size. The external pressure generation cell was a 100 ml. flask containing degassed water. When the equilibrium cell pressure exceeded the pressure of the head of water within the burette, the degassed water within the flask was heated to a temperature sufficient for the saturated vapour pressure to exceed the cell pressure. (Any condensed water can be vacuumed off through valves M2 and M4). A supply of an inert gas could be substituted in this method, provided the gas is removed through the vacuum system as soon as the addition is completed.

The cell is of approximately the same internal dimensions as that of the simple rig, these not being critical to the method. The stems between the cell and valve pockets are constructed to the minimum length to decrease the dead space. The two inlets for the components were positioned diametrically opposite in the apparatus; this is now thought unadvisable as water occasionally became trapped in the dead space of the methanol inlet arm. The connections were also placed near the top of the cell as this was initially considered desirable because the accuracy in measuring the liquid level in the cell would be impaired by the sidearms. This point is discussed in Section 6.4 where it is now considered desirable to have the sidearms at the lower levels.

The cell was calibrated as outlined in Section 5.3 and the cathetometer again used to measure the cell liquid levels. A magnetic stirrer was inserted to promote equilibrium. The stirrer was activated by an electrical agitator positioned underneath the cell. This can be seen on plate 1.

6.3 Vacuum System

The vacuum system is shown in figure 34. Many of the features of the simple rig were incorporated. The system as before is split into a high vacuum side (pressure $<$ 0.001mmHg) for the cell vacuum and a low vacuum side (pressure approximately 3mmHg) for the degassing apparatus.

In the diagram, the burettes appear on the low vacuum side. However they are initially evacuated to the high vacuum requirements by isolating them from the low vacuum side. This is achieved by opening the cell connections and closing valves M5, M4, M9 and M7. After the burettes have been charged with the degassed liquids they are reconnected to the low vacuum side for any further degassing. Each side is served individually by an Edwards Rotary Vacuum pump. These could be coupled together if required.

A Whatman filter was positioned at the air inlet to the bourdon gauge to prevent any harmful particles entering the sensitive bourdon tube. The other apparatus is detailed in Section 5.4.

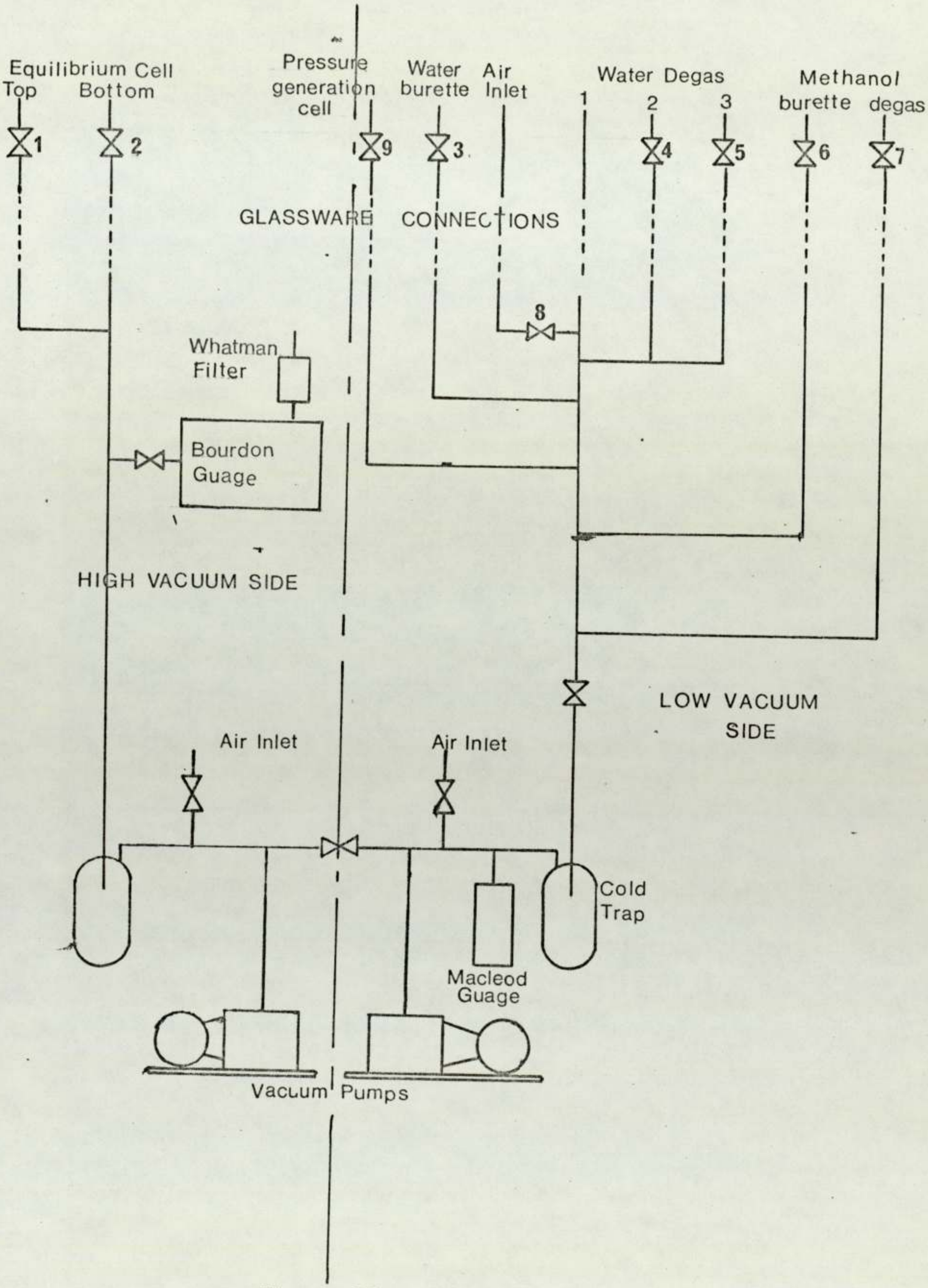


Figure 34
Vacuum System; Main Rig

6.3. Data Acquisition Operation

The glassware is individually cleaned using the method described in Section 5.5. before every run. The glassware is pieced together and the stopcocks adjusted ensuring that no grease or dust enters the apparatus. The diaphragm is positioned across the cell with the L.V.D.T. core located to give a minimal voltage output at it's central position. The backstop on the core support is adjusted to prevent overstretching of the diaphragm. The equilibrium cell is placed vertically and checked using the cathetometer in the water bath.

The two sections of the water bath are filled so that the level of the interior chamber is sufficient to completely immerse the equilibrium cell below the diaphragm. The cold traps are filled with liquid nitrogen as described in Section 5.6 and the valves degassed prior to leak testing the equipment.

When the equipment is functional the two components are degassed (Section 5.1) and the required system temperature obtained within the water bath (Section 5.2).

On completion of the degassing, water is charged from the reservoir to both the burette, via valve M5, and to the pressure generation cell. Water is allowed to enter the burette from the top in order to completely immerse the piston within the burette. Methanol is also charged to the appropriate burette. Checks are made at this stage for any signs of air within the components and if required further degassing undertaken.

Before commencing the data acquisition, the pressure measurement apparatus is checked to be functioning correctly and the initial voltage from the L.V.D.T. recorded using a D.C. microvoltmeter. A measured amount of methanol is then introduced into the equilibrium cell, and allowed to acquire the system temperature; this is assumed to have occurred when the voltage output is steady. Temperature stabilisation was normally found to require several minutes although voltage reductions could also have been taking place due to adsorption of the methanol on the p.t.f.e. of the valves. When the voltage is steady, an equalising pressure is supplied to the top of the diaphragm using the servo control of the bourdon gauge. The equalising pressure is obtained when the voltage from the L.V.D.T. changes rapidly for a small pressure input as detailed in Section 6.1. This equalising pressure is recorded.

After ensuring that the head in the water burette is greater than the pressure within the equilibrium cell, a measured quantity of water is passed into the cell. If the water pressure head is insufficient, the degassed water in the pressure generation cell is heated until it's saturated vapour pressure is adequate. The equilibrium cell mixture is stirred vigorously for between 5 to 10 minutes to promote equilibrium. The stirring times will be discussed later. When it is assumed that equilibrium has been reached, an equalising pressure is applied to the top of the diaphragm as before and recorded. The water bath temperature is also checked at this stage and any changes noted.

The procedure is then repeated with another water charge until the cell is full. Usually between 20 to 30 readings were taken in any one run. A complete run usually took two days, the initial preparation of the apparatus being performed in one day with the actual data acquisition taking around 8 - 10 hours minimum.

6.4 Practical Problems During Data Acquisition and Suggestions for Improvement of the Apparatus

During the data acquisition runs, numerous unforeseen difficulties arose. A problem that occurred during every run and was not satisfactorily solved, was the formation of globules of the mixture on the walls of the equilibrium cell. These originated from two sources, the initial introduction of the water and from the stirring action. The stirring source was decreased as experience in the use of the stirrer was obtained; a judicial control of the input to the magnetic stirrer creates a deep vortex without splashing. The creation of a vortex was used to remove as much of the globules from the walls as possible. These globules produce inaccuracies in both the measurement of the liquid level in the cell and in the total pressure, as the composition of the globules will differ from the bulk composition.

The possibility of coating the walls with a non-wetting agent was investigated but the problem of adsorption on the coating is always prevalent. The obvious way to overcome the difficulty when introducing the degassed water is to have the two sidearms near the bottom of the cell. This is now considered to be advantageous.

A further problem that arose initially during data acquisition was the tendency for the mixture to condense on the bottom of the diaphragm. This creates a possible error in the measurement of the cell mixture level and could alter the characteristics of the diaphragm due to the extra weight. This difficulty was solved by either immersing the equilibrium cell to a depth well below that of the diaphragm or by use of a hot-air heater on the top section of the cell.

At the conclusion of a run air was thought to be present in the cell, even with all the precautions described within the procedure. This is corroborated by the results. It has been concluded after various tests that the main source of this air is from the 'Rotaflo' valves. Over a long period of time air will diffuse through the p.t.f.e. valves. The 'Rotaflo' valves have proved unsatisfactory in other aspects. The stopcocks operate with only one seal between the p.t.f.e. seat and the glass walls. Over a long period of time under constant operation it was often found that dust would become trapped in the chamber. This would then prevent a continous seal being formed. In addition, to create an adequate seal, the valves required tightening to an extent that operating the valves required considerable force. With the fragility of the glassware and the positioning of certain valves this often lead to breakages.

It is suggested that in future apparatus these valves are replaced by J. Young O-ring valves (see figure 35). These valves

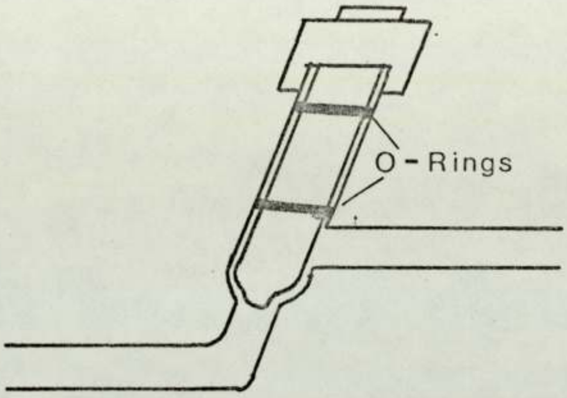


Figure 35
O-Ring Valve

are manufactured with a glass body and two thin O-rings. The use of glass almost eliminates errors attributable to adsorportion, and to diffusion of air through the valves. The use of the two O-rings eliminates the probability of any dust preventing an effective seal. The valves have been provisionally tested and found to be very light and easy to operate.

The pressure technique was not entirely satisfactory. At low temperatures especially, and when the total pressure within the equilibrium cell was low, the 'peak' was often difficult to locate with any accuracy. As the technique was only adopted as a temporary measure, no discussion of this is considered relevant to the improvement of the technique.

7.0 Discussion of Results.

7.1 Previous Experimental Work.

The data obtained in this work cannot be tested for thermodynamic consistency because the Gibbs-Duhen equation is employed in the calculational technique. The performance of the apparatus therefore, will be analysed by comparison with data available in the literature.

Considering the fundamental importance of the two systems, data in the literature is extremely scarce. Both systems are well documented for isobaric conditions but workers have neglected the systems when employing isothermal techniques.

Data on the methanol-water system appears to be limited to that of Butler, Thomson and MacLennan (99) and Wolfbauer (100). The latter was acquired only recently (1971) so that Butlers data of 1932 has been used as the standard by later workers, for instance Ho, Boshko and Lu (26) in 1961. This is surprising as data on alcohol-water systems are inherently unreliable and data of this period has frequently been shown to be thermodynamically inconsistent.

The result on the consistency test on Butlers data is shown on Figure 36. The consistency routine adopted was the area test of Herrington (101). In this procedure the two functions I, and I_2 are calculated.

$$I_1 = \int_{x_1 = 0}^{x'_1} x_1 \, d \ \ln \gamma_1 = \int_{\ln \gamma_{1,0}}^{\ln \gamma \ x'_2} x_1 \, d\ln \gamma_1$$

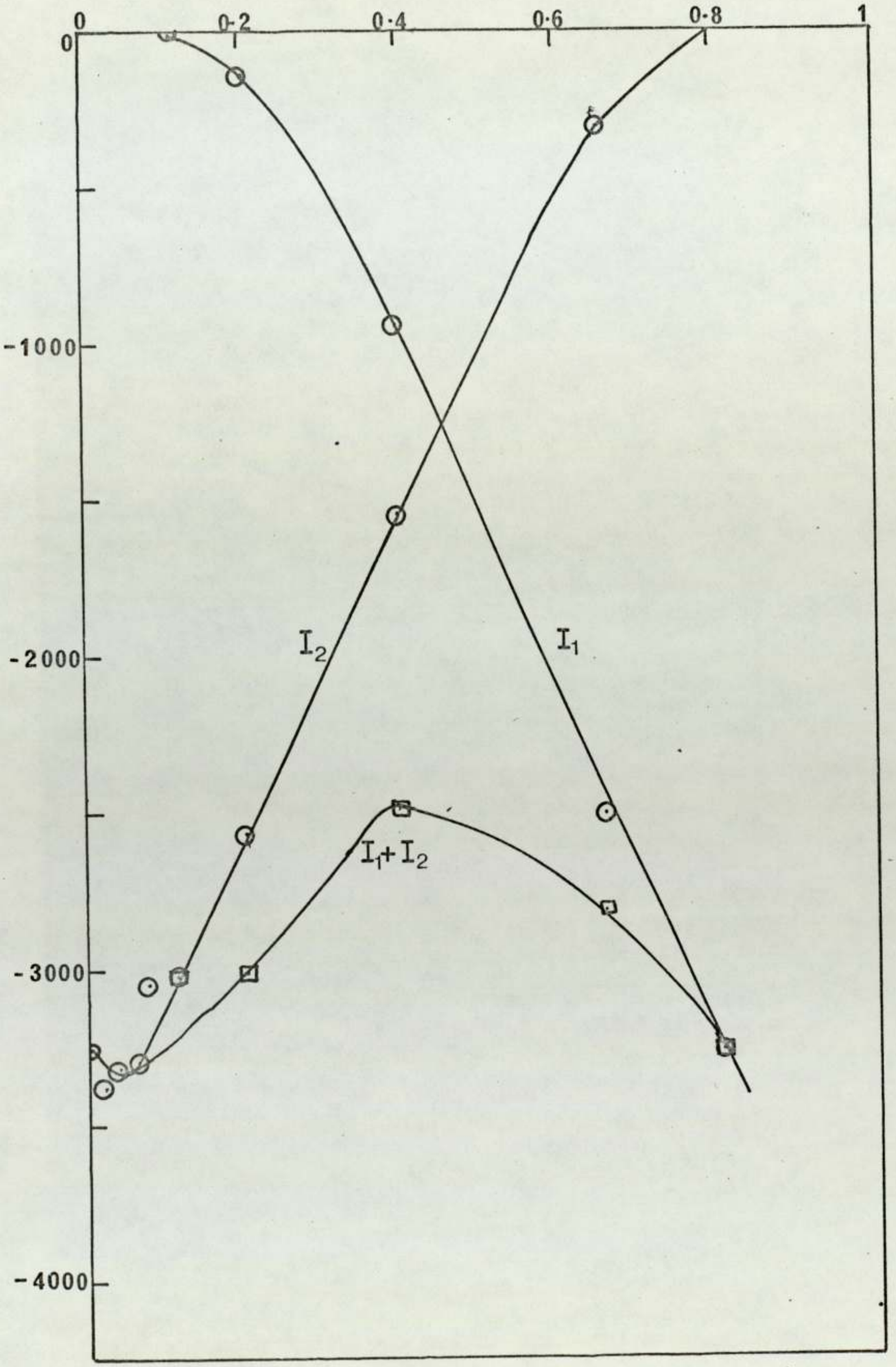


Figure 36
Consistency Testing of Methanol-Water Data of Butler

$$I_2 = \int_{x_1 = 1}^{x_1'} x_2 \, d\ln \gamma_2 = \int_{\ln \gamma_2, 1}^{\ln \gamma_2, x_1'} x_2 \, . \, d\ln \gamma_2$$

For thermodynamic consistent data

$$I_1 + I_2 = C$$

so that if $I_1 + I_2$ is plotted against mole fraction in liquid phase a horizontal line is obtained. Butler's data can be seen to be badly inconsistent and as such no basis for comparison will be made with these results. The shape of the function $I_1 + I_2$ indicates that the inconsistency in the data can be attributed to errors in the pressure.

Data on ethanol-water mixture is more copious than methanol-water. The data of Dobson (102) used by Ho, Boshko and Lu is earlier than that of Butler. The data of Dornte (103) and Wrewski (104) have been tested for consistency by Null (105). The data of Dornte is at 25°C. and of Wrewski is at 39.76°C., 54.81°C. and 74.79°C. Null demonstrated that the results of Dornte were badly inconsistent and those of Wrewski were only marginally acceptable. The only other set of data available is that of Silva and d'Avilia (106). They obtained data at 5°C. intervals from 10°C. to 30°C. The data was obtained using Barker's method and as such should automatically be consistent. They compared that data with Dobson's and showed very good agreement. The consistency test has however been applied to the data and as shown on Figure 37 the $I_1 + I_2$ function is not consistent. This surprising result is probably due to the use of the Redlich-Kister expansion in the method.

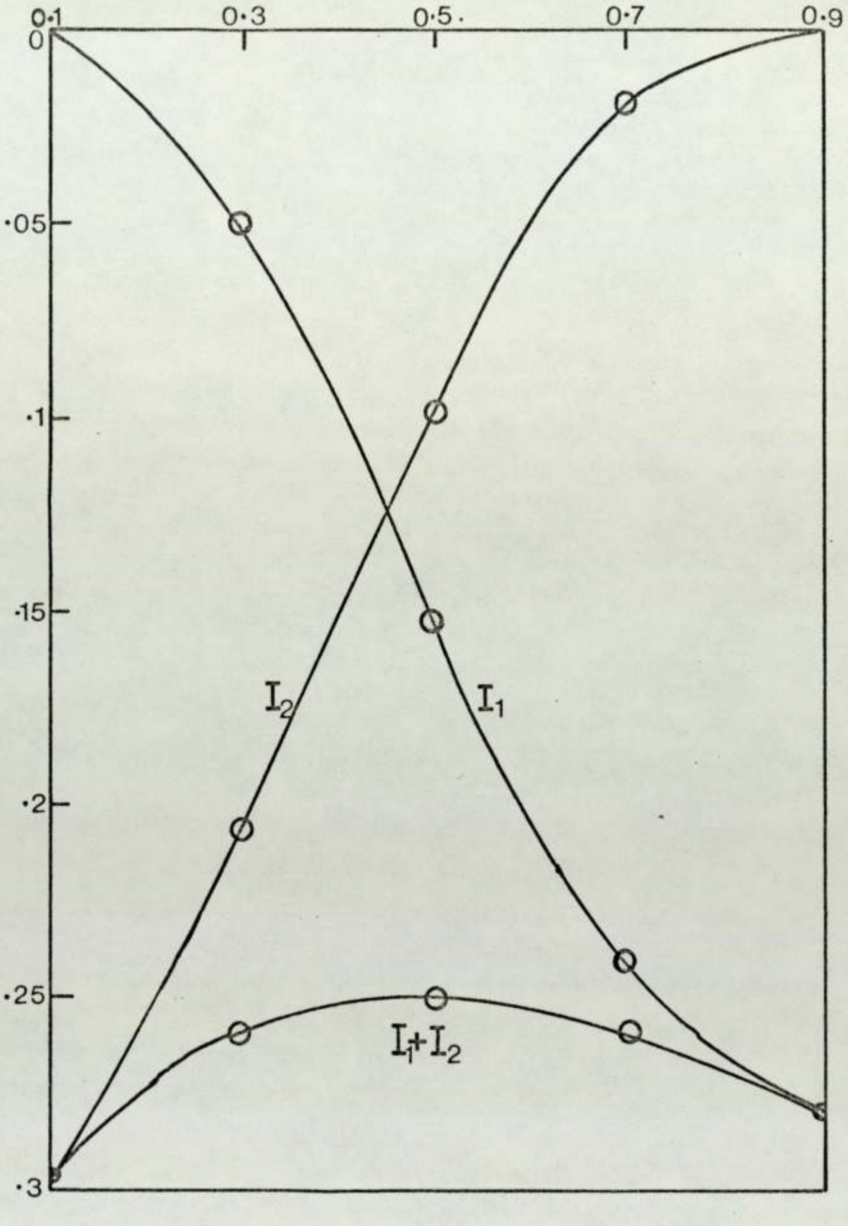


Figure 37
Consistency Testing of Ethanol-Water Data
of d'Avila & Silva

The sets of data of Silva and Wrewski, being the best available, will be used as the standard. Together they have the advantage of producing results over a large temperature range.

It is considered possible that all data on these two systems is not entirely consistent and this could manifest itself when workers have tried to correlate the data. Hudson and Van Winkle (83) for example, found that the poorest ternary predictions for the twenty systems they tested was given by the water-methanol-ethanol mixtures. Their work concluded that comparison with other ternary systems negated the possibility of hydrogen bonding being the cause of the poor fit. The similar work of Rohoutova et al (107) on binary systems, showed that the Wilson equation excellently described the data on systems such as methanol-2-propanol and 2-propanol-water but not methanol-water. They suggested that this could be caused by a 30% inaccuracy in their estimation of the cross-virial coefficient.

7.2 Evaluation and Accuracy of Results from Main Apparatus

The raw data and results are given in Appendices 1 and 2. The results were calculated using the computer program 'DATACALC' which is detailed in Appendix 3. Before any discussion of the performance of the apparatus, the effect of experimental errors in the data ought to be considered.

Errors can occur during data acquisition in the recorded values of the water and alcohol quantities, the cell liquid volume and the total pressure in the equilibrium cell. Of the two possible calculational procedures it was found that method B using data from two comparable runs required accuracy in the measurement of the cell liquid volume beyond that accorded by the present apparatus. Errors in the cell liquid volume were present because of the problem discussed earlier, of mixture globules adhering to the cell walls. Improvements for this method will be considered later.

The effect of certain errors on the final values of the activity coefficients and K ratio have been ascertained for the alternative method for the system ethanol-water. This procedure is insensitive to expected errors in the cell liquid volume, an error of 0.2 mls. producing an imperceptible error in both values. The effect of introducing an error of 0.1 mmHg. in the total pressure in the equilibrium cell is shown on Figure 38. The trends are similar for the activity coefficients and K. ratio with the former being the more sensitive. The effects are as expected with the percentage error decreasing with increase in temperature due to the increase in the saturated vapour pressure.

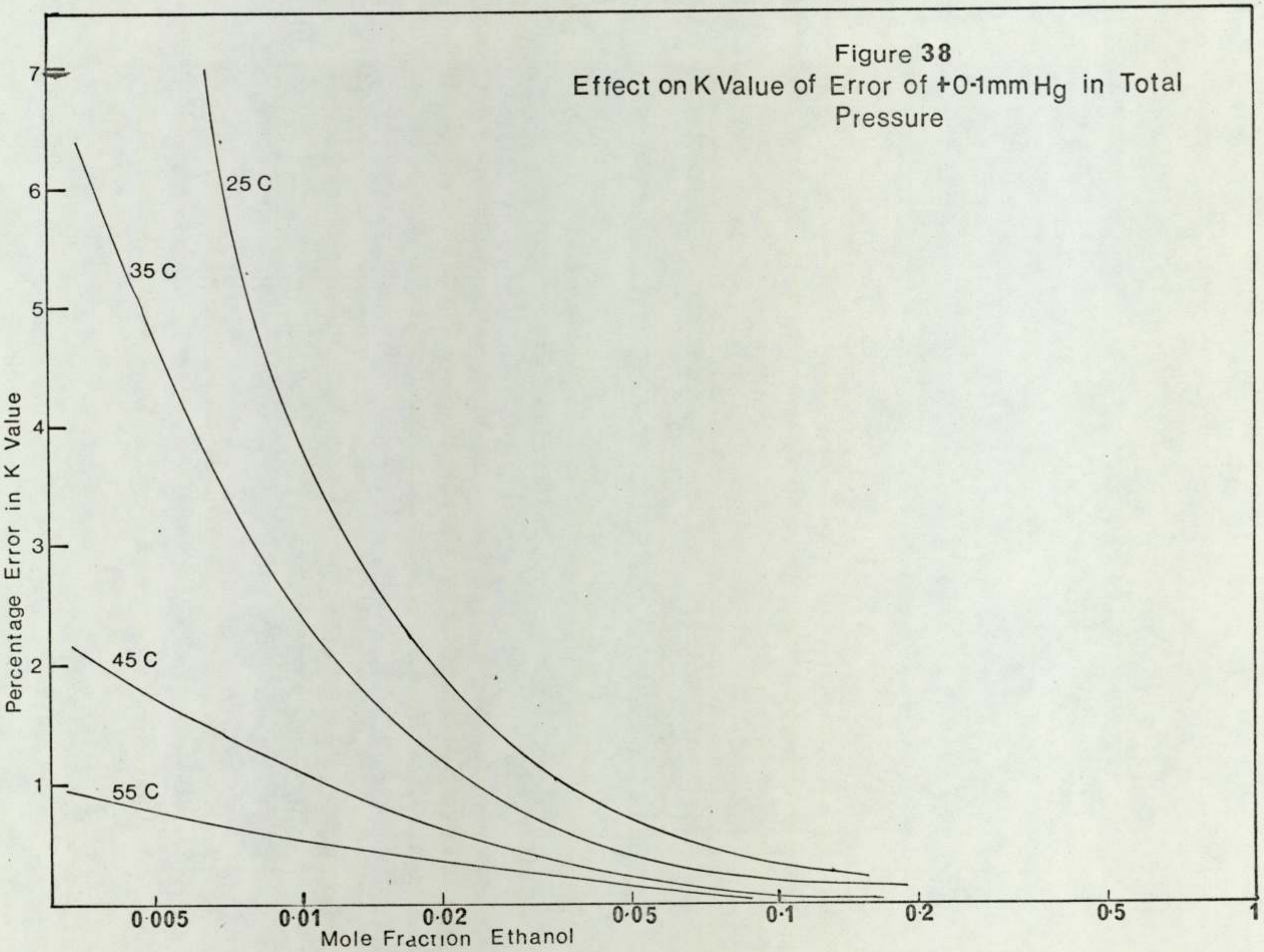


Figure 38
Effect on K Value of Error of +0·1mm Hg in Total Pressure

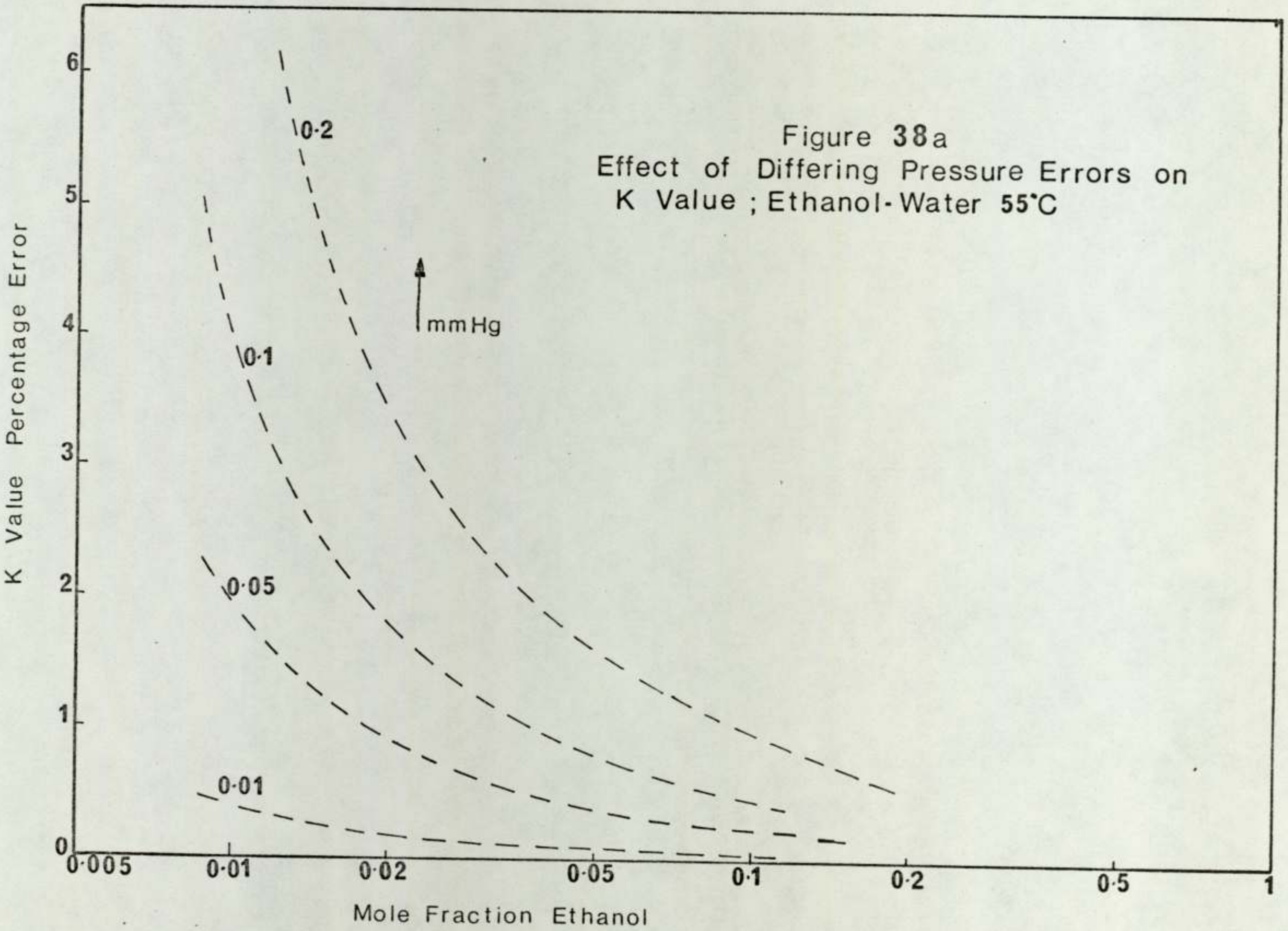


Figure 38a
Effect of Differing Pressure Errors on K Value ; Ethanol-Water 55°C

The error for compositions greater than 0.1 is small (less than 0.25%) but increases significantly at lower concentrations. This error is independent of individual runs at any one temperature.

The effect of introducing an error in the water charge measurement is shown in Figure 39. The effect is principally dependent on the relevant quantities of each component within the cell.

The observations indicate that in general, over the main concentration range for one temperature, the overall accuracy remains both reasonably constant and high. It will become apparent from the results that the sharp decline in accuracy with respect to pressure errors is not a crucial drawback to the method. Before the overall error becomes critical (ca 5%) infinite dilution will usually have been reached and Henry's Law will be obeyed. In this region, errors are readily detectable. The overall effect of differing pressure errors is shown on figure 38a and therefore when the apparatus is capable of providing the anticipated pressure control of 0.01 mmHg, the error will be within 2 %.

A preliminary inspection of the raw data to remove poor results before the calculational procedure, can be performed by plotting pressure against moles water per mole alcohol. This produces an elliptical curve as Figure 40 illustrates. Using this basis, individual runs at one temperature will form one curve.

Inspection of the data at this stage revealed certain inadequacies in the experimental procedure. It was continually found that in the first few recordings of each data acquisition run the pressure

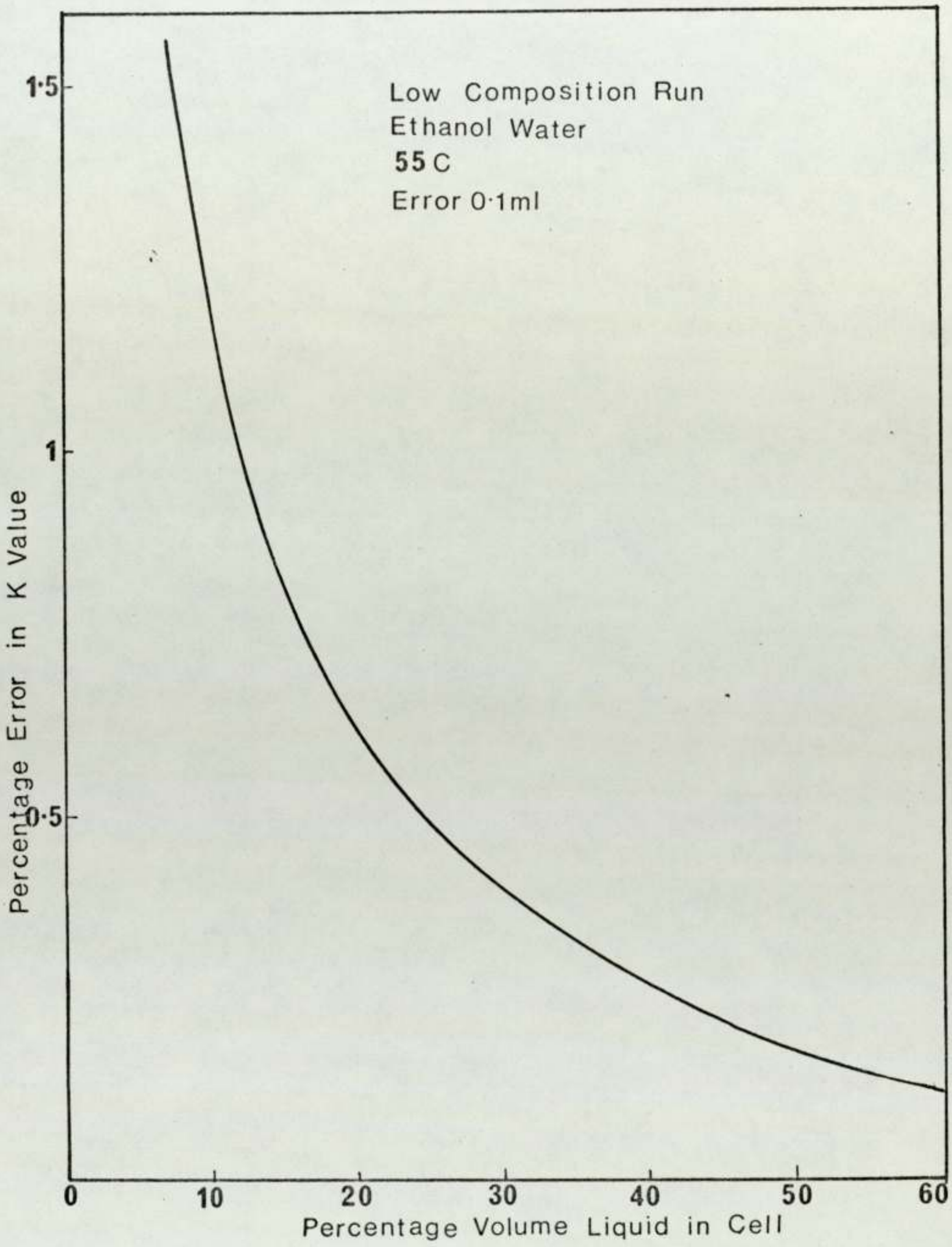
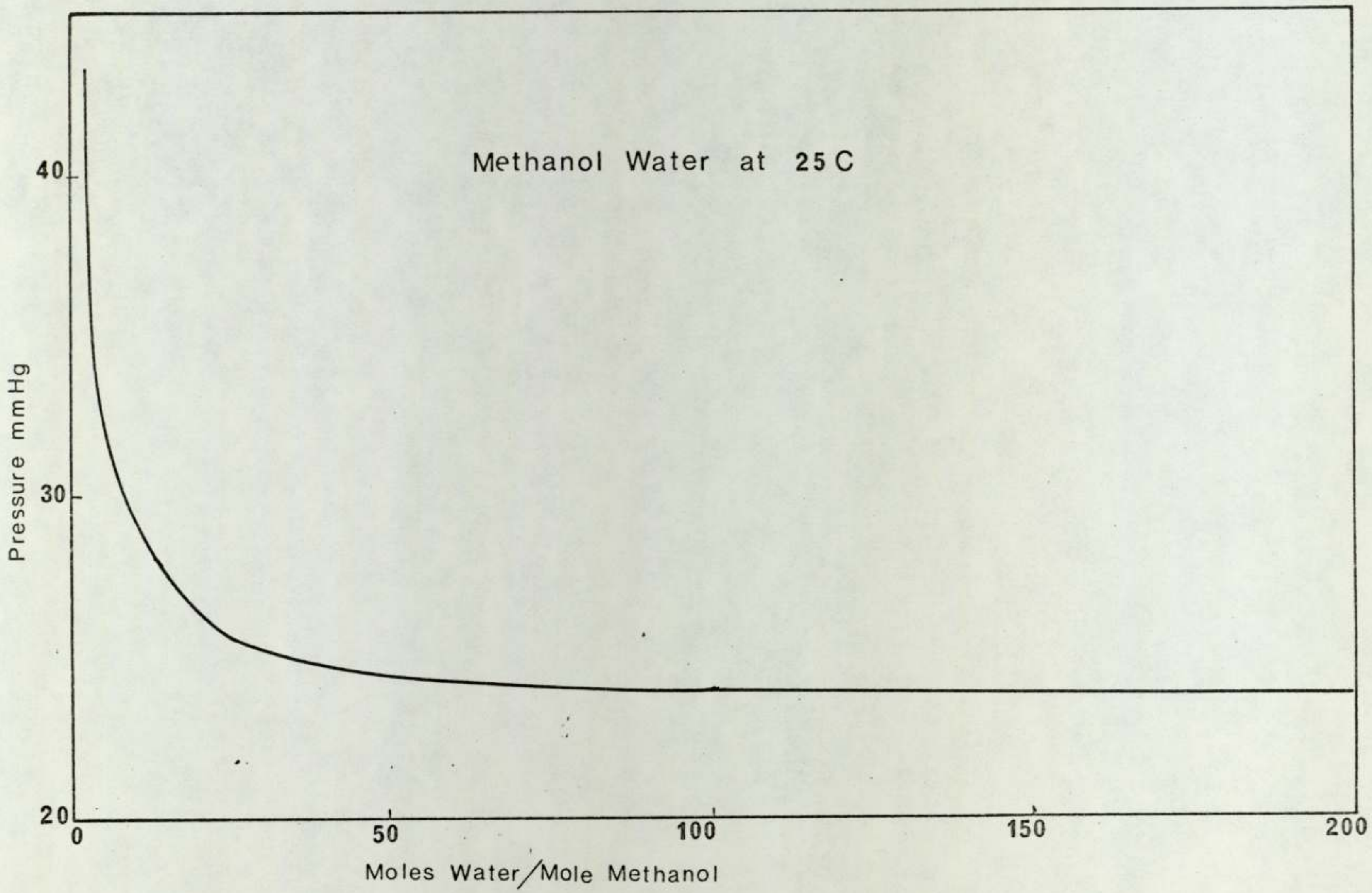


Figure 39

Effect of Error in Water Measurements

Figure 40



Methanol Water at 25 C
Pressure mmHg
40
30
20
0
50
100
150
200
Moles Water/Mole Methanol

was too high. This is the result of an insufficient stirring period in the cell for the relatively large vapour phase. It is recommended that initially the minimum agitation period be 15-20 minutes, this reducing to 5 minutes as the vapour phase volume decreases. The pressure recordings at the conclusion of a run were, in addition, often too high. These occured usually after approximately 20 recordings i.e. a run period of 3-4 hours plus. The inadequacies in the apparatus which caused this have been detailed earlier.

The results for the K-values and activity coefficients for each temperature range on both systems are shown on Figures 41 to 50. In order to extract the important features of the results, 'screened' data for each system is shown on Figures 51 and 52. 'Screening' was conducted by removing suspect results from the extremities of each run as indicated above.

Before considering the implications of the results the performance of the apparatus will initially be assessed. This can be gauged from the mole fraction of the vapour phase-temperature relationship for a constant mole fraction in the liquid phase. The data, from the considerations discussed above should be most reliable at a liquid phase mole fraction of 0.1. This is also when the imperfect behaviour of the system is nearing a maximum. The results from this work and other workers are shown on Figure 53 for ethanol-water.

The diagram shows that the results from this work fall on that predicted and interpolated by the other workers. The relationship obtained at this x-value shows the highly imperfect behaviour of the

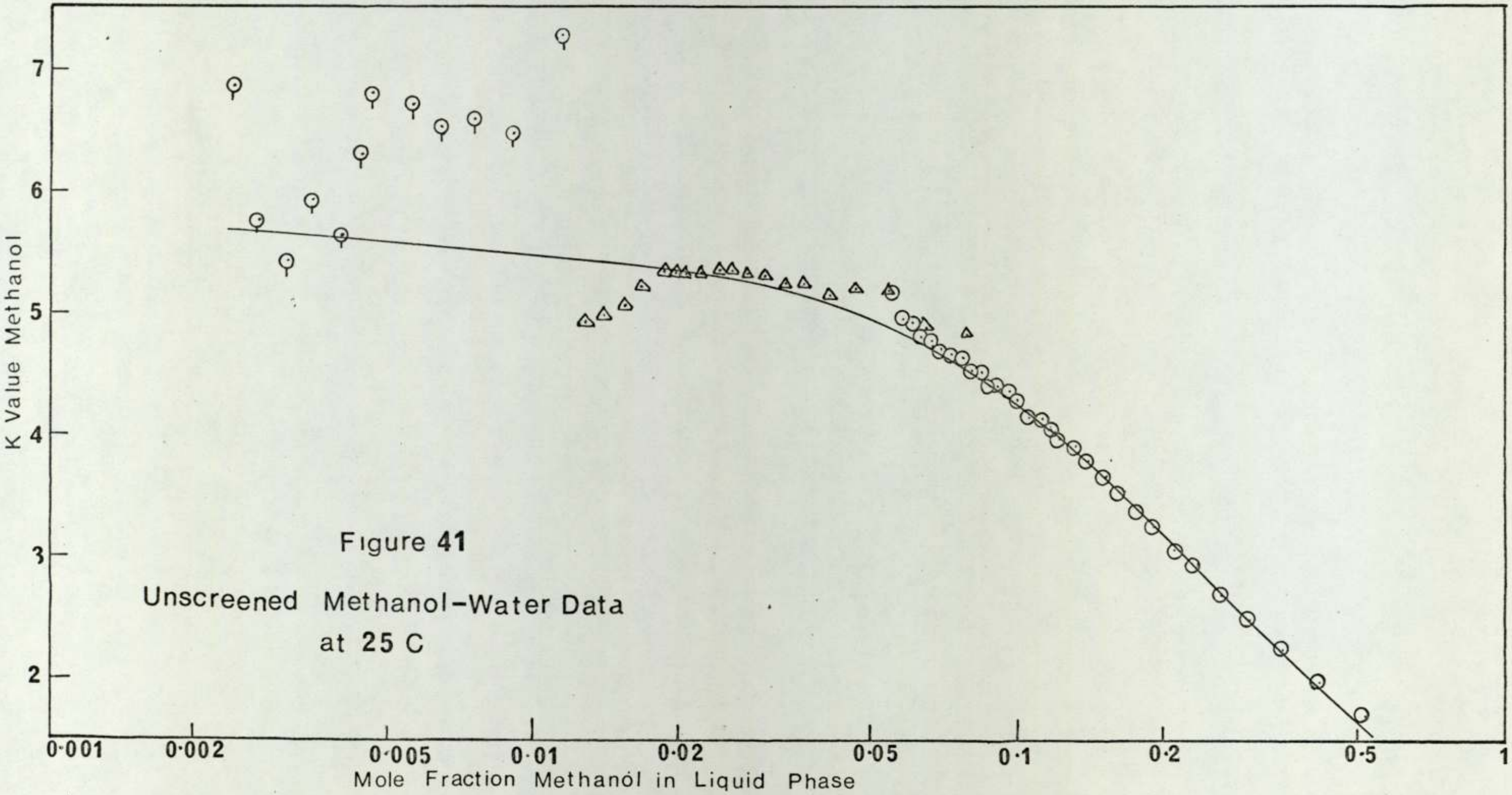


Figure 41

Unscreened Methanol-Water Data at 25 C

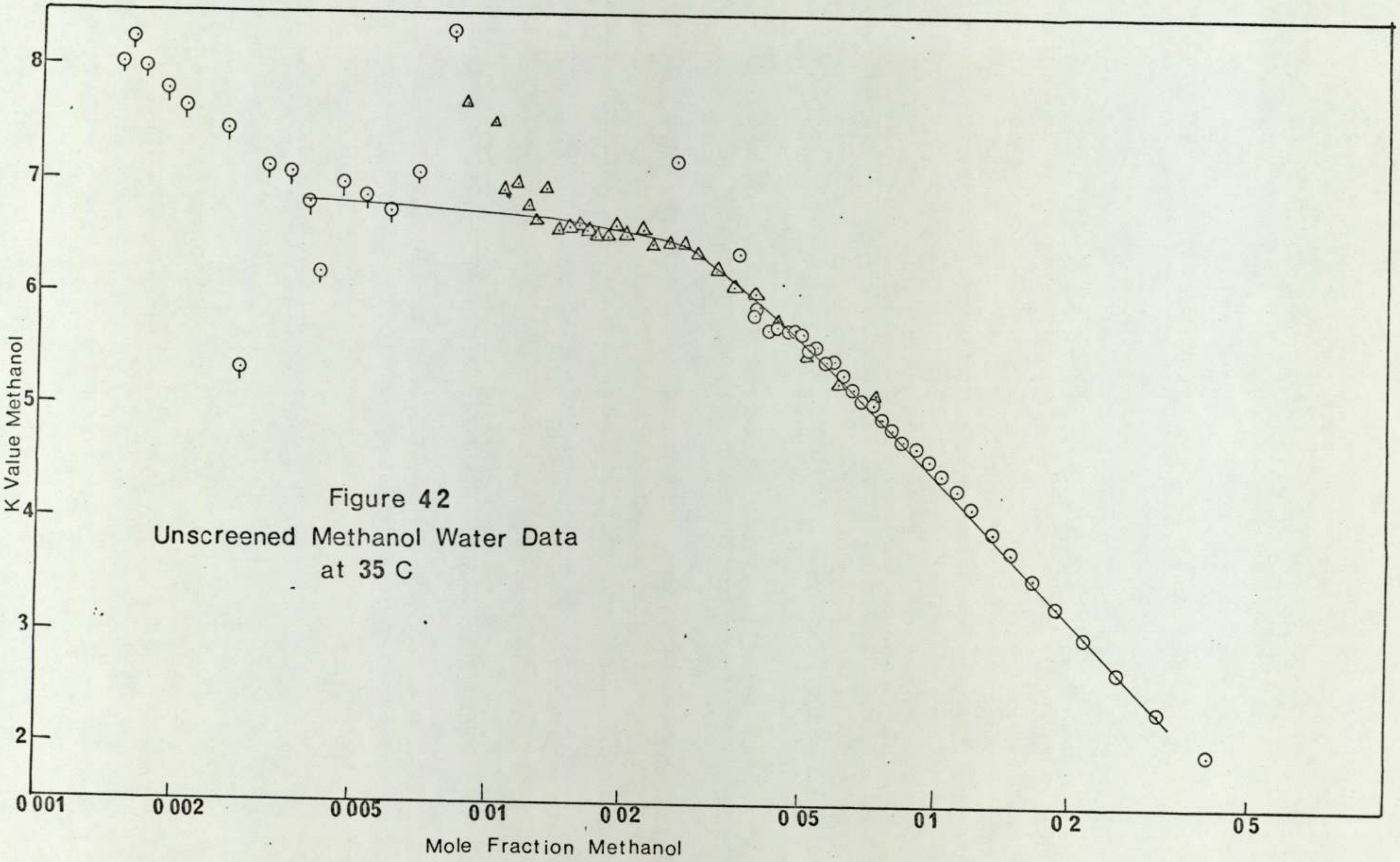


Figure 42
Unscreened Methanol Water Data
at 35 C

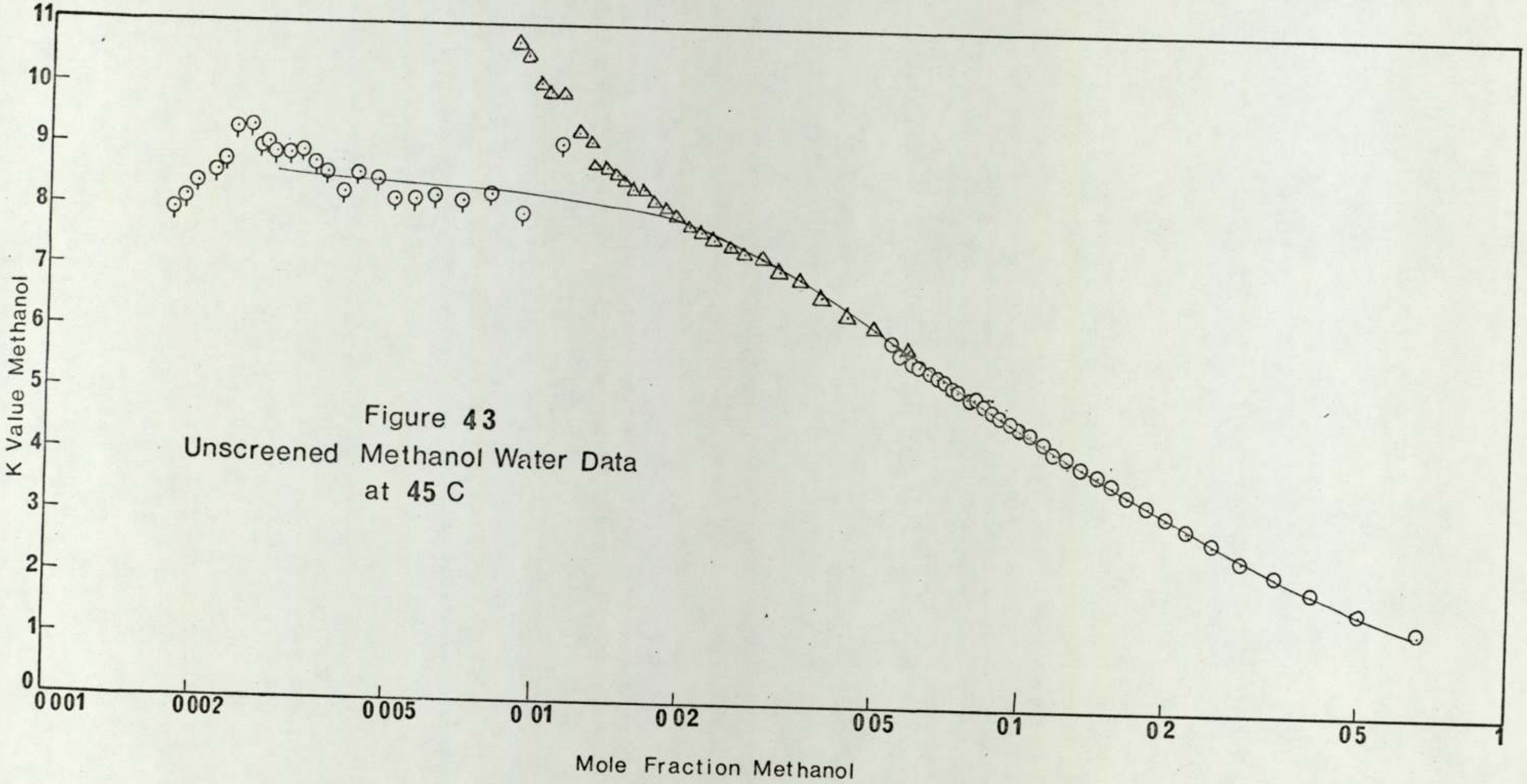


Figure 43
Unscreened Methanol Water Data
at 45 C

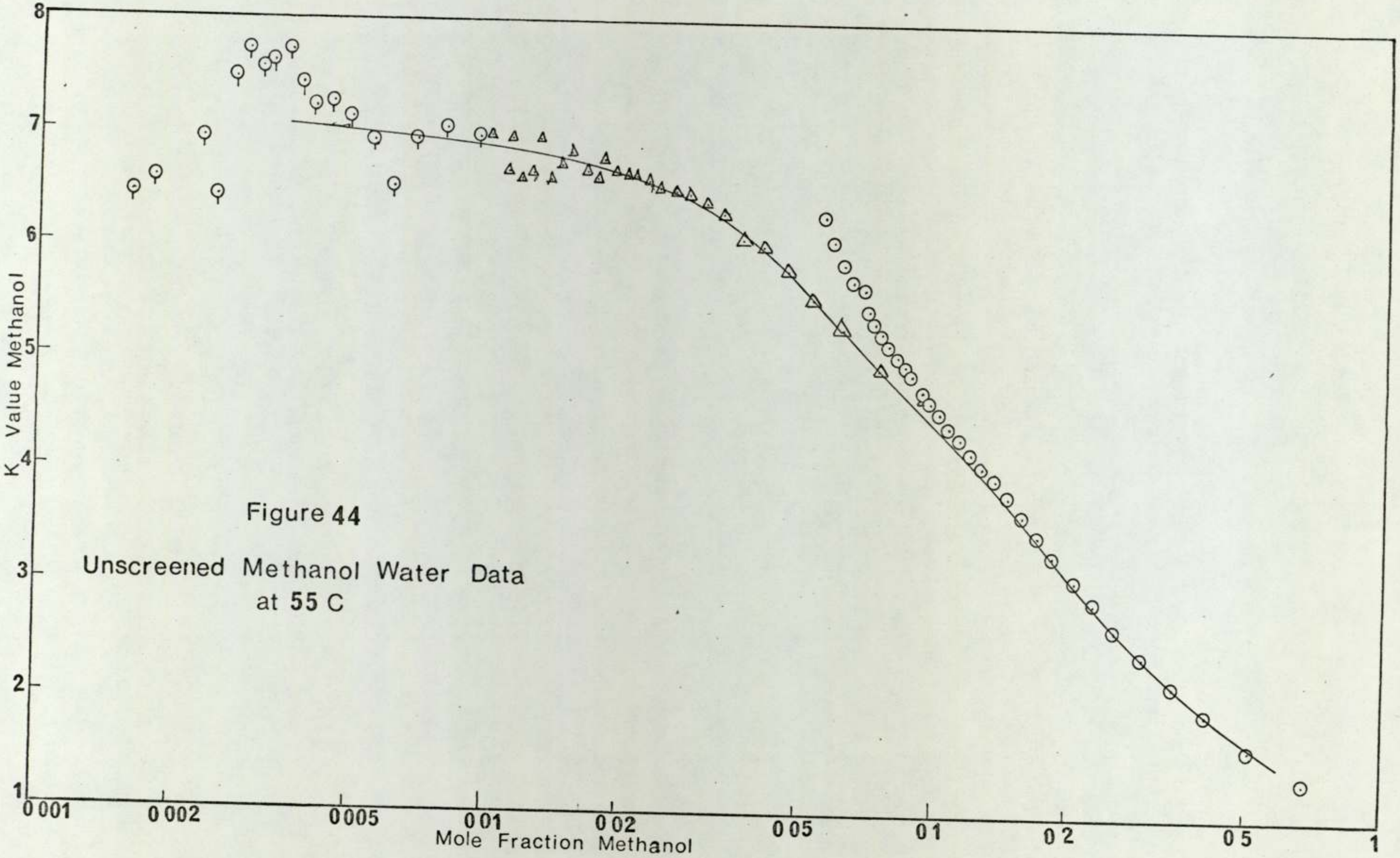


Figure 44

Unscreened Methanol Water Data at 55 C

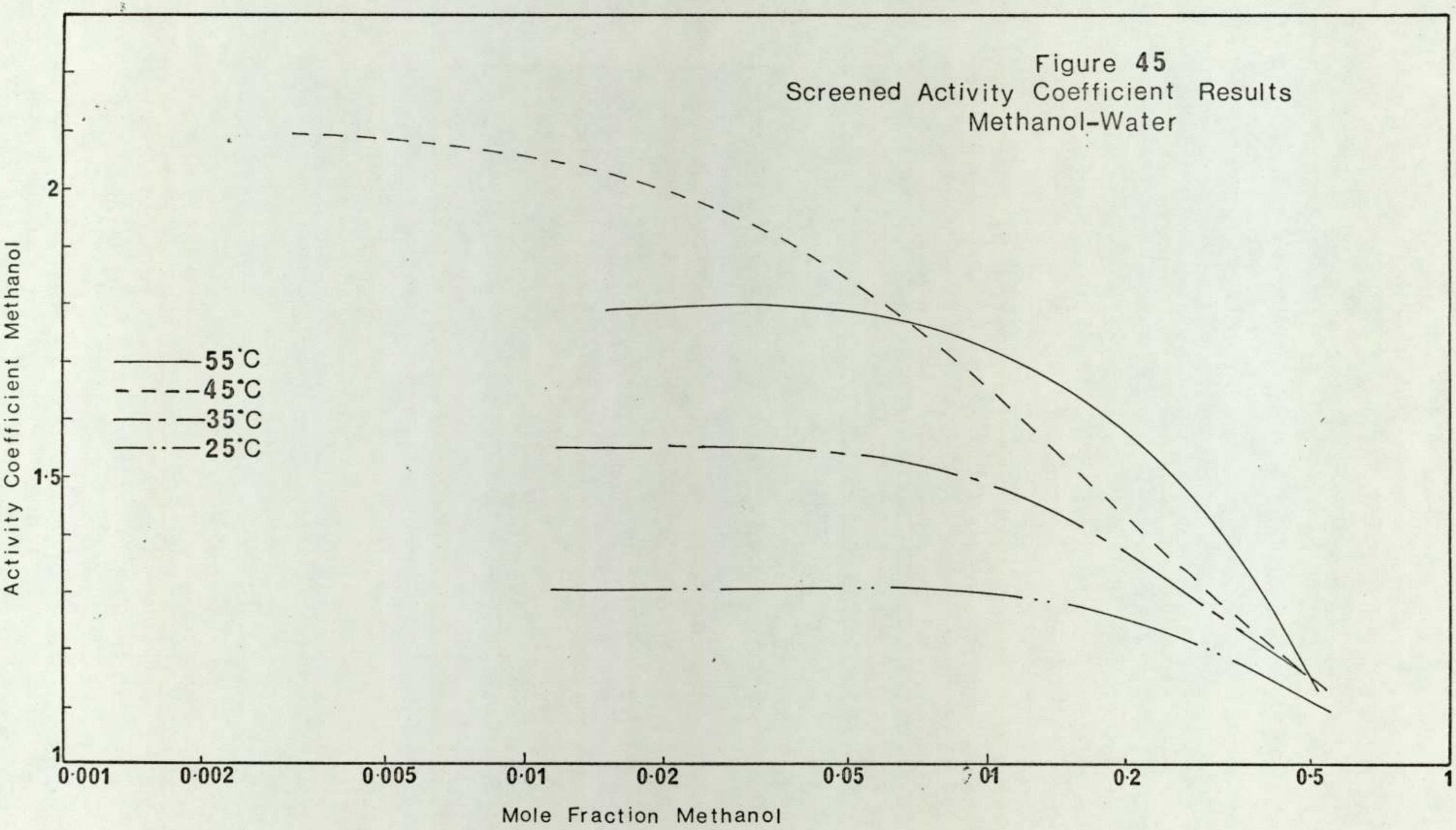


Figure 45
Screened Activity Coefficient Results
Methanol-Water

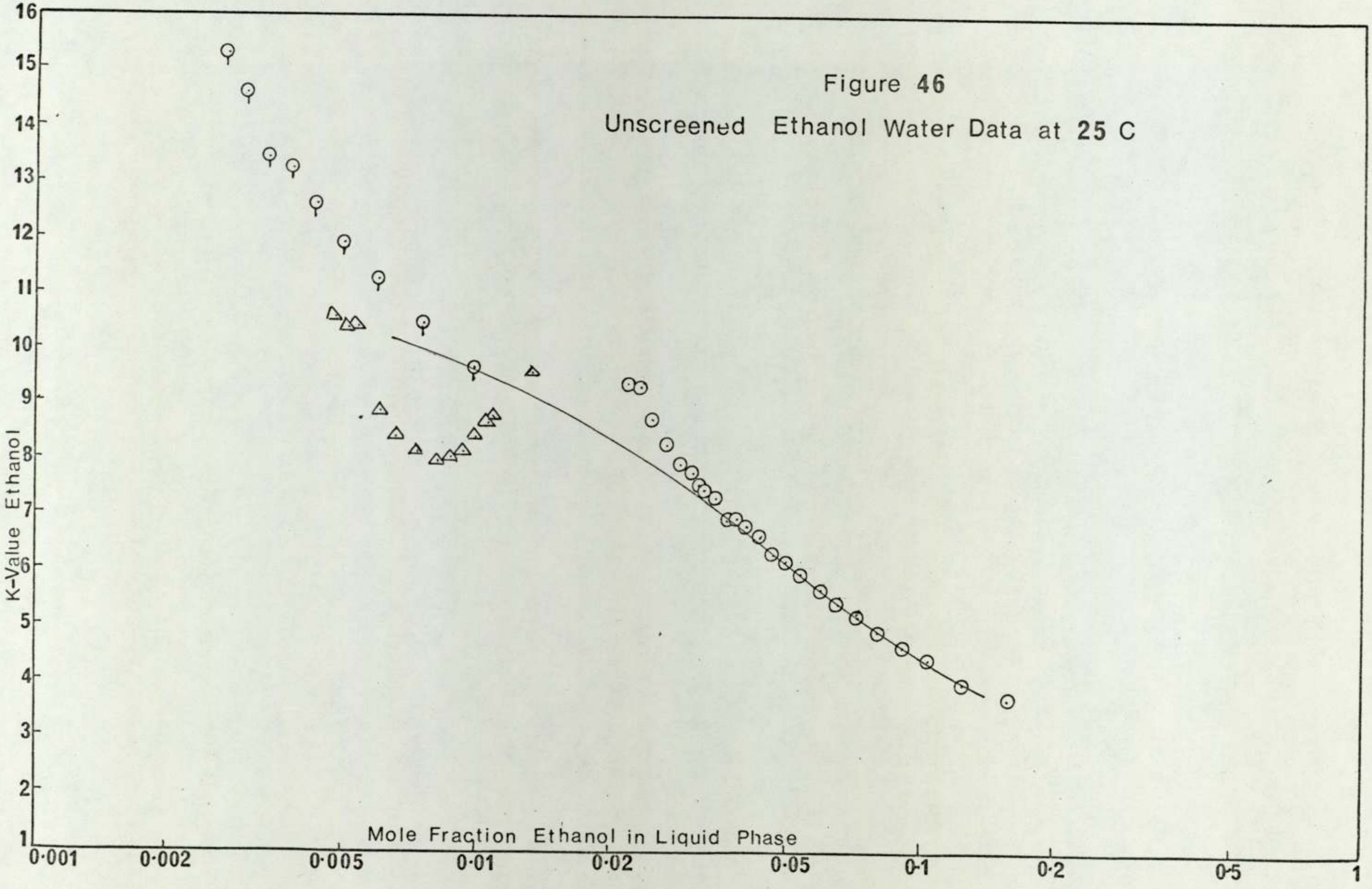


Figure 46

Unscreened Ethanol Water Data at 25 C

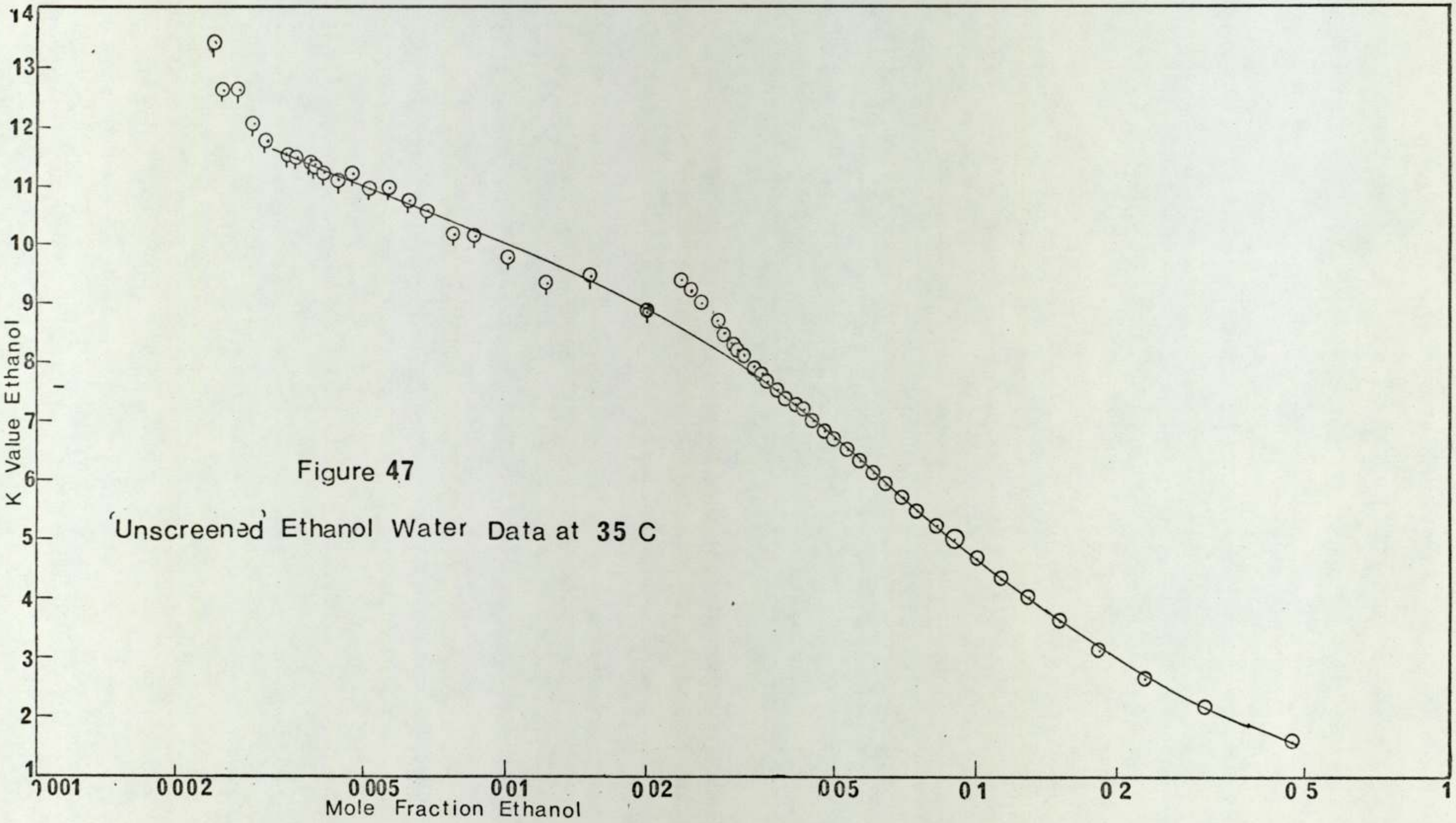


Figure 47

'Unscreened' Ethanol Water Data at 35 C

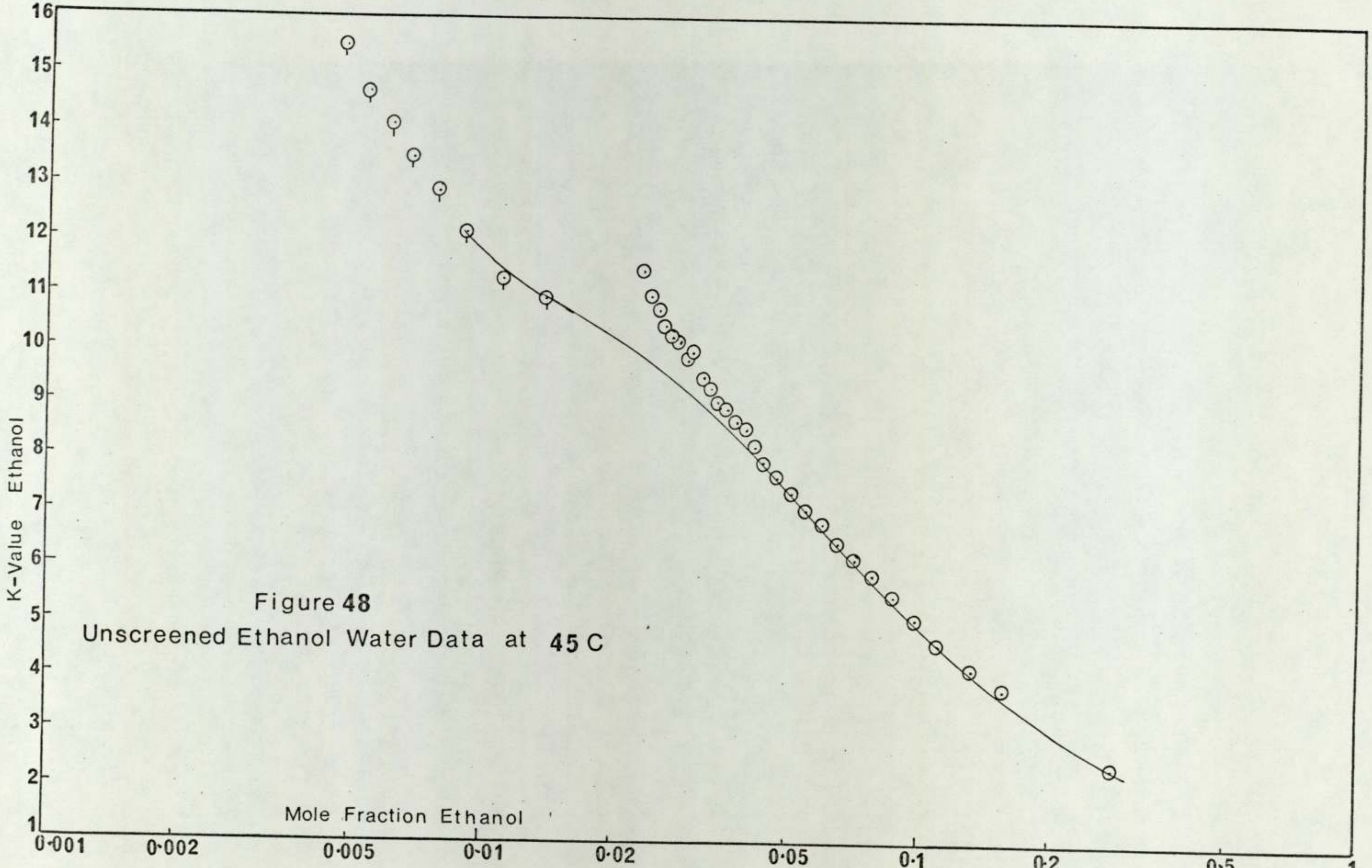


Figure **48**
Unscreened Ethanol Water Data at **45** C

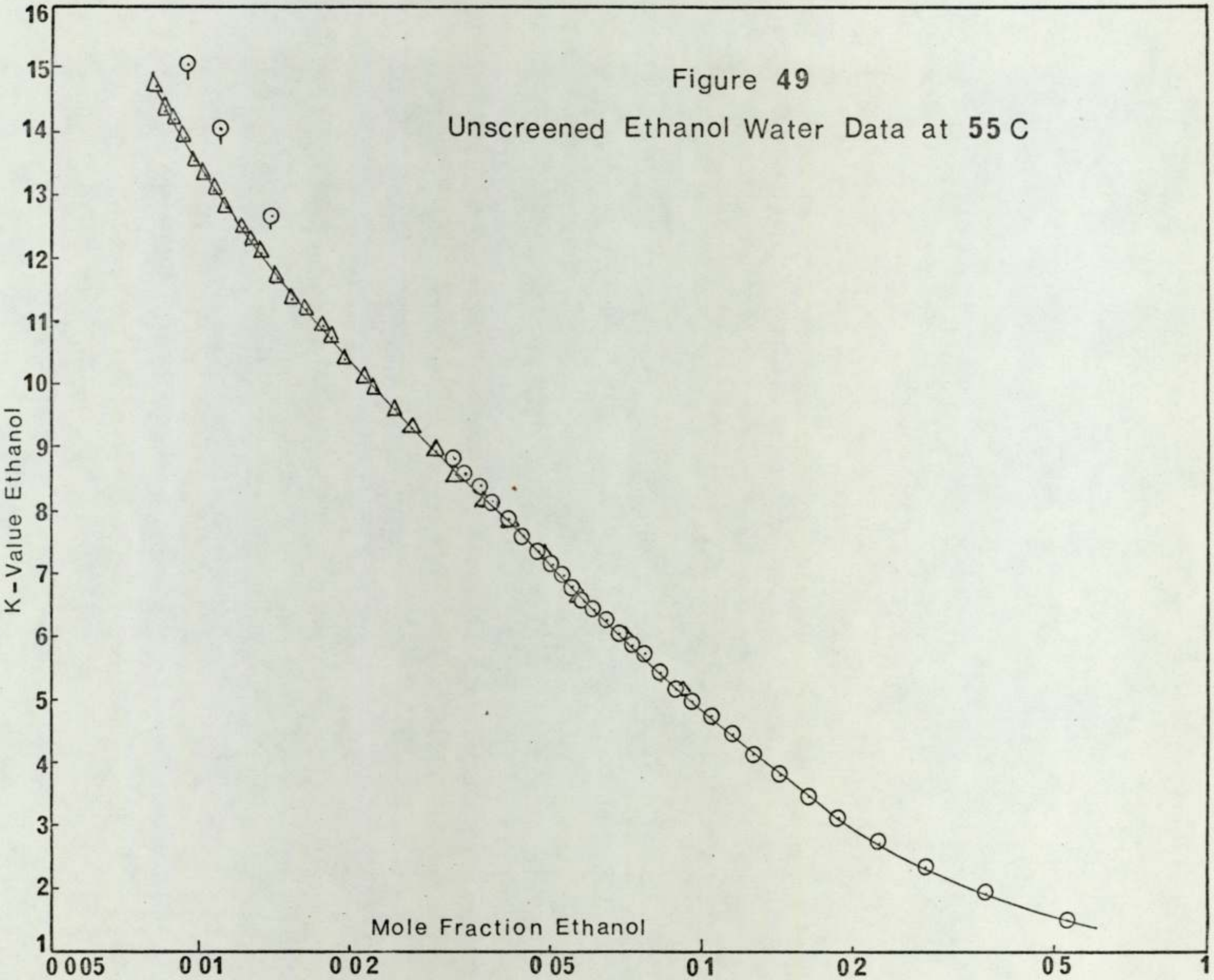


Figure 49

Unscreened Ethanol Water Data at 55 C

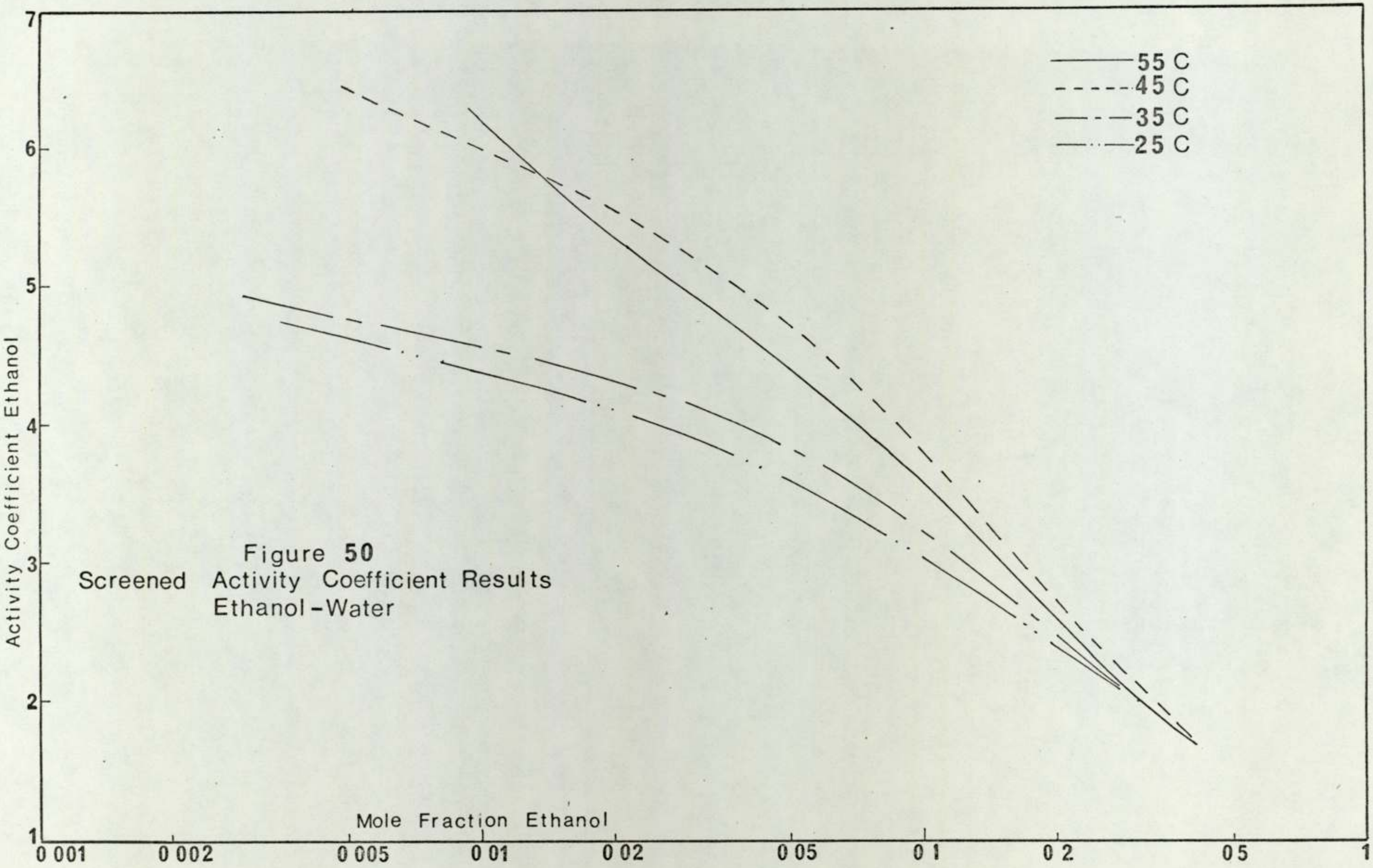


Figure **50**
Screened Activity Coefficient Results
Ethanol-Water

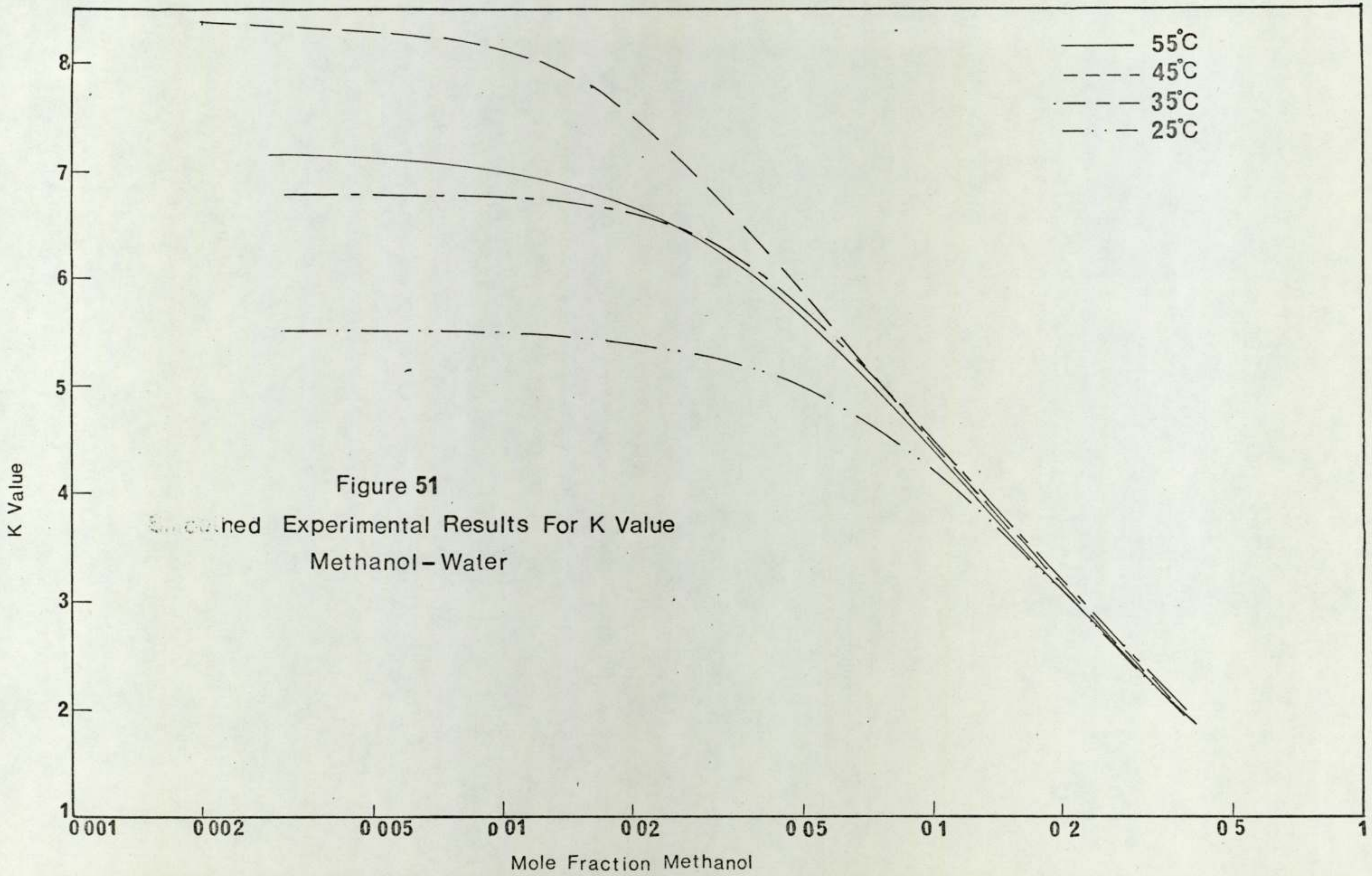


Figure 51

Combined Experimental Results For K Value

Methanol – Water

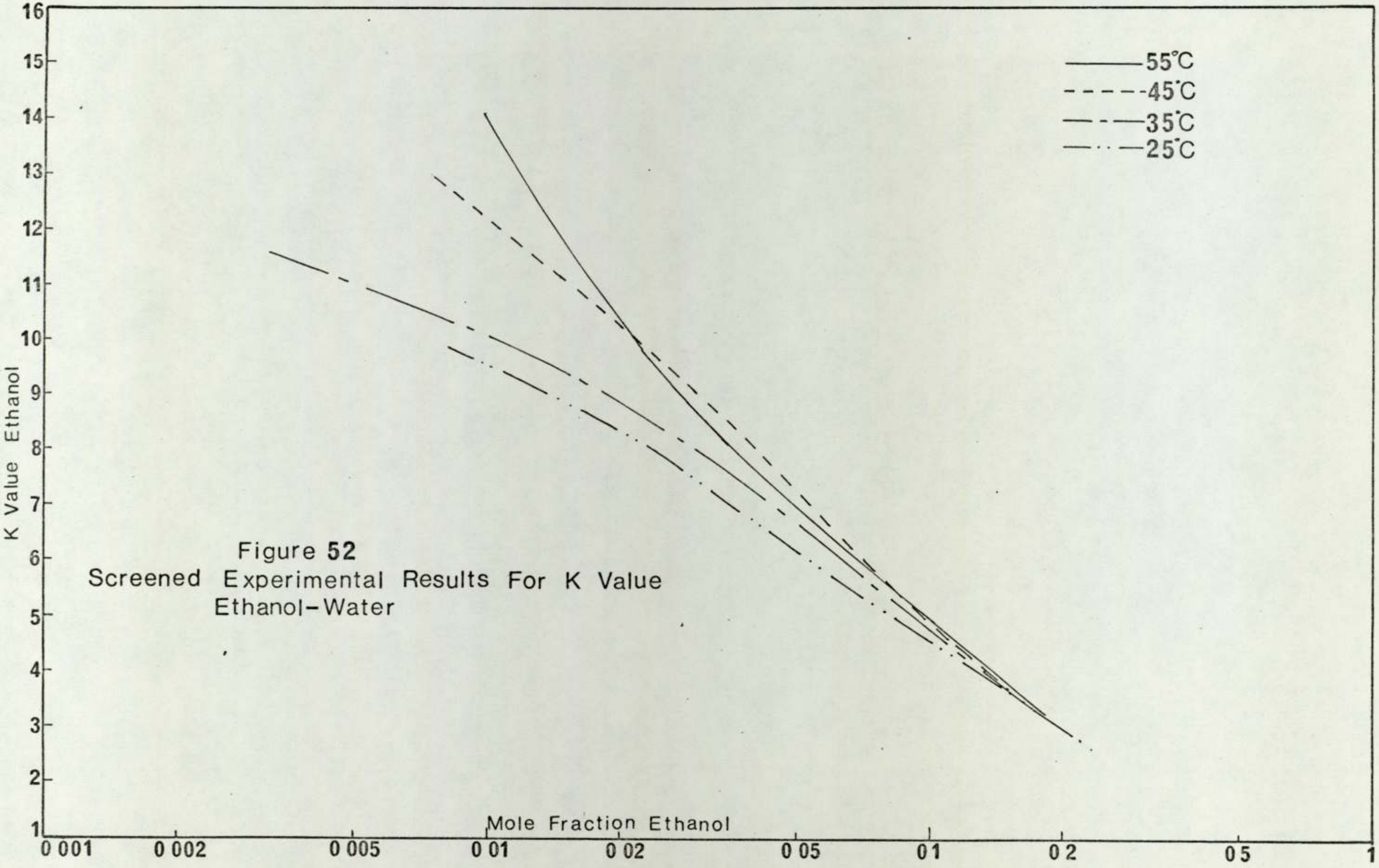
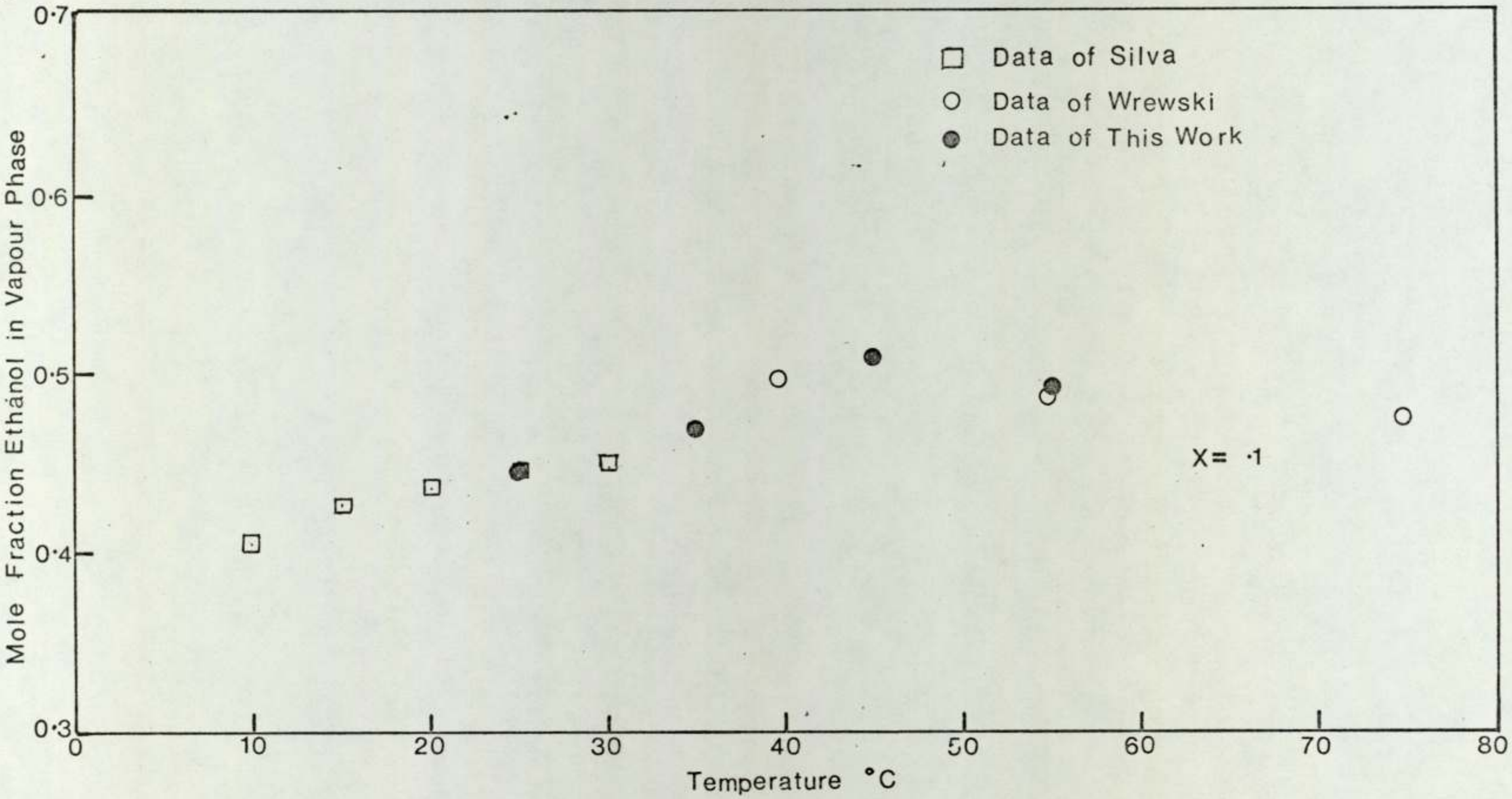


Figure **52**
Screened Experimental Results For K Value
Ethanol-Water

Figure 53



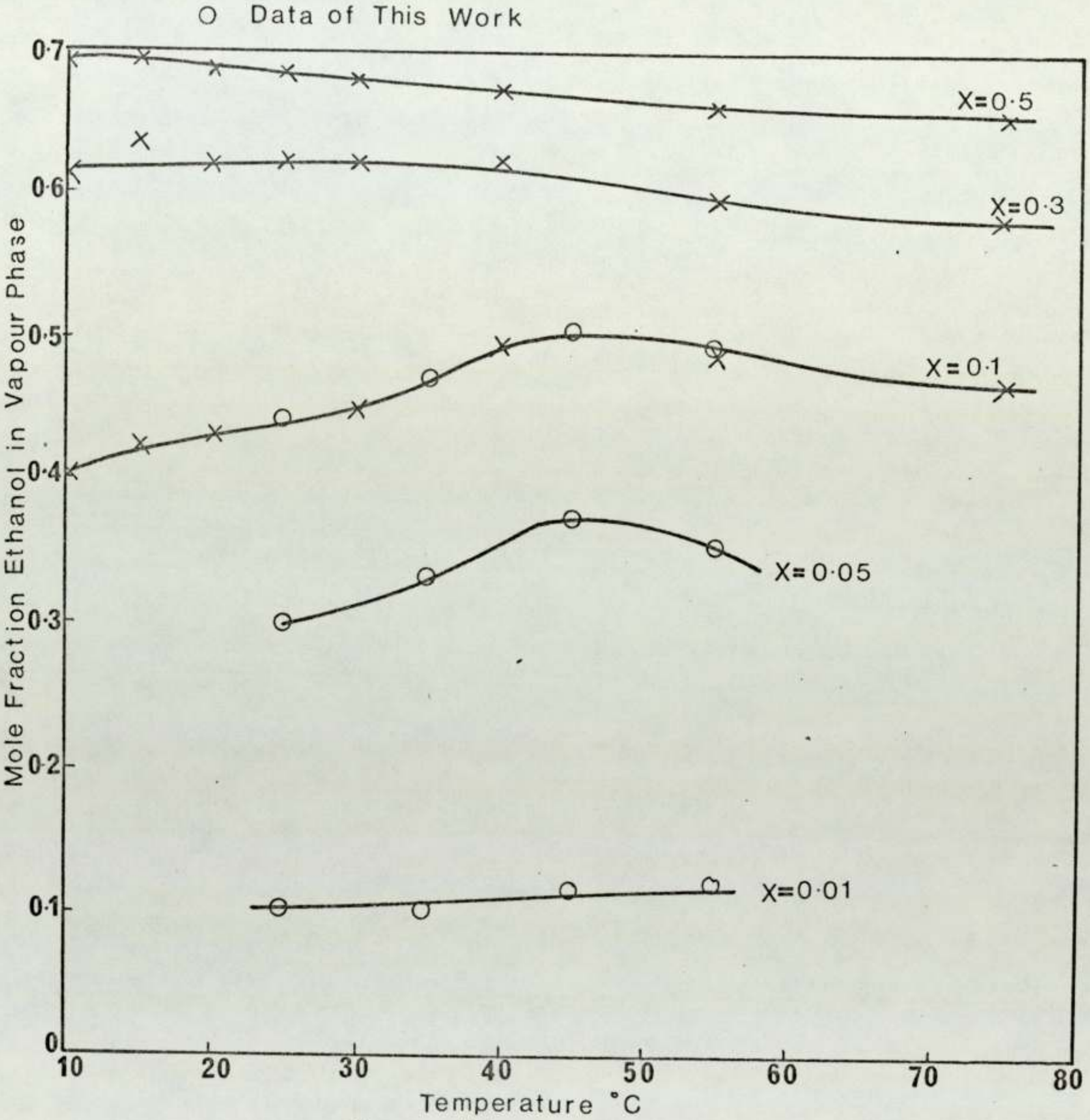
□ Data of Silva
○ Data of Wrewski
● Data of This Work
X= ·1
Mole Fraction Ethanol in Vapour Phase
0·3
0·4
0·5
0·6
0·7
Temperature °C
0
10
20
30
40
50
60
70
80

ethanol-water system. The relationship is that expected; both of these systems have been ignored by the chemists over the last twenty years due to this behaviour, the last detailed discussions being in 1953 (108).

From these discussions it is obvious that a strict physical interpretation of the behaviour of these systems is not possible. The behaviour of the water and alcohol molecules is complicated, for instance it is known that the water and alcohol molecules tend to associate with themselves and that the water structure in particular will not break down until large quantities of alcohol are present.

The figure shown above indicates the excellence of the data. Data on the same basis at differing x values is also illustrative of both the reliability and behaviour of the results. Figure 54 shows data for the ethanol-water system and Figure 55 for the methanol-water system over mole fractions between 0.5 and 0.01. The trends obtained follow roughly those anticipated from known relationships. (Principally G^E-temperature relationships) and from expected theory. At mid-concentration (x_1 = 0.5) the intermolecular forces behave in a manner approaching Raoult's Law. The imperfect behaviour increases with decrease in mole fraction until infinite dilution is reached when the molecular behaviour is that predicted by Henry's Law.

Observation of the data over the full composition range tested for K-values shows the trends found by Dalager where Henry's Law is obeyed. The results at the lower concentrations for certain temperatures are scattered more than desired. This is specifically true at 25°C. where the diaphragm movement is less detectable and a pressure error has the greater effect. Figures 51 and 52 of the 'screened' data show



○ Data of This Work
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
Mole Fraction Ethanol in Vapour Phase
10
20
30
40
50
60
70
80
Temperature °C
X=0·5
X=0·3
X=0·1
X=0·05
X=0·01

Figure 54

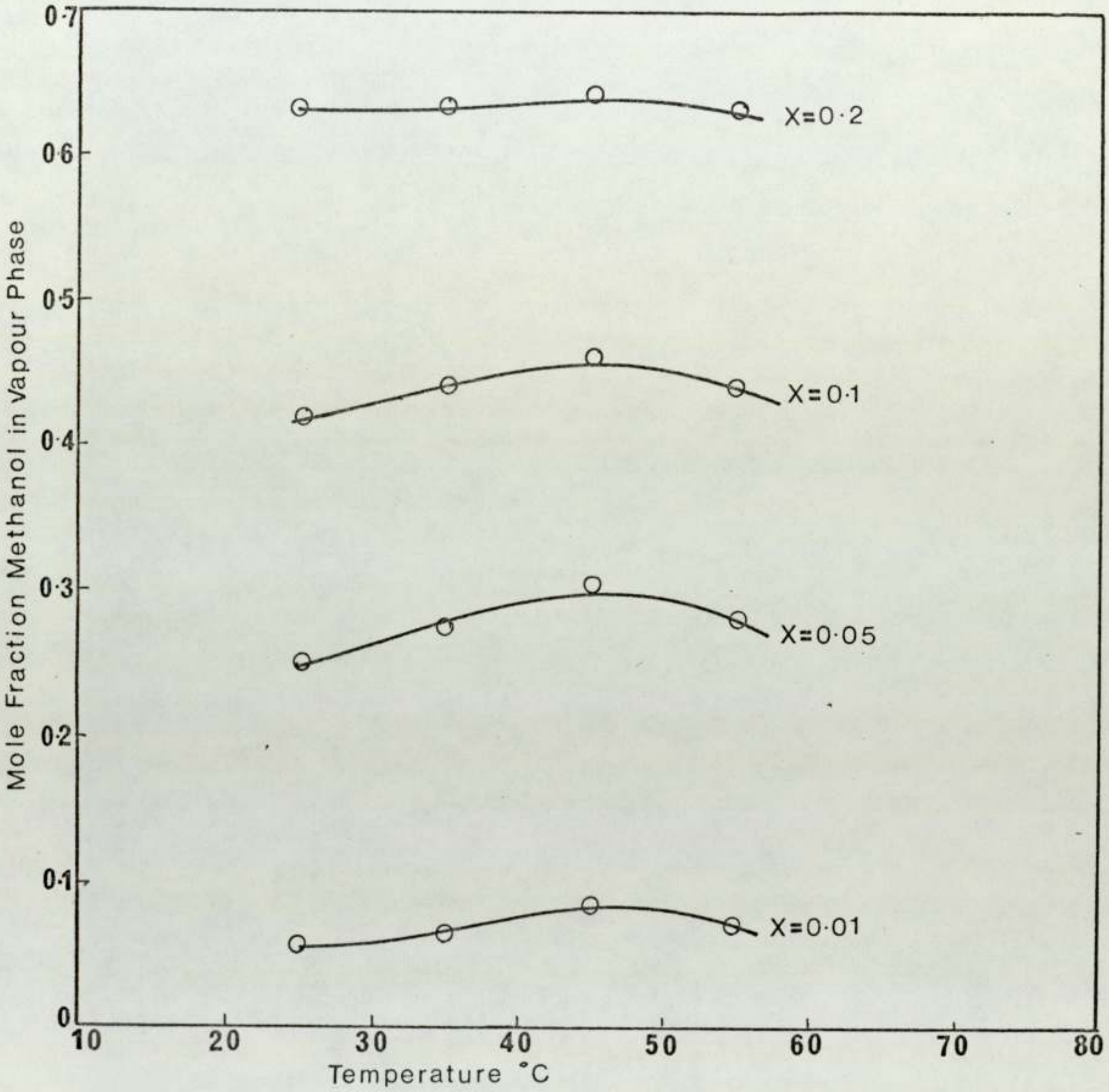

0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
Mole Fraction Methanol in Vapour Phase
10
20
30
40
50
60
70
80
Temperature °C
X=0·2
X=0·1
X=0·05
X=0·01

Figure 55

the beginning of the infinite dilution range and the temperature effect on this range. It is noted that the start of the infinite dilution range is not constant but differs both with the system and the temperature. Dalager showed the data from both his systems reaching infinite dilution at approximately the same concentration (x = 0.005). The flattering of the curve is at lower values for the system ethanol-water than the methanol-water system. This is to be expected from the higher activity coefficients of the ethanol-water system. The infinite dilution concentration is also at lower concentrations for an increase in temperature. Again this is to be expected as a result of the higher internal energy of the molecules at higher temperatures.

The data from this work fits in reasonably well with that of Dalager. Dalagers results are isobaric at 760 mmHg and are therefore at higher temperatures than this work. At higher temperatures especially the ethanol-water results do not follow the expected trend. It is difficult to state without further experimental work whether this is entirely due to experimental errors. Results have been reported for higher alcohol-water systems with activity coefficients greater than those obtained in this work.

Experimental work on the two systems was undertaken at the alcohol rich ends of the composition range. It is to be appreciated that the apparatus in it's present form is unsuitable for this concentration region; the apparatus being incapable of producing sufficient quantities of completely degassed water. This can be easily overcome in an improved apparatus as the degassing sections can be made interchangeable. This concentration region was considered worthwhile investigating because of the known azeotrope of the ethanol-water system at approximately 95% ethanol at 25°C. (104).

The unscreened results are shown on Figures 56 to 59. As to be expected from considerations stated above, the accuracy of the data approaching the end of a run badly falls away. The screened data however, shown on Figures 60 and 61, are considered to be both fairly reliable and fairly accurate. Figure 60 for the ethanol-water results shows the existence of the azeotrope, however, the azeotropic concentrations are in disagreement with those of Wrewski. Wrewski predicted the azeotropes at ethanol mole fractions of 0.9552 and 0.8945 at tem temperatures of 39.76°C, 54.81°C and 74.79°C. respectively. This temperature - mole fraction relationship is directly opposed to that found in this work, these azeotropic ethanol mole fractions being about 0.955, 0.97, 0.987 at temperatures of 25°C, 35°C and 45°C. respectively. The same trend is obtained with the methanol-water results.

Explanation of this discrepancy is difficult without further experimental work. It is noted however that Dalager did not find an azeotrope for either system. From Wrewski's data, at the temperatures used by Dalager, it would have been expected that Dalager would have found the azeotrope for the ethanol-water system.

To the authors knowledge the methanol-water azeotrope has not been previously reported in the literature. If the data of this work is correct, this would be expected from the lack of work on the system at these low water concentrations and temperatures.

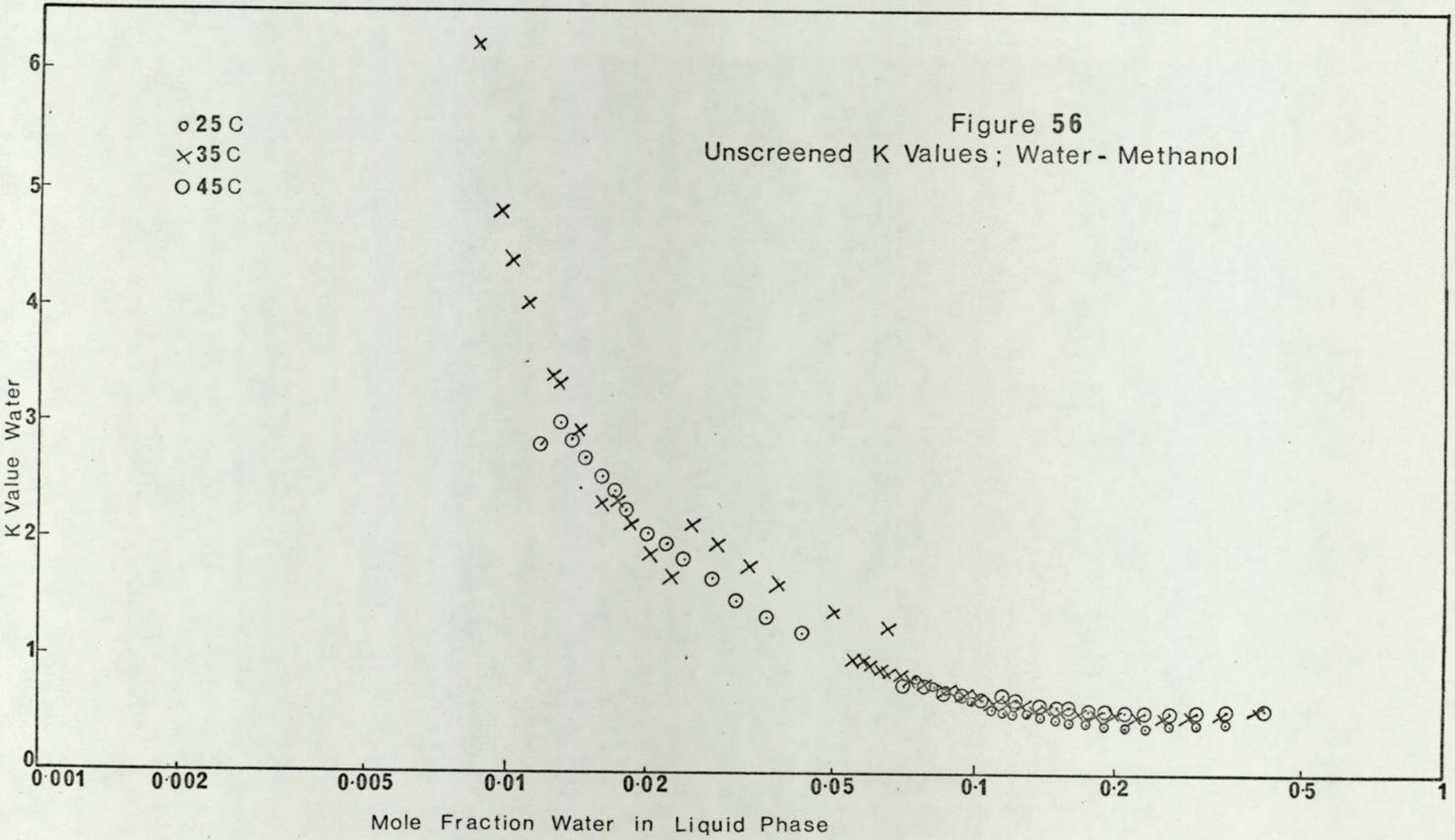


Figure 56

Unscreened K Values; Water-Methanol

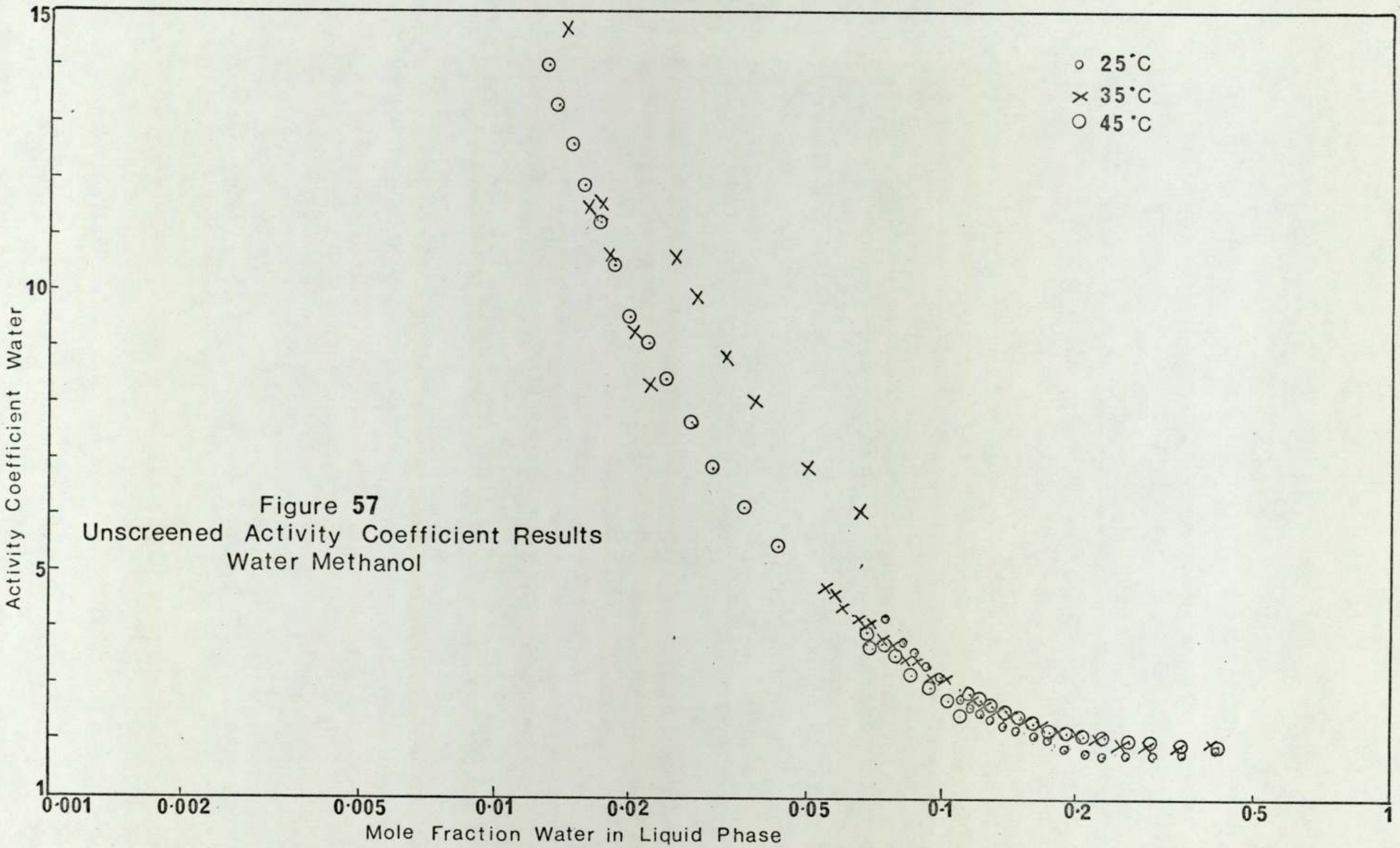


Figure **57**
Unscreened Activity Coefficient Results
Water Methanol

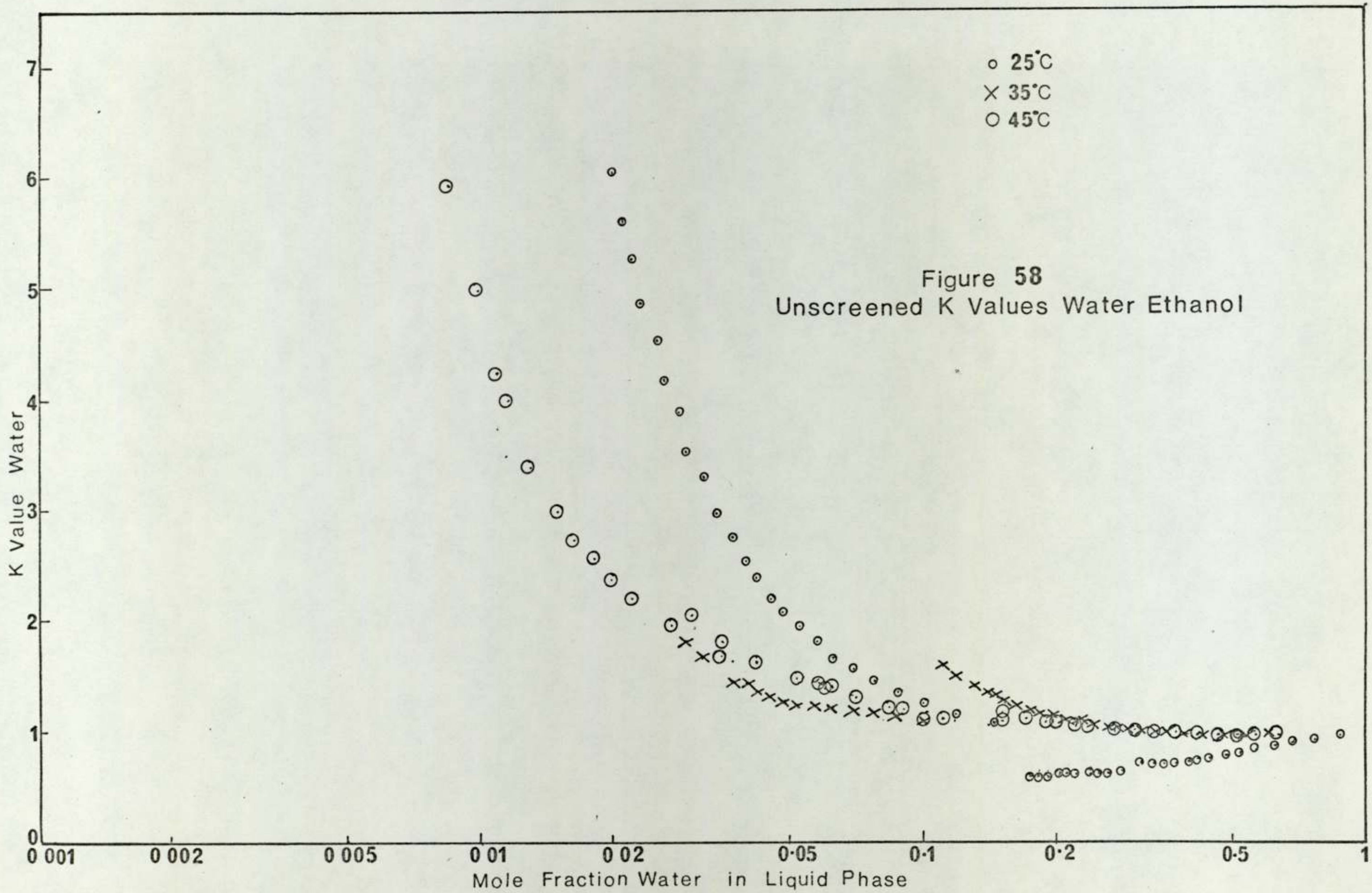


Figure 58
Unscreened K Values Water Ethanol

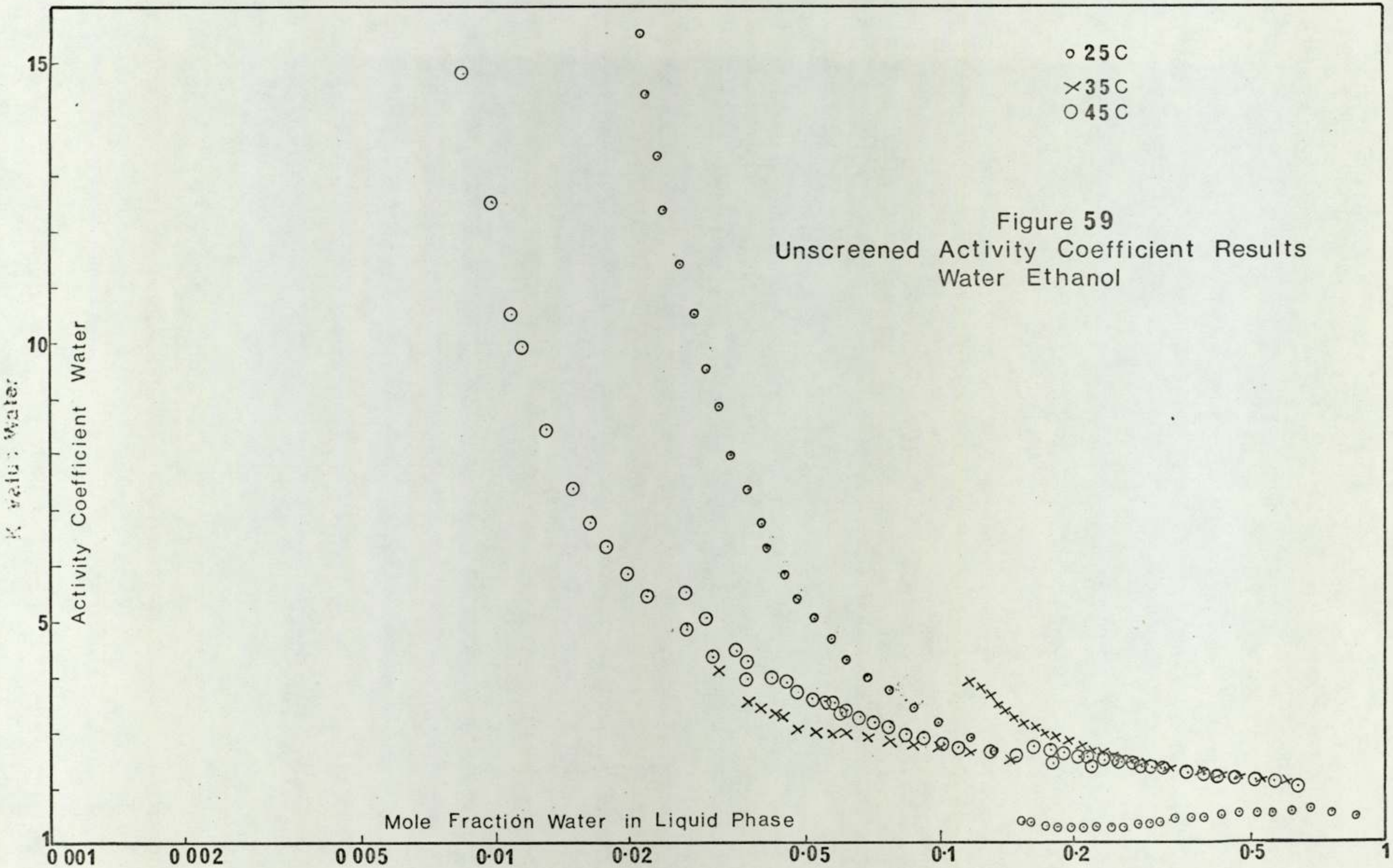


Figure 59
Unscreened Activity Coefficient Results
Water Ethanol

Figure 60

'Screened' Ethanol-Water Results; Low Water Region

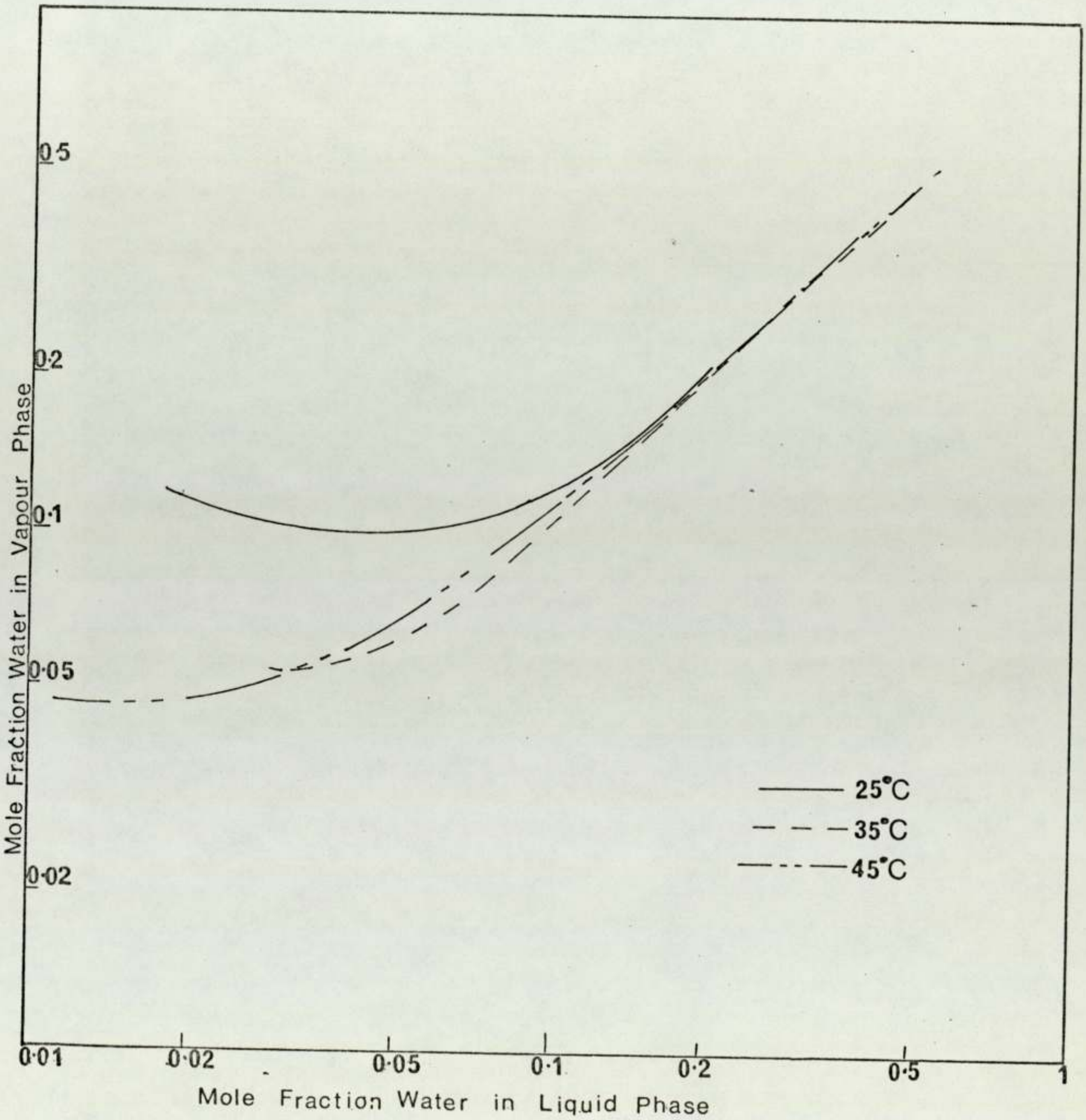
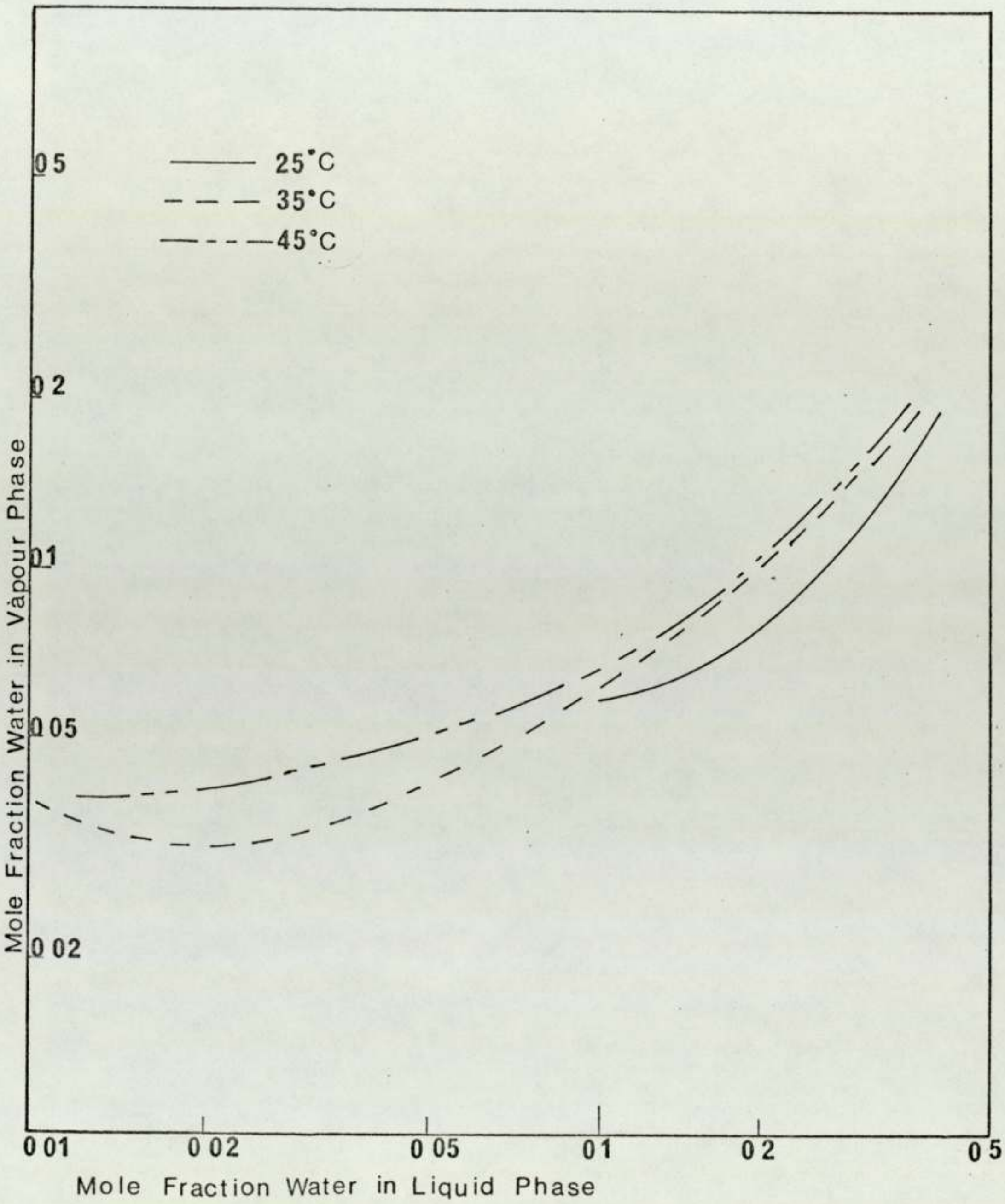


Figure **61**

Screened Methanol Water Results; Low Water Region



7.3 Fitting of the Data to activity coefficient-mole fraction correlations

The fitting of the data to activity coefficient-mole fraction correlations requires the development of a computer program to calculate the required parameters. The principal section of the program is the technique employed to minimise the error in a selected criterion. There are two main approaches to minimising a function, those based on gradient methods and those on hill-climbing methods. Gradient methods are the more powerful and from a literature survey, the minimisation technique called 'MULTIFIT' presented by Coggan (109) was selected. This technique is based on the method of Fletcher and Powell (110) and later modified by Davidson (111).

After comprehensive testing it has been concluded that this technique and probably the majority of gradient techniques are unsuitable in their present forms for fitting vapour-liquid data to many of the more recent correlations. The reason for this conclusion can be shown by considering figures 9, 10 and 16 presented earlier for possible parameter pairs for a certain error in the Wilson and NRTL equations. Gradient techniques estimate their step length from the value of the gradient from the initial point to one nearer the minimum. When the error function curve is that of a narrow valley then a very large range of parameter pairs will give a reasonable fit. This produces a very flat gradient and hence a very small step length. This results in the method minimising to values differing only minimally from the original values, the technique being incapable of proceeding along the valley. From the figures above it is seen that the problem increases with data at low concentrations when the valley narrows and lengthens.

Unsuccessful attempts were made to overcome this difficulty by altering the step length. Gibson-Robinson (112) has found the same problem when attempting to employ a more recent and powerful gradient technique called 'SPIRAL'. 'MULTIFIT' was found to be successful when fitting the Redlich-Kister 2 and 3 parameter forms but not the 4 parameter form.

The results have been fitted to the Wilson equations, NRTL equations and Redlich-Kister expansions using a program incorporating a modified form of the Rosenbrock method. The program minimises the error in the sum of the pressures $(P_{calc} - P_{exp})^2$ This was found to accord a better fit than an error in activity coefficients, which is in agreement with Holmes and Van Winkle (83). Detailed listing of the program is held at the University of Aston. The behaviour of a non-ideal vapour phase is treated using subroutines based on those presented by Prausnitz et al (113) and partly outlined in Appendix 4.

The isoboric data of Dalager has been fitted to the Wilson 2-parameter equation and the NRTL 2 and 3 parameter equations. The fits are shown on Figure 62. For both systems only the 3 parameter NRTL equation adequately predicts the non-ideal behaviour. For the other two correlations, the Wilson equation is superior at infinite dilution but is badly inferior at mole fractions above 0.1.

To produce the fits shown for the 3 parameter NRTL equation, the optimised values of α were 1.2685 for the methanol-water system and 0.5710 for the ethanol-water system. Both values are beyond the limits

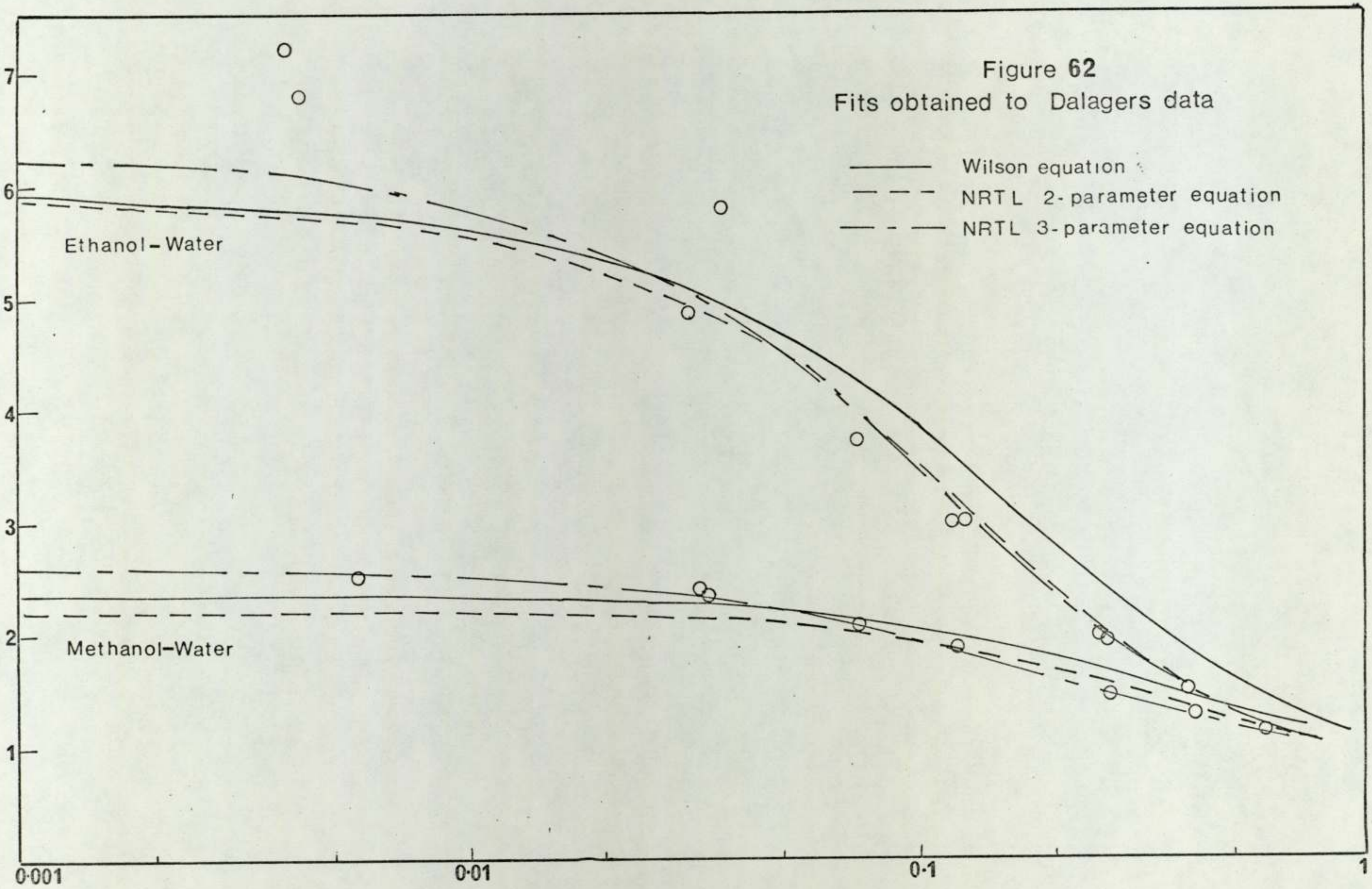


Figure 62
Fits obtained to Dalagers data

set by Renon. The NRTL equation in this form was being allowed to operate as a purely 3 parameter fitting equation in a similar manner to for example, the Redlich-Kister expansion.

The behaviour of the 3 parameter NRTL equation with α restricted within it's limiting values can be gauged from Table 4 . This table shows the results obtained when the correlations cited were fitted to part of the data obtained in this work. Each data set consisted of thirty unscreened values taken from all the runs performed at the one temperature. The sum of least squares values are based on the pressures, and were calculated from

$$\left[\frac{P_{exp} - P_{calc}}{P_{exp}}\right]^2$$

The results cannot be used to consider the performance of any one correlation for different temperatures or systems as the accuracy within each data set is different.

The results obtained for the NRTL equation show little or no difference between the two forms. This indicates that the improvement in fit of Dalagers data by the 3 parameter NRTL equation can be attributed to allowing the α value to obtain an unconstrained optimised value.

From the table 4 , the Redlich-Kister 3 and 4 parameter expansions appear to be vastly superior to the Wilson and NRTL equations. This however, is a characteristic of the data, which is illustrated on

T A B L E : 4

SYSTEM	TEMPERATURE °C.	Sum of Least Squares					
		WILSON	NRTL		Redlich-Kister Expansion		
			fixed	optimised	2 parameters	3 parameters	4 parameters
METHANOL	25	0.1271	0.1450	0.1450	2.9940	0.5862	0.0240
WATER	55	0.1412	0.1482	0.1384	0.0439	0.0395	0.0365
ETHANOL	25	0.0770	0.0732	0.0732	0.0791	0.0719	0.0726
WATER	45	0.1089	0.1167	0.1167	0.1221	0.1108	0.0956
	55	0.1699	1.2888	0.9664	0.2121	0.1893	0.1461

Figure 63. The Redlich-Kister expansions produce low error values because they manage to describe the whole data set, including those values obviously incorrect and which would have been removed by screening. In contrast the Wilson and NRTL equations produce fits very similar to that which is produced by screening. This leads to the possibility of using either of these two equations within or instead of the screening process described earlier.

The least squares values produced by these two correlations do not differ markedly, and more reliable data is required before conclusions on the superiority of either in this respect can be drawn. Figure 63 again shows the deterioration in fit of both correlations approaching the middle concentration range.

This cursory investigation of the fitting characteristics at low concentrations shows that for the systems chosen, the best fit is usually produced by the NRTL equation with α being allowed to find it's optimum value without any limits. This is especially the case when the data is to be extrapolated to higher mole fractions.

7.4 Suggestions for Further Improvements to Apparatus

The results discussed and analysed in this work were calculated using the procedure referred to as Method A. This involves some assumption regarding the vapour phase. The alternative method using data from corresponding runs has the advantage that no such assumption is necessary. This method is therefore the more desirable of the two. This method was not used because of the insufficient accuracy acquired in the measurement of the cell liquid volume. It is considered preferable

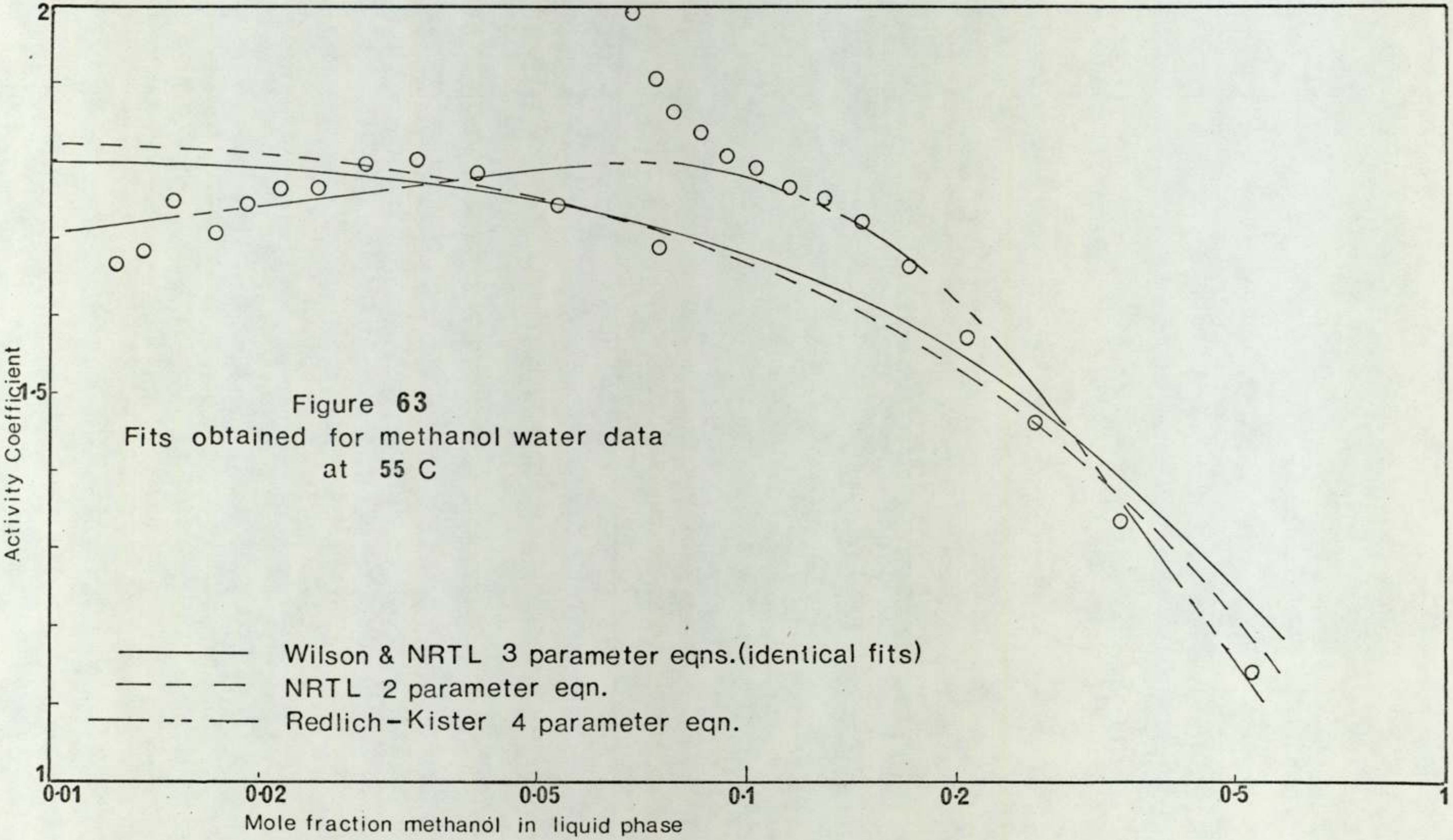


Figure 63
Fits obtained for methanol water data at 55 C

for the dimensions of the equilibrium cell to be varied for the two methods. Method A, where the total pressure is the main criterion governing the accuracy of the data, requires the equilibrium cell to have a high a diameter/height ratio as practical. The larger the diameter of the cell, the larger is the active diameter of the diaphragm and hence the more sensitive is the pressure measurement.

For the alternative method obtaining a high accuracy in the cell liquid volume measurement, requires a smaller diameter equilibrium cell. The total pressure measurement being of less significance.

8.0 GENERAL CONCLUSION

The work described in this thesis was undertaken to develop a technique for the rapid determination of isothermal vapour-liquid equilibrium data. The apparatus constructed requires certain modifications but the results obtained show the feasibility of the technique.

The results acquired on the binary mixtures methanol-water, ethanol-water demonstrate the technique to be superior to existing isothermal techniques in

(a) It's rapidity; producing more than 30 data points in one experimental run

(b) It's ability to produce data at low concentrations

The full composition range to infinite dilution at both ends of the binary should be covered adequately by 4 experimental runs.

The work demonstrates that for the systems investigated, at infinite dilution the K-value and activity coefficient behave in the manner predicted by Henry's Law. Infinite dilution is shown to be at lower concentrations than that normally taken by extrapolating existing data. This infinite dilution concentration is also demonstrated to be dependent on both the binary components and the temperature.

Fitting of activity coefficient correlations to the data shows that even the more powerful equations cannot completely predict the low concentration behaviour. The best fit is obtained by the NRTL equation with the third parameter α being optimised. This optimised value of α is however, usually outside the limits set by it's physical interpretation.

The modified apparatus should prove valuable in providing the copious data required at low concentrations for a physical interpretation of the behaviour of the forces involved.

APPENDIX 1.0

RAW DATA

A.1.1 SYSTEM:- METHANOL (1) - WATER (2)

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
Temperature 25.074°C.		
Methanol Charge 4.84 cm^3		
2.025	81.50	6.70
3.04	72.56	7.71
4.05	66.78	8.62
5.11	61.92	9.77
6.135	58.51	10.70
7.145	54.52	11.79
8.155	51.72	12.855
9.155	49.29	13.79
10.165	47.69	14.90
11.19	45.85	15.82
12.22	44.51	16.83
13.23	43.21	17.845
14.26	42.04	18.82
15.265	40.83	19.87
16.285	39.82	20.81
17.315	38.90	21.91
18.355	38.08	22.86
19.365	37.29	23.945
20.465	36.69	24.07
21.465	35.97	26.03
22.475	35.37	27.03
23.485	34.98	28.04
24.505	34.40	29.06
26.105	33.87	30.65
27.545	33.29	32.05

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
29.01	32.80	33.53
30.585	32.31	35.15
32.085	31.87	36.59
33.645	31.66	38.19
35.195	31.27	39.69
36.720	31.41	41.20
Methanol Charge 0.77cm^3		
3.995	35.28	4.37
5.005	32.19	5.34
6.025	31.13	6.375
7.05	29.79	7.41
8.08	28.81	8.50
9.04	28.27	9.435
10.055	27.74	10.53
11.06	27.38	11.49
12.075	27.06	12.47
13.075	26.78	13.53
14.08	26.55	14.55
15.10	26.33	15.71
16.11	26.14	16.615
17.13	25.98	17.65
18.14	25.87	18.61
20.145	25.57	20.71
22.165	25.34	22.88
24.225	25.16	24.855
26.265	25.03	26.97
Methanol Charge 0.1cm^3		
3.885	25.58	3.92
4.885	25.00	4.89
5.885	24.80	5.70
6.885	24.63	6.81
7.925	24.54	7.70
9.945	24.33	9.89
10.975	24.21	10.86

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
12.52	24.18	12.43
14.08	24.09	14.10
16.13	24.07	15.98
18.16	24.10	18.16
Temperature 35.103°C		
Methanol Charge 3.24 cm^3		
2.06	126.52	4.56
3.06	109.37	5.58
4.08	102.05	6.70
5.15	93.78	7.70
6.155	89.01	8.73
7.19	83.61	9.78
8.21	80.35	10.815
9.225	76.70	11.85
10.435	73.83	13.07
11.435	71.48	14.10
12.435	69.28	15.12
13.445	67.56	16.14
14.465	65.98	17.17
15.475	64.21	18.40
16.475	63.12	19.22
17.435	62.10	20.20
18.455	61.43	21.42
19.55	60.09	22.35
20.59	59.31	23.41
21.64	59.00	24.63
22.655	57.98	25.505
23.78	57.41	26.65
24.84	57.12	27.67
25.83	56.27	28.73
26.85	56.11	29.77
27.85	55.53	30.79
29.40	54.41	32.36
30.91	53.92	33.96

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
32.43	53.15	35.44
33.95	53.14	36.99
35.25	52.46	38.31
36.96	52.04	40.04
38.16	52.76	41.36
<u>Methanol Charge 0.78 cm^3</u>		
4.38	62.25	4.79
5.38	57.79	5.78
6.38	55.57	6.76
7.39	54.19	7.78
8.39	53.10	8.75
9.395	51.84	9.75
10.395	50.97	10.77
11.405	50.30	11.79
12.405	49.69	13.03
13.405	49.06	13.78
14.415	48.48	14.795
15.415	48.14	15.78
16.435	47.68	16.95
17.435	47.44	18.145
18.45	47.01	19.01
19.45	46.78	19.97
20.495	46.53	20.75
21.505	46.34	22.40
22.51	46.11	22.95
23.53	45.90	24.08
25.54	45.83	26.285
26.55	45.51	27.10
28.05	45.38	28.54
29.59	45.32	30.45
31.60	45.07	32.20
33.62	45.17	34.505
35.63	45.91	36.28
38.66	44.83	39.65

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
Methanol Charge 0.10 cm^3		
4.405	45.75	4.425
5.305	44.88	5.22
6.305	44.04	6.185
7.305	43.68	7.18
8.305	43.52	8.17
9.29	43.40	9.27
10.29	43.13	10.28
11.305	43.15	11.29
12.305	43.11	12.38
13.835	43.01	13.89
15.435	42.70	15.51
16.95	42.89	17.01
18.57	42.99	18.64
20.63	42.78	20.69
22.89	42.73	22.98
25.355	42.69	25.79
27.385	42.67	27.47
29.435	42.62	29.53
31.44	42.75	31.53
Temperature 45.052°C.		
Methanol Charge 4.65cm^3		
1.025	257.62	5.25
2.025	225.31	6.20
3.025	205.77	7.19
4.015	192.53	8.05
5.015	180.25	9.04
6.025	172.18	10.09
7.025	164.08	11.08
8.035	156.03	12.16
9.035	150.37	13.15
10.055	144.36	14.20
11.075	140.85	15.21
12.095	135.42	16.24

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
13.165	131.04	17.36
14.175	128.19	18.38
15.185	124.91	19.60
16.185	122.80	20.60
17.23	121.88	21.65
18.25	118.41	22.68
19.27	116.49	23.73
20.28	115.24	24.77
21.30	112.80	25.79
22.34	111.51	26.76
23.34	110.99	27.75
24.36	108.69	28.78
25.36	107.62	29.79
26.38	106.38	30.83
27.39	105.57	31.86
28.425	104.50	32.90
29.435	103.86	34.00
30.945	102.42	35.52
32.465	101.34	37.08
33.975	100.18	38.63
35.49	99.85	40.20
Methanol Charge 0.81 cm^3		
3.71	116.45	3.91
5.71	102.43	6.00
6.73	98.68	7.01
7.74	95.44	8.01
8.76	93.37	9.02
9.77	91.78	10.03
10.79	90.01	11.06
11.805	88.77	12.17
12.81	87.42	13.19
13.825	86.43	14.24
14.835	85.44	15.33
15.85	84.77	16.38

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
16.88	84.08	17.42
17.90	83.52	18.48
18.92	83.08	19.57
19.95	82.57	20.55
20.97	82.30	21.56
21.98	81.80	22.58
23.00	81.52	23.58
24.01	81.22	24.57
25.04	80.96	25.67
26.055	80.70	26.69
27.065	80.65	27.79
29.095	80.16	29.85
31.105	80.16	31.90
33.11	79.67	33.74
35.01	79.47	35.69
37.05	79.28	37.70
39.065	79.10	39.08
Methanol Charge 0.13cm^3		
5.005	79.02	4.575
6.005	76.85	5.56
7.015	76.30	6.51
8.025	75.66	7.52
9.03	75.26	8.54
10.055	74.87	9.63
11.065	74.59	10.69
12.065	74.47	11.74
13.085	74.29	12.80
14.085	74.02	13.83
15.095	73.97	14.87
16.115	73.88	15.85
17.115	73.80	16.89
18.115	73.68	17.91
19.125	73.59	18.93
20.125	73.53	19.94

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
21.135	73.44	20.97
22.135	73.43	22.01
23.145	73.36	23.05
24.665	73.17	24.66
26.185	73.07	26.17
27.695	72.97	27.65
29.195	72.88	29.20
30.705	72.80	30.72
Temperature 54.937°C.		
Methanol Charge 4.82 cm^3		
0.98	408.76	4.29
1.95	354.93	5.36
2.95	332.35	6.33
3.92	310.81	7.38
4.92	292.58	8.30
5.94	278.64	9.32
6.965	268.73	10.35
7.975	258.16	11.38
8.995	249.20	12.49
9.995	243.21	13.37
11.01	236.19	14.82
12.02	229.47	16.17
13.04	223.51	16.86
14.06	217.48	18.05
15.07	211.81	19.58
16.09	207.16	20.17
17.09	202.92	21.19
18.10	199.55	22.81
19.12	195.96	23.30
20.13	192.80	24.36
21.14	191.07	25.77
22.16	187.89	26.52
23.16	185.78	27.55
24.19	183.61	28.62

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
25.20	181.96	29.66
26.22	180.31	30.71
27.24	178.85	31.82
28.26	179.33	32.94
29.78	175.84	34.56
31.32	174.21	36.04
33.32	172.72	38.18
35.32	171.64	40.22
Methanol Charge 0.845 cm^3		
3.435	193.75	3.63
4.445	173.63	4.61
5.455	165.08	5.60
6.455	158.64	6.61
7.455	154.20	7.61
8.495	150.27	8.68
9.505	146.53	9.83
10.505	144.66	10.81
11.515	142.35	11.86
12.525	140.44	12.91
13.535	138.57	13.98
14.635	136.91	15.01
15.685	135.66	16.08
16.69	134.63	17.11
17.71	133.58	18.19
18.71	132.71	19.21
19.72	132.16	20.20
20.74	130.96	21.26
21.74	130.47	22.27
23.76	129.68	24.305
24.78	128.91	25.35
26.31	128.10	26.96
27.87	128.02	28.59
28.91	127.11	29.69
30.48	126.52	31.24

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
32.04	126.65	32.82
34.09	125.67	31.87
36.115	125.66	36.95
Methanol Charge 0.12 cm^3		
5.35	125.20	4.905
6.36	124.14	5.93
7.37	123.17	6.96
8.395	122.19	7.91
9.40	122.03	8.93
10.41	121.77	10.00
11.41	121.51	11.02
12.425	121.20	12.11
13.485	121.04	13.18
14.495	120.95	14.37
15.515	120.71	15.32
16.515	120.53	16.31
17.525	120.45	17.35
19.045	120.16	18.87
20.575	119.68	20.375
22.17	119.71	21.89
23.69	119.51	23.49
25.20	119.32	25.03
26.71	119.12	26.71
28.745	119.25	28.89
31.785	119.11	31.79

A1.2 ETHANOL (1) - WATER (2)

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
Temperature 25.071°C.		
Methanol Charge 2.320 cm^3		
3.77	49.06	5.79
4.97	42.20	6.82
6.07	39.98	7.98
7.07	37.95	8.99
8.07	36.72	10.02
9.075	35.73	10.91
10.075	34.77	11.81
11.095	34.16	13.08
12.415	33.39	14.34
13.425	32.90	15.41
14.425	32.35	16.40
15.675	32.01	17.64
16.575	31.77	18.58
17.605	31.40	19.63
18.635	30.75	20.49
19.535	30.97	21.58
20.555	30.67	22.32
21.565	30.41	23.63
22.585	30.29	24.82
24.095	29.96	26.25
25.615	29.83	27.58
27.635	29.76	29.67
29.725	29.74	31.83
31.705	29.32	33.98
33.705	29.29	35.82

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
Ethanol Charge 0.46 cm^3		
4.29	35.43	4.51
5.29	33.76	5.33
5.30	31.80	6.31
7.30	29.99	7.34
8.25	28.74	8.33
9.27	32.75	9.36
10.30	26.96	10.41
12.66	26.04	12.85
13.31	25.84	13.45
14.32	25.63	14.48
15.32	25.47	15.51
16.34	25.32	16.55
17.36	25.20	17.61
19.34	25.07	19.69
21.34	24.99	21.77
23.54	24.95	23.99
25.91	25.05	26.47
27.45	24.95	27.95
28.98	24.92	29.52
Ethanol Charge 0.10 cm^3		
3.06	26.03	3.01
4.06	25.60	4.00
5.08	25.34	4.98
6.08	25.15	5.87
7.09	25.02	6.91
8.11	24.92	7.96
9.12	24.80	8.95
10.14	24.78	10.05
11.16	24.73	11.15
12.17	24.71	12.17
13.18	24.68	13.18
14.01	24.67	14.035

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
15.215	24.64	15.21
16.23	24.62	16.26
17.25	24.61	17.29
Temperature 35.112°C.		
Ethanol Charge 2.995 cm^3		
1.02	95.52	3.28
2.05	90.60	4.30
3.08	85.32	5.46
4.10	82.03	6.44
5.13	79.15	7.49
6.165	77.30	8.59
7.18	74.02	9.60
8.21	71.83	10.63
9.205	70.36	11.66
10.215	68.19	12.66
11.235	66.61	13.63
12.245	65.25	14.645
13.245	64.16	15.67
14.255	63.17	16.70
15.255	62.25	17.72
16.265	61.28	18.73
17.285	60.48	19.77
18.295	59.70	20.875
19.305	59.16	21.905
20.38	58.47	22.98
21.39	57.78	24.02
22.40	57.29	25.09
23.40	56.79	26.11
24.42	56.31	27.235
25.43	55.92	28.23
26.44	55.55	29.28
27.44	55.37	30.28
28.46	54.97	31.28
29.48	54.75	32.29

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
30.485	54.48	33.27
31.995	54.17	34.82
33.525	54.00	36.395
35.035	53.72	37.91
36.595	53.47	39.46
Ethanol Charge 0.205 cm^3		
3.06	50.20	2.98
4.06	48.47	4.01
5.06	47.02	5.01
6.07	46.36	6.04
7.08	45.89	7.06
8.07	45.40	8.08
9.07	45.16	9.06
10.09	44.88	10.20
11.09	44.69	11.23
12.10	44.47	12.12
13.13	44.33	13.19
14.14	44.15	14.24
15.14	44.04	15.21
16.16	43.94	16.23
17.17	43.85	17.295
18.18	43.77	18.29
19.18	43.69	19.30
20.20	43.63	20.32
21.73	43.56	21.85
23.24	43.54	23.37
24.75	43.45	24.92
26.265	43.46	26.455
Temperature 45.047°C.		
Ethanol Charge 2.58 cm^3		
2.04	153.93	3.61
4.19	151.01	5.94
5.19	137.08	6.70
6.21	132.56	7.73

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
7.22	128.34	8.76
8.24	125.01	9.79
9.25	121.93	10.84
10.27	118.55	11.95
11.29	116.03	12.99
12.32	114.00	14.01
13.39	111.47	15.10
14.42	110.30	16.18
15.78	107.57	17.58
16.80	106.40	18.70
17.82	105.31	19.79
18.84	104.43	20.83
19.90	102.98	21.85
20.94	102.00	23.01
21.97	100.92	23.85
23.00	100.19	24.86
24.01	99.45	25.90
25.04	99.65	27.35
26.06	97.71	27.361
27.17	97.62	29.45
28.23	96.61	30.55
29.29	96.11	31.75
30.31	95.84	32.79
31.33	95.46	33.85
33.34	95.16	35.91
Ethanol Charge 0.18 cm^3		
3.855	83.44	3.665
4.86	81.16	4.61
5.88	80.08	5.64
6.88	79.30	6.66
7.90	78.62	7.69
8.91	78.13	8.71
9.97	77.65	9.78
11.49	77.16	11.31
13.025	76.74	12.92

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
14.53	76.51	14.35
16.08	76.31	16.09
17.61	76.05	17.64
20.115	75.90	20.24
21.645	75.67	21.75
24.195	75.54	24.61
26.24	75.41	26.40
28.27	75.37	28.42
Temperature 54.796°C. Ethanol Charge 3.91 cm^3		
1.025	264.94	4.21
2.06	253.91	5.18
3.08	244.95	6.19
4.09	236.40	7.21
5.105	230.89	8.24
6.125	225.16	9.25
7.125	220.48	10.27
8.15	216.12	11.31
9.16	211.60	12.35
10.18	206.89	13.39
11.18	203.11	14.40
12.205	198.89	15.475
13.205	195.43	16.49
14.225	192.18	17.53
15.245	189.58	18.57
16.255	186.60	19.60
17.265	184.31	20.64
18.265	182.12	21.69
19.265	179.96	22.67
20.285	178.09	23.69
21.295	176.37	24.70
22.30	174.65	25.72
23.88	172.28	27.41

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
25.53	169.71	29.16
27.73	166.88	31.47
29.835	164.28	33.42
31.94	162.27	35.60
34.02	160.24	37.74
35.615	159.06	39.38
Ethanol Charge 1.005 cm^3		
3.05	196.56	3.61
4.06	186.02	4.52
5.06	175.19	5.40
6.08	168.94	6.47
7.095	163.12	7.60
8.14	157.96	8.61
9.16	155.14	9.66
10.19	151.87	10.67
11.215	149.78	11.66
12.24	147.56	12.73
13.27	145.96	13.82
14.27	144.28	14.82
15.29	142.87	15.94
16.295	141.85	16.97
17.30	140.82	17.99
18.33	139.94	18.95
19.34	138.87	19.96
20.85	137.80	21.56
22.37	136.93	23.29
23.91	135.79	24.89
25.44	134.88	26.19
26.96	134.23	27.73
28.50	133.57	29.37
30.05	132.82	30.94
31.75	132.29	32.35
33.075	131.98	33.86
34.605	131.59	35.50

Volume Water added cm^3	Cell Pressure mmHg.	Cell Liquid volume cm^3
36.095	131.09	37.03
37.655	130.79	38.66
Ethanol Charge 0.2 cm^3		
4.115	139.79	3.935
5.18	136.80	4.98
6.20	134.57	6.02
7.25	132.96	7.05
8.28	131.93	8.08
9.30	131.01	9.11
10.305	130.52	10.12
11.305	129.83	11.15
12.325	129.34	12.24
13.335	128.80	13.31
14.845	128.42	14.87
16.415	127.93	16.43
17.93	127.56	17.95
19.48	126.76	19.54
21.07	127.02	21.21
22.59	126.65	22.81
24.09	126.49	24.20
25.62	126.41	25.75
27.14	126.16	27.28
28.67	126.09	28.82
30.15	125.83	30.14
31.685	125.77	31.67
33.215	125.75	33.21
34.735	126.09	34.74

A1.3 WATER (1) - METHANOL (2)

Volume Methanol added	Cell Pressure mmHg.	Cell Liquid volume
Temperature 25.060°C.		
Water Charge 0.995		
3.015	91.03	34.49
4.01	95.62	4.59
5.00	99.58	5.60
6.00	102.83	6.57
7.015	105.27	7.58
8.025	107.44	8.60
9.045	109.28	9.62
10.055	111.41	10.63
11.08	112.59	11.65
12.12	113.80	12.67
13.18	115.03	13.67
14.18	116.01	14.70
15.19	116.61	15.67
16.18	117.35	16.70
17.18	118.14	17.71
19.185	119.70	19.73
20.695	120.38	21.25
22.205	121.21	22.78
23.715	121.74	24.31
26.195	122.75	26.91
Temperature 35.104°C.		
Water Charge 0.960		
2.99	155.87	3.66
3.99	163.50	4.61
4.99	170.35	5.62
6.00	174.79	6.64
7.01	179.32	7.71
8.03	182.87	8.70
9.03	184.93	9.71

Volume Methanol added	Cell Pressure mmHg.	Cell Liquid volume
10.03	187.58	10.72
11.04	189.47	11.74
12.03	191.11	12.75
13.04	192.58	13.78
14.04	193.81	14.81
15.04	195.31	15.82
16.05	196.10	16.83
17.66	198.17	18.45
19.19	198.79	19.99
20.76	200.21	21.50
22.27	200.75	23.06
23.77	201.88	24.67
25.29	202.41	26.17
26.80	203.44	27.70
28.35	203.61	29.24
29.81	204.11	30.71
31.32	204.58	31.41
32.85	205.20	33.73
34.36	205.40	35.27
35.88	205.79	36.74
<u>Water Charge 0.105</u>		
3.13	209.25	2.64
4.14	209.98	3.71
5.49	210.86	5.06
6.50	211.17	6.10
7.50	211.65	7.14
8.51	211.84	8.20
9.54	208.99	10.01
10.54	209.50	11.03
11.56	210.23	12.02
12.57	210.58	13.07
13.59	210.13	14.11
15.10	211.62	15.63
16.62	212.13	17.22

Volume Methanol added	Cell Pressure mmHg.	Cell Liquid volume
17.13	212.21	18.73
19.65	212.92	20.20
21.17	213.12	21.71
22.68	213.54	23.48
25.71	215.25	26.60
28.72	216.58	29.60
Temperature 45.060°C.		
Water Charge 1.005		
2.97	249.04	3.49
3.95	263.40	4.48
4.95	272.88	5.50
5.90	279.81	6.69
6.91	287.05	7.50
7.90	290.87	8.51
8.86	295.51	9.48
9.83	298.21	10.50
10.82	302.61	11.60
11.82	304.75	12.61
12.87	307.83	13.64
13.84	309.63	14.67
14.84	311.81	15.68
15.86	313.83	16.68
16.86	311.37	17.68
18.02	314.29	18.87
20.07	316.72	20.98
22.06	319.45	23.06
24.10	322.01	25.08
26.13	323.85	27.275
28.17	324.93	29.28
Water Charge 0.110		
3.00	323.49	2.58
5.01	330.97	4.59
6.01	332.21	5.68
7.01	333.17	6.91

Volume Methanol added	Cell Pressure mmHg.	Cell Liquid volume
8.01	334.17	7.97
9.07	334.78	8.99
10.08	335.12	10.01
11.09	335.13	11.10
12.09	335.79	12.10
13.09	336.11	13.08
14.10	336.30	14.13
15.13	336.56	15.18
16.14	336.68	16.19
17.15	336.84	17.34
19.19	335.07	19.50

A1.4 WATER (1) - ETHANOL (2)

Volume Ethanol added	Cell Pressure mmHg.	Cell Liquid volume
Temperature 25.057°C.		
Water Charge 2.010		
1.01	38.76	2.34
2.04	42.48	3.39
3.07	44.91	4.43
4.08	45.81	5.48
5.10	46.74	6.52
6.12	47.27	7.61
7.14	48.07	8.65
8.16	48.59	9.63
9.18	49.22	10.52
10.19	49.48	11.53
11.20	49.87	12.55
12.21	50.36	13.56
13.23	50.54	14.58
14.25	50.82	15.61
15.27	51.01	16.67
16.78	51.43	18.18
18.32	51.70	19.71
19.84	52.12	21.23
21.38	52.43	22.81
22.90	52.72	24.34
24.37	53.00	25.79
25.89	53.28	27.32
27.43	53.49	28.90
28.95	53.85	30.43
30.49	54.09	32.06
32.00	54.42	33.61
33.53	54.79	35.08
35.04	54.98	36.60
36.54	55.40	38.11

Volume Ethanol added	Cell Pressure mmHg.	Cell Liquid volume
Temperature 25.057°C. Water Charge 0.205		
3.97	59.72	3.73
4.98	60.28	4.78
6.01	60.71	5.83
7.01	61.03	6.89
8.01	61.38	8.03
9.03	61.61	8.99
10.055	61.80	9.975
11.055	62.09	10.99
12.075	62.34	12.03
13.08	32.51	13.07
14.07	62.66	14.10
15.09	62.91	15.15
16.09	63.11	16.23
17.13	63.42	17.25
18.64	63.60	18.83
20.16	63.95	20.36
21.67	64.08	21.90
23.15	64.46	23.40
24.65	64.68	24.91
26.175	64.96	26.64
27.685	65.17	28.15
29.215	65.46	29.57
30.715	65.68	31.07
32.235	66.01	32.60
33.745	66.28	34.11
35.265	66.61	35.71
Temperature 35.104°C. Water Charge 1.395		
3.035	94.88	3.84
4.05	96.61	4.86
5.16	98.52	5.91
6.16	99.66	6.93
7.18	100.60	7.95

Volume Ethanol added	Cell Pressure mmHg.	Cell Liquid volume
8.18	101.35	8.99
9.18	102.09	10.00
10.19	102.68	11.01
11.20	103.47	11.99
12.20	103.72	13.02
13.21	104.20	14.04
14.22	104.56	15.12
15.23	105.06	16.18
16.25	105.44	17.23
17.255	105.89	18.31
18.78	106.32	19.28
20.245	106.82	21.29
21.755	107.20	22.80
23.255	107.80	24.35
24.765	108.04	25.88
26.315	108.52	27.53
27.825	108.87	29.07
29.335	109.39	30.60
30.845	109.75	32.11
32.375	110.20	33.61
33.885	110.57	35.11
35.395	111.04	36.72
36.895	111.43	38.23
38.425	112.05	39.86
<u>Water Charge 0.205</u>		
4.02	103.64	3.78
5.03	104.20	4.83
6.04	104.40	5.93
7.04	104.50	6.92
8.05	104.59	7.94
9.05	104.59	8.94
10.07	104.57	9.96
11.09	104.55	10.95
12.09	104.54	11.93

Volume Ethanol added	Cell Pressure mmHg.	Cell Liquid volume
13.10	104.58	12.98
14.11	104.82	14.14
15.12	104.88	15.17
16.12	104.98	16.15
17.13	105.08	17.15
20.15	105.58	20.29
22.20	105.86	22.49
Temperature 45.062°C.		
Water Charge 1.570		
2.975	157.26	4.00
4.015	161.01	5.10
5.035	163.70	6.15
6.02	165.47	7.10
7.02	167.15	8.08
8.02	168.41	9.10
9.01	169.96	10.15
10.01	170.92	11.17
11.005	171.66	12.17
12.01	172.58	13.23
12.97	172.82	14.58
13.97	173.80	15.47
14.93	174.23	16.57
15.91	174.67	17.67
16.905	174.70	18.75
17.935	174.72	19.69
18.935	174.72	19.69
19.925	175.40	21.63
20.925	175.75	22.65
21.925	176.00	23.97
22.92	176.34	24.67
23.93	176.75	25.69
24.95	176.91	26.72

Volume Ethanol added	Cell Pressure mmHg.	Cell Liquid volume
26.99	177.22	28.99
30.00	177.82	32.36
34.015	179.05	36.515
Water Charge 0.290		
3.30	172.82	3.09
4.34	173.88	4.23
5.37	174.95	5.41
6.40	175.34	6.49
7.48	175.82	7.67
8.44	176.10	8.85
9.44	176.47	9.97
10.47	176.68	10.98
11.48	177.00	12.00
12.49	177.18	13.05
13.49	177.35	14.06
14.50	177.56	15.10
15.50	177.78	16.22
16.50	177.70	17.25
17.54	177.69	18.32
19.54	177.15	20.34
21.59	178.07	22.39
24.59	178.26	25.56
26.09	178.42	27.08
27.59	178.91	28.59
30.605	178.94	31.78
33.64	179.38	34.80
36.575	179.74	37.73
Water Charge 0.060		
3.04	177.37	2.70
5.11	177.37	4.82
6.11	177.58	5.80
7.11	177.86	6.77
8.69	177.99	8.47
9.70	178.08	9.50

Volume Ethanol added	Cell Pressure mmHg.	Cell Liquid volume
10.74	178.21	10.51
11.75	178.30	11.57
12.77	178.58	12.68
14.79	178.84	14.76
16.80	179.39	16.95
17.80	179.54	18.01
19.83	180.29	20.14
22.83	180.79	23.36
25.88	182.10	26.44
28.90	183.25	29.56

APPENDIX 2.0

CALCULATED RESULTS

A2.1 METHANOL (1) - WATER (2)

X = Mole fraction liquid phase
Y = Mole fraction vapour phase
A = Activity coefficient

MOLE FRACTION X_1	VAPOUR PHASE			
	IDEAL		NON-IDEAL	
	Y_1	A_1	Y_1	A_1
Temperature 25.074°C.				
Methanol Charge 4.840 cm^3				
0.5143	0.8584	1.092	0.8697	1.117
0.4136	0.8080	1.132	0.8197	1.163
0.3462	0.7674	1.188	0.7787	1.214
0.2957	0.7298	1.1227	0.7403	1.252
0.2591	0.6992	1.267	0.7090	1.292
0.2310	0.6649	1.260	0.6737	1.283
0.2083	0.6364	1.268	0.6442	1.289
0.1899	0.6096	1.270	0.6165	1.290
0.1743	0.5887	1.293	0.5950	1.311
0.1609	0.5653	1.293	0.5708	1.310
0.1494	0.5460	1.306	0.5510	1.322
0.1396	0.5270	1.309	0.5313	1.324
0.1308	0.5089	1.312	0.5127	1.326
0.1233	0.4899	1.302	0.4932	1.314
0.1165	0.4729	1.298	0.4757	1.309
0.1103	0.4567	1.293	0.4590	1.302
0.1047	0.4415	1.289	0.4435	1.297
0.0998	0.4265	1.279	0.4281	1.286
0.0950	0.4140	1.284	0.4153	1.291

0.0909	0.3996	1.269	0.4006	1.274
0.0872	0.3870	1.260	0.3876	1.264
0.0838	0.3778	1.260	0.3783	1.270
0.0806	0.3651	1.251	0.3653	1.254
0.0760	0.3519	1.259	0.3520	1.261
0.0723	0.3380	1.249	0.3378	1.250
0.0689	0.3257	1.244	0.3253	1.244
0.0656	0.3130	1.237	0.3124	1.236
0.0627	0.3014	1.229	0.3006	1.227
0.0600	0.2947	1.248	0.2939	1.246
0.0575	0.2840	1.239	0.2830	1.236
0.0553	0.2855	1.303	0.2845	1.300
METHANOL CHARGE 0.770 cm^3				
0.0786	0.3796	1.367	0.3802	1.371
0.0638	0.3091	1.252	0.3085	1.250
0.0536	0.2778	1.295	0.2768	1.291
0.0462	0.2394	1.240	0.2380	1.233
0.0405	0.2089	1.192	0.2074	1.183
0.0364	0.1903	1.186	0.1887	1.177
0.0328	0.1718	1.165	0.1702	1.154
0.0299	0.1584	1.162	0.1568	1.151
0.0275	0.1463	1.155	0.1447	1.143
0.0255	0.1355	1.144	0.1340	1.132
0.0237	0.1265	1.138	0.1250	1.124
0.0221	0.1178	1.125	0.1163	1.111
0.0208	0.1101	1.113	0.1087	1.098
0.0195	0.1035	1.104	0.1022	1.090
0.0185	0.0987	1.109	0.0974	1.094
0.0167	0.0865	1.064	0.0853	1.049
0.0152	0.0768	1.029	0.0757	1.014
0.0139	0.0690	1.002	0.0679	0.986
0.0128	0.0631	0.988	0.0622	0.972
METHANOL CHARGE 0.100 cm^3				
0.0113	0.0818	1.491	0.0806	1.469
0.0090	0.0583	1.303	0.0574	1.282
0.0075	0.0493	1.313	0.0485	1.291
0.0064	0.417	1.289	0.0410	1.267

0.0056	0.0374	1.323	0.0368	1.300
0.0044	0.0280	1.230	0.0275	1.208
0.0040	0.0227	1.098	0.0223	1.078
0.0035	0.0210	1.157	0.0207	1.136
0.0031	0.0170	1.047	0.0167	1.028
0.0027	0.0158	1.112	0.0155	1.092
0.0024	0.0167	1.330	0.0164	1.303

TEMPERATURE 35.103°C.

METHANOL CHARGE 3.240 cm^3

0.4079	0.8026	1.210	0.8224	1.257
0.3170	0.7366	1.236	0.7548	1.279
0.2583	0.6935	1.332	0.7101	1.377
0.2163	0.6476	1.365	0.6618	1.406
0.1876	0.6151	1.419	0.6276	1.458
0.1651	0.5789	1.425	0.5893	1.460
0.1477	0.5526	1.462	0.5616	1.494
0.1336	0.5236	1.461	0.5310	1.490
0.1200	0.4973	1.488	0.5034	1.513
0.1107	0.4753	1.493	0.4803	1.515
0.1027	0.4538	1.488	0.4577	1.507
0.0957	0.4355	1.494	0.4387	1.511
0.0896	0.4181	1.497	0.4205	1.511
0.0842	0.3985	1.477	0.4002	1.488
0.0795	0.3850	1.485	0.3861	1.494
0.0755	0.3721	1.488	0.3728	1.495
0.0716	0.3626	1.512	0.3630	1.518
0.0679	0.3458	1.488	0.3458	1.492
0.0647	0.3349	1.493	0.3345	1.494
0.0617	0.3293	1.530	0.3287	1.531
0.0591	0.3156	1.505	0.3147	1.503
0.0565	0.3069	1.516	0.3057	1.513
0.0542	0.3017	1.545	0.3004	1.541
0.0523	0.2897	1.517	0.2881	1.511
0.0504	0.2862	1.550	0.2846	1.544
0.0486	0.2775	1.540	0.2757	1.532
0.0462	0.2607	1.493	0.2586	1.483
0.0440	0.2523	1.502	0.2501	1.490
0.0421	0.2399	1.474	0.2375	1.461
0.0403	0.2383	1.529	0.2359	1.516
0.0388	0.2273	1.493	0.2248	1.478

0.0371	0.2197	1.497	0.2171	1.481
0.0360	0.2294	1.637	0.2269	1.621
0.0255	0.1834	1.763	0.1806	1.738

METHANOL CHARGE 0.780 cm^3

0.0724	0.3715	1.554	0.3713	1.554
0.0598	0.3138	1.476	0.3124	1.470
0.0509	0.2797	1.485	0.2778	1.475
0.0443	0.2562	1.525	0.2540	1.513
0.0392	0.2369	1.560	0.2346	1.545
0.0352	0.2151	1.542	0.2127	1.525
0.0319	0.1990	1.546	0.1965	1.527
0.0292	0.1860	1.560	0.1836	1.540
0.0269	0.1741	1.565	0.1716	1.543
0.0249	0.1618	1.549	0.1594	1.525
0.0232	1.1503	1.526	0.1479	1.502
0.0217	0.1430	1.539	0.1407	1.514
0.0204	0.1336	1.516	0.1313	1.490
0.0193	0.1282	1.533	0.1260	1.507
0.0182	0.1192	1.494	0.1171	1.467
0.0173	0.1131	1.484	0.1111	1.457
0.0164	0.1085	1.493	0.1065	1.465
0.0157	0.1042	1.496	0.1022	1.467
0.0150	0.0991	1.481	0.0272	1.452
0.0144	0.0944	1.467	0.0925	1.438
0.0132	0.0920	1.547	0.0902	1.516
0.0127	0.0851	1.478	0.0834	1.447
0.0121	0.0819	1.496	0.0802	1.465
0.0115	0.0801	1.541	0.0784	1.508
0.0107	0.0743	1.517	0.0728	1.485
0.0101	0.0758	1.648	0.0742	1.613
0.0095	0.0901	2.111	0.0884	2.068
0.0088	0.0675	1.674	0.0661	1.638

METHANOL CHARGE 0.100 cm^3

0.0098	0.0872	1.974	0.0855	1.931
0.0082	0.0680	1.812	0.0666	1.771
0.0069	0.0490	1.519	0.0479	1.483
0.0060	0.0403	1.432	0.0393	1.397
0.0053	0.0360	1.451	0.0352	1.415

0.0047	0.0328	1.473	0.0321	1.436
0.0042	0.0263	1.300	0.0257	1.267
0.0039	0.0264	1.432	0.0258	1.396
0.0036	0.0252	1.485	0.0246	1.448
0.0032	0.0226	1.490	0.0220	1.452
0.0028	0.0151	1.107	0.0148	1.078
0.0026	0.0192	1.553	0.0188	1.513
0.0024	0.0213	1.887	0.0208	1.839
0.0021	0.0163	1.593	0.0159	1.551
0.0019	0.0149	1.617	0.0145	1.575
0.0017	0.0138	1.657	0.0135	1.614
0.0016	0.0132	1.712	0.0129	1.667
0.0016	0.0120	1.661	0.0117	1.618
0.0014	0.0149	2.213	0.0145	2.156

<u>TEMPERATURE 45.052°C</u>

<u>METHANOL CHARGE 4.650 cm^3</u>

0.6628	0.9059	1.074	0.9185	1.104
0.4990	0.8402	1.157	0.8555	1.192
0.4002	0.7905	1.239	0.8059	1.276
0.3347	0.7516	1.318	0.7662	1.356
0.2872	0.7158	1.370	0.7291	1.406
0.2512	0.6874	1.437	0.6996	1.473
0.2235	0.6599	1.477	0.6708	1.512
0.2011	0.6320	1.495	0.645	1.527
0.1829	0.6095	1.528	0.6178	1.557
0.1675	0.5855	1.539	0.5927	1.565
0.1545	0.5685	1.581	0.5749	1.606
0.1433	0.5453	1.571	0.5505	1.593
0.1333	0.5246	1.573	0.5288	1.592
0.1250	0.5094	1.593	0.5129	1.610
0.1170	0.4923	1.594	0.4950	1.608
0.112	0.4798	1.616	0.4820	1.629
0.1052	0.4723	1.669	0.4742	1.682
0.0999	0.4536	1.640	0.4548	1.649
0.0951	0.4417	1.650	0.4424	1.657
0.0908	0.4330	1.676	0.4334	1.682
0.0868	0.4182	1.656	0.4182	1.661
0.0831	0.4090	1.673	0.4086	1.676
0.0799	0.4042	1.713	0.4036	1.715

0.0768	0.3895	1.681	0.3885	1.681
0.0740	0.3816	1.693	0.3803	1.691
0.0713	0.3726	1.694	0.3711	1.691
0.0689	0.3661	1.711	0.3644	1.707
0.0665	0.3580	1.714	0.3561	1.709
0.0644	0.3526	1.734	0.3505	1.727
0.0615	0.3414	1.735	0.3391	1.726
0.0587	0.3324	1.749	0.3300	1.739
0.0563	0.3229	1.753	0.3203	1.741
0.0540	0.3191	1.799	0.3164	1.786
METHANOL CHARGE 0.810 cm^3				
0.0865	0.4360	1.795	0.4367	1.799
0.0580	0.3390	1.828	0.3367	1.816
0.0497	0.3078	1.866	0.3049	1.849
0.0435	0.2797	1.873	0.2764	1.850
0.0387	0.2600	1.917	0.2565	1.891
0.0348	0.2441	1.965	0.2405	1.935
0.0316	0.2267	1.970	0.2230	1.937
0.0290	0.2138	1.998	0.2101	1.962
0.0268	0.1999	1.991	0.1961	1.953
0.0249	0.1891	2.005	0.1854	1.965
0.0232	0.1783	2.002	0.1746	1.960
0.0218	0.1706	2.027	0.1670	1.983
0.0205	0.1627	2.039	0.1591	1.993
0.0193	0.1561	2.058	0.1526	2.011
0.0183	0.1507	2.087	0.1473	2.038
0.0174	0.1447	2.097	0.1413	2.047
0.0165	0.1411	2.142	0.1378	2.090
0.0158	0.1352	2.136	0.1319	2.083
0.0151	0.1317	2.167	0.1284	2.112
0.0145	0.1279	2.188	0.1247	2.132
0.0139	0.1246	2.214	0.1214	2.157
0.0134	0.1213	2.234	0.1182	2.176
0.0129	0.1203	2.299	0.1172	2.239
0.0120	0.1141	2.329	0.1111	2.266
0.0112	0.1134	2.472	0.1105	2.406
0.0105	0.1074	2.474	0.1045	2.406

0.0105	0.1074	2.474	0.1045	2.406
0.0100	0.1046	2.541	0.1018	2.471
0.0094	0.1020	2.613	0.0992	2.540
0.0090	0.0995	2.681	0.0968	2.605
METHANOL CHARGE 0.130 cm^3				
0.0111	0.1006	2.182	0.0978	2.116
0.0093	0.0735	1.852	0.0713	1.793
0.0080	0.0655	1.912	0.0636	1.850
0.0070	0.0567	1.873	0.0549	1.811
0.0062	0.0509	1.882	0.0493	1.819
0.0056	0.0454	1.855	0.0440	1.793
0.0051	0.0413	1.850	0.0400	1.787
0.0047	0.0394	1.918	0.0381	1.852
0.0043	0.0367	1.933	0.0355	1.866
0.0040	0.0329	1.857	0.0318	1.792
0.0037	0.0320	1.933	0.0309	1.866
0.0035	0.0306	1.939	0.0296	1.901
0.0033	0.0293	2.003	0.0284	1.933
0.0031	0.0276	1.990	0.0266	1.920
0.0029	0.0262	1.995	0.0253	1.925
0.0028	0.0253	2.022	0.0244	1.951
0.0027	0.0240	2.009	0.0231	1.938
0.0026	0.0237	2.082	0.0229	2.008
0.0024	0.0227	2.079	0.0219	2.005
0.0023	0.0200	1.947	0.0193	1.878
0.0022	0.0185	1.912	0.0179	1.844
0.0020	0.0171	1.860	0.0165	1.793
0.0019	0.0157	1.806	0.0152	1.742
0.0018	0.0146	1.756	0.0141	1.693
TEMPERATURE 54.937°C.				
METHANOL CHARGE 4.820 cm^3				
0.6782	0.9071	1.079	0.9222	1.117
0.5148	0.8386	1.141	0.8573	1.183
0.4124	0.7913	1.258	0.8103	1.305
0.3458	0.7515	1.333	0.7696	1.380
0.2965	0.7162	1.394	0.7326	1.441
0.2489	0.6860	1.457	0.7009	1.502

0.2296	0.6616	1.528	0.6750	1.572
0.2066	0.6372	1.571	0.6491	1.613
0.1876	0.6151	1.613	0.6256	1.652
0.1721	0.5981	1.668	0.6075	1.706
0.1588	0.5795	1.701	0.5877	1.736
0.1474	0.5614	1.724	0.5684	1.756
0.1375	0.5445	1.746	0.5503	1.775
0.1288	0.5271	1.756	0.5319	1.781
0.1213	0.5102	1.759	0.5140	1.780
0.1145	0.4954	1.769	0.4983	1.787
0.1085	0.4814	1.776	0.4835	1.792
0.1031	0.4694	1.793	0.4709	1.806
0.0981	0.4567	1.799	0.4575	1.810
0.0937	0.4451	1.807	0.4453	1.815
0.0896	0.4375	1.841	0.4375	1.847
0.0859	0.4256	1.838	0.4250	1.841
0.0825	0.4170	1.854	0.4160	1.855
0.0792	0.4080	1.866	0.4066	1.865
0.0763	0.4007	1.886	0.3990	1.883
0.0736	0.3935	1.903	0.3915	1.899
0.0710	0.3868	1.923	0.3846	1.917
0.0686	0.3869	1.995	0.3846	1.989
0.0654	0.3725	1.978	0.3698	1.968
0.0623	0.3646	2.011	0.3616	1.999
0.0588	0.3567	2.067	0.3535	2.053
0.0557	0.3505	2.132	0.3471	2.116
METHANOL CHARGE 0.845 cm^3				
0.0950	0.4486	1.806	0.4492	1.809
0.0753	0.3713	1.690	0.3687	1.678
0.0623	0.3294	1.723	0.3256	1,702
0.0532	0.2955	1.738	0.2908	1.710
0.0465	2.2700	1.769	0.2650	1.735
0.0410	0.2466	1.783	0.2414	1.743
0.0369	0.2241	1.758	0.2187	1.715
0.0335	0.2113	1.802	0.2059	1.754
0.0306	0.1961	1.798	0.1908	1.748
0.0283	0.1832	1.797	0.1779	1.744
0.0262	0.1704	1.778	0.1653	1.723
0.0243	0.1587	1.765	0.1537	1.708

0.0227	0.1496	1.763	0.1447	1.704
0.0214	0.1419	1.764	0.1372	1.703
0.0202	0.1341	1.752	0.1295	1.691
0.0191	0.1275	1.746	0.1230	1.683
0.0182	0.1230	1.766	0.1186	1.702
0.0173	0.1142	1.707	0.1100	1.643
0.0165	0.1101	1.718	0.1061	1.653
0.0151	0.1034	1.750	0.0996	1.683
0.0145	0.0975	1.709	0.0938	1.642
0.0137	0.0911	1.682	0.0875	1.615
0.0129	0.0898	1.755	0.0863	1.684
0.0125	0.0829	1.667	0.0795	1.598
0.0118	0.0780	1.645	0.0748	1.577
0.0113	0.0784	1.739	0.0752	1.667
0.0106	0.0706	1.652	0.0677	1.582
0.0100	0.0700	1.733	0.0671	1.659
METHANOL CHARGE 0.120 cm^3				
0.0095	0.0661	1.715	0.0633	1.637
0.0080	0.0567	1.729	0.0543	1.649
0.0069	0.0482	1.687	0.0461	1.608
0.0061	0.0398	1.569	0.0380	1.495
0.0055	0.0379	1.670	0.0362	1.590
0.0049	0.0353	1.719	0.0337	1.637
0.0045	0.0329	1.747	0.0314	1.663
0.0041	0.0300	1.732	0.0286	1.649
0.0038	0.0284	1.777	0.0271	1.691
0.0036	0.0274	1.842	0.0262	1.753
0.0033	0.0253	1.812	0.0241	1.724
0.0031	0.0236	1.799	0.0225	1.711
0.0029	0.0228	1.841	0.0217	1.751
0.0027	0.0202	1.768	0.0193	1.681
0.0025	0.0161	1.513	0.0153	1.438
0.0023	0.0162	1.637	0.0154	1.557
0.0022	0.0144	1.552	0.0137	1.476
0.0021	0.0127	1.453	0.0121	1.381
0.0019	0.0109	1.322	0.0104	1.257
0.0018	0.0118	1.548	0.0113	1.471
0.0016	0.0105	1.517	0.0100	1.441

A2.2 ETHANOL (1) - WATER (2)

TEMPERATURE 25.071°C.				
ETHANOL CHARGE 2.320				
0.1591	0.5928	3.092	0.6008	3.146
0.1256	0.5078	2.886	0.5123	2.922
0.1052	0.4684	3.009	0.4719	3.040
0.0917	0.4315	3.019	0.4339	3.043
0.0813	0.4057	3.099	0.4075	3.118
0.0730	0.3837	3.177	0.3849	3.193
0.0662	0.3620	3.216	0.3628	3.227
0.0605	0.3467	3.311	0.3471	3.320
0.0544	0.3273	3.396	0.3273	3.401
0.0505	0.3144	3.463	0.3143	3.465
0.0472	0.3003	3.482	0.2999	3.481
0.0436	0.2902	3.604	0.2897	3.601
0.0413	0.2832	3.682	0.2825	3.677
0.0390	0.2730	3.716	0.2722	3.709
0.0369	0.2560	3.605	0.2550	3.594
0.0353	0.2600	3.859	0.2591	3.849
0.0336	0.2515	3.882	0.2504	3.870
0.0321	0.2439	3.910	0.2428	3.896
0.0307	0.2398	4.005	0.2387	3.989
0.0288	0.2300	4.045	0.2287	4.026
0.0271	0.2253	4.187	0.2240	4.166
0.0252	0.2219	4.430	0.2206	4.407
0.0235	0.2077	4.712	0.2187	4.687
0.0220	0.1890	4.670	0.2063	4.642
ETHANOL CHARGE 0.460				
0.0319	0.3508	6.609	0.3514	6.620
0.0260	0.3146	6.916	0.3145	6.912
0.0219	0.2694	6.608	0.2685	6.586
0.0190	0.2226	5.953	0.2217	5.918
0.0169	0.1874	5.404	0.1859	5.360
0.0150	0.2855	10.543	0.2846	10.518
0.0136	0.1308	4.400	0.1294	4.350
0.0111	0.0978	3.895	0.0966	3.843

0.0105	0.0904	3.750	0.0892	3.699
0.0098	0.0822	3.639	0.0811	3.587
0.0092	0.0750	3.567	0.0748	3.515
0.0086	0.0690	3.481	0.0689	3.429
0.0081	0.0645	3.502	0.0644	3.448
0.0073	0.0593	3.459	0.0584	3.405
0.0066	0.0557	3.568	0.0548	3.511
0.0060	0.0536	3.779	0.0528	3.719
0.0054	0.0569	4.428	0.0560	4.358
0.0051	0.0528	4.336	0.0520	4.267
0.0049	0.0514	4.450	0.0506	4.379
ETHANOL CHARGE 0.100				
0.0099	0.0964	4.281	0.0952	4.218
0.0075	0.0790	4.561	0.0779	4.490
0.0050	0.0602	5.094	0.0593	5.010
0.0043	0.0547	5.358	0.0538	5.269
0.0038	0.0503	5.619	0.0496	5.524
0.0034	0.0454	5.661	0.0446	5.654
0.0030	0.0443	6.135	0.0435	6.029
0.0027	0.0421	6.401	0.0414	6.291
0.0025	0.0411	6.808	0.0404	6.690
0.0023	0.0397	7.120	0.0391	6.996
0.0022	0.0392	7.464	0.0386	7.334
0.0020	0.0379	7.818	0.0372	7.682
0.0019	0.0370	8.133	0.0363	7.991
0.0018	0.0365	8.522	0.0359	8.373
TEMPERATURE 35.112°C.				
ETHANOL CHARGE 2.995				
0.4722	0.7670	1.502	0.7817	1.544
0.3081	0.6779	1.930	0.6917	1.983
0.2287	0.6188	2.235	0.6305	2.291
0.1822	0.5796	2.526	0.5897	2.584
0.1512	0.5477	2.776	0.5564	2.834
0.1291	0.5249	3.043	0.5325	3.101
0.1129	0.4946	3.139	0.5008	3.191
0.1002	0.4717	3.274	0.4769	3.322

0.0904	0.4548	3.429	0.4593	3.474
0.0822	0.4324	3.474	0.4359	3.513
0.0753	0.4145	3.551	0.4174	3.586
0.0695	0.3986	3.623	0.4009	3.653
0.0646	0.3852	3.703	0.3870	3.730
0.0603	0.3727	3.779	0.3740	3.802
0.0566	0.3609	3.843	0.3619	3.863
0.0533	0.3485	3.881	0.3491	3.897
0.0503	0.3378	3.933	0.3381	3.945
0.0476	0.3272	3.970	0.3273	3.978
0.0453	0.3194	4.041	0.3194	4.048
0.0430	0.3097	4.079	0.3094	4.082
0.0410	0.3001	4.090	0.2995	4.089
0.0393	0.2928	4.136	0.2920	4.132
0.0377	0.2853	4.167	0.2845	4.161
0.0361	0.2781	4.196	0.2771	4.187
0.0348	0.2720	4.238	0.2709	4.226
0.0335	0.2662	4.278	0.2650	4.264
0.0323	0.2629	4.365	0.2616	4.350
0.0312	0.2567	4.383	0.2553	4.365
0.0301	0.2529	4.451	0.2515	4.431
0.0292	0.2485	4.495	0.2470	4.472
0.0278	0.2431	4.583	0.2415	4.558
0.0266	0.2398	4.715	0.2381	4.688
0.0255	0.2349	4.797	0.2333	4.768
0.0244	0.2305	4.889	0.2288	4.857
ETHANOL CHARGE 0.205				
0.0199	0.1766	4.313	0.1746	4.253
0.0151	0.1431	4.444	0.1410	4.371
0.0122	0.1140	4.262	0.1121	4.183
0.0102	0.0996	4.390	0.0978	4.305
0.0087	0.0890	4.523	0.0874	4.432
0.0077	0.0782	4.474	0.0767	4.379
0.0068	0.0725	4.633	0.0711	4.533
0.0062	0.0661	4.663	0.0647	4.561
0.0056	0.0616	4.753	0.0603	4.647
0.0051	0.0565	4.731	0.0553	4.624
0.0047	0.0532	4.810	0.0520	4.700
0.0044	0.490	4.751	0.0479	4.641

0.0041	0.0463	4.797	0.0453	4.685
0.0039	0.0439	4.840	0.0429	4.727
0.0036	0.0417	4.876	0.0408	4.761
0.0034	0.0398	4.912	0.0389	4.795
0.0033	0.0379	4.920	0.0370	4.802
0.0031	0.0364	4.971	0.0355	4.851
0.0029	0.0346	5.079	0.0338	4.956
0.0027	0.0340	5.331	0.0332	5.201
0.0025	0.0318	5.304	0.0311	5.175
0.0024	0.0319	5.643	0.0312	5.506

TEMPERATURE 45.047°C.

ETHANOL CHARGE 2.580

0.2763	0.6621	2.130	0.6789	2.202
0.1568	0.5987	3.330	0.6129	3.433
0.1307	0.5442	3.297	0.5546	3.379
0.1116	0.5183	3.554	0.5272	3.634
0.0976	0.4946	3.757	0.5020	3.831
0.0866	0.4748	3.960	0.4811	4.029
0.0779	0.4565	4.127	0.4616	4.191
0.0707	0.4366	4.227	0.4407	4.283
0.0648	0.4207	4.353	0.4240	4.402
0.0597	0.4072	4.492	0.4098	4.535
0.0552	0.3908	4.559	0.3927	4.593
0.0514	0.3819	4.729	0.3834	4.760
0.0472	0.3634	4.780	0.3641	4.801
0.0445	0.3546	4.896	0.3549	4.913
0.0421	0.3462	5.006	0.3462	5.018
0.0399	0.3392	5.130	0.3390	5.138
0.0378	0.3285	5.162	0.3279	5.164
0.0360	0.3208	5.243	0.3199	5.241
0.0344	0.3123	5.291	0.3112	5.283
0.0329	0.3063	5.383	0.3050	5.371
0.0316	0.3001	5.458	0.2987	5.442
0.0303	0.3006	5.706	0.2992	5.689
0.0292	0.2859	5.530	0.2841	5.504
0.0280	0.2844	5.722	0.2825	5.695
0.0270	0.2761	5.707	0.2741	5.674
0.0260	0.2717	5.789	0.2695	5.753
0.0252	0.2690	5.910	0.2668	5.870
0.0244	0.2655	6.000	0.2632	5.957
0.0230	0.2621	6.273	0.2597	6.227

ETHANOL CHARGE 0.180				
0.0138	0.1505	5.257	0.1475	5.127
0.0110	0.1242	5.288	0.1213	5.146
0.0091	0.1107	5.607	0.1080	5.450
0.0078	0.1008	5.900	0.0982	5.730
0.0068	0.0921	6.125	0.0896	5.944
0.0061	0.0857	6.379	0.0833	6.187
0.0054	0.0794	6.569	0.0772	6.368
0.0047	0.0729	6.896	0.0708	6.681
0.0042	0.0673	7.171	0.0654	6.944
0.0037	0.0641	7.589	0.0622	7.348
0.0034	0.0613	8.007	0.0595	7.750
0.0031	0.0579	8.237	0.0561	7.971
0.0027	0.0556	9.023	0.0539	8.729
0.0025	0.0526	9.144	0.0509	8.845
0.0022	0.0507	9.833	0.0491	9.510
0.0021	0.0489	10.263	0.0474	9.924
0.0019	0.0482	10.902	0.0467	10.542
TEMPERATURE 54.796°C. ETHANOL CHARGE 3.910				
0.5336	0.7922	1.405	0.8158	1.469
0.3629	0.7038	1.759	0.7273	1.841
0.2760	0.6511	2.064	0.6723	2.155
0.2231	0.6121	2.317	0.6308	2.411
0.1871	0.5844	2.576	0.6012	2.674
0.1610	0.5601	2.798	0.5751	2.897
0.1417	0.5404	3.005	0.5538	3.103
0.1261	0.5227	3.199	0.5346	3,297
0.1138	0.5056	3.357	0.5162	3.451
0.1036	0.4885	3.484	0.4977	3.573
0.0953	0.4742	3.611	0.4822	3.695
0.0880	0.4587	3.703	0.4656	3.781
0.0819	0.4454	3.797	0.4514	3.869
0.0765	0.4327	3.884	0.4378	3.950
0.0717	0.4220	3.983	0.4263	4.044
0.0676	0.4101	4.044	0.4137	4.098
0.0639	0.4004	4.125	0.4033	4.174
0.0606	0.3911	4.197	0.3934	4.240

0.0577	0.3819	4.256	0.3837	4.294
0.0549	0.3735	4.326	0.3749	4.358
0.0525	0.3658	4.392	0.3667	4.420
0.0502	0.3580	4.447	0.3585	4.469
0.0471	0.3470	4.537	0.3470	4.553
0.0442	0.3351	4.599	0.3345	4.606
0.0408	0.3215	4.695	0.3203	4.692
0.0381	0.3088	4.761	0.3070	4.748
0.0356	0.2984	4.854	0.2963	4.832
0.0335	0.2880	4.915	0.2855	4.886
0.0321	0.2816	4.987	0.2790	4.952
ETHANOL CHARGE 1.005				
0.0892	0.4608	3.679	0.4680	3.743
0.0687	0.4174	4.096	0.4215	4.141
0.0560	0.3730	4.227	0.3744	4.246
0.0471	0.3437	4.464	0.3435	4.465
0.0407	0.3157	4.583	0.3143	4.565
0.0357	0.2896	4.642	0.2873	4.606
0.0319	0.2738	4.828	0.2711	4.779
0.0288	0.2558	4.893	0.2526	4.830
0.0262	0.2435	5.038	0.2399	4.965
0.0241	0.2304	5.113	0.2266	5.028
0.0223	0.2205	5.236	0.2166	5.142
0.0207	0.2102	5.295	0.2062	5.192
0.0194	0.2013	5.371	0.1972	5.260
0.0182	0.1946	5.486	0.1905	5.367
0.0172	0.1879	5.574	0.1837	5.448
0.0162	0.1820	5.678	0.1778	5.545
0.0154	0.1750	5.710	0.1707	5.570
0.0143	0.1676	5.845	0.1634	5.695
0.0134	0.1615	5.997	0.1573	5.838
0.0125	0.1538	6.044	0.1496	5.878
0.0118	0.1474	6.118	0.1433	5.944
0.0111	0.1427	6.242	0.1386	6.060
0.0105	0.1380	6.342	0.1339	6.153
0.0100	0.1326	6.388	0.1287	6.193
0.0095	0.1288	6.485	0.1248	6.283
0.0091	0.1263	6.646	0.1224	6.437
0.0087	0.1234	6.768	0.1195	6.552
0.0083	0.1197	6.821	0.1159	6.600

0.0080	0.1174	6.958	0.1136	6.731
ETHANOL CHARGE 0.200				
0.0141	0.1793	6.431	0.1752	6.233
0.0113	0.1590	6.978	0.1548	6.748
0.0095	0.1435	7.381	0.1394	7.126
0.0081	0.1319	7.815	0.1280	7.536
0.0071	0.1243	8.233	0.1204	8.019
0.0064	0.1174	8.755	0.1137	8.430
0.0058	0.1136	9.335	0.1099	8.985
0.0053	0.1084	9.710	0.1048	9.341
0.0048	0.1047	10.168	0.1011	9.779
0.0045	0.1006	10.517	0.0971	10.110
0.0040	0.0975	11.305	0.0941	10.864
0.0036	0.0937	11.954	0.0904	11.484
0.0033	0.0908	12.604	0.0875	12.106
0.0031	0.0848	12.697	0.0817	12.187
0.0028	0.0865	14.027	0.0833	13.467
0.0026	0.0836	14.492	0.0806	13.910
0.0025	0.0823	15.185	0.0793	14.574
0.0023	0.0816	15.992	0.0786	15.348
0.0022	0.0797	16.496	0.0767	15.830
0.0021	0.0791	17.274	0.0761	16.576
0.0020	0.0771	17.662	0.0742	16.946
0.0019	0.0765	18.419	0.0736	17.671
0.0018	0.0763	19.242	0.0734	18.462
0.0017	0.0787	20.815	0.0758	19.978

A2.3 WATER (1) - METHANOL (2)

TEMPERATURE 25.060°C				
WATER CHARGE 0.995				
0.4130	0.1966	1.824	0.1817	1.685
0.3459	0.1477	1.719	0.1341	1.558
0.2978	0.1214	1.709	0.1089	1.529
0.2610	0.1047	1.735	0.0930	1.539
0.2320	0.0910	1.739	0.0803	1.530
0.2089	0.0826	1.788	0.0725	1.564
0.1898	0.0762	1.848	0.0666	1.609
0.1740	0.0763	2.056	0.0665	1.785
0.1605	0.0710	2.097	0.0616	1.814
0.1487	0.0680	2.191	0.0589	1.891
0.1384	0.0668	2.337	0.0578	2.013
0.1299	0.0656	2.464	0.0566	2.119
0.1223	0.0623	2.498	0.0536	2.143
0.1157	0.0611	2.610	0.0526	2.236
0.1097	0.0611	2.769	0.0525	2.370
0.0994	0.0626	3.173	0.0537	2.711
0.0928	0.0611	3.334	0.0523	2.845
0.0870	0.0616	3.609	0.0527	3.077
0.0819	0.0604	3.780	0.0517	3.218
0.0748	0.0609	4.208	0.0520	3.578
TEMPERATURE 35.104 °C				
WATER CHARGE 0.960				
0.4032	0.2125	1.948	0.1949	1.786
0.3360	0.1647	1.900	0.1480	1.706
0.2879	0.1402	1.967	0.1244	1.742
0.2516	0.1193	1.966	0.1047	1.720
0.2234	0.1092	2.079	0.0951	1.805
0.2007	0.1009	2.181	0.0874	1.882
0.1825	0.0907	2.180	0.0781	1.870
0.1673	0.0869	2.311	0.0745	1.974
0.1543	0.0820	2.386	0.0700	2.031
0.1434	0.0781	2.468	0.0665	2.094
0.1338	0.0749	2.555	0.0636	2.161
0.1255	0.0719	2.633	0.0609	2.222

0.1181	0.0713	2.794	0.0603	2.354
0.1115	0.0681	2.839	0.0575	2.386
0.1024	0.0683	3.136	0.0576	2.632
0.0950	0.0636	3.156	0.0534	2.640
0.0884	0.0635	3.409	0.0533	2.848
0.0829	0.0604	3.466	0.0506	2.890
0.0781	0.0607	3.722	0.0508	3.101
0.0737	0.0587	3.824	0.0491	3.181
0.0699	0.0596	4.115	0.0598	3.422
0.0663	0.0568	4.135	0.0474	3.433
0.0633	0.0560	4.287	0.0467	3.556
0.0604	0.0553	4.443	0.0461	3.682
0.0577	0.0555	4.678	0.0462	3.875
0.0553	0.0540	4.755	0.0449	3.935
0.0531	0.0536	4.924	0.0446	4.073

<u>WATER CHARGE 0.105</u>

0.0656	0.0815	6.167	0.0686	5.155
0.0504	0.0698	6.900	0.0583	5.729
0.0384	0.0620	8.071	0.0516	6.667
0.0326	0.0578	8.861	0.0479	7.301
0.0284	0.0558	9.856	0.0462	8.107
0.0251	0.0534	10.687	0.0442	8.778
0.0225	0.0380	8.359	0.0312	6.833
0.0204	0.0383	9.309	0.0315	7.606
0.0186	0.0399	10.660	0.0328	8.709
0.0172	0.0400	11.640	0.0329	9.507
0.0159	0.0367	11.506	0.0302	9.387
0.0143	0.0420	14.703	0.0345	12.006
0.0130	0.0430	16.609	0.0354	13.561
0.0126	0.0430	17.114	0.0354	13.972
0.0110	0.0446	20.420	0.0367	16.672
0.0103	0.0448	22.072	0.0368	18.018
0.0096	0.0460	24.327	0.0378	19.862
0.0085	0.0525	31.710	0.0433	25.929
0.0076	0.0575	39.000	0.0474	31.929

<u>TEMPERATURE 4</u>5·060°C

<u>WATER CHARGE 1.005</u>

0.4126	0.2265	1.902	0.2078	1.746
0.3454	0.1850	1.963	0.1662	1.763

0.2962	0.1541	1.975	0.1362	1.744
0.2608	0.1336	1.995	0.1167	1.739
0.2314	0.1219	2.104	0.1056	1.818
0.2084	0.1075	2.087	0.0923	1.787
0.1901	0.1012	2.188	0.0864	1.863
0.1746	0.0922	2.192	0.0783	1.855
0.1612	0.0909	2.374	0.0769	2.003
0.1495	0.0848	2.403	0.0715	2.018
0.1390	0.0827	2.548	0.0695	2.134
0.1305	0.0790	2.609	0.0663	2.178
0.1228	0.0774	2.733	0.0647	2.277
0.1158	0.0760	2.865	0.0635	2.382
0.1097	0.0623	2.459	0.0517	2.032
0.1033	0.0643	2.722	0.0534	2.248
0.0938	0.0616	2.895	0.0510	2.384
0.0860	0.0617	3.186	0.0509	2.619
0.0793	0.0623	3.519	0.0514	2.889
0.0736	0.0618	3.786	0.0509	3.103
0.0686	0.0599	3.948	0.0493	3.231

WATER CHARGE 0.100

0.0706	0.0577	3.681	0.0475	3.012
0.0433	0.0520	5.530	0.0425	4.486
0.0363	0.0487	6.190	0.0396	5.006
0.0313	0.0464	6.878	0.0378	5.551
0.0275	0.0455	7.706	0.0370	6.210
0.0243	0.0442	8.460	0.0359	6.809
0.0220	0.0428	9.100	0.0347	7.315
0.0200	0.0410	9.551	0.0332	7.669
0.0184	0.0412	10.493	0.0334	8.422
0.0170	0.0408	11.238	0.0330	9.015
0.0158	0.0402	11.911	0.0325	9.550
0.0147	0.0399	12.686	0.0322	10.167
0.0138	0.0394	13.341	0.0318	10.687
0.0130	0.0390	14.054	0.0315	11.254
0.0117	0.0326	13.045	0.0263	10.423

A2.4 WATER (1) - ETHANOL (2)

TEMPERATURE 25.057°C.				
WATER CHARGE 2.010				
0.8660	0.7956	1.499	0.7974	1.506
0.7618	0.6685	1.569	0.6684	1.572
0.6800	0.5787	1.609	0.5761	1.604
0.6153	0.5034	1.578	0.4985	1.565
0.5613	0.4450	1.560	0.4384	1.538
0.5160	0.3946	1.522	0.3867	1.492
0.4774	0.3573	1.514	0.3486	1.478
0.4443	0.3238	1.491	0.3145	1.449
0.4154	0.2978	1.485	0.2882	1.437
0.3903	0.2715	1.449	0.2617	1.397
0.3681	0.2508	1.430	0.2410	1.374
0.3482	0.2348	1.429	0.2250	1.369
0.3302	0.2165	1.395	0.2068	1.332
0.3140	0.2019	1.376	0.1924	1.310
0.2993	0.1878	1.348	0.1786	1.280
0.2799	0.1722	1.332	0.1632	1.261
0.2626	0.1566	1.298	0.1481	1.226
0.2474	0.1463	1.297	0.1379	1.222
0.2338	0.1359	1.283	0.1279	1.206
0.2217	0.1271	1.273	0.1194	1.194
0.2111	0.1200	1.268	0.1125	1.187
0.2012	0.1136	1.266	0.1063	1.184
0.1921	0.1070	1.254	0.1000	1.170
0.1839	0.1039	1.281	0.0970	1.194
0.1762	0.0995	1.286	0.0928	1.198
0.1693	0.0975	1.319	0.0908	1.227
0.1628	0.0966	1.368	0.0900	1.272
0.1569	0.0934	1.377	0.0869	1.279
0.1515	0.0944	1.454	0.0878	1.350
WATER CHARGE 0.205				
0.1435	0.1520	2.663	0.1423	2.489
0.1178	0.1347	2.902	0.1256	2.700
0.0996	0.1231	3.159	0.1144	2.930
0.0866	0.1151	3.415	0.1068	3.161
0.0766	0.1105	3.728	0.1024	3.446
0.0686	0.1061	4.015	0.0982	3.706

0.0620	0.1026	4.305	0.0948	3.970
0.0537	0.1017	4.690	0.0940	4.322
0.0522	0.1010	5.084	0.0933	4.682
0.0483	0.0999	5.437	0.0922	5.004
0.0451	0.0990	5.789	0.0913	5.326
0.0422	0.0998	6.267	0.0920	5.765
0.0397	0.1003	6.720	0.0925	6.180
0.0373	0.1025	7.332	0.0945	6.744
0.0344	0.1023	7.963	0.0944	7.323
0.0319	0.1049	8.857	0.0968	8.145
0.0297	0.1048	9.502	0.0966	8.737
0.0279	0.1083	10.541	0.0999	9.695
0.0262	0.1099	11.401	0.1013	10.487
0.0247	0.1123	12.415	0.1036	11.422
0.0234	0.1140	13.351	0.1052	12.284
0.0222	0.1169	14.486	0.1078	13.333
0.0212	0.1189	15.526	0.1097	14.293
0.0202	0.1224	16.846	0.1130	15.514
0.0193	0.1252	18.094	0.1156	16.669
0.0185	0.1288	19.536	0.1190	18.005

TEMPERATURE 35.104°C.

WATER CHARGE 1.395

0.6005	0.5652	2.117	0.5600	2.104
0.5297	0.4973	2.151	0.4887	2.118
0.4692	0.4436	2.209	0.4324	2.157
0.4254	0.4046	2.247	0.3918	2.179
0.3884	0.3722	2.286	0.3582	2.201
0.3579	0.3458	2.321	0.3309	2.223
0.3319	0.3242	2.364	0.3088	2.253
0.3091	0.3052	2.403	0.2894	2.280
0.2893	0.2907	2.465	0.2747	2.329
0.2721	0.2752	2.488	0.2591	2.342
0.2566	0.2563	2.535	0.2471	2.378
0.2428	0.2521	2.575	0.2360	2.408
0.2304	0.2435	2.633	0.2273	2.456
0.2191	0.2352	2.684	0.2191	2.497
0.2090	0.2286	2.746	0.2125	2.550
0.1953	0.2184	2.819	0.2025	2.610

0.1838	0.2109	2.907	0.1951	2.685
0.1733	0.2036	2.987	0.1878	2.752
0.1639	0.1990	3.104	0.1834	2.855
0.1555	0.1928	3.176	0.1772	2.916
0.1477	0.1889	3.292	0.1734	3.017
0.1408	0.1850	3.392	0.1696	3.105
0.1345	0.1829	3.528	0.1675	3.225
0.1288	0.1802	3.642	0.1649	3.326
0.1234	0.1786	3.780	0.1632	3.449
0.1186	0.1768	3.908	0.1615	3.564
0.1141	0.1761	4.063	0.1607	3.703
0.1100	0.1751	4.208	0.1598	3.832
0.1061	0.1761	4.412	0.1606	4.016

WATER CHARGE 0.205

0.1429	0.1459	2.510	0.1330	2.282
0.1175	0.1254	2.636	0.1136	2.381
0.0998	0.1096	2.717	0.0988	2.442
0.0869	0.0976	2.784	0.0877	2.493
0.0768	0.0885	2.856	0.0792	2.550
0.0689	0.0807	2.903	0.0721	2.585
0.0624	0.0740	2.943	0.0660	2.616
0.0570	0.0685	2.981	0.0610	2.646
0.0525	0.0640	3.022	0.0569	2.678
0.0486	0.0606	3.087	0.0538	2.732
0.0453	0.0594	3.260	0.0527	2.883
0.0424	0.0571	3.349	0.0507	2.959
0.0399	0.0555	3.465	0.0492	3.060
0.0376	0.0542	3.589	0.0480	3.168
0.0322	0.0533	4.151	0.0472	3.661
0.0293	0.0530	4.546	0.0469	4.007

TEMPERATURE 45.062°C.

WATER CHARGE 1.570

0.6347	0.5977	2.061	0.5938	2.055
0.5627	0.5298	2.109	0.5212	2.082
0.5065	0.4779	2.149	0.4659	2.101
0.4618	0.4368	2.178	0.4222	2.109
0.4239	0.4032	2.212	0.3867	2.125
0.3918	0.3746	2.241	0.3567	2.136

0.3644	0.3524	2.287	0.3335	2.166
0.3404	0.3317	2.318	0.3121	2.181
0.3194	0.3135	2.344	0.2933	2.194
0.3007	0.2984	2.382	0.2779	2.219
0.2848	0.2834	2.393	0.2627	2.217
0.2699	0.2726	2.442	0.2517	2.254
0.2570	0.2616	2.467	0.2407	2.269
0.2451	0.2516	2.495	0.2307	2.286
0.2340	0.2408	2.501	0.2200	2.283
0.2236	0.2305	2.506	0.2099	2.280
0.2143	0.2226	2.530	0.2022	2.295
0.2058	0.2160	2.561	0.1957	2.317
0.1979	0.2098	2.591	0.1896	2.339
0.1906	0.2037	2.617	0.1837	2.356
0.1839	0.1986	2.650	0.1788	2.381
0.1775	0.1942	2.691	0.1745	2.413
0.1715	0.1890	2.714	0.1695	2.429
0.1606	0.1798	2.761	0.1607	2.462
0.1469	0.1692	2.851	0.1506	2.531
0.1318	0.1604	3.031	0.1421	2.679

WATER CHARGE 0.290

0.2243	0.2227	2.388	0.2027	2.169
0.1802	0.1836	2.465	0.1647	2.206
0.1518	0.1595	2.574	0.1418	2.282
0.1297	0.1405	2.643	0.1240	2.325
0.1131	0.1265	2.737	0.1110	2.393
0.1015	0.1165	2.812	0.1018	2.449
0.0917	0.1088	2.911	0.0948	2.527
0.0835	0.1017	2.996	0.0884	2.592
0.0767	0.0967	3.106	0.0838	2.681
0.0709	0.0920	3.198	0.0796	2.755
0.0660	0.0881	3.293	0.0760	2.831
0.0617	0.0849	3.402	0.0732	2.921
0.0579	0.0824	3.519	0.0710	3.017
0.0546	0.0788	3.566	0.0677	3.053
0.0515	0.0757	3.632	0.0650	3.106
0.0464	0.0732	3.904	0.0627	3.334
0.0423	0.0687	4.025	0.0588	3.431
0.0373	0.0649	4.311	0.0554	3.668
0.0352	0.0637	4.486	0.0544	3.814

0.0334	0.0645	4.805	0.0551	4.085
0.0302	0.0615	5.072	0.0525	4.306
0.0276	0.0613	5.550	0.0522	4.710
0.0254	0.0611	6.014	0.0521	5.101
WATER CHARGE 0.060				
0.0607	0.0830	3.374	0.0717	2.894
0.0370	0.0599	3.992	0.0512	3.389
0.0311	0.0553	4.384	0.0471	3.714
0.0269	0.0526	4.843	0.0448	4.096
0.0221	0.0486	5.451	0.0413	4.601
0.0198	0.0469	5.859	0.0399	4.942
0.0180	0.0458	6.323	0.0389	5.329
0.0164	0.0448	6.761	0.0380	5.695
0.0151	0.0450	7.390	0.0382	6.224
0.0131	0.0444	8.443	0.0377	7.106
0.0115	0.0459	9.917	0.0389	8.345
0.0109	0.0461	10.551	0.0390	8.877
0.0098	0.0490	12.539	0.0415	10.553
0.0085	0.0504	14.874	0.0427	12.519
0.0075	0.0562	18.959	0.0477	15.973
0.0067	0.0614	23.260	0.0522	19.615

A3. Computer Program 'DATACALC'

A3.0 General Introduction

Program 'DATACALC' calculates phase composition-activity coefficient results from the raw data obtained on the main apparatus using method A. The theory has been outlined in Section 4.1 where a flowchart is also presented. The behaviour of a non-ideal vapour-phase is treated using subroutines based on those presented by Prausnitz et al (113). The program is written in FORTRAN IV for use on the ICL 1905 computer at the University of Aston in Birmingham.

A3.1 Program details

The first section of the program reads in the experimental data and the required pure component properties. The volumes of component 2 charged to the cell and the cell liquid volumes are held in the arrays DATA (1 ,J), DATA(2,J) respectively.

The vapour phase can be assumed ideal by giving VW the value 0. For a non-ideal vapour phase (VW = 1) the virial equation is employed. The values of the virial coefficients may be calculated using the subroutine virial or inserted directly. The calculation of the virial coefficients is based on that given by Prausnitz, however it has been found that the values calculated using these procedures give values significantly different to literature values at lower temperatures. (ca $< 50^{\circ}$C.). This has also been confirmed by Sunal (114) who suggests the use of the method presented by Halm and Stiel (115). This however requires the fitting of a polynomial and has not been included in the present program. In this work, experimental values for the virial coefficients were always employed.

The fugacity coefficients and activity coefficients are unity initially and the values of the mole concentrations calculated as described in Section 4.1. For an ideal vapour phase these are the required results.

For a non-ideal vapour phase, the fugacity coefficients are calculated in subroutine 'FUGVAP'. From these values, the activity coefficients are calculated from

$$A = \frac{Py_a}{P_a^o \, x_a \, \phi_a} \qquad (A\ 3.1)$$

New mole fractions are computed using these new values in 'XCALC'. This procedure is then repeated until errors in successive vapour phase mol fractions are within the acceptable error. The output presents the values of the mol fractions, activity coefficients, fugacity coefficients, K values and ratio mole as component 2 mole component 1.

A3.2 Calculational Procedures

A3.2.1. Saturated Vapour Pressure

The saturated vapour pressures are calculated using the Antoine equation.

$$\ln P\ (\text{atm}) = C_1 + \frac{C_2}{C_3 + T} + C_4 T + C_5 T^2 + C_6 \ln T \qquad (A3.2)$$

A3.2.2. Liquid Molar Volume

The molar volume of a component at any temperature (^{o}K) is calculated using

$$V^L = a + bT + cT^2 \qquad (A3.3)$$

A3.2.3. Critical Properties for Binary Interactions

The mixing rules for calculating the critical temperature and pressure for binary interactions are

$$T_{c_{12}} = (T_{c_1} \times T_{c_2})^{\frac{1}{2}}$$

$$P_{c_{12}} = 4 \; T_{c_{12}} \left[\frac{P_{c_1} \; V_{c_1}}{T_{c_1}} + \frac{P_{c_2} \; V_{c_2}}{T_{c_2}} \right] \Bigg/ \left[V_{c_1}^{\frac{1}{3}} + V_{c_2} \right]^3 \qquad (A3.4)$$

A3.2.4. Second Virial Coefficients for the Pure Gases

For non-polar gases, the Pitzer and Curl (116) correlation based on the three parameter theory of corresponding states is used

$$\frac{P_{c_i} \; B_{ii}}{RT_{ci}} = f_B^{\circ} \; (T_R) + W_i \, f_B^{(1)} \; (T_R) \qquad (A3.5)$$

where W_i = accentric factor of i

$$f_B^{(o)} (T_R) = 0.1445 - \frac{0.330}{T_R} - \frac{0.1385}{T_R^{\,2}} - \frac{0.0121}{T_R^{\,3}} \qquad (A3.6)$$

$$f_B^{(1)} \; (T_R) = 0.073 + \frac{0.46}{T_R} - \frac{0.50}{T_R^{\,2}} - \frac{0.097}{T_R^{\,3}} - \frac{0.0073}{T_R^{\,8}} \qquad (A3.7)$$

$$T_R = T \; / \; Tci$$

For polar gases, Prausnitz developed the following correlation based on an extended corresponding states theory.

$$\frac{P_{c_i} B_{ii}}{RT_{ci}} = f_B^{(o)}(T_R) + W_{Hi}\, f_B^{(1)}(T_R) + f\mu(\mu_R\, T_R) + \eta_i\, fa\,(T_R) \qquad (A3.8)$$

Where W_{hi} = acentric factor of the polar components homomorph

η_i = association constant

$$f\mu\,(\mu_{R1}\cdot T_R) = -\,5.237220 + 5.665807(\ln \mu_R) - 2.133816\,(\ln \mu_R)^2$$
$$+\,0.2525373\,(\ln \mu_R)^3 + \frac{1}{T_R}\,(\,5.769770 - 6.181427 \ln \mu_R$$
$$+\,2.283270\,(\ln\mu_R)^2 - 0.2649074\,(\ln \mu_R)^3) \qquad (A3.9)$$

The reduced dipole moment is given by

$$\mu_R = \frac{10^5\, \mu_i^2\; P_{c_1}}{T_{c_i}^2} \qquad (A.3.10)$$

Where u_i is the dipole moment of i in Debye

The association function $fa(T_R)$ is given by

$$fa\,(T_R) = \exp\,(6 - 6\,(0.7 - T_R) \qquad A3.11)$$

If μ_R is less than 4, equation A3.9 is not applicable and the polar contributions are ignored.

A3.2.5 Density

Densities of the two alcohols are calculated from the following equation using parameter values given in International Critical Tables'

$$= D_1 + D_2\,(T=273 : 15\ ) + D_3(T-273.15)^2\, D_4(T-273.15)^3$$

A3.3 Program Nomenclature

ACF	Acentric factor
ACFH	Acentric factor of polar components homomorph
ACT	Activity coefficient
ASC	Association constant
B	Second virial coefficient
BL	Flag to indicate if second virial coefficient is to be employed
CPSAT	Parameters in vapour pressure calculation
CV	Critical volume
D	Parameters for density calculation
DATA	Array to contain volume component 2 changed to equilibrium cell and cell liquid volume
DENS	Density of component 2 at experimental temperature
DMOLES	Ratio moles component 2| mole component 1.
FUGC	Fugacity coefficient
INSD	Flag used if more than one data set to be computed
JVP	Set equal to one if an ideal vapour phase is to be assumed in addition to a non-ideal vapour phase
MIX	Set equal to one automatically when binary mixture properties calculated
MOLWT	Molecular weight of component 2
MU	Dipole moment in Debye
N	Number of data points
NI	Number of iterations
NL	Number of gm moles in liquid phase of one component
MO	Overall number of gm moles present

NSD	Number of sets of data to be computed
NV	Number of gm moles in vapour phase of one component
P	Total pressure (mmHg)
PC	Critical pressure
PP	Partial pressure
PSAT	Saturated vapour pressure (mmHg)
R	Gas constant
SECVER	Reduced second virial coefficient
TC	Critical temperature (°K)
TEMP	Experimental temperature (°K)
VC	Cell volume (cm^3)
VG	Set equal to one if second virial coefficients are to be calculated, o if coefficients are given.
VOL	Volume of component 2 added
VW	Set equal to o for ideal vapour phase, equals one for a non-ideal vapour phase.
X	Mole fraction in liquid phase
XG	Initial guess for mole fraction component 2
Y	Mole fraction in vapour phase

```
***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P
***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P
***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P
***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P
***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P***P

#LISTING OF :ECP0707.DATACALC(1/B1B0)   PRODUCED ON  9JAN74 AT 23.50.28

#G7.70  AT ASTON    IN ':ECP0707.DATACALC' ON  9JAN74 AT 23.52.55

DOCUMENT     :ECP0707.DATACALC(/B1B0)


STARTED :ECP0707,DATACALC, 9JAN74  22.36.26 TYPE:BACK
22.36.26+ RJ :ECP0707,DATACALC,:JOBS.JOBZ(304)
22.36.27+ JOBZ
22.36.27+ UAERJOBZ    0304
22.36.29+ ER :JOBS.JOBZ(0304)
END OF MACRO
22.36.35+ JOBTIME 200
22.36.37+ MAXSIZE 32768
22.36.37+ JD    6,  32768
22.36.39+ UAFORTRAN
22.36.42+      IF MOP,(TA NONE)ELSE(TA CE,DP,OL,LS)
22.36.42+ TA CE,DP,OL,LS

FURTRAN COMPILATION BY #XFAT MK 4C    DATE  09/01/74  TIME  23/18/18


                     LIST (LP)
                     PROGRAM (FXXX)
                     INPUT  1 = CR0
                     INPUT  3 = TR0
                     INPUT  5 = CR1
                     OUTPUT 2 = LP0
                     OUTPUT 6 = LP1
                     COMPRESS INTEGER AND LOGICAL
                     COMPACT
                     TRACE 2
                     END



                     TRACE 1
                     READ FROM (CR)
                     MASTER MDATACALC
               C
               C     MDATACALC CALCULATES THE X-Y-ACTIVITY COEFFICIENT DATA
               C     FROM RAW DATA OF THE MAIN APPARATUS VIA METHOD A.
               C
                     REAL NO,NV,NL,MU,MOLWT,MUR
                     INTEGER VW,VG
                     DIMENSION TITLE(9),COMP(2),DATA(2,80),VW(2),IVP(2),MQ(2),CPSAT(2,6
                    1),TC(2,2),PC(2,2),CV(2),ACF(2),ASC(2),        MU(2),PSAT(2)
                    2,B(2,2),NO(2),P(80),PP(2),NV(2),NL(2),X(2,80),Y(2,80),ACT(2,80),MO
                    3LWT(2),DENS(2),VG(2),ACFH(2),FUGC(2,80),YOX(80),DMOLES(80)
                     COMMON TC,PC,CV,ACF,ACFH,MU,ASC,TEMP,R,B,MQ,Y,FUGC,H,DATA,MOLWT,X,
                    1PSAT,P,VW,VC,DENS,ACT,NO,VG
               C
               C     COMPONENT 1 IS THE INITIAL COMPONENT IN CELL
```

```
C     DATA(1,J) IS VOLUME COMPONENT ADDED (CMS**3)
C     DATA(2,J) IS LIQUID VOLUME IN CELL (CM**3)
C     P(J) IS TOTAL PRESSURE (MM.HG)
C     VOL IS VOLUME COMPONENT 1 ADDED (CM**3)
C
      MIX=0
      READ(1,2) NSD
    2 FORMAT(I2)
      INSD=0
    1 READ(1,4) (TITLE(I),I=1,9)
      READ(1,5) (COMP(I),I=1,2)
      WRITE(2,4) (TITLE(I),I=1,9)
      WRITE(2,6)
      WRITE(2,7) (I,COMP(I),I=1,2)
      READ(1,8) N,TEMP,VC,VOL
      READ(1,9) (DATA(1,J),DATA(2,J),P(J),J=1,N)
      WRITE(2,10)
      WRITE(2,11)
      WRITE(2,12) COMP(1),VOL
      WRITE(2,13) COMP(2)
      WRITE(2,14) (DATA(1,J),DATA(2,J),P(J),J=1,N)
C     VW VALUE INDICARES WHETHER VIRIAL EQUATION TO BE EMPLOYED
C     VW=0  IDEAL VAPOUR PHASE,VW=1 VIRIAL
C     IVP (=1) INDICATES THAT AN IDEAL VAPOUR PHASE IS TO BE ASSUMED AS
C     AN EXTRA CALCULATION, EQUALS 0 OTHERWISE.
C     VG=1,PURE SECOND VIRIAL COEFFICIENTS TO BE INSERTED
C     VG=0 VIRIAL COEFFICIENTS TO BE CALCULATED
      DO 16 I=1,2
      READ(1,18) VW(I),IVP(I),VG(I)
      READ(1,20) (CPSAT(I,J),J=1,6)
   16 CONTINUE
      DO 30 K=1,2
      IF(VW(K)) 0,25,0
      IF(VG(K).EQ.0) GOTO 21
      READ(1,23) B(K,K)
   23 FORMAT(F10.0)
   21 READ(1,22) TC(K,K),PC(K,K),CV(K),ACF(K),ACFH(K),MU(K),ASC(K)
      DO 24 I=1,2
   24 IF(MU(I).EQ.0.) ACFH(I)=ACF(I)
      MQ(K)=0
   250PSAT(K)=EXP(CPSAT(K,1)+CPSAT(K,2)/(TEMP+CPSAT(K,3))+CPSAT(K,4)*TEM
     1P+CPSAT(K,5)*(TEMP**2)+CPSAT(K,6)*ALOG(TEMP))
      PSAT(K)=PSAT(K)*760.0
   30 CONTINUE
      DO 901 K=1,2
  901 CALL VIRIAL(K)
      WRITE(2,35)
      WRITE(2,36)
      DO 50 I=1,2
      IF(VW(I)) 0,45,0
      IF(VG(I).EQ.0) GOTO 41
      WRITE(2,43) B(I,I)
   43 FORMAT(34H SECOND VIRIAL COEFFICIENT(GIVEN) ,F8.4)
      GOTO 45
      WRITE(2,38) COMP(I)
   41 WRITE(2,40)
      WRITE(2,42) TC(K,K),PC(K,K),CV(K),ACF(K),ACFH(K),MU(K),ASC(K)
      IF(MQ(I)) 47,48,47
   47 WRITE(2,44) B(I,I)
      GOTO 45
   48 WRITE(2,49) B(I,I)
   45 WRITE(2,46) PSAT(I)
   50 CONTINUE
```

```
      RT=62400,0*TEMP
      READ(1,55) (MOLWT(I),DENS(I),I=1,2)
      DO 60 I=1,2
      IF(DENS(I).NE.0) GOTO 60
      READ(1,58) D1,D2,D3,D4
   58 FORMAT(4F12.0)
      DENS(I)=D1+D2*(TEMP-273,15)+D3*((TEMP-273.15)**2)+D4*((TEMP-273.15
     1)**3)
   60 CONTINUE
      NO(1)=VOL*DENS(1)/MOLWT(1)
   63 DO 57 I=1,2
      DO 59 J=1,N
      FUGC(I,J)=1.0
      ACT(I,J)=1.0
   59 CONTINUE
   57 CONTINUE
      DO 80 J=1,N
      CALL XCALC(J)
      IF(VW(1).EQ.0.AND.VW(2).EQ.0) GOTO 73
      NI=0
   82 YI=Y(2,J)
      NI=NI+1
      CALL FUGVAP(J)
      DO 84 I=1,2
   84 ACT(I,J)=(P(J)*Y(I,J))/(FUGC(I,J)*X(I,J)*PSAT(I))
      CALL XCALC(J)
      IF(NI.GT.15) GOTO 78
      IF(ABS(Y(2,J)-YI).GT.1.E-05) GOTO 82
      GOTO 77
   78 WRITE(2,79) Y(2,J),YI
   79 FORMAT(2F8.6)
      GOTO 77
   73 DO 74 I=1,2
   74 ACT(I,J)=(P(J)*Y(I,J))/(X(I,J)*PSAT(I))
   77 YOX(J)=Y(1,J)/X(1,J)
      DMOLES(J)=NO(2)/NO(1)
   80 CONTINUE
      WRITE(2,6)
      IF(VW(2)) 0,90,0
      WRITE(2,85)
      GOTO 91
   90 WRITE(2,92)
   91 IF(VW(2)) 0,98,0
      WRITE(2,94)
      WRITE(2,95)
      WRITE(2,96) (X(1,J),Y(1,J),ACT(1,J),ACT(2,J),FUGC(1,J),FUGC(2,J),Y
     1OX(J),DMOLES(J),J=1,N)
      GOTO 105
   98 WRITE(2,99)
      WRITE(2,100)
      WRITE (2,102) (X(1,J),Y(1,J),ACT(1,J),ACT(2,J),YOX(J),DMOLES(J),J=
     11,N)
  105 IF(VW(2)) 0,120,0
      IF(IVP(2).NE.1) GOTO 120
      VW(1)=0
      VW(2)=0
      GOTO 63
  120 CONTINUE
    4 FORMAT(2X,9A8)
    5 FORMAT(2A8)
    6 FORMAT(72(1H*))
    7 FORMAT(/5X,11H COMPONENT ,I1,4H IS ,A8)
    8 FORMAT(I2,3F0.0)
```

```
    9 FORMAT(3F10.0)
   10 FORMAT(//5X,11H RAW DATA. )
   11 FORMAT(5X,11(1H*))
   12 FORMAT(/5X,A8,11H CHARGE IS ,F6.3,7H CM**3 )
   13 FORMAT(/5X,8H VOLUME ,A8,5X,16H LEVEL PRESSURE ,5X,20H CELL LIQUID
     1 VOLUME )
   14 FORMAT(9X,F8.4,13X,F8.4,15X,F8.4)
   18 FORMAT(3I2)
   20 FORMAT(6F12.0)
   22 FORMAT(7F10.0)
   35 FORMAT(22H PURE COMPONENT DATA. )
   36 FORMAT(24(1H*))
   38 FORMAT(//2X,A8)
   40 FORMAT(//3X,4H TC ,6X,4H PC ,6X,4H AC ,6X,5H ACF ,5X,5H ASC ,5X,5H
     1 CPD ,5X,4H MU )
   42 FORMAT(7F10.5)
   44 FORMAT(74H SECOND VIRIAL COEFFICIENT (CALCULATED USING PITZER AND
     1CURL CORRELATION. ,F8.5)
   49 FORMAT(68H SECOND VIRIAL COEFFICIENT (CALCULATED USING PRAUSNITZ C
     1ORRELATION.) ,F8.5)
   46 FORMAT(27H SATURATED VAPOUR PRESSURE ,F8.4,7H MM HG )
   55 FORMAT(2F10.0)
   62 FORMAT(2F10.0)
   85 FORMAT(///57H RESULTS CALCULATED EMPLOYING SECOND VIRIAL COEFFICIE
     1NT. )
   92 FORMAT(///48H RESULTS CALCULATED ASSUMING IDEAL VAPOUR PHASE )
   94 FORMAT(//5X,13H LIQUID MOLE ,2X,13H VAPOUR MOLE ,2X,23H ACTIVITY C
     1OEFFICIENTS ,2X,23H FUGACITY COEFFICIENTS ,2X,9H K VALUE ,2X,16H M
     2OLES 2/MOLE 1 )
   95 FORMAT(5X,13H FRACTION X1 ,2X,13H FRACTION Y1 ,5X,3H 1 ,7X,3H 2 ,1
     12X,3H 1 ,7X,3H 2 )
   96 FORMAT(8X,F6.4,10X,F6.4,7X,F6.3,4X,F6.3,9X,F6.3,4X,F6.3,7X,F6.4,7X
     1,F5.1)
   99 FORMAT(//5X,13H LIQUID MOLE , 2X,13H VAPOUR MOLE ,2X,23H ACTIVITY
     1COEFFICIENTS ,2X,9H K VALUE ,2X,16H MOLES 2/MOLE 1 )
  100 FORMAT(5X,13H FRACTION X1 ,2X,13H FRACTION Y2 ,5X,3H 1 ,7X,3H 2 )
  102 FORMAT(8X,F6.4,10X,F6.4,7X,F6.3,4X,F6.3,7X,F6.4,7X,F5.1)
      INSD=INSD+1
      IF(NSD.NE.INSD) GOTO 1
      END

END OF SEGMENT, LENGTH   970, NAME  MDATACALC

      SUBROUTINE VIRIAL(K)
      REAL NO,NV,NL,MU,MOLWT,MUR
      INTEGER VW,VG
      DIMENSION TITLE(9),COMP(2),DATA(2,80),VW(2),IVP(2),MQ(2),CPSAT(2,6
     1),TC(2,2),PC(2,2),CV(2),ACF(2),ASC(2),        MU(2),PSAT(2)
     2,B(2,2),NO(2),P(80),PP(2),NV(2),NL(2),X(2,80),Y(2,80),ACT(2,80),MO
     3LWT(2),DENS(2),VG(2),ACFH(2),FUGC(2,80),YOX(80),DMOLES(80)
      COMMON TC,PC,CV,ACF,ACFH,MU,ASC,TEMP,R,B,MQ,Y,FUGC,N,DATA,MOLWT,X,
     1PSAT,P,VW,VC,DENS,ACT,NO,VG
      FRDP(TR,RD)=-5.237220+ALOG(RD)*(5.665807+ALOG(RD)*(-2.133816+ALOG(
     1RD)*0.2525373))+(5.769770+ALOG(RD)*(-6.181427+ALOG(RD)*(2.283270-A
     2LOG(RD)*0.2649074)))/TR
C     CALCULATION OF CRITICAL PROPERTIES FOR BINARY INTERACTIONS
      IF(MIX.EQ.1) GOTO 245
      DO 240 I=1,2
      DO 241 J=1,2
      TC(I,J)=SQRT(TC(I,I)*TC(J,J))
      PC(I,J)=4.0*TC(I,J)*(PC(I,I)*CV(I)/TC(I,I)+PC(J,J)*CV(J)/TC(J,J))/
```

```
     1(CV(I)**0.33333333+CV(J)**0.33333333)**3
      TC(J,I)=TC(I,J)
      PC(J,I)=PC(I,J)
      MIX=1
  241 CONTINUE
  240 CONTINUE
  245 DO 202 I=1,NCOMP
      DO 201 J=1,NCOMP
      SECVIR=1.0
      IF(VG(I).EQ.1) GOTO 210
      TR=TEMP/TC(I,J)
      AACF=(ACFH(I)+ACFH(J))/2.0
C
C     CALCULATION OF NONPOLAR SECOND VIRAL COEFFICIENT FROM
C     CORRELATION OF PITZER-AND CURL
C
     0SECVTR=(0.1445-(0.330+(0.1385+0.0121/TR)     /TR)/TR+AACF*(0.073+(0
     1.46-(0.50+(0.097+0.0073/TR**5)/TR)/TR)/TR))
C
C     ADD POLAR CONTRIBUTION AT REDUCED TEMP BELOW 0.95 WHEN
C     REDUCED DIPOLE MOMENT RD LARGER THAN 4.0
C
      IF(MU(I)*MU(J)) 210,210,215
  215 IF(0.95-TR) 210,210,217
  217 RD=10.E04*MU(I)*MU(J)*PC(I,J)/(TC(I,J)**2)
      IF(RD-4.0) 210,210,219
  219 SECVIR=SECVIR+FRDP(TR,RD)
C
C     ADD CONTRIBUTION FOR MOLECULAR ASSOCIATION
C
      IF(ASC(I)+ASC(J))210,210,221
  221 SECVIR=SECVIR-0.5*(ASC(I)+ASC(J))*EXP(6.6*(0.7-TR))
  210 IF(VG(I).EQ.1.AND.I.EQ.J) GOTO 201
      B(I,J)=SECVIR*82.057*TC(I,J)/PC(I,J)
      B(J,I)=B(I,J)
  201 CONTINUE
  202 CONTINUE
      RETURN
      END

END OF SEGMENT, LENGTH   400, NAME  VIRIAL

      SUBROUTINE FUGVAP(J)
      REAL NO,NV,NL,MU,MOLWT,MUR
      INTEGER VW,VG
      DIMENSION TITLE(9),COMP(2),DATA(2,80),VW(2),IVP(2),MQ(2),CPSAT(2,6
     1),TC(2,2),PC(2,2),CV(2),ACF(2),ASC(2),          MU(2),PSAT(2)
     2,B(2,2),NO(2),P(80),PP(2),NV(2),NL(2),X(2,80),Y(2,80),ACT(2,80),MO
     3LWT(2),DENS(2),VG(2),ACFH(2),FUGC(2,80),YOX(80),DMOLES(80)
      COMMON TC,PC.CV,ACF,ACFH,MU,ASC,TEMP,R,B,MQ,Y,FUGC,N,DATA,MOLWT,X,
     1PSAT,P,VW,VC,DENS,ACT,NO,VG
C
C     CALCULATION OF MOLAR VOLUME OF MIXTURE
      PORT=(P(J)/760.0)/(82.057*TEMP)
      BMIX=0.0
      DO 15 I=1,2
      DO 10 K=1,2
   10 BMIX=BMIX+Y(I,J)*Y(K,J)*B(I,K)
   15 CONTINUE
      IF(MARK) 20,20,22
   20 SQARG=0.25+BMIX*PORT
```

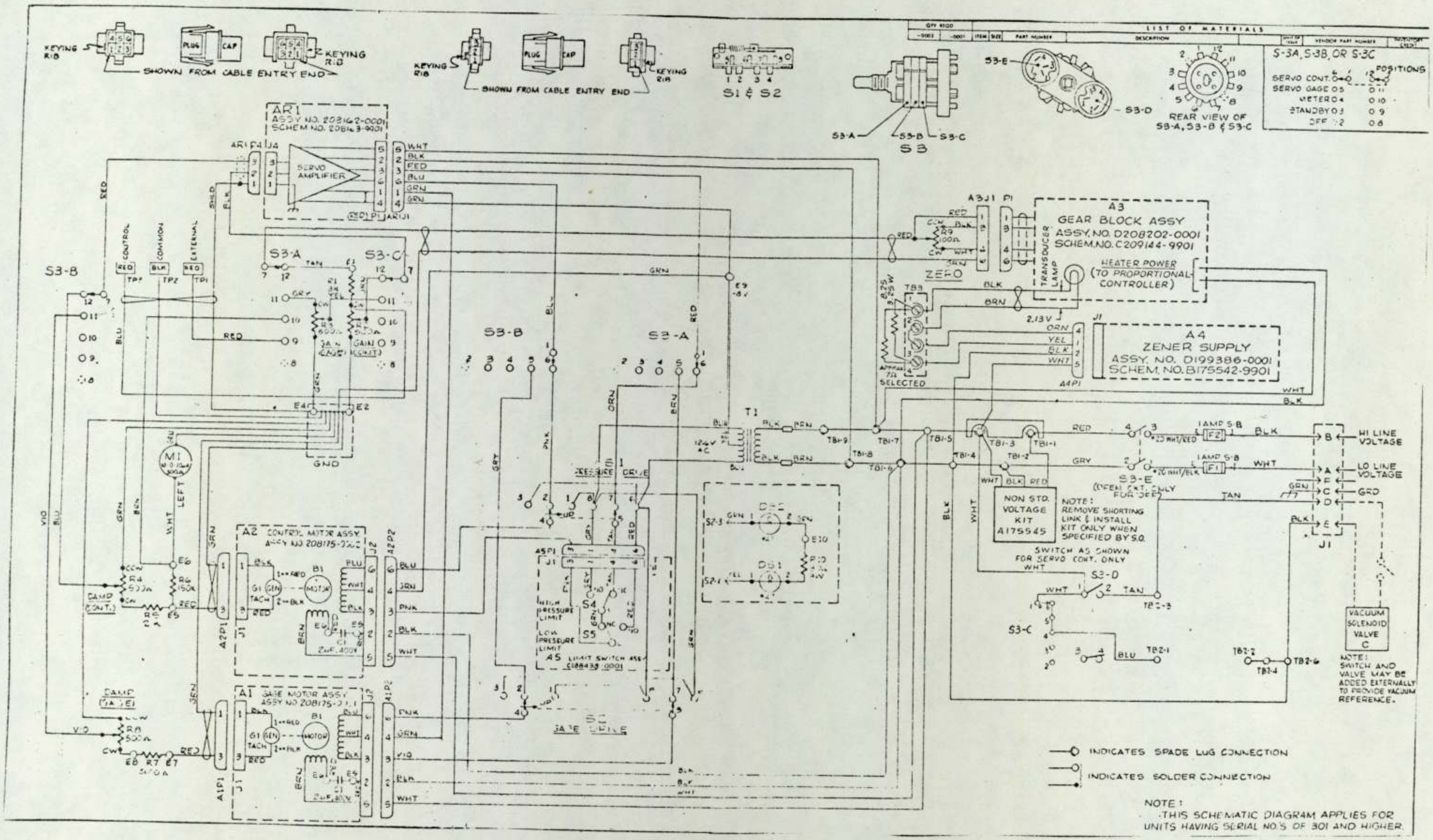
```
C
C     IF SQRG  MORE NEGATIVE THAN 0.25 USE PRESSURE SERIES VIRIAL FQN.
C
      IF(SQARG) 22,25,25
   22 VMIX=BMIX+1./PORT
      ZMIX=PORT*VMIX
      DO24 I=1,2
      SUMB=0.0
      DO 23 K=1,2
      SUMB=SUMB+Y(K,J)*B(I,K)
   23 CONTINUE
      FUGC(I,J)=EXP((2.0*SUMB-BMIX)*PORT)
   24 CONTINUE
      MARK=MARK+1
      GOTO 50
   25 VMIX=(0.5+SQRT(SQARG))/PORT
      ZMIX=PORT*VMIX
      DO 40 I=1,2
      SUMB=0.0
      DO 30 K=1,2
      SUMB=SUMB+Y(K,J)*B(I,K)
   30 CONTINUE
      FUGC(I,J)=EXP(2.0*SUMB/VMIX)/ZMIX
   40 CONTINUE
   50 RETURN
      END

END OF SEGMENT, LENGTH   184, NAME  FUGVAP

      SUBROUTINE XCALC(J)
      REAL NO,NV,NL,MU,MOLWT,MUR
      INTEGER VW,VG
      DIMENSION TITLE(9),COMP(2),DATA(2,80),VW(2),IVP(2),MQ(2),CPSAT(2,6
     1),TC(2,2),PC(2,2),CV(2),ACF(2),ASC(2),        MU(2),PSAT(2)
     2,B(2,2),NO(2),P(80),PP(2),NV(2),NL(2),X(2,80),Y(2,80),ACT(2,80),MO
     3LWT(2),DENS(2),VG(2),ACFH(2),FUGC(2,80),YOX(80),DMOLES(80)
      COMMON TC,PC,CV,ACF,ACFH,MU,ASC,TEMP,R,B,MQ,Y,FUGC,N,DATA,MOLWT,X,
     1PSAT,P,VW,VC,DENS,ACT,NO,VG
      RT=62400.0*TEMP
      NO(2)=DATA(1,J)*DENS(2)/MOLWT(2)
      XG=NO(2)/(NO(1)+NO(2))
   64 PP(2)=(XG*PSAT(2)*FUGC(2,J)*ACT(2,J))
      PP(1)=P(J)-PP(2)
      DO 70 I=1,2
      IF(VW(I)) 0,65,0
      VB=((RT/PP(I))+SQRT(((RT/PP(I))**2)+((4.*B(I,I)*RT)/PP(I)))/2.)
      NV(I)=(VC-DATA(2,J))/VB
      GOTO 68
   65 NV(I)=PP(I)*(VC-DATA(2,J))/RT
   68 NL(I)=NO(I)-NV(I)
   70 CONTINUE
      X(2,J)=NL(2)/(NL(1)+NL(2))
      IF(ABS(X(2,J)-XG)-1.E-08) 75,75,0
      XG=X(2,J)
      GOTO 64
   75 X(1,J)=1.0-X(2,J)
      Y(1,J)=NV(1)/(NV(1)+NV(2))
      Y(2,J)=1.0-Y(1,J)
      RETURN
      END
```

A4 MODIFICATIONS TO THE INTERNAL CIRCUITRY OF THE BOURDON PRESSURE GAUGE

The reason and purpose of the modifications have been described in Section 6.1. The modifications are detailed diagramatically on Figures 64 and 65. Figure 64 shows the original circuitry and Figure 65 the modified version.

The modifications are based mainly on the introduction of a second amplifier. The connections for the amplifier are indicated in Figure 66. The working of the pressure gauge can be outlined as follows; the voltage charge from the L.V.D.T. caused by a pressure change in the equilibrium cell is passed to the new amplifier. This out of balance is then equalised by an opposing voltage generated from the pressure applied to the top of the equilibrium cell signified by the bourdon tube. The equalising pressure is registered on the bourdon gauge utilising the original amplifier.

When these changes alone were concluded it was found that the system could not be satisfactorily stabilised and after a short initial period the pressure would drift towards atmospheric pressure. Intensive testing finally indicated that this instability could be attributed to the fact that both amplifiers were being driven by the same voltage supply of 115 volts. It is believed that this was producing a loop in the circuitry. The second transformer shown on Figure 65 was therefore introduced to provide a separate supply for the new amplifier.



NOTE: THIS SCHEMATIC DIAGRAM APPLIES FOR UNITS HAVING SERIAL NO.'S OF 301 AND HIGHER.

Figure 64

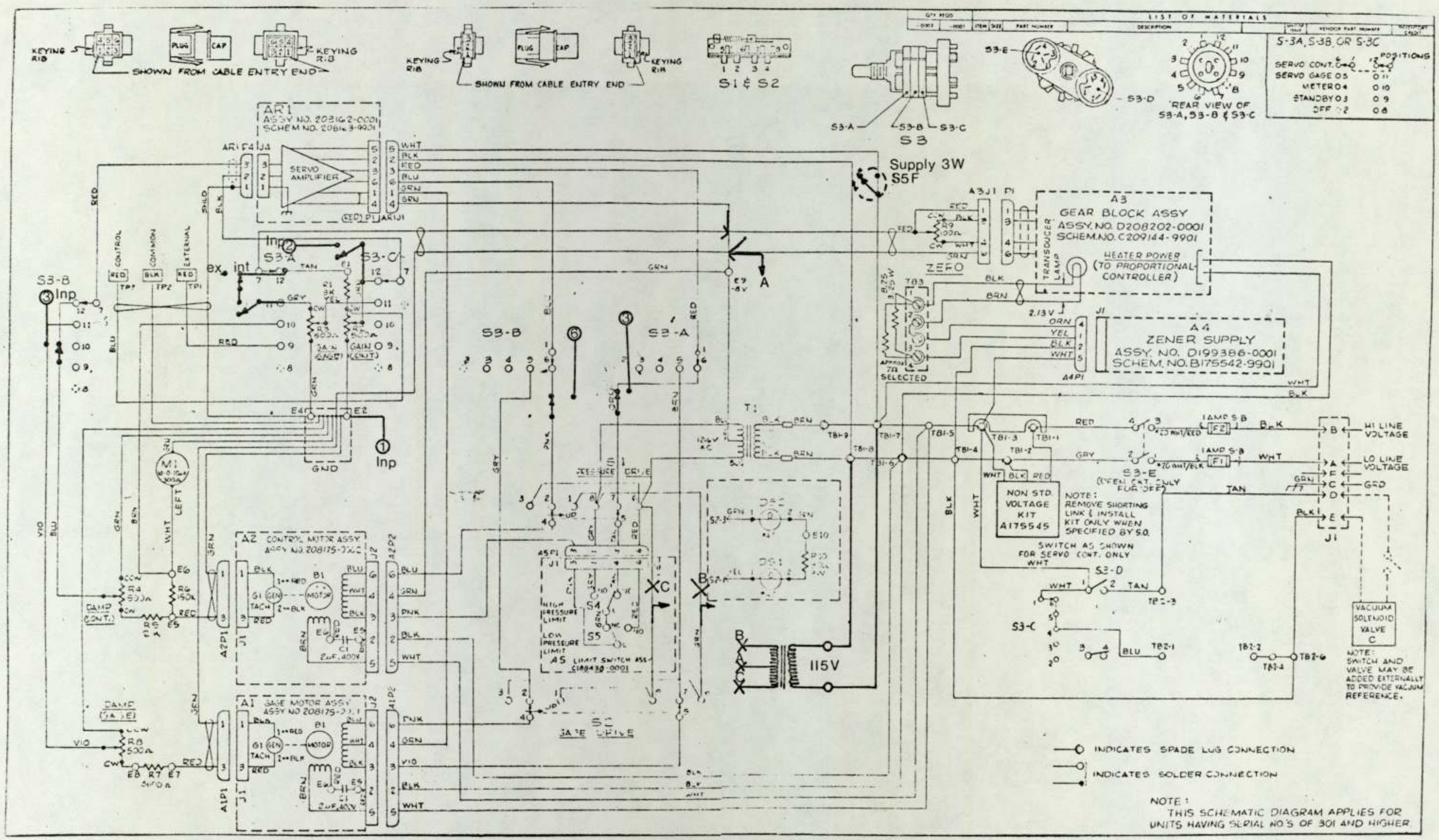
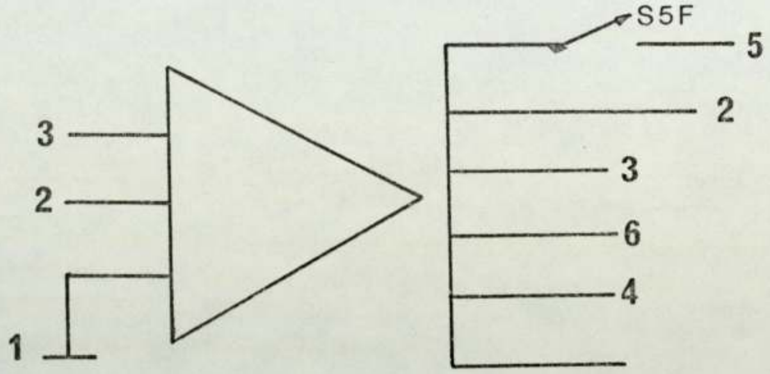

LIST OF MATERIALS
KEYING RIB
PLUG
CAP
SHOWN FROM CABLE ENTRY END
S1 & S2
S3-A
S3-B
S3-C
S3-D
S3-E
S3
REAR VIEW OF S3-A, S3-B & S3-C
S-3A, S-3B, OR S-3C
POSITIONS
SERVO CONT. 6
SERVO GAGE 05
METER 04
STANDBY 03
OFF 2
AR1
ASSY NO. 208162-0001
SCHEM NO. 208163-9901
SERVO AMPLIFIER
Supply 3W
S5F
A3
GEAR BLOCK ASSY
ASSY. NO. D208202-0001
SCHEM. NO. C209144-9901
HEATER POWER
(TO PROPORTIONAL CONTROLLER)
TRANSDUCER LAMP
ZERO
A4
ZENER SUPPLY
ASSY. NO. D199386-0001
SCHEM. NO. B175542-9901
Inp
ex
int
CONTROL
COMMON
EXTERNAL
TP3
TP2
TP1
GAIN (GAGE)
GAIN (CONT)
GND
M1
A2 CONTROL MOTOR ASSY
ASSY NO. 208175-0002
A1 GAGE MOTOR ASSY
ASSY NO. 208175-0001
TACH
MOTOR
DAMP (CONT.)
DAMP (GAGE)
PRESSURE DRIVE
GAGE DRIVE
HIGH PRESSURE LIMIT
LOW PRESSURE LIMIT
A5 LIMIT SWITCH ASSY
C188430-0001
S4
S5
DS2
DS1
T1
12.6V AC
115V
HI LINE VOLTAGE
LO LINE VOLTAGE
GRD
NON STD. VOLTAGE KIT A175545
NOTE: REMOVE SHORTING LINK & INSTALL KIT ONLY WHEN SPECIFIED BY S.O.
S3-E (OPEN CKT. ONLY FOR OFF)
SWITCH AS SHOWN FOR SERVO CONT. ONLY
VACUUM SOLENOID VALVE C
NOTE: SWITCH AND VALVE MAY BE ADDED EXTERNALLY TO PROVIDE VACUUM REFERENCE.
INDICATES SPADE LUG CONNECTION
INDICATES SOLDER CONNECTION
NOTE: THIS SCHEMATIC DIAGRAM APPLIES FOR UNITS HAVING SERIAL NO'S OF 301 AND HIGHER
A
B
C
①
③
⑥

Figure 65



Fig

Figure 66

Secondary Amplifier Connections

Although this configuration was not utilised in the actual data acquisition, the bourdon gauge has been tested with the modifications and demonstrated to be operative both in the original modes and the new mode.

APPENDIX 5.

Results from testing of diaphragms.

Material:- Tantalum.

Diaphragm Configuration:- Flat.

Diaphragm Thickness					
0.025mm.		0.05mm.		0.1mm.	
Bourdon Gauge reading	Voltage change v.	Bourdon Gauge reading	Voltage Change microvolts	Bourdon Gauge reading	Voltage change microvolts
0	0.02	000	0	0	0
119	0.04	015	80	480	120
250	0.06	035	240	1095	240
377	0.08	065	280	1530	420
479	0.10	085	420	2095	580
698	0.12	105	660	2540	720
1146	0.14	135	840	3035	820
2247	0.16	275	1840	4025	1120
3139	0.18	440	8600	4990	1360
4342	0.20	725	17320	5990	1620
		978	20820	7045	1840
		1165	23960	8030	2200
		1340	25160	8980	2400
		1735	32660	10010	2680
		2060	33720	11120	2920
				12075	3160
				13025	3460

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