MASS TRANSFER AND CHEMICAL REACTION ON A DISTILLATION PLATE

by

BRUCE DAVIES

A thesis submitted to the University of Aston in Birmingham as a requirement for the Degree of Doctor of Philosophy.

Department of Chemical Engineering.
University of Aston in Birmingham.

October, 1971.

To my wife and my parents.

SUMMARY

A multistage distillation column in which mass transfer and a reversible chemical reaction occurred simultaneously, has been investigated to formulate a technique by which this process can be analysed or predicted.

A transesterification reaction between ethyl alcohol and butyl acetate, catalysed by concentrated sulphuric acid, was selected for the investigation and all the components were analysed on a gas liquid chromatograph.

The transesterification reaction kinetics have been studied in a batch reactor for catalyst concentrations of 0.1 - 1.0 weight percent and temperatures between 21.4 and 85.0 °C. The reaction was found to be second order and dependent on the catalyst concentration at a given temperature.

The vapour liquid equilibrium data for six binary, four ternary and one quaternary systems are measured at atmospheric pressure using a modified Cathala dynamic equilibrium still. The systems with the exception of ethyl alcohol - butyl alcohol mixtures, were found to be non-ideal. Multicomponent vapour liquid equilibrium compositions were predicted by a computer programme which utilised the Van Laar constants obtained from the binary data sets. Good agreement was obtained between the predicted and experimental quaternary equilibrium vapour compositions.

Continuous transesterification experiments were carried out in a six stage sieve plate distillation column. The column was 3" in internal diameter and of unit construction in glass. The plates were 8" apart and had a free area of 7.7%. Both the liquid and vapour streams were analysed. The component conversion was dependent on the boilup rate and the reflux ratio. Because of the presence of the reaction, the concentration of one of the lighter components increased below the feed plate. In the same region a highly developed foam was formed due to the presence of the catalyst.

The experimental results were analysed by the solution of a series of simultaneous enthalpy and mass equations. Good agreement was obtained between the experimental and calculated results.

ACKNOWLEDGEMENTS

The author would like to express his thanks to the following:-

The Department of Chemical Engineering, The University of Aston in Birmingham for the provision of research facilities.

Professor G. V. Jeffreys for his supervision of the research work.

Dr. J. D. Jenkins for his interest and helpful suggestions.

The technical staff from the Department of Chemical Engineering for their help in constructing the equipment.

Mrs. B. Davies for typing the thesis.

CONTENTS.

CONTENTS. Page

Section 1.

THE SELECTION OF A SYSTEM.

1. THE SELECTION OF A SYSTEM.

A review of the factors necessary for the study of distillation with a reversible chemical reaction revealed that information would be required about the following subjects:-

a). The thermal and volumetric properties of the system.

b). An analytical technique for all the components.

c). The kinetics of the reaction.

d). The vapour liquid equilibrium data of the system.

e). The behaviour of the reacting system in a distillation column so that the validity of a proposed mathematical model could be ascertained.

The selected system should be the simplest available and one which would clearly demonstrate both the distillation and chemical reaction aspects.

Other considerations which would have to be taken into account are:-

1). The components should be available in a reasonably pure form and be relatively inexpensive particularly as the distillation column would be operating under continuous conditions.

2). All the components should be amenable to chemical analysis.

3). It would be preferable if the system contained a small number of components and the components were miscible in all proportions.

4). The difference in the components' boiling points should be as wide as possible as this will aid the separation of the components in the distillation column. Also the column should be operated at atmospheric pressure and no azeotropes be formed during the operation.

5). In the selection of the reaction it would be preferable if no solid deposition and no side reactions occurred.

6). All the components should be non-toxic, non-corrosive and non-inflammable.

7). Any other data required for the system should either be readily available or easily determined.

An appraisal of the literature revealed the following reversible reactions which might be suitable for a study of distillation with a reversible chemical reaction:-

a). ESTERIFICATION.

$ROH + RCOOH \rightleftharpoons RCOOR + H_2O$

b). ALCOHOLYSIS OF A HALIDE.

$ROH + RX \rightleftharpoons RX + ROH$

c). HYDROLYSIS OF AN ESTER.

$RCOOR + H_2O \rightleftharpoons ROH + RCOOH$

d). TRANSESTERIFICATION.

$ROH + RCOOR \rightleftharpoons ROH + RCOOR$

All the reactions contain four components and require a catalyst which will complicate both the analytical and theoretical solutions. Due to the presence of water, both the esterification and hydrolysis reactions could split into two phases creating a difficulty in the sampling and analytical procedures. Also esters and alcohols are inflammable and can be expensive.

A review of the literature revealed a complete lack of any information regarding the alcoholysis of a halide.

The transesterification of an ester by an alcohol does present problems in that a catalyst is necessary and the components may be inflammable, but they are readily amenable to certain chemical analytical techniques and can have a wide range of boiling points.

A further appraisal of the literature revealed that a considerable amount of research had been carried out in processes involving a transesterification reaction.

A number of research workers have studied the transesterification reaction between ethylene glycol and di-methyl terephthalate which is a stage in the production of the polymer poly (ethylene terephthalate). The majority of the work could be categorised as follows:-

a). An investigation into the equipment in which the reaction was carried out and often further modifications were suggested and used to improve the performance of the equipment.

b). An investigation into the characteristics of a catalyst which would enable the reaction to be carried out more quickly or would enable the polymer which would be formed from the condensation of the prepolymer, to have the correct or better characteristics and be more free from impurities.

A summary of the appropriate references are given in Table 1.1 & Table 1.2.

TABLE 1.1

The equipment used in the transesterification of di-methyl terephthalate.

EQUIPMENT	REFERENCE
Reaction Tower and Evaporator	29
Plate Column	30
Column	31
Column Distillation	6
Continuous Rotary Drum	32
Review	33

TABLE 1.2

Catalysts used in the transesterification of di-methyl terephthalate.

CATALYST	TEMPERATURE °C	REFERENCE
Lead Formate & Oxalate, Metal Acetates	—	1
Zinc Acetate	140-215	2-5
Manganese & Sodium Acetate	150-210	6
Cobalt, Lead & Zinc Acetate	—	7
Monocarboxylic Acid Salts	110-260	8
Zinc Stearate	—	9
Salts of Salicylic & Lactic Acids	110-260	10
Electronegative Metals	—	11
NaOH	—	12
PbO	260	13,14
$LiNH_2$	197	15,16
$PbSiF_6$, $KSnF_3$	197	17,18
Cadmium, Zinc & Cobalt Cyanides	197	19
Metal Thiocyanates	197	20
Sodium & Potassium Carbonate	120-140	21
LiH	—	8,18
$NaBH_4$, KBH_4	—	22
Metallic Oxides & Salts	200	23
Alumino Silicates	150	24
Boric Acid	—	25
Alkyl Substituted Guanidines	—	26
Metal Alkyls	—	27
$Sb(OR)_3$	—	4
$Ti(OC_4H_9)_4$	—	5
$(C_4H_9)_2SnR_2$: R= mono Methyl Terephthalate	190-220	28

Although the reaction between ethylene glycol and di-methyl terephthalate has been extensively studied, very little data was available for the kinetics and vapour liquid equilibria of the system. Also if the conditions were correct, there was the additional hazard that the reactants could suddenly polymerise.

From a review of the aliphatic transesterification reactions, the published research work was mainly concerned with (a) following the reaction by labelling techniques (b) the performance of certain catalysts for a given reaction (c) carrying out the reaction in the vapour phase using a solid catalyst.

Data has been published for one aliphatic transesterification reaction concerning the kinetics of the reaction in the liquid phase using (a) an acid catalyst (b) an ion-exchange catalyst (c) selective solvents containing the reaction mixture. Also some vapour liquid equilibria and thermal data are available.

Thus in view of the above considerations, the transesterification of butyl acetate by ethyl alcohol was selected for the investigation.

$$C_2H_5OH + CH_3COOC_4H_9 \rightleftharpoons C_4H_9OH + CH_3COOC_2H_5$$

Transesterification reactions can be catalysed by a wide range of catalysts as was shown in Table 1.2. Some of the commonly used catalysts are:- acids, alkalis, metal esters, ion-exchange resins, metal alkoxy derivatives, metals, metal hydrides and oxides. However, it was desirable that the catalyst would remain in the liquid phase. It was decided to select sulphuric acid as the catalyst particularly as other workers had used it to catalyse the reaction between butyl acetate and ethyl alcohol and thus some comparison could be made. Sulphuric acid is relatively inexpensive but very corrosive and consequently certain precautions were taken in the design and operation of all the research equipment.

It was found necessary to use 100 weight per cent sulphuric acid in order to eliminate the possibility of it containing any unreacted water which could cause separation into phases, side reactions and difficulties with the method of analysis.

In order to prevent any side reactions, the actual concentration of the acid would be kept to about one weight per cent of the total reacting mixture.

Section 2.

THE ANALYTICAL TECHNIQUE.

2. THE ANALYTICAL TECHNIQUE.

2.1 Literature Survey

Several methods have been described in the literature for the analysis of a mixture of alcohols and esters. A fractionation technique was used by Fehlandt & Adkins (34) to remove the lower boiling ester and alcohol and the higher boiling alcohol and ester were determined in the residue by saponification. This method was unsuitable due to the composition change in the fractionation stage.

Ester - alcohol mixtures have also been analysed by several workers (35, 36) using the turbidity technique developed by Bogin (37). Binary mixtures were analysed by Bogin (37) by titrating with water and using the degree of turbidity as the indicator. This technique was extended by Mainkar et al (35) to apply to a ternary ethyl acetate - ethyl alcohol - butyl alcohol mixture but it was concluded that the method could only be applied to a very limited range which could be increased by the addition of a known quantity of one of the components such that the mixture would be brought back into the limited measurable range.

Samples which had been taken from a reaction cell were analysed by Barker & White (38) by using a recording double-beam infra-red spectrophotometer. Samples of all compositions could be analysed with an accuracy comparable with the results obtained by Farkas et al (39).

Furnas & Leighton (40) analysed samples obtained from an Othmer Still by making density determinations at 25°C with 10cm^3 pycnometers. A calibration of specific gravity against weight per cent ethyl alcohol was obtained for the ethyl alcohol - ethyl acetate mixtures.

The percentage of ethyl acetate was estimated by

Farkas et al (39) and Mainkar et al (36), by hydrolysis with alcoholic potassium hydroxide and a back titration technique.

In their study of the mechanism of a transesterification reaction, an aqueous extraction technique followed by the addition of a known excess of sodium hydroxide and a back titration with hydrochloric acid was used by Buess-Thiernagand & Fierens (41). The results were compared with a pre-determined calibration curve.

The composition of various mixtures of the reactants and products of a transesterification reaction were determined by Farkas et al (39) who analysed the quantity of ester in an aqueous extract. The saponification number was determined for the ester content in the aqueous extract by a back-titration method. The reaction mixture composition was related to the saponification number by an empirical calibration curve which had been obtained by analysing synthetic mixtures which corresponded to the interval which the reaction had progressed. A linear calibration curve was determined with an accuracy of 0.5% and the analysis time was claimed to be less than one hour.

Several workers have analysed ester - alcohol mixtures using gas liquid chromatographic techniques. Butyl alcohol - butyl acetate mixtures were analysed by Shaposhnikov et al (42) using a thermal conductivity detector and a column packing of diatomaceous brick with a stationary phase of poly (ethylene adipidate). With an oven temperature of 85°C, air as the carrier gas and iso amyl alcohol as the internal standard, samples were analysed giving results to an accuracy of ±5%.

Propyl alcohol was used as the internal standard by Curry et al (43) for the determination of ethyl alcohol in blood samples. However, samples were analysed using a flame ionization detector with an automatic integrator at the same oven temperature but using columns containing 10% poly ethylene glycol (molecular weight 400) as the stationary phase on 100-120 mesh celite as the support. The carrier gas was argon. By comparing the peak heights of ethyl alcohol and propyl alcohol a calibration was obtained with an accuracy of ±3%.

In their studies of a transesterification reaction in the presence of an alkyl aluminium catalyst, ethyl acetate was analysed at 95°C by Selwitz & Walde (44) using a gas chromatographic technique. For the transesterification of ethyl aceto acetate and methyl alcohol (45), the progress of the reaction was monitored by analysing samples on a column containing celite 545 as the support and a mixture of 13 weight per cent sebacate and two weight per cent poly ethylene glycol (molecular weight 400) as the stationary phases. The analysis was carried out at 120°C with hydrogen as the carrier gas.

2.2 Selection of Analytical Technique

The main requirements for the analytical technique were:-

1). An accurate method.

2). A method which would be applicable to all the components used in the reaction and which would be suitable for all the experimental equipment.

3). The method must not be time consuming.

The earlier methods (fractionation, turbidity, density, extraction and back titration, saponification) which have been reviewed are considered to be very time consuming. As a large number of samples would have to be analysed, it was considered that it was imperative that an analytical technique with a short analysis time should be selected.

As a transesterification reaction requires a catalyst, it was realised that as soon as the sample had been removed from the equipment that it would either have to be neutralised or immediately analysed. A similar problem was resolved by Juvet & Wachi (46) in their transesterification studies by immediately analysing the sample on a gas liquid chromatograph. It was found that the catalyst and reactants separated so quickly in the column that no change in composition was observed.

Although the accuracy of the analysis using a gas chromatograph has been previously reported as being low, the speed with which the analysis could be determined is very favourable. Thus after considering all the methods available for analysing ester-alcohol mixtures, a Gas Liquid Chromatograph (G.L.C.) with a Flame Ionization Detector (F.I.D.) (47) was used to analyse all the samples in this research.

2.3 The Gas Liquid Chromatograph

2.3.1 Description of the Equipment

The Gas Liquid Chromatograph and the ancillary equipment are shown in Fig. 2.1 and Plate 1.

Argon was used as the carrier gas and was passed through the two stainless steel columns which were contained in a constant temperature oven. A hydrogen-air flame was burnt in each detector head. The gas flowrates were controlled by pressure gauge regulators which were attached to the gas cylinders and by the flow restrictors which were situated on the top of the oven. The gas flowrates were measured by using a bubble flowmeter.

The constant temperature oven was controlled by a temperature programming unit. The oven could be maintained at a required temperature under isothermal conditions for any given time interval

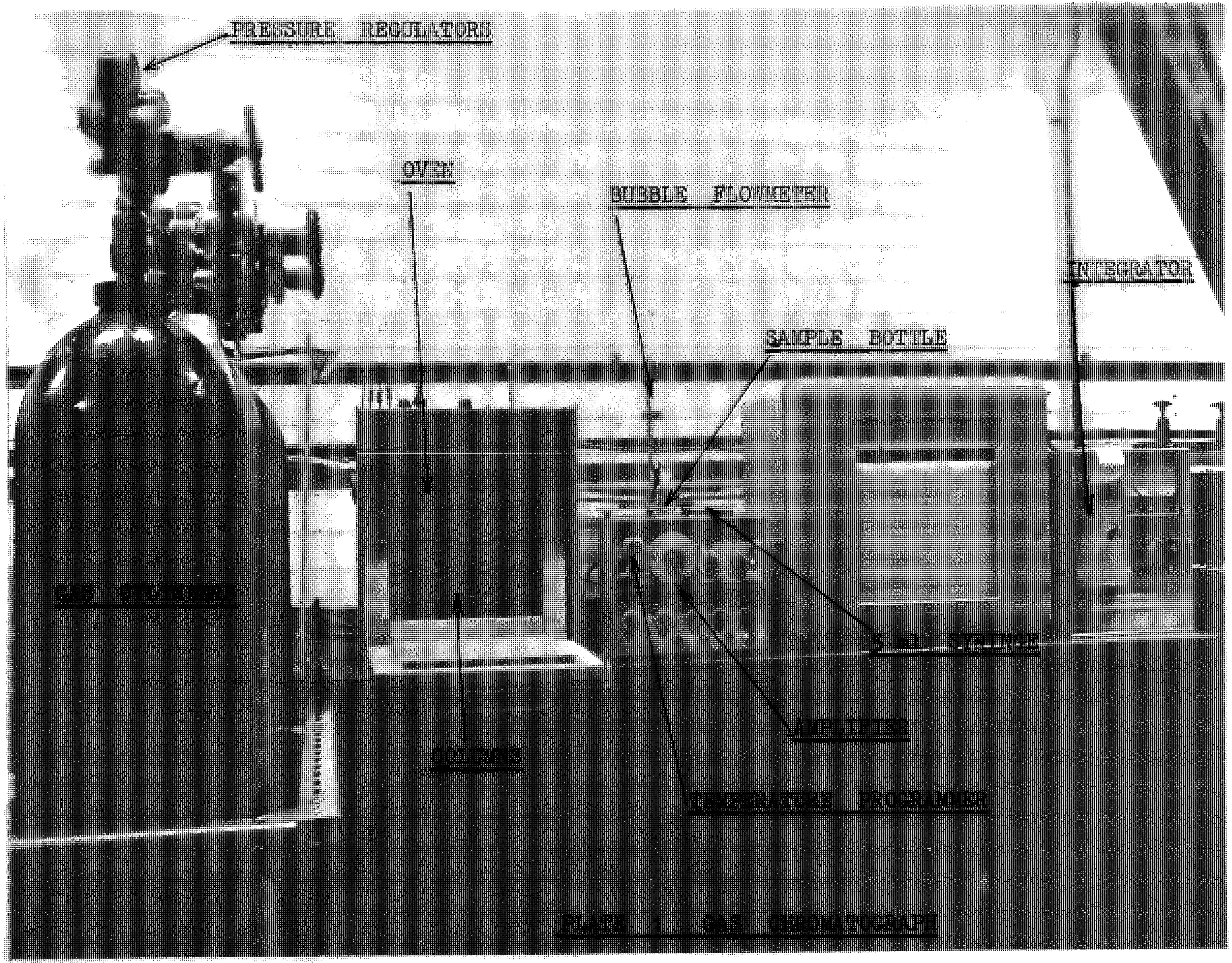


PLATE 1 GAS CHROMATOGRAPH

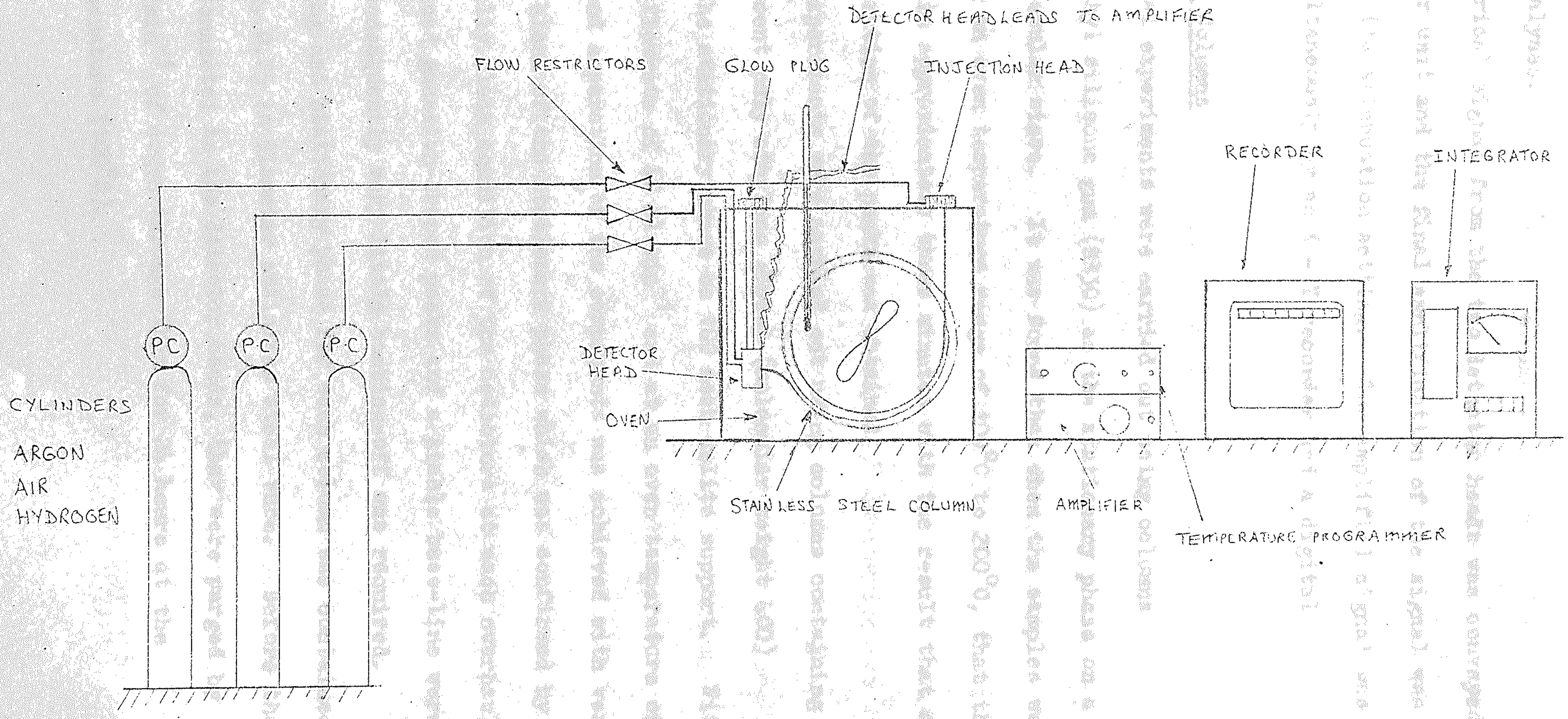


FIG 2.1 GAS LIQUID CHROMATOGRAPH

or it could be heated at a predetermined rate for temperature programming analyses.

The electrical signal from the two detector heads was conveyed to an amplifier unit and the final amplification of the signal was dependent upon the attenuation setting. The amplified signal was displayed simultaneously by an X - Y recorder and a digital integrator.

2.3.2 The Columns

The initial experiments were carried out using columns containing methyl silicone gum (SE30) as the stationary phase on a support of molecular sieve. It was found that when the samples were analysed using an oven temperature range of 100°C to 200°C, that they were resolved in approximately three minutes with the result that a very poor separation of the peaks was obtained.

Further experiments were carried out using columns containing 10 weight per cent poly ethylene glycol (molecular weight 400) (PEG 400) as the stationary phase on 100 mesh celite support. With a carrier gas flowrate of 40 ml min^{-1} and at an oven temperature of 100°C, very good separation of the components was achieved with very little column bleed of the stationary phase which was confirmed by the exceptionally clean condition of the detectors at each overhaul. Hence well spaced gaussian-shaped peaks and a stable base-line were obtained and consequently very little backing-off was required.

The packing and stationary phase for each column was contained in a 5 ft long, 0.25 in diameter stainless steel tube. Before the columns were connected to the detector heads, they were purged by passing 45 ml min^{-1} of argon through them for 24 hours at the operating temperature (100°C).

2.3.3 The Gas Flowrates

To prevent base-line drift and recorder-pen fluctuations pure gases are required. It was thought to be essential that the air should not contain any water (as this could extinguish the flame) and any hydrocarbons (which could cause constant or erratic background signals such as base-line drift or recorder-pen fluctuations). For these reasons high purity air, white-spot hydrogen and commercial-grade argon were used and the specifications are listed in Appendix A1.

In the selection of the gas flowrates, the retention time of each component in the sample has to be considered because the retention time of the sample is directly related to the gas flowrates and in particular to the carrier gas flowrate (48). Also the degree of separation of each component is a function of the carrier gas flowrate.

The hydrogen, air and argon pressure regulators were calibrated for flowrate against gauge pressure over a range of 0-700 ml min^{-1} for air and 0-200 ml min^{-1} for argon and hydrogen using a bubble flowmeter.

In order to prevent too much condensation in the detectors it was recommended (47) that a 15:1 air:hydrogen flowrate was used. It was concluded by Batt & Cruickshank (49) that to obtain good flame stability and hence reproducible results it was necessary to have an extremely high flowrate of compressed air.

After considering the above comments, the carrier gas (argon) and hydrogen flowrates were each set to 40 ml min^{-1} whilst an air flowrate of 500 ml min^{-1} was found to be satisfactory.

2.3.4 The Start-up and Shut-down Procedure

The recommended (47) start-up and shut-down procedures (which are tabulated below) are designed to prevent any damage to the equipment in particular the column packings and the detector heads and to allow sufficient time for the electrical equipment to warm up.

1). The amplifier was switched onto warm up for 30 minutes.

2). The integrator and pen recorder were switched on.

3). The carrier gas was turned on and set to 40 ml min^{-1}.

4). The oven fan was switched onto boost and the oven was heated to 100°C at a set rate of 12 degC min^{-1}.

5). The air and hydrogen flows were turned on and set to 100 ml min^{-1} and 40 ml min^{-1} respectively. Both flames were ignited, the detector head caps were removed to prevent excess condensation in the detectors. After five minutes, the air flowrates were gradually increased to 500 ml min^{-1}.

6). The oven fan was switched to slow speed.

7). The amplifier was zeroed after the warm up period had elapsed.

8). The detector head caps were replaced, the co-axial cable from the detectors to the amplifier was connected and the amplifier was zeroed again.

9). The required attenuation was selected and any column-bleed was backed-off.

10). The integrator was zeroed, set to correct percentage cut-off and the appropriate dip-detector was chosen.

11). The pen recorder was switched to the correct chart speed.

The shut-down sequence was:-

1). The amplifier was switched to set-zero range.

2). The oven fan was switched to boost, the oven heaters were switched off and the oven door was opened to allow the oven to cool.

3). The co-axial cable from the detectors to the amplifier was disconnected.

4). The hydrogen and air were turned off.

5). The integrator, pen recorder and amplifier were switched off.

6). The oven fan was switched off when the oven temperature was 30°C.

7). The argon was turned off.

2.4 The Chromatograms

2.4.1 Evaluation of Chromatograms

Various techniques can be used to calculate the peak area as each component is eluted. It has been found (50) that for quantitative work, more accurate results can be obtained using peak areas rather than peak heights.

The peak area can be determined by (a) planimetry (b) triangulation (c) peak height x width at half peak height (d) cut & weigh (e) peak height x retention time (f) digital integrator.

It was found that techniques (a)-(e) inclusive were dependent upon the operator's skill and the accuracy of the measuring instrument. A similar conclusion was reported by Gill & Tao (51). It was stated by Condal-Bosch (52) that methods (b) & (c) only compute about 97% the actual peak area whilst it was found by Knox (50) that methods (b), (c) & (e) were inaccurate for unsymmetrical peaks. Techniques (a)-(e) inclusive are dependent on the accuracy of the X - Y recorder, a fact which was observed by Gill & Tao (51) and Girling & Gigg (53). In the comparison of seven

X - Y recorders it was noted that the error in the recorders was approximately three times greater than that of the integrator which was monitoring the same signal. Girling & Gigg (53) concluded that the error was due to irregular chart travel. Techniques (a)-(e) inclusive (50-53) were reported as being tedious and time consuming whilst it was stated by Gill & Tao (51) that method (f) was more accurate and faster.

As the whole of the research programme was dependent upon an accurate and fast analytical technique, it was concluded that all the peak areas should be evaluated using a Chromalog digital integrator (54) in parallel with an X - Y recorder.

2.4.2 The Relationship between Peak Area and Composition

The peak area can be related to the sample composition by using a normalisation technique and it is assumed that all of the injected sample is eluted. The weight percentage of a particular component X in a sample is given by:-

$$\% X = \left(\frac{A_x}{A_w + A_x + A_y + A_z} \right) \times 100 \qquad 2.1$$

where A_w, A_x, A_y, & A_z, are the peak areas of the components W, X, Y & Z respectively. From 2.1 a calibration curve relating weight composition and peak area can be constructed.

However, the peak areas obtained from the chromatograms are not always related to the composition because the detector response can be different for each molecular type or class of compounds. Thus a response factor is introduced which corrects for the detector response. Damm et al (55) found that if the response factors were made relative to an added internal reference compound whose response factor was set equal to unity, then the accuracy of a calibration could be improved if the relative response factors were used in conjunction with the normalisation technique.

The response factor (f) of a pure component X is obtained by analysing a standard sample and is defined as:-

$$f_x = \frac{A_r}{A_x} \times \frac{W_x}{W_r} \times f_r \qquad 2.2$$

where A_x = Peak area of component X

A_r = Peak area of internal reference R

W_x = Concentration of component X (wt %)

W_r = Concentration of reference R (wt %)

f_r = Response factor of reference R.

2.5 Selection of the Reference Compound

The selection of the internal reference compound was based upon the following criteria:-

1). The compound must not react with the components of the system.

2). The compound must be a liquid.

3). The compound should not be eluted at the same time as the other components of the system and preferably it should be eluted before the other components.

Benzene, toluene, acetone and ethyl methyl ketone were all tried as the reference compounds but when they were tested, they were found to have retention times which were similar to the components of the system.

Other reference compounds which have been reported in the literature and used successfully are iso amyl alcohol (42, 43), nonane (56, 58), iso-octane (57) and 1,1 dichlorobutane (55). After further investigations iso-octane (trimethyl pentane) was found to have a retention time of 56 seconds and thus as it was a compound which would not react with the components of the system and it would also have the advantage of being the first component to be resolved, it was selected as the internal reference compound.

2.6 The Sampling Technique

The quantity of iso-octane which had to be added to a sample had to be determined so that for a given attenuation, on-scale peaks would be obtained for all the components. Greater accuracy could be obtained by changing the attenuation as each component was resolved but it was decided that a constant attenuation setting was more desirable so that whilst each sample was being analysed the operator would be able to monitor other equipment.

If the sample : reference compound was 6:1 (mass basis) and the attenuation was 50×10^3, on-scale peaks were obtained for each component in the sample over a concentration range of 0-100 mole % of each component.

Before each sample was taken, the syringe was flushed out and then a 3ml sample was removed and added to a predetermined quantity of iso-octane which was contained in a sample bottle. For a 3ml sample and a 6:1 sample : reference compound, 0.42g of iso-octane was required. The sample bottle was tightly stoppered, shaken vigorously and a 0.1μL sample was injected into the chromatograph using a 0-1.0μL syringe which had been flushed out prior to taking the sample.

With the above analytical technique, the interval between the sample being removed from the reactor, equilibrium still or distillation column and being injected into the chromatograph was very short and usually was less than 20 seconds, whilst the time taken to analyse the sample in the chromatograph was seven minutes.

2.7 Typical Chromatogram.

A typical chromatogram is illustrated in Fig. 2.2 with the integrated areas for each peak. The relationship between the peak area traced by the pen recorder and the integrated value can be determined as follows:-

$$\text{chart speed} \times \text{full scale deflection} = 2{,}500 \text{ counts min}^{-1} \qquad 2.3$$

The operating conditions for the results illustrated in Fig. 2.2 were:-

Argon = 40 ml min^{-1} Hydrogen = 40 ml min^{-1} Air = 500 ml min^{-1}

Columns = 10 weight per cent poly ethylene glycol (PEG 400) on 100-120 mesh celite.

Oven temperature = 100°C Attenuation = 50×10^3

Sample : reference = 6:1 (mass basis) Sample injected = 0.1μL

Pen recorder chart speed = 15 in min^{-1}

Integrator = 0.5% scale cut-off V-dip detector set.

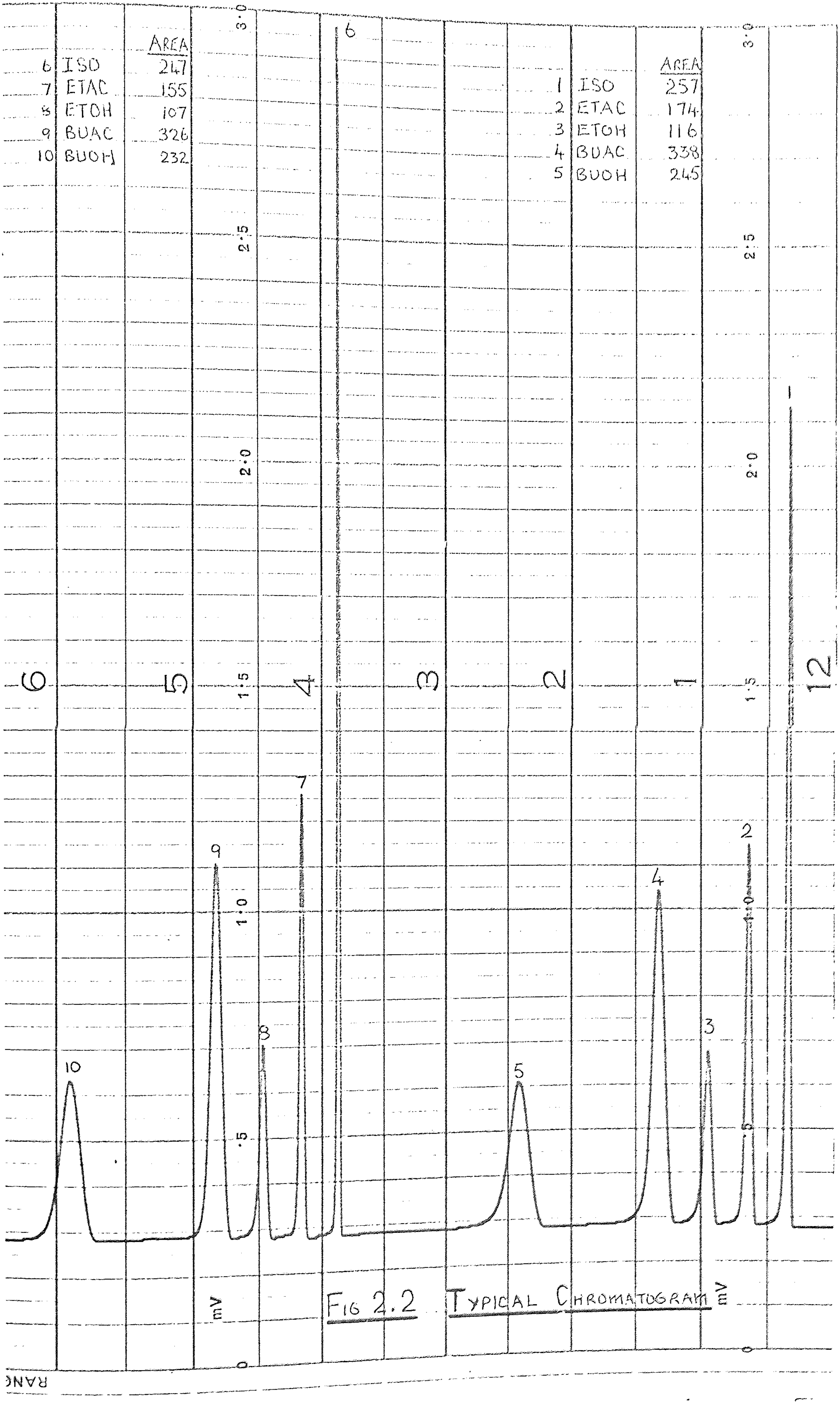
The component retention times were:-

Iso-Octane		56 seconds
Ethyl Acetate	1 minute	28 seconds
Ethyl Alcohol	2 minutes	9 seconds
Butyl Alcohol	3 minutes	6 seconds
Butyl Acetate	5 minutes	40 seconds

2.8 The Calibration of the Chromatograph

2.8.1 To Evaluate the Response Factors.

A sample containing 10g of one component and 1.67g of iso-octane was made up. The chromatograph was set into operation as outlined in 2.3.4 and a 0.1μL sample was injected into the chromatograph. The sample was analysed ten times and an average value was used. The same procedure was repeated for the remaining three components. The value of the response factor of the reference compound was set to unity and the response factors were calculated



		AREA
6	ISO	247
7	ETAC	155
8	ETOH	107
9	BUAC	326
10	BUOH	232

		AREA
1	ISO	257
2	ETAC	174
3	ETOH	116
4	BUAC	338
5	BUOH	245

FIG 2.2 TYPICAL CHROMATOGRAM

for the four components of the system. The results are tabulated in Appendix A2.

2.8.2 To Calibrate the Chromatograph

Binary samples of the four components were made up, each sample weighing 10g. 1.67g of iso-octane was added to each sample and the compositions of these standard solutions are tabulated in Appendix A3. A 0.1μL sample of the binary mixture and the reference compound was injected into the chromatograph and each sample was analysed ten times and an average value was determined. From the results $\frac{f_x A_x}{\Sigma f A}$ was determined for each component where

f_x = response factor of component X

A_x = peak area of component X

ΣfA = summation of the product fA of all the components in the sample.

The results of the analysis of the binary and reference samples are tabulated in Tables 1-27 of Appendix A4. It was observed that for each component in the sample (i.e. including the reference compound) that the factor $\left(\frac{f_x A_x}{\Sigma f A}\right)$ was directly equal to the weight fraction of the component in the sample. The same conclusion was observed by Damm et al (55) who calibrated a mixture of nonane, 1:1 dichlorobutane and ethyl benzene using nonane as the internal reference compound and from their results the worst error was calculated as 1.5%.

From Table 28 Appendix A4 and Fig. 2.3 it can be seen that the worst error involved in equating $\frac{fA}{\Sigma fA}$ to the measured (true) weight per cent was $\mp 2.16\%$ and this error occurred when small percentages were being measured whilst for large percentages being measured the error was of the order of ±0.2%. The average error was found to

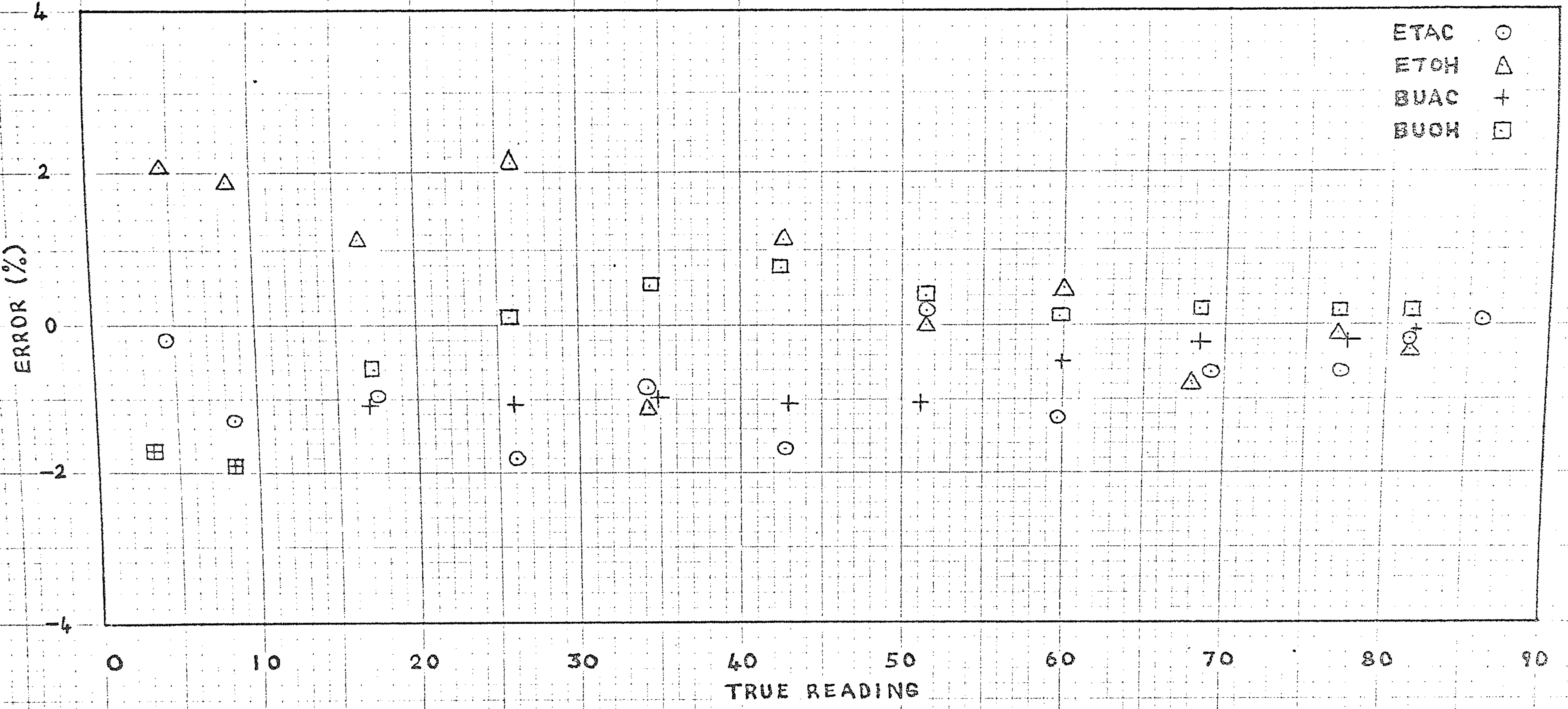


Fig 2.3 Percentage Error vs True Reading.

be ±0.73%.

Thus a computer programme was formulated to calculate the composition of a sample. The only data which was inputted was the number of samples being analysed, the peak areas of the reference compound and the four components. The calculation time for each sample was one minute and the outputs were displayed as weight and mole per cents of the four components in the original sample. The computer flow diagram, programme and typical results sheet are tabulated in Appendix A5.

2.9 Operating Checks and Maintenance of the Chromatograph

It was observed that as the chromatograph was in continual use that the properties of the column would gradually change with time. The response factors were periodically checked and continually updated in the computer programme. The gas flowrates were checked weekly whilst the carrier gas flowrate was checked before each experiment. The condition of the columns was found to remain good with very little column bleed being detected. This was substantiated by the excellent condition of the detector heads which was observed at each annual overhaul.

Section 3.

THE REACTION KINETICS.

3. THE REACTION KINETICS.

3.1 Introduction

Stoichiometrically, the transesterification reaction can be written as:-

$$C_2H_5OH + CH_3COOC_4H_9 \overset{H_2SO_4}{\rightleftharpoons} C_4H_9OH + CH_3COOC_2H_5$$

where one mole of ethyl alcohol reacts with one mole of butyl acetate in the presence of concentrated sulphuric acid as the catalyst to give one mole of butyl alcohol and one mole of ethyl acetate as the reaction products.

3.2 Literature Survey

Farkas et al (39) studied the reaction in a batch reactor. The reactants were mixed in a reactor together with the catalyst which was contained in a sealed ampoule. The reactor was immersed in a thermostat whose temperature was controlled to $\pm 0.1^\circ C$ and the reactants were heated to the required reaction temperature. The ampoule was broken, the vessel shaken, a sample was taken and the timing of the reaction commenced. Samples were taken at varying intervals.

Martin & Krchma (59) considered the reverse reaction and their objective was to displace the equilibrium of the reaction in favour of the products. The reaction was carried out in a hydrocarbon-water system which forms two phases. Both the reactants preferentially dissolved in the hydrocarbon phase. As the reaction proceeded, the product (ethyl alcohol) preferentially dissolved in the aqueous phase whilst the other product (butyl acetate) dissolved in the hydrocarbon phase. Thus as one reaction product was removed from the reaction zone, the reaction was claimed to proceed to almost 100% completion. The reaction was carried out under total reflux for three hours. The aqueous phase was distilled off at $85^\circ C$

leaving a dry ester-hydrocarbon mixture from which the ester was recovered by distillation.

Haken (60) in his studies on the transesterification of n-alkyl methacrylates used a reaction flask fitted with a 48" fractionating column. When the reflux temperature had reached the required value the distillate which mainly contained the alcohol product of the reaction was continuously removed. The ester was contained in the residue in the reactor.

In a later publication, Haken & McKay (61) pointed out that the equilibrium of the reaction between an alcohol and a methacrylate could be displaced in favour of the products by the continuous removal of an azeotrope containing a high percentage of the product alcohol and a small quantity of the reacting ester. It was found that if the temperature at which the azeotrope distilled off was not accurately controlled, then the azeotrope composition would rapidly change for a very small change of temperature and the reaction would not proceed to completion.

So that the azeotrope could be removed accurately at the required temperature, Haken & McKay (61) constructed a temperature controlled swinging funnel head which enabled the reflux to be removed whilst the temperature was below the required temperature. The temperature controller unit also regulated the heat input to the reactor and a manometer was used to control the column pressure drop. If the pressure drop increased, the reactor heat input was decreased thereby reducing the possibility of polymerisation.

Farkas et al (39) carried out the reaction at 60, 70 and 80°C using butyl:ethyl group ratios of 1:1 and 1.55:1 and a catalyst concentration of 0.1 and 0.2 weight per cent of anhydrous 100 weight per cent sulphuric acid. Two reactions were carried out in the reverse direction whilst the remainder were in the forward direction and a blank experiment was performed in the absence of any catalyst and after 90 hours no reaction had taken place. The equilibrium constant was measured at 60°C and 80°C and was found to be independent of temperature having a mean value of 0.96 which compared favourably with the value of 0.97 at 200°C which was calculated from Fehlandt & Adkin's (34) data.

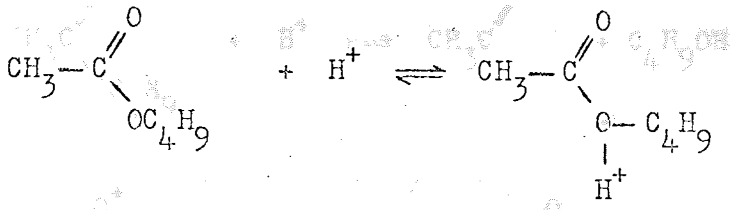
Martin & Krchma (59) used sulphuric acid as the catalyst but they considered that either hydrochloric acid or phosphoric acid could be used as the catalyst. One volume of butyl alcohol, 1.6 volumes of a mixture containing 85% ethyl acetate and 15% ethyl alcohol, three volumes of water, 0.45 volume of sulphuric acid and three volumes of a hydrocarbon whose boiling point was between 200°C and 250°C were used to carry out the reaction, but unfortunately no further data was given for the reaction.

Barker & White (38) used a cation-exchange resin catalyst in their fixed bed reactor. The bed was contained in a 31mm I.D. glass reactor and the feed was preheated. The majority of the experiments were carried out with the feed flowing up through the resin bed which was supported on a 200 mesh stainless steel screen. The catalyst was Dowex-50, a low breakage resin which essentially is a monosulfonated, cross-linked polystyrene resin. The resin was screened into five increments between 20 and 115 mesh size and a quantity of resin from each fraction was then treated with 10% hydrochloric acid to convert the resin into the hydrogen form. The beads were air dried and non-spherical particles were removed.

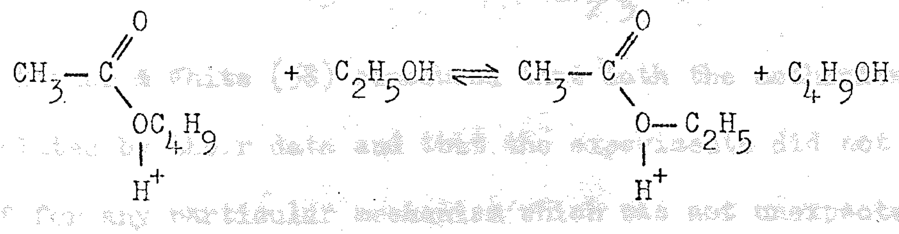
The reaction was carried out with a feed composition of between 0.5 and 4.0 mole ratio of ethyl alcohol to butyl acetate flowing at between 6 and 60 $gh^{-1}cm^{-2}$. Most of the experiments were carried out at 60°C whilst some were carried out at 50, 70 and 80°C and the equilibrium constant was measured at 25°C and was found to be 0.96 which agreed well with the previously published data.

Esterification mechanisms were applied to the transesterification reactions by both Farkas et al (39) and Carroll (62) with some success which might be expected due to the simularity of the reactions.

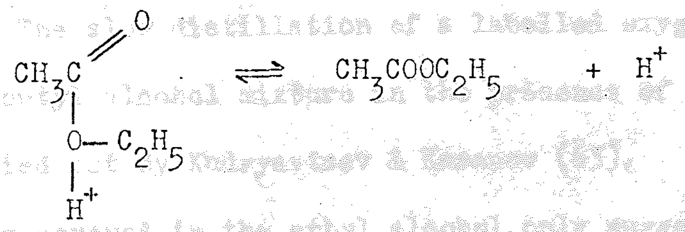
Barker & White (38) suggested the following mechanisms for the transesterification reaction:-



3.1



3.2



3.3

The same reaction sequence was also applied by Farkas et al (39) who assumed that reactions 3.1, 3.3 were fast and that reaction 3.2 was controlling and quoted the following rate expression:-

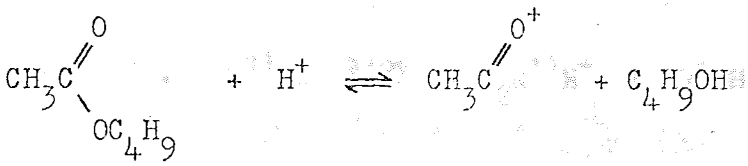
$$r_v = k_1 \, (H^+) \left[(BUAC)(ETOH) - \frac{(BUOH)(ETAC)}{K} \right] \qquad 3.4$$

where mole fractions were used instead of concentrations. Barker & White (38) commented that in using this procedure it amounted to using the following rate expression:-

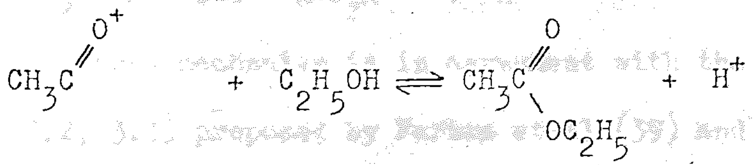
$$r_v = \frac{k_2 (H^+)}{\rho_L} \left[(BUAC)(ETOH) - \frac{(BUOH)(ETAC)}{K} \right] \qquad \text{———} \quad 3.5$$

Barker & White (38) stated that 3.5 correlated their data better than 3.4 although 3.5 was not theoretically valid.

A different mechanism for the formation of the ester was also formulated by Barker & White (38).



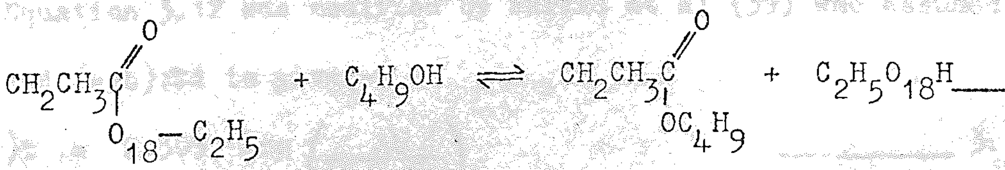
$$CH_3C(=O)OC_4H_9 + H^+ \rightleftharpoons CH_3C{=}O^+ + C_4H_9OH \qquad \text{———} \quad 3.6$$



$$CH_3C{=}O^+ + C_2H_5OH \rightleftharpoons CH_3C(=O)OC_2H_5 + H^+ \qquad \text{———} \quad 3.7$$

Barker & White (38) concluded that both the mechanisms were correlated by their data and that the experiments did not represent proof for any particular mechanism which was not unexpected for such a non-ideal quatenary mixture.

The slow distillation of a labelled oxygen atom ethyl propionate and butyl alcohol mixture in the presence of metallic sodium was carried out by Kudryavtsev & Kwsanov (63). The labelled oxygen atom was recovered in the ethyl alcohol only suggesting that the reaction proceeds through the acyl-oxygen fission as proposed by Barker & White (38) (3.6 & 3.7) :



$$CH_2CH_3C(=O)O_{18}-C_2H_5 + C_4H_9OH \rightleftharpoons CH_2CH_3C(=O)OC_4H_9 + C_2H_5O_{18}H \text{———} 3.8$$

The transesterification of 0^{18} labelled vinyl and alkenyl acetates with palladium chloride or platinum as catalysts was considered by Sabel et al (64) who concluded that the reaction proceeded through alkenyl-oxygen fission.

The transesterification of primary alkyl esters such as methyl and butyl propionates and acrylates was studied by Buess-Thiernagand & Fierens (41) using an acidic catalyst and they concluded that the mechanism was bimolecular and was demonstrated as follows:-

$$RCO_2R^1 + H^+ \rightleftharpoons RCO_2R^1H^+ \qquad \_\_\_\_\_\_\_\_ \; 3.9$$

$$RCO_2R^1H^+ + R^{11}OH \overset{\text{slow}}{\rightleftharpoons} RCO_2R^{11}H^+ + R^+OH \qquad \_\_\_\_\_\_\_\_ \; 3.10$$

$$RCO_2R^{11}H^+ \rightleftharpoons RCO_2R^{11} + H^+ \qquad \_\_\_\_\_\_\_\_ \; 3.11$$

The above mechanism is in agreement with the mechanism (3.1, 3.2, 3.3) proposed by Farkas et al (39) and Barker & White (38) but Buess-Thiernagand & Fierens (41) stated that the mechanism for the transesterification in a basic solution was bimolecular and occurred with the rupture of the acyl-oxygen bond whilst in a neutral solution the mechanism was monomolecular again with the rupture of the acyl-oxygen bond.

The only quantitative rate data was determined and evaluated by Farkas et al (39) who integrated 3.4 to obtain:-

$$k_1(H^+)t = \frac{1}{\sqrt{(a+b)^2 - 4ab(1-\frac{1}{K})}} \ln\left(\frac{2ab-x\left[a+b-\sqrt{(a+b)^2 - 4ab(1-\frac{1}{K})}\right]}{2ab-x\left[a+b+\sqrt{(a+b)^2 - 4ab(1-\frac{1}{K})}\right]}\right)$$

$$\_\_\_\_\_\_\_\_ \; 3.12$$

Equation 3.12 was modified by Farkas et al (39) who assumed that $K \hat{=} 1$ and $(a+b) \hat{=} 1$ to give:-

$$k_1(H^+)t = 2.303 \log\left(\frac{ab}{ab - x}\right) \qquad \_\_\_\_\_\_\_\_ \; 3.13$$

From their experimental results the parameter $\log\left(\frac{ab}{ab - x}\right)$ was plotted against time and a series of straight lines were obtained from which they evaluated a first order forward rate constant for each temperature. It was concluded that the rate constants were independent of alcohol to ester reactant ratio and the direction of the reaction but was dependent on the catalyst concentration and the temperature.

The rate data was reduced to a common acid concentration and a graph of $\log k_1$ against $\frac{1}{T}$ was plotted from which a value for the activation energy was obtained.

The reactions between a series of esters and alcohols were considered by Fehlandt & Adkins (34) who computed the equilibrium constant for each reaction. From the data a numerical comparison of the reactivities of the alcohols was made by calculating the ratio of the product ester to the reactant ester and equating this result to the reactivity of the reacting alcohol. The reactivities were then made relative to methyl alcohol. Fehlandt & Adkins (34) concluded that a substituted group for a hydrogen atom, reduced the reactivity whilst branching or a double bond also reduced the reactivity.

The same technique was used by Hatch & Adkins (65) who concluded that a primary alcohol had a greater reactivity than a secondary alcohol, that the introduction of an unsaturated group into the alcohol also reduced the reactivity whilst the value of reactivity did not change progressively as a homologeous series (aliphatic or aromatic) was being ascended.

The results of the various investigators may be summarised as follows:-

1). A variety of equipment has been used to study the transesterification reactions.

2). The transesterification of butyl acetate by ethyl alcohol has been investigated over a limited temperature and catalyst concentration range.

3). The reaction has been catalysed by different acidic catalysts.

4). The reaction has been carried out from both directions and to its equilibrium.

5). The reaction has been investigated under continuous conditions in an ion-exchange resin bed.

6). Some reaction mechanisms have been proposed and one mechanism has been confirmed by the use of "labelling" the acetate with O^{18}.

7). For approximately equimolar conditions, the reaction mechanism is second order but the only available kinetic data is based on a first order approximation.

In conclusion, although the transesterification of butyl acetate and ethyl alcohol has been investigated previously, the reaction rate kinetics have been considered by only one worker. The research was carried out over a very limited temperature and catalyst concentration range and most of the data was evaluated for the forward reaction with equimolar reactants only. The equilibrium constant and the activation energy for the reaction have been either measured or derived by other workers.

As an accurate knowledge of the reaction rate data is important, particularly in the study of distillation with a chemical reaction, since any errors in the data would cause inaccuracies in the application of any theoretical model, it was decided that a practical determination of the rate data should be carried out.

3.3 Materials Specification

The materials used were of "Analar" grade with one exception, that being butyl acetate which could only be economically obtained in the "Laboratory General Purpose" grade. The same grade for each component was used throughout the whole of the research work.

The exact specification for each component is quoted in Appendix A1. For kinetic work, highly purified materials are normally used, but in this case "Analar" grade materials were used because the object of the work was to obtain operating data rather than absolute values.

3.4 Description of the Equipment

A diagram of the Batch Reactor Equipment is shown in Fig. 3.1 (See also Plates 2 and 3).

A one litre batch reactor (A) was connected to a preheater (B) of the same volume. The reactor was electrically stirred, the stirrer passing through a double walled ground glass gland, and the gland contained a silicone rubber insert and was packed with silicone grease. During the experiments, the reactor was vented to the atmosphere through vent (D) and any vapours escaping from the reactor were condensed by a line condenser (G). Liquid samples were removed from the sample point (S) using a 5cc capacity hypodermic syringe.

The reactants were fed into the reactor either through the feed funnel (H) or were transferred from the feed preheater through the feed inlet (C) by pressurising the feed preheater.

Both the reactor and feed preheater were connected to a pressure system such that both vessels could be pressurised and consequently emptied. The reactor was emptied through the waste product line (K). The pressure system was controlled by an Edwards pressure controller

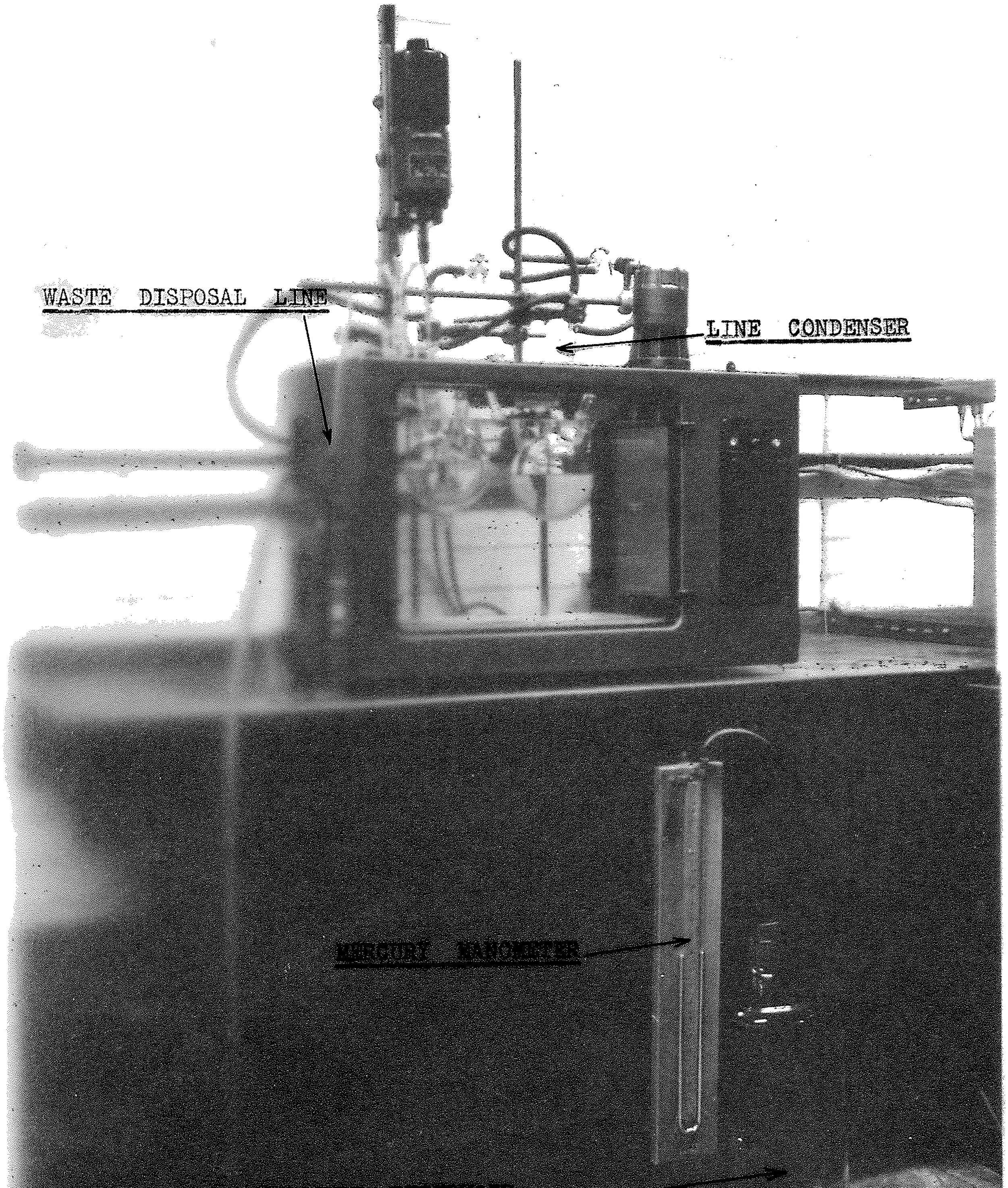


PLATE 2 BATCH REACTOR

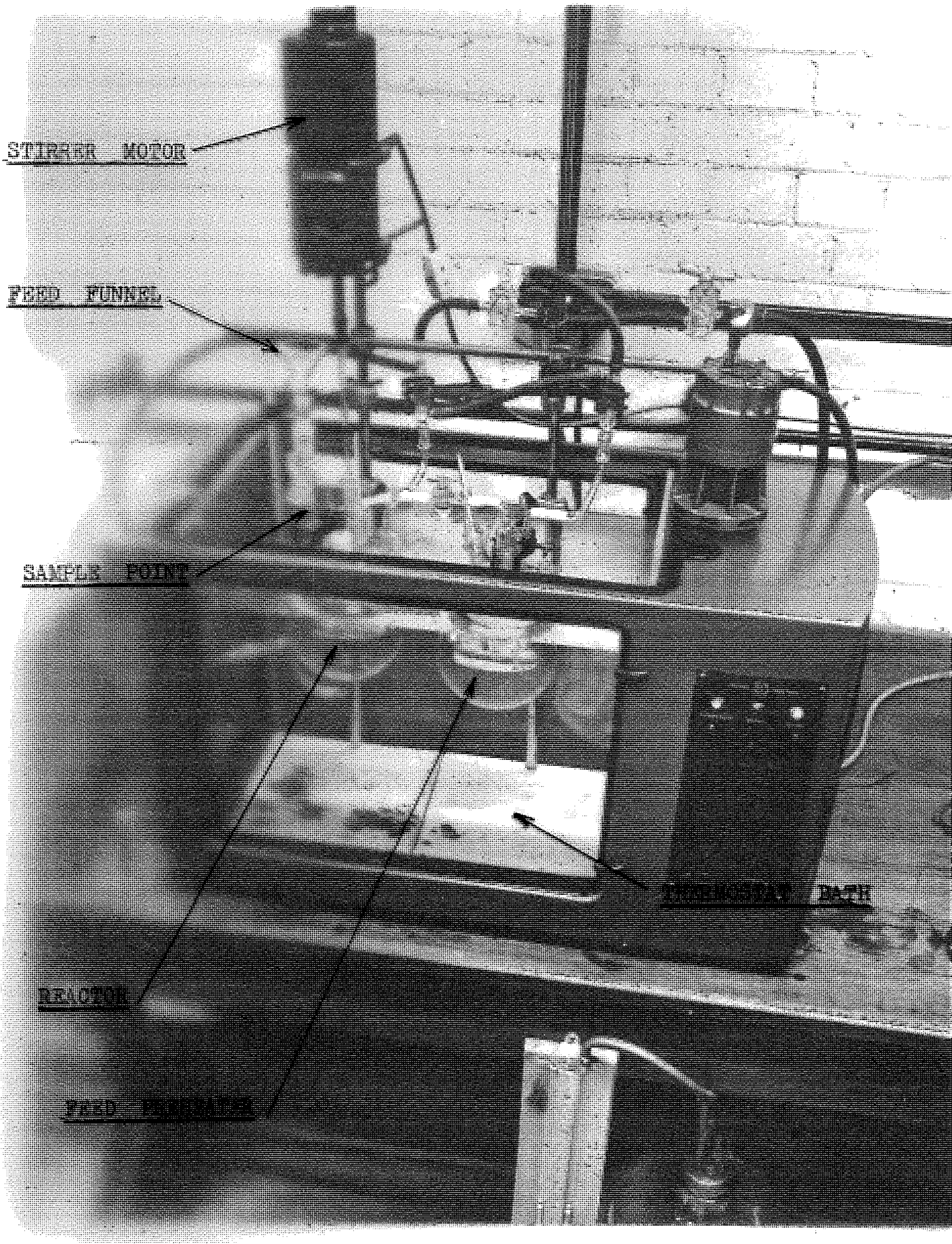


PLATE 3 BATCH REACTOR

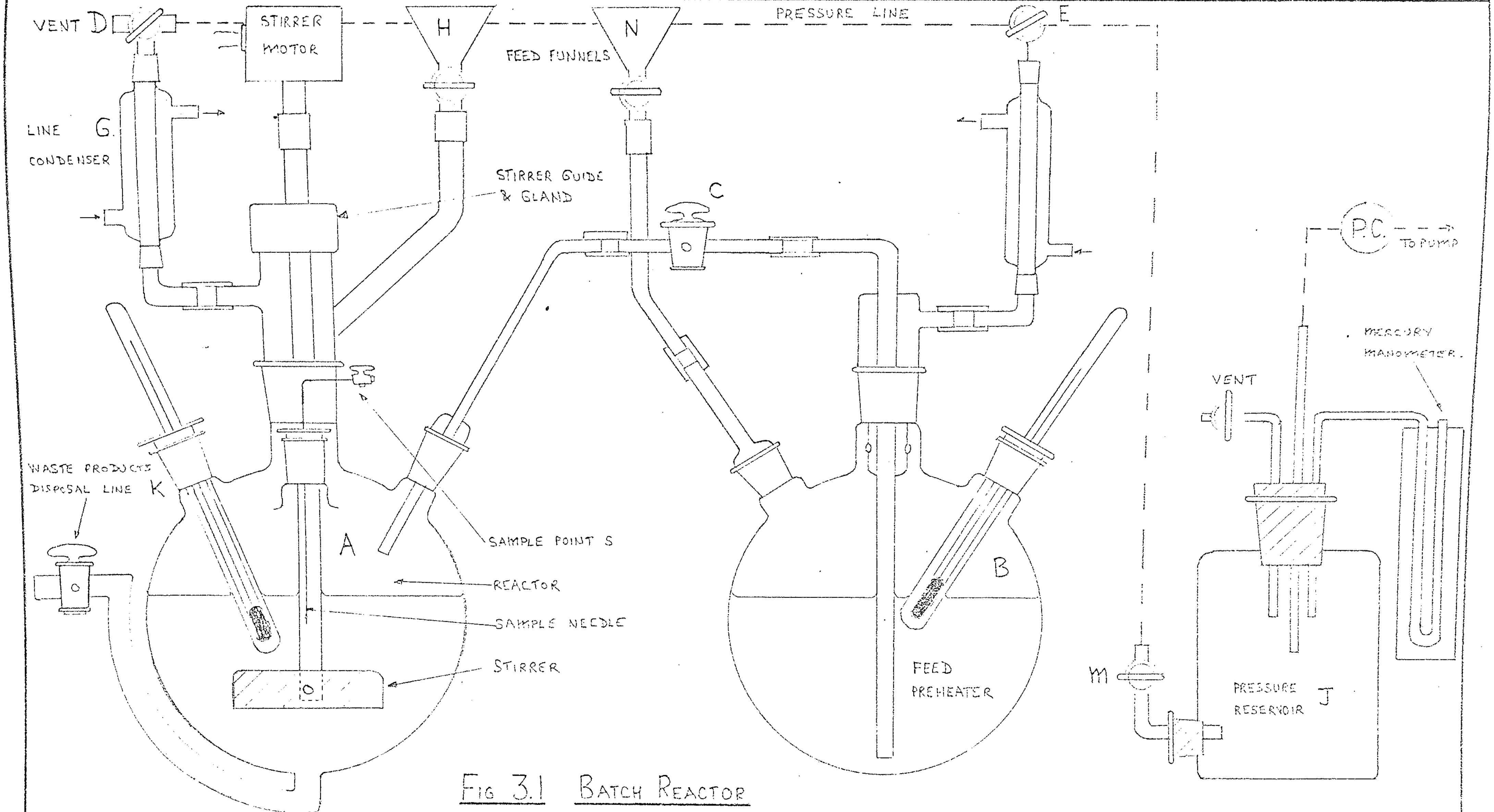


Fig 3.1 Batch Reactor

which allowed the pressure reservoir (J) to be pressurised to 10cm of mercury. The pressure of the reservoir was measured by a mercury manometer.

The reactor and feed preheater were immersed in a Townson & Mercer constant temperature oil bath and the temperatures of the reactor and feed preheater were measured by mercury in glass thermometers graduated to 0.1°C intervals.

3.5 Method of Operation

The oil bath was set to the approximate temperature required to maintain the reactor and feed preheater at the desired temperature. The ester and the catalyst were mixed together (a previous experiment had shown that there was no reaction between these reactants) and fed into the reactor through the feed funnel (H). The stirrer was started. The alcohol was fed into the feed preheater through the feed funnel (N).

When both of the reactants had reached the required temperature, reservoir (J) was pressurised to approximately 10cm of mercury. Valve (E) was set to the feed preheater, valve (C) and vent (D) were opened and then valve (M) was carefully opened pressurising the feed preheater causing the contents of the feed preheater to be transferred to the reactor. The transfer operation took about 15 seconds.

As soon as the transfer of the alcohol was complete, the hypodermic syringe and needle were flushed out and a sample was taken. During the subsequent calculations, this composition and time were taken as the starting point of the reaction. The length of an experiment varied between one and seven hours and the sampling frequency varied between one sample per seven minutes and one sample per hour. The syringe and hypodermic needle were always flushed out before each sample was taken.

The stirrer speed was such that almost all of the inside surface of the reactor was covered with liquid but not too great so that a vortex was formed which would cause both the temperature sheath and the sample needle to become uncovered from the liquid.

It was observed that the reactor temperature remained very constant for all the temperatures, the fluctuation being less than ±0.1°C. It was found that for temperatures in excess of 85°C boiling commenced for equimolar mixtures of the reactants and hence the practicable upper limit for the system was set to 85°C.

During the initial experiments two major difficulties were identified and subsequently the mode of operation had to be modified. The transfer of the ethyl alcohol from the feed preheater to the reactor always left some of the alcohol in the feed preheater due to a "dead-volume" of approximately 25cc occurring between the bottom of the delivery tube and the inside surface of the feed preheater.

A second and more major difficulty was that, when the two reactants were mixed together there was a drop in temperature of more than 5°C and the solution would take at least 15 minutes to return to the required reaction temperature.

In the study of the hydrolysis of acetic anhydride, a similar problem was resolved by Mamers (66) who after mixing the reactants allowed them to reach the required temperature. At that point, the first sample was taken and the timing of the reaction commenced. However, at high temperatures and acid concentrations when the reaction was completed in one hour or less, a severe limitation of this procedure was that only a few samples could be taken in the time available.

The difficulties were resolved by eliminating the use of the feed preheater. The reactants were fed into the reactor through the feed funnel (H) with the exception of about 10cc of the butyl acetate, and they were allowed to reach the required temperature. The catalyst was added through the feed funnel followed immediately by the remaining butyl acetate which ensured that all the catalyst had been added to the reactants. The first sample was taken and the reaction timing commenced. Using this technique in which the addition of the catalyst followed by the ester and the withdrawal of the first sample and the commencement of the timing took less than 15 seconds, no temperature drop at the start of the reaction was noticed.

The equilibrium constant data was measured by using the same apparatus. The same technique for the loading of the reactants and the catalyst into the reactor and the timing of the reaction was used. The reaction was allowed to proceed for three weeks at the required temperature before the reaction mixture was sampled, analysed and the equilibrium data was calculated.

3.6 Experimental Programme.

As the data reported in the literature had only been evaluated for a limited temperature range of 60-80°C and a catalyst concentration range of 0.1-0.2 weight per cent, it was decided to investigate the reaction as follows:-

1). A temperature range of 20-85°C

2). A catalyst concentration range of 0.1-1.0 weight per cent.

3). Equimolar and non-equimolar reactant ratios.

4). The forward and the reverse reaction.

5). The equilibrium constant.

By carrying out the above programme a comparison between these results and the published data could be made to ascertain the accuracy of the data, and the range of the data would be considerably extended.

3.7 The Kinetics of a Reversible Reaction

It has been shown that within the range of concentration used in these experiments, the reaction

$$CH_3COOC_4H_9 + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + C_4H_9OH$$

is second order(39).

Let a and b be the initial concentrations of ethyl alcohol and butyl acetate respectively, x be the decrease in each after time t.

The reaction rate equation may be written as:-

$$\frac{dx}{dt} = k_1(a-x)(b-x) - k_2\,(x)(x) \qquad \text{———— } 3.14$$

at equilibrium $\frac{dx}{dt} = 0$

$$\text{hence } \frac{k_1}{k_2} = K = \frac{x^2}{(a-x)(b-x)} \qquad \text{———— } 3.15$$

Thus equation 3.14 becomes:-

$$\frac{dx}{dt} = k_1\left\{\left[(a-x)(b-x)\right] - \frac{x^2}{K}\right\} \qquad \text{———— } 3.16$$

integrating equation 3.16 between $t = 0$ & $t = t$

$x = 0$ & $x = x$

$$\int_0^x \frac{dx}{\left[(a-x)(b-x) - \frac{x^2}{K}\right]} = \int_0^t k_1 dt$$

$$\text{hence } \int_0^x \frac{dx}{\left[ab+x^2 - ax - bx - \frac{x^2}{K}\right]} = k_1 t \qquad \text{———— } 3.17$$

$$\text{let } C = \left[(a+b)^2 - 4ab\left(1-\frac{1}{K}\right)\right] \qquad \text{———— } 3.18$$

Equation 3.17 is solved by separating the integral into partial fractions and at the same time substituting equation 3.18.

On integrating the modified form of equation 3.17

$$\frac{1}{\sqrt{C}} \quad \ln\left[\frac{2ab-x\ (a+b-\sqrt{C})}{2ab-x\ (a+b+\sqrt{C})}\right] = k_1 t \qquad \text{———— 3.19}$$

Hence a plot of the lefthand side of equation 3.19 against time t should be linear for a second order reaction and from the gradient of the graph the value for the second order forward velocity constant k_1 can be calculated.

The temperature dependence of the forward velocity constant k_1 can be expressed by the Arrhenius equation

$$\log k_1 = B - \frac{A}{T}$$

where A and B are constants.

The value of the activation energy for the reaction can be calculated from the gradient (A) of the Arrhenius equation.

Equation 3.19 can be simplified as follows:-

Assume that 1) $a+b \triangleq 1$

2) $K \triangleq 1$ hence $C \triangleq 1$

3.19 reduces to

$$\ln\left(\frac{ab}{ab-x}\right) = k_1 t \qquad \text{———— 3.20}$$

A plot of the lefthand side of equation 3.20 against time t should be linear for a first order reaction from which the value of the rate constant can be calculated.

3.8 Experimental Results

In the tabulated results the parameter

$$\frac{1}{\sqrt{C}} \quad \ln\left[\frac{2ab-x(a+b-\sqrt{C})}{2ab-x(a+b+\sqrt{C})}\right]$$

will be referred to as Y

If the units of a, b and x are mole fractions then the units of

$\sqrt{C}$ will also be mole fractions and consequently the log term of Y will be dimensionless. Thus the log term can be calculated by adapting the gas chromatographic computer programme (see Appendix A4). If the $\sqrt{C}$ term outside the log term of Y is calculated from the values of a, b where a and be are in g mole litre^{-1} units, $\sqrt{C}$ will also have g mole litre^{-1} units. Thus with the catalyst concentration (H^+) expressed in g mole litre^{-1} and the time t in minutes, the units of the forward velocity constant k_1 will be litre g mole^{-1} min^{-1}. This technique only involves the initial measurement of the volume of the reactants to determine the parameters a and b which are constants whereas Mamers (66) used an average volume of the reactants which was derived from the initial and final volumes so that he could express his concentrations in terms of g mole litre^{-1}. A typical calculation is shown in Appendix B1.

Series K1 Temperature 85°C

Run K1.1 Catalyst Concentration 0.1 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4822	0.5108	0.0062	0.0000
10	0.0165	0.4640	0.4983	0.0204	0.0166
20	0.0320	0.4641	0.4666	0.0365	0.0348
30	0.0462	0.4470	0.4555	0.0506	0.0523
40	0.0589	0.4382	0.4391	0.0630	0.0689
50	0.0674	0.4281	0.4309	0.0728	0.0817
60	0.0849	0.4098	0.4161	0.0883	0.1065
70	0.0939	0.4066	0.3968	0.1019	0.1250
80	0.1038	0.3947	0.3919	0.1088	0.1395
90	0.1141	0.3858	0.3808	0.1185	0.1579

Run K1.2 Catalyst Concentration 0.2 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4865	0.5079	0.0039	0.0000
10	0.0281	0.4688	0.4655	0.0360	0.0336
20	0.0598	0.4248	0.4495	0.0643	0.0721
30	0.0782	0.3984	0.4326	0.0891	0.1038
40	0.1020	0.3832	0.4029	0.1062	0.1379
50	0.1241	0.3618	0.3837	0.1287	0.1810
60	0.1375	0.3546	0.3573	0.1488	0.2189
70	0.1534	0.3372	0.3457	0.1620	0.2570
80	0.1644	0.3258	0.3340	0.1742	0.2918
90	0.1734	0.3147	0.3267	0.1835	0.3234

Run K1.3 Catalyst Concentration 0.5 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4865	0.5035	0.0057	0.0000
10	0.0676	0.4353	0.4213	0.0717	0.0818
25	0.1351	0.3512	0.3646	0.1449	0.2102
40	0.1778	0.3171	0.3059	0.1950	0.3527
50	0.1981	0.2946	0.2963	0.2068	0.4287
60	0.2076	0.2820	0.2838	0.2224	0.5092
70	0.2120	0.2647	0.2789	0.2402	0.6103
80	0.2241	0.2675	0.2637	0.2412	0.6904
90	0.2236	0.2542	0.2684	0.2496	0.7661

Run K1.4 Catalyst Concentration 1.0 weight per cent.

t min	mole fractions ETAC (x)	 ETOH (a)	 BUAC (b)	 BUOH (x)	Y
0	0.0000	0.4993	0.4862	0.0061	0.0000
7	0.0919	0.4077	3.3890	0.1031	0.1266
14	0.1318	0.4053	0.3071	0.1475	0.2116
21	0.1191	0.1941	0.4070	0.2715	0.3973
28	0.2024	0.2888	0.2829	0.2176	0.4813
35	0.2146	0.2731	0.2728	0.2311	0.5867
42	0.2225	0.2681	0.2628	0.2382	0.6766
50	0.2266	0.2554	0.2590	0.2507	0.8358
60	0.2347	0.2518	0.2533	0.2519	1.0016

Table 3.1

Reaction Rates Series K1

Run No.	(H^+) g mole litre^{-1}	Rate Constant k_1	 $\log k_1$	Temperature ^{o}C	 $\frac{1000}{T}$ (^{o}K)
K1.1	0.00883	0.00174	-2.7595	85	2.793
K1.2	0.01760	0.00358	-2.4461	85	2.793
K1.3	0.04390	0.00858	-2.0665	85	2.793
K1.4	0.08780	0.01680	-1.7747	85	2.793

Series K2 Temperature 80°C

Run K2.1 Catalyst Concentration 0.1 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4851	0.5091	0.0050	0.0000
10	0.0133	0.4630	0.5077	0.0152	0.0126
20	0.0230	0.4506	0.4993	0.0263	0.0256
30	0.0368	0.4402	0.4857	0.0364	0.0384
40	0.0520	0.4386	0.4588	0.0515	0.0563
50	0.0604	0.4347	0.4432	0.0608	0.0693
60	0.0692	0.4154	0.4400	0.0747	0.0852
70	0.0750	0.4133	0.4278	0.0830	0.0957
80	0.0861	0.3977	0.4221	0.0933	0.1123
90	0.0939	0.3918	0.4134	0.1002	0.1244
100	0.1015	0.3879	0.4022	0.1077	0.1375
110	0.1123	0.3783	0.3856	0.1229	0.1617
120	0.1206	0.3653	0.3806	0.1226	0.1698

Run K2.2 Catalyst Concentrations 0.2 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4915	0.5012	0.0056	0.0000
10	0.0236	0.4697	0.4792	0.0258	0.0244
20	0.0455	0.4390	0.4646	0.0493	0.0515
30	0.0646	0.4328	0.4298	0.0712	0.0790
40	0.0809	0.4079	0.4189	0.0906	0.1057
50	0.0968	0.3915	0.4013	0.1086	0.1338
60	0.1155	0.3818	0.3792	0.1218	0.1633
70	0.1276	0.3626	0.3759	0.1327	0.1864
80	0.1411	0.3531	0.3560	0.1481	0.2201
90	0.1479	0.3411	0.3465	0.1628	0.2478
100	0.1590	0.3317	0.3380	0.1696	0.2733
110	0.1685	0.3262	0.3259	0.1777	0.3012
120	0.1729	0.3171	0.3199	0.1877	0.3267

Run K2.3 Catalyst Concentration 0.5 weight per cent.

t min	mole fractions ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	Y
0	0.0000	0.5044	0.4845	0.0069	0.0000
10	0.0537	0.4673	0.4061	0.0686	0.0691
20	0.0955	0.4060	0.3940	0.1003	0.1251
30	0.1350	0.3808	0.3801	0.0999	0.1606
40	0.1757	0.2864	0.3569	0.1767	0.3118
50	0.1816	0.2796	0.3321	0.2024	0.3740
60	0.1925	0.3036	0.2946	0.2051	0.4060
70	0.1983	0.2929	0.2842	0.2204	0.4654
80	0.2104	0.2833	0.2748	0.2273	0.5342
90	0.2145	0.2807	0.2727	0.2278	0.5545

Run K2.4 Catalyst Concentration 1.0 weight per cent.

t min	mole fractions ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	Y
0	0.0000	0.4747	0.5107	0.0062	0.0000
8	0.0998	0.3941	0.3954	0.1024	0.1330
14	0.1418	0.3379	0.3552	0.1567	0.2362
21	0.1785	0.3142	0.3159	0.1831	0.3358
28	0.1981	0.2998	0.2882	0.2056	0.4329
35	0.2074	0.2809	0.2807	0.2226	0.5199
42	0.2179	0.2695	0.2757	0.2287	0.5941
48	0.2257	0.2708	0.2620	0.2331	0.6677
60	0.2305	0.2580	0.2562	0.2471	0.8477

Table 3.2

Reaction Rates Series K2

Run No.	(H^+) g mole litre^{-1}	Rate Constant		Temperature	
		k_1	$\log k_1$	^oC	$\frac{1000}{T}$ (^oK)
K2.1	0.00882	0.001395	-2.8541	80	2.833
K2.2	0.01747	0.002685	-2.5711	80	2.833
K2.3	0.04380	0.006720	-2.1726	80	2.833
K2.4	0.08770	0.014000	-1.8539	80	2.833

Series K3 Temperature 70^{o}C

Run K3.1 Catalyst Concentration 0.1 weight per cent.

t min	mole fractions				Y
	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.5074	0.4848	0.0069	0.0000
15	0.0110	0.4759	0.4934	0.0188	0.0123
30	0.0219	0.4720	0.4782	0.0270	0.0230
45	0.0299	0.4661	0.4652	0.0371	0.0340
60	0.0405	0.4551	0.4543	0.0493	0.0474
75	0.0499	0.4421	0.4486	0.0586	0.0594
90	0.0633	0.4313	0.4383	0.0663	0.0736
110	0.0723	0.4185	0.4292	0.0791	0.0892
120	0.0808	0.4179	0.4188	0.0817	0.0974
135	0.0862	0.4076	0.4140	0.0914	0.1092
150	0.0957	0.4023	0.4054	0.0957	0.1205
165	0.1014	0.3857	0.4064	0.1057	0.1338
180	0.1068	0.3889	0.3934	0.1096	0.1421

Run K3.2 Catalyst Concentration 0.2 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4898	0.5058	0.0027	0.0000
15	0.0196	0.4733	0.4785	0.0268	0.0240
30	0.0440	0.4503	0.4601	0.0438	0.0489
45	0.0602	0.4205	0.4500	0.0676	0.0755
60	0.0762	0.4073	0.4365	0.0782	0.0949
75	0.0926	0.4069	0.3997	0.0991	0.1247
90	0.1045	0.3975	0.3840	0.1123	0.1469
105	0.1189	0.3810	0.3695	0.1290	0.1772
120	0.1342	0.3575	0.3719	0.1347	0.1999
135	0.1444	0.3610	0.3481	0.1449	0.2241
150	0.1502	0.3413	0.3512	0.1556	0.2455
165	0.1610	0.3367	0.3344	0.1662	0.2761
180	0.1639	0.3229	0.3317	0.1798	0.3025

Run K3.3 Catalyst Concentration 0.5 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4999	0.4873	0.0082	0.0000
15	0.0487	0.4478	0.4447	0.0547	0.0555
30	0.0899	0.4045	0.4056	0.0989	0.1155
45	0.1209	0.3710	0.3703	0.1338	0.1790
60	0.1519	0.3500	0.3404	0.1536	0.2385
75	0.1693	0.3289	0.3227	0.1750	0.2954
90	0.1799	0.3155	0.3078	0.1927	0.3467
105	0.1882	0.2940	0.3046	0.2091	0.4015
120	0.2071	0.2911	0.2852	0.2125	0.4636
135	0.2105	0.2813	0.2775	0.2266	0.5257
150	0.2157	0.2806	0.2745	0.2258	0.5434

Run K3.4 Catalyst Concentration 1.0 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4938	0.4919	0.0060	0.0000
10	0.0630	0.4339	0.4253	0.0695	0.0764
20	0.1168	0.3808	0.3782	0.1160	0.1613
30	0.1493	0.3502	0.3379	0.1544	0.2425
40	0.1738	0.3229	0.3098	0.1852	0.3301
50	0.1898	0.3042	0.2952	0.2025	0.4016
60	0.2053	0.2860	0.2860	0.2144	0.7419
70	0.2184	0.2812	0.2771	0.2150	0.5309
80	0.2198	0.2737	0.2740	0.2242	0.5785
90	0.2291	0.2659	0.2641	0.2326	0.6837
100	0.2311	0.2604	0.2586	0.2417	0.7817
110	0.2289	0.2596	0.2559	0.2473	0.8210
120	0.2340	0.2543	0.2559	0.2475	0.8983

Table 3.3

Reaction Rates Series K3

Run No.	(H^+) g mole litre^{-1}	Rate Constant		Temperature	
		k_1	log k_1	^oC	$\frac{1000}{T}$ (^oK)
K3.1	0.00881	0.000780	-3.1079	70	2.915
K3.2	0.01747	0.001645	-2.7838	70	2.915
K3.3	0.04380	0.003880	-2.4112	70	2.915
K3.4	0.08770	0.007740	-2.1113	70	2.915

Series K4 Temperature 60°C

Run K4.1 Catalyst Concentration 0.1 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4796	0.5137	0.0059	0.0000
20	0.0075	0.4757	0.5007	0.0154	0.0090
40	0.0174	0.4819	0.4762	0.0238	0.0192
60	0.0233	0.4813	0.4654	0.0292	0.0256
80	0.0324	0.4643	0.4630	0.0395	0.0371
100	0.0392	0.4616	0.4531	0.0447	0.0444
120	0.0484	0.4469	0.4525	0.0515	0.0545
140	0.0552	0.4436	0.4425	0.0579	0.0631
160	0.0608	0.4398	0.4285	0.0702	0.0754
180	0.0668	0.4244	0.4310	0.0771	0.0846
200	0.0780	0.4262	0.4148	0.0801	0.0951
220	0.0828	0.4204	0.4089	0.0871	0.1042
240	0.0907	0.4107	0.4060	0.0919	0.1143

Run K4.2 Catalyst Concentration 0.2 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4948	0.4983	0.0052	0.0000
20	0.0148	0.4881	0.4727	0.0228	0.0175
40	0.0318	0.4667	0.4625	0.0363	0.0352
63	0.0487	0.4445	0.4519	0.0533	0.0563
80	0.0601	0.4380	0.4349	0.0653	0.0720
100	0.0732	0.4233	0.4221	0.0797	0.0917
120	0.0884	0.4101	0.4091	0.0907	0.1120
140	0.0986	0.3990	0.3982	0.1024	0.1304
160	0.1061	0.3850	0.3879	0.1194	0.1524
183	0.1184	0.3795	0.3747	0.1257	0.1705
200	0.1274	0.3680	0.3733	0.1295	0.1838
220	0.1360	0.3589	0.3617	0.1417	0.2069
240	0.1445	0.3637	0.3375	0.1526	0.2305

Run K4.3 Catalyst Concentration 0.5 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4969	0.4914	0.0075	0.0000
20	0.0360	0.4567	0.4621	0.0411	0.0393
40	0.0710	0.4244	0.4196	0.0809	0.0896
60	0.1009	0.4009	0.3862	0.1078	0.1355
80	0.1243	0.3742	0.3665	0.1308	0.1802
100	0.1456	0.3504	0.3480	0.1518	0.2289
120	0.1611	0.3331	0.3323	0.1692	0.2746
140	0.1742	0.3229	0.3096	0.1892	0.3299
160	0.1860	0.3096	0.3095	0.1908	0.3565
180	0.1941	0.2997	0.2995	0.2026	0.4015
200	0.2043	0.2948	0.2837	0.2130	0.4585
225	0.2130	0.2847	0.2808	0.2174	0.5025

Run K4.4 Catalyst Concentration 1.0 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.5043	0.4814	0.0061	0.0000
20	0.0658	0.4167	0.4326	0.0768	0.0849
40	0.1212	0.3705	0.3696	0.1306	0.1807
60	0.1587	0.3348	0.3324	0.1606	0.2722
80	0.1799	0.3050	0.3126	0.1944	0.3603
100	0.2006	0.2932	0.2875	0.2106	0.4530
120	0.2143	0.2795	0.2757	0.2223	0.5443
140	0.2172	0.2687	0.2729	0.2331	0.6110
160	0.2266	0.2632	0.2664	0.2357	0.6878
180	0.2289	0.2665	0.2594	0.2371	0.7166
200	0.2341	0.2606	0.2607	0.2364	0.7584
225	0.2410	0.2201	0.2540	0.2267	0.7316

Table 3.4

Reaction Rates Series K4

Run No.	(H^+) g mole litre^{-1}	Rate Constant		Temperature	
		k_1	log k_1	°C	$\frac{1000}{T}$ (°K)
K4.1	0.00875	0.000460	-3.3372	60	3.003
K4.2	0.01770	0.000923	-3.0348	60	3.003
K4.3	0.04380	0.002240	-2.6498	60	3.003
K4.4	0.08780	0.004445	-2.3521	60	3.003

Series K5 Temperature 50°C

Run K5.1 Catalyst Concentration 0.1 weight per cent.

t min	mole fractions				Y
	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.5044	0.4904	0.0044	0.0000
30	0.0084	0.4860	0.4962	0.0086	0.0067
60	0.0124	0.4866	0.4832	0.0170	0.0135
90	0.0204	0.4729	0.4807	0.0252	0.0225
120	0.0297	0.4661	0.4729	0.0305	0.0310
150	0.0335	0.4695	0.4572	0.0389	0.0383
180	0.0423	0.4594	0.4532	0.0443	0.0470
210	0.0486	0.4445	0.4576	0.0485	0.0537
240	0.0522	0.4386	0.4507	0.0577	0.0620
270	0.0600	0.4334	0.4442	0.0616	0.0699
300	0.0630	0.4339	0.4328	0.0695	0.0775
330	0.0709	0.4239	0.4316	0.0728	0.0855
360	0.0763	0.4268	0.4140	0.0821	0.0964

Run K5.2 Catalyst Concentration 0.2 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.5063	0.4871	0.0049	0.0000
30	0.0112	0.4876	0.4842	0.0153	0.0116
60	0.0267	0.4681	0.4738	0.0299	0.0284
90	0.0390	0.4646	0.4466	0.0481	0.0470
120	0.0514	0.4445	0.4457	0.0568	0.0606
150	0.0627	0.4319	0.4345	0.0691	0.0767
180	0.0772	0.4194	0.4264	0.0754	0.0917
210	0.0845	0.4196	0.4072	0.0920	0.1102
240	0.0930	0.3918	0.4100	0.1034	0.1267
270	0.1009	0.3909	0.3972	0.1093	0.1387
300	0.1129	0.3852	0.3846	0.1158	0.1557
330	0.1196	0.3841	0.3681	0.1260	0.1724
360	0.1292	0.3667	0.3620	0.1410	0.1986

Run K5.3 Catalyst Concentration 0.5 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4937	0.4993	0.0029	0.0000
30	0.0300	0.4672	0.4622	0.0365	0.0359
60	0.0626	0.4369	0.4320	0.0643	0.0752
90	0.0855	0.4126	0.4042	0.0936	0.1147
120	0.1109	0.3945	0.3836	0.1069	0.1484
150	0.1237	0.3673	0.3681	0.1367	0.1915
180	0.1436	0.3512	0.3509	0.1501	0.2309
210	0.1593	0.3387	0.3345	0.1634	0.2708
240	0.1684	0.3263	0.3274	0.1738	0.3016
275	0.1844	0.3121	0.3136	0.1857	0.3219
300	0.1857	0.2972	0.3097	0.2032	0.3952

Run K5.4 Catalyst Concentration 1.0 weight per cent.

t min	mole fractions				Y
	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4989	0.4882	0.0046	0.0000
30	0.0578	0.4358	0.4289	0.0692	0.0750
60	0.1033	0.3908	0.3841	0.1135	0.1479
90	0.1364	0.3518	0.3493	0.1541	0.2280
120	0.1639	0.3217	0.3231	0.1830	0.3117
150	0.1788	0.3017	0.3049	0.2009	0.3765
180	0.2000	0.2935	0.2861	0.2121	0.4619
210	0.2072	0.2833	0.2795	0.2217	0.5203
240	0.2149	0.2779	0.2759	0.2230	0.5582
275	0.2183	0.2628	0.2718	0.2389	0.6637
300	0.2229	0.2675	0.2640	0.2372	0.6850

Table 3.5

Reaction Rates Series K5

Run No.	(H^+) g mole litre^{-1}	Rate Constant		Temperature	
		k_1	$\log k_1$	^oC	$\frac{1000}{T}$ (^oK)
K5.1	0.00877	0.000258	-3.5867	50	3.096
K5.2	0.01761	0.000510	-3.2924	50	3.096
K5.3	0.04390	0.001290	-2.8894	50	3.096
K5.4	0.08780	0.002530	-2.5969	50	3.096

Series K6 Temperature Range 21.4°C - 40°C

Run K6.1 Temperature 40°C Catalyst Concentration 0.5 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4899	0.4984	0.0075	0.0000
60	0.0341	0.4508	0.4721	0.0389	0.0369
120	0.0620	0.4295	0.4328	0.0716	0.0764
180	0.0898	0.4110	0.4006	0.0945	0.1148
240	0.1133	0.3826	0.3865	0.1135	0.1521
272	0.1175	0.3631	0.3755	0.1396	0.1824
435	0.1646	0.3264	0.3346	0.1701	0.2814
480	0.1663	0.3128	0.3244	0.1925	0.3216
540	0.1795	0.3109	0.3188	0.1867	0.3355

Run K6.2 Temperature 40°C Catalyst Concentration 1.0 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.5067	0.4782	0.0068	0.0000
60	0.0634	0.4367	0.4241	0.0675	0.0759
120	0.1094	0.3847	0.3783	0.1193	0.1566
180	0.1390	0.3433	0.3409	0.1685	0.2467
240	0.1684	0.3281	0.3126	0.1826	0.3142
272	0.1784	0.3087	0.3104	0.1942	0.3555
420	0.2082	0.2764	0.2793	0.2279	0.5392
480	0.2164	0.2694	0.2718	0.2341	0.6089
540	0.2231	0.2621	0.2709	0.2356	0.6586

Run K6.3 Temperature 30°C Catalyst Concentration 0.5 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4907	0.5016	0.0036	0.0000
60	0.0165	0.4792	0.4776	0.0226	0.0194
120	0.0337	0.4581	0.4630	0.0410	0.0404
180	0.0520	0.4481	0.4450	0.0508	0.0583
225	0.0651	0.4359	0.4292	0.0657	0.0773
270	0.0755	0.4204	0.4226	0.0774	0.0935
315	0.0811	0.4186	0.4084	0.0878	0.1058
360	0.0912	0.4019	0.4082	0.0947	0.1195

Run K6.4 Temperature 30°C Catalyst Concentration 1.0 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4939	0.4926	0.0054	0.0000
60	0.0369	0.4561	0.4546	0.0442	0.0437
120	0.0640	0.4390	0.4105	0.0783	0.0852
180	0.0907	0.3964	0.4054	0.0993	0.1229
225	0.1099	0.3838	0.3854	0.1127	0.1521
270	0.1262	0.3663	0.3688	0.1305	0.1867
315	0.1357	0.3573	0.3583	0.1404	0.2085
360	0.1506	0.3483	0.3421	0.1509	0.2404

Run K6.5 Temperature 21.4°C Catalyst Concentration 0.5 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4808	0.5101	0.0052	0.0000
60	0.0073	0.4907	0.4854	0.0126	0.0079
120	0.0173	0.4628	0.4861	0.0232	0.0196
180	0.0256	0.4587	0.4739	0.0379	0.0327
240	0.0341	0.4518	0.4693	0.0408	0.0396
300	0.0459	0.4492	0.4551	0.0457	0.0500
360	0.0512	0.4432	0.4423	0.0593	0.0624
420	0.0542	0.4238	0.4588	0.0593	0.0643

Run K6.6 Temperature 21.4°C Catalyst Concentration 1.0 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.4930	0.4886	0.0051	0.0000
60	0.0208	0.4295	0.4650	0.0264	0.0234
120	0.0386	0.4557	0.4491	0.0484	0.0475
180	0.0523	0.4446	0.4429	0.0636	0.0643
240	0.0652	0.4308	0.4253	0.0714	0.0813
300	0.0818	0.4279	0.3989	0.0933	0.1107
360	0.0902	0.4020	0.4008	0.0987	0.1222
420	0.1044	0.3922	0.3912	0.1039	0.1392

Table 3.6

Reaction Rates Series K6

Run No.	(H^+) g mole litre^{-1}	Rate Constant		Temperature	
		k_1	log k_1	^oC	$\frac{1000}{T}$ (^oK)
K6.1	0.0438	0.000650	-3.1871	40	3.195
K6.2	0.0877	0.001280	-2.8928	40	3.195
K6.3	0.0438	0.000330	-3.4815	30	3.300
K6.4	0.0879	0.000670	-3.1739	30	3.300
K6.5	0.0439	0.000170	-3.7696	21.4	3.390
K6.6	0.0881	0.000345	-3.4622	21.4	3.390

Series K7 The Reverse Reaction Temperature 75°C

Run K7.1 Catalyst Concentration 0.1 weight per cent.

t min	mole fractions				Y
	ETAC (a)	ETOH (x)	BUAC (x)	BUOH (b)	
0	0.4859	0.0000	0.0000	0.5130	0.0000
10	0.4877	0.0116	0.0117	0.4880	0.0125
20	0.4724	0.0251	0.0252	0.4763	0.0278
30	0.4577	0.0265	0.0332	0.4816	0.0294
40	0.4563	0.0395	0.0445	0.4588	0.0451
50	0.4424	0.0489	0.0563	0.4514	0.0572
60	0.4316	0.0561	0.0647	0.4459	0.0676
75	0.4153	0.0723	0.0781	0.4333	0.0897
90	0.4005	0.0812	0.0915	0.4258	0.1031
105	0.4143	0.0969	0.1079	0.3800	0.1287
120	0.3868	0.0941	0.1135	0.4047	0.1239
135	0.3748	0.1087	0.1225	0.3933	0.1499
150	0.3707	0.1170	0.1315	0.3798	0.1658

Run K7.2 Catalyst Concentration 0.2 weight per cent.

t	mole fractions				Y
min	ETAC (a)	ETOH (x)	BUAC (x)	BUOH (b)	
0	0.4804	0.0000	0.0000	0.5175	0.0000
10	0.4606	0.0197	0.0246	0.4932	0.0215
20	0.4491	0.0459	0.0441	0.4590	0.0533
30	0.4305	0.0595	0.0633	0.4448	0.0716
40	0.4059	0.0743	0.0815	0.4363	0.0929
50	0.4003	0.0857	0.0961	0.4159	0.1106
60	0.3843	0.1013	0.1134	0.3989	0.1369
75	0.3668	0.1199	0.1285	0.3827	0.1724
95	0.3378	0.1354	0.1554	0.3694	0.2060
105	0.3409	0.1507	0.1585	0.3478	0.2442
120	0.3255	0.1604	0.1763	0.3358	0.2833
135	0.3150	0.1702	0.1868	0.3290	0.3028
150	0.3046	0.1776	0.1965	0.3193	0.3289

Run K7.3 Catalyst Concentration 0.5 weight per cent.

t	mole fractions				Y
min	ETAC (a)	ETOH (x)	BUAC (x)	BUOH (b)	
0	0.4599	0.0000	0.0000	0.5351	0.0000
10	0.4353	0.0548	0.0549	0.4501	0.0657
20	0.3956	0.0884	0.0967	0.4163	0.1161
30	0.3752	0.1206	0.1318	0.3675	0.1758
40	0.3384	0.1431	0.1574	0.3561	0.2276
50	0.3244	0.1661	0.1780	0.3264	0.2938
60	0.3024	0.1788	0.1911	0.3227	0.3391
75	0.2847	0.1923	0.2184	0.2996	0.3983
90	0.2800	0.2150	0.2235	0.2765	0.5443
105	0.2701	0.2216	0.2358	0.2675	0.6080
120	0.2639	0.2262	0.2430	0.2619	0.6653
135	0.2563	0.2320	0.2452	0.2615	0.7624
150	0.2602	0.2411	0.2471	0.2466	1.0799

Run K7.4 Catalyst Concentration 1.0 weight per cent.

t	mole fractions				Y
min	ETAC (a)	ETOH (x)	BUAC (x)	BUOH (b)	
0	0.4628	0.0000	0.0000	0.5272	0.0000
10	0.3863	0.0964	0.1019	0.4054	0.1314
20	0.3374	0.1459	0.1614	0.3452	0.2379
30	0.3030	0.1777	0.1973	0.3120	0.3399
40	0.2828	0.2051	0.2176	0.2845	0.4787
50	0.2750	0.2197	0.2353	0.2600	0.6011
60	0.2569	0.2225	0.2440	0.2666	0.6331
70	0.2485	0.2323	0.2457	0.2561	0.7916

Table 3.7

Reaction Rates Series K7 - The Reverse Reaction.

Run No.	(H^+) g mole litre^{-1}	Rate Constant		Temperature	
		k_1	log k_1	^oC	$\frac{1000}{T}$ (^oK)
K7.1	0.00876	0.00111	-2.9547	75	2.874
K7.2	0.01750	0.00222	-2.6536	75	2.874
K7.3	0.04310	0.00567	-2.2464	75	2.874
K7.4	0.08780	0.01130	-1.9469	75	2.874

Series K8 Non Equimolar Ratios of Reactants - Temperature 70°C

Run K8.1 Catalyst Concentration 0.1 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.3787	0.6162	0.0070	0.0000
15	0.0122	0.3783	0.5888	0.0195	0.0149
30	0.0257	0.3661	0.5764	0.0307	0.0307
45	0.0387	0.3560	0.5608	0.0434	0.0481
60	0.0483	0.3376	0.5587	0.0543	0.0629
75	0.0624	0.3320	0.5371	0.0674	0.0837
90	0.0729	0.3183	0.5306	0.0777	0.1008
105	0.0809	0.3110	0.5022	0.1048	0.1323
120	0.0924	0.3014	0.5137	0.0913	0.1305
135	0.0987	0.2906	0.5051	0.1045	0.1495
150	0.1071	0.2812	0.5008	0.1099	0.1638
165	0.1145	0.2745	0.4925	0.1175	0.1803
180	0.1213	0.2692	0.4838	0.1245	0.1965

Run K8.2 Catalyst Concentration 0.2 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.3858	0.6060	0.0063	0.0000
15	0.0259	0.3662	0.5735	0.0325	0.0321
30	0.0470	0.3500	0.5485	0.0528	0.0606
45	0.0680	0.3202	0.5402	0.0698	0.0897
60	0.0886	0.3020	0.5194	0.0881	0.1230
75	0.1043	0.2915	0.5005	0.1019	0.1513
90	0.1177	0.2785	0.4774	0.1246	0.1905
105	0.1335	0.2707	0.4515	0.1425	0.2329
120	0.1426	0.2552	0.4411	0.1594	0.2708
135	0.1516	0.2471	0.4408	0.1587	0.2842
150	0.1596	0.2381	0.4308	0.1696	0.3174
165	0.1665	0.2289	0.4264	0.1764	0.3439
180	0.1735	0.2233	0.4140	0.1874	0.3836

Run K8.3 Catalyst Concentration 0.5 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.3937	0.5943	0.0070	0.0000
15	0.0554	0.3356	0.5448	0.0596	0.0707
30	0.0975	0.2914	0.4999	0.1067	0.1473
45	0.1335	0.2639	0.4652	0.1329	0.2172
60	0.1553	0.2332	0.4366	0.1705	0.3062
92	0.1939	0.2032	0.4018	0.1966	0.4553
105	0.1968	0.1884	0.3995	0.2108	0.5137
120	0.2052	0.1866	0.3877	0.2160	0.5712
135	0.2063	0.1764	0.3814	0.2313	0.6619
150	0.2110	0.1749	0.3821	0.2275	0.6676
165	0.2173	0.1719	0.3725	0.2339	0.7695
180	0.2232	0.1675	0.3747	0.2302	0.7920

Run K8.4 Catalyst Concentration 1.0 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.3984	0.5861	0.0070	0.0000
10	0.0720	0.3257	0.5108	0.0829	0.1031
20	0.1243	0.2720	0.4519	0.1432	0.2198
30	0.1541	0.2454	0.4178	0.1741	0.3121
40	0.1809	0.2182	0.4042	0.1881	0.3981
50	0.1904	0.2127	0.3786	0.2098	0.4889
60	0.2054	0.1939	0.3753	0.2169	0.5787
70	0.2095	0.1835	0.3695	0.2288	0.6696
80	0.2123	0.1864	0.3649	0.2279	0.6822
90	0.2161	0.1834	0.3611	0.2308	0.7345
100	0.2213	0.1726	0.3583	0.2392	0.8846
110	0.2196	0.1736	0.3592	0.2390	0.8583
120	0.2180	0.1747	0.3510	0.2477	0.9756

Run K8.5 Catalyst Concentration 0.1 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.5893	0.3991	0.0106	0.0000
15	0.0074	0.5765	0.3998	0.0153	0.0078
30	0.0201	0.5619	0.3919	0.0252	0.0217
45	0.0302	0.5602	0.3750	0.0336	0.0335
60	0.0387	0.5412	0.3717	0.0470	0.0438
75	0.0441	0.5355	0.3624	0.0570	0.0505
90	0.0550	0.5256	0.3565	0.0619	0.0648
105	0.0614	0.5198	0.3457	0.0720	0.0735
120	0.0657	0.4929	0.3618	0.0787	0.0795
135	0.0794	0.5064	0.3259	0.0873	0.0998
150	0.0867	0.4945	0.3215	0.0963	0.1113
165	0.0894	0.4876	0.3145	0.1076	0.1158
180	0.1076	0.4175	0.3445	0.1295	0.1478

Run K8.6 Catalyst Concentration 0.2 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.5657	0.4244	0.0079	0.0000
15	0.0218	0.5579	0.3928	0.0255	0.0238
30	0.0378	0.5500	0.3692	0.0410	0.0428
45	0.0532	0.5209	0.3617	0.0621	0.0626
60	0.0711	0.5189	0.3319	0.0761	0.0876
75	0.0843	0.4974	0.3230	0.0934	0.1078
90	0.0933	0.4882	0.3127	0.1037	0.1228
105	0.1241	0.5451	0.1897	0.1391	0.1812
120	0.1205	0.4678	0.2880	0.1217	0.1736
135	0.1423	0.5143	0.1786	0.1629	0.2235
150	0.1367	0.4459	0.2701	0.1453	0.2099
165	0.1476	0.4365	0.2612	0.1526	0.2375
180	0.1502	0.4253	0.2602	0.1622	0.2446

Run K8.7 Catalyst Concentration 0.5 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.5963	0.3889	0.0098	0.0000
15	0.0476	0.5325	0.3628	0.0521	0.0550
30	0.0830	0.5103	0.3114	0.0903	0.1056
45	0.1129	0.4764	0.2831	0.1226	0.1582
60	0.1383	0.4461	0.2655	0.1451	0.2138
75	0.1526	0.4298	0.2489	0.1637	0.2514
90	0.1701	0.4106	0.2330	0.1812	0.3069
105	0.1821	0.4070	0.2171	0.1888	0.3537
120	0.1883	0.3889	0.2146	0.2032	0.3820
135	0.1999	0.3901	0.1978	0.2072	0.4451
150	0.1959	0.3725	0.1860	0.2407	0.4212
165	0.2061	0.3781	0.1867	0.2271	0.4860
180	0.2128	0.3648	0.1841	0.2333	0.5411

Run K8.8 Catalyst Concentration 1.0 weight per cent.

t	mole fractions				Y
min	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)	
0	0.0000	0.5729	0.3990	0.0181	0.0000
10	0.0652	0.5197	0.3346	0.0704	0.0833
20	0.1061	0.4677	0.3004	0.1158	0.1547
30	0.1385	0.4463	0.2652	0.1399	0.2308
40	0.1613	0.4266	0.2379	0.1643	0.3029
50	0.1786	0.4014	0.2249	0.1851	0.3766
70	0.2018	0.3848	0.1975	0.2059	0.5313
80	0.2050	0.3666	0.1945	0.2239	0.5628
90	0.2090	0.3609	0.1825	0.2376	0.6094
100	0.2226	0.3675	0.1772	0.2226	0.9038
110	0.2214	0.3660	0.1776	0.2251	0.8576
120	0.2202	0.3590	0.1774	0.2334	0.8195

Table 3.8

Reaction Rates Series K8

Run No.	Mole Ratio ETOH:BUAC	(H^+) g mole litre^{-1}	Rate Constant		Temperature	
			k_1	log k_1	^oC	$\frac{1000}{T}$ (K)
K8.1	0.5565	0.00897	0.00110	-2.9586	70	2.915
K8.2	0.5395	0.01770	0.00221	-2.6556	70	2.915
K8.3	0.4470	0.04320	0.00484	-2.3152	70	2.915
K8.4	0.4978	0.08860	0.00977	-2.0101	70	2.915
K8.5	1.4360	0.00862	0.00073	-3.1397	70	2.915
K8.6	1.3100	0.01720	0.00144	-2.8432	70	2.915
K8.7	1.4950	0.04310	0.00339	-2.4705	70	2.915
K8.8	1.3740	0.08640	0.00725	-2.1397	70	2.915

Table 3.9

Summary of the Rate Constants and Temperatures.

Run No.	log k_1	$\frac{1000}{T}$ (^oK)	Run No.	log k_1	$\frac{1000}{T}$ (^oK)
K1.1	-2.7595	2.793	K5.4	-2.5969	3.096
K1.2	-2.4461	2.793	K6.1	-3.1871	3.195
K1.3	-2.0665	2.793	K6.2	-2.8928	3.195
K1.4	-1.7747	2.793	K6.3	-3.4815	3.300
K2.1	-2.8541	2.833	K6.4	-3.1739	3.300
K2.2	-2.5711	2.833	K6.5	-3.7696	3.390
K2.3	-2.1726	2.833	K6.6	-3.4622	3.390
K2.4	-1.8539	2.833	K7.1	-2.9547	2.874
K3.1	-3.1079	2.915	K7.2	-2.6536	2.874
K3.2	-2.7838	2.915	K7.3	-2.2464	2.874
K3.3	-2.4112	2.915	K7.4	-1.9469	2.874
K3.4	-2.1113	2.915	K8.1	-2.9586	2.915
K4.1	-3.3372	3.003	K8.2	-2.6556	2.915
K4.2	-3.0348	3.003	K8.3	-2.3152	2.915
K4.3	-2.6498	3.003	K8.4	-2.0101	2.915
K4.4	-2.3521	3.003	K8.5	-3.1397	2.915
K5.1	-3.5867	3.096	K8.6	-2.8432	2.915
K5.2	-3.2924	3.096	K8.7	-2.4705	2.915
K5.3	-2.8894	3.096	K8.8	-2.1397	2.915

Table 3.10

Equilibrium Constant   Series K9

Run No.	Temp. °C	Equilibrium Concentrations				K
		ETAC	ETOH	BUAC	BUOH	
K9.1	60	0.2283	0.2351	0.2690	0.2676	0.967
K9.2	70	0.2080	0.2171	0.2874	0.2875	0.962
K9.3	80	0.2427	0.2117	0.2985	0.2471	0.951

3.9 Discussion

A graph of log k_1 against $\frac{1}{T}$ (see Fig. 3.13-3.16) has shown that these two parameters can be correlated satisfactorily by a linear relationship of the general form for each catalyst concentration

$$y = mx + c \qquad \text{——— 3.21}$$

where m = gradient of the line

c = a constant

The values of m and c were calculated by the method of least mean squares (67).

$$m = \frac{\Sigma xy - \dfrac{(\Sigma x)(\Sigma y)}{N}}{\Sigma x^2 - \dfrac{(\Sigma x)^2}{N}} \qquad \text{——— 3.22}$$

$$c = \frac{(\Sigma x)(\Sigma xy) - (\Sigma y)(\Sigma x^2)}{(\Sigma x)^2 - N(\Sigma x^2)} \qquad \text{——— 3.23}$$

where N = The number of (x,y) values.

For this calculation, the values of k_1 were obtained for the forward reaction rate data (series K1, K2, K3, K4, K5 and K6) and the reverse reaction data (series K7) from the gradients of the graphs of Y against t in Figs. 3.2 - 3.12 giving a total of 30 values

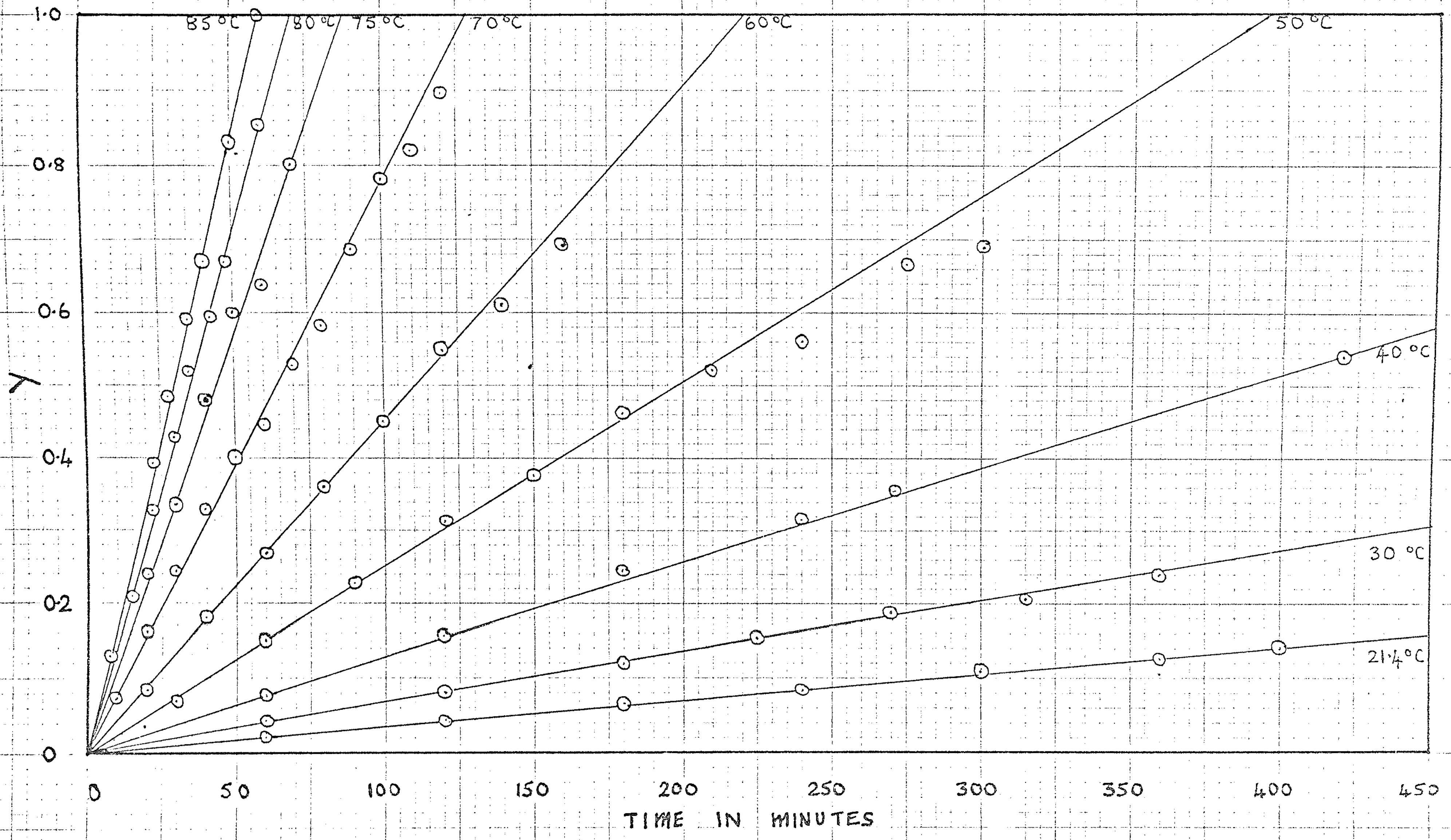


FIG 3.2 Y VS TIME CATALYST CONCENTRATION 1·0 W/W %.

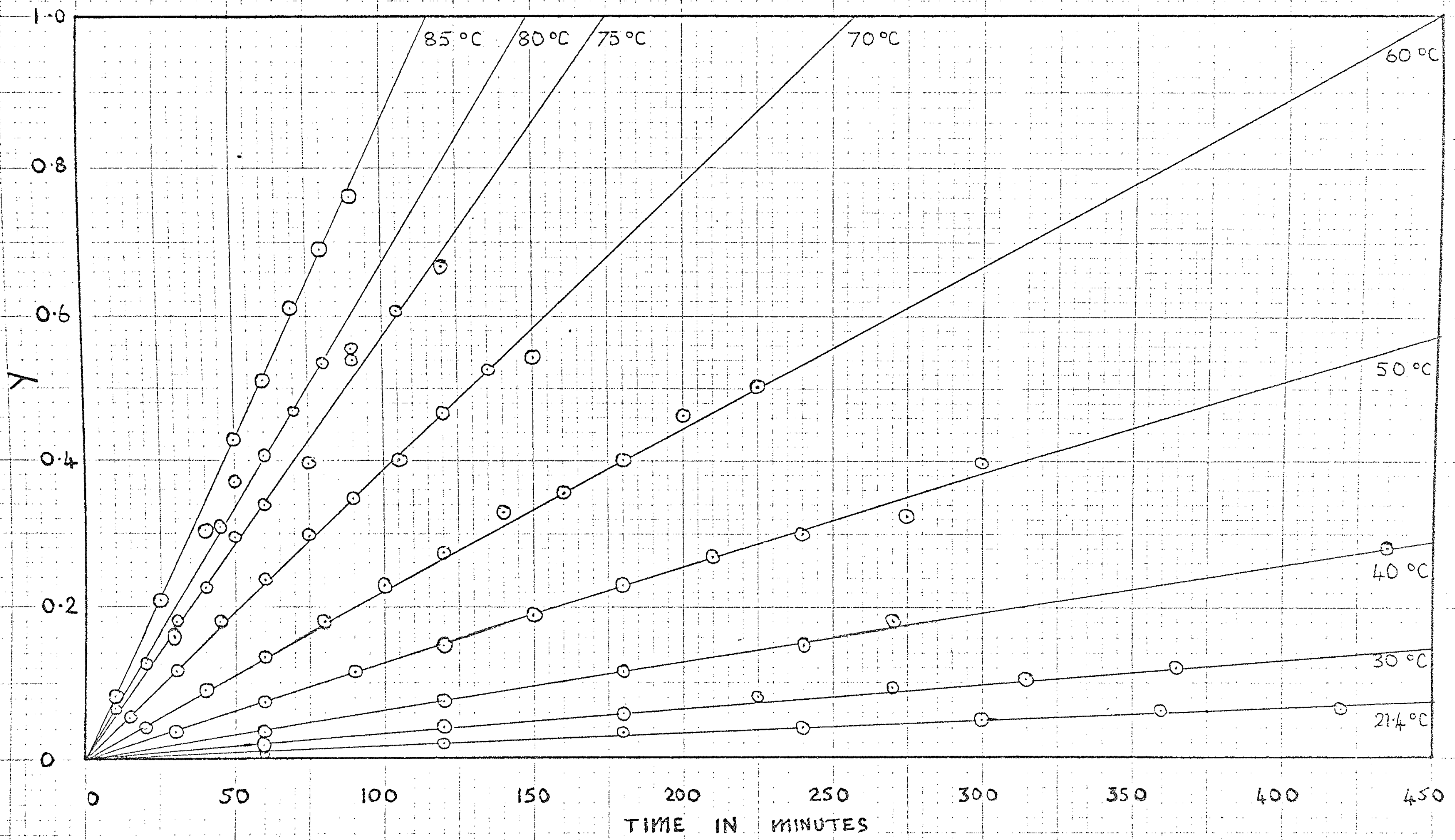


Fig 3.3 Y vs Time Catalyst Concentration 0·5 W/W %.

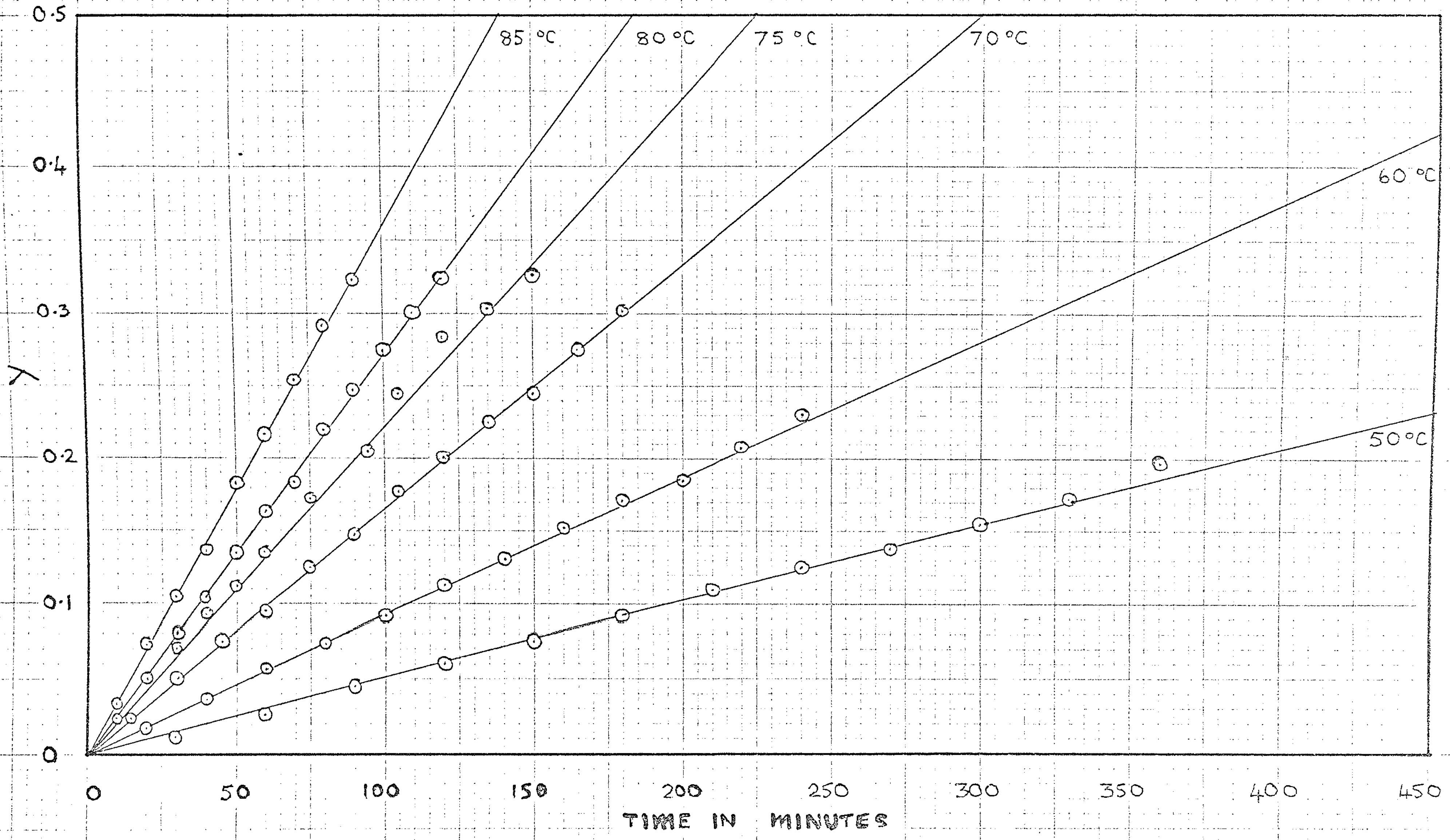


FIG 3.4 Y VS TIME CATALYST CONCENTRATION 0.2 W/W %.

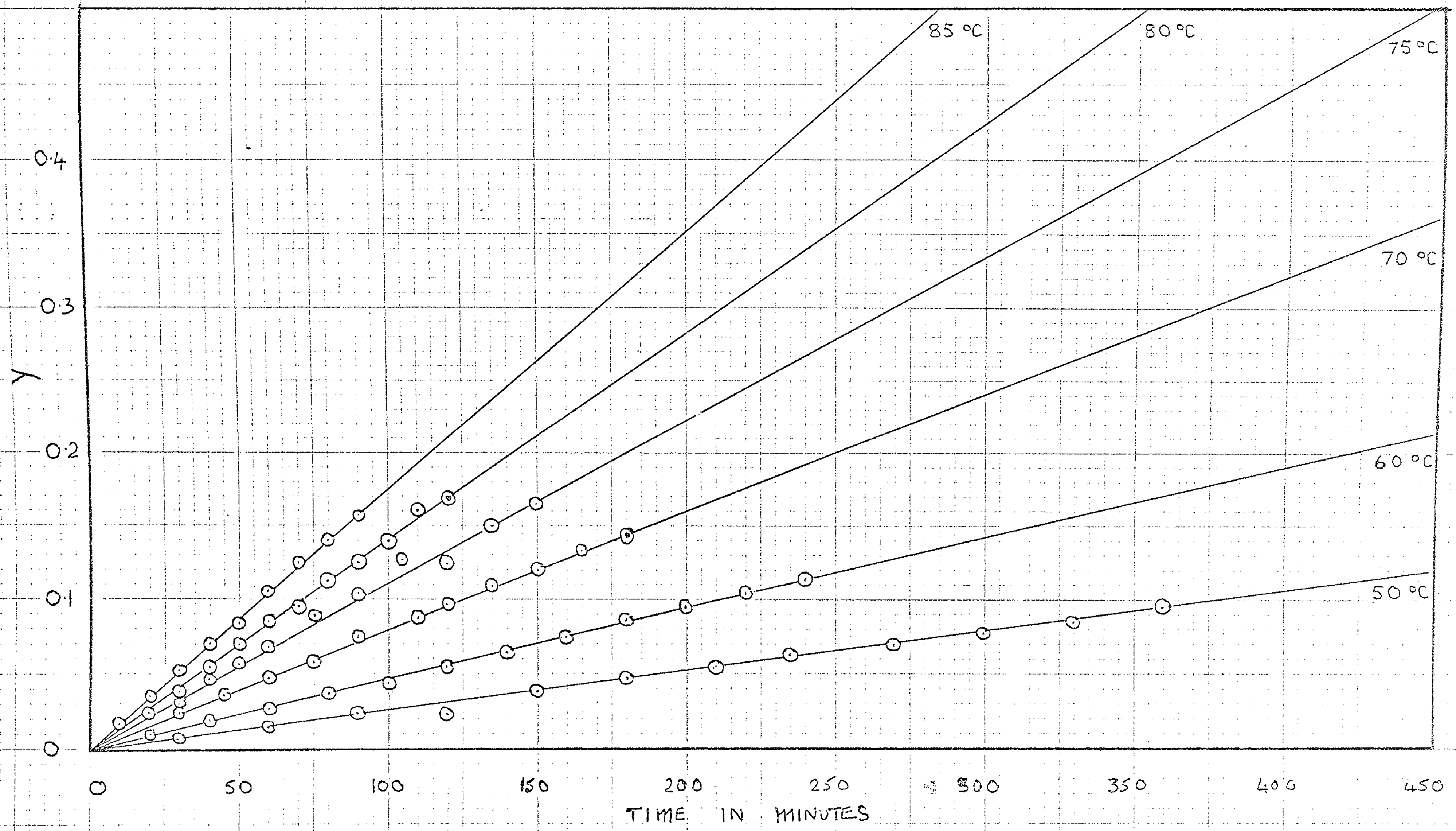


FIG 3.5 Y VS TIME CATALYST CONCENTRATION 0·1 W/W %

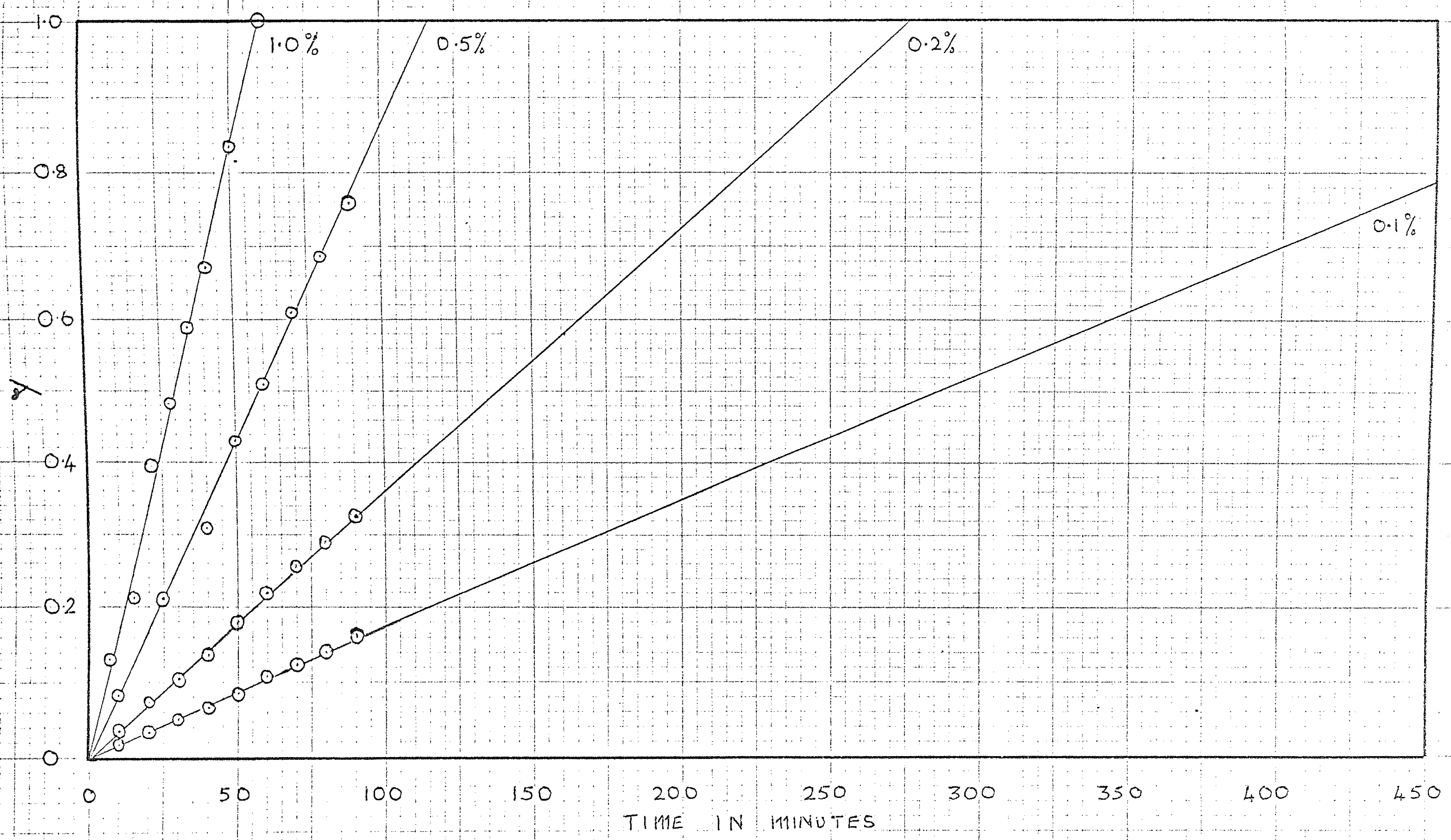


Fig 3.6 Y vs Time Temperature 85 °C

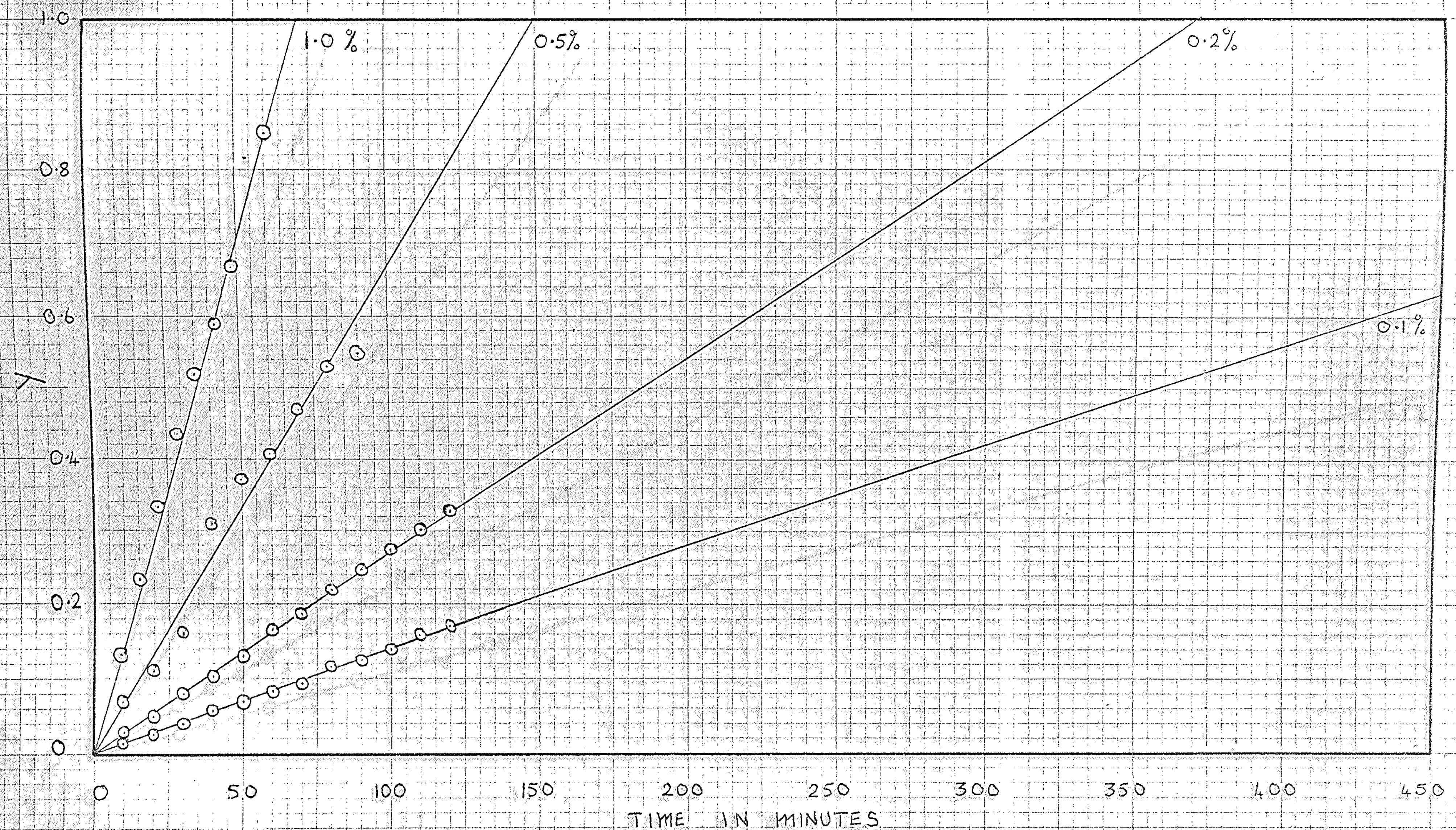


Fig 3.7 Y vs Time Temperature 80 °C

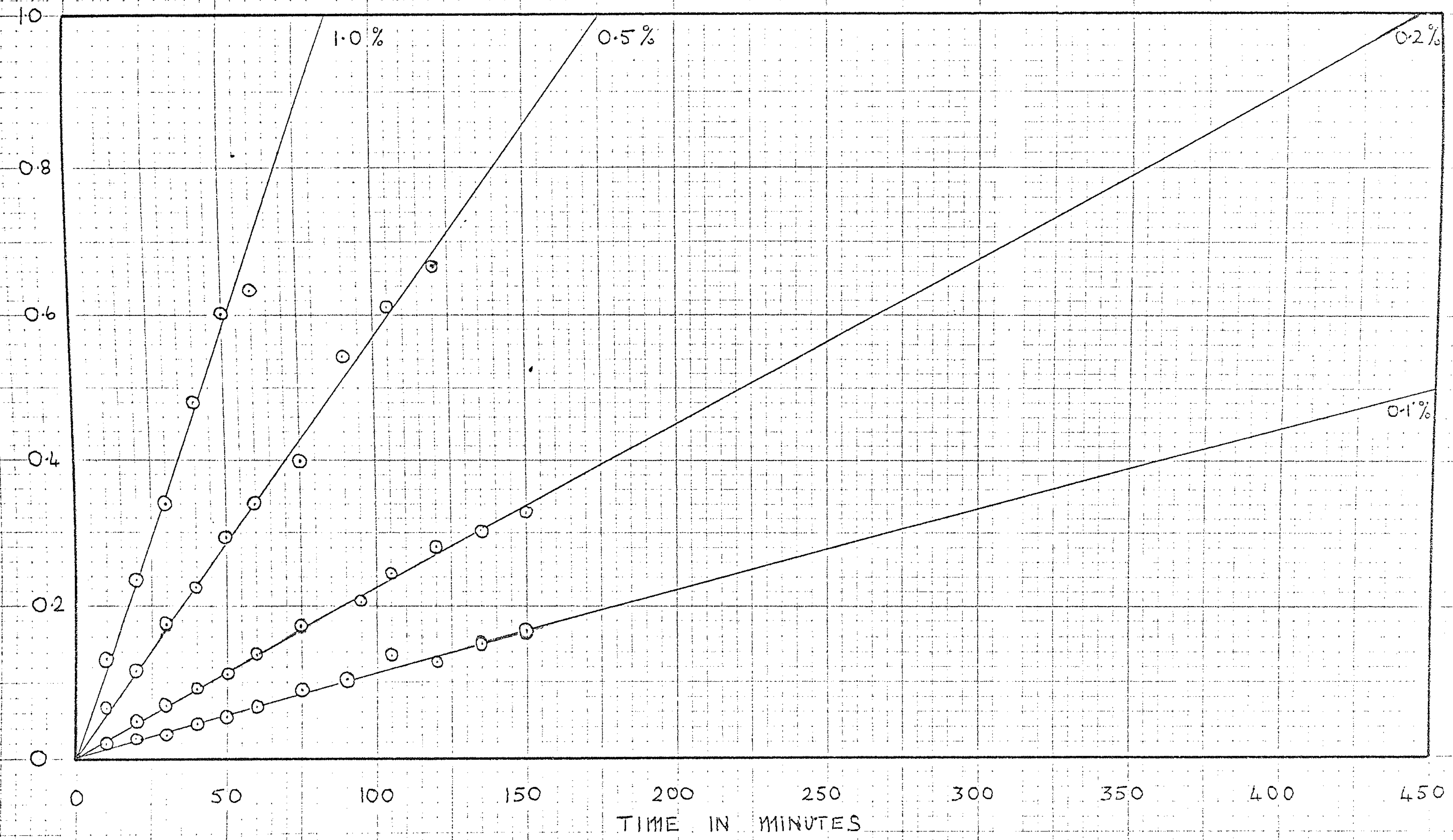


FIG 3.8 Y VS TIME TEMPERATURE 75 °C

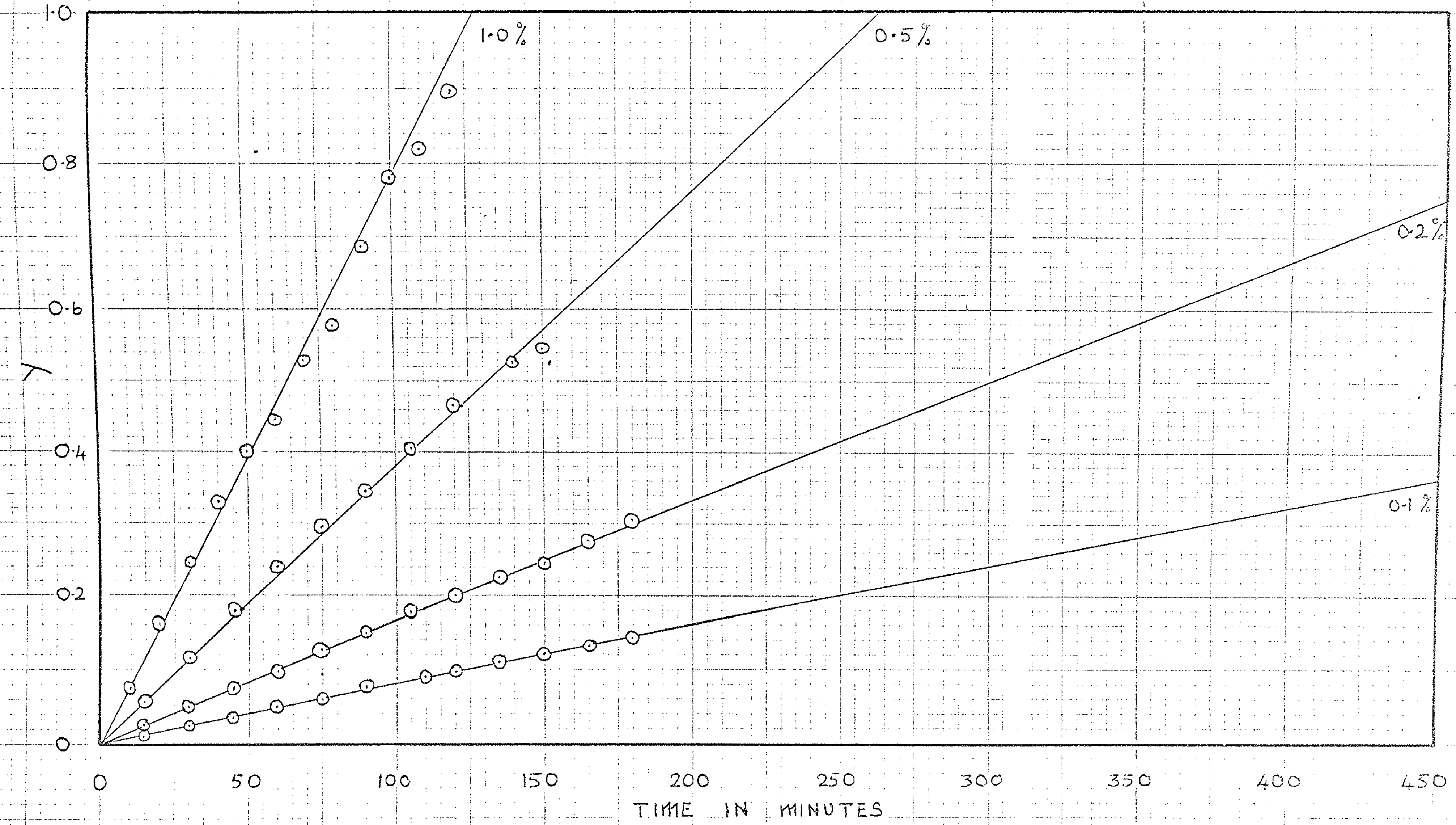


Fig 3.9 Y vs Time Temperature 70 °C

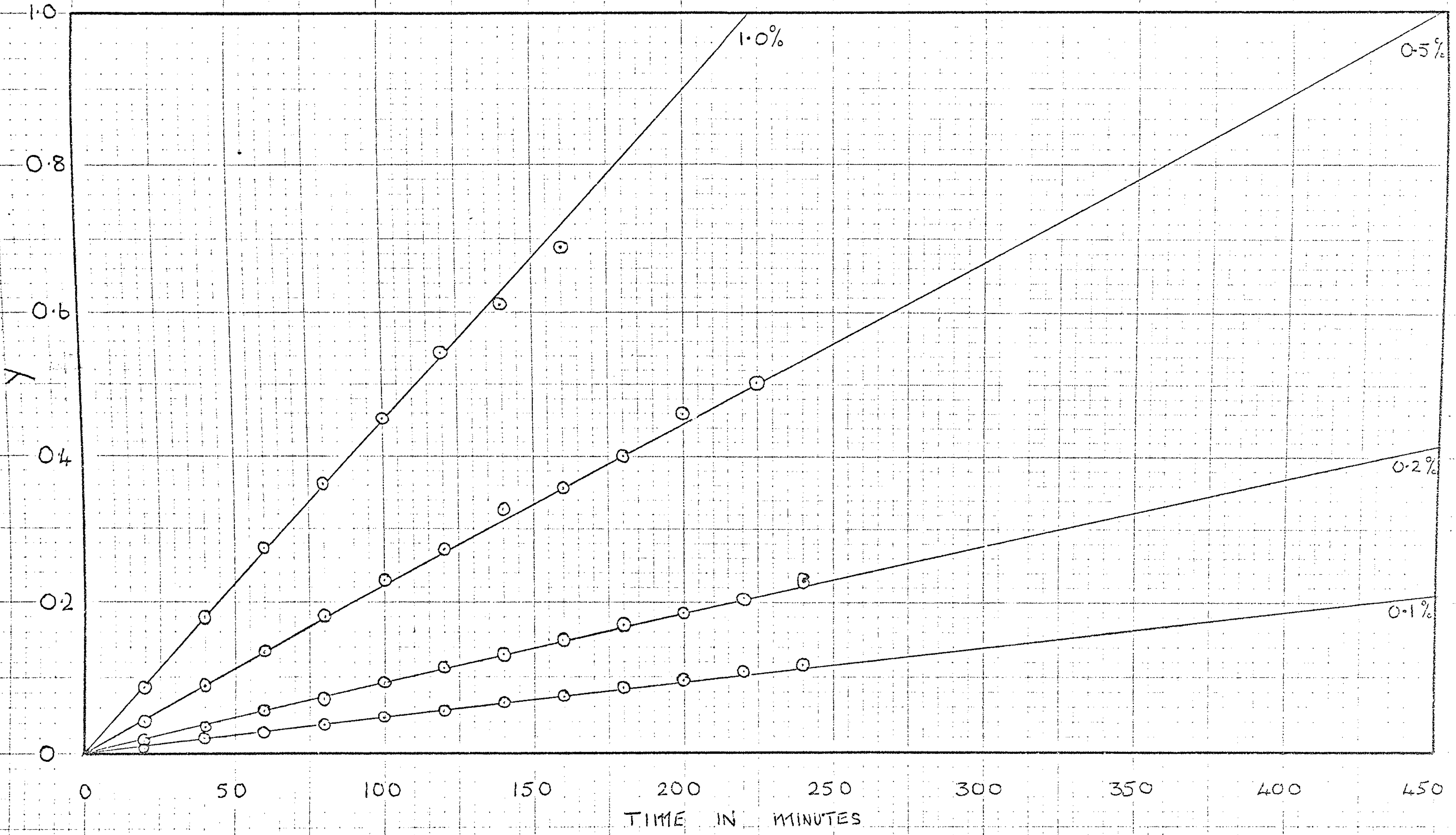


FIG. 3.10 Y VS TIME TEMPERATURE 60°C

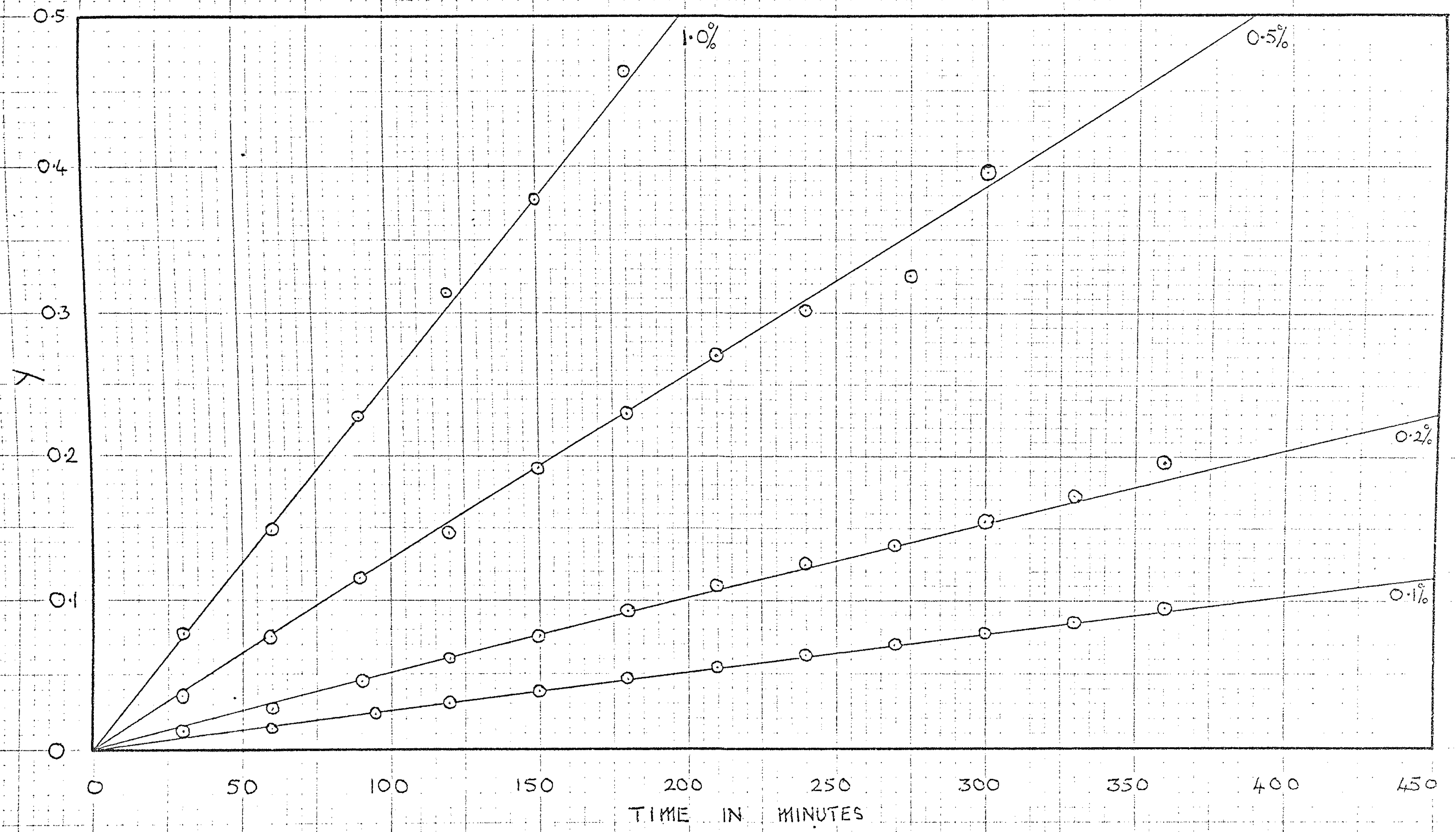


Fig 3.11 Y vs Time Temperature 50°C

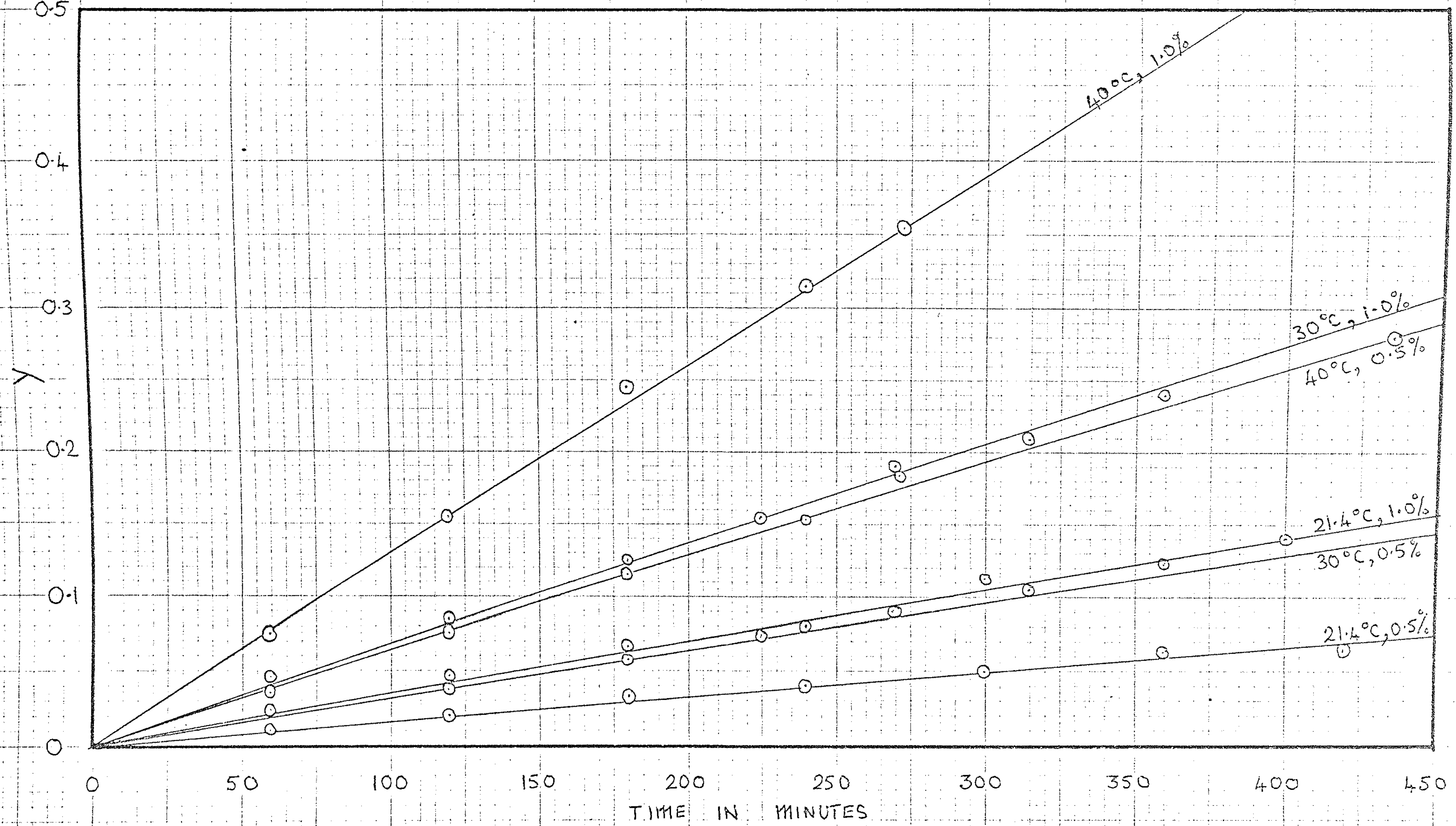


FIG 3.12 Y VS TIME TEMPERATURES OF 40, 30 & 21·4 °C

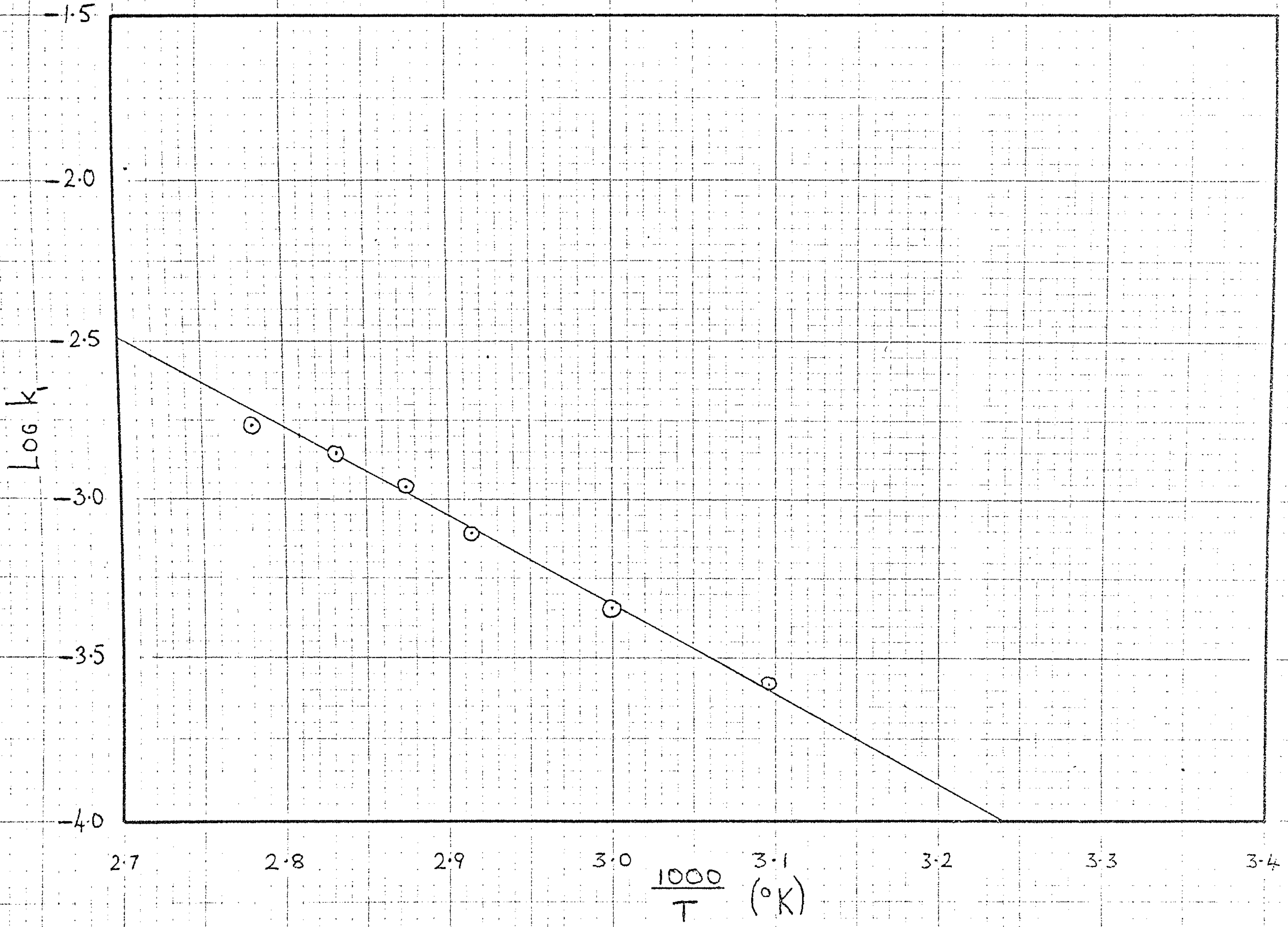


Fig 3.13 Log k_1 vs Absolute Temperature, Catalyst Concentration 0.1 w/w %

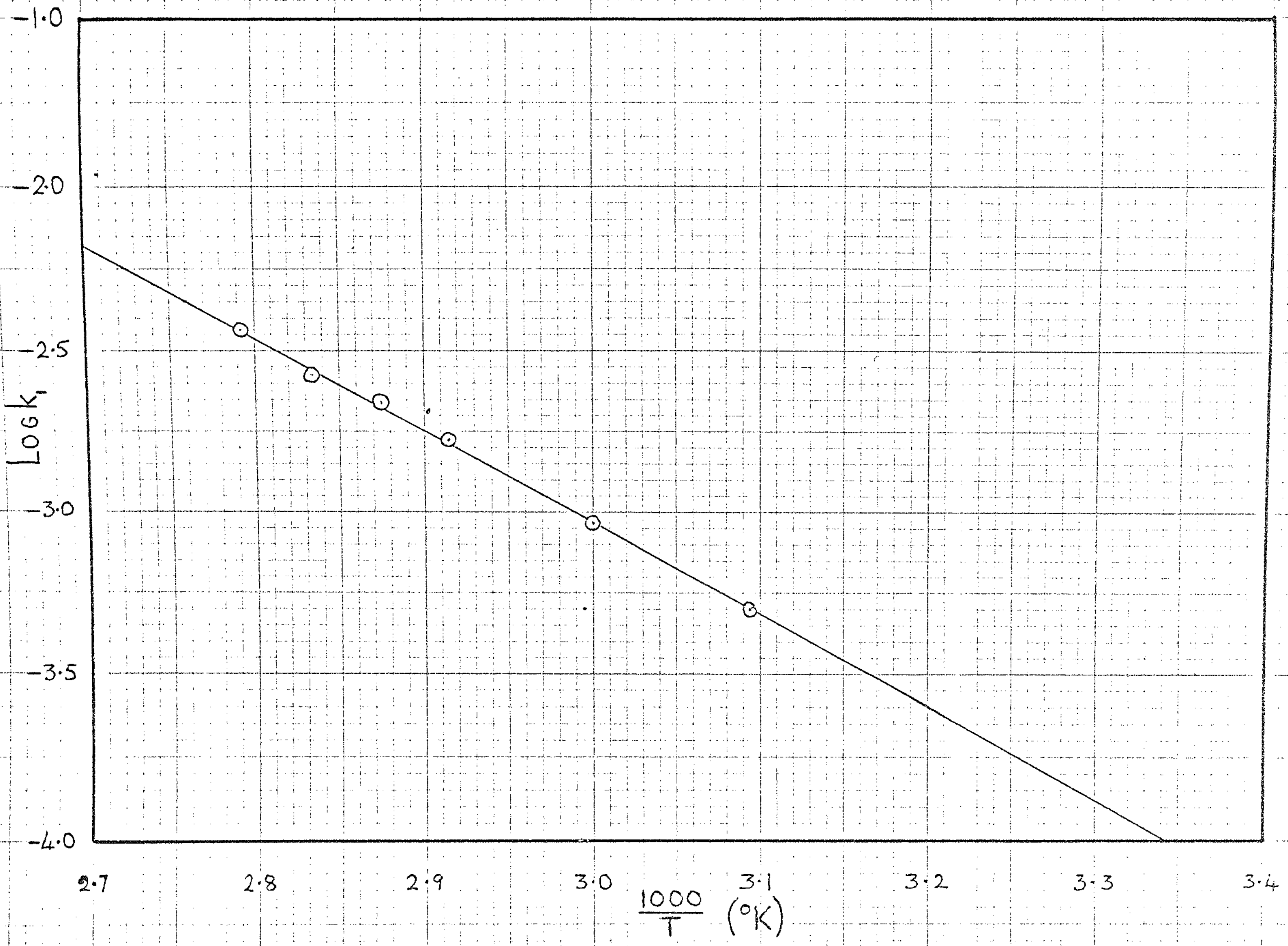


Fig 3.14 Log k_1 vs Absolute Temperature, Catalyst Concentration 0·2 w/w%.

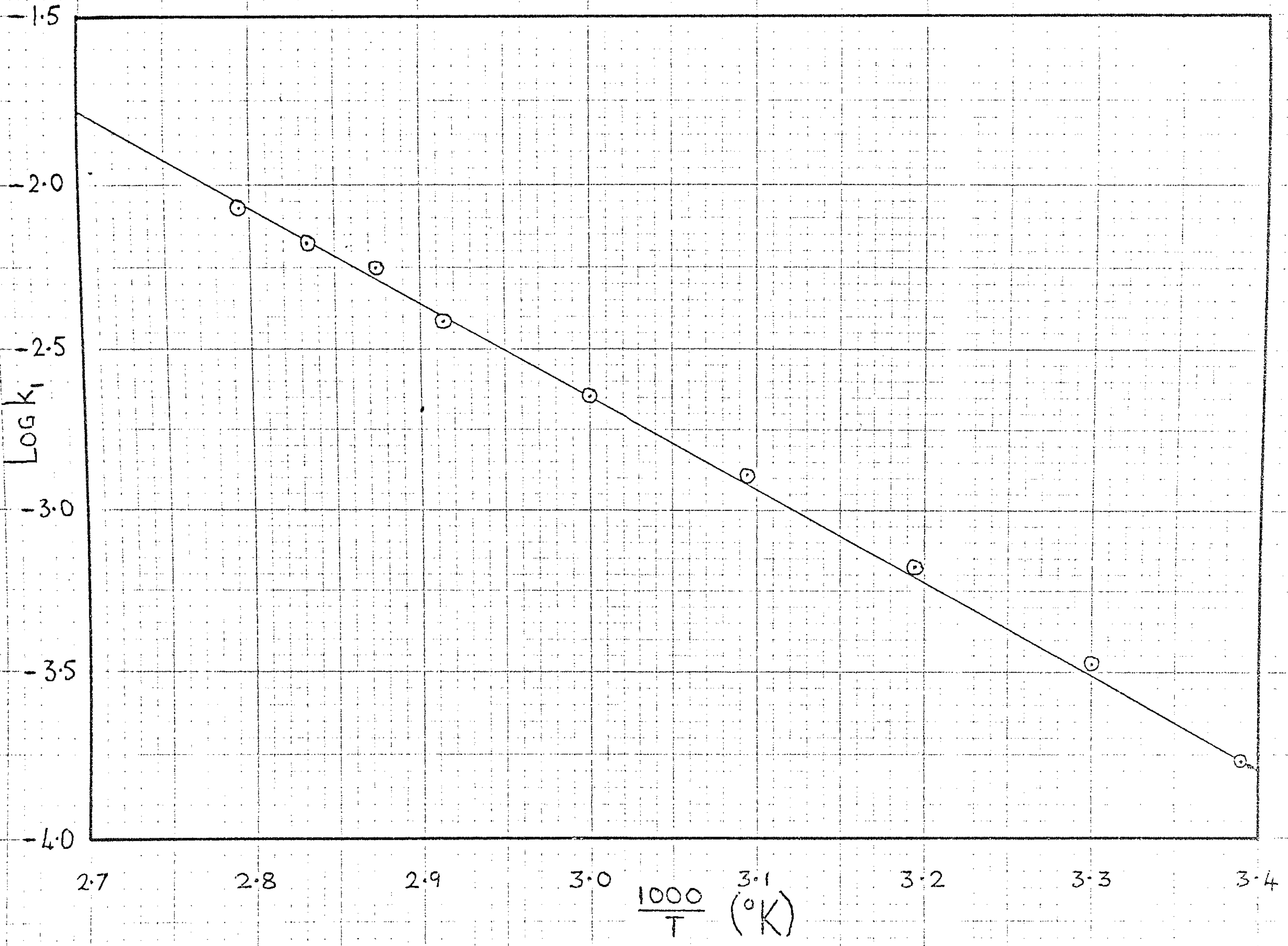


FIG 3.15 LOG k_1 VS ABSOLUTE TEMPERATURE, CATALYST CONCENTRATION 0.5 W/W %

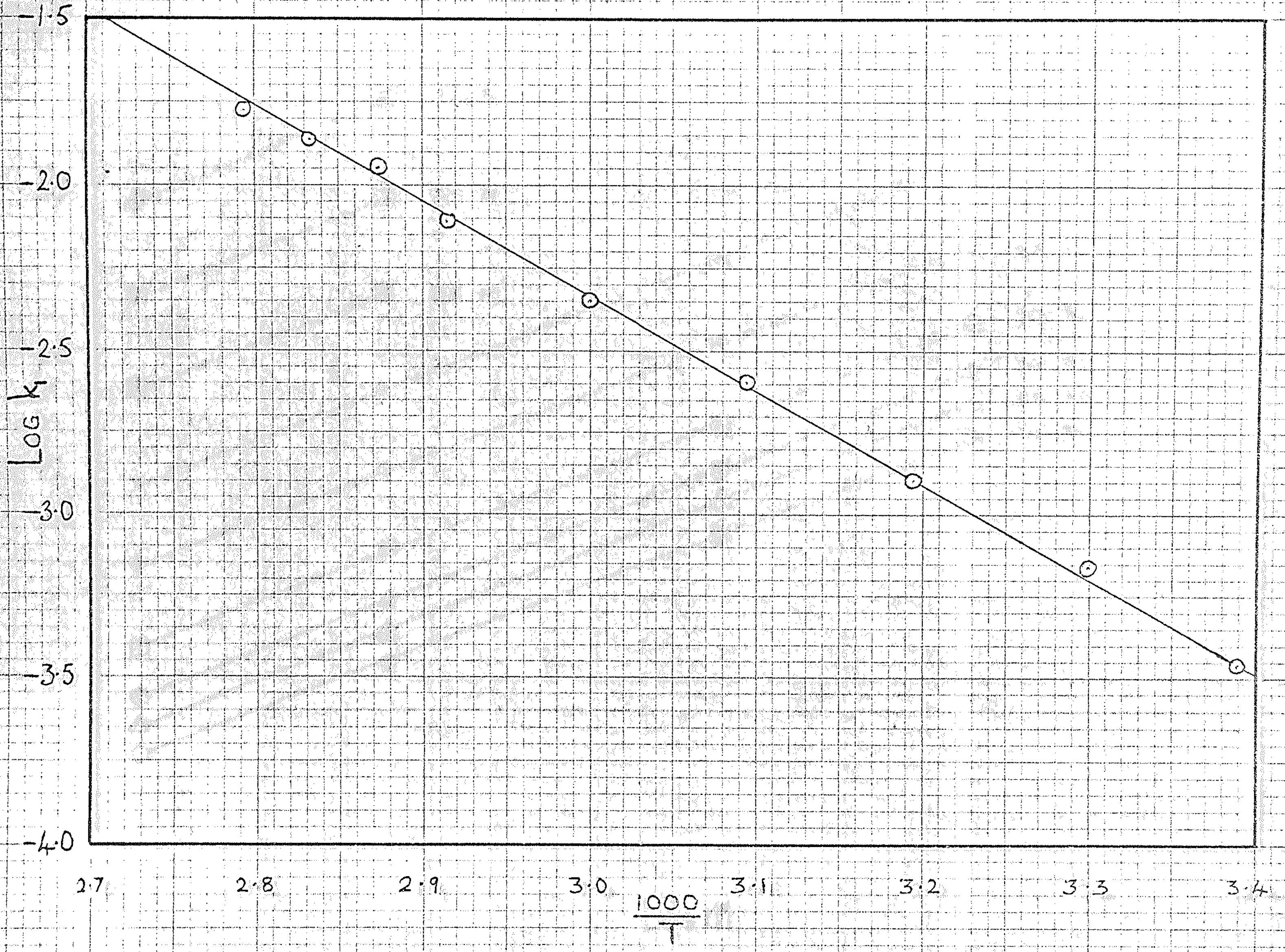


Fig 3.16 Log k_1 vs Absolute Temperature, Catalyst Concentration 1·0 w/w%

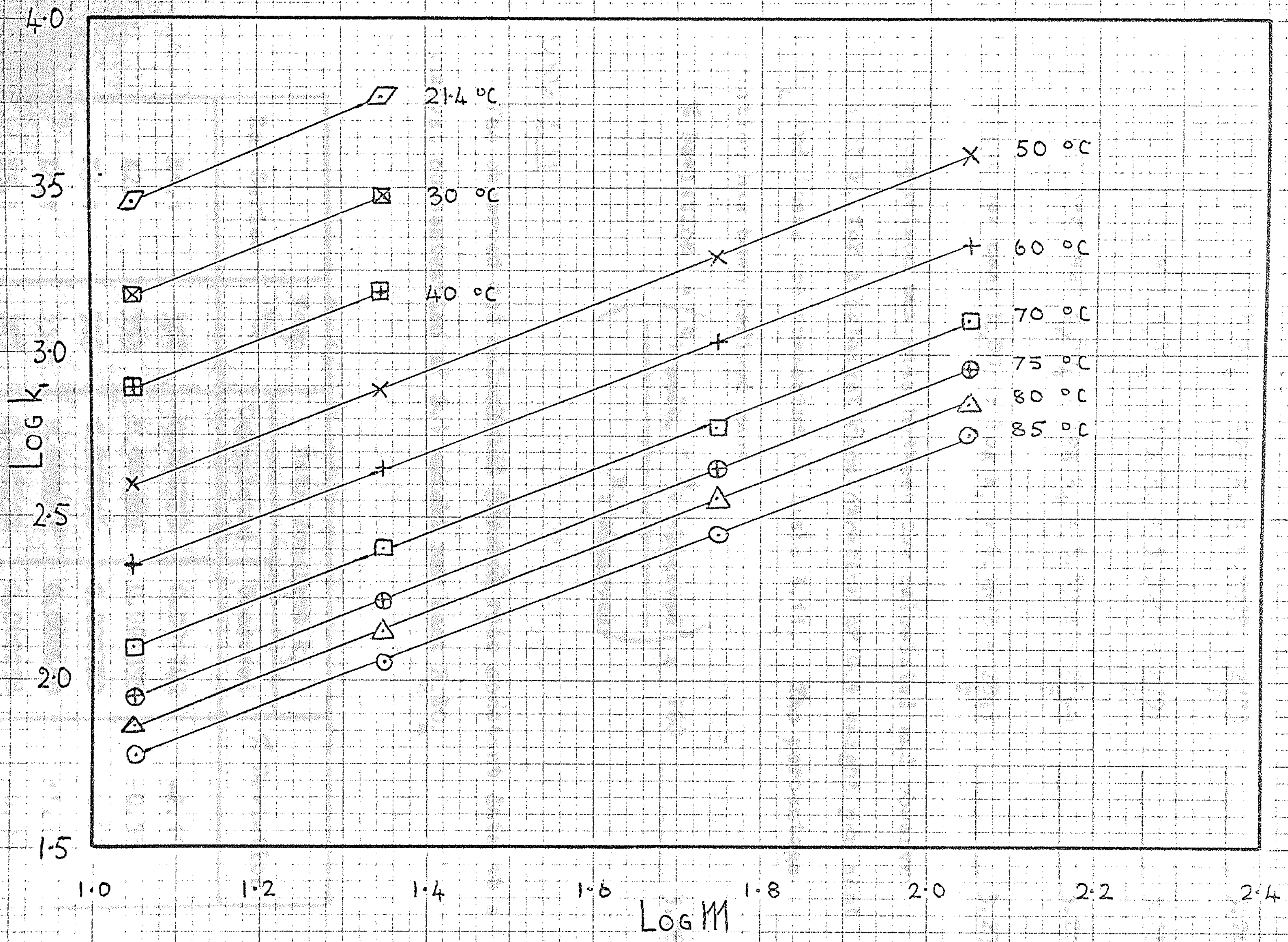


Fig 3.17 Log k_1 vs Log M

which were used to determine the values of m and c. From the computations equations 3.24-27 relating log k_1 and $\frac{1}{T}$ were formulated:-

$$0.1 \text{ weight per cent } H_2SO_4 : \log k_1 = 4.9939 - \frac{2773}{T} \qquad 3.24$$

$$0.2 \text{ weight per cent } H_2SO_4 : \log k_1 = 5.3511 - \frac{2791}{T} \qquad 3.25$$

$$0.5 \text{ weight per cent } H_2SO_4 : \log k_1 = 5.8992 - \frac{2846}{T} \qquad 3.26$$

$$1.0 \text{ weight per cent } H_2SO_4 : \log k_1 = 6.1873 - \frac{2841}{T} \qquad 3.27$$

A comparison was made between the calculated and observed values of k_1 for a catalyst concentration of 0.1 weight per cent H_2SO_4 and these are presented in Table 3.11. The percentage deviation has been defined as:-

$$\% \text{ Deviation} = \left(\frac{k_{1 \text{ calc.}} - k_{1 \text{ observed}}}{k_{1 \text{ observed}}} \right) \times 100 \qquad 3.28$$

Table 3.11

The observed and calculated forward rate constant data at a catalyst concentration of 0.1 weight per cent H_2SO_4

Run Series	Temp. °K	Rate Constant k_1		% Deviation
		Calculated	Observed	
K1.1	358	0.001778	0.001740	+2.19
K2.1	353	0.001382	0.001395	-0.95
K3.1	343	0.000816	0.000780	+4.60
K4.1	333	0.000467	0.000460	+1.46
K5.1	323	0.000258	0.000258	-0.08
K7.1	348	0.001065	0.001110	+4.06

The mean percentage deviation from the calculated relationship was 1.88%.

The Activation energy for the reaction maybe calculated from the gradients of equations 3.24 - 3.27.

0.1% $E = 12.69$ kcal g mole^{-1}

0.2% $E = 12.77$ kcal g mole^{-1}

0.5% $E = 13.02$ kcal g mole^{-1}

1.0% $E = 13.00$ kcal g mole^{-1}

$E_{mean} = 12.87$ kcal g mole^{-1}

These values are in good agreement with the previously published data of 12.1 x 10^3 kcal g mole^{-1} and 12.8 kcal g mole^{-1}.

It is difficult to compare the values of the forward velocity constant which have been obtained as the only other values which can be found are those published by Farkas et al (39). A direct comparison of the values is not possible because the data presented by Farkas et al (39) is based on a first order velocity constant which has been calculated from the approximate form of the rate equation i.e. equation 3.20 and the approximate form was calculated using mole fractions as the concentrations. However, it was concluded that both sets of results demonstrated similar trends for the forward rate velocity and that the rate constant was proportional to the catalyst concentration.

The average value of the equilibrium constant measured over the temperature range 60, 70 and 80°C was found to be 0.96. This value compares favourably with the published data listed in Table 3.12.

Table 3.12

Equilibrium Constant

Temp. °C	Equilibrium Constant K	Reference
25	0.96	Barker
60 80	0.96	Farkas
60 70 80	0.96	Present Work
200	0.97	Fehlandt & Adkins

A general appraisal of the results has indicated that there is a good agreement with the data reported in the literature.

However, some differences have been discovered which might have been expected due to the wider range of temperature and catalyst concentration and the purity of the reactants which have been employed.

The materials used were either analar or in the case of butyl acetate, laboratory reagent grade. It was observed in the preliminary experiments, that when the first sample was removed from the reactor (i.e. immediately after the addition of the catalyst) and analysed, that it contained approximately one mole per cent of butyl alcohol. As the reaction was not instantaneous, it was realised that the butyl alcohol must have originated from the reactant butyl acetate as an "impurity". Thus in the calculation of the mole fraction of the reaction products (x) a modified procedure had to be adopted. The actual concentration of the butyl alcohol which was formed by the reaction (x) being calculated as follows:-

Butyl alcohol formed by the reaction at time (t) =

Butyl alcohol analysed at time (t) - Butyl alcohol present at t = 0. Thus the mole fraction for the reaction products (x) would equal the average of the ethyl acetate concentration and the modified butyl alcohol concentration. Using this technique, more consistent values for Y were obtained.

The forward rate constant k_1 was evaluated by Farkas et al (39) using an approximate form of the integrated rate equation i.e.

$$\ln \frac{ab}{(ab - x)} = k_1 (H^+) t \qquad 3.29$$

In the development of the reaction kinetics computer programme from the analytical computer programme (see Appendix A5) both the approximated and full forms of the integrated rate equations (i.e. 3.20 & 3.19) were calculated so that a comparison could be made of the error incurred in using the approximate equation. The results for the experimental series are tabulated in Appendix B2.

From these results it is clear that the values used from the approximate equation (3.20) would be greater than those from the normal equation (3.19) and this casts further doubts on Farkas's (39) data particularly as there is about a 10% error between the values at the high concentrations.

A series of reactions (K8) was carried out at 70°C with an excess of one of the reactants. From the analysis of the results it was noted that the rate constant increased when a mixture containing an excess of butyl acetate (BUAC : ETOH = 1.97:1) was reacted whilst the value of the rate constant remained approximately constant when a mixture containing an excess of ethyl alcohol (ETOH : BUAC = 1.40:1) was reacted.

It was stated by Farkas et al (39) that the reaction rate constant was not affected by the ester : alcohol reactant molar ratio, although it was observed from their results that when excess ester was present the reaction rate constant increased by 6.0 per cent. It was concluded by Kolhatkar (68) that as the ester concentration was increased, the rate constant was increased by approximately the same magnitude. However, the affect of a large excess of alcohol in a transesterification reaction has been observed by Hrivnak et al (45), Kolhatkar (68) and Juvet et al (46) who concluded that under such conditions the reaction becomes first order.

The increase in the reaction rate when as excess of butyl acetate was present could in the reaction mixture possibly be due to a change in reaction order or mechanism and it is clear that this could be clarified by a further investigation.

It was observed that at high catalyst concentrations and/or high temperatures, when the concentration of the products exceeded 20 mole per cent, that the reaction rate 'tailed-off' as the reaction equilibrium was approached. A similar phenomenon was noticed by Juvet et al (46) in their study of a transesterification reaction using gas liquid chromatography techniques and they reported that the calculated reaction rate constant decreased by as much as 12% as the reaction approached equilibrium.

It was observed from the graphs of parameter Y versus time t (Figs. 3.2 - 3.12) that as the catalyst concentration was increased the reaction rate increased and this is clearly demonstrated in Fig. 3.17 where log of the rate constant is plotted against the log of the Molarity. As the catalyst concentration increased from 0.1 to 1.0 weight per cent, the rate constant increased by a factor of ten. This could be attributed to the change in the hydrogen ion concentration affecting the rate determining steps in the appropriate mechanism.

Section 4.

THE VAPOUR LIQUID EQUILIBRIA.

4. THE VAPOUR LIQUID EQUILIBRIA.

4.1 Introduction

In order to assess the performance of the distillation column which will be used in the later experimental work, it will be necessary to determine the vapour liquid equilibrium data at atmospheric pressure for the following systems:-

1) ethyl acetate - ethyl alcohol
2) ethyl acetate - butyl alcohol
3) ethyl acetate - butyl acetate
4) ethyl alcohol - butyl alcohol
5) ethyl alcohol - butyl acetate
6) butyl alcohol - butyl acetate
7) ethyl acetate - ethyl alcohol - butyl alcohol
8) ethyl acetate - ethyl alcohol - butyl acetate
9) ethyl acetate - butyl alcohol - butyl acetate
10) ethyl alcohol - butyl alcohol - butyl acetate
11) ethyl acetate - ethyl alcohol - butyl acetate - butyl alcohol.

The following systems have all been studied at atmospheric pressure and equilibrium data is available:-

1) ethyl acetate - ethyl alcohol : (40), (69) & (70).
2) ethyl acetate - butyl alcohol : (71).
4) ethyl alcohol - butyl alcohol : (72), (73).
6) butyl alcohol - butyl acetate : (74), (75).
7) ethyl acetate - ethyl alcohol - butyl alcohol : (36).

In the study of the ethyl acetate - ethyl alcohol mixtures, the investigators have all detected an azeotrope but the reported composition of the azeotrope has varied from 42.7 to 46.4 mole per cent ethyl alcohol whilst the temperature of the minimum boiling azeotrope has varied from 71.8 to 72.8°C. For the ethyl alcohol - butyl alcohol mixtures, the values of the 3rd order Van Laar constants calculated by both research workers (72, 73) were found to be almost zero, although the values calculated by Van Winkle & Hellwig (73) were some what greater than those of Brunjes & Bogart (72). The butyl alcohol - butyl acetate equilibrium compositions were determined by two investigators (74, 75) one of whom determined a minimum boiling azeotrope of 72.9 mole per cent butyl alcohol at 116.5°C (74) whilst the other investigator (75) did not detect an azeotrope.

Thus in view of the general lack of data, particularly for the multicomponent mixtures, and the discrepancies which occurred within the available data, it was concluded that it would be necessary to determine the vapour liquid equilibrium compositions. Thus vapour liquid equilibrium compositions could be determined directly from the experimental data or the experimental data could be used to formulate a mathematical model from which any equilibrium compositions could be predicted.

4.2 A Literature Survey of The Vapour Liquid Equilibrium Stills

4.2.1 Introduction

The various techniques available for the experimental determination of vapour liquid equilibrium can be categorised as follows:-

1) The Distillation Method
2) The Dew & Bubble Point Methods
3) The Static Method
4) The Circulation Method
5) The Flow Method

In examining the various techniques which are available for the experimental determination of V.L.E. data, it was important to realise that in the eventual selection of an apparatus, the systems which were to be investigated were non-ideal due to the presence of polar components, azeotropes could be formed by some of the binary mixtures and finally a reversible reaction could occur. The apparatus which was to be selected would have to cope with all these possibilities.

4.2.2 The Distillation Method

In this technique which has been used by Taylor (76) and Rayleigh (77), a small quantity of liquid is distilled off from a large amount of liquid which is contained in a flask. The liquid distilled off is assumed to be in equilibrium with the mean composition of the bulk liquid.

4.2.3 The Dew & Bubble Point Methods

These techniques are used to investigate the behaviour of the system's compositions under iso thermal conditions when the pressure is changed. A simple cell has been described by Hala et al (79) for the determination of dew and bubble point data. The method has also been used to study the phase behaviour of hydrocarbon mixtures, particularly those with lower molecular weights. In particular the work of Sage and Lacey (78) who studied the propane - pentane system, is typical. However, due to the large residence times, this type of apparatus would be unsuitable.

4.2.4. The Static Method

In this type of apparatus, a liquid sample is placed into a closed and evacuated cylinder which is contained in a thermostat. The cylinder and its contents are either rotated or agitated until equilibrium is established between the liquid and vapour phases. Then samples are taken from both phases. Although the procedure seems to be relatively simple, the main difficulty lies in the removal of the vapour sample. When carrying out the experiment at low pressures, most of the vapour above the liquid phase has to be removed in order to provide a reasonably sized sample and thus the equilibrium is disturbed. Hence this technique is usually confined to high pressure studies and the work of Verchoyle (80) who investigated the hydrogen - nitrogen - carbon monoxide system at 225 atmospheres, is typical.

4.2.5 The Circulation Method

These stills whether they are vapour recirculating stills (69, 81-3) or liquid condensate recirculating stills (84-8), are usually based upon a common design concept. That is, a large quantity of liquid is loaded into a boiler. The vapours emerging from the boiling mixture are condensed and collected in a reservoir where the condensate is sampled. In the case of liquid condensate recirculation stills, the condensate is fed directly back to the liquid phase in the boiler whilst in the case of vapour recirculating stills, the condensate is vaporised before being passed back to the equilibrium chamber.

These stills which are generally considered to be simple to construct and use, are widely used for V.L.E. determinations and consequently new designs or modifications to existing stills appear at regular intervals. Othmer (84) suggested some design criteria for the recirculation stills. He proposed that concentration gradients should not occur in the boiling liquid and the vapour should disengage evenly from the liquid phase causing minimum liquid phase entrainment. He also recommended that the liquid phase sample point in the equilibrium chamber should be positioned well away from the condensate return inlet. The size of the sample should always be as small as possible to minimize any disturbances to the vapour liquid equilibrium.

Most of the circulation stills will only operate at medium pressures, a fact which was observed by Bloom et al (81). They also paid specific attention to the prevention of heat losses from the equipment particularly as in their measurements they were trying to obtain the enthalpies of the equilibrium compositions. Adiabatic conditions were achieved by containing the boiler and the equilibrium chamber of the still within two lengths of aluminium pipe. The space between the equipment and the pipe's inside wall was filled with an insulating material whilst the external surfaces of the aluminium pipes were wrapped with heating tapes. The whole apparatus was finally enclosed by rock-wool insulation.

For their design of a vapour recirculating still, Colburn et al (82) ensured that proper mixing occurred in the equilibrium chamber. This was achieved by directing the inlet vapour stream away from the liquid sampling point and onto the thermocouple. Thus good mixing and temperature measurements were obtained.

Ellis (85) in the design of his recirculating still, reiterated and emphasised the design concepts suggested by Othmer (84) particularly with respect to the liquid sampling arrangements which Ellis (85) thought had been unsatisfactory. It was also observed that partial condensation had occurred in some of the other investigators' apparatus. Ellis (85) overcame the liquid sampling problem by using a double-walled glass boiler and equilibrium chamber.

The returning condensate and the equilibrium liquid phase were boiled in a boiling chamber by a bayonet heater. The boiling mixture was expanded up through an equilibrium coil and impinged onto a thermometer pocket. The vapour disengaged whilst the liquid phase descended down the outside of the boiling chamber and passed into the base of the chamber through four small port holes which were designed so that only the returning liquid phase could enter the boiling chamber. The disengaged vapour flowed up the inner part of a column to another thermometer before returning down the outside of the same column (thus providing a vapour jacket as insulation) to a finger condenser where the condensate was sampled. The column was heated by an externally wound resistance wire heater. The still was charged with about 250 ml of liquid and equilibrium was reached after operating for one hour. The attainment of equilibrium was judged by the constancy of the thermometer readings and when the distillation rate was such that 40-70 drops per minute of liquid fell from the finger condenser.

Gillespie (86) tried to overcome the problem of partial condensation by using a vapour jacket technique and also by applying externally mounted jacket heaters. The apparatus uses the Cottrell pump technique and the conditions in the Cottrell tube were designed to achieve equilibrium between the liquid and vapour phases. The boiler had a 100 ml capacity and equilibrium was achieved after two hours.

Malenko et al (87) have designed a simple circulating still to study the equilibrium of a quaternary mixture containing esters, a ketone and a hydrocarbon. The boiler had a capacity of 700 ml and the apparatus was operated for one hour before equilibrium was achieved. In order to avoid disturbing the equilibrium, the samples were returned to the still after being analysed.

Recently, a still has been designed to examine non-ideal positive and negative mixtures which are contained in ternary acrylonitrile mixtures (88). The equilibrium chamber was surrounded by a vapour jacket. The boiling liquid was well mixed by a magnetic stirrer but it would appear that the liquid phase sampling point was situated near to the condensate return inlet.

Hipkins & Myers (83) used a vapour jacket arrangement to overcome heat losses in their vapour recirculating still. They claimed that this was a better technique than using external heaters which they thought were difficult to control and could cause local hot spots. They were one of the few investigators who checked the amount of entrainment which occurred in the still. This was achieved by boiling a sodium chloride solution and analysing the condensate for chloride ions with silver nitrate solution. No precipitation was observed at the highest vapour flowrate of 18 mole h^{-1}.

4.2.6 The Flow Method

The usual technique for flow stills is to pass a preheated liquid phase stream and a separate vapour phase stream into a contacting device where equilibrium of the two phases is quickly achieved. The phases are separated and sampled. Normally the composition of each stream can be adjusted independently from the other stream and thus a whole series of experimental determinations can be carried out.

A flow still was designed by Colburn et al (89) to determine the vapour liquid equilibrium of partially miscible liquids. A constant flow of saturated vapour was bubbled through 15 ml of liquid which was contained in an adiabatic contacting unit. The contactor was surrounded by a vapour jacket and a dead-air jacket. Vapour liquid equilibrium was considered to have been reached when a constant liquid level and a temperature variation of less than 0.1°C were observed. After sampling both phases, the vapour composition was changed and the procedure was repeated. The still was calibrated by using an ethylene dichloride-toluene system.

A simple flow still has been designed by Villim et al (90). The liquid mixture was placed in a reservoir below which there was a float mechanism. The float established a constant level in the vaporiser. The boiling liquid-vapour mixture leaving the vaporiser, impinged on a thermometer in the disengager unit. The phases separated, were condensed, cooled and sampled. The heat input to the vaporiser was adjusted to give a liquid to vapour ratio of 10:1. 300 ml of liquid was placed in the reservoir when large samples were required but generally a charge of 50-100 ml of liquid was sufficient. Each equilibrium determination took between 10 and 15 minutes.

Rius et al (91) have designed a flow still specifically for reacting mixtures. The reactants which were stored in reservoirs were mixed at the correct rate in an agitator and fed at 50 ml min^{-1} to a 10 cm long vaporiser. The heating time of the liquid took about 30 seconds. The boiling mixture was fed into a contactor which was contained in a Dewar flask. The phases separated by gravity, were condensed, cooled and sampled. The time for each determination was about 15 minutes and equilibrium was achieved when a constant temperature was reached. The still was calibrated using an ethyl alcohol-water system. The data which was obtained, was found to compare well with other experimental data for the system. Finally the still was used to obtain data for the V.L.E. of esterification reactions and the results were correlated by the Redlich-Kister Equations. It was observed that when a catalyst was not used, no reaction occurred.

Cathala (92, 93) has constructed a still for reacting mixtures which differs considerably from the previously designed flow stills. Basically, the vapour and the preheated liquid were mixed in a contacting chamber. The mixture passed up into an equilibrium chamber. It was proposed to investigate the vapour liquid equilibrium of the thermally unstable sulphuric acid-nitric acid-water system in the still and the equipment which was used is illustrated in Fig. 4.1.

Superheated steam was generated by boiling water in an internally heated flask (A) and the vapour was superheated in an external electrically heated side arm. The vapour was fed into the base of the contacting chamber (C) where it was mixed with a preheated liquid phase which entered onto the first of two sieve plates (25 mm dia. 60 0.10 mm dia. holes) through port (D). The mixture passed up into a vigreux column (E) in the equilibrium chamber where the rate of approach to equilibrium was considered to be accelerated by the degree of superheat of the vapour (94). The mixture jetted out from the top of the vigreux column through four port holes onto a thermometer well and from there it passed to the de-entrainer. The liquid flowed down the inside surface of a thermal shield (F) and was syphoned away whilst the vapour flowed up the outside of the shield and passed to a condenser through exit (G). The whole of the equilibrium chamber was surrounded by a resistance wire heater. The whole still was well lagged to prevent partial condensation.

Marek (95, 96) used a slightly modified version of Cathala's

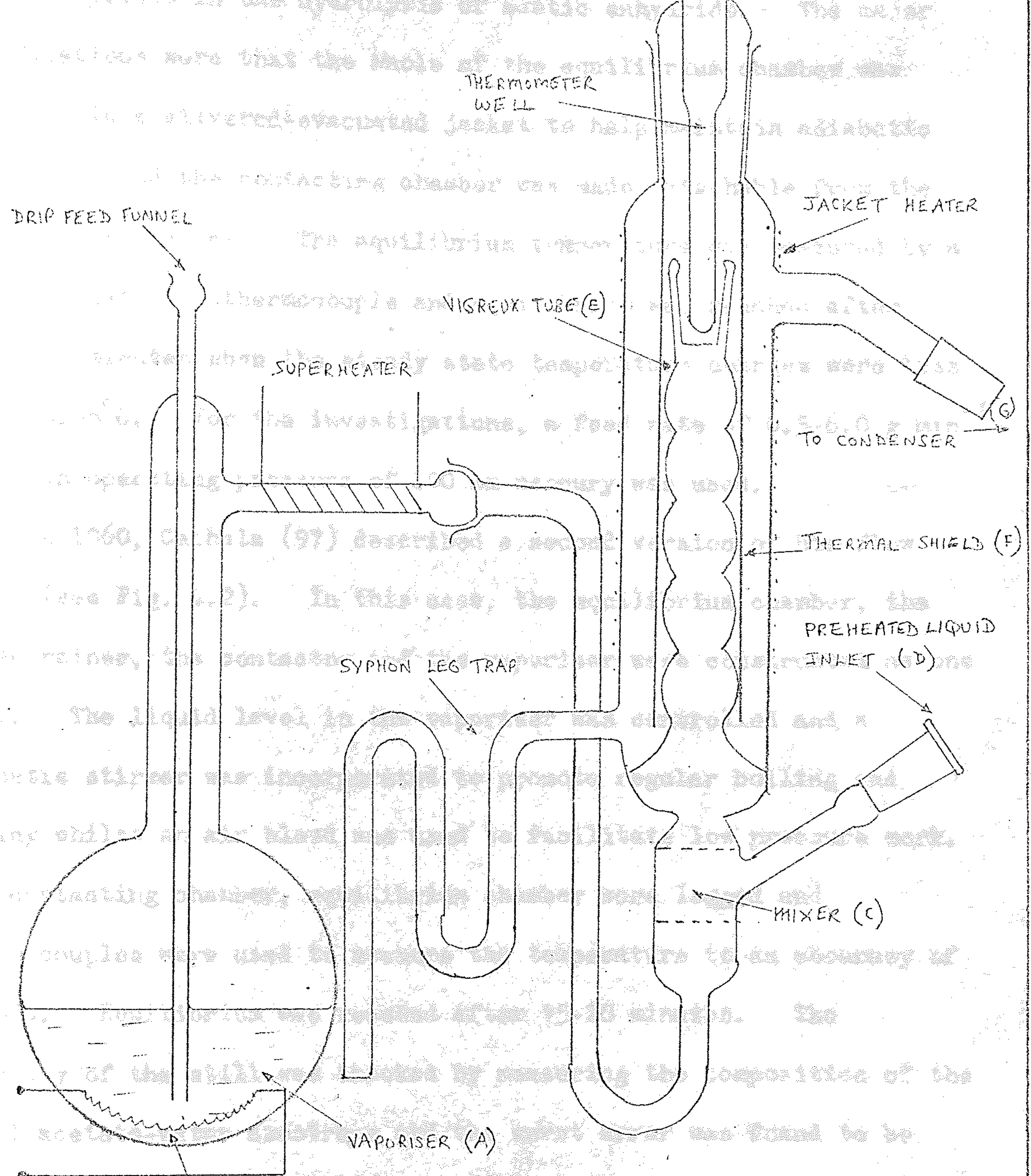


FIG 4.1 ORIGINAL CATHALA STILL (1950)

original still to investigate the vapour liquid equilibrium of the various systems in the hydrolysis of acetic anhydride. The major modifications were that the whole of the equilibrium chamber was enclosed in a silvered-evacuated jacket to help maintain adiabatic conditions and the contacting chamber was made detachable from the equilibrium chamber. The equilibrium temperature was measured by a copper-constantan thermocouple and equilibrium was reached after 10 to 20 minutes when the steady state temperature changes were less than ±0.05°C. For the investigations, a feed rate of 0.5-6.0 g min^{-1} under an operating pressure of 400 mm mercury was used.

In 1960, Cathala (97) described a second version of his flow still (see Fig. 4.2). In this case, the equilibrium chamber, the de-entrainer, the contactor and the vaporiser were constructed as one unit. The liquid level in the vaporiser was controlled and a magnetic stirrer was incorporated to promote regular boiling and mixing whilst an air bleed was used to facilitate low pressure work. The contacting chamber, equilibrium chamber were lagged and thermocouples were used to measure the temperature to an accuracy of 0.05°C. Equilibrium was reached after 15-20 minutes. The accuracy of the still was checked by measuring the composition of the ethyl acetate-water azeotrope and the worst error was found to be ±0.158 mole per cent. Liquid entrainment was estimated by boiling a solution containing potassium dichromate and analysing the vapour phase. It was concluded that entrainment was very small.

A major modification to the Cathala stills was made by Mamers (66) who separated the vaporiser from the equilibrium chamber unit. As in the case of Marek's design (95, 96) the equilibrium chamber was surrounded by an evacuated jacket and the still was well

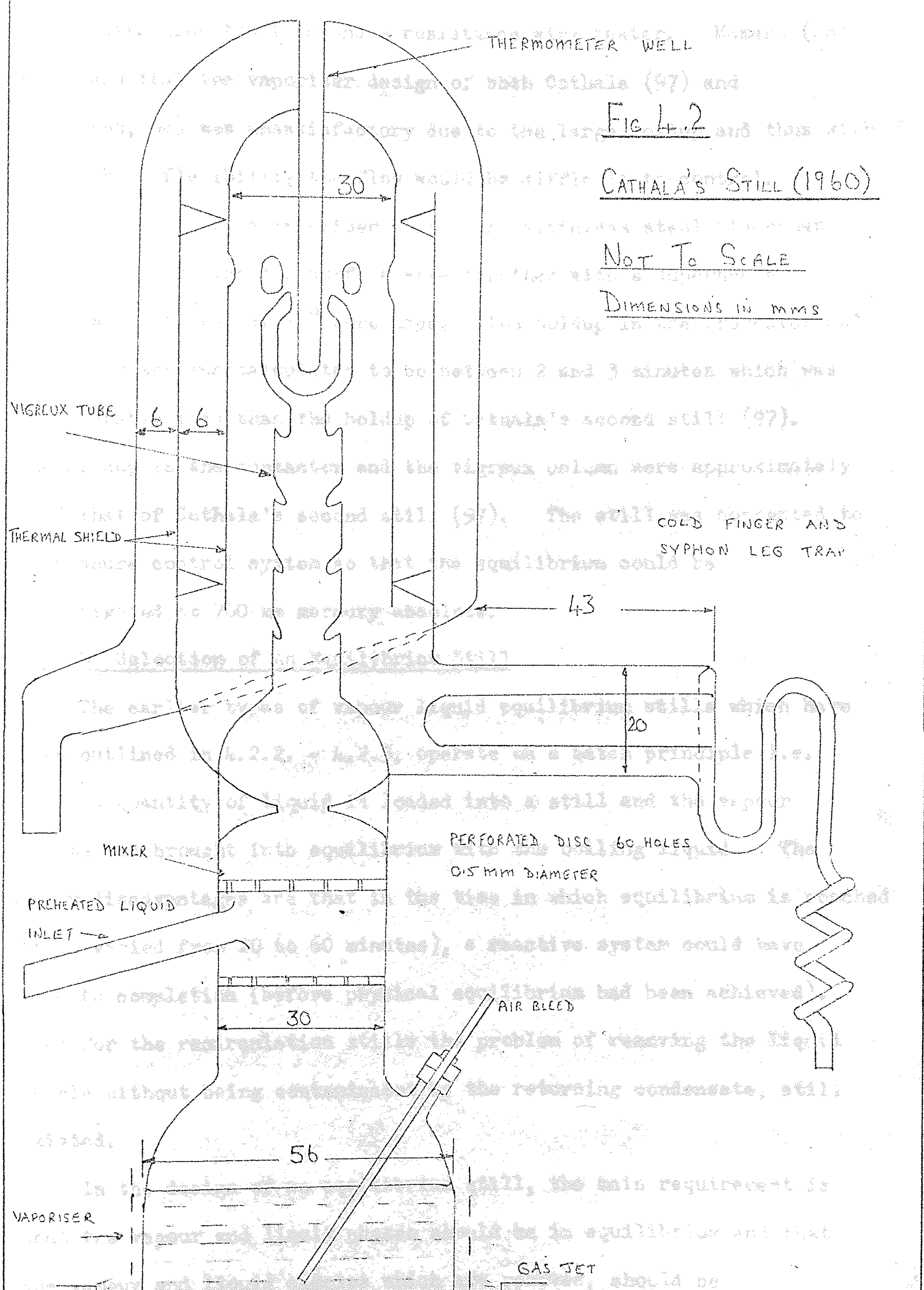


FIG 4.2

CATHALA'S STILL (1960)

NOT TO SCALE

DIMENSIONS IN MMS

lagged with asbestos tape and a resistance wire heater. Mamers (66) concluded that the vaporiser design of both Cathala (97) and Marek (95, 96) was unsatisfactory due to the large holdup and thus with the lack of flexibility the flow would be difficult to control. Hence a falling film vaporiser containing stainless steel Oldershaw packing to increase the surface area together with a superheater which was inclined at 15° were used. The holdup in the preheater and the vaporiser was calculated to be between 2 and 3 minutes which was considerably less than the holdup of Cathala's second still (97). The holdup in the contactor and the vigreux column were approximately half that of Cathala's second still (97). The still was connected to a pressure control system so that the equilibrium could be investigated at 760 mm mercury absolute.

4.3 The Selection of An Equilibrium Still

The earlier types of vapour liquid equilibrium stills which have been outlined in 4.2.2. - 4.2.5, operate on a batch principle i.e. a large quantity of liquid is loaded into a still and the vapour created is brought into equilibrium with the boiling liquid. The major disadvantages are that in the time in which equilibrium is reached (this varied from 20 to 60 minutes), a reactive system could have gone to completion (before physical equilibrium had been achieved). Also for the recirculation stills the problem of removing the liquid sample without being contaminated by the returning condensate, still existed.

In the design of an equilibrium still, the main requirement is that the vapour and liquid phases should be in equilibrium and that the vapour and liquid samples which are removed, should be representative of the equilibrium conditions. For this to occur a number of factors should be taken into account (85):-

1) Concentration gradients must not exist in the boiling liquid.
2) The vapour and liquid should separate and be analysed as quickly as possible.
3) Partial condensation of the equilibrium phase should not occur.
4) Liquid entrainment by the vapour should not occur.
5) The equilibrium vapour and liquid mixture should impinge onto a thermometer which must be capable of accurate measurements of all boiling points.
6) The apparatus should be easy to operate.

Thus bearing in mind the above criteria and the comments concerning the distillation, dew & bubble point, static and circulation stills, it was appreciated that a flow still of the Cathala type would be suitable for the determination of the V.L.E. data of a reacting system although it was realised that quaternary data for a transesterification system could be obtained without the presence of a reaction by avoiding the use of a catalyst.

Hence after examining the available information on the modified Cathala stills, it was decided to use a still which was based upon the design proposed and used by Mamers (66).

4.4 Description of The Equipment

4.4.1 The General Layout

The general layout of the equipment is illustrated in Fig. 4.3 and Plates 4 and 5.

The components were stored in 5 litre overhead aspirators (1). The liquid stream flowed down through feed control valves (2) into a flowrator (3) where the flowrate was metered. The liquid from the two flowrators was mixed and fed into a liquid preheater (4) which

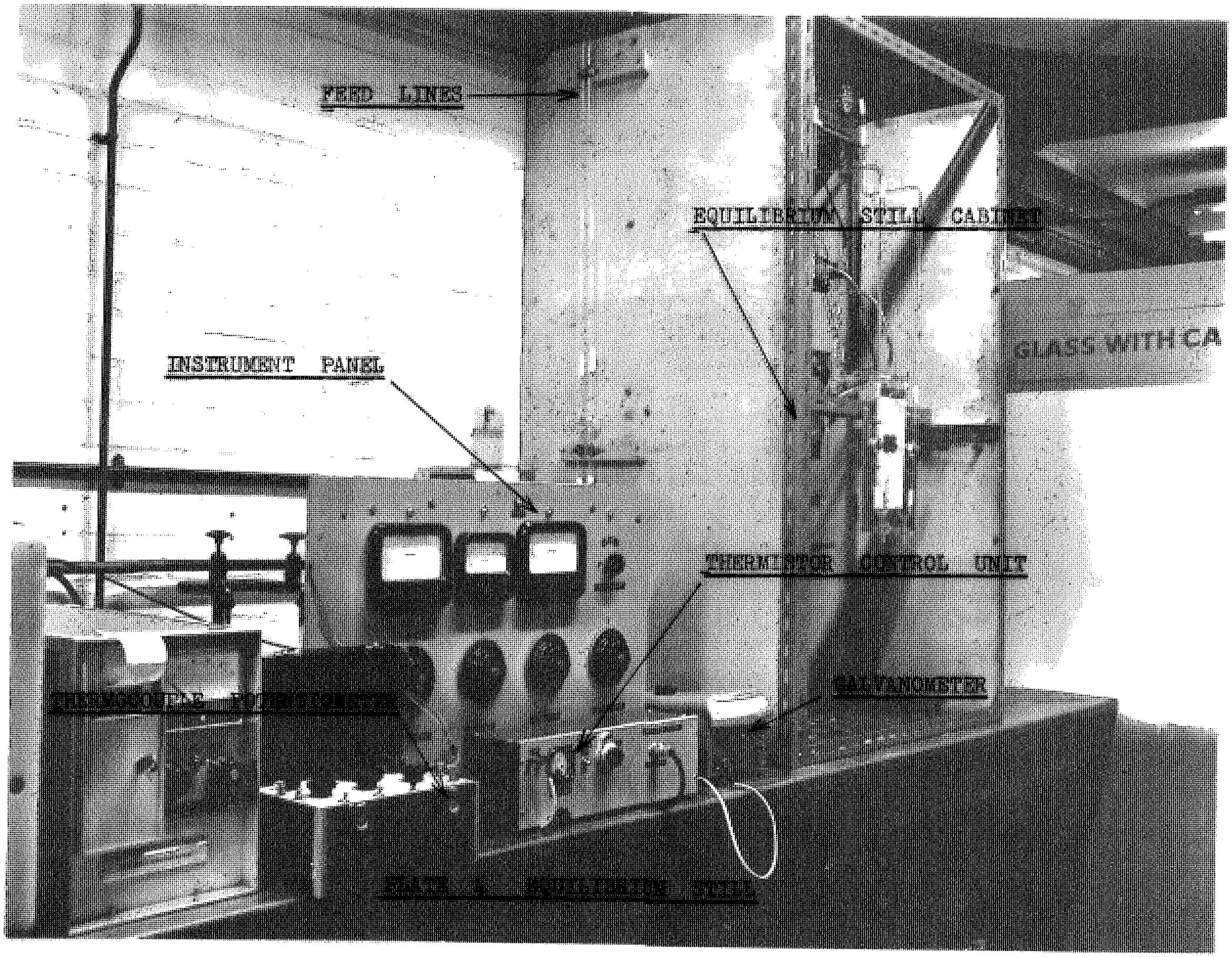


PLATE 4. EQUILIBRIUM STILL

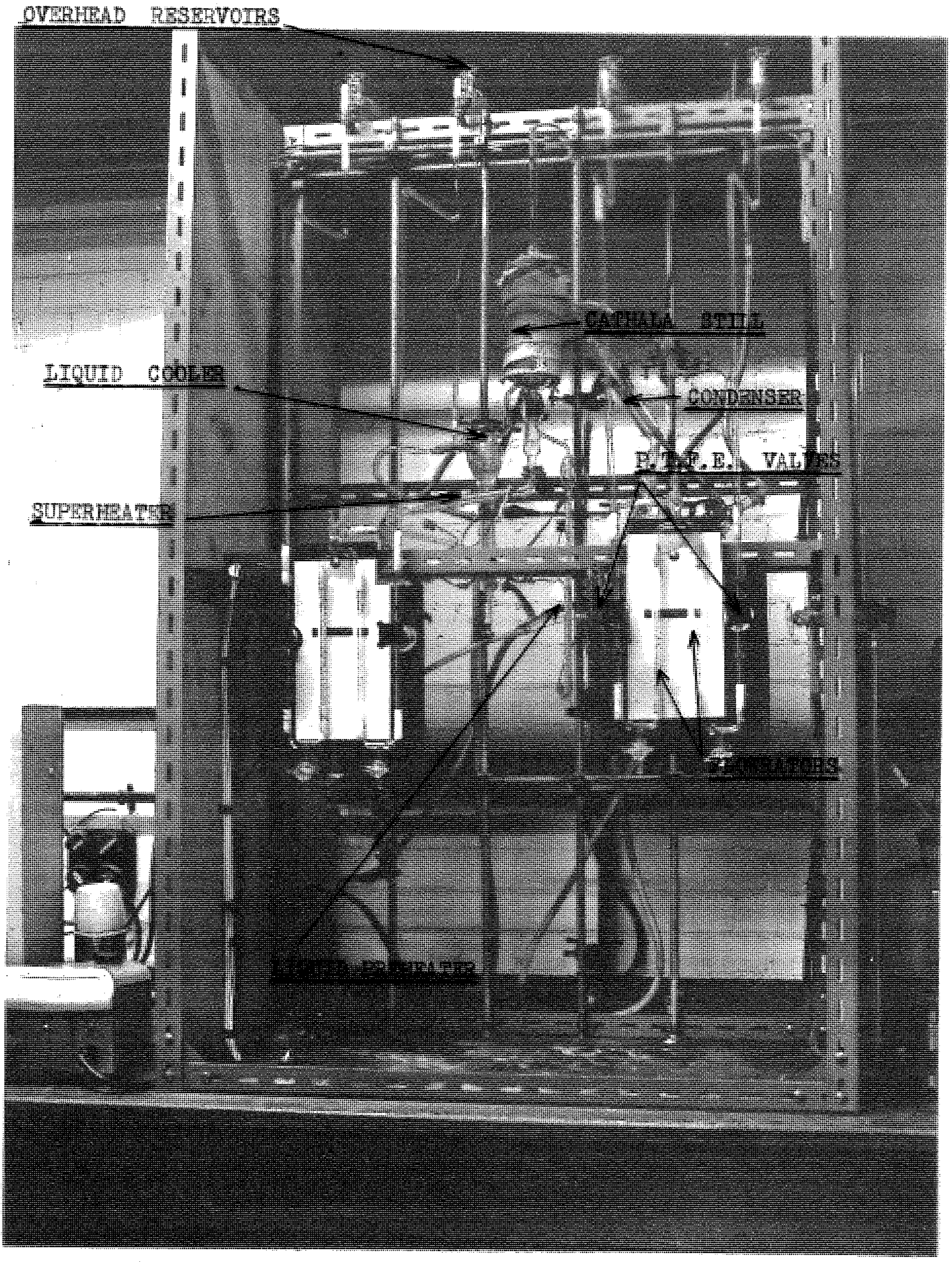


PLATE 5 EQUILIBRIUM STILL

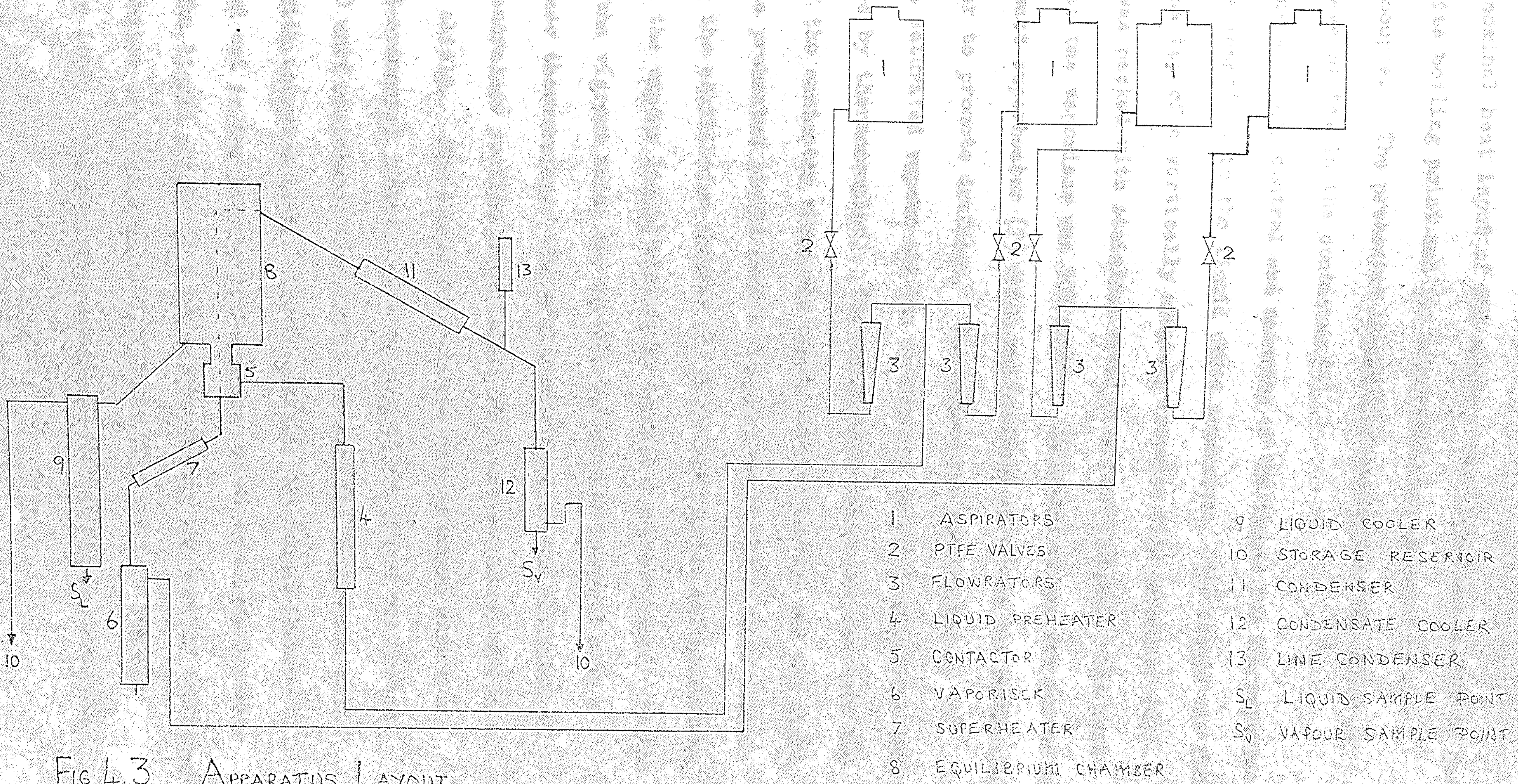


FIG 4.3 APPARATUS LAYOUT

had a nominal heat input of 250 watts. The liquid was heated to just below its boiling point and its temperature was measured by a thermocouple. The preheated liquid then passed onto the first of two sieve plates in the contactor (5).

The storage, control and metering of the liquid for the vaporiser (6) was identical to the liquid phase apparatus. The liquid was fed into the top of a vertically mounted, dropwise film vaporiser (6) which was packed with stainless steel Oldershaw packing. The heat input to the vaporiser was 500 watts. Saturated vapour was passed to a 100 watt superheater (7) which was inclined at 15° to the horizontal in order to promote drainage. The vapour was superheated by 10° and the saturated vapour and the superheated vapour temperatures were measured by thermocouples. The superheated vapour was fed into the base of the contactor where the vapour bubbled through and was mixed with the preheated liquid feed. The gaseous-liquid mixture flowed up into the equilibrium chamber (8) where equilibrium was reached by passing the vapour liquid mixture up through a vigreux tube. At the top of the vigreux tube, the equilibrium mixture impinged onto a resistance thermometer. The equilibrium mixture was separated in the de-entrainer section of the still which was contained within a thermal shield. The equilibrium chamber was contained within a silvered-evacuated jacket. The outside of the jacket was heated by a 150 watt resistance wire heater and also the jacket was well lagged with asbestos tape. Due to gravity, the liquid phase separated out in the de-entrainer and was cooled in a liquid cooler (9). The liquid sample (S_L) was withdrawn from the base of the liquid cooler whilst the liquid phase flowed continuously to a storage reservoir (10). The equilibrium vapour after separating from the liquid in the de-entrainer, flowed out of the still to a condenser (11) and a condensate cooler (12) from the base of which a liquid phase sample for the equilibrium vapour (S_V) was removed. The remainder of the condensate flowed to the storage reservoir (10). The whole of the apparatus was designed so that it could be operated under vacuum or pressure conditions and this was achieved by connecting pressure lines to the vapour condenser through a line condenser (13), to the liquid exit from the liquid cooler and to the product storage lines. The pressure system was controlled by an Edwards Pressure Controller (98) which was working against the pressure in a surge tank.

The whole of the apparatus was situated within a cabinet and the necessary electrical control equipment was mounted on a panel to the immediate left of the cabinet.

The individual units of the equipment are now described in greater detail.

4.4.2 The Feed Layout

Previous investigators who have used a Cathala still (66, 92, 93, 95, 96), have operated with vapour and liquid flow rates of 3-12 ml min^{-1}. These figures were taken as the basis for the design capacity and in particular for the selection of the flowrators' range.

It was realised that stable flow conditions would be essential in order to obtain accurate results particularly as the principle of the still is such that stable flow conditions would be needed for 15-20 minutes. It was felt that overhead aspirators would operate satisfactorily as storage reservoirs and hence four 5 litre aspirators were used, two for the vaporiser stream and two for the

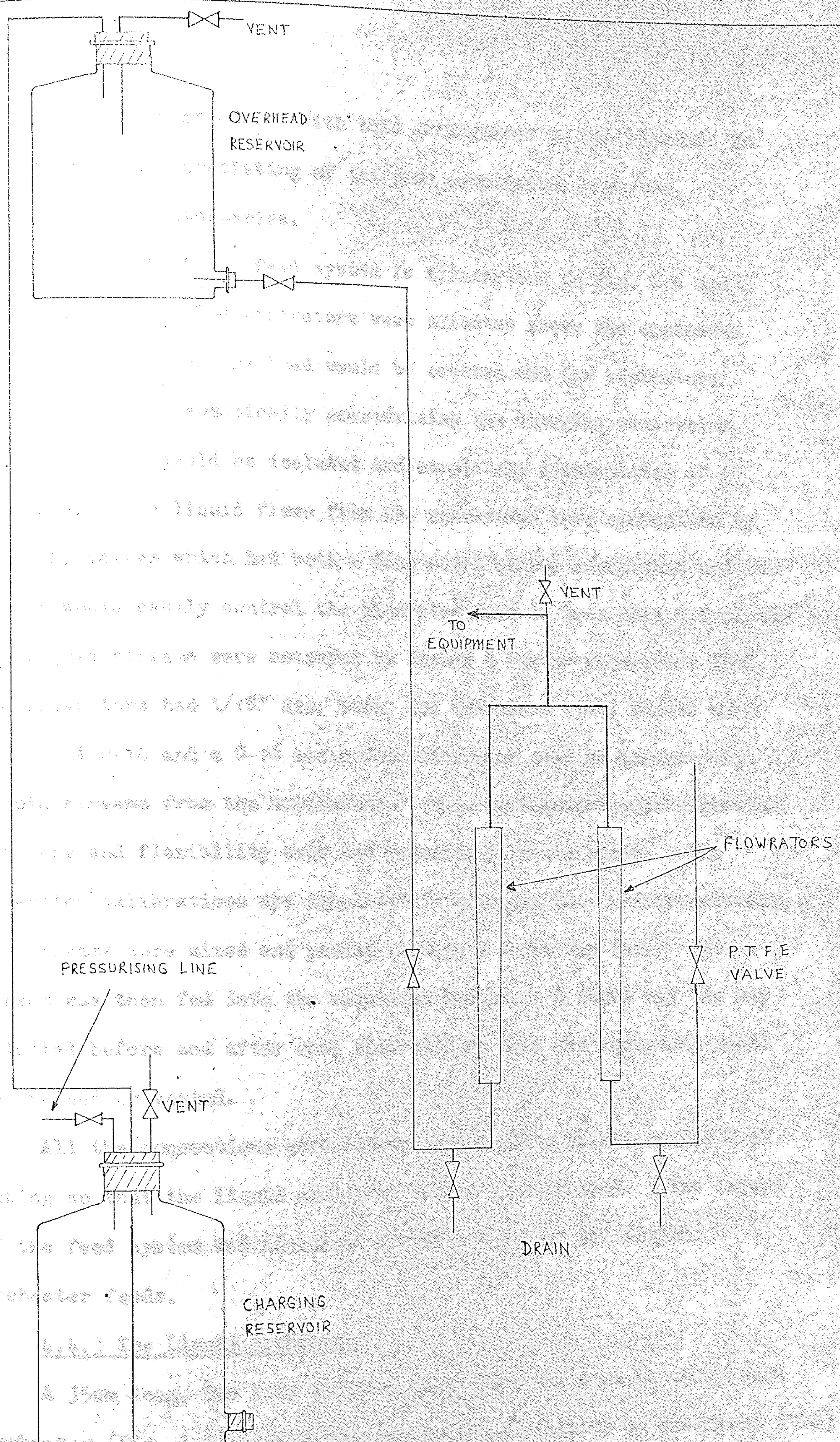


Fig 4.4 Feed System

liquid preheater stream. With this arrangement it was possible to have feed inputs consisting of the pure components, binaries, ternaries and quaternaries.

The layout of the feed system is illustrated in Fig. 4.4 and Plates 4 and 5. The aspirators were situated above the apparatus so that a good pressure head would be created and the aspirators were filled by pneumatically pressurising the charging reservoirs. Each aspirator could be isolated and completely disconnected if required. The liquid flows from the reservoirs were controlled by P.T.F.E. valves which had both a fine and a coarse adjustment and the valves would easily control the flowrates down to less than 0.5 ml min^{-1}. The liquid streams were measured by Fisher & Porter flowrators (99). The flowrators had 1/16" dia. bore, and stainless steel floats were used. A 0-10 and a 0-16 scale flowrator were used to measure the liquid streams from the aspirators. This arrangement gave a greater accuracy and flexibility over the required flowrate range. The flowrator calibrations are tabulated in Appendix C1. After metering, the streams were mixed and passed through a three way tap. The stream was then fed into the requisite heater. A three way tap was situated before and after each flowrator so that the equipment could be drained or vented.

All the connections were either ground glass joints or P.T.F.E. tubing so that the liquid would not become contaminated. The layout of the feed system was identical for the vaporiser and liquid preheater feeds.

4.4.3 The Liquid Preheater

A 35cm long, 8mm bore vertical glass tube was used as the liquid preheater (Fig. 4.5). The tube was externally heated by Brightray (100)

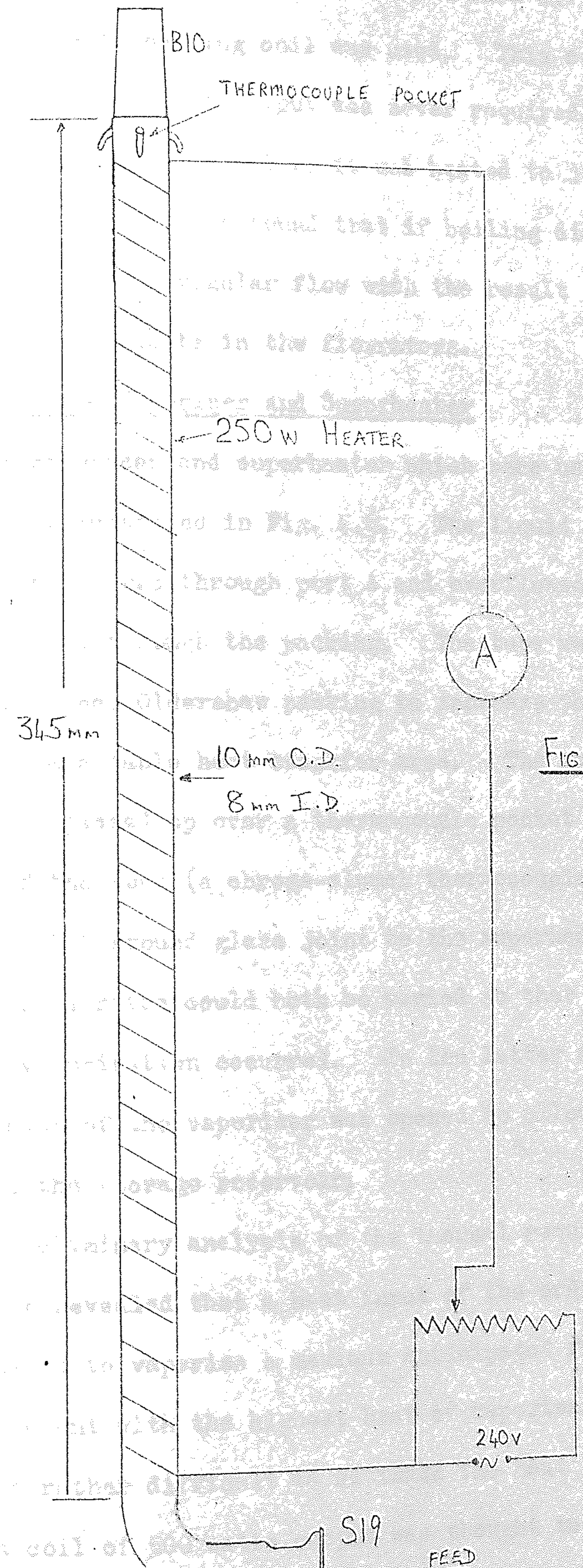


Fig 4.5 Liquid Preheater

NOT TO SCALE

resistance wire. Due to difficulty in estimating the inside wall temperature, heat transfer calculations were difficult to compute and hence a 250 watt heating coil was used. This coil was found to be adequate and full heat output was never required. When the liquid flowed through the preheater, it was heated to just below its boiling point as it was found that if boiling did commence, the agitation caused irregular flow with the result that it was difficult to control the floats in the flowrators.

4.4.4 The Vaporiser and Superheater

The vaporiser and superheater which were used in the equilibrium still are illustrated in Fig. 4.6. The liquid feed from the flowrators entered through port A and overflowed the weir to run down the walls and through the packing. The tube was filled with stainless steel Oldershaw packing to increase the liquid path and hence the available heat transfer area. The saturated vapour which was formed passed up over a thermocouple pocket which protruded to the centre of the tube (a chrome-alumel thermocouple was used) and out through a B19 ground glass joint to the superheater. The heat input and the feed rates could both be varied so that total vaporisation or partial vaporisation occurred. In the latter case, the drain tap at the base of the vaporiser was opened to allow the excess liquid to drain to the storage reservoir.

A preliminary analysis of the thermal requirements of the vaporiser revealed that a heat input of the order of 200 watts would be required to vaporise a maximum anticipated flowrate of 10g min^{-1} of the component with the highest heat of vaporisation. However, as it would be rather difficult to estimate the heat losses from the vaporiser an open coil of 500 watts output was thought to be sufficient. It was

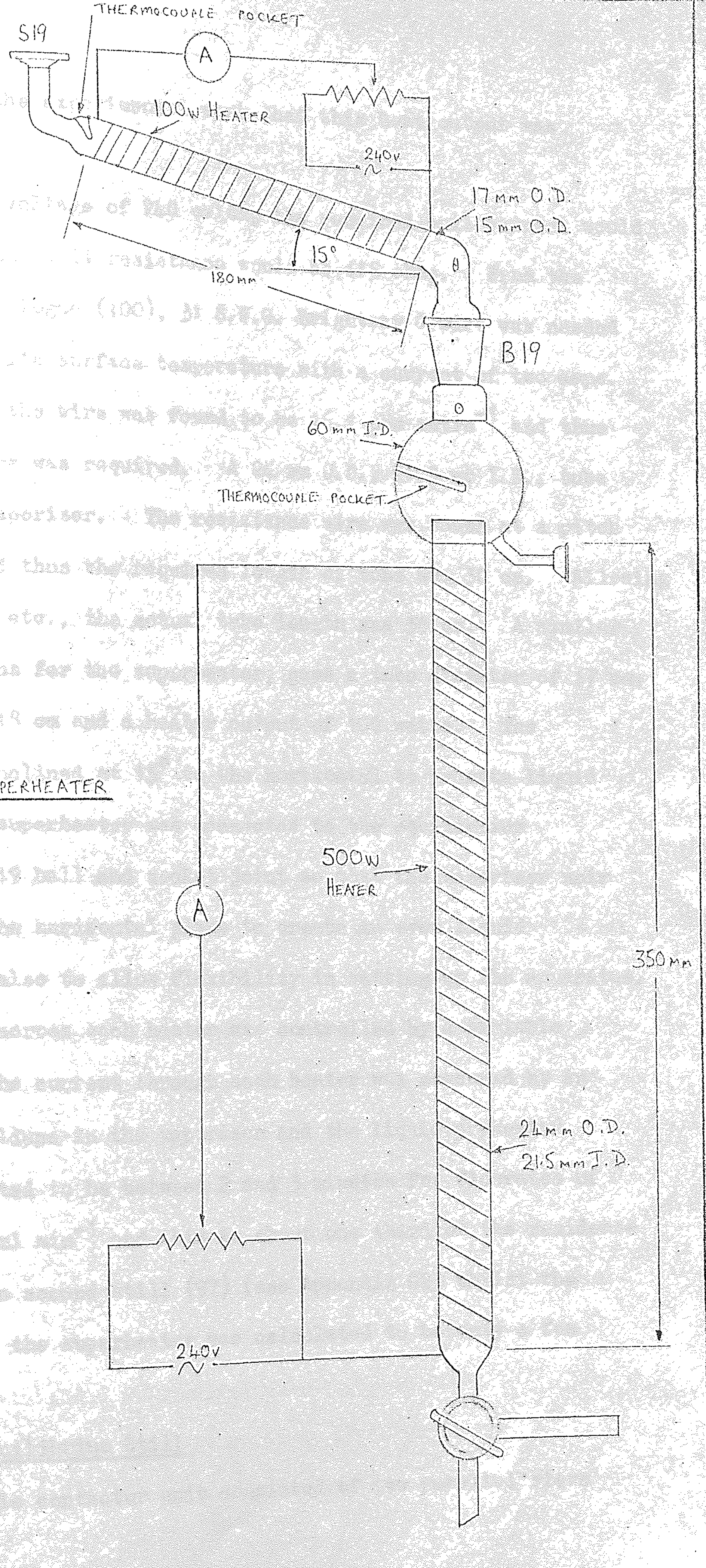


Fig 4.6

Vaporiser & Superheater

Not To Scale

later found from the experimental work that this heat output was adequate.

With a mains voltage of 240 volts, the required coil current would be 2.08 amps and the coil resistance would be 115 ohms. From the manufacturer's catalogue (100), 31 S.W.G. Brightray C wire was needed to give the requisite surface temperature with a current of two amps. The resistance of the wire was found to be 16.1 ohm metre^{-1} and thus 7.14 metres of wire was required. A 24 mm O.D., 21.5 mm I.D., tube was used as the vaporiser. The resistance wire was wound at a pitch of 3 turn cm^{-1} and thus the required length of tube was 30 cm. Allowing for the coil ends etc., the actual tube length was 35 cm. A similar set of calculations for the superheater, gave a tube diameter of 17 mm, a tube length of 18 cm and a heater output of 100 watts. The superheater was inclined at 15° to the horizontal to promote liquid drainage and the superheater was connected to the equilibrium contactor by an S19 ball and socket joint so that the vaporiser weir could be set in the horizontal plane to create an even liquid distribution and also to allow flexibility in setting up the apparatus.

The voltage across each heater was controlled by a variable transformer and the current through each heater was measured by an ammeter. The holdups in the vaporiser and the liquid preheater have been calculated to be between 2 and 3 minutes for flowrates of between 8 and 12 ml min^{-1} and this is about one third of the residence time for Cathala's second still (97) (see Appendix C2) whilst the residence time in the superheater was calculated to be only a few seconds.

4.4.5 The Equilibrium Still

The detachable contactor unit consisted of two parallel sieve plates of 16 mm and 24 mm diameter, each plate having 52 0.5 mm diameter holes. The superheated vapour entered through the base of the contactor and bubbled through the preheated liquid which entered between the two sieve plates (see Fig. 4.7). The liquid vapour mixture flowed up through the vigreux column before the mixture spurted out through the four discharge port holes onto the resistance thermometer well. It was hoped that the co-current passage of the vapour and liquid together with the mixing effect caused by the vigreux points would eliminate any concentration gradients and that the effect of the superheat in the vapour would promote the achievement of equilibrium.

The diameter of the thermal shield was restricted to 26 mm by the B34 ground glass socket through which it had to pass. The resistance thermometer pocket of the shield just fitted into the discharge head of the vigreux column and there was about 10 mm clearance between the end of the thermal shield and the base of the de-entrainer.

It has been calculated that the largest droplet diameter which could be entrained under the extremest operating conditions would be 0.076 mm (Appendix C3) although it was concluded that due to the turbulence and the change of direction of the vapour stream, that the majority of the entrainment would be eliminated due to coalescence on thermal shield and de-entrainer walls.

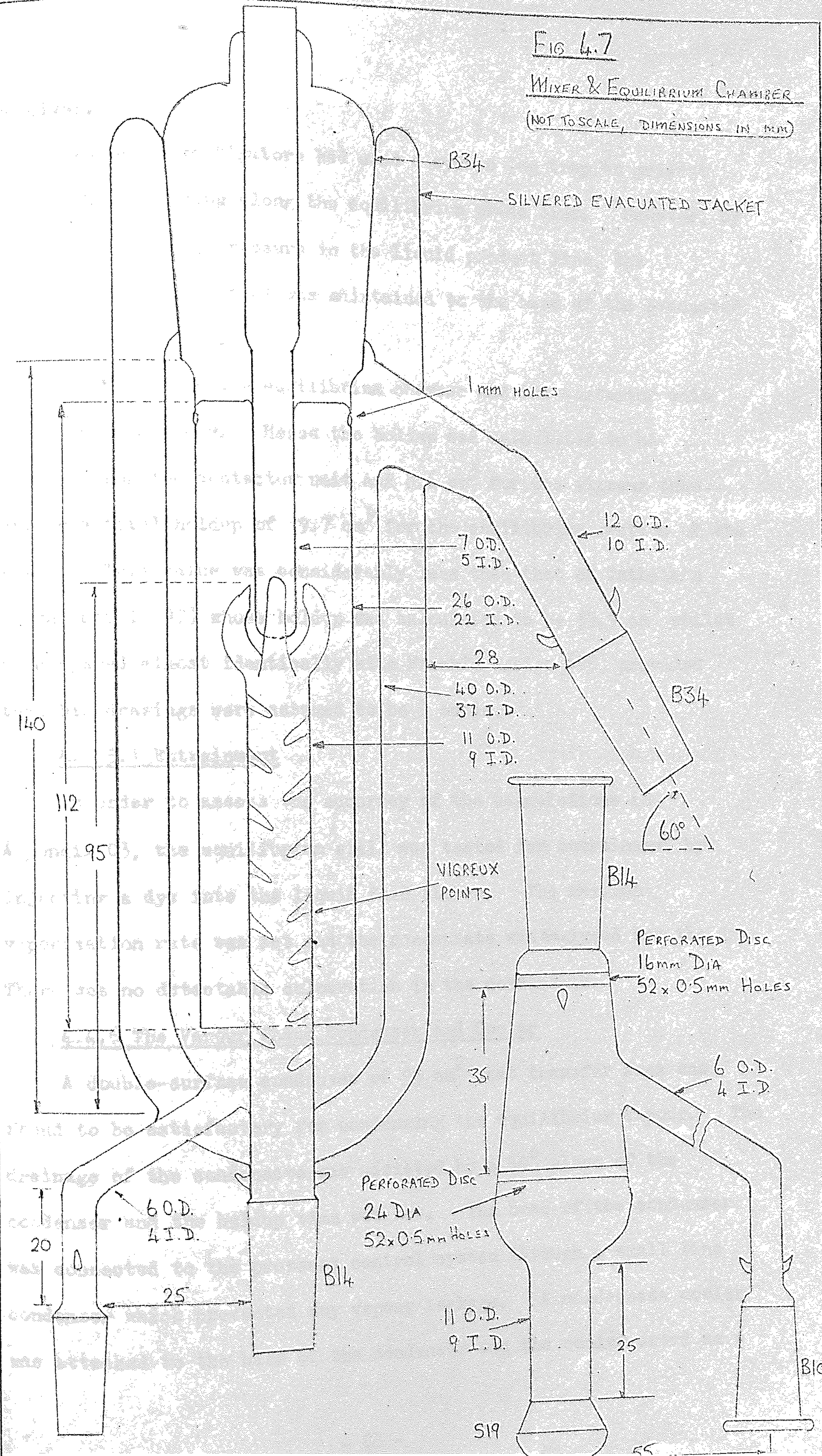
To prevent partial condensation of the equilibrium vapour on the surfaces of the de-entrainer, the whole of the equilibrium chamber was enclosed in a silvered evacuated jacket. A 150 watt resistance wire heater was wound round the external surface of the evacuating jacket and the still was well lagged with asbestos tape.

The vapour off take line was inclined at 60° with the horizontal to promote drainage of any condensation into the product

Fig 4.7

Mixer & Equilibrium Chamber

(Not to scale, dimensions in mm)



receiver.

Previous investigators had used a syphon leg trap to prevent vapour from escaping along the equilibrium phase line. However, by adjusting the back pressure in the liquid product line, the equilibrium liquid level was maintained to the base of the evacuated jacket of the still.

The holdup in the equilibrium chamber and the contactor unit should be a minimum. Hence the holdup was calculated to be 11.3 cm^3 for the contactor unit and 8.6 cm^3 for the vigreux tube giving a total holdup of 19.7 cm^3 for the equilibrium section of the still. This value was considerably less than that of Cathala's second still (97) whose holdup was calculated to be 35.5 cm^3 whilst it compared almost identically with Marek's design (95) provided that his drawings were assumed to be $\frac{1}{4}$ scale.

4.4.5.1 Entrainment

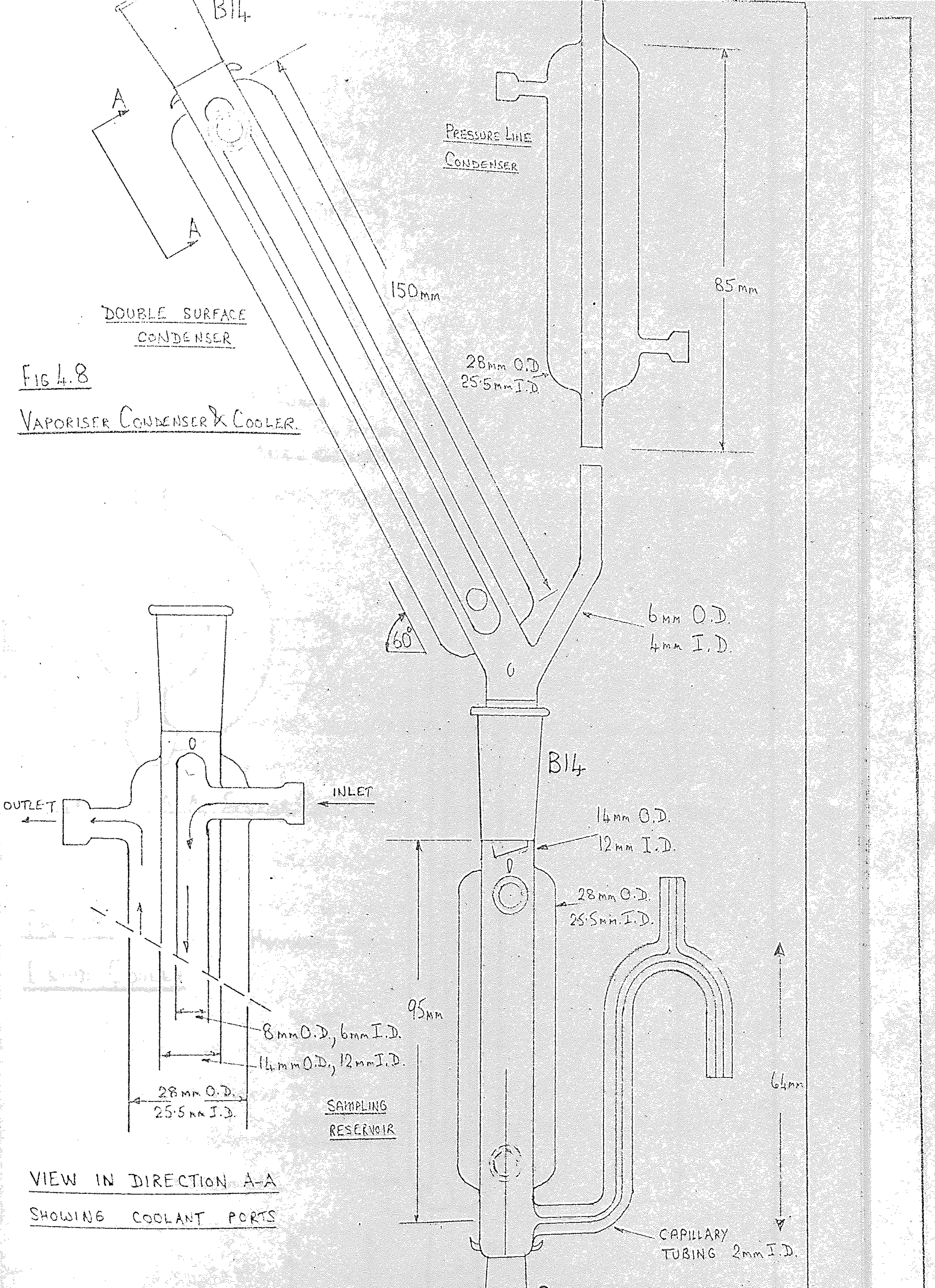
In order to assess the accuracy of the calculations in Appendix C3, the equilibrium still was tested for entrainment by injecting a dye into the liquid feed stream. The maximum vaporisation rate was set and the condensate was analysed for the dye. There was no detectable colouration in the condensate.

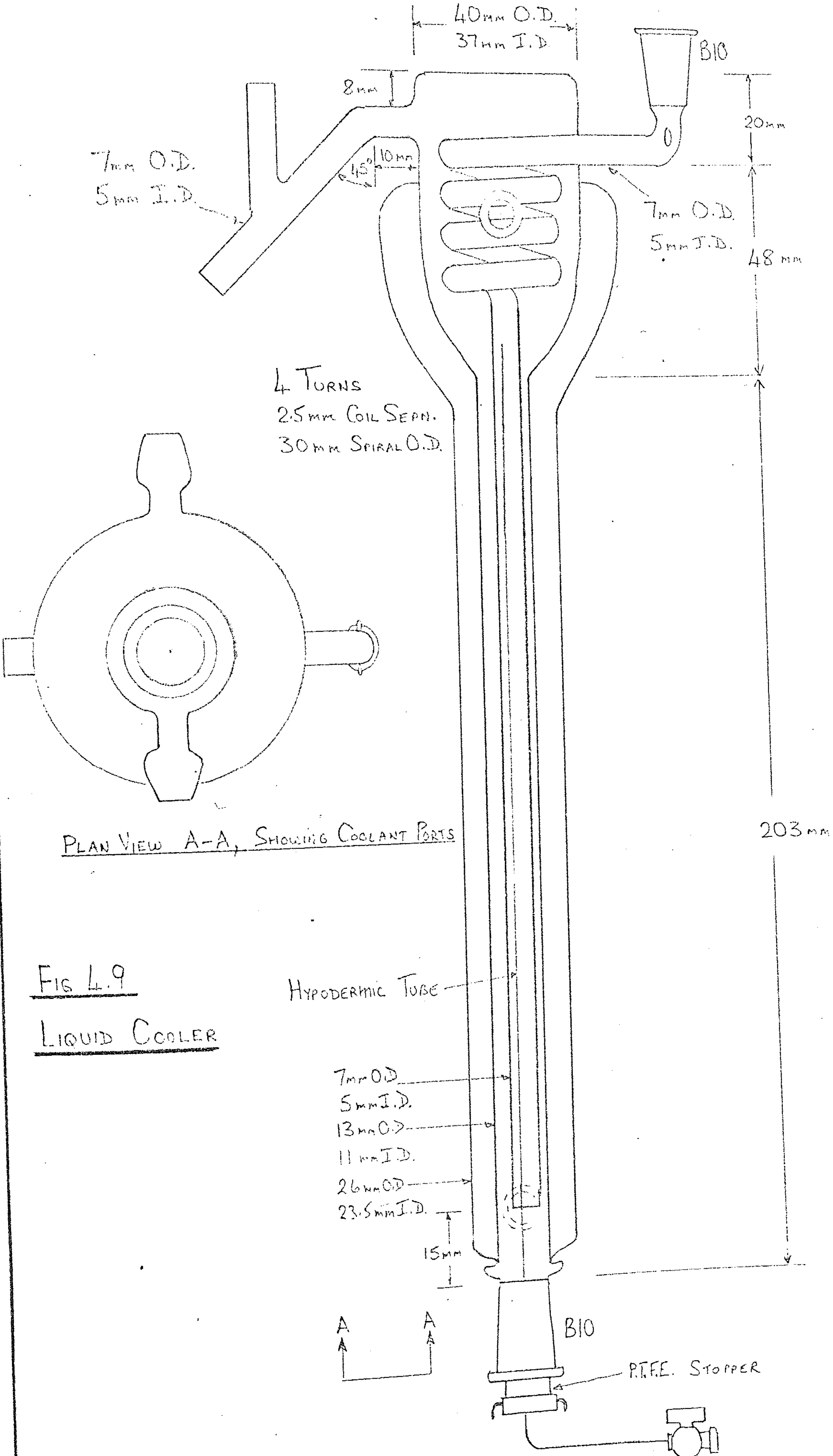
4.4.6 The Vapour Phase Condenser and Cooler

A double-surface condenser of 95 cm^2 heat transfer area was found to be satisfactory for condensing the equilibrium vapour. The drainage of the condensate was assisted by a 60° slope of the condenser and the holdup time was low. The base of the condenser was connected to the pressure control system through a small line condenser which prevented any vapour leakage. A condensate cooler was attached to the base of the condenser and the cooler acted as a

Fig 4.8

Vaporiser Condenser & Cooler.





Plan View A-A, Showing Coolant Ports

Fig 4.9

Liquid Cooler

Not To Scale

product sampling reservoir (see Fig. 4.8). The holdup of the cooler was approximately 8 cm^3. The condensate flowed continually to the main storage reservoir via a capillary outlet weir which controlled the height of the liquid in the cooler. The condensate in the cooler was cooled by an external water jacket and condensate samples were taken with a 5 ml hypodermic syringe which fitted into a hypodermic needle which was located in the P.T.F.E. plug.

4.4.7 The Liquid Cooler and Product Storage Reservoir

The liquid cooler which was used is shown in Fig. 4.9. The cooler had a heat transfer area of approximately 30 cm^2 and this was found to be adequate to cope with flowrates which were less than the expected maximum liquid flowrate. The liquid cooler was connected to the liquid outlet from the equilibrium still by a B10 ground glass joint. From this connection, the liquid flowed in and through a spiral coil which was then connected to a 44 cm long downcomer tube. From the exit of the downcomer tube at the base of the cooler, the liquid flowed up the outside surfaces of the downcomer tube and the spiral coil. The liquid flowed out of the cooler to the product storage reservoir through outlet port which was at a higher level than the inlet port. Cooling water circulated through an external jacket. The liquid sample was again removed through a hypodermic needle probe. The length of the probe was such that the required sample was collected from within the volume of the downcomer so that any back mixing at the base of the downcomer tube was avoided. The holdup in the downcomer tube was calculated to be 8.7 cm^3 and at the expected liquid flowrates, this would correspond to a holdup of approximately 50 seconds but as the sample was withdrawn from only half of the tube, the presampling holdup was approximately half that time.

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

4.4.8 The Pressure Control Circuit

The pressure control circuit is illustrated in Fig. 4.10. A water ejector which was capable of pulling a vacuum of about 20 cm of mercury was coupled to a 15 litre surge tank and the tank pressure was regulated by an Edwards Pressure Controller (98). Also an air bleed system could be connected to the surge tank through the pressure controller.

Daily barometric readings over a period of about one month prior to the commencement of the experimental work had indicated that the pressure was generally below 760 mm of mercury and that on two occasions only did the pressure rise above 760 mm of mercury. Thus so that the experimental work could proceed under an absolute pressure of 760 mm of mercury, both vacuum and pressure bleeds were used so that the correction applied by the pressure controller would enable an absolute pressure of 760 mm mercury to exist in the equilibrium still.

4.4.9 Temperature Measurement

The equilibrium boiling point temperatures were measured by the change in resistance of a silicon transistor element which had a base resistance of 4.95 k ohm at 100°C and a negative characteristic of approximately 100 ohm deg C^{-1}. The thermistor and a 20.4 k ohm resistor were constructed as one arm of a Wheatstone Bridge circuit, whilst the corresponding arm of the bridge was a variable 5 k ohm resistor in series with a 2 k ohm resistor. The remaining two arms of

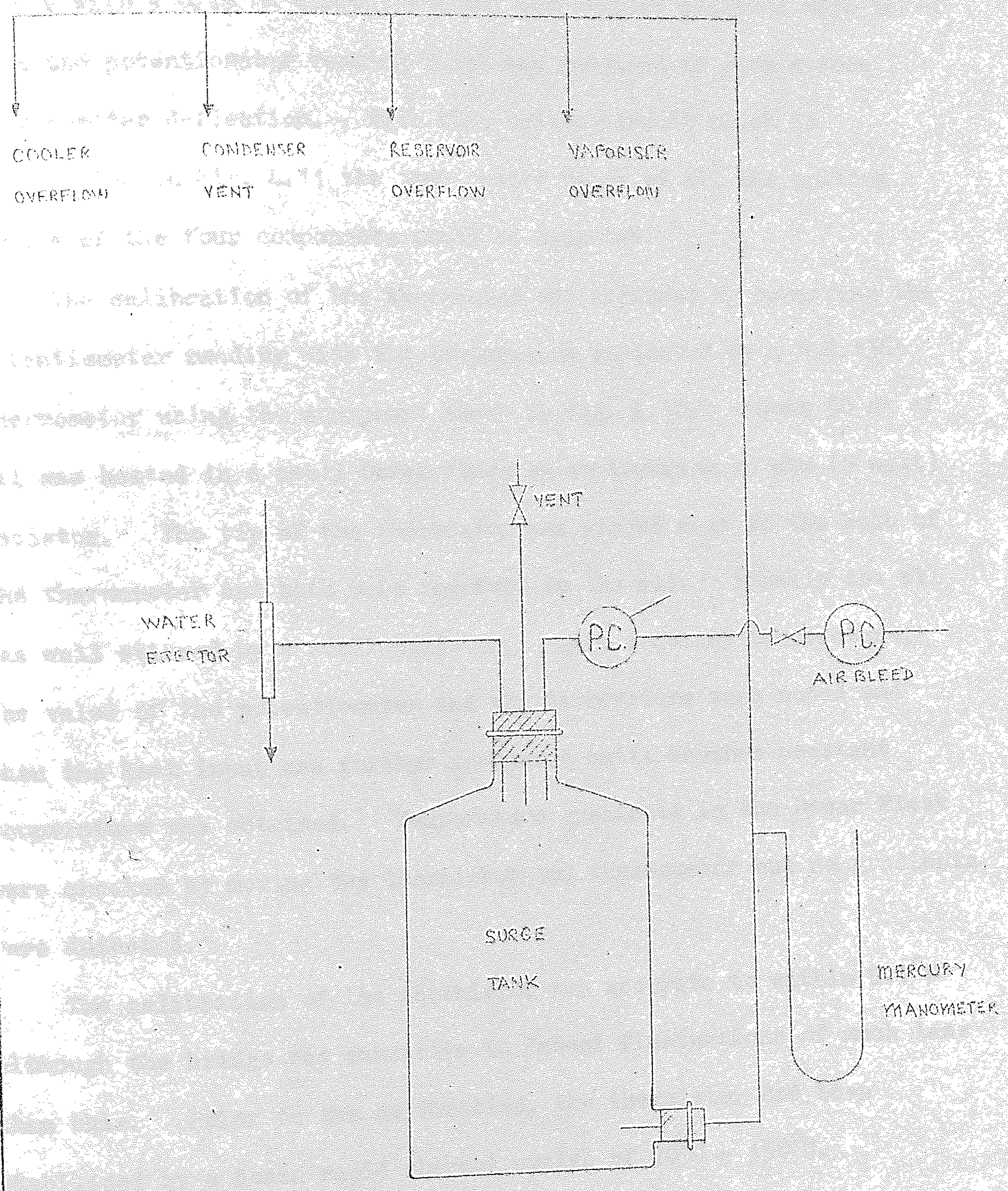


Fig 4.10 Pressure Control Circuit

the bridge were made with 1.75 k ohm resistors. The bridge operated at 9 V with a 0.25 mA current and the temperature readings were taken from the potentiometer reading which was required to give a zero galvanometer deflection. With this bridge circuit which is illustrated in Fig. 4.11 the temperature range of all the boiling points of the four components could be measured.

The calibration of the thermistor was achieved by comparing the potentiometer reading with the temperature indicated by a B.S.1365 thermometer using the equipment shown in Fig. 4.12. About 50 ml of oil was heated in a small Dewar Flask by an immersed 25 ohm (5 watt) resistor. The tip of the thermistor was placed next to the bulb of the thermometer and both were immersed in the oil. Finally the oil was well stirred by a small agitator. At a constant temperature, the value of the potentiometer and the temperature were noted and then the heat input was further increased until another constant temperature was obtained. Temperature gradients in the Dewar Flask were checked by moving the thermistor and thermometer but no gradients were detected.

The calibration of the thermistor was accurate to within 0.1°C although the bridge was sensitive to detect fluctuations of much less than this. Prior to the calibration, the thermistor had been stabilised by a dozen rapid thermal cycles of 20°C - 150°C.

Three chrome-alumel thermocouples were used to monitor the temperatures in the vaporiser, the superheater and the liquid preheater. A common cold junction was immersed crushed ice contained in a Dewar Flask and the outputs were fed via a multipoint switch to a "Doran" thermocouple potentiometer. The calibration technique was similar to that used for the calibration of the thermistor.

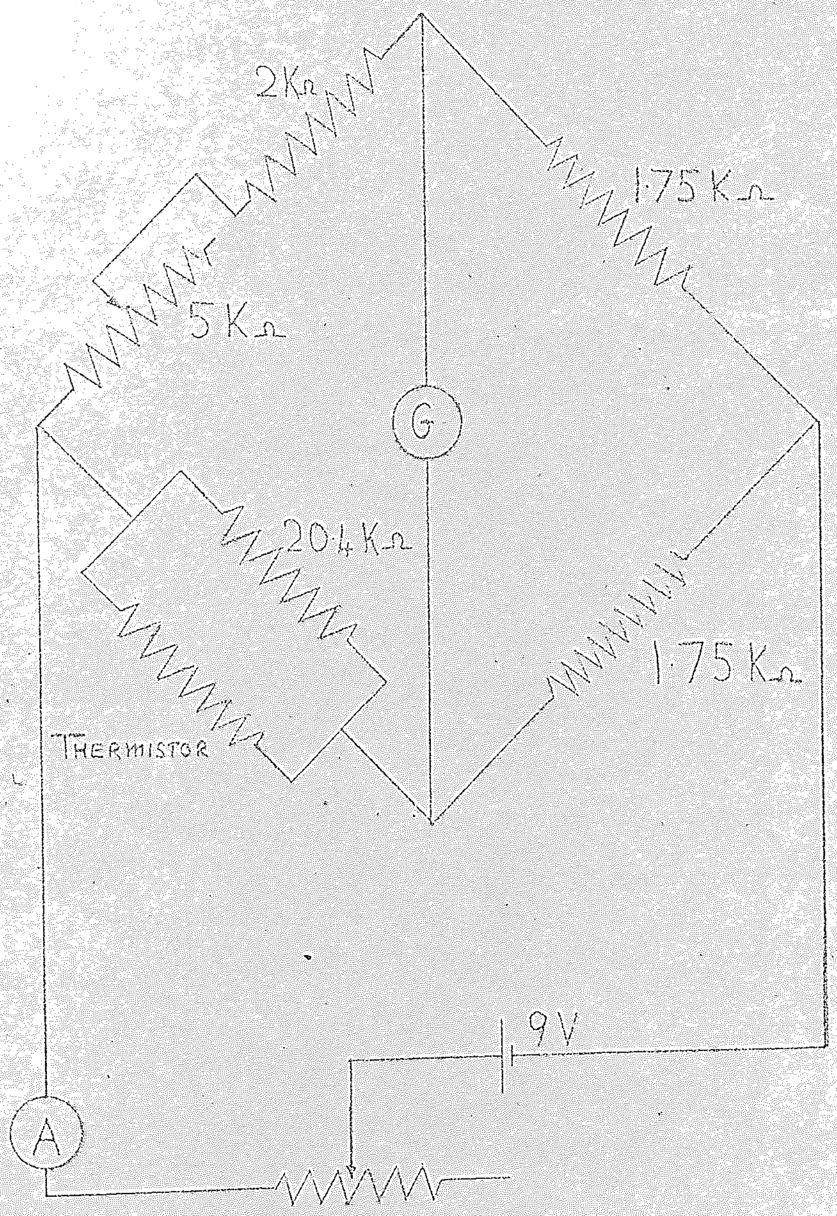


Fig 4.11 THERMISTOR BRIDGE CIRCUIT

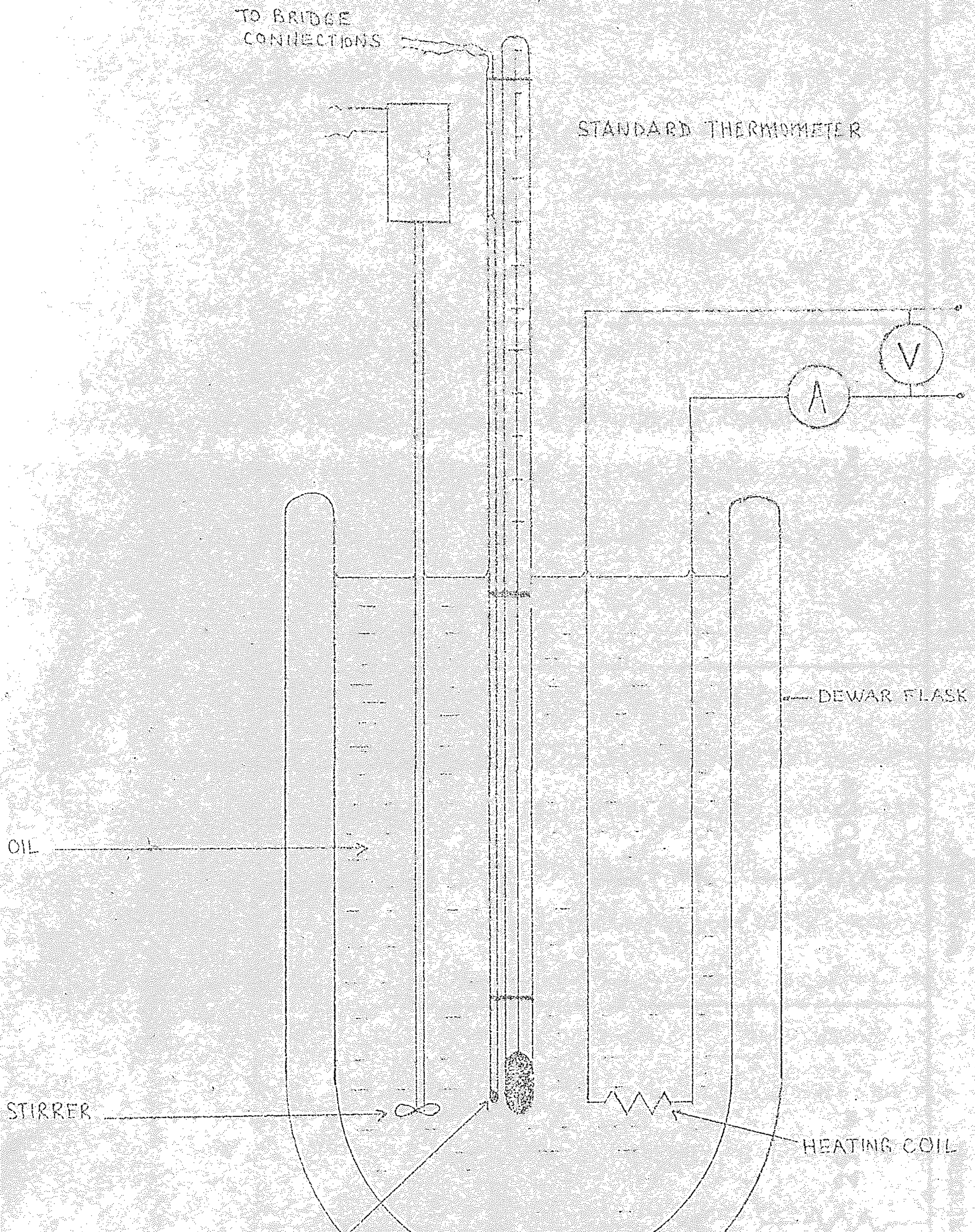
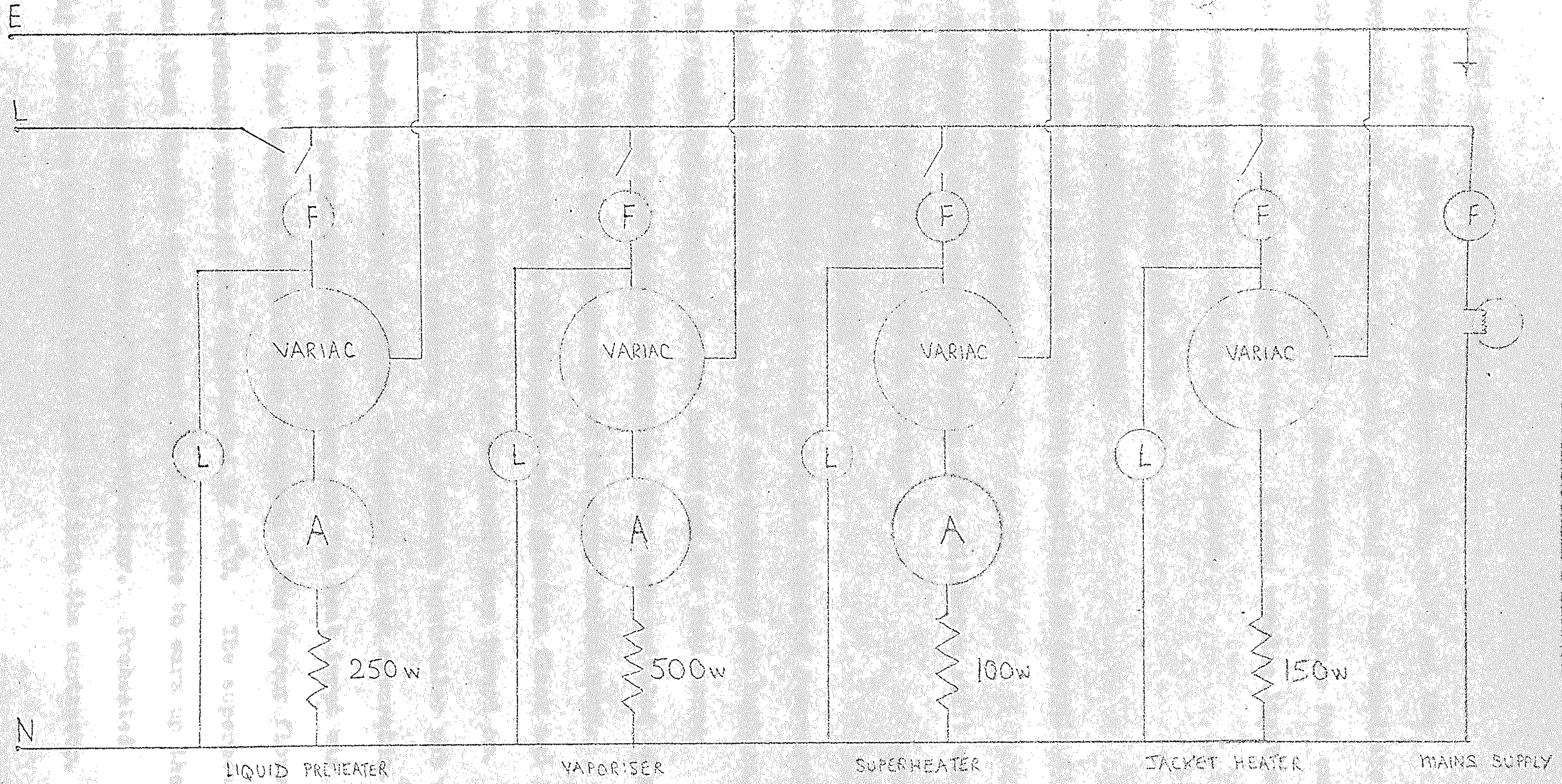


Fig 4.12 Thermistor Calibration Apparatus

Fig 4.13 Electrical Circuits



4.4.10 The Electrical Panel Circuits

The electrical wiring circuit is shown in Fig. 4.13 and the control apparatus was contained in a panel situated to the immediate left of the equilibrium still cabinet. The control sequence for each heater was switch-fuse-variac-ammeter-load. A neon warning light was connected across the input terminals of the variacs.

4.5 The Measurement of the V.L.E. Data

4.5.1 The Materials Specification

The materials used are those which are specified in Appendix A1.

4.5.2 The Method of Analysis

All the samples which were taken from the equilibrium still were analysed by the technique outlined in Section 2.

4.5.3 The Method of Operation

The overhead reservoirs were loaded with the required components and the liquid feed lines were cleared of any entrapped air bubbles. As both the equilibrium chamber jacket heater and the resistance thermometer required some time to stabilise, they were switched on at least one hour before the commencement of the experimental work. Crushed ice was placed in the thermocouple cold junction flask and the cooling water and water ejector pump (if required) were turned on. After reading the barometric pressure, the pressure controller was set to give an absolute pressure of 760 mm of mercury in the apparatus.

The feed was passed into the vaporiser and the heat input was selected so that complete vaporisation occurred. The vapour flowed to the superheater where it was superheated by 10°C. The superheated vapour was blown through the equipment for 5 minutes to warm up the vigreux column and the surfaces of the de-entrainer. Preheated liquid at just below its boiling point was fed into the contactor.

The combined through put rate for each stream was between 3 and 12 ml min^{-1}. - a range which was utilised by both Marek (95, 96) and Cathala (97).

Equilibrium was judged to have been reached when the vapour-liquid temperature recorded by the resistance thermometer remained steady within ± 0.05°C. After 10 minutes of steady operation, the requisite samples were taken. The condensate sample line was drained by removing about 1 ml of liquid before a 3 ml sample was taken with the hypodermic syringe. The liquid cooler sample line was also flushed out in a similar manner before the 3 ml sample was taken with the hypodermic syringe.

After the samples had been taken the feed rates of the components in the streams were altered in such a manner so that the feed stream flowrates remained constant and thus the adjustments to the heat inputs were kept to a minimum. Then the above procedure was repeated until the new equilibrium condition was established.

The shut down order for the equipment was : resistance thermometer, thermocouples, all the heaters, the feed streams, the water ejector and the water supply to the condensers and coolers. The condensate cooler, the liquid cooler and the vaporiser were drained of any excess liquid.

4.5.4 The Experimental Programme

For the majority of the binary concentrations, the feed streams were made up from separately metered pure components which were mixed at the junction of the flowrator outlets. This had two advantages. Firstly, constant flowrates could easily be maintained throughout a series of experiments by just increasing one stream flowrate and decreasing the second stream flowrate by a corresponding amount.

Thus the required changes to the heaters were minimised and hence the time taken for a new equilibrium condition to be achieved would be small. Secondly, small composition increments could readily be achieved because a relatively large change in the flowrates of one component did not greatly affect its final liquid phase composition.

For the values where the component composition was low, feed streams of one pure component and one diluted component were used.

The ternary and quaternary mixtures were investigated by loading each of the pure components into the overhead reservoirs and by adjusting the relative flowrates, the required composition range was obtained. As it was anticipated that the ternary and quaternary mixtures would be predicted from a mathematical model requiring binary data only, the experimental ternary and quaternary data was measured for the purpose of assessing the accuracy of the prediction model.

In all about 24 measurements were carried out for each binary, 40 for each ternary and 101 for the quaternary system.

4.6 Experimental Results

4.6.1. Experimental Equilibrium Compositions

Table 4.1 Ethyl Acetate - Ethyl Alcohol, P = 1 atm.

	Mole per cent - ETAC		K_{ETAC}	K_{ETOH}	T °C
	x	y			
1	0.00	0.00	-	1.00	78.7
2	2.23	5.28	2.36	0.97	78.2
3	4.84	9.47	1.95	0.95	77.2
4	5.65	11.41	2.02	0.94	77.0
5	9.89	19.92	2.01	0.89	76.1
6	14.98	26.04	1.73	0.87	75.1
7	21.47	32.54	1.51	0.86	74.0
8	25.00	35.86	1.44	0.86	73.3
9	36.13	44.42	1.23	0.87	72.7
10	43.12	47.70	1.11	0.92	72.5
11	49.90	52.97	1.06	0.94	72.3
12	56.43	57.61	1.02	0.97	72.0
13	56.53	57.67	1.02	0.97	72.0
14	59.32	58.25	0.98	1.02	72.0
15	61.96	59.80	0.97	1.06	72.3
16	74.69	69.01	0.92	1.22	72.5
17	80.01	73.83	0.92	1.31	73.3
18	83.82	77.45	0.92	1.39	73.5
19	91.70	87.05	0.95	1.56	74.8
20	100.00	100.00	1.00	-	77.5

Table 4.2 Ethyl Acetate - Butyl Alcohol, P = 1 atm.

	Mole per cent - ETAC		K_{ETAC}	K_{BUOH}	T °C
	x	y			
1	0.00	0.00	-	1.00	117.3
2	3.78	14.10	3.73	0.89	114.5
3	7.60	25.30	3.33	0.81	111.2
4	12.41	38.62	3.11	0.70	107.2
5	13.69	41.60	3.03	0.68	106.1
6	16.40	47.18	2.88	0.63	104.1
7	19.78	52.87	2.67	0.59	102.0
8	21.14	57.08	2.70	0.54	100.7
9	25.18	62.69	2.49	0.50	97.7
10	27.43	65.87	2.40	0.47	97.3
11	29.83	68.40	2.29	0.45	96.4
12	35.20	71.96	2.04	0.43	94.2
13	39.50	73.30	1.85	0.44	93.3
14	39.57	76.08	1.92	0.40	92.2
15	42.84	78.47	1.83	0.38	91.5
16	52.45	83.84	1.60	0.34	88.3
17	58.87	84.78	1.44	0.37	86.8
18	61.22	86.18	1.41	0.36	86.5
19	66.89	88.32	1.32	0.35	85.0
20	69.21	90.06	1.30	0.32	83.7
21	72.98	91.75	1.24	0.32	82.5
22	79.41	93.56	1.18	0.31	81.3
23	88.63	97.03	1.09	0.26	79.3
24	92.89	98.13	1.06	0.26	28.1
25	100.00	100.00	1.00	-	77.4

Table 4.3 Ethyl Acetate - Butyl Acetate, P = 1 atm.

	Mole per cent - ETAC		K_{ETAC}	K_{BUAC}	T
	x	y			°C
1	0.00	0.00	-	1.00	125.5
2	3.17	7.24	2.28	0.96	125.4
3	5.14	13.10	2.55	0.92	121.9
4	8.18	18.98	2.32	0.88	120.1
5	12.85	28.65	2.23	0.82	117.3
6	14.57	34.04	2.33	0.77	115.5
7	16.81	38.61	2.29	0.74	113.9
8	18.69	40.62	2.17	0.73	112.8
9	25.08	51.25	1.95	0.68	109.8
10	25.38	55.57	2.19	0.60	106.8
11	28.88	58.46	2.01	0.58	105.3
12	29.46	60.23	2.04	0.56	103.3
13	33.78	64.36	1.91	0.54	102.5
14	42.41	70.10	1.65	0.52	99.8
15	42.47	72.91	1.68	0.48	98.0
16	43.53	75.28	1.73	0.44	97.0
17	44.03	75.86	1.72	0.41	96.1
18	47.99	79.78	1.66	0.39	94.3
19	51.80	82.14	1.58	0.37	92.7
20	54.78	83.37	1.52	0.37	91.3
21	62.64	88.12	1.41	0.32	88.2
22	67.94	90.55	1.33	0.30	86.2
23	72.97	92.66	1.27	0.27	84.8
24	78.23	94.20	1.20	0.27	82.8
25	83.74	96.05	1.15	0.24	81.0
26	84.54	97.04	1.11	0.24	79.9
27	91.02	98.15	1.08	0.21	78.9
28	94.82	98.96	1.04	0.20	77.8
29	97.30	100.00	1.03	-	77.2
30	98.24	100.00	1.02	-	76.9
31	100.00	100.00	1.00	-	76.5

Table 4.4 Ethyl Alcohol - Butyl Alcohol, P = 1 atm.

	Mole per cent - ETOH		K_{ETOH}	K_{BUOH}	T
	x	y			°C
1	0.00	0.00	-	1.00	117.5
2	4.85	17.20	3.55	0.87	112.8
3	6.59	24.01	3.64	0.81	111.8
4	11.22	33.52	2.99	0.75	108.5
5	18.27	44.95	2.46	0.67	104.8
6	20.60	49.75	2.42	0.63	103.4
7	25.09	53.22	2.12	0.62	102.3
8	27.53	59.23	2.15	0.56	100.1
9	34.29	67.10	1.96	0.50	96.8
10	39.52	68.57	1.74	0.52	94.5
11	46.36	76.48	1.65	0.51	93.2
12	49.28	80.83	1.64	0.38	90.8
13	58.36	83.44	1.43	0.40	89.6
14	60.75	86.19	1.42	0.35	87.8
15	63.35	88.64	1.40	0.31	86.7
16	71.01	90.61	1.28	0.32	85.2
17	71.16	91.14	1.28	0.31	84.4
18	87.61	96.58	1.10	0.28	80.5
19	88.13	96.20	1.09	0.32	80.1
20	91.30	97.78	1.07	0.26	79.0
21	100.00	100.00	1.00	-	78.5

Table 4.5 Ethyl Alcohol - Butyl Acetate, P = 1 atm.

	Mole per cent - ETOH		K_{ETOH}	K_{BUAC}	T
	x	y			°C
1	0.00	0.00	–	1.00	124.7
2	5.46	30.33	5.55	0.74	114.4
3	11.83	49.03	4.14	0.58	106.3
4	16.30	56.59	3.47	0.52	102.3
5	25.32	67.93	2.68	0.43	95.1
6	33.06	73.93	2.23	0.39	91.5
7	39.46	75.45	1.91	0.41	90.4
8	42.18	78.46	1.86	0.37	88.5
9	51.55	80.77	1.57	0.40	85.5
10	53.26	82.93	1.56	0.37	85.0
11	53.92	82.65	1.53	0.38	85.5
12	60.58	85.45	1.41	0.37	83.0
13	69.16	88.54	1.28	0.37	81.5
14	79.69	92.31	1.16	0.38	79.4
15	86.10	94.52	1.10	0.39	79.0
16	93.07	97.36	1.05	0.38	78.0
17	97.38	98.89	1.02	0.42	78.0
18	100.00	100.00	1.00	—	77.6

Table 4.6 Butyl Alcohol - Butyl Acetate, P = 1 atm.

	Mole per cent - BUOH		K_{BUOH}	K_{BUAC}	T
	x	y			°C
1	0.00	0.00	-	1.00	124.9
2	5.33	8.34	1.56	0.97	123.8
3	6.90	10.51	1.52	0.96	123.6
4	9.22	14.07	1.53	0.95	123.1
5	9.31	15.04	1.62	0.94	122.8
6	13.64	19.94	1.46	0.93	122.1
7	14.39	21.14	1.47	0.92	121.7
8	16.99	24.32	1.43	0.91	121.5
9	19.73	27.71	1.40	0.90	120.8
10	22.58	31.47	1.40	0.88	120.5
11	24.68	33.10	1.34	0.89	120.1
12	30.17	38.70	1.28	0.88	119.4
13	30.86	39.36	1.27	0.88	119.2
14	35.16	43.51	1.24	0.87	118.8
15	37.12	45.51	1.22	0.87	118.5
16	45.78	51.87	1.13	0.89	118.0
17	50.00	56.36	1.12	0.87	117.7
18	55.21	59.94	1.08	0.90	117.4
19	58.40	64.10	1.10	0.86	117.0
20	65.40	68.12	1.04	0.92	116.9
21	65.20	70.90	1.09	0.84	116.8
22	68.60	71.30	1.04	0.91	116.7
23	77.80	79.16	1.02	0.94	116.6
24	86.80	87.80	1.01	0.92	116.6
25	100.00	100.00	1.00	-	117.3

Table 4.7   Ethyl Acetate - Ethyl Alcohol - Butyl Alcohol, P = 1 atm.

	x (Mole per cent)			y (Mole per cent)			K			T
	ETAC	ETOH	BUOH	ETAC	ETOH	BUOH	ETAC	ETOH	BUOH	°C
1	1.47	3.36	95.16	3.35	8.19	88.46	2.28	2.43	0.93	115.5
2	1.95	4.54	93.51	4.31	11.53	84.16	2.21	2.54	0.90	114.4
3	2.37	4.97	92.66	7.37	14.03	78.60	3.11	2.82	0.85	113.0
4	2.38	90.66	6.96	3.34	95.08	1.57	1.40	1.05	0.23	80.2
5	2.44	4.47	93.10	4.89	8.91	86.20	2.01	1.98	0.93	115.0
6	2.48	4.05	93.47	6.72	9.80	83.48	2.71	2.42	0.89	114.1
7	2.51	86.58	10.91	3.87	94.10	2.03	1.54	1.09	0.19	80.9
8	2.67	84.10	13.23	4.98	91.61	3.41	1.86	1.09	0.26	81.6
9	2.82	78.65	18.53	5.02	80.56	5.42	1.78	1.02	0.29	82.7
10	2.83	23.08	74.09	5.85	52.50	41.65	2.06	2.27	0.56	100.7
11	3.15	2.28	94.57	8.90	6.29	84.81	2.82	2.75	0.90	114.5
12	3.45	25.08	71.47	10.56	52.83	36.61	3.05	2.10	0.51	98.2
13	3.56	56.31	40.13	6.90	79.93	13.17	1.94	1.42	0.33	87.8
14	3.88	85.00	11.11	9.88	86.75	3.37	2.54	1.02	0.30	80.6
15	4.65	22.76	72.58	4.97	52.45	42.58	1.07	2.31	0.59	101.5
16	4.80	2.61	92.60	13.70	6.75	79.55	2.85	2.58	0.86	113.3
17	5.31	55.62	39.07	11.69	75.80	12.50	2.20	1.36	0.32	86.8
18	7.65	8.84	83.51	23.72	19.58	56.69	3.10	2.21	0.68	105.7
19	7.66	16.64	75.70	22.43	35.64	41.94	2.92	2.14	0.55	100.8
20	8.10	23.88	68.01	21.91	46.49	31.60	2.70	1.94	0.47	95.7
21	8.69	5.90	85.41	26.83	14.33	58.85	3.08	2.43	0.69	106.2
22	11.02	53.48	35.50	21.18	68.18	10.69	1.93	1.27	0.30	84.6
23	17.97	51.41	30.62	31.83	60.36	7.81	1.77	1.17	0.26	82.2
24	23.70	48.44	27.86	38.03	55.29	6.68	1.61	1.14	0.24	80.3
25	26.13	52.84	21.04	38.20	57.12	4.68	1.46	1.08	0.22	78.8
26	30.67	55.43	13.90	41.07	56.28	2.65	1.34	1.02	0.19	76.4
27	31.68	28.18	40.14	50.69	37.75	11.56	1.60	1.34	0.29	83.6
28	32.31	23.49	44.20	52.43	32.20	15.37	1.62	1.37	0.35	84.5
29	34.12	18.54	47.34	57.42	27.30	15.27	1.68	1.47	0.32	86.0
30	34.34	5.22	60.44	70.39	8.57	21.04	0.89	1.12	0.18	90.6
31	36.00	13.97	50.03	60.39	22.46	17.15	1.68	1.61	0.34	87.5
32	36.13	10.04	53.83	63.17	15.23	21.60	1.75	1.52	0.40	89.2
33	39.82	36.64	23.54	54.25	40.39	5.36	1.36	1.10	0.23	78.1
34	76.71	9.08	13.30	81.56	14.77	3.66	1.06	1.48	0.28	78.2
35	80.94	9.00	10.07	83.54	13.50	2.96	1.03	1.50	0.29	77.7
36	82.32	8.01	9.67	84.28	13.00	2.73	1.02	1.62	0.28	77.9
37	82.44	7.78	9.79	85.68	11.30	3.02	1.04	1.45	0.31	78.5
38	86.93	5.64	7.43	89.91	7.56	2.54	1.03	1.34	0.34	78.4

Table 4.8 Ethyl Acetate - Ethyl Alcohol - Butyl Acetate, P = 1 atm.

	x (Mole per cent)			y (Mole per cent)			K			T
	ETAC	ETOH	BUAC	ETAC	ETOH	BUAC	ETAC	ETOH	BUAC	°C
1	4.73	52.93	42.35	7.39	76.96	15.65	1.56	1.45	0.37	84.5
2	6.23	51.39	42.38	9.55	74.34	16.11	1.53	1.45	0.38	84.0
3	7.95	32.06	59.99	6.26	72.11	21.64	0.79	2.25	0.36	95.1
4	11.93	29.17	58.89	13.24	64.66	22.10	1.11	2.22	0.38	94.6
5	13.42	52.62	33.96	22.81	60.23	16.96	1.70	1.14	0.50	80.6
6	17.49	24.98	57.53	20.70	58.26	21.05	1.18	2.33	0.37	94.6
7	21.17	39.56	39.27	30.18	55.78	14.05	1.43	1.41	0.36	81.7
8	21.51	22.20	56.28	28.24	51.35	20.41	1.31	2.31	0.36	94.6
9	23.71	37.63	38.66	31.00	57.24	11.76	1.31	1.52	0.30	82.1
10	24.60	19.56	55.84	34.97	45.42	19.60	1.42	2.32	0.35	94.3
11	27.10	17.47	55.43	37.99	41.70	20.31	1.40	2.39	0.37	96.3
12	28.73	13.75	57.51	42.54	36.62	20.85	1.48	2.66	0.36	96.8
13	29.23	36.72	34.00	36.78	54.14	9.08	1.26	1.47	0.27	80.6
14	32.69	10.54	56.77	48.50	28.75	22.75	1.48	2.73	0.40	95.0
15	33.39	34.96	31.65	43.88	48.49	7.63	1.13	1.39	0.24	81.3
16	37.18	7.71	55.12	56.94	19.87	23.20	1.53	2.58	0.42	95.8
17	40.05	33.01	26.94	45.86	47.15	6.99	1.15	1.43	0.26	88.5
18	40.50	20.52	38.98	48.16	39.74	12.09	1.19	1.94	0.31	88.1
19	40.53	37.57	21.90	43.58	50.69	5.72	1.08	1.35	0.26	78.8
20	41.50	6.92	51.57	63.28	15.58	21.15	1.52	2.25	0.41	92.5
21	42.19	32.07	25.74	51.17	41.56	7.28	1.21	1.30	0.28	85.7
22	42.30	28.36	29.34	47.67	45.99	6.34	1.13	1.60	0.22	85.4
23	42.86	38.94	18.20	48.71	47.76	3.53	1.14	1.23	0.19	82.9
24	43.80	38.23	17.98	48.06	47.86	4.08	1.10	1.25	0.23	82.9
25	44.28	16.13	39.50	54.60	33.64	11.76	1.23	2.09	0.30	86.4
26	44.37	38.80	16.91	47.15	48.87	3.97	1.06	1.24	0.24	81.5
27	45.55	44.16	10.30	49.96	48.12	1.93	1.10	1.09	0.19	80.8
28	45.63	41.00	13.37	48.70	48.27	3.02	1.07	1.18	0.23	81.2
29	46.17	45.81	8.03	49.32	48.82	1.86	1.07	1.07	0.23	80.2
30	46.52	12.75	40.73	60.07	28.00	11.93	1.29	2.20	0.29	87.3
31	46.80	34.37	18.83	49.57	45.90	4.53	1.06	1.34	0.24	83.0
32	48.47	8.14	43.39	66.67	19.39	13.96	1.35	2.38	0.32	91.0
33	49.25	36.65	14.10	51.80	44.97	3.23	1.05	1.23	0.23	81.8
34	50.73	37.06	12.21	53.62	44.08	2.30	1.06	1.19	0.19	81.7
35	51.00	8.08	41.82	70.74	14.12	15.14	1.39	1.75	0.36	90.2
36	51.30	41.63	7.07	52.68	46.17	1.15	1.03	1.11	0.16	78.8
37	52.25	42.95	4.80	53.85	45.16	0.98	1.03	1.05	0.20	78.7
38	54.43	43.08	2.50	54.23	45.26	0.52	0.99	1.05	0.21	76.7
39	54.47	42.16	3.28	54.72	44.69	0.58	1.00	1.06	0.18	76.7
40	55.36	40.97	3.68	26.51	72.84	0.65	0.48	1.78	0.78	77.2

Table 4.9 Ethyl Acetate - Butyl Alcohol - Butyl Acetate, P = 1 atm.

	x (Mole per cent)			y (Mole per cent)			K			T
	ETAC	BUOH	BUAC	ETAC	BUOH	BUAC	ETAC	BUOH	BUAC	°C
1	4.31	35.05	60.65	11.14	39.91	48.95	2.59	1.14	0.81	116.0
2	4.94	39.32	55.74	13.11	40.89	46.00	2.67	1.04	0.83	115.4
3	5.20	33.51	61.29	13.81	36.52	49.68	2.66	1.09	0.81	115.5
4	5.86	34.25	59.89	10.45	39.66	49.89	1.79	1.16	0.83	116.6
5	6.96	33.58	59.46	19.91	33.90	46.18	2.86	1.01	0.78	113.8
6	8.71	32.77	58.52	19.91	33.94	46.15	2.29	1.03	0.79	113.6
7	9.28	29.36	61.36	24.09	30.50	45.41	2.60	1.04	0.74	113.0
8	10.04	29.42	60.54	26.81	29.80	43.40	2.67	1.01	0.72	111.6
9	11.25	27.60	61.14	28.10	28.56	43.33	2.50	1.03	0.71	111.7
10	11.51	25.73	62.76	30.42	25.80	43.78	2.64	1.00	0.70	111.2
11	13.91	27.26	58.83	33.61	26.16	40.23	2.42	0.96	0.68	110.3
12	14.52	13.16	72.31	38.26	14.09	47.65	2.63	1.07	0.66	110.5
13	15.26	19.75	64.99	34.64	20.31	45.05	2.27	1.03	0.69	110.8
14	15.70	8.41	75.89	38.48	9.29	52.23	2.45	1.10	0.69	111.2
15	16.75	33.84	49.41	39.26	29.84	30.90	2.35	0.88	0.63	107.0
16	17.20	28.86	53.94	42.29	24.56	33.15	2.46	0.85	0.61	106.8
17	17.35	5.45	77.19	41.57	5.90	52.53	2.39	1.08	0.68	110.6
18	17.61	39.09	43.30	40.14	33.11	26.76	2.28	0.85	0.62	106.0
19	19.61	40.82	39.57	44.00	31.09	24.91	2.24	0.76	0.63	105.3
20	36.69	14.39	48.92	67.20	10.25	22.55	1.83	0.71	0.46	98.4
21	38.05	15.75	46.20	68.60	11.52	21.69	1.75	0.73	0.47	97.7
22	39.14	11.90	48.96	69.14	7.67	23.19	1.77	0.64	0.47	97.5
23	41.92	10.28	47.80	54.86	27.70	17.45	1.31	2.70	0.37	96.9
24	42.73	7.31	49.96	73.21	5.14	21.65	1.71	0.70	0.43	96.8
25	43.41	19.25	37.33	73.97	11.16	14.87	1.70	0.58	0.40	95.6
26	47.72	22.37	29.91	75.79	12.73	11.48	1.59	0.57	0.38	92.8
27	55.13	28.19	16.68	82.17	12.79	5.04	1.49	0.45	0.30	88.9
28	57.64	30.51	11.85	83.95	12.51	3.54	1.45	0.41	0.30	88.1
29	59.46	30.65	9.89	84.06	12.95	2.99	1.41	0.42	0.30	87.3
30	61.72	33.59	4.69	85.63	13.35	1.03	1.39	0.40	0.22	86.5
31	67.75	29.27	2.97	87.97	11.36	0.66	1.30	0.39	0.22	85.2
32	72.42	25.04	2.55	89.64	9.46	0.90	1.24	0.38	0.35	84.3
33	77.86	19.76	2.38	90.91	8.13	0.96	1.17	0.41	0.40	83.2
34	78.02	21.98	-	92.81	6.52	0.67	1.18	0.30	-	82.6
35	84.02	12.77	3.21	93.26	5.09	1.65	1.11	0.40	0.52	81.9

Table 4.10 Ethyl Alcohol - Butyl Alcohol - Butyl Acetate, P = 1 atm.

	x (Mole per cent)			y (Mole per cent)			K			T
	ETOH	BUOH	BUAC	ETOH	BUOH	BUAC	ETOH	BUOH	BUAC	°C
1	3.30	64.80	31.91	10.86	59.61	29.53	3.29	0.93	0.92	121.8
2	4.69	59.88	35.43	21.25	48.31	30.44	4.53	0.81	0.86	113.0
3	4.96	61.51	33.53	15.03	56.28	28.69	3.03	0.92	0.86	113.5
4	6.00	62.84	31.15	20.86	54.10	25.04	3.49	0.86	0.80	111.6
5	7.54	57.36	35.10	27.75	46.45	25.80	3.59	0.81	0.74	110.0
6	8.38	58.88	32.73	28.13	47.45	24.42	3.35	0.81	0.75	109.1
7	10.46	60.05	29.49	35.41	43.30	21.29	3.39	0.72	0.72	107.9
8	10.80	55.80	33.40	32.65	43.07	24.28	3.03	0.77	0.73	107.2
9	13.43	31.95	54.61	41.44	24.64	33.92	3.09	0.77	0.62	105.6
10	13.62	34.87	51.51	42.21	24.99	32.80	3.10	0.72	0.64	104.7
11	16.87	55.35	27.79	46.11	35.11	18.78	2.73	0.64	0.68	103.0
12	19.31	55.78	24.91	48.36	33.95	17.69	2.50	0.61	0.74	102.5
13	20.26	27.23	52.51	54.02	17.14	28.83	2.67	0.63	0.55	100.4
14	21.49	58.66	19.86	52.32	33.77	13.91	2.43	0.58	0.70	100.9
15	22.03	29.30	48.67	56.63	17.47	25.90	2.57	0.60	0.53	98.8
16	22.83	32.86	44.31	53.20	20.94	25.87	2.33	0.64	0.58	100.6
17	26.88	50.25	22.87	59.31	26.17	14.52	2.20	0.52	0.64	98.5
18	26.91	3.29	69.80	69.41	0.94	29.65	2.58	0.29	0.43	94.5
19	27.15	15.81	57.04	65.42	8.10	26.48	2.41	0.51	0.47	95.6
20	27.17	39.33	33.50	60.99	19.89	19.12	2.24	0.52	0.57	97.4
21	29.89	55.47	14.64	64.95	26.27	8.78	2.17	0.47	0.60	96.7
22	32.75	7.52	59.73	72.96	3.86	23.19	2.23	0.51	0.39	91.5
23	34.66	59.15	6.19	69.17	27.33	3.50	1.99	0.46	0.57	95.5
24	35.74	3.04	55.22	73.99	3.84	22.16	2.07	1.27	0.40	90.6
25	36.70	60.80	2.50	70.72	27.73	1.55	1.93	0.46	0.62	95.1
26	36.93	21.76	41.31	71.15	9.85	19.00	1.93	0.45	0.46	91.3
27	40.24	47.06	12.70	71.46	20.29	8.25	1.77	0.43	0.65	93.0
28	41.02	52.48	6.50	65.68	27.54	6.78	1.60	0.53	1.04	92.8
29	41.19	33.04	25.77	73.14	13.42	13.44	1.77	0.41	0.52	91.5
30	43.68	4.60	51.71	78.11	1.15	20.73	1.79	0.25	0.40	87.9
31	44.40	6.63	48.97	73.85	5.84	20.31	1.66	0.87	0.41	87.1
32	48.39	17.97	33.64	80.50	5.58	13.92	1.66	0.31	0.41	87.7
33	50.60	10.92	38.49	81.25	3.43	15.32	1.61	0.31	0.40	86.7
34	51.43	4.77	43.81	82.63	1.41	15.95	1.61	0.30	0.36	86.0
35	53.72	1.98	44.30	83.82	-	16.18	1.56	-	0.37	85.3
36	61.31	19.05	19.64	84.22	5.08	10.70	1.37	0.27	0.55	85.1
37	65.53	19.46	15.01	85.19	6.73	8.07	1.30	0.35	0.54	84.4
38	78.42	9.33	12.26	91.77	2.45	5.78	1.17	0.26	0.47	81.4

Table 4.11 Ethyl Acetate - Ethyl Alcohol - Butyl Acetate - Butyl Alcohol, P = 1 atm.

	x				y				K				T
	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	^oC
1	1.63	39.33	31.84	27.20	3.12	69.74	15.30	11.83	1.91	1.77	0.48	0.44	91.4
2	3.71	37.43	32.07	26.79	5.80	68.65	14.49	11.06	1.56	1.83	0.45	0.41	91.3
3	5.37	38.49	30.70	25.45	8.77	66.91	14.05	10.26	1.63	1.73	0.46	0.40	90.4
4	7.54	73.59	40.01	28.86	13.47	51.99	19.88	14.67	1.79	2.20	0.50	0.51	95.7
5	8.85	35.45	30.24	25.46	15.30	61.76	12.97	9.97	1.73	1.74	0.43	0.39	89.9
6	10.68	4.80	50.27	34.25	21.59	10.79	35.73	31.89	2.02	2.25	0.71	0.93	110.0
7	11.23	24.41	37.04	27.31	19.78	49.67	17.02	13.53	1.76	2.03	0.46	0.50	93.7
8	11.88	31.21	31.17	25.74	20.00	57.07	12.91	10.02	1.69	1.84	0.41	0.39	90.0
9	12.19	24.05	37.21	26.55	21.63	49.67	16.61	12.09	1.77	2.07	0.45	0.46	93.2
10	12.25	3.57	50.98	33.21	26.54	9.89	33.76	29.82	2.16	2.77	0.66	0.90	108.6
11	14.37	4.32	48.98	32.33	31.90	10.51	30.26	27.33	2.22	2.43	0.62	0.85	107.3
12	15.29	5.80	45.85	33.07	32.59	12.22	28.95	26.24	2.13	2.11	0.63	0.79	105.8
13	15.40	30.74	30.24	23.62	24.94	54.75	11.66	8.64	1.62	1.78	0.39	0.37	88.7
14	15.65	4.98	47.79	31.59	33.19	12.24	29.43	25.14	2.12	2.46	0.61	0.80	101.7
15	16.67	26.61	32.98	23.75	27.16	50.61	12.80	9.44	1.63	1.90	0.39	0.40	89.8
16	17.29	40.14	14.71	27.86	27.95	58.37	5.08	8.59	1.62	1.45	0.35	0.31	84.9
17	18.05	28.12	38.74	15.09	27.38	53.66	13.28	5.68	1.52	1.91	0.34	0.39	88.0
18	18.25	31.05	33.69	17.01	28.01	53.91	11.97	6.12	1.54	1.74	0.36	0.36	87.0
19	18.47	43.21	9.39	28.93	30.79	57.12	3.72	8.35	1.67	1.32	0.39	0.29	83.8
20	18.52	33.97	45.92	1.58	25.85	60.20	13.28	0.67	1.40	1.77	0.29	0.42	84.5
21	18.54	43.42	7.82	30.21	32.01	57.36	2.86	7.78	1.73	1.32	0.37	0.26	83.2
22	18.60	29.08	31.76	20.56	28.74	51.70	11.77	7.80	1.55	1.78	0.37	0.38	88.2
23	18.69	29.91	40.71	10.69	27.57	56.19	12.71	3.54	1.48	1.88	0.31	0.35	86.3
24	18.74	29.90	28.18	23.18	29.30	50.62	11.48	8.59	1.56	1.69	0.41	0.37	88.3
25	18.90	4.62	46.41	30.06	42.07	7.38	27.34	23.21	2.22	1.60	0.59	0.77	103.9

Table 4.11 (Cont'd.)

	x				y				K				T
	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	°C
26	19.49	32.35	25.55	22.62	30.40	53.24	8.66	7.70	1.56	1.65	0.34	0.34	86.6
27	19.76	32.99	27.93	19.31	30.48	53.79	9.50	6.23	1.54	1.63	0.34	0.32	85.1
28	20.09	32.75	43.91	3.26	26.88	59.43	12.78	0.91	1.34	1.81	0.29	0.28	84.8
29	20.20	37.90	12.55	29.34	31.12	55.01	3.67	10.20	1.54	1.45	0.29	0.35	85.0
30	20.27	3.07	47.32	29.34	42.20	6.01	28.52	23.26	2.08	1.96	0.60	0.79	104.8
31	20.51	2.93	47.77	28.79	42.47	3.80	29.47	24.26	2.07	1.30	0.62	0.84	105.0
32	20.80	30.48	40.68	8.04	28.98	55.62	12.71	2.68	1.39	1.82	0.31	0.33	85.8
33	20.93	24.17	37.89	17.00	33.25	46.91	13.28	6.56	1.59	1.94	0.35	0.39	88.6
34	20.94	30.99	41.48	6.60	28.82	56.38	12.68	2.12	1.37	1.82	0.31	0.32	85.5
35	20.96	44.43	6.41	28.20	33.79	56.26	2.33	7.62	1.61	1.27	0.36	0.27	82.4
36	20.99	5.92	42.70	30.38	41.76	12.08	23.81	22.35	1.99	2.04	0.56	0.74	102.8
37	21.07	42.42	15.60	20.91	32.06	57.24	4.17	5.73	1.56	1.35	0.27	0.27	81.7
38	21.23	46.62	10.85	21.30	33.04	58.62	3.15	5.39	1.56	1.25	0.29	0.25	80.8
39	21.23	32.05	27.37	19.36	33.26	52.68	8.21	5.85	1.57	1.64	0.30	0.30	85.5
40	21.26	31.45	42.71	4.58	28.91	57.13	12.76	1.20	1.36	1.82	0.30	0.26	85.1
41	21.28	36.13	15.26	27.32	32.87	53.15	4.69	9.29	1.54	1.47	0.31	0.34	84.9
42	21.30	41.05	14.18	23.47	34.62	56.45	4.12	4.82	1.63	1.37	0.29	0.21	82.2
43	21.55	6.17	42.59	29.69	44.33	11.41	23.51	20.75	2.05	1.85	0.55	0.70	101.5
44	21.84	32.99	43.85	1.32	30.02	57.28	12.24	0.46	1.37	1.74	0.28	0.35	84.0
45	22.17	25.82	33.16	18.85	31.03	50.59	11.45	6.93	1.40	1.96	0.35	0.37	88.9
46	22.28	51.97	4.72	21.03	34.84	59.00	1.17	4.99	1.56	1.13	0.25	0.24	79.2
47	22.36	49.16	7.86	20.62	34.54	58.28	2.22	4.96	1.54	1.19	0.28	0.24	79.9
48	22.37	27.36	28.79	21.48	33.86	46.91	11.01	8.22	1.52	1.71	0.38	0.38	88.2
49	22.38	39.72	16.87	20.93	34.10	56.06	5.02	4.82	1.52	1.41	0.30	0.23	82.7
50	22.39	33.10	18.37	26.14	34.37	50.67	5.45	9.51	1.53	1.53	0.30	0.36	85.4

Table 4.11 (Cont'd.)

	x				y				K				T
	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	°C
51	22.62	25.97	28.40	22.01	36.52	48.09	8.91	6.49	1.62	1.85	0.30	0.30	87.2
52	22.75	49.76	6.22	21.27	35.08	58.42	1.50	5.01	1.54	1.17	0.24	0.24	79.4
53	22.84	42.32	10.51	24.33	36.65	55.25	3.12	4.98	1.60	1.31	0.30	0.21	81.4
54	23.00	29.07	32.59	15.34	35.29	48.10	8.90	7.72	1.53	1.66	0.27	0.50	86.4
55	23.23	6.61	45.96	23.20	45.50	14.96	23.32	16.22	1.96	2.27	0.50	0.70	100.4
56	23.27	46.13	3.28	27.31	38.68	55.02	0.98	5.33	1.66	1.19	0.30	0.20	80.3
57	23.70	18.48	34.10	23.73	40.71	38.80	11.49	9.00	1.72	2.10	0.34	0.38	
58	27.78	29.26	44.80	2.15	31.92	53.54	13.91	0.63	1.34	1.83	0.31	0.29	85.6
59	24.16	15.50	40.83	19.51	41.48	33.43	15.86	9.24	1.72	2.15	0.40	0.47	92.0
60	24.47	44.43	5.04	26.06	39.12	54.03	1.47	5.39	1.60	1.22	0.29	0.21	80.6
61	25.01	27.87	40.84	6.28	34.58	49.89	13.28	2.27	1.38	1.79	0.33	0.36	85.7
62	25.06	29.18	41.09	4.67	33.82	51.66	13.06	1.46	1.35	1.77	0.32	0.31	85.3
63	25.09	10.87	38.40	25.64	45.27	28.94	14.05	11.74	1.81	2.66	0.37	0.42	93.7
64	25.39	42.61	7.66	24.35	39.94	52.74	2.13	5.19	1.57	1.24	0.28	0.21	80.8
65	25.65	40.05	27.88	6.42	31.96	58.14	8.27	1.63	1.25	1.45	0.30	0.25	81.6
66	25.75	8.64	39.48	26.16	49.23	21.96	15.79	13.02	1.91	2.54	0.40	0.50	96.2
67	25.99	25.82	29.18	19.01	40.18	43.88	9.21	6.74	1.55	1.70	0.32	0.36	86.0
68	26.23	22.69	29.47	21.61	40.32	38.95	11.28	9.45	1.54	1.71	0.38	0.44	88.7
69	26.53	46.65	17.85	8.97	34.11	57.87	5.97	2.05	1.29	1.24	0.33	0.23	
70	26.76	3.79	41.86	27.59	54.10	10.54	18.36	16.99	2.02	2.79	0.44	0.61	98.8
71	27.39	47.56	19.76	5.29	33.95	60.99	4.41	0.65	1.24	1.28	0.22	0.12	77.2
72	27.51	54.17	14.65	3.67	34.31	62.20	3.32	0.18	1.25	1.15	0.23	0.49	76.3
73	27.64	52.57	14.92	4.87	34.12	59.29	4.17	2.42	1.23	1.13	0.28	0.50	79.3
74	27.80	54.48	6.97	10.76	58.16	35.09	1.73	5.01	2.09	0.64	0.25	0.47	77.5
75	28.10	7.10	39.09	25.72	51.68	17.93	15.73	14.67	1.84	2.53	0.40	0.57	96.8

Table 4.11 (Cont'd.)

	x				y				K				T
	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	°C
76	28.32	17.32	31.05	23.31	45.52	32.58	11.78	10.12	1.61	1.88	0.38	0.43	90.1
77	28.59	9.93	40.97	20.51	50.35	21.73	16.78	11.14	1.76	2.19	0.42	0.54	93.7
78	28.60	0.72	38.47	32.21	58.43	3.07	17.55	20.96	2.04	4.26	0.46	0.65	100.7
79	28.70	6.69	24.78	39.83	53.05	15.80	10.95	20.20	1.85	2.36	0.44	0.51	96.3
80	28.75	53.44	14.02	3.79	35.59	59.52	4.27	0.62	1.24	1.11	0.31	0.16	77.3
81	28.80	0.48	39.17	31.56	57.58	1.77	19.35	21.30	2.00	3.69	0.49	0.68	101.2
82	28.91	1.79	38.51	30.79	57.53	4.90	17.61	19.97	1.99	2.74	0.46	0.65	99.9
83	28.97	8.04	29.27	33.73	53.40	15.45	13.48	17.67	1.84	1.92	0.46	0.52	95.4
84	29.37	6.75	21.13	42.75	53.09	14.66	9.70	22.55	1.81	2.17	0.46	0.53	95.8
85	29.56	2.57	38.49	29.38	56.59	6.69	17.93	18.79	1.92	2.60	0.47	0.64	99.5
86	30.73	4.05	18.93	46.29	56.87	9.16	9.47	24.49	1.85	2.26	0.50	0.53	97.2
87	30.94	8.85	44.24	15.97	52.56	17.71	19.67	10.07	1.70	2.00	0.44	0.63	95.4
88	31.68	13.56	31.77	22.98	48.92	26.59	12.71	11.77	1.54	1.96	0.40	0.51	91.3
89	32.27	5.20	17.41	45.11	56.90	9.68	8.61	24.81	1.76	1.86	0.49	0.55	96.8
90	33.82	3.45	42.21	20.53	63.81	2.76	19.84	13.59	1.89	0.80	0.47	0.66	98.2
91	34.14	8.89	21.06	35.91	59.48	18.41	6.91	15.19	1.74	2.07	0.33	0.42	95.3
92	34.35	8.30	51.26	6.09	58.02	18.74	19.50	3.74	1.69	2.26	0.38	0.61	94.2
93	34.97	3.17	11.36	50.50	59.55	7.25	6.28	26.92	1.70	2.29	0.61	0.53	96.9
94	35.22	3.83	35.26	25.69	63.45	6.21	15.30	15.05	1.80	1.62	0.43	0.59	95.8
95	35.51	8.77	32.52	23.19	57.94	15.63	3.58	12.85	1.63	1.78	0.42	0.55	93.7
96	37.35	5.80	33.12	23.73	59.78	11.60	14.34	14.28	1.60	2.00	0.43	0.60	94.4
97	37.97	10.32	4.10	47.62	66.63	17.98	1.29	14.10	1.75	1.74	0.32	0.30	86.1
98	38.45	10.33	50.29	0.93	58.70	22.05	18.69	0.56	1.53	2.14	0.37	0.60	90.2
99	38.80	10.20	47.28	3.71	60.02	22.37	16.04	1.56	1.55	2.19	0.34	0.42	90.5
100	39.29	9.79	15.60	40.32	63.47	18.35	3.40	14.78	1.61	1.87	0.32	0.37	88.1
101	41.03	10.48	6.61	41.88	65.69	16.91	1.87	15.54	1.60	1.61	0.28	0.37	87.2

4.6.2 Calculated Results

Vapour Pressure Data references.

ETAC	(101)
ETOH	(102)
BUAC	(104)
BUOH	(103)

Table 4.12 Activity Coefficients, Ethyl Acetate - Ethyl Alcohol.

	γ		$(\log \gamma)^{\frac{1}{2}}$		$\log\left(\frac{\gamma_{ETAC}}{\gamma_{ETOH}}\right)$
	ETAC	ETOH	ETAC	ETOH	
1	—	—	—	—	—
2	2.25	1.00	0.59	0.03	0.352
3	2.02	1.00	0.55	0.03	0.305
4	2.11	1.01	0.57	0.06	0.320
5	1.95	1.03	0.54	0.12	0.277
6	1.89	1.01	0.53	0.06	0.272
7	1.72	1.04	0.49	0.13	0.218
8	1.66	1.06	0.47	0.16	0.196
9	1.46	1.12	0.41	0.22	0.115
10	1.33	1.20	0.35	0.28	0.045
11	1.29	1.23	0.33	0.30	0.021
12	1.25	1.29	0.31	0.33	-0.014
13	1.25	1.29	0.31	0.33	-0.014
14	1.20	1.36	0.28	0.37	-0.054
15	1.17	1.39	0.26	0.38	-0.078
16	1.11	1.59	0.21	0.45	-0.155
17	1.08	1.65	0.18	0.47	-0.184
18	1.07	1.73	0.17	0.49	-0.209
19	1.05	1.84	0.14	0.51	-0.244
20	—	—	—	—	—

Table 4.13 Activity Coefficients, Ethyl Acetate - Butyl Alcohol

	γ		$(\log \gamma)^{\frac{1}{2}}$		$\log\left(\frac{\gamma_{ETAC}}{\gamma_{BUOH}}\right)$
	ETAC	BUOH	ETAC	BUOH	
1	—	—	—	—	—
2	1.27	1.01	0.32	0.05	0.10
3	1.23	1.03	0.30	0.12	0.08
4	1.28	1.04	0.33	0.13	0.09
5	1.28	1.05	0.33	0.15	0.09
6	1.28	1.05	0.33	0.15	0.09
7	1.26	1.06	0.32	0.16	0.08
8	1.32	1.03	0.35	0.12	0.11
9	1.32	1.07	0.35	0.17	0.09
10	1.29	1.03	0.33	0.11	0.10
11	1.26	1.01	0.32	0.08	0.10
12	1.21	1.08	0.29	0.18	0.05
13	1.26	1.14	0.23	0.24	0.05
14	1.20	1.06	0.28	0.16	0.05
15	1.17	1.05	0.26	0.15	0.05
16	1.12	1.09	0.22	0.19	0.01
17	1.06	1.27	0.16	0.32	-0.08
18	1.03	1.23	0.11	0.30	-0.08
19	1.03	1.30	0.11	0.34	-0.10
20	1.05	1.26	0.14	0.32	-0.08
21	1.04	1.31	0.13	0.34	-0.10
22	1.03	1.36	0.11	0.37	-0.12
23	1.02	1.26	0.09	0.32	-0.09
24	1.03	1.33	0.11	0.35	-0.11
25	—	—	—	—	—

Table 4.14 Activity Coefficients, Ethyl Acetate - Butyl Acetate

	γ			γ	
	ETAC	BUAC		ETAC	BUAC
1	—	—	17	0.96	1.06
2	0.58	0.95	18	0.98	1.04
3	0.71	1.01	19	0.98	1.04
4	0.68	1.02	20	0.98	1.10
5	0.71	1.04	21	0.99	1.06
6	0.77	1.03	22	1.00	1.07
7	0.79	1.04	23	0.99	1.04
8	0.76	1.07	24	1.00	1.09
9	0.74	1.09	25	1.01	1.07
10	0.90	1.05	26	1.01	1.08
11	0.87	1.08	27	1.01	0.99
12	0.93	0.89	28	1.02	1.02
13	0.89	0.87	29	1.00	—
14	0.83	1.15	30	1.00	—
15	0.89	1.13	31	—	—
16	0.94	1.06			

Table 4.15 Activity Coefficients, Ethyl Alcohol - Butyl Alcohol

	γ			γ	
	ETOH	BUOH		ETOH	BUOH
1	—	—	12	1.01	1.06
2	1.04	1.03	13	0.93	1.18
3	1.09	1.00	14	0.98	1.13
4	1.01	1.04	15	1.01	1.04
5	0.94	1.09	16	0.98	1.17
6	0.97	1.08	17	1.01	1.14
7	0.97	1.11	18	1.01	1.23
8	0.98	1.10	19	1.02	1.46
9	0.97	1.10	20	1.04	1.23
10	0.94	1.26	21	—	—
11	0.94	1.09			

Table 4.16   Activity Coefficients, Ethyl Alcohol - Butyl Acetate

	γ		$(\log \gamma)^{\frac{1}{2}}$		$\log\left(\frac{\gamma_{ETOH}}{\gamma_{BUAC}}\right)$
	ETOH	BUAC	ETOH	BUAC	
1	—	—	—	—	—
2	1.55	1.02	0.44	0.09	0.18
3	1.50	1.04	0.42	0.13	0.16
4	1.44	1.07	0.40	0.17	0.13
5	1.33	1.11	0.39	0.21	0.11
6	1.35	1.15	0.36	0.25	0.07
7	1.19	1.24	0.28	0.31	-0.02
8	1.25	1.23	0.31	0.30	0.01
9	1.19	1.47	0.27	0.41	-0.09
10	1.21	1.39	0.29	0.38	-0.06
11	1.16	1.41	0.25	0.31	-0.08
12	1.18	1.52	0.27	0.43	-0.11
13	1.13	1.63	0.23	0.46	-0.16
14	1.11	1.81	0.21	0.51	-0.21
15	1.07	1.91	0.17	0.53	-0.25
16	1.06	2.02	0.16	0.55	-0.28
17	1.03	2.15	0.11	0.58	-0.32
18	—	—	—	—	—

Table 4.17 Activity Coefficients, Butyl Alcohol - Butyl Acetate

	γ		$(\log\ \gamma)^{\frac{1}{2}}$		$\log\left(\frac{\gamma_{BUOH}}{\gamma_{BUAC}}\right)$
	BUOH	BUAC	BUOH	BUAC	
1	—	—	—	—	—
2	1.28	1.00	0.33	0.03	0.107
3	1.26	1.00	0.31	0.05	0.100
4	1.28	1.00	0.33	0.16	0.107
5	1.36	1.00	0.37	0.19	0.134
6	1.27	1.01	0.32	0.08	0.100
7	1.29	1.01	0.33	0.10	0.107
8	1.27	1.01	0.32	0.15	0.100
9	1.27	1.02	0.32	0.13	0.097
10	1.27	1.01	0.32	0.25	0.100
11	1.24	1.03	0.31	0.15	0.079
12	1.22	1.04	0.29	0.17	0.068
13	1.22	1.05	0.29	0.18	0.065
14	1.20	1.05	0.28	0.19	0.057
15	1.20	1.05	0.28	0.21	0.057
16	1.12	1.10	0.23	0.17	0.009
17	1.12	1.09	0.22	0.21	0.013
18	1.09	1.12	0.19	0.18	-0.012
19	1.12	1.10	0.22	0.29	0.009
20	1.06	1.08	0.16	0.20	-0.008
21	1.12	1.07	0.22	0.48	0.021
22	1.06	1.19	0.16	0.27	-0.054
23	1.06	1.19	0.16	0.27	-0.050
24	1.03	1.20	0.11	0.28	-0.066
25	—	—	—	—	—

4.6.3 Predicted Vapour Compositions

Table 4.18 Predicted Vapour Compositions for Ethyl Acetate - Ethyl Alcohol - Butyl Alcohol

	y (mole fractions)			T
	ETAC	ETOH	BUOH	°C
1	0.049	0.113	0.838	113.5
2	0.063	0.148	0.790	112.4
3	0.075	0.159	0.766	111.8
4	0.036	0.949	0.015	78.9
5	0.078	0.144	0.778	112.1
6	0.080	0.132	0.789	112.4
7	0.039	0.937	0.025	79.8
8	0.041	0.928	0.030	80.3
9	0.045	0.910	0.045	81.6
10	0.070	0.523	0.407	100.8
11	0.102	0.076	0.822	113.2
12	0.083	0.545	0.372	99.5
13	0.065	0.809	0.127	87.5
14	0.059	0.917	0.025	79.7
15	0.112	0.503	0.385	100.0
16	0.150	0.084	0.766	110.8
17	0.094	0.786	0.120	87.0
18	0.208	0.236	0.556	105.9
19	0.188	0.387	0.425	101.5
20	0.182	0.490	0.328	97.7
21	0.241	0.164	0.595	107.1
22	0.183	0.717	0.100	85.4
23	0.274	0.648	0.078	83.6
24	0.342	0.591	0.067	82.4
25	0.354	0.600	0.046	80.4
26	0.385	0.588	0.027	78.4
27	0.483	0.401	0.117	86.2
28	0.510	0.352	0.138	87.7
29	0.551	0.292	0.157	89.0
30	0.638	0.100	0.262	94.6
31	0.594	0.230	0.176	90.0
32	0.620	0.175	0.205	91.6
33	0.511	0.437	0.052	80.8
34	0.836	0.134	0.031	79.0
35	0.856	0.121	0.023	78.2
36	0.869	0.109	0.023	78.2
37	0.871	0.106	0.023	78.2
38	0.904	0.079	0.017	77.9

Table 4.19 Predicted Vapour Compositions for Ethyl Acetate - Ethyl Alcohol - Butyl Acetate

	y (mole fractions)			T
	ETAC	ETOH	BUAC	°C
1	0.059	0.811	0.130	85.9
2	0.078	0.793	0.130	86.0
3	0.120	0.659	0.221	92.4
4	0.181	0.605	0.215	92.3
5	0.160	0.745	0.096	83.8
6	0.266	0.526	0.208	92.2
7	0.265	0.623	0.113	85.4
8	0.328	0.471	0.201	92.1
9	0.297	0.594	0.110	85.4
10	0.378	0.422	0.200	92.2
11	0.419	0.382	0.199	92.3
12	0.463	0.320	0.217	93.7
13	0.354	0.555	0.091	84.0
14	0.533	0.252	0.216	94.0
15	0.398	0.520	0.082	83.3
16	0.606	0.186	0.208	93.8
17	0.463	0.472	0.065	82.0
18	0.527	0.362	0.110	86.2
19	0.453	0.497	0.051	80.6
20	0.653	0.161	0.186	92.4
21	0.484	0.455	0.062	81.7
22	0.500	0.427	0.073	82.8
23	0.468	0.492	0.040	79.5
24	0.478	0.483	0.040	79.5
25	0.588	0.297	0.115	86.8
26	0.481	0.483	0.037	79.1
27	0.481	0.498	0.021	77.4
28	0.486	0.486	0.028	78.2
29	0.485	0.500	0.016	76.7
30	0.633	0.246	0.122	87.5
31	0.512	0.447	0.041	79.7
32	0.692	0.170	0.138	89.0
33	0.524	0.447	0.029	78.4
34	0.534	0.441	0.025	77.8
35	0.708	0.163	0.129	88.0
36	0.530	0.456	0.014	76.4
37	0.536	0.455	0.009	75.8
38	0.553	0.442	0.005	75.1
39	0.555	0.439	0.006	75.3
40	0.562	0.432	0.007	75.4

Table 4.20 Predicted Vapour Compositions for Ethyl Acetate - Butyl Acetate - Butyl Alcohol

	y (mole fractions)			T
	ETAC	BUAC	BUOH	°C
1	0.129	0.497	0.373	117.1
2	0.147	0.450	0.404	116.3
3	0.153	0.494	0.352	116.6
4	0.171	0.476	0.353	116.0
5	0.200	0.462	0.338	115.3
6	0.244	0.438	0.318	114.2
7	0.258	0.456	0.287	114.0
8	0.275	0.443	0.282	113.5
9	0.305	0.437	0.260	112.9
10	0.309	0.447	0.244	112.8
11	0.360	0.399	0.242	111.1
12	0.378	0.495	0.127	111.8
13	0.389	0.433	0.178	110.8
14	0.405	0.513	0.082	111.4
15	0.414	0.314	0.272	109.0
16	0.423	0.342	0.236	109.0
17	0.440	0.508	0.052	110.6
18	0.431	0.269	0.300	108.0
19	0.466	0.236	0.298	106.8
20	0.693	0.222	0.085	100.0
21	0.706	0.204	0.090	99.3
22	0.718	0.214	0.068	97.9
23	0.743	0.200	0.057	96.6
24	0.752	0.208	0.040	96.3
25	0.752	0.151	0.098	95.6
26	0.784	0.112	0.103	93.5
27	0.833	0.056	0.111	90.2
28	0.848	0.038	0.114	89.0
29	0.858	0.031	0.111	88.3
30	0.870	0.014	0.116	87.4
31	0.898	0.008	0.094	85.4
32	0.916	0.007	0.077	84.0
33	0.936	0.006	0.058	82.5
34	0.937	0.000	0.064	82.4
35	0.957	0.008	0.036	80.9

Table 4.21 Predicted Vapour Compositions for Ethyl Alcohol - Butyl Acetate - Butyl Alcohol

	y (mole fractions)			T °C
	ETOH	BUAC	BUOH	
1	0.119	0.266	0.615	115.4
2	0.165	0.286	0.550	114.5
3	0.172	0.269	0.558	114.2
4	0.203	0.246	0.551	112.3
5	0.248	0.267	0.485	113.3
6	0.270	0.245	0.485	111.6
7	0.321	0.214	0.467	110.1
8	0.331	0.238	0.431	109.9
9	0.409	0.353	0.238	108.2
10	0.410	0.334	0.256	108.1
11	0.455	0.180	0.365	106.0
12	0.497	0.157	0.347	104.5
13	0.537	0.296	0.168	103.6
14	0.530	0.123	0.347	103.2
15	0.560	0.268	0.172	102.6
16	0.567	0.245	0.188	102.2
17	0.607	0.129	0.264	100.4
18	0.666	0.317	0.017	98.3
19	0.644	0.275	0.082	99.2
20	0.617	0.179	0.204	100.0
21	0.641	0.083	0.277	99.0
22	0.713	0.253	0.034	95.7
23	0.691	0.035	0.275	97.0
24	0.762	0.226	0.013	94.5
25	0.711	0.014	0.275	96.1
26	0.729	0.182	0.090	95.1
27	0.742	0.194	0.064	94.5
28	0.748	0.034	0.218	94.3
29	0.753	0.118	0.129	93.8
30	0.796	0.188	0.016	90.8
31	0.797	0.180	0.023	90.7
32	0.809	0.132	0.059	90.4
33	0.827	0.139	0.034	89.1
34	0.836	0.150	0.014	88.2
35	0.850	0.145	0.006	87.1
36	0.873	0.075	0.052	86.6
37	0.891	0.058	0.051	85.6
38	0.936	0.044	0.020	82.0

Table 4.22 Predicted Quaternary Vapour Compositions

	y (mole fractions)				T
	ETAC	ETOH	BUAC	BUOH	°C
1	0.028	0.728	0.139	0.106	93.6
2	0.063	0.695	0.138	0.104	93.6
3	0.088	0.691	0.127	0.094	92.5
4	0.143	0.524	0.191	0.142	93.3
5	0.145	0.638	0.122	0.095	92.4
6	0.263	0.151	0.321	0.266	108.6
7	0.202	0.511	0.164	0.124	96.3
8	0.197	0.578	0.126	0.099	93.0
9	0.217	0.501	0.163	0.119	96.1
10	0.301	0.113	0.325	0.261	108.7
11	0.338	0.130	0.294	0.238	106.9
12	0.346	0.166	0.262	0.227	105.3
13	0.246	0.552	0.115	0.087	91.8
14	0.357	0.145	0.276	0.222	105.7
15	0.273	0.504	0.129	0.094	93.0
16	0.262	0.603	0.052	0.084	87.6
17	0.278	0.524	0.142	0.057	91.6
18	0.275	0.546	0.120	0.060	90.4
19	0.277	0.609	0.032	0.082	86.1
20	0.251	0.598	0.146	0.005	88.3
21	0.280	0.608	0.027	0.085	86.0
22	0.289	0.520	0.116	0.075	91.2
23	0.276	0.545	0.142	0.038	90.4
24	0.292	0.523	0.103	0.082	90.9
25	0.415	0.130	0.255	0.201	104.3
26	0.295	0.540	0.090	0.076	89.6
27	0.292	0.548	0.096	0.063	89.2
28	0.275	0.575	0.140	0.011	88.4
29	0.305	0.564	0.043	0.088	87.4
30	0.449	0.088	0.262	0.201	104.7
31	0.454	0.084	0.265	0.198	104.7
32	0.296	0.542	0.135	0.027	89.3
33	0.330	0.463	0.141	0.066	92.3
34	0.293	0.570	0.135	0.002	89.2

Table 4.22 (Cont'd.)

	y (mole fractions)				T
	ETAC	ETOH	BUAC	BUOH	°C
35	0.307	0.597	0.021	0.075	84.8
36	0.438	0.156	0.220	0.187	102.2
37	0.295	0.599	0.050	0.057	85.5
38	0.294	0.618	0.034	0.054	84.1
39	0.312	0.531	0.095	0.063	89.0
40	0.294	0.554	0.137	0.015	88.6
41	0.318	0.548	0.052	0.083	87.6
42	0.304	0.585	0.046	0.065	86.0
43	0.444	0.161	0.216	0.180	101.8
44	0.291	0.570	0.135	0.004	87.6
45	0.342	0.470	0.119	0.069	91.2
46	0.306	0.631	0.014	0.049	82.1
47	0.305	0.622	0.024	0.050	83.0
48	0.343	0.479	0.102	0.076	90.5
49	0.314	0.574	0.054	0.058	86.0
50	0.335	0.520	0.063	0.082	88.3
51	0.351	0.464	0.106	0.080	91.0
52	0.312	0.619	0.019	0.051	82.6
53	0.323	0.579	0.033	0.065	85.0
54	0.336	0.502	0.110	0.052	89.4
55	0.462	0.172	0.229	0.137	100.8
56	0.334	0.587	0.010	0.068	83.4
57	0.395	0.371	0.134	0.100	94.0
58	0.326	0.525	0.141	0.007	88.4
59	0.413	0.333	0.165	0.089	95.2
60	0.346	0.573	0.016	0.065	83.6
61	0.350	0.497	0.131	0.021	88.8
62	0.344	0.512	0.129	0.015	88.2
63	0.458	0.247	0.167	0.128	97.3
64	0.354	0.561	0.023	0.062	83.9
65	0.322	0.583	0.078	0.017	84.4
66	0.482	0.203	0.177	0.137	98.2
67	0.387	0.448	0.099	0.066	89.7
68	0.406	0.410	0.105	0.080	91.0

Table 4.22 (Cont'd.)

	y (mole fractions)				T
	ETAC	ETOH	BUAC	BUOH	°C
69	0.326	0.606	0.048	0.021	82.3
70	0.536	0.098	0.203	0.163	100.8
71	0.325	0.612	0.051	0.012	81.7
72	0.317	0.640	0.036	0.007	80.0
73	0.322	0.631	0.038	0.010	80.3
74	0.619	0.341	0.018	0.022	79.7
75	0.524	0.168	0.174	0.135	98.1
76	0.457	0.334	0.115	0.094	92.6
77	0.504	0.225	0.171	0.101	96.3
78	0.590	0.019	0.193	0.198	101.7
79	0.544	0.148	0.110	0.199	97.6
80	0.330	0.628	0.034	0.008	79.7
81	0.595	0.013	0.197	0.195	101.8
82	0.583	0.046	0.188	0.183	100.9
83	0.532	0.177	0.126	0.165	96.9
84	0.554	0.145	0.093	0.208	97.0
85	0.583	0.065	0.183	0.170	100.1
86	0.593	0.089	0.085	0.233	96.8
87	0.537	0.204	0.181	0.079	96.0
88	0.516	0.270	0.119	0.096	93.0
89	0.601	0.110	0.074	0.215	96.4
90	0.621	0.084	0.184	0.111	97.8
91	0.586	0.177	0.082	0.155	94.0
92	0.573	0.196	0.200	0.030	94.7
93	0.651	0.065	0.048	0.236	96.0
94	0.633	0.088	0.149	0.130	96.7
95	0.590	0.183	0.124	0.103	93.9
96	0.635	0.125	0.130	0.110	94.7
97	0.629	0.179	0.015	0.178	91.0
98	0.590	0.229	0.177	0.004	91.9
99	0.596	0.222	0.166	0.016	91.8
100	0.636	0.174	0.038	0.153	91.1
101	0.649	0.178	0.023	0.150	90.0

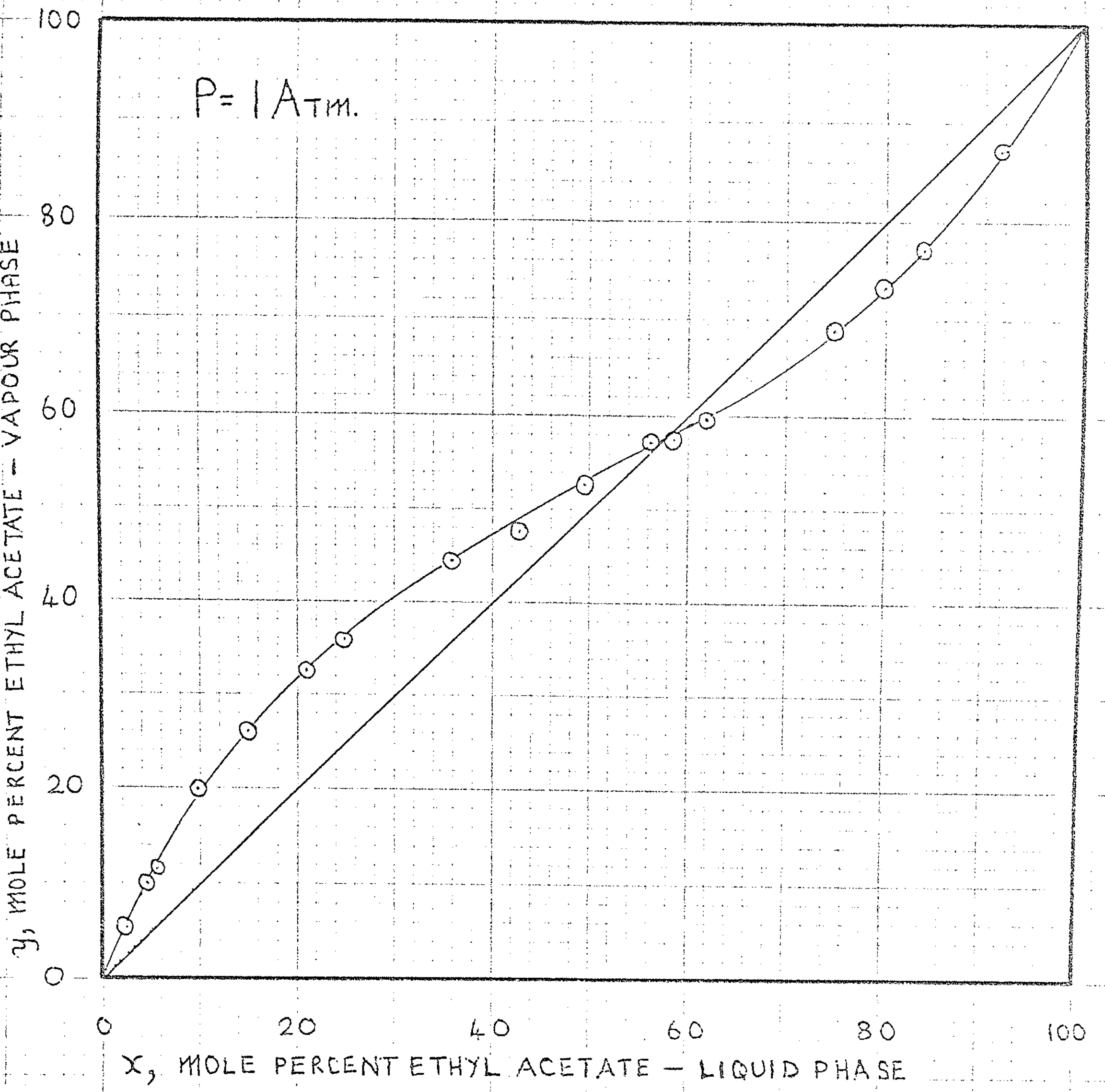


Fig 4.14 V.L.E. Curve For Ethyl Acetate–Ethyl Alcohol

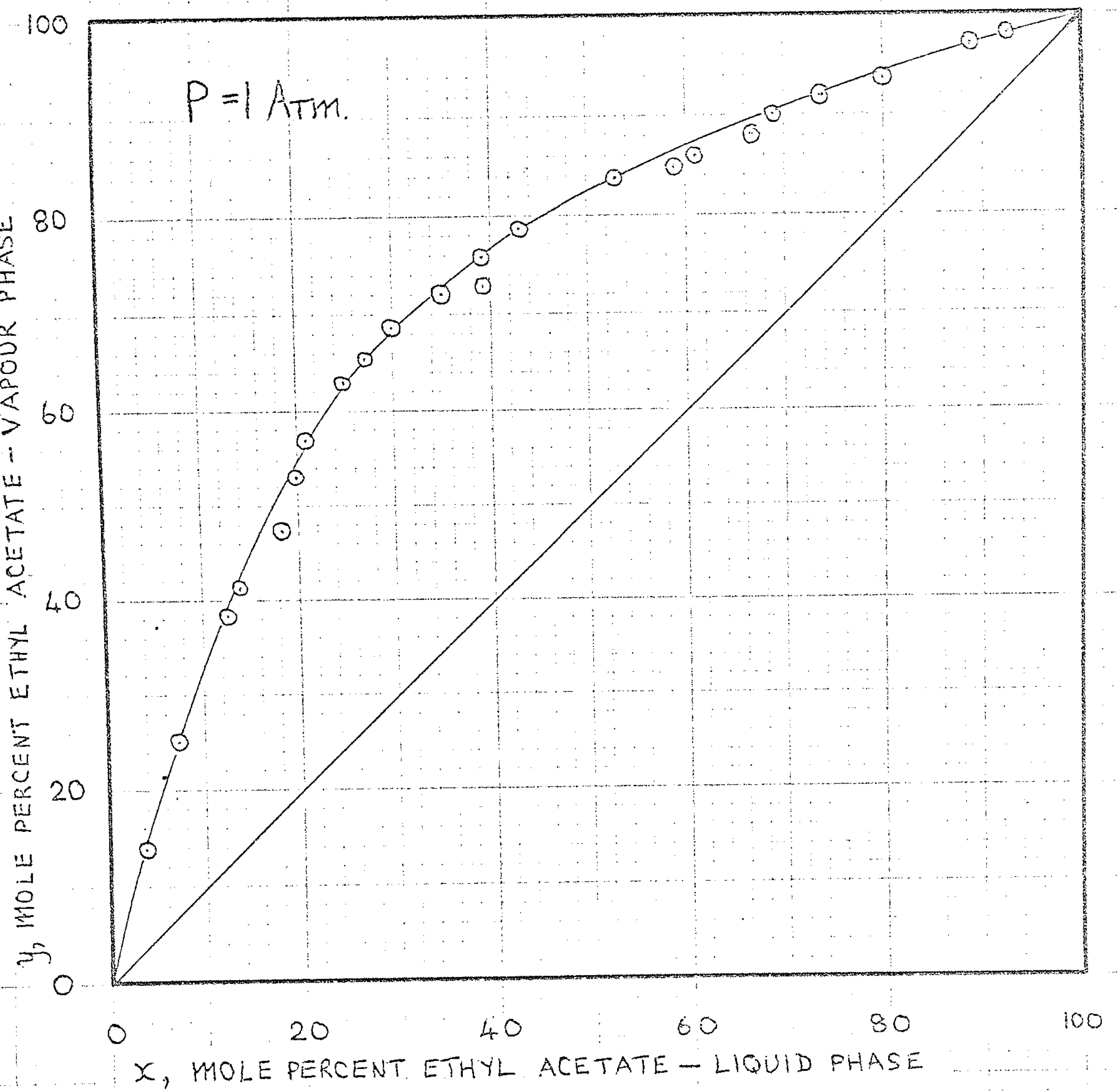


Fig 4.15 V.L.E. Curve For Ethyl Acetate-Butyl Alcohol

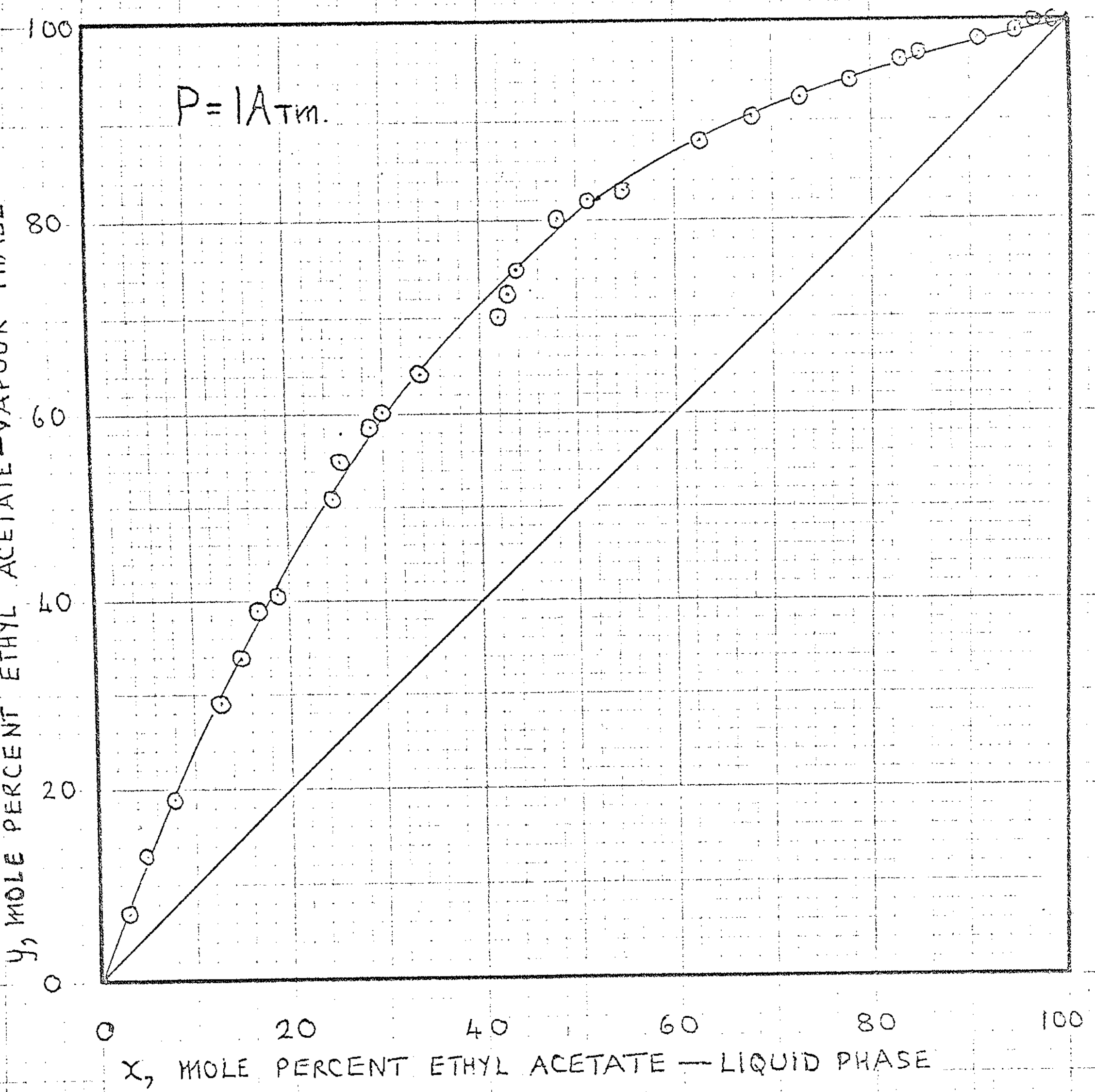


FIG 4.16 V. L. E. CURVE FOR ETHYL ACETATE—BUTYL ACETATE

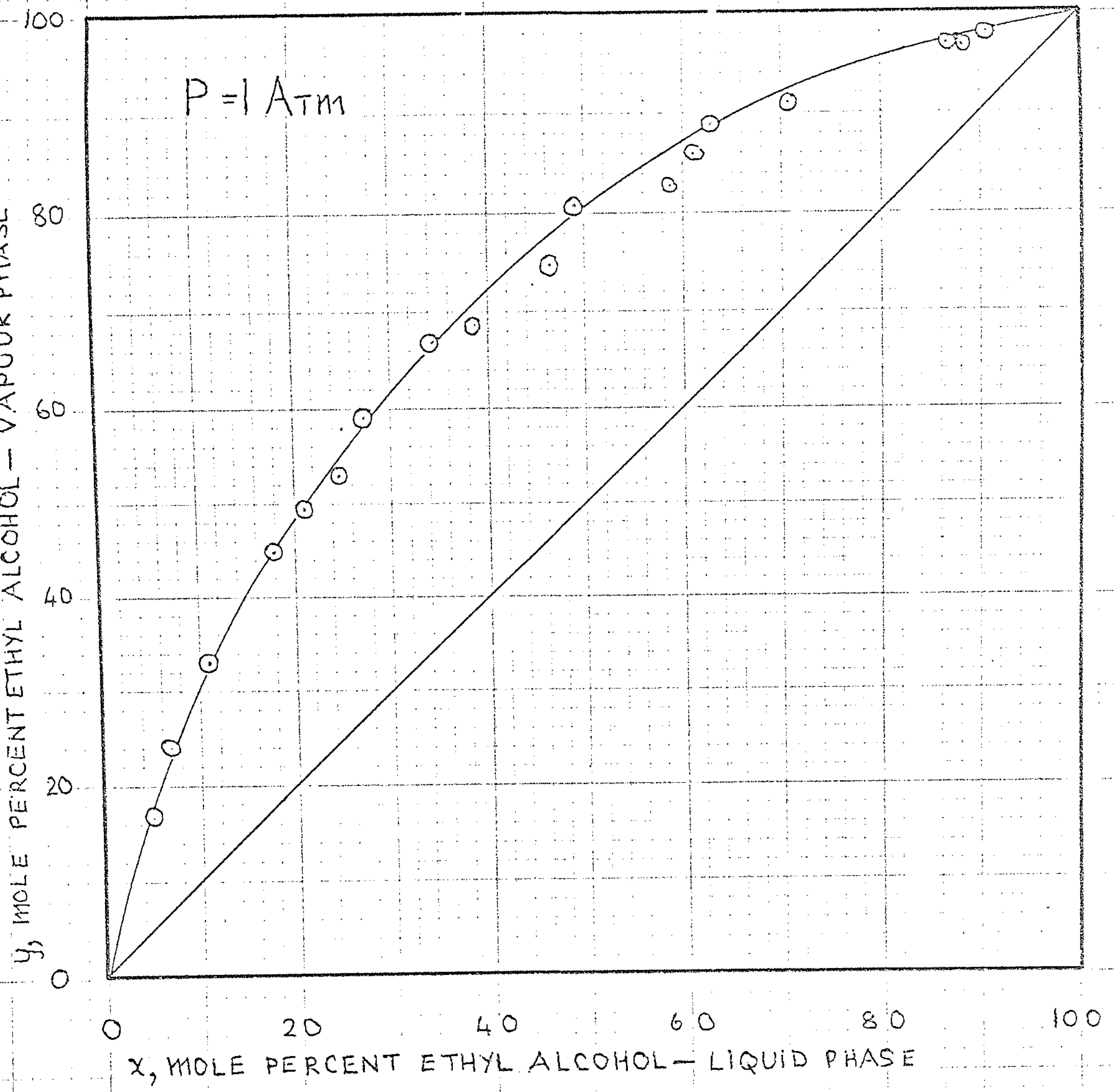


Fig 4.17 V.L.E. Curve For Ethyl Alcohol—Butyl Alcohol

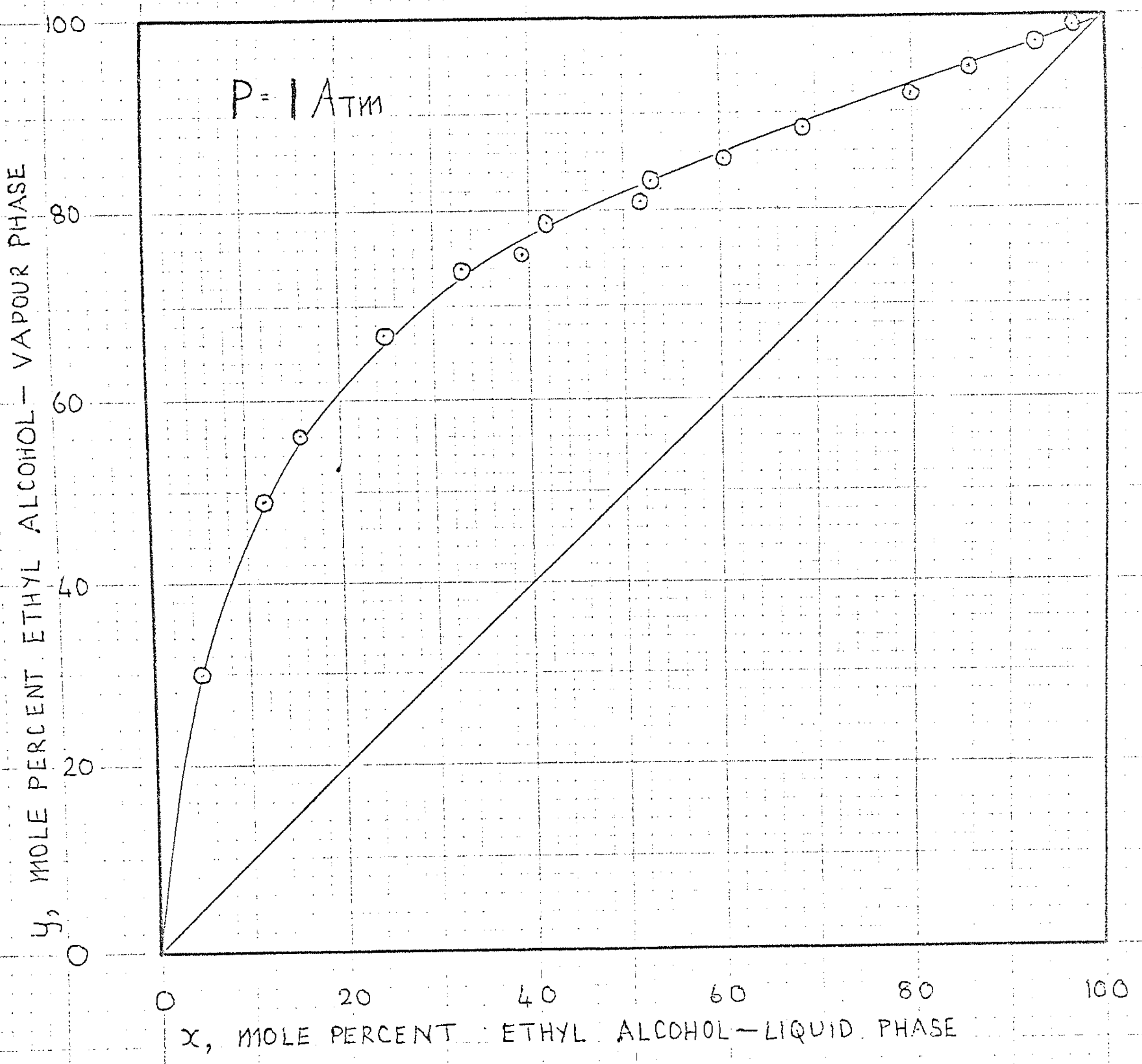


Fig 4.18 V.L.E. Curve Ethyl Alcohol Butyl Acetate

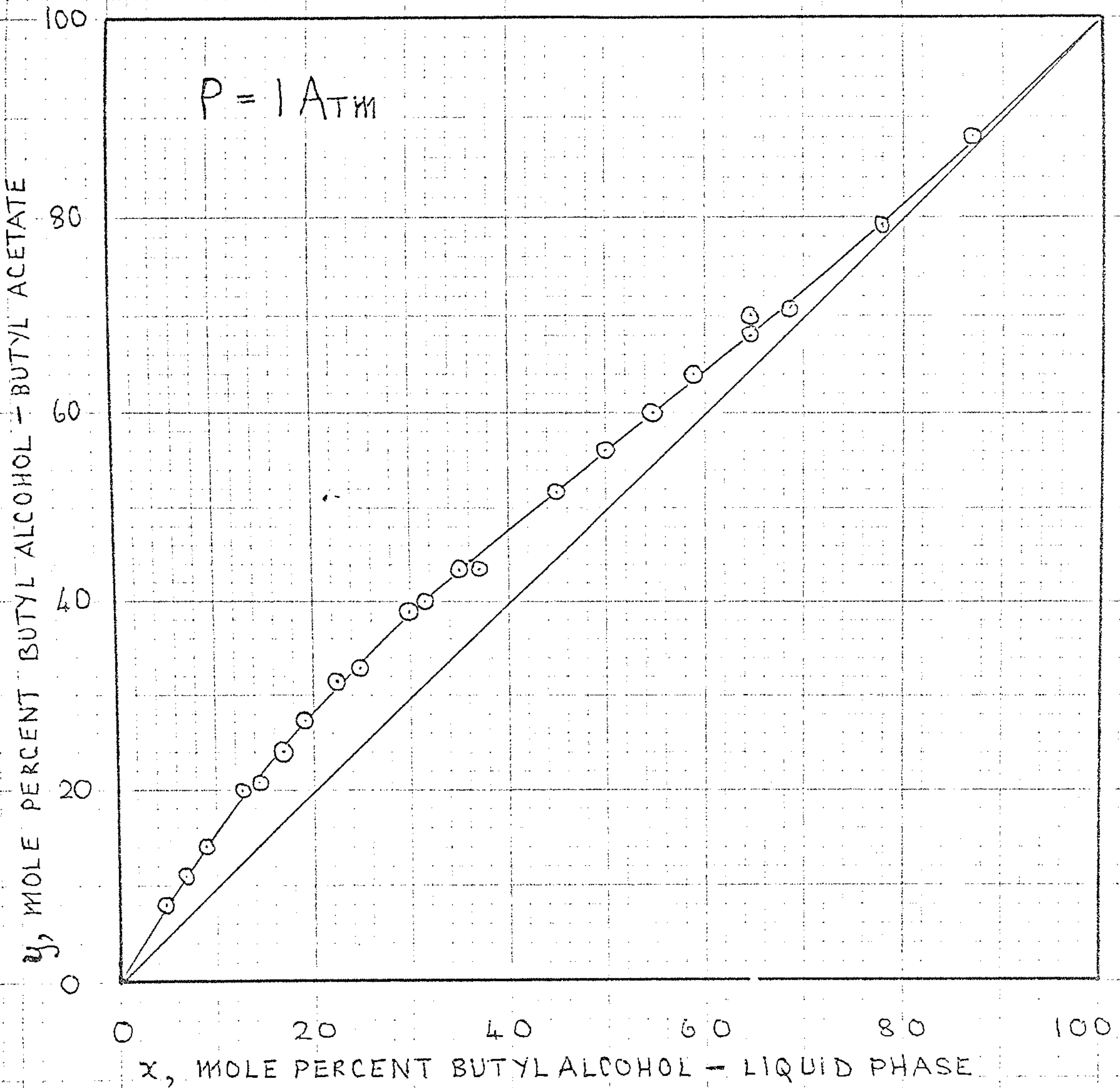


Fig 4.19 V.L.E. Curve Butyl Alcohol Butyl Acetate

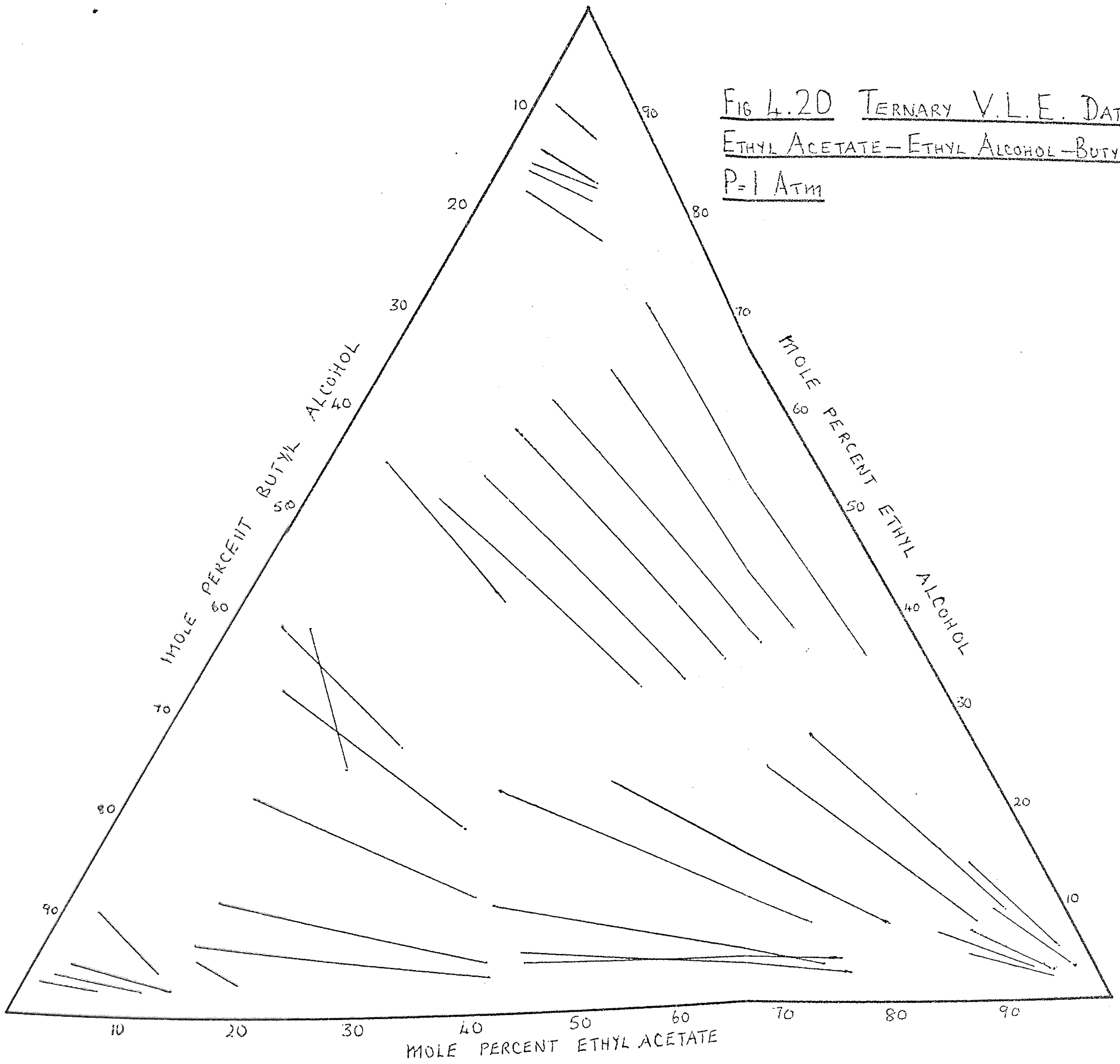


Fig 4.20 Ternary V.L.E. Data
Ethyl Acetate—Ethyl Alcohol—Butyl Alcohol.
P=1 Atm

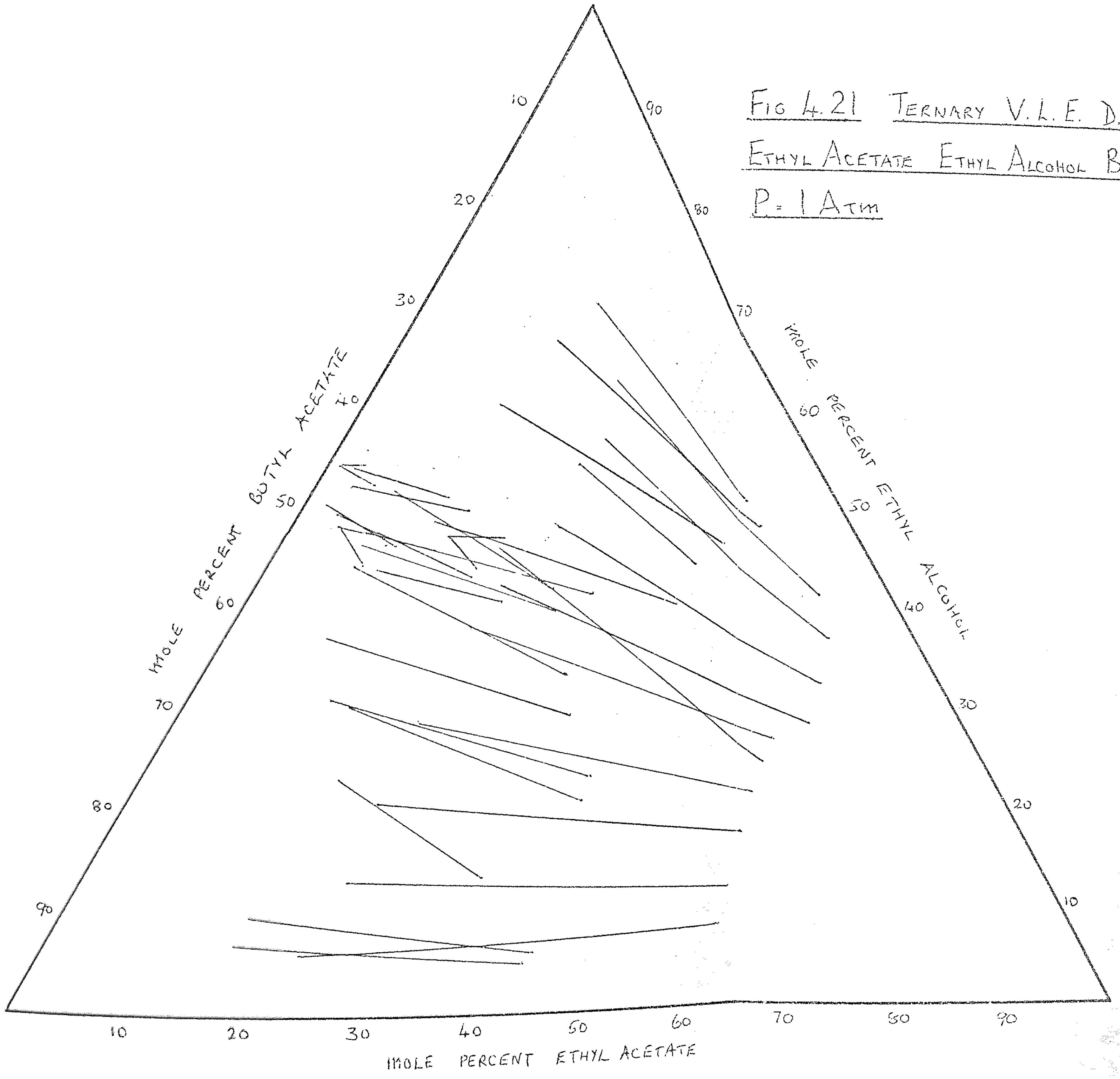


Fig 4.21 Ternary V.L.E. Data
Ethyl Acetate Ethyl Alcohol Butyl Acetate
P = 1 Atm

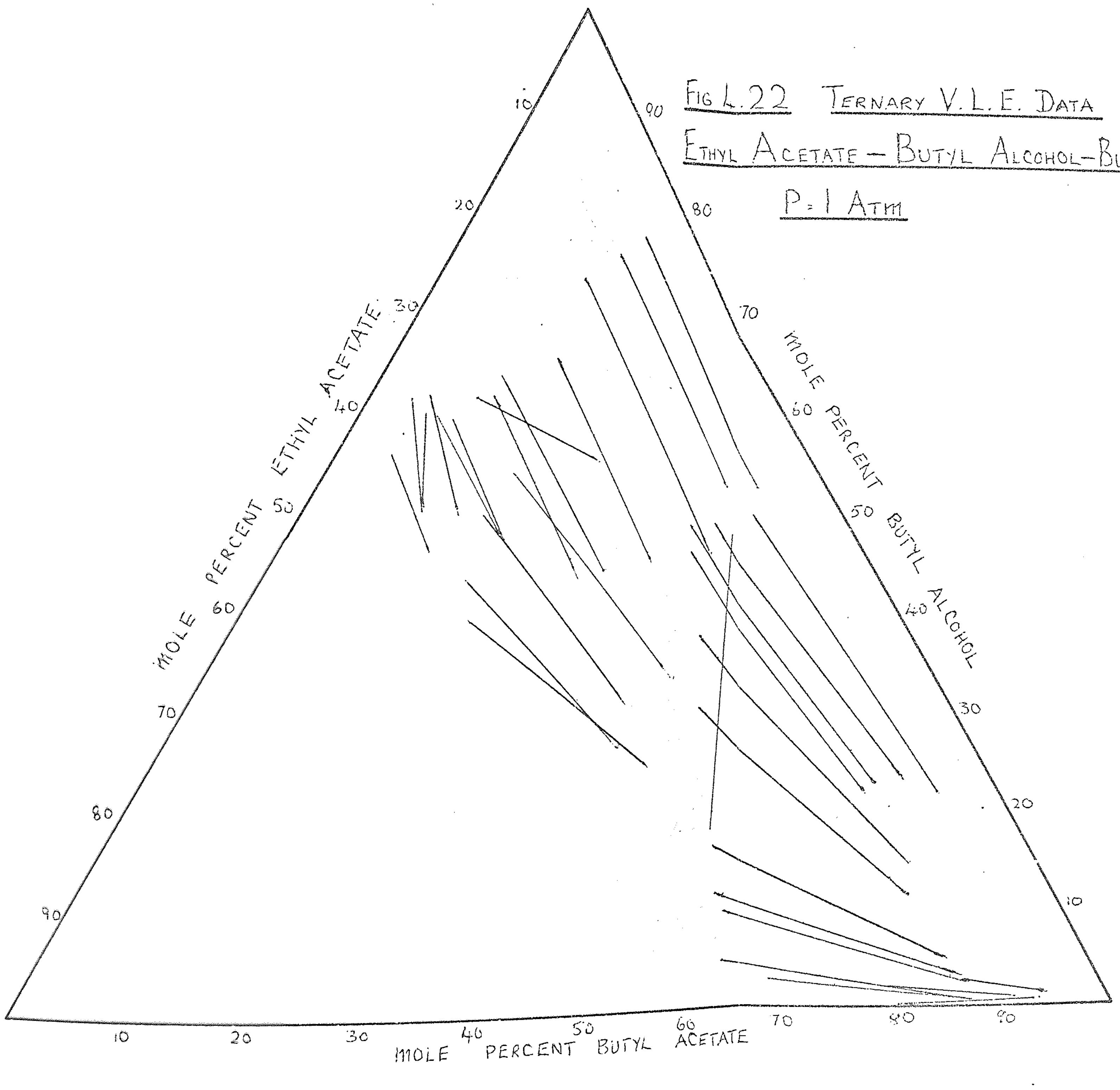


Fig 4.22 Ternary V.L.E. Data

Ethyl Acetate — Butyl Alcohol — Butyl Acetate

P = 1 Atm

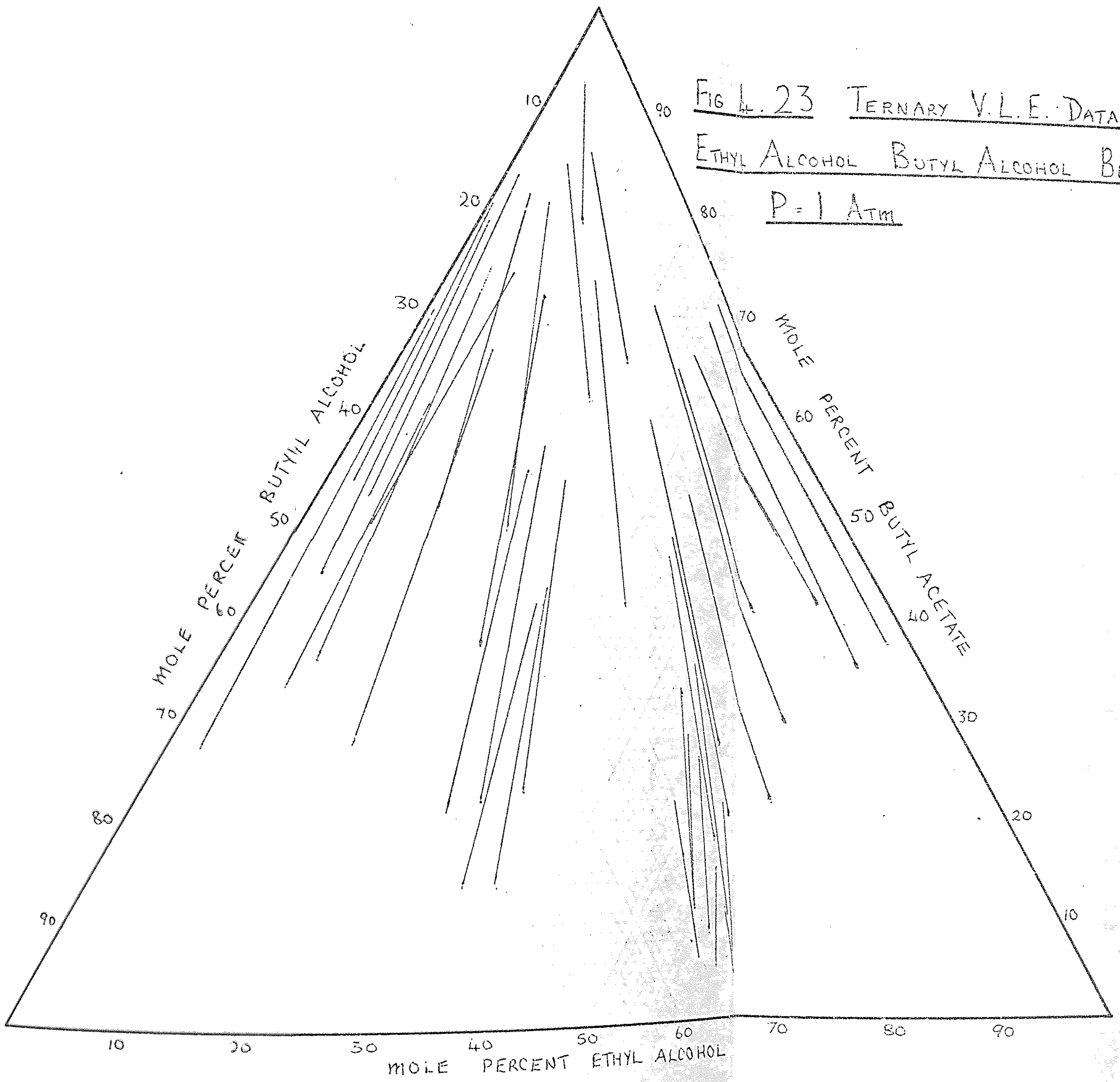


FIG 4.23 TERNARY V.L.E. DATA

ETHYL ALCOHOL BUTYL ALCOHOL BUTYL ACETATE

P = 1 ATM

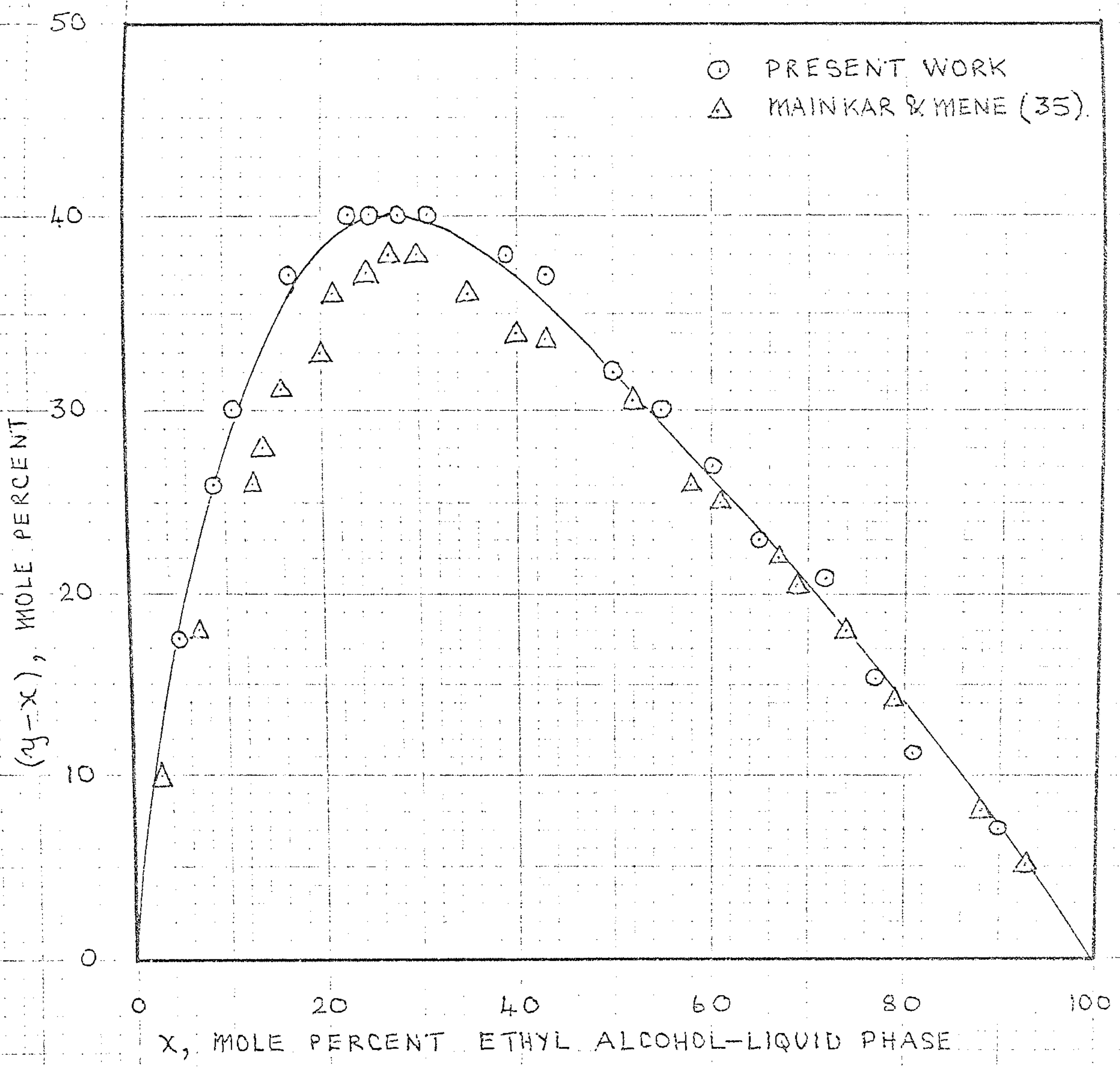


Fig 4.24 (y-x) vs x, Ethyl Alcohol-Butyl Acetate

4.7 Discussion

In general, quaternary mixtures can be bounded by six sets of experimentally determined binary data. Hence Tables 4.1 - 4.6 contain the experimental binary data for ethyl acetate - ethyl alcohol, ethyl acetate - butyl alcohol, ethyl acetate - butyl acetate, ethyl alcohol - butyl alcohol, ethyl alcohol - butyl acetate and butyl alcohol - butyl acetate systems respectively whilst Tables 4.7 - 4.10 contain the experimental ternary data for ethyl acetate - ethyl alcohol - butyl alcohol, ethyl acetate - ethyl alcohol - butyl acetate, ethyl acetate - butyl alcohol - butyl acetate, ethyl alcohol - butyl alcohol - butyl acetate respectively. The quaternary ethyl alcohol - ethyl acetate - butyl alcohol - butyl acetate data is tabulated in Table 4.11 and all the experimental determinations were carried out at an absolute pressure of one atmosphere.

The experimental binary data were visually fitted to an x - y composition graph and these are contained in Figs. 4.14 - 4.19, and the ternary data was plotted in Figs. 4.20 - 4.23. The ethyl acetate - ethyl alcohol system was found to have an azeotrope. The azeotrope composition was 57 mole per cent ethyl acetate and the equilibrium temperature was 72°C (see Table 4.1 & Fig. 4.14). These values compare favourably with those of Skljarenko & Baranajev (69) and Murti & Van Winkle (70) who obtained values of 57.3 and 57.0 mole per cent ethyl acetate for the equilibrium composition and 72.8 and 72.2 °C respectively for the equilibrium temperature. It would appear that the values obtained by Furnas & Leighton (40) of 53.8 mole per cent for the equilibrium composition were slightly in error although the equilibrium temperature of 71.8 °C was accurate. The ethyl acetate - butyl alcohol mixtures (Table 4.2 & Fig. 4.15) have been investigated by Mainkar & Mene (35) but it was difficult to compare the results due to the fact that their data had been determined at a pressure of 725 mm Hg. If a graph of (y - x) against x was drawn for the most volatile component for both sets of data, quite a close agreement is obtained for 0 - 50 mole per cent ethyl acetate liquid phase is obtained whilst the two curves coincide for the 50 - 100 mole per cent range (see Fig. 4.24). After making allowances for the difference in operating pressure it was concluded that the data was in close agreement. For the ethyl acetate - butyl acetate system, it was not possible to compare the experimental data (Table 4.3 & Fig. 4.16) as no other experimental data was available. In the determination of the activity coefficients from the data, it was observed that the behaviour of the butyl acetate was almost ideal but the behaviour of the ethyl acetate was completely different and activity coefficients which were considerably less than one were obtained, particularly for the low liquid phase concentration region of ethyl acetate. Hence the data which has been presented was not used in the later prediction model, particularly as due to the low ethyl acetate activity coefficients it was not possible to apply a consistency test. It was concluded that the unusual behaviour of the ethyl acetate could be due to analytical errors in determining the liquid phase compositions where small changes in the liquid composition could cause a large variation in the value of the activity coefficients as the ratio of small numbers was used to calculate the activity coefficient.

The equilibrium data for ethyl alcohol - butyl alcohol (see Table 4.4 & Fig. 4.17) was found to compare well with the previously reported data (72 & 73). Both the components were found to exert near ideal behaviour in the liquid phase over the whole concentration range with the activity coefficients varying by ± 0.1. As the system was almost ideal, with some activity coefficients being less than one, it was difficult to apply any consistency tests because this would involve the square roots of negative numbers. The ethyl alcohol - butyl acetate data (Table 4.5 & Fig. 4.18) demonstrated that whilst the ethyl alcohol was almost ideal over the whole concentration range, butyl acetate was non-ideal in the liquid phase. This would be expected due to the highly polar nature of butyl acetate as it had the highest di-pole moment of all the components (see Appendix C4). For the butyl alcohol - butyl acetate system (Table 4.6 & Fig. 4.19) no azeotrope was detected from the experimental observations although a fluctuation in the temperature below the lower boiling component was observed whilst in the same region the liquid phase composition was only very slightly less than the vapour phase composition for the more volatile component. Hence slight analytical errors could have disguised the presence of an azeotrope although one author (74) detected an azeotrope at 116.5 °C and 72.9 mole per cent liquid phase butyl alcohol whilst another worker (75) did not observe an azeotrope.

Before the experimental binary data could be used for predicting quaternary vapour liquid equilibrium compositions, it was decided to perform consistency tests on the data so that a sound basis for the prediction technique would exist. There are a number of thermodynamic consistency tests available for both isothermal and isobaric binary data. Herington (107) has developed the equal-area method for isobaric and isothermal data from the Gibbs-Duhen equation. The log of the ratio of the activity coefficients is plotted against the more volatile component liquid phase composition over the whole composition range, and a smooth curve is obtained. The areas under the two halves of the curve (A, B) are calculated and related by equations 4.1 & 4.2:-

$$I = |(A - B)| \qquad 4.1$$

$$\Sigma = |(A + B)| \qquad 4.2$$

Using 4.1 & 4.2, the percentage deviation (D) can be calculated from 4.3:-

$$D = \frac{100 \times I}{\Sigma} \qquad 4.3$$

The function J is calculated from 4.4 using the binary boiling point data:-

$$J = \frac{150 \times \theta}{T_i} \qquad 4.4$$

where T_i = the absolute temperature of the lower boiling point component unless there is an azeotrope when it equals the boiling point of the minimum boiling azeotrope.

θ = The boiling point difference of the pure components if no azeotrope is formed.

θ = The difference of the minimum boiling point azeotrope and the higher component boiling point.

Herington (107) applied the above equations to a wide range of binary systems whose boiling point data (θ) varied between 10 and 94 deg C. The data was found to be consistent if equation 4.5 held

$$(D - J) < 10 \qquad 4.5$$

For four of the binary equilibrium determinations, ethyl acetate - ethyl alcohol, ethyl acetate - butyl alcohol, ethyl alcohol - butyl acetate and butyl alcohol - butyl acetate, the values of the log of the ratio of the activity coefficients were plotted against the liquid phase equilibrium composition. From these graphs (Figs. 4.25 - 4.28) the areas for each part of the curve above and below the abscissa were determined and the Herington consistency test was applied. For all the four binary equilibrium mixtures, equation 4.5 was found to hold and hence the systems were judged to be consistent (see Table 4.23).

Table 4.23 Consistency Tests

	D	J	D - J
ETAC - ETOH	7.45	2.82	4.63
ETAC - BUOH	11.06	17.08	-6.02
ETOH - BUAC	29.39	20.53	8.86
BUOH - BUAC	10.75	3.19	7.46

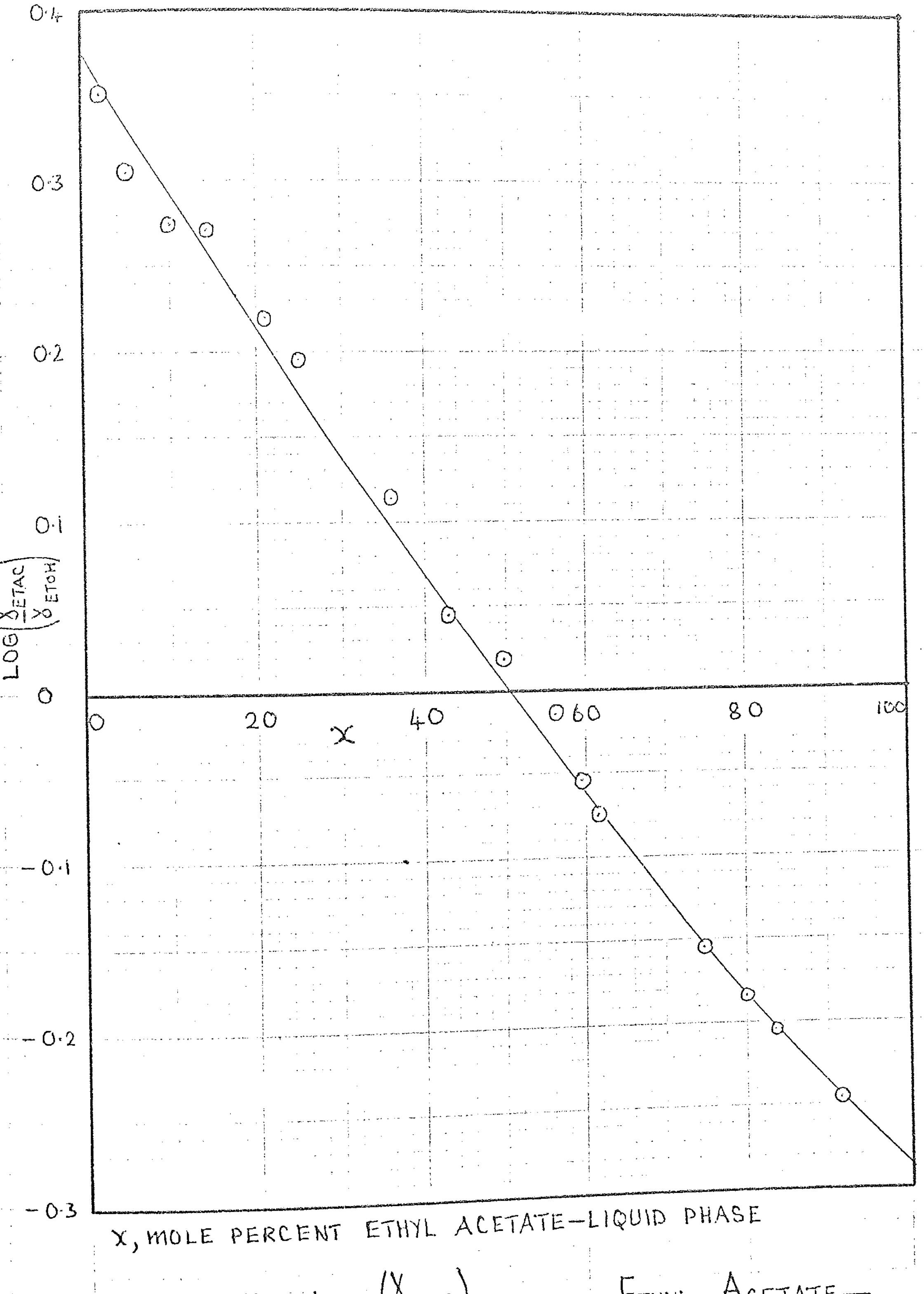


FIG 4.25 $\text{LOG}\left(\frac{\gamma_{ETAC}}{\gamma_{ETOH}}\right)$ VS x, ETHYL ACETATE–ETHYL ALCOHOL.

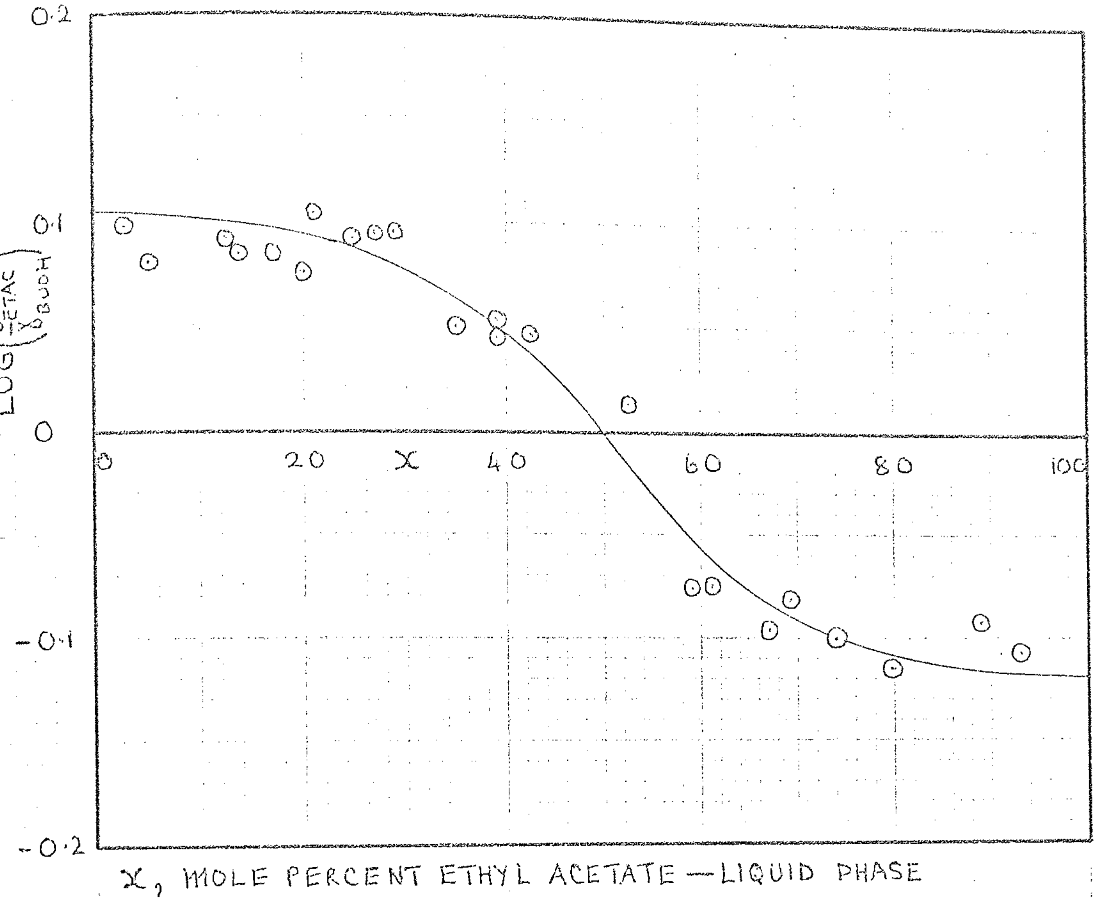


Fig 4.26 $Log\left(\frac{\gamma_{ETAC}}{\gamma_{BUOH}}\right)$ vs x, Ethyl Acetate — Butyl Alcohol

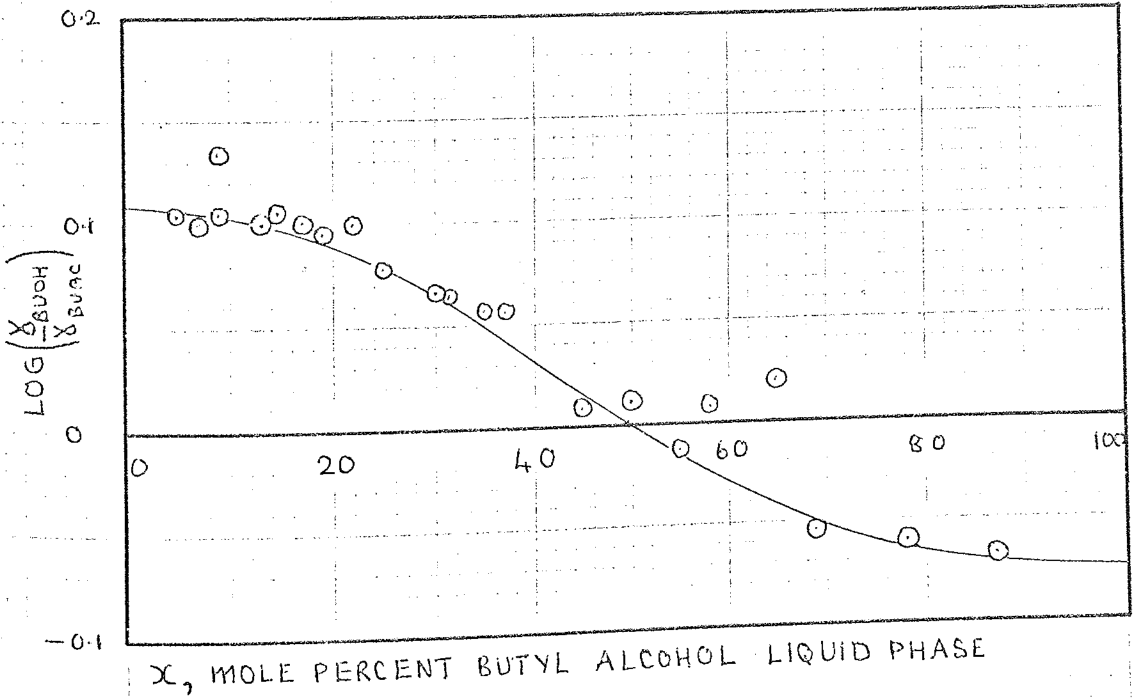


Fig 4.27 $Log\left(\frac{\gamma_{BUOH}}{\gamma_{BUAC}}\right)$ vs x, Butyl Alcohol — Butyl Acetate

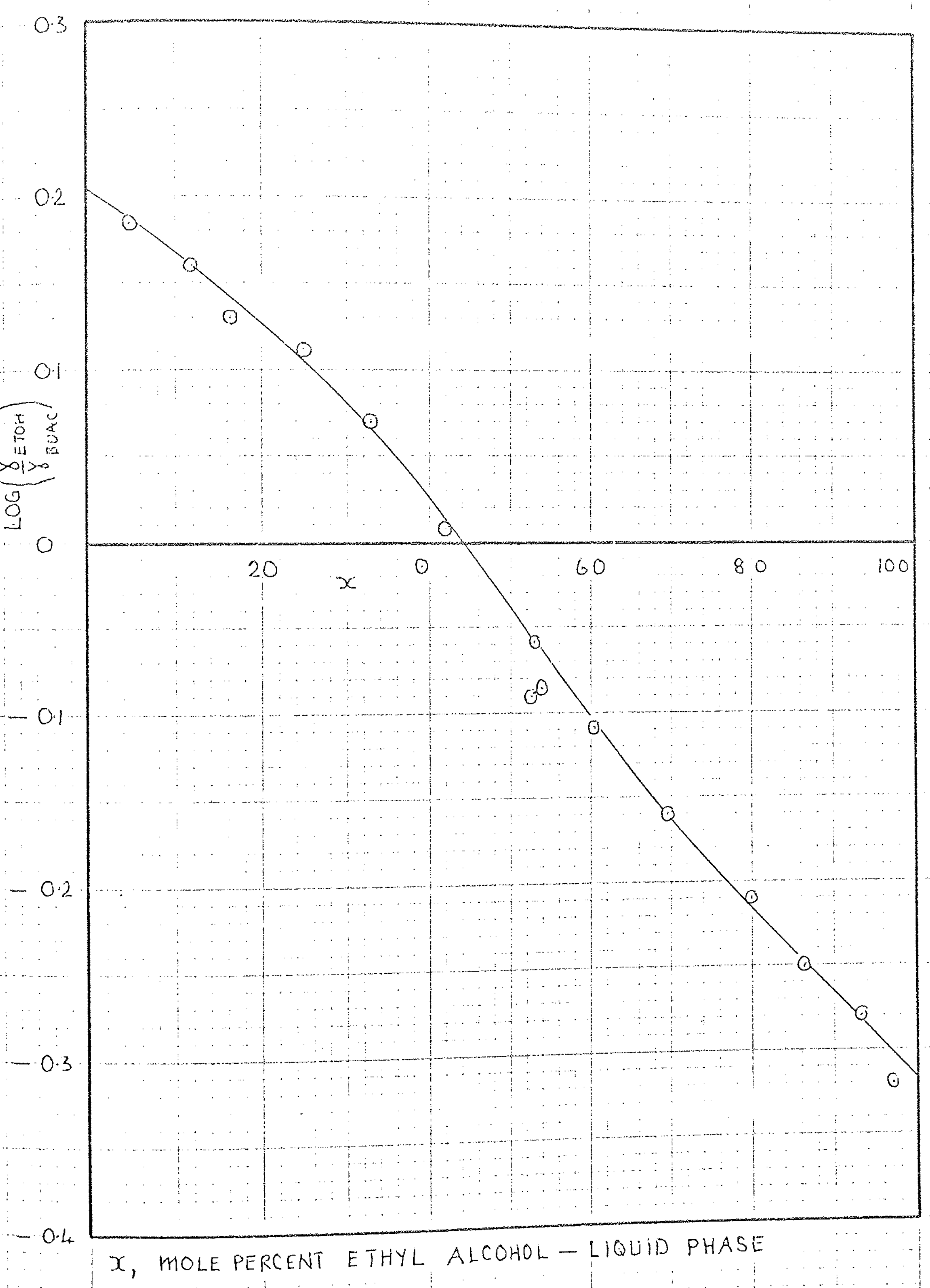


FIG 4.28 LOG $\left(\frac{\gamma_{ETOH}}{\gamma_{BUAC}}\right)$ VS x, ETHYL ALCOHOL—
BUTYL ACETATE

In the study of continuous distillation with a reversible chemical reaction where the transesterification reaction between an alcohol and an ester was involved, it was appreciated that a technique would be required to predict accurately quaternary vapour liquid equilibrium mixtures over a wide composition range. In the past graphical construction and interpolation techniques have been used but they are limited in their application and accuracy. Mamers (66) used a graphical technique to predict ternary mixtures by constructing an equilibrium graph relating the x - y data for two of the components in a constant concentration band of the third component. From a set of six graphs which completely bounded the ternary data, it was possible to predict K values of all the components for a given liquid phase composition from either of the concentration of the remaining two components. Therefore it was possible to obtain two K values for each component in the mixture and these values did not necessarily agree and were often in error by about 5 per cent. A graphical method has also been proposed by Hollo & Lengyel (109) which is a quaternary diagram based upon a two dimensional projection of a tetrahedron. As graphical techniques can involve construction errors and also be time consuming, it was decided to predict quaternary mixtures from a mathematical basis.

Suzuki et al (110) have investigated techniques available for predicting the quaternary vapour liquid equilibrium mixtures obtained in the continuous distillation of esters. They concluded that if the system was almost in equilibrium, the data could be predicted from the component binary data which was correlated by the Wilson parameters. In the correlation, allowance was made for the association into dimers and trimers of acetic acid. A good correlation of the reactive quaternary was obtained from the six binary systems assuming that no reaction occurred in the binaries. Sabylin & Aristovich (111) have made a recent comparison of the various ways of predicting quaternary and ternary data from the binary isothermal data. Data for thirty ternary and four quaternary systems all of which deviated from ideality, were predicted by Wilson, Van Laar, Margules, Wohl and Hala equations. It was concluded that the Wilson equation gave the best predictions and the Wohl and Hala equations gave the poorest prediction for multicomponent data from the binary data. Although not quite as accurate as the Wilson equation, the Van Laar equation still predicted the data well.

As a first approach it was decided to predict the quaternary data using the Van Laar equations and constants. King (112) has quoted the following relationships between the two Van Laar constants A_{AB} and A_{BA} for a binary system containing components A and B:-

$$\left(\log \gamma_A\right)^{\frac{1}{2}} = \left(A_{AB}\right)^{\frac{1}{2}} - \left(\frac{A_{AB}}{A_{BA}}\right)^{\frac{1}{2}} \left(\log \gamma_B\right)^{\frac{1}{2}} \quad \text{———} \quad 4.6$$

A graph of $\left(\log \gamma_A\right)^{\frac{1}{2}}$ against $\left(\log \gamma_B\right)^{\frac{1}{2}}$ should be linear for a binary system which obeys the Van Laar equation. From the graph, the values of A_{AB} and A_{BA} can be calculated from the intercept on the ordinate and the gradient respectively.

$\left(\log \gamma_A\right)^{\frac{1}{2}}$ was plotted against $\left(\log \gamma_B\right)^{\frac{1}{2}}$ for ethyl acetate - ethyl alcohol, ethyl acetate - butyl alcohol, ethyl alcohol - butyl acetate and butyl alcohol - butyl acetate systems (see Tables 4.12, 13, 16, 17 & Figs. 4.30 - 4.33). The straight lines were fitted by

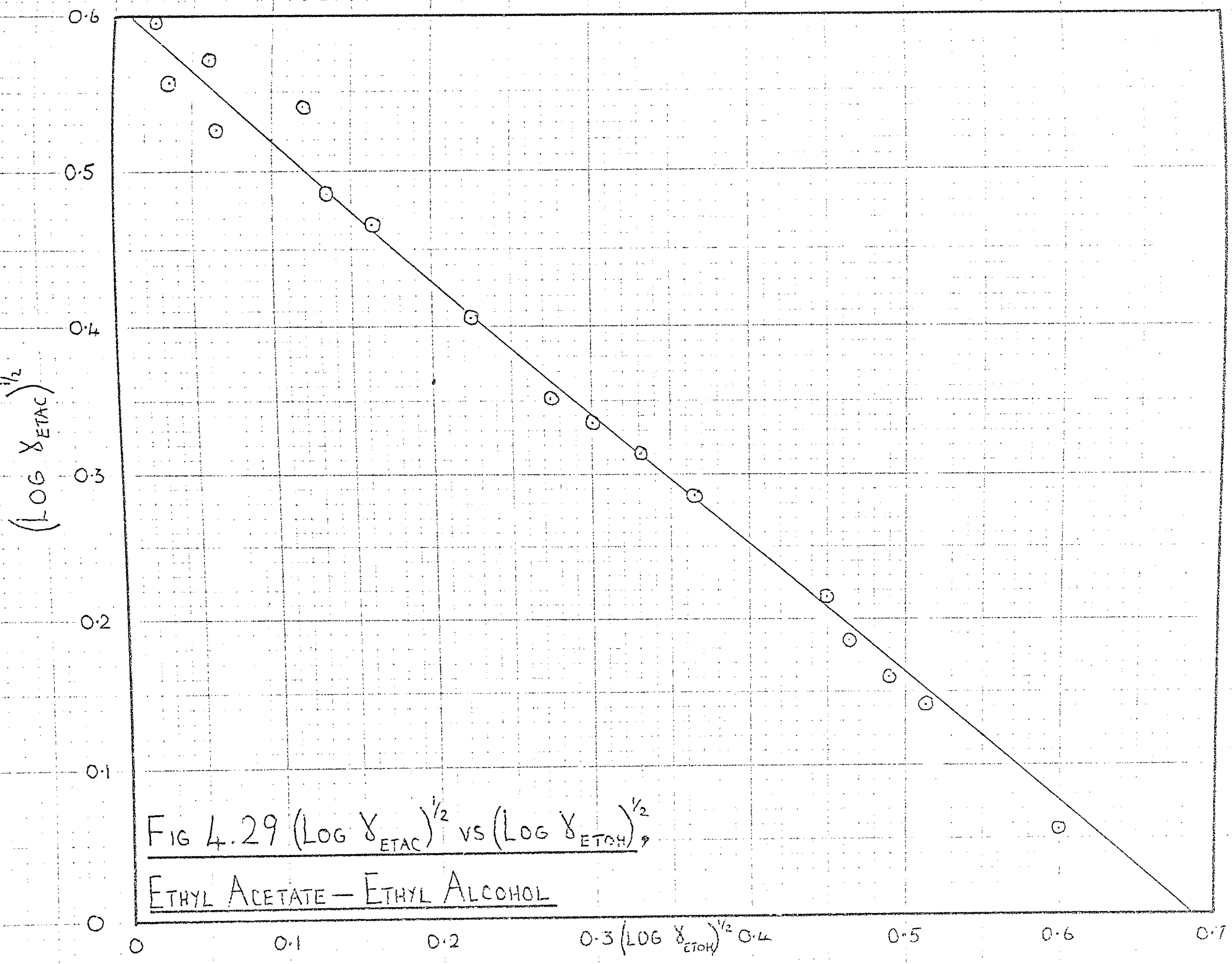


Fig 4.29 $(\log \gamma_{ETAC})^{1/2}$ vs $(\log \gamma_{ETOH})^{1/2}$,

Ethyl Acetate — Ethyl Alcohol

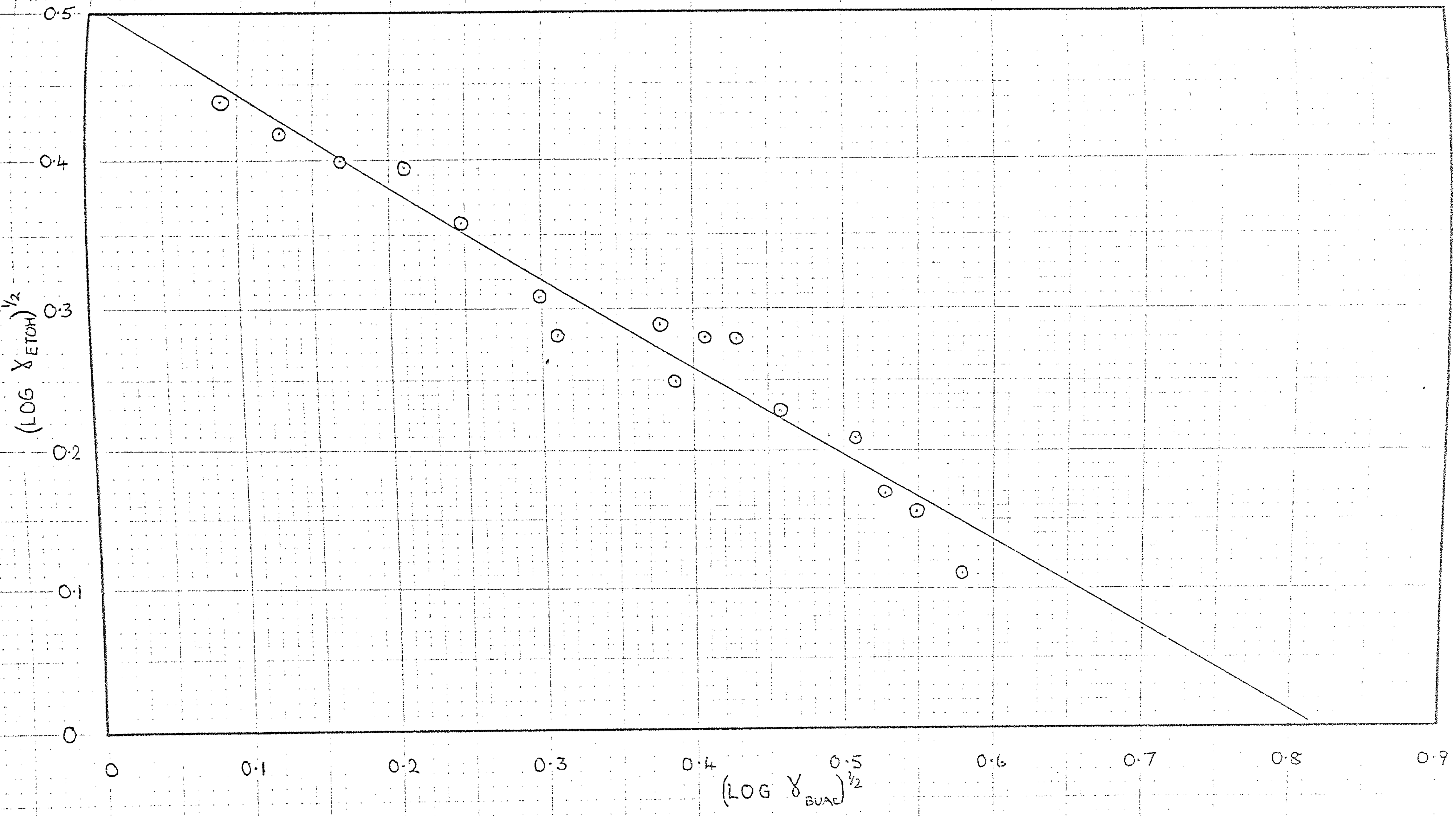


Fig 4.30 $(\text{Log}\ \gamma_{\text{ETOH}})^{1/2}$ vs $(\text{Log}\ \gamma_{\text{BUAC}})^{1/2}$, Ethyl Alcohol – Butyl Acetate

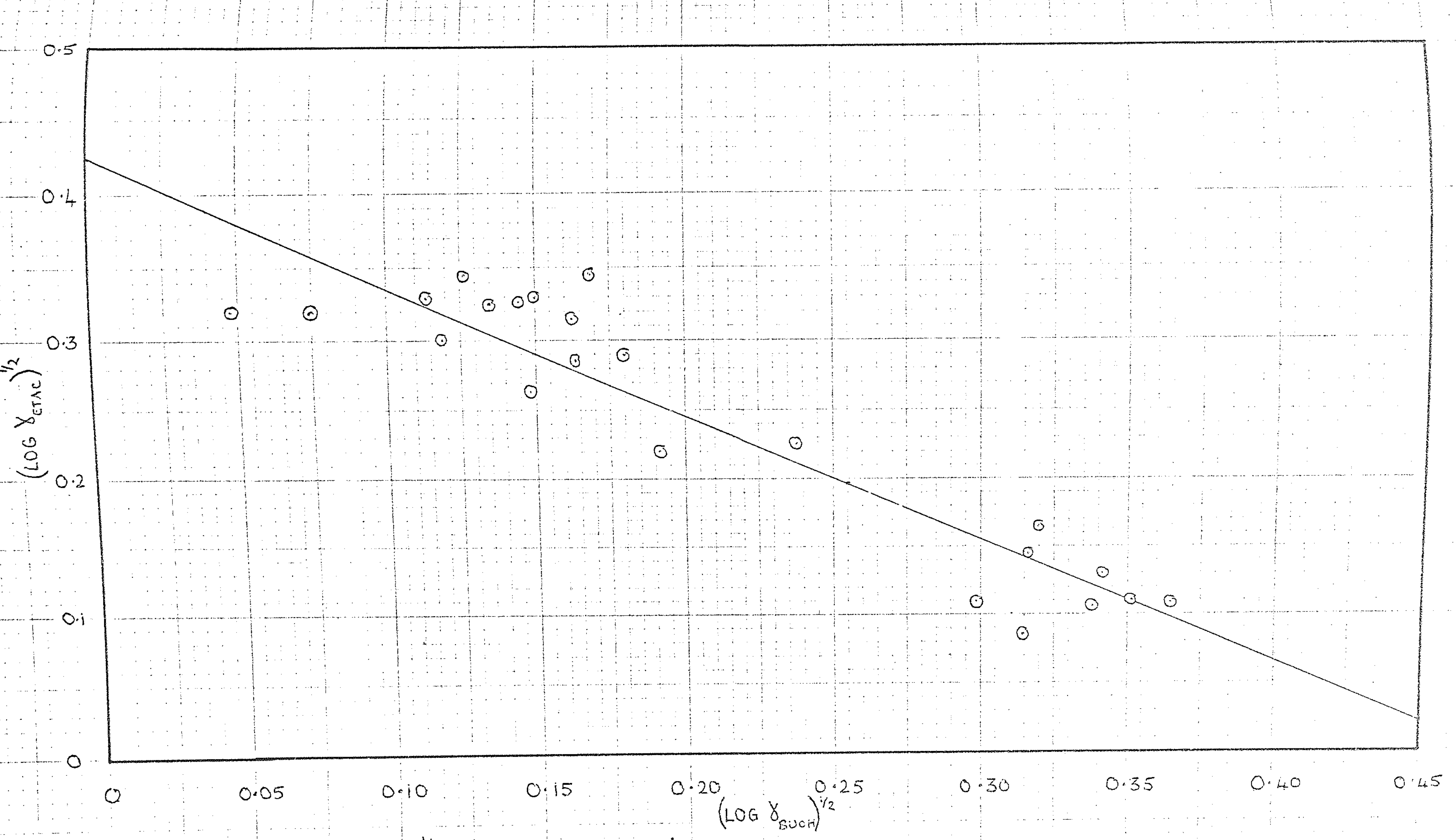


FIG 4.31 $(\text{LOG } \gamma_{\text{ETAC}})^{1/2}$ VS $(\text{LOG } \gamma_{\text{BUOH}})^{1/2}$, ETHYL ACETATE — BUTYL ALCOHOL

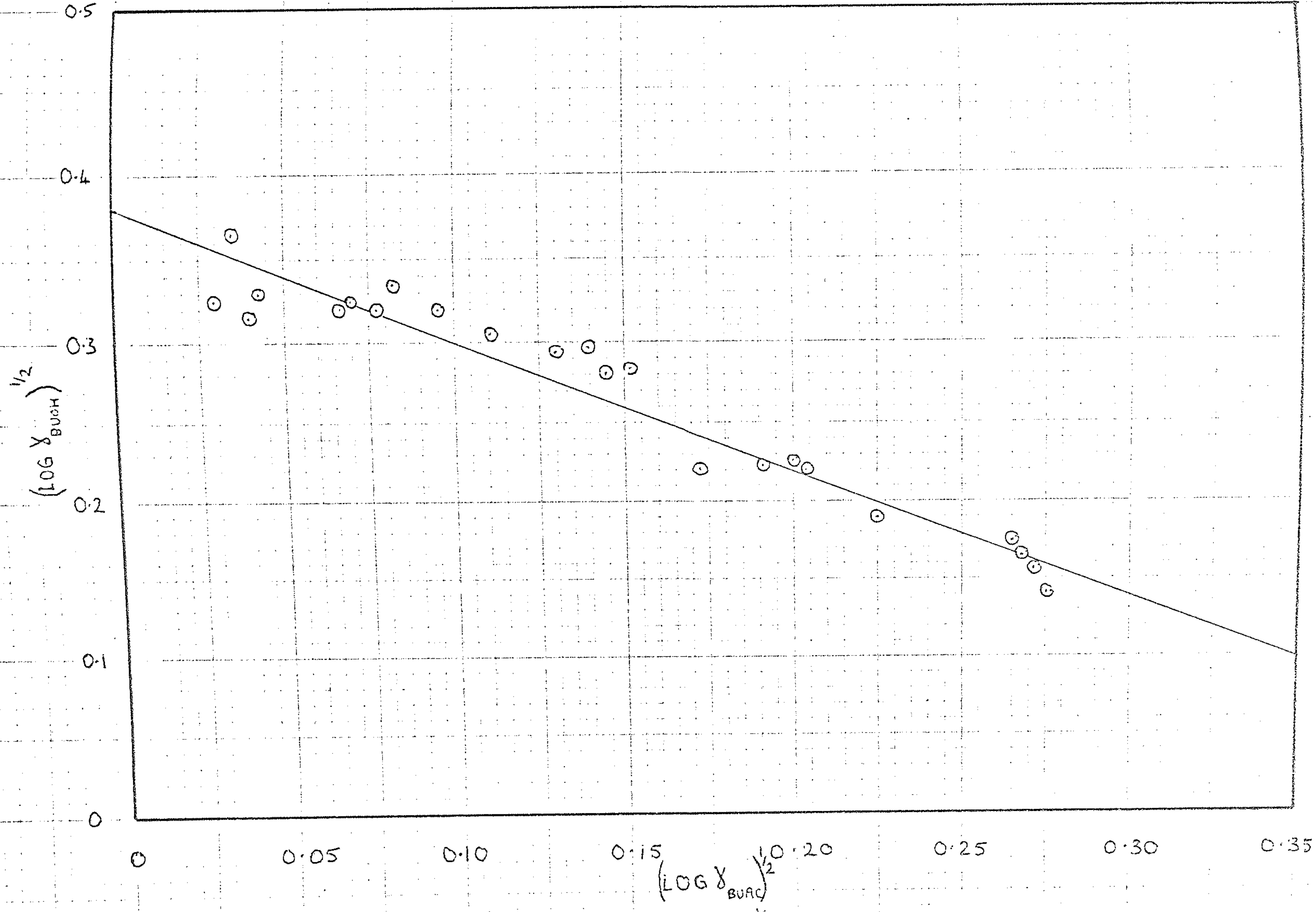


Fig 4.32 $(\log \gamma_{BUOH})^{1/2}$ vs $(\log \gamma_{BUAC})^{1/2}$, Butyl Alcohol — Butyl Acetate

the least mean squares technique (67) and the Van Laar constants were calculated from the gradients and intercepts. The Van Laar constants for ethyl acetate - butyl acetate and ethyl alcohol - butyl alcohol systems were set to zero as for the former ideality had to be assumed due to the low experimental values of the ethyl acetate activity coefficients whilst for the latter the system was almost ideal. As some of the activity coefficients were less than one it was not possible to calculate the square root of a negative log. Hala (113) has calculated the Van Laar constants from Brunje's and Bogart's (72) data and values of $A_{AB} = 0.0011$ & $A_{BA} = -0.0013$ were obtained and consequently it was thought that using zero Van Laar constants for the ethyl alcohol - butyl alcohol system were justified. The values of all the Van Laar constants are summarised in Table 4.24:-

Table 4.24 Van Laar Constants

System	A_{AB}	A_{BA}
ethyl alcohol - ethyl acetate	0.455	0.370
ethyl alcohol - butyl alcohol	0.000	0.000
ethyl alcohol - butyl acetate	0.253	0.667
ethyl acetate - butyl alcohol	0.182	0.226
ethyl acetate - butyl acetate	0.000	0.000
butyl alcohol - butyl acetate	0.225	0.144

The quaternary and ternary mixtures were predicted from the liquid phase compositions using the bubble point computer programme of Prausnitz et al (114). The pure component data which was required for the operation of the programme is tabulated in Appendix C4.

In order to test the accuracy of the prediction programme, the values of the vapour compositions which had been predicted by the programme (see Tables 4.18 - 4.22) were compared with the experimentally determined vapour compositions. The vapour compositions were predicted from the experimentally determined equilibrium liquid phase compositions. A comparison was made for 101 quaternary results (see Table 4.22). Ma et al (115) have used a similar method to judge the accuracy of a computer programme which was predicting the vapour liquid equilibrium of the moderately non-ideal 1,2 dichloroethane—n-propanol—toluene—acetone system from a total of 266 experimental points which had a 54 deg C boiling range at 700 mm Hg. Binary Wilson constants were used in the prediction of the quaternary equilibrium data and the accuracy of the technique was determined from the root mean square deviation of the vapour phase concentration which is defined by equation 4.7:-

$$\sqrt{\left\{\left[\sum_{j=1}^{M}\sum_{i=1}^{N}\left(y_{ji,\ exp} - y_{ji,\ pred.}\right)^{2}\right]\Big/_{MN}\right\}} \qquad \text{—— 4.7}$$

and the temperature error was calculated from equation 4.8:-

$$\sqrt{\left[\left\{\sum_{j=1}^{M}\left(T_{j,\ exp} - T_{j,\ pred.}\right)^{2}\right\}\Big/_{M}\right]} \qquad \text{—— 4.8}$$

where M = number of experimental determinations

N = number of components

$y_{ji,pred.}$ = correlated vapour concentration of the i^{th} component in the j^{th} experimental point (mole fractions)

$y_{ji,\ exp}$ = experimental vapour concentration of the i^{th} component in the j^{th} experimental point (mole fractions).

For the moderately non-ideal quaternary system, Ma et al (115) concluded that if a set of data could be shown (to be well correlated by a multicomponent thermodynamic equation) such as the Wilson equation, then the assumption that the data was inconsistent could not be justified. In conjunction with this premise, an arbitary limit for the root mean square deviation in the vapour concentration of 0.015 mole fraction was used to indicate a good correlation. Using a similar approach, the root mean square deviation for the vapour phase concentrations were calculated for the 101 quaternary points and the four ternary experimental systems (totalling 151 points) and they are tabulated in Table 4.25:-

Table 4.25 Root mean square deviations for the vapour phase concentration and the equilibrium mixture's boiling point

System	No. of Points	R. M. S. D.	
	M	y mole fraction	T °C
ETAC - ETOH - BUOH	38	0.024	1.78
ETAC - ETOH - BUAC	40	0.022	2.61
ETAC - BUOH - BUAC	35	0.018	1.13
ETOH - BUOH - BUAC	38	0.017	2.83
ETAC - ETOH - BUAC - BUOH	101	0.019	2.63

It was found that the quaternary root mean square deviation was 1.87 mole per cent which was slightly greater than the arbitary limit set by Ma et al (115). It was recognised that a greater error could be obtained from a prediction model which was based upon the Van Laar constants rather than the Wilson parameters. Suzuki et al (110) in their prediction model for esters and alcohols (a system containing polar, hydrogen-bonding and associating components) obtained errors in the vapour phase compositions for a four component system of between 1.17 and 4.15 mole per cent whilst the temperature error was 2.0492 °C and they observed that for the particular system in question, a good correlation had been obtained.

It was concluded from the root mean square deviations of the vapour phase concentration and in particular with reference to the previously reported errors obtained in using the Wilson prediction model, that the Van Laar correlation would be accurate enough to be used as a prediction model particularly as from an examination of the distillation column concentration profiles, the quaternary system predominated.

Section 5.

DISTILLATION WITH CHEMICAL REACTION.

5.1 Literature Survey

5.1.1 Introduction

A large amount of patent literature exists concerning distillation with chemical reaction. This literature refers to the design of the equipment or to the application of a particular process and it can be further categorised into the columns where the chemical reaction takes place in the reboiler and is generally a batch-reactor or where the reaction takes place in the column is generally a continuous reaction system.

The latter system is exemplified by a distillation column where an esterification is taking place. As the reaction is

$$\text{ALCOHOL} + \text{ACID} \rightleftharpoons \text{ESTER} + \text{WATER}$$

an equilibrium reaction, the reaction equilibrium can be displaced in favour of the product ester by the continual removal of the product water. Such a distillation column is typified by the use of large plate and reboiler holdups, low liquid and vapour flowrates which give the necessary large residence times to provide completion of the reaction.

Distillation columns in which a chemical reaction is being carried out are sometimes used where it is necessary to suppress a side reaction. The suppression is achieved by the continual removal of a volatile product which would cause a side reaction with one of the reactants. An example of this phenomenon occurs in the transvinylation of vinyl acetate by stearic acid. The reaction is normally carried out in a batchwise reactor but recent workers (118-9) have utilised a distillation with chemical reaction technique with the result that the product vinyl stearate is removed from the bottom of the column free from the impurity ethylidene acetate. This impurity is normally formed in the batch reactor from the side reaction between acetic acid and vinyl acetate.

The design of batch-reactor columns where the bulk of the reaction takes place in the reboiler, can be predicted by the use of traditional design techniques.

5.1.2 Equipment

An early patent was awarded to Backhaus (120) in 1921 relating distillation with chemical reaction for the design of a distillation reaction plate. Since then Keyes (121) has reviewed the subject in the period 1921-32 whilst Rose (122) has surveyed the period of 1941-54 and Mamers (66) has listed some of the patents granted between 1955 and 1960. Bolles and Fair (123) have reviewed the advances in the distillation field since 1962 but the only references to distillation and chemical reaction are in connection with chemical reaction and absorption in a packed or plate column. The same conclusion can be drawn from two recent reviews of the distillation field by Holdsworth (124).

An apparatus has been described for producing esters from their reactants by avoiding the formation of the ester-alcohol azeotrope. This is achieved by introducing an organic azeotropic agent into the top of the packed distillation column. The agent acts as a dehydrating agent and removes the product water from the reaction zone thus causing the reaction to proceed to near completion. The product ester is removed continuously from the bottom of the column whilst the organic agent and water mixture is removed from the top of the column. The organic agent is recovered by separation in a gravity settler and then is returned to the column (108).

5.1.3 Processes

A number of processes have been recorded in the literature and the majority of these have been carried out in bubble-cap plate distillation columns whilst some have been carried out in sieve plate distillation columns. The systems which have been studied can be divided into irreversible reactions and reversible reactions. The hydrolysis of acetic anhydride is the irreversible reaction which has been most frequently used whilst esterifications are the reversible reactions which have been widely studied.

Parker (125) has used a column to react ethylene oxide with water to produce ethylene glycol. As water is one of the more volatile components, it was distilled away from the feed plate whilst ethylene glycol being the least volatile component, passed down the column. Thus the reaction product and one of the reactants were quickly removed from the reaction zone and consequently the conversion of ethylene glycol to diethylene and triethylene glycol was minimised and conversions approaching one hundred per cent were obtained. No details concerning the mechanical construction of the column, the flowrates and compositions were given but it was stated that a stoichiometric feed was used.

The production of hydrocarbon halides using phosphorus and methyl alcohol was reported by Matz (126) using the following reaction:-

$$3CH_3OH + 3X + P \longrightarrow 3CH_3X + H_3PO_3$$

However, the only information published was that the reaction was carried out in a packed column and the overhead products were condensed from which the methyl alcohol-methyl halide azeotrope was separated by a liquid-liquid extraction using water as the continuous phase.

Four studies have been made of the hydrolysis of acetic anhydride. A 30 bubble-cap plate, 60 cm diameter, 10 m high industrial distillation column was used by Marek (127). As the components used were very corrosive, a stainless steel and aluminium column was used and it was operated at 400 mm Hg pressure. The feed plate was the sixteenth plate from the bottom of the column. The rates of all the main streams were measured whilst the liquid compositions were analysed for the main streams and the liquid overflow from six plates within the column. The reboiler was filled to 250 litre whilst the plate holdup was 3.1 litre. The time taken to reach steady state conditions was two hours and the column was operated for six to eight hours at steady state which was indicated by a constant temperature profile and constant composition determinations. However, data for one experiment was listed.

A 6 sieve plate glass column, 3 in diameter, 5 ft high with external interchangeable liquid downcomers and the feed on the fourth plate was used by both Legg (128) and Mamers (66) to study the continuous hydrolysis of acetic anhydride. Legg (128) used a constant feed rate and composition whilst Mamers (66) varied the feed rate between 65.0 and 79.0 g min^{-1} and the feed composition. Both workers used the same reflux ratio of 4:1 although Mamers (66) carried out one experiment under total reflux conditions. Liquid samples were taken from the main streams and the liquid overflow from each plate by both workers but Mamers (66) also sampled the vapour stream between each plate. The vapour was withdrawn by a vacuum system and condensed in a test tube which was immersed in an ice-bath. Both workers reported that the column was well-lagged and was situated in a heated cabinet.

To minimise the effects of corrosion, the apparatus used by Mamers (66) was constructed from either glass or P.T.F.E. whilst the three copper heating elements in the reboiler were silver-plated. The reboiler holdup initially was 3.9 litre but this was later reduced to 2.5 lire. The reflux divider was a solenoid-operated ball and socket joint for making and breaking the reflux stream from the overhead condenser. The column reached steady state after one hour and was maintained for a further two hours at steady state which was indicated by a constant temperature profile before sampling commenced.

Costa (129) has also investigated the continuous hydrolysis of acetic anhydride comparing a theoretical treatment with some experimental results. The distillation column had ten plates and was operated at 400 mm. Hg pressure with a reboiler holdup of 6 litre and a reflux ratio of 1.62:1. Data for only one experiment was recorded.

The continuous esterification of butyl alcohol by acetic acid was studied by Leyes & Othmer (130) in a five stage system. Berman et al (131) later used the same equipment to investigate the continuous production of dibutyl phthalate from phthalic anhydride and butyl alcohol. Each stage including the reboiler consisted of a 2 litre flask. The plate holdup could be varied between 150 and 950 ml whilst the reboiler holdup was equal to twice the plate holdup. The plates were externally heated with nichrome wires whilst the reboiler had a variable heat input. Steady state conditions were achieved after five hours operation and were maintained for a further three to four hours before sampling commenced and this took between one and half and two hours.

Two authors have investigated the production of vinyl stearate from vinyl acetate and stearic acid the reaction being catalysed by a mixture of mercuric acetate and sulphuric acid. Geelen and Wijffels (118) carried out the reaction in a 20 plate glass Oldershaw bubble cap column which was 120 cm high and 5 cm in diameter. The feed was mixed, metered and passed to a pre-heater where it was heated to 72°C before being pumped to the top plate of the column. The top product containing acetic acid and excess vinyl acetate were condensed, cooled and separated by distilling in a packed column containing raschig rings. The vinyl acetate from the top of the packed column was further heated and recycled to the bottom of the reaction column. The column was considered to be operating under adiabatic conditions because it was externally electrically heated to minimise any heat losses. Eight experiments were carried out in which a variety of column parameters such as the feed rate, boil-up rate and residence times were changed. However, only the compositions of the feed, top and bottom streams were analysed. Buselli and Rutledge (119) used a 15 plate bubble-cap column, 3 ft high and 6 in diameter, with a liquid holdup of 2-3 inches per plate. Each plate had one bubble-cap. The feed was passed through a pre-reactor where the residence time was one hour whilst the residence time in the column was two hours. The top products were condensed, separated and the vinyl acetate was recycled to the bottom of the reaction column. No measurements of the compositions were recorded but details of the flowrates were given and a 95 per cent yield is claimed.

Corrigan & Ferris (132) have investigated the continuous esterification of methyl alcohol by acetic acid catalysed by sulphuric acid in a 30 plate Oldershaw sieve-plate column. The reactants were mixed in a ten gallon feed tank before being fed into the column whose reboiler had a capacity of ten gallons. The column was free-floating supported only at the base whilst the reflux divider was an on-off reflux splitter. Three experiments were carried out (two batch and one continuous) and the latter gave a 90 per cent methyl acetate composition in the top product.

Schniepp & Dunning (133) prepared 2:3 butylene glycol diacetate from butylene glycol and acetic acid using sulphuric acid as the catalyst. The glycol and the catalyst were fed into the top of the column whilst a continuous stream of glacial acetic acid was fed into the base of the column. The column consisted of an interconnected series of 12 reaction vessels each containing a single bubble-cap. The plate holdup was 100 ml and each plate was heated with a ring burner to prevent any internal condensation. The top product (containing mainly acetic acid) was separated and the acetic acid was returned to the column. Two experiments were carried out each having a different feed composition and a 97 per cent yield of good quality ester was produced.

The survey may be concluded as follows:-

a) Liquid Residence Time

Marek (127) concluded from an analysis of the hydrolysis of acetic anhydride in a distillation column that the concentration of the reaction products was increased due to the presence of a chemical reaction and in particular was proportional to the plate holdup. He also concluded that the influence of hydrolysis was equal from plate to plate assuming an equal plate holdup.

Similarly Legg (128) observed for the same system that the maxiumum reaction occurred on a plate of high liquid holdup whilst more recently Mamers (66) confirmed this conclusion for the same reaction.

However, Leyes & Othmer (130) observed from the continuous esterification of butyl alcohol that the reaction was not affected by the plate holdup but the results may have been masked by a large heat loss of 43.5% in the esterification section.

In the study of the continuous production of vinyl stearate, Geelen & Wijffels (118) varied the column holdup between 0.06 and 3.2 hours and they observed that the extent of the conversion increased from 74 to 98 per cent with the increase in column holdup.

b) Feed Composition & the Position of the Feed Plate

Marek (127), Legg (128), Leyes & Othmer (130) and Geelen & Wijffels (118) all used constant composition feeds. In the investigation of the continuous production of ethylene glycol Corrigan & Miller (134) studied the effect of the feed composition with a view of increasing the selectivity of the reaction. It was hoped that by using lower water : ethylene oxide molar feed ratios (and thereby reducing the amount of water which had to be recycled and evaporated) the reaction by-products (di, tri and higher ethylene glycols) could be minimised. It was observed that at stoichiometric molar feed ratios, the conversion in the distillation column was better than that of a plug or perfect flow reactor but the by-product formation was higher than could be tolerated for commercial use. However, at higher molar feed ratios (up to 20:1) the performance of the column did not surpass that of the plug or perfect flow reactor.

A similar approach was postulated by Parker (125) who thought that by carrying out the hydrolysis of ethylene oxide in a distillation column with a stoichiometric molar feed ratio, a high conversion and selectivity could be obtained. He deduced that the more volatile component in the feed (ethylene oxide) would separate on the feed plate leaving a water-rich mixture. The product ethylene (the least volatile component) would immediately pass down the column away from the reaction zone, thus avoiding the possibility of any side reactions. By utilising the difference in volatilities he predicted a yield of mono ethylene glycol approaching 100 per cent. However, there were no practical experiments to confirm his predictions.

Mamers (66) adjusted the feed composition by a factor of ten. In the first series there was an excess of water in the feed, the bulk of the reaction was on the feed plate (due to the high concentration of the reactants) and in the reboiler (due to the large volume). In the second series where there was just an excess of water, the reaction on the feed plate was less and the reaction zone moved up the column so that more of the reaction took place on plate 3. In the third series the acetic anhydride was in excess and the bulk of the reaction occurred on the higher plates in the column. As the excess of water in the feed decreased the percentage conversion of the water increased

c) Column Concentration Profile

In a theoretical treatment, Marek (135) observed that where a reaction occurred between a least volatile and a most volatile component, and when the reaction rate was proportional to these two components, the influence of the reaction should be detected near the feed plate where a shift in the reaction product concentration would be observed. In the continuous hydrolysis of acetic anhydride Marek (127) confirmed his previous ideas in one experiment when the concentration of the acetic anhydride initially decreased below the feed plate and only increased on the plates where there was no water present. Similarly the water concentration decreased above the feed plate and only increased on the top plates.

The reversal of the anhydride concentration below the feed plate was observed once by Mamers (66) and this was when the column was operating at near stoichiometric feed conditions. In one experiment when the column was operating with a large excess of water in the feed, the concentration of the heavy component decreased either side of the feed plate - a phenomenon which is not observed in conventional distillation. In two experiments carried out at near stochiometric feed conditions, the effect of the reaction was noticed when the acetic acid concentration was higher above and below the feed plate. The influence of the reaction was such that the reaction components concentration decreased more quickly. Mamers (66) predicted that with a ternary system it was possible to obtain eight different column concentration profiles although he only observed three of these profiles.

d) Plate Efficiencies

Mamers (66) was the only research worker to analyse the performance of a distillation column in which a chemical reaction is being carried out, in terms of plate efficiencies. He calculated both the vaporisation efficiency and the Murphree efficiency. It was concluded however that the effects of the chemical reaction would be demonstrated best by the Murphree efficiencies and subsequently positive, zero and negative values were calculated. It was concluded that the negative values were partly due to the volatility of acetic acid being depressed by water and due to the initial increase of its concentration from the reaction.

The values of the efficiency varied differently for each component. The efficiency for acetic anhydride increased above the feed plate whereas it was observed that there was a large scatter of the values below the feed plate. This was partly attributed to the fact that the anhydride acted as a pseudo-light component below the feed plate. The concentration of the light component, water, increased up the column less rapidly than in normal distillation. This was due to its removal by the reaction. The efficiency was lower on reactive plates than on non-reactive plates and the efficiency was lowest on the plate adjacent to the plate with the highest percentage conversion. The converse, however, was true for acetic acid and was most noticeable around the feed plate and the plate above it.

Finally the effect of the exothermic heat of reaction on the plate efficiencies was considered. It was thought that if there was a region of high heat release (such as the feed plate and the reboiler) and the volatile component concentration was small, then a small change due to the vaporisation by the heat of reaction could lead to a large change in plate efficiency. It was observed that on the feed plate, when the water concentration was low the heat release was high and the efficiencies were very high and also the water concentration increased, the heat release and the efficiencies decreased thus confirming that the heat of reaction could influence the plate efficiencies of the most volatile component.

e) The Catalyst Concentration

Sulphuric acid was used as the catalyst for the continuous esterification of methyl alcohol (132) and as the catalyst for the continuous acetylation of 2:3 butylene glycol (133) but the concentration was not specified in either case.

However, in the continuous esterification of butyl alcohol, 0.03 to 0.13 per cent sulphuric acid was used as the catalyst. Leyes & Othmer (130) observed that at the low concentration the reaction proceeded too slowly whilst at the high concentration, the reaction proceeded to completion and they concluded that the conversion was related to the catalyst concentration.

For a hypothetical reversible reaction, $2A \rightleftharpoons B$, (136) with a high boiling point product, the catalyst was fed in at the top of the column and removed below the equilibrium plate so that the influence of the reverse reaction would be eliminated. However, the effect of the catalyst concentration was not discussed.

In the production of vinyl stearate (118), mercuric acetate and sulphuric acid mixtures were used as the catalyst but although eight experiments were carried out it would appear that the catalyst concentration remained constant. In an investigation of the above reaction with the same catalysts, Buselli & Rutledge (119) observed that if the acid concentration was too low the yield decreased, whilst if it was too high, impurities were obtained due to polymerisation of the reaction products. The same effects were noticed respectively if the mercury salt was too low or too high.

f) Temperature Profile

Marek (127) noted that in the hydrolysis of acetic anhydride, the reaction rate is directly proportional to the temperature. However, in a distillation column, the temperature decreases from the bottom to the top of the column and thus the effect of the reaction should also decrease in the same direction. Also the temperature of the column may well promote unwanted side reactions such as in the production of vinyl stearate where ethylidene diesters could be produced (118).

g) The Reflux Ratio

Marek (127) operated his column at 5.18:1 reflux ratio and he assumed that the reflux was returned at its boiling point whilst Legg (130) only used a 4:1 reflux ratio.

Mamers (66) also operated the column at a 4:1 reflux ratio with one exception where the column was operated at total reflux. From this he compared the conversion obtained at total reflux with one experiment at 4:1 reflux ratio where the heat input was the same although the feed compositions were different. From this comparison Mamers (66) concluded that conversion was dependent on the reflux ratio which would be expected because as the reflux ratio is increased, the concentration of the most volatile component (water - one of the reactants) in the reaction zone should increase thereby increasing the conversion.

Corrigan & Ferris (132) concluded that it should be possible to obtain a product on the ester rich side of the ester-alcohol azeotrope in the continuous esterification of methyl alcohol by making the correct choice of the reflux ratio. However, Berman et al (131) thought that for equimolar reactants in the feed, the optimum conversion was obtained at low reflux ratios.

h) Boilup Rate

Legg (128) observed that the boilup rate affected the concentration profile. Mamers (66), who varied the boilup rate between 63.3 and 259 g min^{-1}, found that the component conversion was dependent on the boilup rate. As the boilup rate was increased, the conversion decreased because the most volatile component was removed more quickly from the reaction zone, although the plate holdup increased with increasing the boilup rate. The limits of the boilup rate were quoted as excessive weeping and droplet entrainment.

i) Conversion

Marek (127) did not quote any overall conversions although he did state that 22.8 per cent of the total reaction took place on the feed plate. Mamers (66) adapted the formulae proposed by Marek (135) to compute the component stagewise conversions. From this approach, good agreement was obtained between the overall component conversions and the sum of the component stagewise conversions.

Geelen & Wijffels (118) quoted an overall component conversion which varied between 74 and 98 per cent whilst for the same reaction. Buselli & Rutledge (119) obtained a 95 per cent conversion.

5.2 Description of the Equipment

5.2.1 The Layout

The reactants which were stored in 10 litre aspirators, were passed down to the flowrators where the feed rate was measured. The feed passed through a feed preheater where it was heated to just below its boiling point. The feed was fed onto the fourth plate of a 3 inch internal diameter, six sieve-plate, glass distillation column. The liquid overflow from each plate flowed down to the next plate through external interchangeable downcomers. Vapour was generated by two 2 kw heaters which were contained in a 9 litre glass reboiler. The bottom product was removed from the column through a weir system. The flowrate was determined by weighing some of the bottom product which had been collected in a flask over a given period of time. The liquid composition on each plate and the composition of the vapour leaving each plate were sampled and analysed. The temperature of each plate and a number of other temperatures which are listed in 5.2.6 were measured and displayed on a cyclic multipoint temperature recorder. The vapour leaving the top plate was condensed in a 2 inch I.D. water condenser. The reflux was divided by an electronically controlled solenoid operated ball and socket valve. The reflux ratio could be varied by adjusting the electronic impulse system. The reflux was returned to the top product whilst the top product flowrate was measured before being stored. The whole of the column, the reflux divider and the reboiler were contained in a heated cabinet in order to minimise heat losses. The column was not lagged so that the plate behaviour could easily be observed. The electrical control panel and the flowrate control panel were mounted adjacent to the distillation column cabinet. The individual sections of the equipment are now described in greater detail.

5.2.2 The Distillation Column

Some of the factors which were considered in the selection of the design of the column are (1) A large diameter column in which heat losses and disturbances due to sampling would be minimised (2) A large diameter column which would clearly demonstrate the respective effects of chemical reaction and physical separation (3) The largest size of column which could be constructed in one unit and preferably from glass (4) Economic considerations.

Thus a 3 inch internal diameter six sieve-plate distillation column was chosen (see Fig. 5.1 and Plates 6 & 7). It was proposed that the reaction would be carried out on three of the plates and the remaining three plates would be for separation of the components but the apparatus had been designed so that a split feed or a feed on a different plate from the fourth plate could easily be accomodated.

Each plate contained approximately 200 holes of 1.5 mm diameter on a triangular pitch of 4.5 mm giving a total free area of 7.7% (see Fig. 5.2). The plate separation was 8 inches whilst the straight sections above the top plate and below the bottom plate were 12 and 8 inches respectively thus giving an overall column length of 5 ft.

Liquid samples were taken from the top product, the six plates and the reboiler. A 5 ml hypodermic syringe was used to remove the samples. The syringe fitted into a luer valve which was mounted on the exterior of the cabinet and the valve was connected to 14 gauge

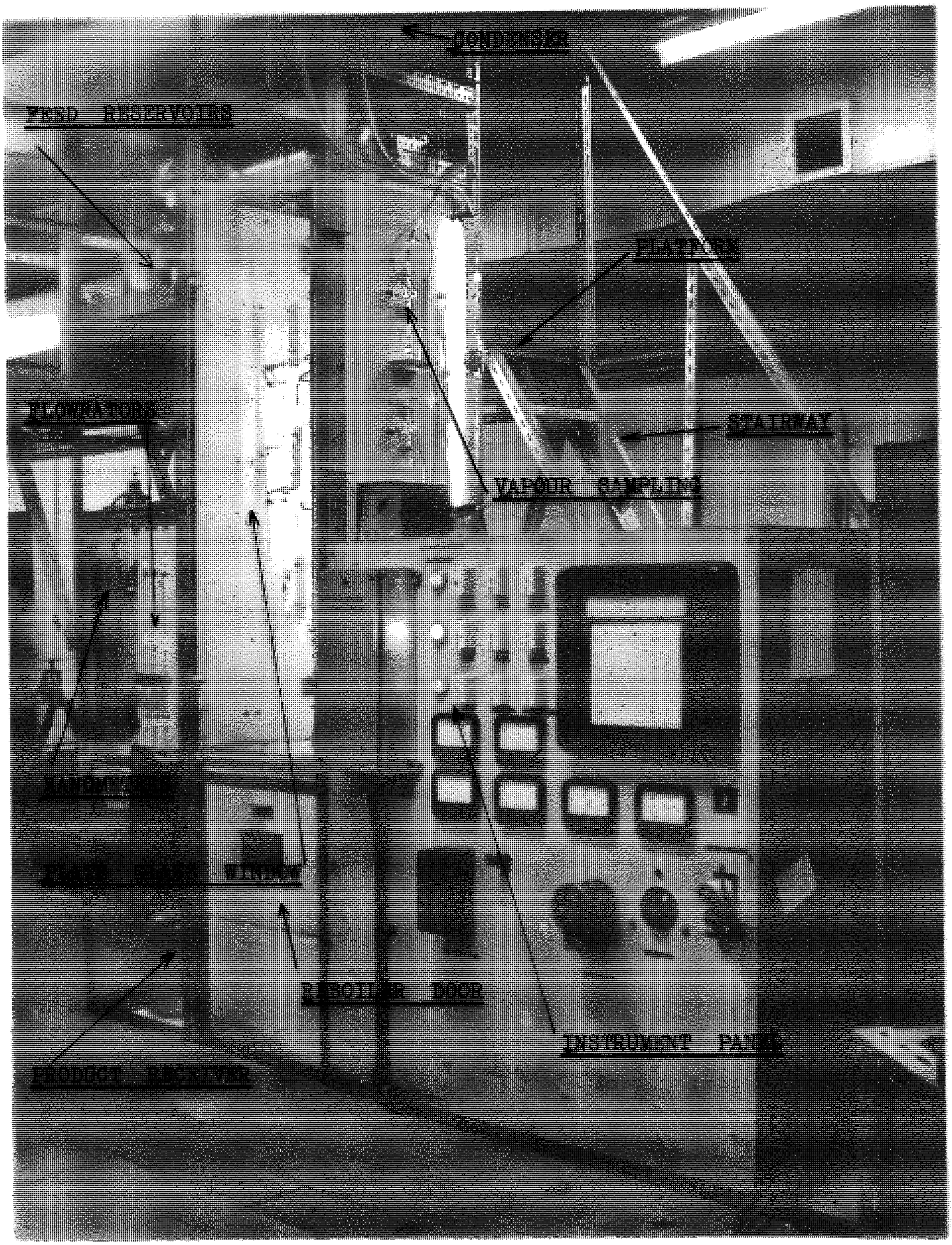


PLATE 6 DISTILLATION COLUMN

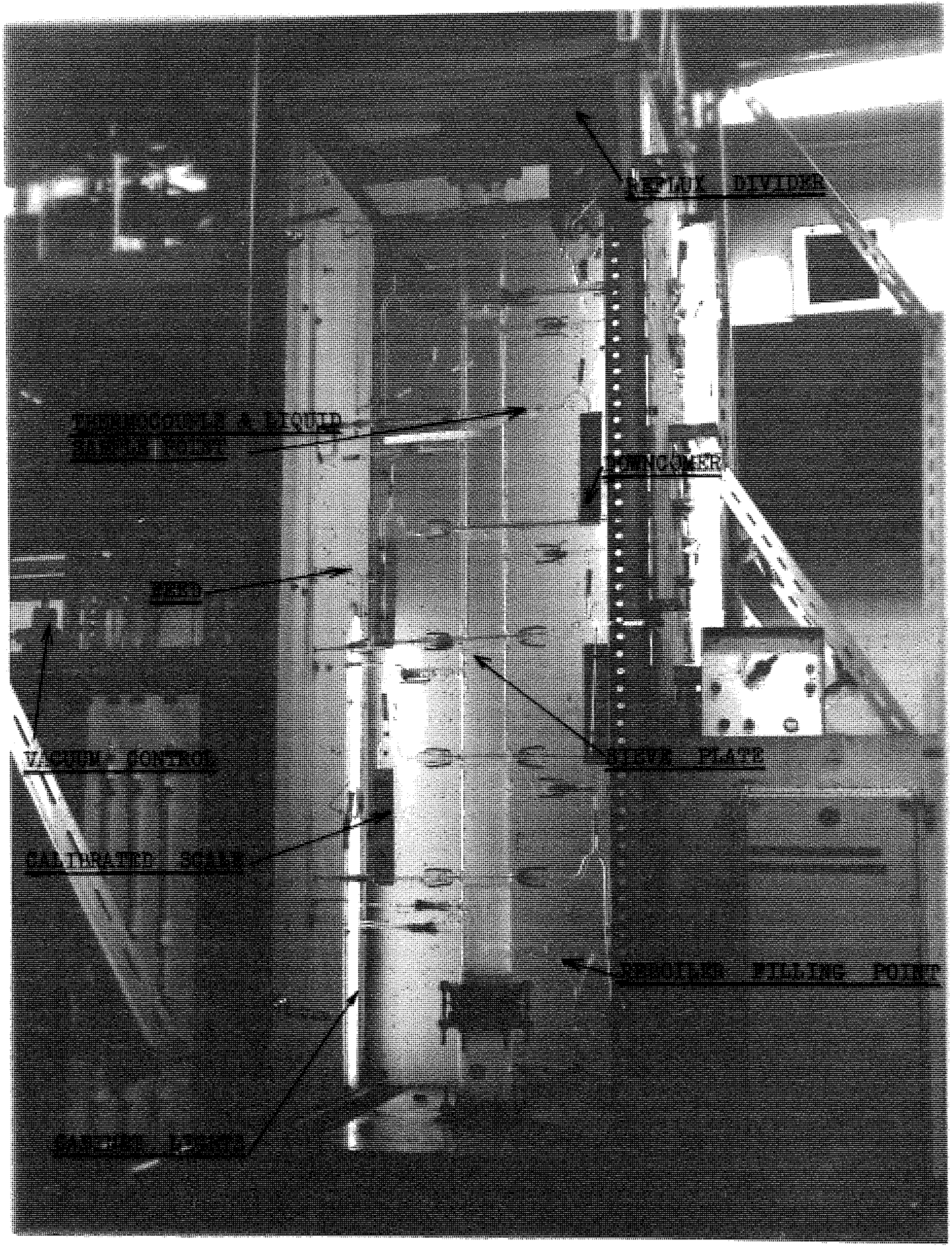


PLATE 7 DISTILLATION COLUMN

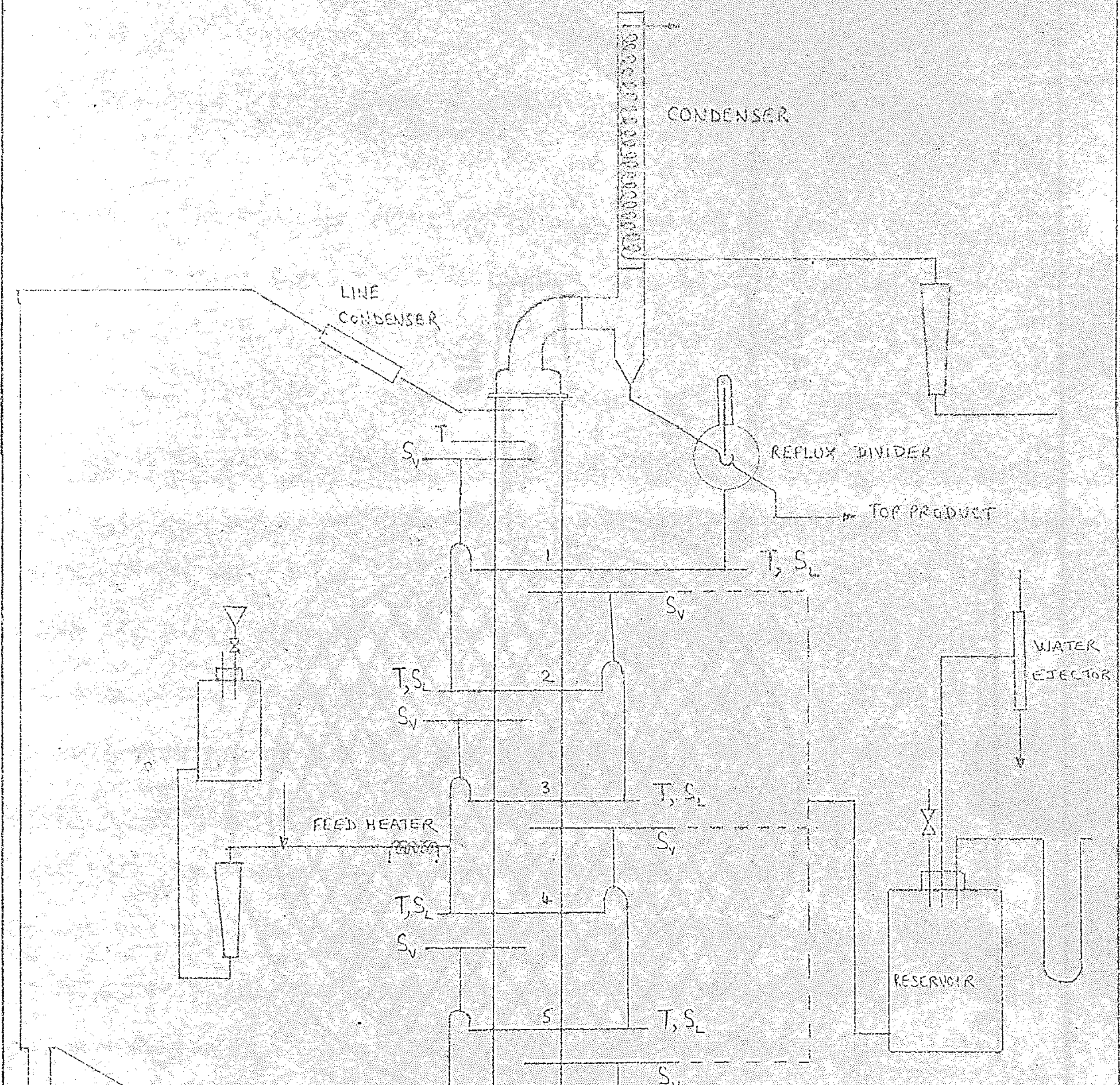


Fig 5.1 Column Layout

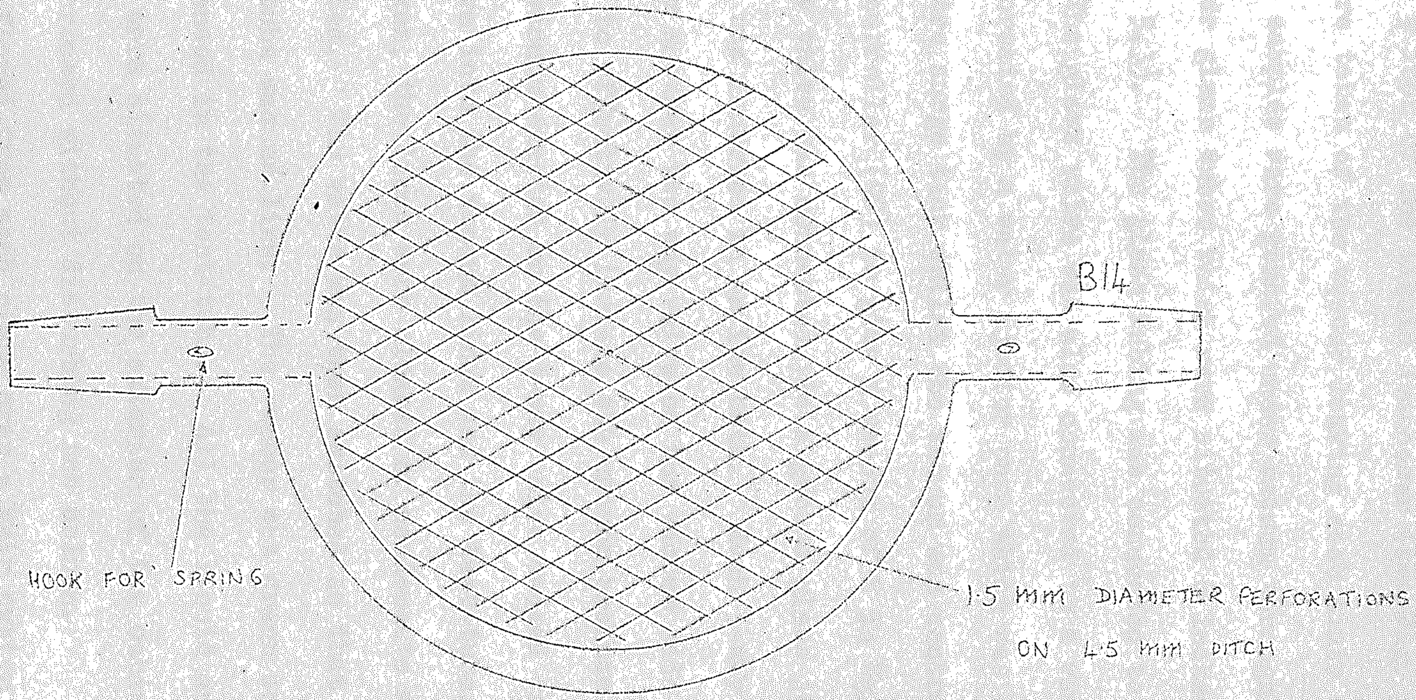


Fig 5.2 Plan of Column Plate.

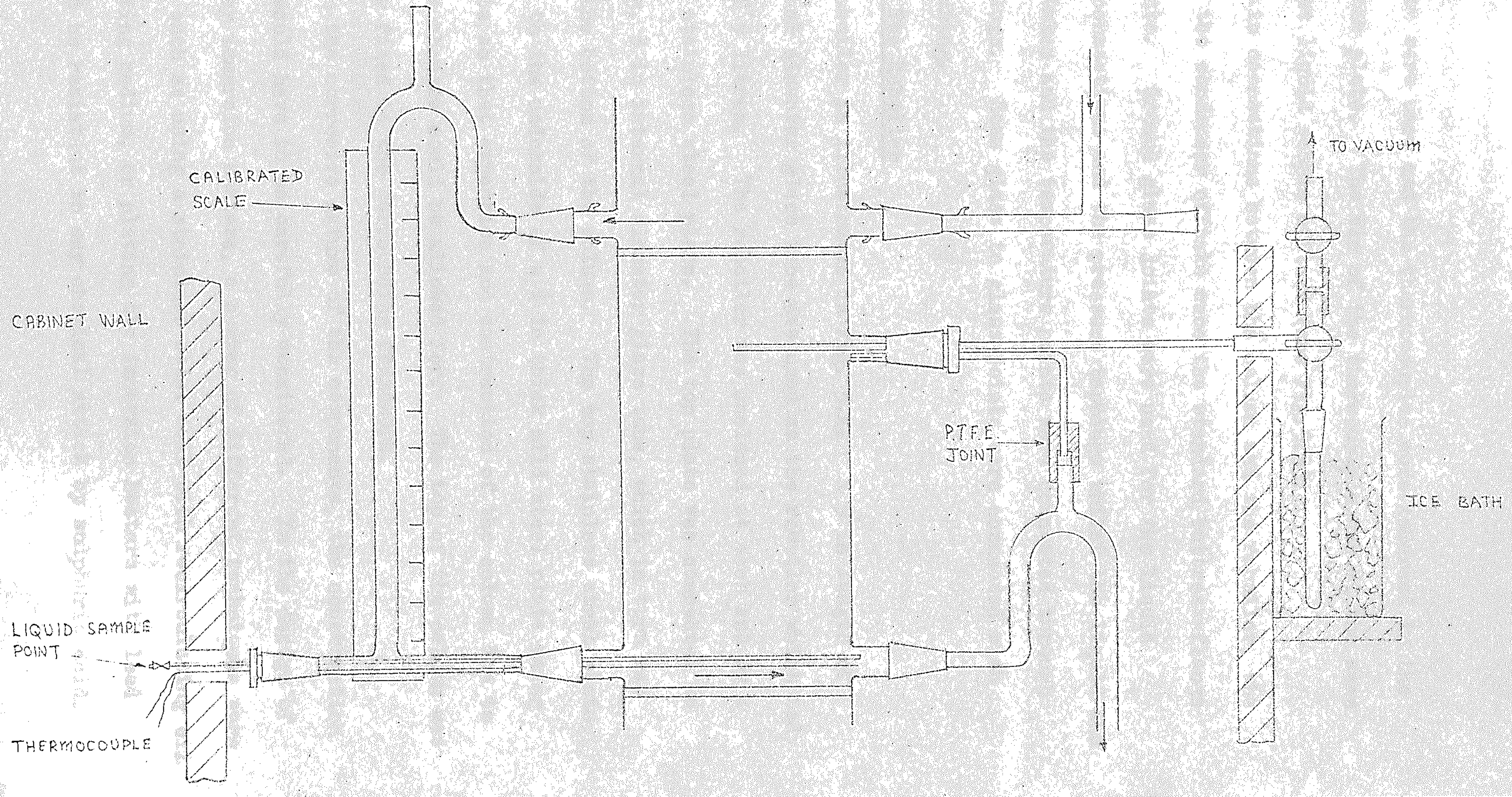
stainless steel hypodermic needle tubing which protruded across the plate to within $\frac{1}{2}$ inch of the liquid downcomer (see Fig. 5.3).

Samples were taken of the vapour leaving each plate and the reboiler. The samples were removed under vacuum through 3 mm internal diameter glass tubes which were situated 6 inches above each plate (see Fig. 5.3). The glass tubing was connected to a 3-way glass valve. The glass valve was also connected to a vacuum system. The vacuum was created by a water ejector pump which was working against a 10 litre surge tank whilst the vacuum was controlled by an Edwards Hivac Controller (98) to give a vacuum of 8 in Hg. The third arm of the 3-way valve was connected via a ground glass joint to a test tube which was immersed in an ice bath. Each 3-way glass valve was protected by another two way valve on the vacuum side of the system in order to effectively isolate the vacuum because it was found that the vacuum exerted on the 3-way valve caused vapour to leak through the valve into the vacuum lines and the test-tube. Before a sample was taken, the lines were cleared of condensate and the test-tube was evacuated. The valve was then switched so that the evacuated test-tube was on line. The vapour was drawn in by the vacuum and condensed in the test-tube. All the liquid and vapour sampling points were situated on the exterior of the cabinet so that sampling could proceed without disturbing the column.

The liquid flowed from each plate over a weir system which was vented to the space above the plate so that syphoning effects would be avoided. The weirs were interchangeable and thus if required, the plate holdups could be altered.

1/16 in chrome-alumel thermocouples contained in a stainless

Fig 5.3 Liquid and Vapour Sampling Points.



steel sheath were used and the thermocouples were immersed in the liquid on the plate. The tip of the thermocouple was at the same point as the liquid sample offtake (see Fig. 5.3).

The main connections between the column and the reboiler, the column and the condenser offtake were the standard buttress-flange gasket joints. Ground glass joints were used for the liquid downcomer connections and the pressure tappings whilst the liquid and vapour offtakes and the temperature points were connected through P.T.F.E. plugs. Some glass to glass joints were connected with P.T.F.E. tubing.

5.2.3 The Reboiler

The reboiler is illustrated in Fig. 5.4. A 9 in length of 9 in internal diameter glass tube was used as the reboiler which had a volume of 9 litres. The reboiler was enclosed at each end by a $\frac{1}{4}$ in thick stainless steel plate. The top plate was connected to a 9 in long, 3 in internal diameter glass tube, which in turn was joined to the bottom of the column. The top stainless steel plate was bolted to the underside of a $\frac{1}{4}$ in thick mild steel plate using sprung bolts so that expansion and contraction of the column due to temperature changes could be allowed for. The top of the column was permanently fixed to the surrounding framework.

Due to the corrosive nature of the components, the construction materials would have to be carefully considered. In the design of the reboiler immersion heaters, a number of different techniques were considered such as using a stainless steel coil with recirculating oil as the heating medium, or plating the immersion heaters with lead which would be resistant to any chemical attack by sulphuric acid.

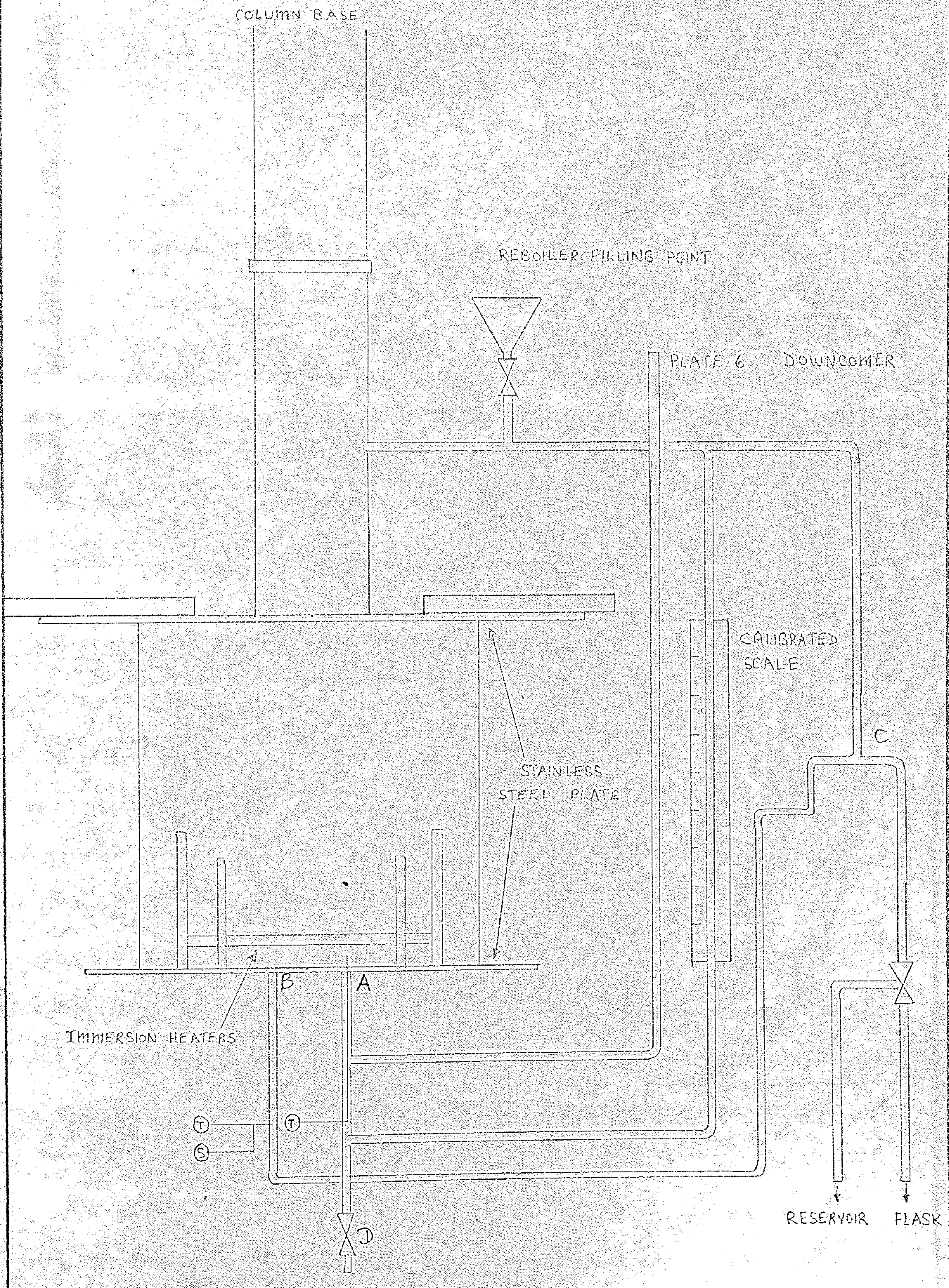
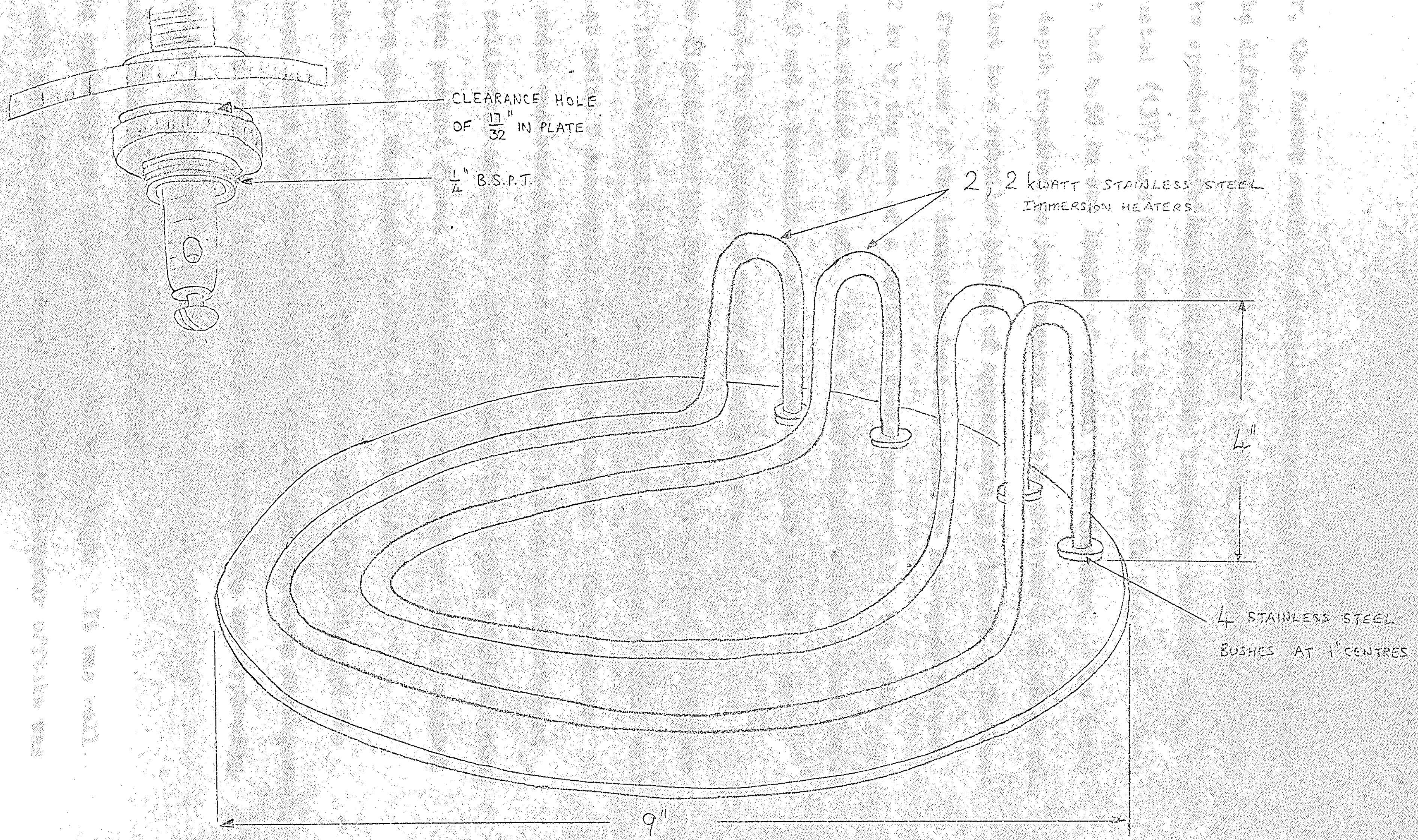


Fig 5.4 The Reboiler

FIG 5.5 THE REBOILER IMMERSION HEATERS



However, the former would be difficult to control whilst the latter would be difficult to construct due to plating difficulties. Thus two 2 kw special stainless steel-sheathed immersion heaters were constructed (137) and the design is illustrated in Fig. 5.5. Each element had a 30 in cut length of nominal $\frac{3}{8}$ in diameter. The total liquid depth required to just immerse the elements was 4 in which was equivalent to a reboiler holdup of approximately 4 litres. The heat output from one of the immersion heaters could be increased between 0 and 2 kw by the use of a variable transformer whilst the other heater was either on or off. Thus an infinitely variable heat input between 0 and 4 kw could be obtained and this was judged to be sufficient for the proposed range of boilup rate.

The liquid overflow from plate 6 entered at point A, the bottom product left at point B whilst the setting of the outlet product weir height at point C determined the reboiler holdup. The reboiler holdup which was varied between 4.6 and 6.5 litres, was determined from a calibrated side-arm. After passing the liquid sampling point the bottom product flowed to the product reservoir or into a weighed flask from which the flowrate could be determined.

Prior to each experiment, the reboiler was filled through the feed funnel which was incorporated in the reboiler side-arm arrangement. The side-arm vented the liquid offtake thus preventing any syphoning. The reboiler was emptied through point D.

5.2.4 The Condenser and Reflux Divider

The condenser was 2 in diameter and 24 in high. It was well lagged with one inch asbestos rope. The column vapour offtake was similarly lagged. The water coolant rate was measured by a 0-2 litre rotameter whilst the inlet and outlet temperatures were measured by chrome-alumel thermocouples.

The reflux divider is illustrated in Fig. 5.6. The divider was constructed in glass. Liquid reflux flowed down through the B14 ground glass connection onto the ball and socket valve. When the valve was shut the liquid flowed over the rim of the B19 valve and down through the line as reflux to the column. However, when the solenoid was activated, causing the valve stem to lift and open the valve, the liquid flowed down through the B19 socket to the top product reservoir.

The valve stem was made from glass tubing to reduce its weight and the seal between the ground glass ball and socket joint was reduced to 2-3 mm in order to reduce liquid surface tension effects. A ferrite rod was sealed into the top of the valve stem. By reducing the weight and the valve contact area, it was hoped that the solenoid would have sufficient power to operate the valve. The whole of the valve assembly was contained inside a 500 ml capacity flask.

The valve was actuated by attracting the ferrite rod into the solenoid's field. The solenoid was controlled by a reflux ratio timer which could be adjusted to give a reflux ratio varying between 1:50 and 50:1.

During the initial commissioning experiments, a number of difficulties arose from the use of the reflux divider. It was observed that the valve leaked when it was closed so that distillate was passing to the top product line. The valve seating and facings were reground until a seal was obtained. The impact of the valve

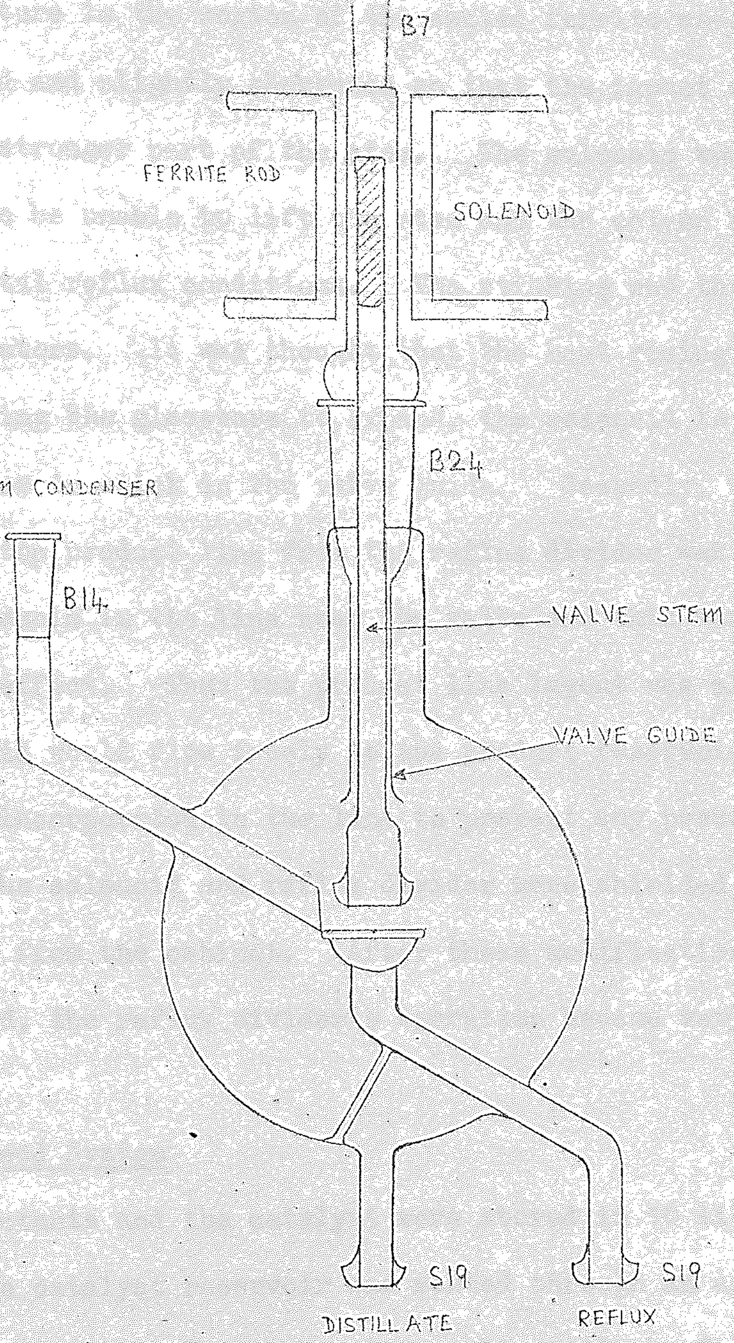


Fig 5.6 Reflux Divider

stem against the stop when the valve was lifted by the solenoid caused the stem to fracture in the region of the sealed ferrite rod. The stem was resealed and slightly shortened so that the impact would be lower down on a stronger part of the stem. The solenoid would at certain instances be unable to lift the stem and the column would thus operate under total reflux conditions. The sticking was thought to be due to two factors. It was thought that the heat rising from the cabinet was causing the glassware to expand, the solenoid to overheat and the valve stem to stick in the valve guide. Secondly, the geometry of the top product line from the reflux divider was causing some liquid to remain in the line near the valve and this was creating a back pressure effect. Thus the product line layout was altered so that the liquid would flow freely to the product reservoir and also a vent was incorporated in the line to prevent any pressure differences. The solenoid and reflux divider were shielded from the warm air issuing from the cabinet. After these modifications had been incorporated, the reflux divider's operation became very satisfactory.

5.2.5 The Feed System

The two reactants and the catalyst were stored in 10 litre overhead aspirators. The catalyst reservoir was vented through an anhydrous calcium chloride bottle. The reservoirs could easily be filled from the overhead walkway. The reactants were fed through 11 mm O.D. glass tubing to the flowrators. For the two reactants, 0-16 scale Fisher & Porter (99) $\frac{1}{8}$ in bore flowrators were used with stainless steel floats, giving a range of 0-50 g min^{-1} for ethyl alcohol and 0-61 g min^{-1} for butyl acetate. A 0-8 scale $\frac{1}{8}$ in bore flowrator with a stainless steel float and a stainless float stop was used for sulphuric acid giving a range of 0-1.55 g min^{-1}.

After measurement, the reactants were mixed, the temperature was measured by a chrome-alumel theromocouple and the mixture flowed to the feed preheater. The preheater consisted of 17 inches of 11 mm O.D. glass tubing wound with Bright Ray Alloy C (100) resistance wire and the maximum output from the heater was calculated as 400 watts (see Appendix D1). The preheated reactants were mixed with the catalyst, the temperature was measured by a chrome-alumel thermocouple and the mixture was fed onto the fourth plate.

The feed system was later modified due to difficulties in obtaining a satisfactory flow in the catalyst lines. The catalyst was mixed with the butyl acetate in the butyl acetate reservoir and thus the storage of large quantities of a highly corrosive liquid was eliminated.

5.2.6 Temperature Measurement

The following temperatures were measured:

Recorder Printout No.	Temperature Point
1	Plate 1
2	Plate 2
3	Plate 3
4	Plate 4
5	Plate 5
6	Plate 6
7	Reboiler
8	Bottom Product
9	Vapour-bottom
10	Vapour-top
11	Water inlet Feed
12	Water outlet Preheated Feed

Pyrotenax (138) chrome-alumel, 1/16 in diameter, stainless steel sheathed, 2 ft long thermocouples were used to measure all the temperatures. The thermocouples were all connected to a common cold junction which was an identical thermocouple placed in crushed melting ice contained in a Dewar flask. The output from the thermocouples was recorded on a Kent (54) 0-1 mv 12 point recorder. The condenser and feed temperatures were recorded by using a switching arrangement so that either the feed or condenser temperatures could be monitored at any given instance. A complete printout was given every two minutes.

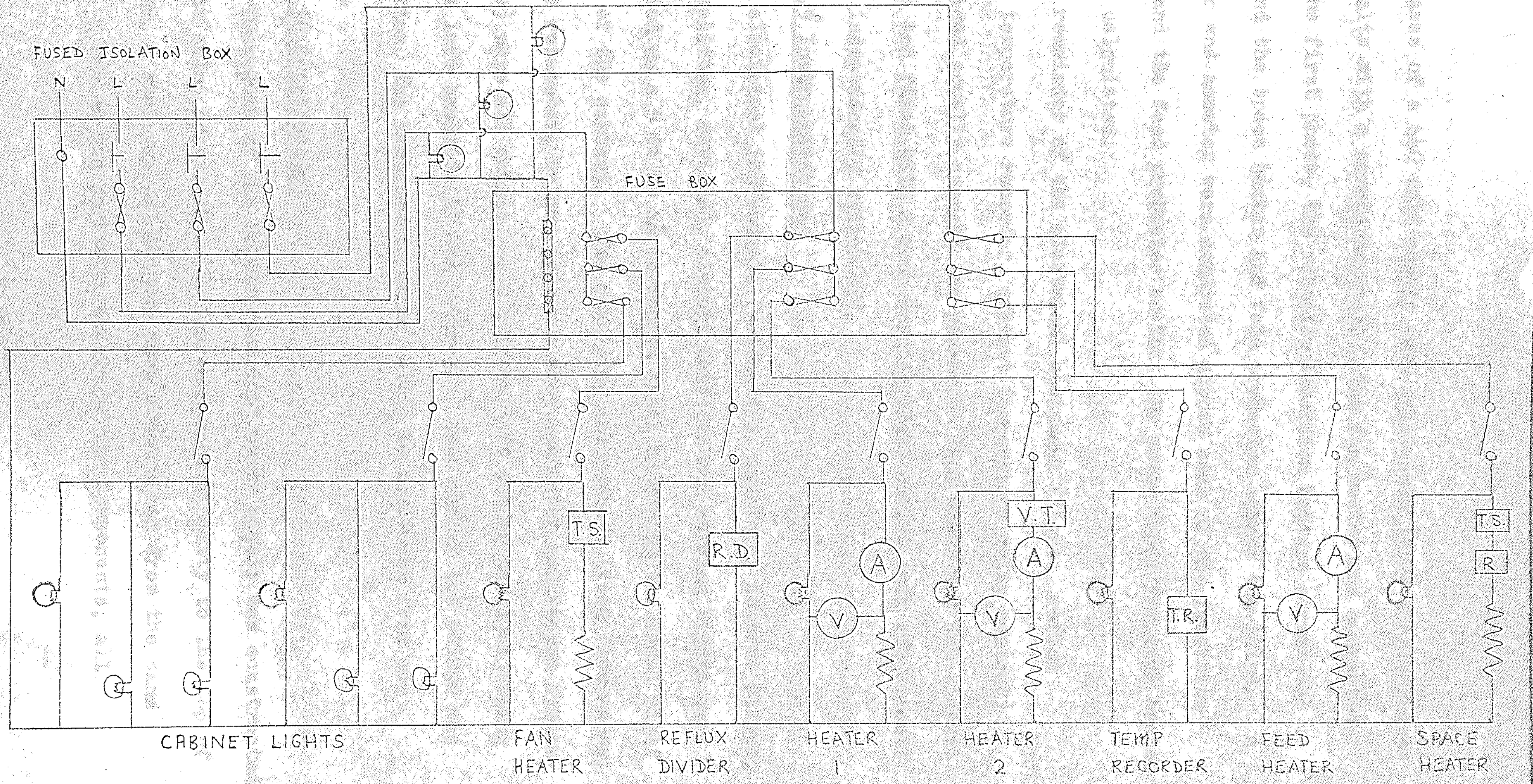
5.2.7 The Cabinet

The distillation column, the reflux divider, the reboiler and all the immediate interconnecting lines were enclosed in a cabinet which was constructed from a light alloy framework and an asbestos composite sheet. The cabinet interior was illuminated by two externally mounted 30 watt strip lights. The reboiler which was also illuminated, could be viewed through a small perspex window which was mounted in a removable door on the lower front of the cabinet. The distillation column was viewed through a $\frac{3}{8}$ in toughened plate glass door. The cabinet was heated by a 3 kw fan heater and a 1 kw space heater. The cabinet temperature in the reboiler was monitored by a 0-200°C thermoregulator which was connected to a relay system which actuated the space heater. Both heaters were connected to Timac time switches so that the heaters would be automatically switched on and reach the required control temperature of 100°C.

5.2.8 The Electrical Circuits

The electrical circuit diagram is illustrated in Fig. 5.7. The

Fig 5.7 Electrical Circuits



three phases of a 440 volt supply were split into three single phases of 240 volts with a common neutral. The fan heater was connected across the first phase, the reboiler immersion heaters across the second and the space heater and feed preheater across the third. A voltmeter and ammeter were connected across each of the immersion heaters and the feed preheater so that the power input for each heater could be calculated.

The remainder of the electrical equipment (lights, reflux divider, temperature recorder, cabinet temperature relay control) were divided equally amongst the phases. Each phase and sub-circuit was fused and fixed with a neon warning light whilst each sub-circuit could be independently switch off.

5.2.9 Instrumentation

The electrical instruments (voltmeters, ammeters, control relays, 3 phase splitter, variacs), circuit switches and warning lights were all mounted on a 5 ft by $4\frac{1}{2}$ ft wooden panel adjoining the front right handside of the cabinet. The remaining instruments (feed flowrators, condenser rotameter, column pressure drop manometer and vacuum system manometer) were all mounted on a 2 ft by 3 ft wooden panel adjoining the front left handside of the cabinet. Thus whilst the column was in operation, the instruments could easily be monitored from one position.

5.2.10 Construction

The framework of the cabinet and instrument panels was constructed from light alloy framework. To increase accessibility to the top of the column, a stairway and gangway were constructed from the same material. Due to the corrosive nature of the components, all connections were made from either ground glass, buttress end joints with bolted flanges and P.T.F.E. lined gaskets, or glass to glass tubing connected with P.T.F.E. tubing. All metal which would be in contact with the liquid or vapour was stainless steel. The column was permanently fixed at the top but it was spring mounted at the bottom to allow for expansion. The column, reboiler, condenser and reflux divider could be removed independently without affecting any other part of the apparatus.

5.3 Calibrations

5.3.1 The Electrical Meters

The ammeters were calibrated against a Sangmo-Weston Ammeter (Model S93 No. AF 19821) and the values could be read in the case of a 0-10 amp scale to 0.02 amp and for the 0-2 amp scale to 0.01 amp. The three ammeters were calibrated at a temperature of 21.6°C and the largest error was 1% on the 0-10 amp scale. The 0.2 amp scale meter was found to have no detectable error.

The voltmeters were calibrated against a Sangmo-Weston Voltmeter (Model S92 No. AF 19820). The three voltmeters were calibrated at a temperature of 21.5°C and the largest error was 1.6% on the 0-240 volt scale.

5.3.2 The Feed Flowrators

From a preliminary investigation it was appreciated that the maximum feed rate would be about 80 g min^{-1}. Thus the individual reactant flowrates would be less. The minimum obtainable flowrate range for a rotameter was calculated as 0-360 g min^{-1} for butyl acetate. Thus for metering the feed rates, the rotameters were discarded and Fisher & Porter (99) flowrators were selected.

The calibration procedure listed in the Fisher & Porter (99) manual was used to obtain a calibration for each flowrator. The calibrations are tabulated in Appendix D2.

5.3.3 The Plate Holdup (Z)

It was necessary to determine the plate holdup because the component conversion on each plate was directly related to it. It would also be required for any theoretical analysis to predict a component conversion on each plate.

Plate holdups can be measured in three ways : plate pressure drop, froth height or liquid holdup in the liquid downcomers. The first technique would be susceptible to variations in density within the liquid on the plate and would be dependent on the dry plate pressure drop. The second method would be difficult to measure particularly as the froth height is a function of the liquid properties. The existence or non-existence of a particular component for a given boilup rate may change the froth height by a considerable degree. It was decided to calibrate the height of liquid in the downcomers against plate holdup.

The downcomers were calibrated using water as the system. The B10 P.T.F.E. stoppers were removed and a glass tap was connected to the socket by a piece of neoprene tubing. The reboiler immersion heat load was set to give the required boilup rate. When the column had attained steady state, the liquid height on the calibrated scale of each downcomer was noted. The holdup rate was reduced until the liquid on each plate did not quite dump and commencing from the top of the column, the liquid was withdrawn from each plate into a beaker and the volume was measured. It was observed that a small quantity of liquid remained on the plate as the liquid offtake was slightly above the plate. The volume of this liquid was estimated by calculating the total volume of the space and halving to allow for the voidage caused by the bubbles.

Initially it was hoped to obtain a general correlation for all the plates but it was found that such a correlation was inaccurate due to differing plate characteristics and hence a calibration was obtained for each plate. Due to the layout of the column, it was not possible to measure the holdup of plate 1 so this was estimated as being the mean of plates 2 and 3.

A correlation of plate holdup against downcomer liquid height (h) was obtained for each plate over the boilup range of 50-80 g min^{-1}.

They are as follows:-

Plate 2	$Z = 48.48h - 61.56$
Plate 3	$Z = 65.76h - 30.48$
Plate 4	$Z = 81.77h - 108.49$
Plate 5	$Z = 74.54h - 119.20$
Plate 6	$Z = 41.26h - 23.94$

The worst error was ± 10% but the majority of the points were well within that limit.

5.3.4 The Reboiler Holdup

The reboiler holdup was determined by adding known volumes of water and observing the reading on the calibrated scale which was attached to the pressure equalisation side-arm (see Fig. 5.4). The side-arm and scale could be clearly seen through the reboiler observation window.

5.3.5 The Thermocouples

All the thermocouples were strapped together and placed in a beaker of water which was well stirred. A thermometer was strapped to the thermocouples. The water was brought to the boiling point and the output of each thermocouple was read on the temperature recorder. The maximum deviation was 1.6°C although most of the thermocouples were reading within 1°C error.

5.3.6 The Reflux Divider

The reflux divider's accuracy was checked in situ by allowing hot water to run from the condenser into the divider and measuring the quantities obtained in the reflux line and the top product line over a given period. It was found that for the operating range of the divider and the control mechanism that both operated accurately and satisfactorily. The timing sequence was based on a 2 second top product interval and thus for a 4:1 ratio the valve was open for 2 seconds for the top product and closed for 8 seconds when the liquid flowed to the column as reflux. In using this timing it was hoped that the column would not be subjected to intermittent reflux flow.

5.3.7 Column Entrainment

The reboiler was filled with water and the heat input was set to give a boilup rate of 125 g min^{-1}. A solution of 7.46 g $litre^{-1}$ of potassium chloride was fed onto the top plate through the reflux divider. After one hour's continuous operation simultaneous liquid and vapour samples were taken and titrated against silver nitrate solution. The ratio of the chloride concentration in the vapour and liquid phase was in all cases below 2%. Thus it was decided that as the entrainment was small, there should not be any serious errors involved in the vapour sampling system.

5.3.8 Liquid Mixing on Each Plate

The equipment was operated at a heat input load of 2 kwatt at total reflux with ethyl acetate, ethyl alcohol and butyl acetate. Samples were removed from plates 2 and 6 at intervals of approximately 0.75 in across the plate. There were no appreciable concentration gradients across each plate and the differences in the concentration of each sample were well within the analytical experimental error for both plates. Thus it was concluded that the liquid on each plate was completely mixed.

5.4 The Method of Operation

5.4.1 The Materials

The same grade of materials which were used in the other experiments, were used for this experimental work and the specifications are tabulated in Appendix A1.

5.4.2 Chemical Analysis

The liquid and vapour compositions were analysed by the technique which was outlined in Section 2.

5.4.3 The Operation of the Column

The overhead reservoirs, each having a capacity of 10 litres, were filled and this was sufficient to last for the anticipated length of each run of five hours. The reboiler was filled with the approximately expected final composition and sufficient liquid was added so that when the column was initially operating under total reflux, there was enough liquid to flood the plates and allow the reboiler to have the correct holdup. The times for the cabinet space heaters were set so that the heaters would be switched on early and the cabinet would reach the required temperature and be ready for operation. Water was turned onto the two pressure line condensers, the column condenser and the water ejector. Crushed ice was placed in the cold junction Dewar flask and the temperature recorder was switched on. The reboiler immersion heaters were initially set to full output to enable the contents to boil quickly. As soon as boiling was achieved the output was reduced by 50 per cent and the column was operated under total reflux until all the plates were completely flooded with liquid and liquid was flowing through the downcomers. When total reflux conditions had been satisfactorily achieved, the feed and feed preheater were switched on and the liquid feed was allowed to flow onto the feed plate. It was observed that if the feed was preheated to its boiling point, the turbulence caused by the boiling affected the liquid flow in the feed line causing the flowrator floats to fluctuate. Thus the feed was preheated to about 5 degrees below its boiling point with the result that the flow was quite steady. The reflux divider was switched on and set to the required ratio whilst the bottom product line valve was opened and the flowrate checked. Next, the reboiler heaters were adjusted to give the required boilup rate which was determined from the top product flowrate. The feed flowrates and feed preheater input rate, the column condenser water rates were all checked and adjusted to the required rates.

The temperatures, ammeter, voltmeter, plate holdup, reboiler holdup, column pressure drop, feed flowrates and condenser flowrates were all read at 15 minute intervals. The time taken to achieve steady state conditions varied between one and two hours of which 30 minutes was required before the top, bottom and feed flowrates were turned on. The column was judged to have reached steady state when a constant temperature profile on the temperature recorder was obtained. The column was operated for a further two hours under equilibrium conditions before samples were taken.

Just prior to the samples being taken, the ice baths for the vapour samples were filled and the test tubes placed in them. A spare test tube was placed in each ice bath so that any condensate which had formed in the vapour sampling line could be removed before the sample was taken. The liquid samples were taken first. A 1 ml sample was removed using a hypodermic syringe to clear the liquid sample line and then a 3 ml sample was taken with the syringe. The liquid samples were taken against the direction of the liquid flow in the column so as to create the smallest disturbance in the column. Thus sampling commenced at the reboiler working up the column. When each liquid sample had been taken the plate temperature was observed. Similarly the same technique was used for the vapour sampling only in this case sampling commenced at the top of the column and proceeded downwards. Immediately before and after sampling, the parameters which were outlined earlier, were all measured.

When all the necessary readings and samples had been taken (in a period lasting about 30 minutes) the feed preheater was switched off and the feed was stopped. The reboiler immersion heaters' input was gradually reduced until the plates almost dumped the liquid. The reflux divider, the top and bottom flows were all turned off and the column was allowed to slowly drain. When the plates were nearly empty, the reboiler heaters were switched off. The temperature recorder, the condenser coolant and the ejector pump were turned off whilst the vacuum reservoir was vented to the atmosphere. The cabinet heaters were switched off, the cabinet door and the reboiler door were opened and the reboiler contents were drained off when they had cooled sufficiently.

5.5 The Experimental Programme

The main parameters which could be investigated are:

1) The feed rate
2) The feed composition
3) The preheating of the feed
4) The position of the feed
5) The plate holdup
6) The reboiler holdup
7) The boilup rate
8) The reflux ratio

Most investigators have used a general approach to their experimental work in distillation with chemical reaction. They have been more concerned with the overall performance of the plant and with the effect of certain modifications to the plant. The performance of the column has usually been quoted in terms of the overall conversion of a component only. One investigator (66) has approached the problem by examining the component conversion on each plate. Consequently it was hoped to analyse the column performance on a plate to plate basis rather than by just examining the effect of changing certain column parameters on the overall column performance.

The position of the feed plate would to a certain extent govern the overall performance of the column. Initially it was anticipated that by having the feed entering on the fourth plate both the physical separation and reaction characteristics would be clearly demonstrated in the upper and lower halves of the column respectively. Although the reaction was not fast, it was hoped that the effect of carrying out a chemical reaction on a distillation plate would be clearly shown by the performance of the three lower plates (4-6). It was also hoped to investigate the effect of using a split feed technique such that the most volatile component would be fed onto the sixth plate whilst the least volatile component and the catalyst would be fed onto the second plate. The design of the column was such that if a split feed system was required the column downcomers could be easily modified. The feedrate would affect the component conversion within the column and on each plate because the conversion is directly related to the liquid residence time. Although it would have been interesting to vary the liquid throughput, other difficulties would have been encountered, particularly with the reactant storage. Thus it was decided to maintain a constant feed rate of approximately 50 g min^{-1} and this feed rate could be maintained for five hours when 10 litre storage reservoirs were used.

After metering, the feed and catalyst were mixed and thus the reaction could proceed in the feed line. However, as the feed was at room temperature the extent of the reaction would be very small. However, it was thought that it would be advisable if the feed should be preheated and consequently the feed was passed through a feed preheater which was described in 5.2.5. The time taken for the reactants to pass through the feed preheater was less than one minute so that the extent of reaction which would have taken place would be small. Thus it was hoped that the advantage of preheating the feed would out weigh the disadvantage due to the reaction starting in the feed. The feed composition was maintained constant using an approximately equimolar ratio of the reactants with about 1 weight per cent of sulphuric acid although if required, it was possible to change the feed composition by adjusting the relative feed flowrates.

The plate holdup has a major effect on the extent of the reaction occurring on each plate as the conversion is directly affected by the liquid holdup and residence time. The plate holdup could be varied by changing the height of the weir on each liquid downcomer. Also the holdup was directly affected by the boilup rate. Thus it was decided to use the variation in plate holdup caused by changes in the boilup rate rather than by changing the liquid downcomers.

It was expected that a considerable proportion of the conversion due to the chemical reaction would take place in the reboiler. This would be due to its large volume which was necessary to completely cover the immersion heater elements, rather than due to the high concentration of the reactants. The reboiler also maintains the equilibrium of the column and equilibrium is reached with a minimum holdup. In order to determine the effect of the reboiler on overall conversion, the minimum holdup would be increased by about 50 per cent.

The boilup rate will directly affect the column and plate performance by its affect on the plate holdup and the liquid residence time. Thus the boilup rate would be increased by over 150 per cent.

Finally the reflux ratio which most investigators had maintained constant would be varied between 2:1, 4:1, 8:1 and infinite reflux.

In all, a total 20 experiments were carried out in which the boilup rate, the reboiler holdup and the reflux ratio were varied by aforementioned proportions. With the exception of the last two experiments when a split feed technique was adopted, a constant feed rate was fed onto the fourth plate. It was anticipated that the changes in the parameters would illustrate the effects of carrying out a chemical reaction in a distillation column.

5.6 The Physical Data

1) Molecular Weights

Ethyl Alcohol	46.07
Ethyl Acetate	88.11
Butyl Alcohol	74.12
Butyl Acetate	116.16

2) Molar Heat Capacities (cal mole^{-1} deg C^{-1}) (103, 139)

Ethyl Alcohol	31.33
Ethyl Acetate	40.40
Butyl Alcohol	50.92
Butyl Acetate	71.67

3) Molar Heat of Vaporisation (kcal mole^{-1}) (103)

Ethyl Alcohol	10.29
Ethyl Acetate	9.40
Butyl Alcohol	9.89
Butyl Acetate	8.97

4) Molar Volume (cm^{3} mole^{-1}) (101, 104, 114, 140-2)

Temperature ^{o}C	0	20	25	34.6	40	50	100
Ethyl Alcohol	57.14	58.37	58.76	-	-	60.36	64.31
Ethyl Acetate	-	97.90	98.89	-	-	-	-
Butyl Alcohol	89.87	91.52	92.00	92.81	-	-	-
Butyl Acetate	-	131.58	132.91	-	134.85	-	-

5) Heat of Reaction (kcal mole^{-1}) (104, 139, 143-4)

22.9 kcal mole^{-1} per ethyl alcohol reacted.

6) Kinetics of the Transesterification Reaction

Section 3.

7) Vapour Liquid Equilibrium Data

Section 4.

Other properties (including those tabulated above) were determined by taking a weighted average for each mixture.

5.7 Experimental Results

Table 5.1 Feed Compositions

Run	Weight Per Cent			Mole Per Cent		
No	ETOH	BUAC	H_2SO_4	ETOH	BUAC	H_2SO_4
1	28.30	70.66	1.04	49.80	49.30	0.90
2	27.90	71.60	0.99	49.30	49.90	0.80
3	28.40	70.55	1.05	49.90	49.20	0.90
4	28.20	70.80	1.00	49.70	49.50	0.80
5	29.10	69.90	1.02	50.80	48.40	0.80
6	29.10	69.87	1.03	50.78	48.37	0.85
7	28.60	70.40	1.02	50.20	49.00	0.80
8	28.60	70.40	1.02	50.25	48.95	0.80
9	28.30	70.70	1.02	49.90	49.30	0.80
10	29.25	69.75	1.00	50.90	48.28	0.82
11	28.30	70.70	1.01	49.90	49.30	0.80
12	28.75	70.25	1.02	50.40	48.80	0.80
13	28.45	70.45	1.07	49.90	49.00	0.90
14	27.96	71.00	1.04	49.30	49.80	0.90
15	28.50	70.50	1.04	50.00	49.10	0.90
16	29.34	69.63	1.03	51.00	48.20	0.80
17	28.70	70.25	1.05	50.30	48.80	0.90
18	28.70	70.30	1.02	50.40	48.80	0.80
19	29.90	69.10	1.03	51.56	47.60	0.84
20	29.65	69.25	1.05	51.46	47.68	0.86

Table 5.2 Mass Flowrate Balance

Run	Input ($g\ min^{-1}$)				Output ($g\ min^{-1}$)			Balance
No	ETOH	BUAC	H_2SO_4	TOTAL	TOP	BOTTOM	TOTAL	%
1	14.30	35.70	0.53	50.53	13.90	37.70	51.60	102.0
2	14.20	36.00	0.51	50.71	23.40	26.60	49.66	98.0
3	13.90	34.60	0.52	49.02	8.07	41.94	50.01	102.0
4	14.20	35.70	0.51	50.41	0.00	51.30	51.30	101.6
5	14.70	35.30	0.52	50.52	13.90	36.40	50.30	99.8
6	14.90	35.80	0.53	51.23	23.40	26.80	50.20	98.2
7	14.70	36.20	0.53	51.43	7.90	43.70	51.60	100.3
8	14.50	35.70	0.51	50.71	0.00	51.50	51.50	101.5
9	14.30	35.70	0.51	50.51	20.10	30.50	50.60	100.2
10	15.10	35.90	0.51	51.51	15.30	35.20	50.50	98.1
11	14.30	35.70	0.51	50.51	11.90	38.30	50.20	99.6
12	14.60	35.70	0.52	50.82	00.00	50.00	50.00	98.4
13	14.60	36.20	0.55	51.35	24.90	25.40	50.30	98.1
14	14.00	35.70	0.53	50.23	30.00	19.80	49.80	99.2
15	14.40	35.70	0.53	50.63	33.30	17.60	50.90	100.3
16	15.30	36.30	0.53	52.13	21.30	29.70	51.00	98.0
17	15.00	36.60	0.55	52.15	11.97	39.05	51.02	98.0
18	14.40	35.30	0.51	50.21	32.80	16.40	49.20	98.1
19	15.80	36.50	0.53	52.83	22.30	29.40	51.70	98.1
20	15.50	36.10	0.55	52.15	21.50	29.50	51.00	98.0

Table 5.3 Molar Flowrate Balance

Run No	Input (g mole min^{-1})				Output (g mole min^{-1})						Balance %
	ETOH	BUAC	H_2SO_4	TOTAL	ETAC	ETOH	BUAC	BUOH	H_2SO_4	TOTAL	
1	0.311	0.307	0.0054	0.6234	0.1123	0.1726	0.2004	0.1355	0.0054	0.6262	100.4
2	0.309	0.311	0.0052	0.6247	0.0260	0.3142	0.2415	0.0211	0.0052	0.6402	102.3
3	0.302	0.298	0.0054	0.6054	0.1077	0.1230	0.1885	0.1694	0.0054	0.5940	98.2
4	0.309	0.307	0.0052	0.6212	0.1105	0.1663	0.1912	0.1517	0.0052	0.6249	100.6
5	0.320	0.305	0.0053	0.6303	0.0691	0.1925	0.1773	0.1940	0.0053	0.6382	101.2
6	0.324	0.309	0.0054	0.6384	0.0203	0.2907	0.2284	0.1094	0.0054	0.6542	102.2
7	0.320	0.312	0.0054	0.6374	0.1010	0.1354	0.1785	0.2080	0.0054	0.6281	98.5
8	0.315	0.307	0.0052	0.6272	0.1075	0.1475	0.1795	0.1865	0.0052	0.6262	99.9
9	0.305	0.307	0.0052	0.6172	0.0400	0.3472	0.2061	0.0945	0.0052	0.6880	111.2
10	0.329	0.310	0.0052	0.6442	0.0245	0.2931	0.2263	0.1119	0.0052	0.6610	102.4
11	0.311	0.307	0.0052	0.6232	0.1536	0.1822	0.1426	0.1523	0.0052	0.6359	102.0
12	0.317	0.307	0.0053	0.6293	0.1390	0.1680	0.1582	0.1500	0.0053	0.6205	98.7
13	0.317	0.312	0.0056	0.6346	0.0155	0.3114	0.2535	0.0636	0.0056	0.6496	102.2
14	0.305	0.307	0.0054	0.6174	0.0108	0.2877	0.2727	0.0507	0.0054	0.6274	101.6
15	0.313	0.307	0.0054	0.6254	0.0352	0.2824	0.2904	0.0110	0.0054	0.6244	99.7
16	0.334	0.314	0.0054	0.6534	0.1656	0.2338	0.1333	0.1312	0.0054	0.6689	102.3
17	0.326	0.315	0.0056	0.6466	0.1623	0.1995	0.1370	0.1508	0.0056	0.6552	101.1
18	0.314	0.305	0.0052	0.6242	0.0340	0.2653	0.2094	0.1237	0.0052	0.6376	102.1
19	0.344	0.315	0.0054	0.6644	0.1569	0.2334	0.1378	0.1363	0.0054	0.6798	102.2
20	0.339	0.312	0.0056	0.6566	0.1594	0.2343	0.1358	0.1343	0.0056	0.6694	101.8

Table 5.4 Overall Conversions

Run	Molar Feed Ratio	Percentage Conversion	
No	ETOH : BUAC	ETOH	BUAC
1	1.012	44.6	33.1
2	0.995	-1.7	22.2
3	1.012	59.7	36.8
4	1.004	46.4	37.7
5	1.048	39.9	41.8
6	1.048	10.3	26.1
7	1.025	57.7	39.6
8	1.026	53.2	41.6
9	0.994	-	33.3
10	1.061	10.9	27.0
11	1.013	41.4	53.6
12	1.032	47.1	48.5
13	1.015	1.8	18.8
14	0.993	5.7	11.2
15	1.019	9.8	5.4
16	1.062	30.0	57.6
17	1.034	38.9	56.5
18	1.028	15.2	31.0
19	1.092	32.1	56.2
20	1.086	30.9	56.6

Table 5.5 Column Operating Conditions

Run No	Reflux Ratio	Feed Plate	Column ΔP Pressure drop cm H_2O	Barometric Pressure mm Hg	Reboiler holdup Litres
1	4	4	21.5	758.2	4.70
2	2	4	21.6	750.3	4.70
3	8	4	22.1	760.3	4.60
4	∞	4	22.9	756.5	4.60
5	4	4	21.6	748.9	5.50
6	2	4	21.9	758.1	6.40
7	8	4	22.1	753.3	6.20
8	∞	4	22.9	757.2	6.10
9	4	4	23.1	757.1	5.85
10	2	4	23.4	755.1	6.35
11	8	4	23.4	749.5	6.35
12	∞	4	23.5	746.8	6.50
13	4	4	24.4	744.1	5.65
14	4	4	26.4	742.9	4.70
15	4	4	27.7	750.0	4.80
16	4	4	23.4	737.9	6.25
17	8	4	23.4	755.6	6.00
18	2	4	23.4	747.1	6.40
19	4	2 & 4	27.2	761.5	5.95
20	4	2 & 6	23.1	736.5	6.05

Table 5.6 Column Loadings

Run No	Boilup Rate g min^{-1}	Vapour Loading lb ft^{-2} h^{-1}	Max. Liquid Loading lb ft^{-2} h^{-1}
1	69.5	187	288
2	70.2	189	259
3	72.6	195	308
4	70.0	188	326
5	69.5	187	285
6	70.2	189	261
7	71.1	191	309
8	70.0	188	327
9	107.5	290	350
10	105.6	284	373
11	107.1	288	392
12	105.0	283	417
13	124.5	336	403
14	150.0	404	457
15	166.5	448	495
16	148.5	400	479
17	108.0	291	396
18	98.4	265	309
19	111.5	300	379
20	107.5	290	369

Table 5.7 Plate Holdup

Run No	Plate Holdup (ml) 1	2	3	4	5	6	Reactive (ml)	Total (ml)	E.W.H.
1	123	79	167	178	149	173	500	869	978
2	154	103	200	178	139	166	483	940	983
3	126	79	173	178	149	180	507	885	1008
4	127	74	180	186	149	180	515	896	1045
5	130	79	180	178	164	176	518	907	983
6	136	84	187	178	157	173	508	915	996
7	123	79	167	178	157	189	524	893	1008
8	126	79	173	186	157	185	528	906	1045
9	144	94	193	194	164	181	539	970	1055
10	152	103	200	194	164	177	535	990	1067
11	129	84	173	186	157	185	528	914	1067
12	132	84	180	194	157	185	536	932	1072
13	158	103	213	202	171	189	562	1036	1113
14	175	123	226	219	179	185	583	1107	1205
15	169	118	219	219	179	189	587	1093	1264
16	136	84	187	186	157	185	528	935	1067
17	132	84	180	186	157	185	528	924	1067
18	132	84	180	186	157	185	528	924	1067
19	136	84	187	194	144	185	523	930	1240
20	136	84	187	194	119	177	490	897	1055

Table 5.8 Enthalpy Balance

Run No	Input (Cal min^{-1})			Output (Cal min^{-1})					Balance %
	Electrical	Feed	Total	Condenser	Tops	Bottoms	Reaction	Total	
1	16750	677	17427	10900	586	2304	2441	16231	93.14
2	22000	361	22361	14850	1224	1904	1580	19558	87.46
3	16050	545	16595	11070	277	2384	2508	16489	99.36
4	19380	514	19894	11350	-	2822	2652	16824	84.57
5	21800	556	22356	12750	641	2580	2924	18895	84.52
6	25900	403	26303	17500	1176	1870	1846	22392	85.13
7	18500	433	18933	12350	313	2700	3057	18420	97.29
8	18480	437	18917	11930	-	2800	2920	17650	93.30
9	25100	436	25536	16450	979	2120	2320	21869	85.64
10	29500	384	29884	19300	1953	1265	1917	24435	81.77
11	20600	382	20982	12570	467	2190	3765	18892	90.52
12	19430	512	19942	13200	-	2596	3408	19204	96.30
13	29980	442	30422	20650	1355	1829	1340	25204	82.85
14	32500	474	32974	22900	1763	1424	785	26872	81.49
15	32700	580	33280	23750	2377	1213	380	27680	83.17
16	22050	676	22726	15300	887	1820	4138	22145	97.44
17	20000	732	20732	12730	476	2369	4076	20651	99.61
18	28200	528	28728	22500	1789	1217	2189	27695	96.40
19	23400	500	23900	16450	987	1819	4058	23314	97.55
20	25500	493	25993	17980	946	1868	4035	25313	97.38

Table 5.9 Column Temperature

Run No	Temperature °C									
	Plate 1	Plate 2	Plate 3	Plate 4	Plate 5	Plate 6	Reboiler	Feed	Top	Bottom
1	76.2	77.0	79.5	83.0	83.9	93.7	106.1	75.0	74.0	98.4
2	89.0	98.0	112.0	113.1	114.0	121.0	122.0	65.0	78.5	118.0
3	75.0	76.0	77.0	81.5	83.0	88.0	103.0	67.0	73.0	94.0
4	72.3	73.5	78.0	81.7	82.5	85.5	91.5	64.8	72.3	90.3
5	78.5	78.8	83.5	88.5	94.7	104.7	116.2	65.2	77.5	111.2
6	94.7	101.3	109.0	112.1	117.4	119.0	119.9	50.0	83.2	111.2
7	73.5	77.8	79.3	83.5	84.3	89.5	103.9	63.7	72.3	98.3
8	76.0	76.5	77.2	80.9	81.7	83.5	93.2	54.5	73.0	89.5
9	79.2	80.7	89.1	98.2	111.7	116.3	117.5	53.8	78.5	112.2
10	96.8	105.8	107.9	109.5	112.7	113.7	115.7	62.5	85.8	113.7
11	77.0	77.1	77.6	81.2	81.9	85.2	96.7	53.0	73.0	93.0
12	72.5	77.4	77.9	81.2	81.3	83.4	91.2	58.5	72.3	86.7
13	89.9	101.8	112.7	116.5	118.5	116.8	119.3	70.0	84.0	115.8
14	99.8	114.0	117.0	115.8	115.5	115.3	114.0	76.3	91.0	116.2
15	99.8	115.3	118.8	120.1	124.8	124.8	121.8	75.0	86.3	112.5
16	76.8	77.4	78.9	82.8	85.3	93.2	104.5	63.7	75.0	98.0
17	75.6	77.8	78.4	80.0	82.2	85.3	96.0	64.2	73.5	90.3
18	96.9	106.4	109.3	112.6	117.5	118.1	119.0	66.2	85.4	115.0
19	79.0	82.7	81.5	79.5	84.2	88.7	104.3	949,62.5	78.0	98.8
20	79.7	82.9	82.7	83.9	84.2	88.8	102.1	949,40.7	78.7	98.9

Table 5.10 Stagewise Conversions, Runs 1 & 2.

Run Number			1				2			
Stage Number			Reboiler	Plate 6	Plate 5	Plate 4	Reboiler	Plate 6	Plate 5	Plate 4
Temperature		$^{\circ}C$	106.1	93.7	83.9	83.0	122.0	121.0	114.0	113.1
Rate Constant	k_1	litre $mole^{-1}$ min^{-1}	0.0496	0.0136	0.0082	0.0080	0.0992	0.0476	0.0352	0.0338
Stage Holdup	Z	litre	4.700	0.173	0.149	0.178	0.700	0.166	0.139	0.178
x_{ETAC}			0.086	0.147	0.148	0.122	0.016	0.014	0.029	0.024
x_{ETOH}			0.063	0.281	0.145	0.572	0.017	0.023	0.053	0.062
x_{BUAC}			0.499	0.383	0.296	0.270	0.803	0.796	0.728	0.722
x_{BUOH}			0.339	0.185	0.077	0.032	0.142	0.161	0.185	0.186
Molar Volume	v	litre $mole^{-1}$	0.105	0.107	0.095	0.090	0.137	0.135	0.131	0.130
$\left(x_{ETOH}\, x_{BUAC} - \frac{1}{K}\, x_{ETAC}\, x_{BUOH}\right) \frac{k_1 Z}{v^2}$		mole min^{-1}	0.0226	0.0161	0.0174	0.0264	0.280	0.0066	0.0093	0.0129
Stage Conversion		%	21.25	15.14	16.25	24.76	405	9.51	13.51	18.66
Heat Absorbed		cal min^{-1}	519	370	398	604	6426	150	213	295

Table 5.10 (Cont'd.) Runs 3 & 4.

Run Number			3				4			
Stage Number			Reboiler	Plate 6	Plate 5	Plate 4	Reboiler	Plate 6	Plate 5	Plate 4
Temperature		°C	103.0	88.0	83.0	81.5	91.5	85.5	82.5	81.7
Rate Constant	k_1	litre $mole^{-1}$ min^{-1}	0.0430	0.0094	0.0072	0.0067	0.0248	0.0077	0.0066	0.0063
Stage Holdup	Z	litre	4.600	0.180	0.149	0.178	4.600	0.180	0.149	0.186
x_{ETAC}			0.111	0.168	0.162	0.147	0.187	0.251	0.244	0.232
x_{ETOH}			0.116	0.384	0.528	0.596	0.187	0.436	0.536	0.572
x_{BUAC}			0.401	0.308	0.258	0.241	0.360	0.233	0.194	0.187
x_{BUOH}			0.361	0.137	0.048	0.018	0.257	0.076	0.023	0.005
Molar Volume	v	litre $mole^{-1}$	0.114	0.100	0.092	0.088	0.104	0.096	0.090	0.088
$\left(x_{ETOH}\,x_{BUAC} - \frac{1}{K}\,x_{ETAC}\,x_{BUOH}\right)\frac{k_1 Z}{v^2}$		mole min^{-1}	0.0727	0.0156	0.0161	0.0215	0.182	.0121	.0118	.0161
Stage Conversion		%	66.41	14.22	14.68	19.64	158	10.42	10.18	13.94
Heat Absorbed		cal min^{-1}	16.68	358	368	492	4177	277	270	369

Table 5.10 (Cont'd.) Runs 5 & 6.

Run Number			5				6			
Stage Number			Reboiler	Plate 6	Plate 5	Plate 4	Reboiler	Plate 6	Plate 5	Plate 4
Temperature		^{o}C	116.2	104.7	94.7	88.5	119.9	119.0	117.4	112.1
Rate Constant	k_1	litre $mole^{-1} min^{-1}$	0.0776	0.0223	0.0139	0.0102	0.0908	0.0440	0.0410	0.0330
Stage Holdup	Z	litre	5.500	0.176	0.164	0.178	0.400	0.173	0.157	0.178
x_{ETAC}			0.024	0.046	0.065	0.065	0.000	0.000	0.006	0.020
x_{ETOH}			0.028	0.138	0.335	0.518	0.033	0.024	0.036	0.074
x_{BUAC}			0.448	0.437	0.362	0.314	0.669	0.646	0.624	0.581
x_{BUOH}			0.486	0.375	0.233	0.099	0.278	0.323	0.328	0.320
Molar Volume	v	litre $mole^{-1}$	0.119	0.114	0.102	0.094	0.129	0.128	0.123	0.123
$\left(x_{ETOH}\, x_{BUAC} - \frac{1}{K}\, x_{ETAC}\, x_{BUOH}\right) \frac{k_1 Z}{v^2}$		mole min^{-1}	0.0118	0.0126	0.0232	0.0318	0.771	0.0072	0.0084	0.0133
Stage Conversion		%	9.22	9.85	18.16	24.87	953	8.90	10.38	16.55
Heat Absorbed		cal min^{-1}	271	288	531	727	17694	164	192	306

Table 5.10 (Cont'd.) Runs 7 & 8.

Run Number			7				8			
Stage Number			Reboiler	Plate 6	Plate 5	Plate 4	Reboiler	Plate 6	Plate 5	Plate 4
Temperature		^{o}C	103.9	89.5	84.3	83.5	93.2	83.5	81.7	80.9
Rate Constant	k_1	litre $mole^{-1} min^{-1}$	0.0448	0.0104	0.00794	0.00762	0.0270	0.00698	0.0063	0.00610
Stage Holdup	Z	litre	6.200	0.189	0.157	0.178	6.100	0.185	0.157	0.186
x_{ETAC}			0.096	0.148	0.144	0.112	0.182	0.239	0.239	0.228
x_{ETOH}			0.127	0.394	0.548	0.593	0.226	0.466	0.549	0.578
x_{BUAC}			0.354	0.304	0.261	0.272	0.287	0.218	0.192	0.186
x_{BUOH}			0.412	0.150	0.044	0.020	0.298	0.074	0.017	0.006
Molar Volume	v	litre $mole^{-1}$	0.111	0.099	0.092	0.090	0.104	0.093	0.089	0.088
$\left(x_{ETOH}\, x_{BUAC} - \frac{1}{K}\, x_{ETAC}\, x_{BUOH}\right) \frac{k_1 Z}{v^2}$		mole min^{-1}	0.0838	0.0198	0.0204	0.0270	0.132	0.0123	0.0131	0.0155
Stage Conversion		%	62.69	14.43	15.26	20.20	104	9.62	10.30	12.14
Heat Absorbed		cal min^{-1}	1911	441	468	618	5003	281	301	354

Table 5.10 (Cont'd.) Runs 9 & 10.

Run Number			9				10			
Stage Number			Reboiler	Plate 6	Plate 5	Plate 4	Reboiler	Plate 6	Plate 5	Plate 4
Temperature		^oC	117.5	116.3	111.7	98.2	115.7	113.7	112.7	109.5
Rate Constant	k_1	litre $mole^{-1} min^{-1}$	0.0820	0.0301	0.0247	0.0133	0.0759	0.0291	0.0278	0.0242
Stage Holdup	Z	litre	5.850	0.181	0.164	0.194	6.350	0.177	0.164	0.194
x_{ETAC}			0.014	0.008	0.014	0.025	0.045	0.040	0.029	0.003
x_{ETOH}			0.030	0.034	0.090	0.277	0.021	0.027	0.037	0.102
x_{BUAC}			0.629	0.624	0.569	0.450	0.684	0.696	0.674	0.634
x_{BUOH}			0.310	0.330	0.324	0.240	0.215	0.233	0.255	0.257
Molar Volume	v	litre $mole^{-1}$	0.127	0.123	0.122	0.109	0.131	0.130	0.128	0.124
$\left(x_{ETOH}\ x_{BUAC} - \frac{1}{K}\ x_{ETAC}\ x_{BUOH}\right) \frac{k_1 Z}{v^2}$		mole min^{-1}	0.428	0.0064	0.0124	0.0661	0.121	0.0029	0.0047	0.0192
Stage Conversion		%	423	6.38	12.29	65.44	144	3.51	5.66	22.89
Heat Absorbed		cal min^{-1}	9823	147	284	1517	2777	67	109	439

Table 5.10 (Cont'd.) Runs 11 & 12.

Run Number			11				12			
Stage Number			Reboiler	Plate 6	Plate 5	Plate 4	Reboiler	Plate 6	Plate 5	Plate 4
Temperature		^{o}C	96.7	85.2	81.9	81.2	91.2	83.4	81.3	81.2
Rate Constant	k_1	litre mole^{-1}min^{-1}	0.0320	0.0063	0.0053	0.0051	0.0245	0.0055	0.0049	0.0050
Stage Holdup	Z	litre	6.350	0.185	0.157	0.186	6.500	0.185	0.157	0.194
x_{ETAC}			0.153	0.221	0.214	0.197	0.234	0.277	0.247	0.264
x_{ETOH}			0.188	0.425	0.553	0.590	0.261	0.471	0.565	0.541
x_{BUAC}			0.313	0.244	0.199	0.198	0.255	0.195	0.175	0.173
x_{BUOH}			0.334	0.107	0.031	0.012	0.242	0.054	0.011	0.019
Molar Volume	v	litre mole^{-1}	0.107	0.096	0.089	0.087	0.102	0.092	0.088	0.089
$\left(x_{ETOH}\, x_{BUAC} - \frac{1}{K}\, x_{ETAC}\, x_{BUOH}\right) \frac{k_1 Z}{v^2}$		mole min^{-1}	0.0996	0.0099	0.0108	0.0113	0.116	0.0089	0.0921	0.0106
Stage Conversion		%	60.47	6.04	6.50	6.86	78.0	6.01	6.19	7.13
Heat Absorbed		cal min^{-1}	2286	227	249	258	2662	205	211	243

Table 5.10 (Cont'd.) Runs 13 & 14.

Run Number			13				14			
Stage Number			Reboiler	Plate 6	Plate 5	Plate 4	Reboiler	Plate 6	Plate 5	Plate 4
Temperature		^oC	119.3	116.8	118.5	116.5	114.0	115.3	115.5	115.8
Rate Constant	k_1	litre $mole^{-1} min^{-1}$	0.0886	0.0285	0.0309	0.0278	0.0705	0.0229	0.0231	0.0233
Stage Holdup	Z	litre	5.65	0.189	0.171	0.202	4.70	0.185	0.179	0.219
x_{ETAC}			0.000	0.000	0.000	0.011	0.000	0.000	0.000	0.031
x_{ETOH}			0.043	0.033	0.021	0.042	0.087	0.060	0.054	0.035
x_{BUAC}			0.798	0.776	0.751	0.684	0.816	0.869	0.868	0.849
x_{BUOH}			0.144	0.187	0.225	0.259	0.068	0.062	0.074	0.081
Molar Volume	v	litre $mole^{-1}$	0.134	0.133	0.133	0.129	0.134	0.136	0.137	0.137
$\left(x_{ETOH}\, x_{BUAC} - \frac{1}{K}\, x_{ETAC}\, x_{BUOH}\right) \frac{k_1 Z}{v^2}$		mole min^{-1}	0.956	0.0077	0.0047	0.0087	1.309	0.0128	0.0100	0.0073
Stage Conversion		%	-	13.18	7.94	14.81	-	37.35	29.18	21.28
Heat Absorbed		cal min^{-1}	21940	481	106	198	30042	294	229	167

Table 5.10 (Cont'd.) Runs 15 & 16.

Run Number			15				16			
Stage Number			Reboiler	Plate 6	Plate 5	Plate 4	Reboiler	Plate 6	Plate 5	Plate 4
Temperature		^{o}C	121.8	124.8	124.8	120.1	104.5	93.2	85.3	82.8
Rate Constant	k_1	litre $mole^{-1} min^{-1}$	0.0984	0.0316	0.0316	0.0233	0.0461	0.0079	0.0054	0.0047
Stage Holdup	Z	litre	4.80	0.189	0.179	0.219	6.25	0.185	0.157	0.186
x_{ETAC}			0.015	0.000	0.000	0.016	0.090	0.144	0.152	0.138
x_{ETOH}			0.019	0.000	0.000	0.019	0.095	0.297	0.516	0.613
x_{BUAC}			0.932	0.971	0.971	0.929	0.413	0.339	0.252	0.220
x_{BUOH}			0.000	0.000	0.000	0.025	0.386	0.218	0.077	0.027
Molar Volume	v	litre $mole^{-1}$	0.143	0.145	0.145	0.141	0.115	0.104	0.092	0.111
$\left(x_{ETOH}\, x_{BUAC} - \frac{1}{K}\, x_{ETAC}\, x_{BUOH}\right) \frac{k_1 Z}{v^2}$		mole min^{-1}	0.450	0.000	0.000	0.0043	0.0664	0.0091	0.0117	0.0068
Stage Conversion		%	-	0.000	0.000	25.9	36.72	5.04	6.47	3.76
Heat Absorbed		cal min^{-1}	10328	0.000	0.000	99	1524	207	269	155

Table 5.10 (Cont'd.) Runs 17 & 18.

Run Number			17				18			
Stage Number			Reboiler	Plate 6	Plate 5	Plate 4	Reboiler	Plate 6	Plate 5	Plate 4
Temperature		^{o}C	96.0	85.3	82.2	80.0	119.0	118.1	117.5	112.6
Rate Constant	k_1	litre $mole^{-1} min^{-1}$	0.0309	0.0072	0.0062	0.0055	0.0874	0.0368	0.0358	0.0268
Stage Holdup	Z	litre	6.00	0.185	0.157	0.186	6.40	0.185	0.157	0.186
x_{ETAC}			0.162	0.223	0.213	0.190	0.021	0.026	0.026	0.021
x_{ETOH}			0.218	0.442	0.554	0.596	0.011	0.021	0.021	0.068
x_{BUAC}			0.290	0.228	0.198	0.200	0.643	0.658	0.643	0.600
x_{BUOH}			0.319	0.104	0.032	0.012	0.293	0.290	0.306	0.306
Molar Volume	v	litre $mole^{-1}$	0.106	0.094	0.089	0.087	0.136	0.129	0.128	0.124
$\left(x_{ETOH}\, x_{BUAC} - \frac{1}{K}\, x_{ETAC}\, x_{BUOH}\right) \frac{k_1 Z}{v^2}$		mole min^{-1}	.155	0.0113	0.0124	0.0156	0.0201	0.0024	0.0018	0.0109
Stage Conversion		%	87.10	6.35	6.97	8.76	21.02	2.50	1.89	11.40
Heat Absorbed		cal min^{-1}	3557	258	285	357	461	55	41	250

Table 5.10 (Cont'd.) Run 19.

Run Number			19					
Stage Number			Reboiler	Plate 6	Plate 5	Plate 4	Plate 3	Plate 2
Temperature		^{o}C	104.3	88.7	84.2	79.5	81.5	82.7
Rate Constant	k_1	litre $mole^{-1} min^{-1}$	0.0457	0.0030	0.0064	0.0050	0.0056	0.0059
Stage Holdup	Z	litre	5.95	0.185	0.144	0.194	0.187	0.084
x_{ETAC}			0.098	0.167	0.179	0.170	0.186	0.199
x_{ETOH}			0.117	0.363	0.528	0.612	0.576	0.557
x_{BUAC}			0.372	0.288	0.230	0.193	0.226	0.235
x_{BUOH}			0.396	0.180	0.061	0.022	0.010	0.006
Molar Volume	v	litre $mole^{-1}$	0.116	0.100	0.091	0.086	0.098	0.090
$\left(x_{ETOH}\, x_{BUAC} - \frac{1}{K}\, x_{ETAC}\, x_{BUOH}\right) \frac{k_1 Z}{v^2}$		mole min^{-1}	0.0624	0.0132	0.0121	0.0148	0.0137	0.0079
Stage Conversion		%	35.22	7.45	6.83	8.35	7.73	4.46
Heat Absorbed		cal min^{-1}	143	303	277	340	314	180

Table 5.10 (Cont'd.) Run 20.

Run Number			20					
Stage Number			Reboiler	Plate 6	Plate 5	Plate 4	Plate 3	Plate 2
Temperature		^oC	102.1	88.8	84.2	83.9	82.7	82.9
Rate Constant	k_1	litre $mole^{-1} min^{-1}$	0.0412	0.0086	0.0068	0.0067	0.0063	0.0064
Stage Holdup	Z	litre	6.05	0.177	0.119	0.194	0.187	0.084
x_{ETAC}			0.103	0.160	0.187	0.206	0.216	0.225
x_{ETOH}			0.135	0.387	0.493	0.532	0.548	0.538
x_{BUAC}			0.352	0.279	0.248	0.232	0.222	0.228
x_{BUOH}			0.393	0.172	0.069	0.027	0.012	0.007
Molar Volume	v	litre $mole^{-1}$	0.111	0.098	0.093	0.091	0.090	0.091
$\left(x_{ETOH}\, x_{BUAC} - \frac{1}{K}\, x_{ETAC}\, x_{BUOH}\right) \frac{k_1 Z}{v^2}$		mole min^{-1}	0.108	0.0124	0.0101	0.0183	0.0122	0.0077
Stage Conversion		%	61.27	7.04	5.73	10.39	9.76	4.37
Heat Absorbed		cal min^{-1}	2479	284	232	420	395	176

Table 5.11 Column Compositions and Stage Efficiencies, Runs 1 & 2.

		Mole Per Cent												% Vaporisation Efficiencies (E_v)				% Murphree Efficiencies (E_m)			
		x				y				y*											
		ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH
1	T	34.3	64.9	0.8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	27.0	71.3	1.7	—	37.2	62.8	—	—	31.5	68.1	0.4	—	118	92	—	—	290	339	—	—
	2	18.1	77.2	4.7	—	28.5	69.9	1.6	—	21.7	77.1	1.3	—	131	91	123	—	∞	-243	88	—
	3	14.0	74.8	10.6	0.6	21.0	75.0	3.9	—	16.4	80.5	3.0	0.1	128	93	130	—	-119	34	83	—
	4	12.2	57.2	27.0	3.2	18.5	72.2	8.4	0.9	14.7	76.7	7.8	0.7	126	94	108	129	33	26	-50	0
	5	14.8	47.5	29.6	7.7	20.4	70.6	8.2	0.9	19.1	69.8	9.1	2.1	107	101	90	43	70	105	115	122
	6	14.7	28.1	38.3	18.5	23.4	53.7	15.3	7.6	23.8	54.0	14.9	7.3	98	99	103	104	33	99	98	98
	B	8.6	6.3	49.9	33.9	23.2	23.5	30.9	23.4	21.3	19.8	32.4	26.5	109	73	95	88	—	—	—	—
2	T	5.4	79.2	11.0	4.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	3.2	51.6	28.0	17.2	5.7	59.5	20.6	14.1	4.7	79.9	10.3	5.1	121	75	200	276	191	51	58	50
	2	3.9	23.9	46.4	25.8	3.6	38.5	34.8	23.1	7.5	56.0	23.1	13.5	48	69	151	171	30	108	53	23
	3	1.5	6.7	67.4	24.4	1.9	24.2	48.0	26.0	4.0	24.3	49.0	22.6	48	100	98	115	-5	97	106	525
	4	2.4	6.2	72.2	18.6	2.0	20.4	55.8	21.8	6.6	23.5	52.3	17.7	30	87	107	123	-16	82	81	-71
	5	2.9	5.3	72.8	18.5	2.5	6.7	20.8	20.1	7.9	20.4	53.6	18.1	32	33	132	111	24	17	33	195
	6	1.4	2.3	79.6	16.1	0.8	3.9	79.2	16.0	4.3	10.2	66.6	18.9	19	38	119	85	-21	-47	8	40
	B	1.6	1.7	80.3	14.2	1.4	5.9	80.3	12.4	5.0	8.1	69.4	17.5	28	73	116	46	—	—	—	—

Table 5.11 (Cont'd.) Runs 3 & 4.

		Mole Per Cent												% Vaporisation Efficiencies (E_v)				% Murphree Efficiencies (E_m)			
		x				y				y*											
		ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH
3	T	44.7	55.0	0.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	35.0	63.8	1.2	—	45.9	54.1	—	—	39.0	60.7	0.3	—	118	89	—	—	323	375	—	—
	2	24.4	71.2	3.7	0.8	35.9	63.1	1.1	—	28.6	70.4	0.9	0.1	126	90	112	—	−∞	-284	89	—
	3	17.9	72.6	8.8	0.7	28.7	68.5	2.8	—	21.0	76.6	2.3	0.1	137	89	121	—	−∞	-31	91	—
	4	14.7	59.6	24.1	1.8	21.1	70.4	7.8	0.7	16.5	76.4	6.7	0.4	128	92	116	175	43	40	15	57
	5	16.2	52.8	25.8	4.8	24.5	66.4	8.0	1.1	19.9	71.6	7.4	1.1	123	93	108	100	39	61	97	0
	6	16.8	38.4	30.8	13.7	27.5	58.2	10.4	3.9	23.7	61.9	10.2	4.2	116	94	102	93	25	85	98	103
	B	11.1	11.6	40.1	36.1	28.8	37.6	18.5	15.1	24.6	30.8	22.3	22.5	117	122	83	67	—	—	—	—
4	T	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	48.7	51.3	—	—	50.9	49.1	—	—	50.7	49.3	—	—	100	100	—	—	105	106	—	—
	2	40.8	57.7	1.5	—	46.9	52.5	0.6	—	44.0	55.7	0.3	—	107	94	162	—	187	209	73	—
	3	31.6	63.2	5.3	—	40.7	57.9	1.4	—	35.1	63.7	1.2	—	116	91	109	—	234	−∞	95	—
	4	23.2	57.2	18.7	0.5	31.0	63.4	5.6	—	26.2	68.9	4.7	0.1	118	92	119	—	16	26	36	—
	5	24.4	53.6	19.4	2.3	31.9	61.5	6.1	0.4	28.2	66.4	5.0	0.5	113	93	122	80	24	49	62	106
	6	25.1	43.6	23.3	7.6	33.1	56.8	7.9	2.3	30.9	60.3	6.9	1.9	107	93	114	120	4	81	87	95
	B	18.7	18.7	36.0	25.7	33.2	42.1	14.4	10.4	33.2	39.7	13.4	11.8	100	106	94	88	—	—	—	—

Table 5.11 (Cont'd) Runs 5 & 6.

		Mole Per Cent												% Vaporisation Efficiencies (E_v)				% Murphree Efficiencies (E_m)			
		x				y				y*											
		ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH
5	T	24.4	74.6	0.9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	15.3	81.7	3.0	—	26.2	72.9	0.9	—	19.0	80.1	0.9	—	138	91	100	—	257	377	0	—
	2	9.5	83.3	6.4	0.8	14.4	82.7	2.9	—	11.8	86.1	2.0	0.2	122	96	145	—	391	-14	76	—
	3	8.4	63.2	22.2	6.3	10.7	83.0	5.8	0.6	10.4	81.5	6.8	1.4	103	102	85	43	130	125	119	147
	4	6.5	51.8	31.4	9.9	9.4	75.4	12.2	3.1	8.8	78.0	10.5	2.7	107	97	116	115	57	85	80	95
	5	6.5	33.5	36.2	23.3	10.2	61.0	18.8	10.0	11.0	64.4	15.3	9.4	93	95	123	106	64	90	81	97
	6	4.6	13.8	43.7	37.5	8.8	29.9	33.9	27.3	10.7	38.2	26.2	24.9	82	78	129	109	57	73	63	83
	B	2.4	2.8	44.8	48.6	6.3	7.9	46.9	39.0	7.3	9.6	35.8	47.4	86	82	131	82	—	—	—	—
6	T	5.2	72.5	13.1	9.2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	2.1	47.6	27.0	23.3	5.4	75.7	11.5	7.4	3.4	78.2	10.8	7.7	159	97	106	96	433	90	95	103
	2	1.2	20.5	42.4	35.9	2.8	54.3	23.7	19.2	2.6	52.2	24.0	21.3	108	104	99	90	150	113	103	145
	3	1.3	9.9	52.6	36.2	2.2	36.3	35.5	26.0	3.3	31.8	35.9	29.0	67	114	99	90	-120	202	104	36
	4	2.0	7.4	58.1	32.0	2.8	27.4	45.5	24.3	5.5	24.7	41.7	28.1	51	111	109	86	0	119	85	445
	5	0.6	3.6	62.4	32.8	2.8	7.8	60.2	29.2	1.8	13.9	50.5	33.8	156	56	119	86	43	49	46	30
	6	—	2.4	64.6	32.3	2.5	2.0	68.3	27.2	—	9.9	54.6	35.5	—	20	125	77	—	5	25	36
	B	—	3.3	66.9	27.8	3.0	1.6	72.8	22.5	—	13.5	56.1	30.4	—	12	130	74	—	—	—	—

Table 5.11 (Cont'd.) Runs 7 & 8.

		Mole Per Cent												% Vaporisation Efficiencies (E_v)				% Murphree Efficiencies (E_m)			
		x				y				y*											
		ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH
7	T	42.4	57.6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	32.3	66.7	1.0	—	42.4	57.6	—	—	36.6	63.2	0.2	—	116	91	—	—	232	270	—	—
	2	21.5	74.8	3.7	—	32.2	66.5	1.3	—	25.5	73.6	1.0	—	126	90	130	—	316	∞	87	—
	3	14.3	76.1	9.1	0.5	22.4	74.3	3.3	—	16.9	80.5	2.6	0.1	133	92	127	—	∞	5	89	—
	4	11.2	59.3	27.2	2.0	16.5	74.0	9.0	0.5	13.3	78.4	7.8	0.4	124	94	115	125	56	54	-9	93
	5	14.4	54.8	26.1	4.4	20.5	68.8	8.9	1.8	17.6	73.9	7.5	1.0	116	93	119	180	48	67	70	85
	6	14.8	39.4	30.4	15.0	23.2	58.3	12.1	6.4	21.1	63.8	10.4	4.7	110	92	116	136	-17	53	86	91
	B	9.6	12.7	35.4	41.2	22.9	52.0	22.5	22.6	21.5	33.0	20.0	25.4	107	158	113	89	—	—	—	—
8	T	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	47.1	52.4	0.5	—	52.8	47.2	—	—	49.4	50.5	0.1	—	107	93	—	—	213	227	—	—
	2	40.5	58.2	1.3	—	46.4	53.1	0.5	—	43.8	56.0	0.3	—	106	95	152	—	160	197	82	—
	3	33.8	62.6	3.6	0.5	39.5	59.0	1.4	—	37.4	61.8	0.8	—	106	95	175	—	132	329	86	—
	4	22.8	57.8	18.6	0.6	30.9	63.9	5.2	—	25.8	69.4	4.7	0.1	120	92	111	—	2	22	38	—
	5	23.9	54.9	19.2	1.7	31.0	63.2	5.5	0.3	27.4	67.3	4.8	0.4	113	94	115	75	41	55	59	106
	6	23.9	46.6	21.8	7.4	33.5	58.1	6.5	2.0	29.5	62.7	6.0	1.8	114	93	108	111	18	70	89	97
	B	18.2	23.6	28.7	29.8	32.9	47.5	10.7	8.9	29.8	46.0	11.8	12.4	110	103	91	72	—	—	—	—

Table 5.11 (Cont'd.) Runs 9 & 10

		Mole Per Cent												% Vaporisation Efficiencies (E_v)				% Murphree Efficiencies (E_m)			
		x				y				y*											
		ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH
9	T	9.3	87.1	3.6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	5.3	86.0	7.0	1.6	10.3	86.9	2.7	—	6.8	90.6	2.3	0.3	151	96	117	—	∞	14	92	—
	2	3.1	75.8	14.6	6.6	6.4	86.3	7.3	—	3.9	89.9	4.8	1.4	164	96	152	—	∞	74	73	—
	3	2.6	54.0	27.7	15.8	4.1	75.8	13.9	6.3	3.7	81.7	10.1	4.6	111	93	138	137	167	80	78	86
	4	2.5	27.7	45.0	24.0	3.1	52.4	28.1	16.4	4.6	62.0	21.7	11.8	67	85	129	139	0	74	69	73
	5	1.4	9.0	56.9	32.4	3.1	25.6	42.6	28.7	3.6	29.8	39.5	27.1	86	86	108	106	58	81	83	71
	6	0.8	3.4	62.4	33.0	2.4	7.3	57.6	32.7	2.5	13.2	50.4	34.0	96	55	114	96	93	45	57	73
	B	1.4	3.0	62.9	31.0	1.1	2.5	67.3	29.1	4.2	12.1	51.3	32.4	26	21	131	90	—	—	—	—
10	T	13.5	56.8	24.2	15.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	2.2	25.6	40.3	31.9	4.5	64.3	20.4	10.9	4.3	58.6	20.6	16.5	105	110	99	66	120	125	101	172
	2	2.3	11.7	51.6	34.4	3.3	35.9	36.5	24.3	5.7	35.6	33.2	25.5	58	101	110	95	48	103	78	∞
	3	2.1	8.3	59.1	30.5	2.0	24.7	47.9	25.5	5.3	27.9	41.0	25.8	38	89	117	99	13	60	62	94
	4	0.3	10.2	63.4	25.7	1.5	19.8	57.9	20.8	0.8	34.3	43.4	21.5	187	58	133	97	-75	48	50	-450
	5	2.9	3.7	67.4	25.5	1.2	6.5	70.6	21.7	8.2	14.6	51.7	25.6	14	45	137	85	4	27	30	56
	6	4.0	2.7	69.6	23.3	0.9	3.5	78.8	16.8	11.3	10.9	53.8	24.0	8	32	146	70	—	21	221	24
	B	4.5	2.1	68.4	21.5	—	1.5	85.9	12.6	13.2	8.6	54.9	23.3	—	17	156	54	—	—	—	—

Table 5.11 (Cont'd.) Runs 11 & 12.

		Mole Per Cent												% Vaporisation Efficiencies (E_v)				% Murphree Efficiencies (E_m)			
		x				y				y*											
		ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH
11	T	47.8	52.2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	42.3	57.3	0.5	—	49.0	51.0	—	—	45.4	54.5	0.1	—	108	94	—	—	78	209	—	—
	2	32.7	65.2	2.2	—	41.7	57.7	0.6	—	36.7	62.9	0.5	—	114	92	120	—	30	∞	93	—
	3	24.9	68.8	6.2	—	34.7	63.5	1.9	—	28.5	70.0	1.5	—	122	91	127	—	19	-81	90	—
	4	19.7	59.0	19.8	1.2	27.9	66.4	5.7	—	22.7	71.9	5.2	0.3	123	92	110	—	32	83	95	—
	5	21.4	55.3	19.9	3.1	30.4	39.6	15.3	14.7	25.1	69.0	5.3	0.7	121	57	289	∞	10	-150	-233	-448
	6	22.1	42.5	24.4	10.7	31.0	57.7	8.3	3.0	28.8	61.2	7.2	2.8	108	94	115	107	222	-195	0	111
	B	15.3	18.8	31.3	33.4	27.0	64.9	7.2	0.9	28.0	41.7	14.4	15.9	96	157	50	6	—	—	—	—
12	T	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	48.7	51.3	—	—	53.4	46.6	—	—	50.7	49.3	—	—	105	95	—	—	193	204	—	—
	2	42.3	56.4	1.3	—	47.8	51.9	0.4	—	45.3	54.5	0.2	—	106	95	146	—	171	208	82	—
	3	33.7	61.7	4.6	—	41.8	56.9	1.3	—	37.2	61.8	1.0	—	112	92	120	—	215	$-\infty$	93	—
	4	26.4	54.1	17.3	1.9	33.2	61.7	5.1	—	30.1	65.2	4.3	0.4	110	95	118	—	16	103	-33	—
	5	24.7	56.5	17.5	1.1	33.8	61.3	4.9	—	28.1	67.4	4.4	0.2	120	91	111	—	28	43	64	—
	6	27.7	47.1	19.5	5.4	36.0	56.7	5.8	1.4	32.9	60.8	5.1	1.2	109	93	114	117	26	70	81	97
	B	23.4	26.1	25.5	24.2	37.1	47.3	8.7	7.0	35.0	47.3	9.2	8.6	106	100	95	81	—	—	—	—

Table 5.11 (Cont'd.) Runs 13 & 14.

		Mole Per Cent												% Vaporisation Efficiencies (E_v)				% Murphree Efficiencies (E_m)			
		x				y				y*											
		ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH
13	T	3.8	73.4	15.8	7.0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	2.5	52.5	25.8	19.2	4.1	77.6	13.7	4.6	3.7	80.8	9.8	5.8	111	96	140	79	133	88	75	110
	2	2.0	22.6	44.5	31.3	2.5	53.9	25.6	18.1	4.0	55.0	23.6	17.4	63	98	108	104	35	95	88	92
	3	0.8	8.1	59.5	31.5	1.7	31.5	40.8	26.1	2.2	28.0	42.4	27.4	77	113	96	95	55	136	112	38
	4	1.1	4.2	68.4	25.9	1.1	18.2	55.4	25.3	3.2	16.6	53.7	26.4	34	112	103	96	0	114	89	27
	5	—	2.1	75.1	22.5	1.1	5.4	68.6	24.9	—	9.1	64.5	26.3	—	59	106	95	-38	48	68	78
	6	—	3.3	77.6	18.7	0.8	2.0	77.2	20.0	—	14.4	64.3	21.3	—	14	120	94	-64	9	24	78
	B	—	4.3	79.8	14.4	2.2	0.7	82.5	14.6	—	19.0	64.7	16.4	—	4	128	89	—	—	—	—
14	T	2.5	61.8	27.0	8.7	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	1.2	26.9	54.7	17.3	1.6	64.5	22.4	11.0	2.2	62.9	26.2	8.8	73	103	85	125	0	105	119	83
	2	1.4	7.3	75.6	15.8	2.2	29.8	45.9	22.1	3.7	27.5	53.9	14.9	59	108	85	148	29	119	179	-67
	3	2.4	2.3	83.8	11.5	1.6	15.3	64.0	19.2	7.1	10.5	68.8	13.6	23	146	93	141	-12	-167	223	∞
	4	3.1	3.5	84.9	8.1	2.2	12.3	72.7	12.9	8.9	15.7	66.3	9.1	25	78	110	142	0	75	67	-138
	5	—	5.4	86.8	7.4	2.2	2.1	85.0	10.7	—	23.6	68.1	8.4	—	9	125	127	—	-11	27	158
	6	—	6.0	86.9	6.2	—	4.3	91.3	4.4	—	28.0	65.4	6.6	—	15	140	67	—	-4	2	84
	B	—	8.7	81.6	6.8	—	5.3	91.9	2.8	—	34.9	58.5	6.7	—	15	157	42	—	—	—	—

Table 5.11 (Cont'd.) Runs 15 & 16.

		Mole Per Cent												% Vaporisation Efficiencies (E_v)				% Murphree Efficiencies (E_m)			
		x				y				y*											
		ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH
15	T	7.0	59.9	30.8	2.4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	4.5	23.6	65.6	6.3	7.3	62.0	28.7	2.1	8.1	58.5	30.0	3.4	90	106	96	62	78	111	104	286
	2	1.7	6.3	88.7	3.4	4.5	26.6	64.8	4.1	4.7	26.6	65.1	3.6	96	100	100	114	92	100	102	136
	3	1.7	2.7	92.7	3.0	2.2	15.8	79.8	2.2	5.2	13.3	77.8	3.8	42	119	103	58	14	214	74	30
	4	1.6	1.9	92.9	2.5	1.7	11.1	85.6	1.5	5.0	9.6	81.0	4.4	34	116	106	34	20	119	70	6
	5	—	—	97.1	—	0.9	1.5	96.2	1.3	—	—	99.9	—	—	—	96	—	—	4	—	—
	6	—	—	97.1	—	—	—	99.9	—	—	—	99.9	—	—	—	100	—	—	0	—	—
	B	1.5	1.9	93.2	—	—	—	99.9	—	5.0	10.0	84.9	—	—	—	118	—	—	—	—	—
16	T	39.9	60.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	30.3	68.1	1.6	—	40.6	59.4	—	—	34.6	65.0	0.4	—	117	91	—	—	287	356	—	—
	2	21.7	74.7	3.7	—	31.5	67.2	1.3	—	25.6	73.4	1.0	—	123	92	130	—	∞	-377	79	—
	3	16.3	74.7	9.0	—	25.5	72.1	2.4	—	19.0	78.6	2.4	—	134	92	100	—	-441	-5	100	—
	4	13.8	61.3	22.0	2.7	20.2	72.4	7.3	—	16.3	77.0	6.2	0.6	124	94	118	—	51	57	21	—
	5	15.2	51.6	25.2	7.7	24.2	66.3	7.6	1.9	19.3	71.3	7.5	1.9	125	93	101	100	0	71	98	100
	6	14.4	29.7	33.9	21.8	24.2	54.1	13.4	8.4	23.3	55.2	13.2	8.4	104	98	102	100	160	96	98	100
	B	9.0	9.5	41.3	38.6	21.8	28.2	25.7	24.3	21.9	26.5	24.4	27.3	100	106	105	89	—	—	—	—

Table 5.11 (Cont'd.) Runs 17 & 18

		Mole Per Cent												% Vaporisation Efficiencies (E_v)				% Murphree Efficiencies (E_m)			
		x				y				y*											
		ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH
17	T	47.1	52.9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	41.0	58.3	0.7	—	48.0	52.0	—	—	44.3	55.5	0.2	—	108	94	—	—	200	203	—	—
	2	32.6	65.4	2.1	—	40.6	58.9	0.5	—	36.6	62.9	0.5	—	111	94	100	—	282	433	100	—
	3	23.8	70.0	6.2	—	34.4	64.1	1.5	—	27.4	71.1	1.5	—	126	90	100	—	567	-100	100	—
	4	19.0	59.6	20.0	1.2	25.9	67.6	6.5	—	21.8	72.7	5.3	0.3	119	93	123	—	—	—	—	—
	5	21.3	55.4	19.8	3.2	—	—	—	—	25.0	69.1	5.2	0.7	—	—	—	—	—	—	—	—
	6	22.3	44.2	22.8	10.4	31.1	60.3	6.3	2.2	28.7	62.0	6.6	2.7	108	97	95	81	25	91	87	105
	B	16.2	21.8	29.0	31.9	31.9	43.0	12.9	12.2	29.2	44.2	12.5	14.0	109	97	103	87	—	—	—	—
18	T	6.4	55.5	22.1	16.0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	2.9	32.3	33.2	31.7	6.8	57.8	21.0	14.5	5.3	65.3	15.5	13.9	128	89	135	104	∞	63	51	94
	2	1.9	13.0	46.1	39.0	5.1	44.8	26.7	23.5	4.7	38.0	29.5	27.9	109	118	91	84	127	183	136	438
	3	1.1	9.3	54.5	35.2	3.2	30.5	37.2	29.2	2.8	30.5	37.8	28.9	114	100	98	101	20	100	107	120
	4	2.1	6.8	60.0	30.5	3.3	23.3	46.0	27.4	5.6	23.9	43.3	27.2	59	97	106	101	-10	96	78	95
	5	2.6	2.1	64.3	30.6	3.5	9.6	55.3	31.6	7.7	8.4	51.9	32.1	45	114	107	98	30	121	76	78
	6	2.6	2.1	65.8	29.0	1.7	2.7	65.9	29.8	7.8	8.6	53.0	30.6	22	31	124	97	18	26	26	85
	B	2.1	1.1	64.3	29.3	0.4	3.9	70.3	25.4	7.1	3.9	55.6	33.4	6	100	126	76	—	—	—	—

Table 5.11 (Cont'd.) Runs 19 & 20.

		Mole Per Cent												% Vaporisation Efficiencies (E_v)				% Murphree Efficiencies (E_m)			
		x				y				y*											
		ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH
19	T	34.8	62.1	3.2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	25.4	67.6	6.9	—	36.1	60.6	3.3	—	28.9	69.5	1.7	—	125	87	187	—	367	-230	59	—
	2	19.9	55.7	23.6	0.6	26.2	66.8	7.0	—	22.9	70.8	6.2	0.1	114	94	113	—	-106	-122	-100	—
	3	18.6	57.6	22.6	1.0	24.5	69.0	6.6	—	21.4	72.4	6.0	0.2	114	95	110	—	-244	-62	0	—
	4	17.0	61.2	19.3	2.2	22.3	70.3	6.6	0.8	19.8	74.5	5.2	0.5	113	94	127	139	9	34	48	80
	5	17.9	52.8	23.0	6.1	22.1	68.1	7.9	2.0	21.9	70.1	6.5	1.4	101	97	122	143	88	85	75	90
	6	16.7	36.3	28.8	18.0	23.5	57.1	12.1	7.3	24.6	59.7	9.9	5.8	96	96	122	126	73	23	85	92
	B	9.8	11.7	37.2	39.6	20.6	30.4	25.0	24.1	22.3	31.3	21.3	25.1	92	97	117	96	—	—	—	—
20	T	38.5	57.1	4.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	28.1	65.1	6.8	—	38.6	57.0	4.4	—	31.6	66.8	1.6	—	82	85	265	—	326	$-\infty$	35	—
	2	22.5	53.8	22.8	0.7	28.5	65.9	5.6	—	25.7	68.2	5.9	0.2	111	97	95	—	-75	-77	∞	—
	3	21.6	54.8	22.2	1.2	27.3	66.9	5.9	—	24.8	69.2	5.8	0.3	110	97	102	—	-150	23	94	—
	4	20.6	53.2	23.2	2.7	25.8	66.2	7.5	0.5	24.2	69.0	6.2	0.6	107	96	121	83	329	-22	24	107
	5	18.7	49.3	24.8	6.9	23.5	66.7	7.9	2.0	23.3	67.9	7.1	1.7	101	98	111	118	113	88	86	95
	6	16.0	38.7	27.9	17.2	21.8	57.8	12.8	7.5	23.1	62.0	9.5	5.4	94	93	135	139	70	88	80	89
	B	10.3	13.5	35.2	39.3	18.8	30.3	25.6	25.3	21.6	35.0	19.7	23.7	87	87	130	107	—	—	—	—

5.8 Discussion

Twenty continuous distillation experiments were carried out and these can be categorised as follows.

The first four experiments (Runs 1 - 4) were carried out under constant feed rate, composition, boilup rate and reboiler holdup conditions and only the reflux ratio was varied between 2:1 and total reflux (Table 5.5). The second series of experiments (Runs 5 - 8) were performed under the same conditions as the first series with the exception of the reboiler holdup which was increased by approximately 30 per cent (Table 5.5). In the next series (Runs 9 - 12), the boilup rate was increased by approximately 50 per cent whilst the same range of reflux ratios and the increased reboiler holdup were used (Tables 5.5 & 5.6). For the fourth series of experiments (Runs 13 - 16) it was hoped to further increase the boilup rate to between 100 and 200 per cent of the initial boilup rate used in runs 1 - 8. However, it was found that the maximum practical boilup rate was approximately 170 g min^{-1}, i.e. an increase of approximately 150 per cent of the initial boilup rate used in Runs 1 - 8 (Table 5.6). For Runs 13 - 16, the reflux ratio was maintained constant at 4:1. Finally for the last series of experiments (Runs 17 - 20), two investigations (Runs 17 & 18) were performed using an initial reboiler change of the reactants only. In these two experiments, a boilup rate of 100 g min^{-1} and two different reflux ratios were utilised (Tables 5.5 & 5.6). In Runs 19 & 20, a split feed technique was utilised. Butyl acetate and sulphuric acid were fed onto Plate 2 for both experiments whilst ethyl alcohol was fed onto Plate 4 for Run 19 and onto Plate 6 for Run 20. The reflux ratio was maintained constant at 4:1 and a boilup rate of 105 g min^{-1} were used for both runs (Tables 5.5 & 5.6).

For all the runs, the feed composition was maintained constant using an approximately equimolar reactant ratio. The actual feed ratio of ethyl alcohol to butyl acetate varied between 0.996 & 1.092:1 (Tables 5.1 & 5.4). The variation in the feed composition was probably due to fluctuations in the flows of each stream caused by temperature and hydrostatic head effects.

The mass and molar balances (Tables 5.2 & 5.3) were accurate to within 2.3% although the majority of the experiments' error was considerably less than this. However, one run (12), the molar balance was in error by 11.2%.

The enthalpy balances were calculated to a datum of 0°C. The heat of reaction was included in the balances although the heat of mixing was ignored as data could only be obtained for the heat of mixing of two of the binary systems (70, 145), although it was noted in Section 3 that butyl acetate - ethyl alcohol also had a negative heat of mixing. For all the experiments, the worst heat loss (through the walls and mixing) was 18.5% of the total heat input and for 11 runs, the heat loss was less than 10% (Table 5.8). The low heat losses indicated that the degree of internal refluxing in the column was small and thus stagewise enthalpy balances could be applied in the development of a theoretical model.

The sum of the individual plate holdups was in good agreement with the holdup calculated from the overall pressure drop (Table 5.7). The slight discrepancies between the two values were due to the variation with boilup rate of the dry plate pressure drop and to the error incurred in taking an average value of Plate 2 and 3 for the Plate 1 holdup.

The limits of the boilup rate in any series of experiments would be excessive weeping at the lower rate and entrainment at the higher rate. However, even at the maximum practicable boilup rate, the column loadings were considerably less than those for commercial units (i.e. a maximum vapour loading of 448 lb ft^{-2} h^{-1} as against 10 - 20,000 lb ft^{-2} h^{-1} for industrial units (146)). Because of the higher liquid loadings in the lower section of the column, the plate holdups below the feed plate were usually greater than those above whilst the overall plate holdup increased with an increase in the boilup rate. However, observations of the column's dynamic behaviour led to the practical limitation in its operation. Initially it was hoped to increase the boilup rate in increments, from 70 to 210 g min^{-1} but it was noticed that as the boilup rate increased so the height of the foam on some of the plates also increased. Thus to avoid excessive entrainment and the foam filling the whole of the inter-plate volume (the latter occurred at boilup rates in excess of 200 g min^{-1}) the maximum practicable boilup rate had to be limited to 166.5 g min^{-1} and under these conditions the foam height was between 3 and 4 inches. The cellular foam was formed on the feed plate and the three plates below the feed plate only whilst the behaviour of the liquid above the feed plate was entirely different and was consistent with a spray-bed. Zuiderweg & Harmens (147) have attributed a foaming plate mixture to a system which has a positive surface tension gradient down the column whilst a spray-bed plate condition is a system which has a negative or neutral surface tension gradient.

From an examination of the liquid behaviour in the upper section of the column (i.e. above the feed plate) it was observed that the concentration of ethyl alcohol increased by the largest proportion and that for a number of the experiments the upper section of the column could be considered as a binary ethyl alcohol - ethyl acetate system. For the boiling point range, ethyl alcohol has the higher surface tension (17.8 dyne cm^{-2} @ 100°C, 19 dyne cm^{-2} @ 75°C) (139) whilst ethyl acetate has the lower (14.4 dyne cm^{-2} @ 100°C, 17.4 dyne cm^{-2} @ 75°C) (139). Thus the surface tension gradient will increase up the column from Plate 3 to Plate 1 due to the increase in the concentration of ethyl alcohol and also due to the temperature effect ($\sigma \propto T^{-1}$). However, the volatilities of ethyl alcohol and ethyl acetate are similar, whilst the actual values of the surface tensions are similar within the temperature range. Zuiderweg & Harmens (147) concluded that when a system comprised of two components with approximately similar volatilities or surface tensions, the system was classified as a neutral one and the plate dynamics would be consistent with a spray-bed. In some of the experiments, both butyl alcohol (15.47 dyne cm^{-2} @ 100°C) (139) and butyl acetate (22.3 dyne cm^{-2} @ 20°C) (104) were present in the above feed plate compositions. Thus for the multi-component systems at the operating conditions it would be difficult to detect the surface tension gradients but it was observed that at 20°C the four components had similar surface tensions (24.3, 24.6, 22.75, 22.3 dyne cm^{-2} for ETAC, ETOH, BUAC & BUOH respectively) (104, 139). At the operating temperatures in the column, the difference between the highest and lowest surface tensions would be approximately similar and hence from a theoretical view point, it would appear that the four component system would have a neutral surface tension gradient and this was confirmed from the visual observations of the liquid behaviour on the plates above the feed plate.

The behaviour of the liquid phase on the plates on and below the feed plate was entirely different. The column feed was fed onto the fourth plate and the feed contained the sulphuric acid catalyst (52.5 dyne cm^{-2} @ 100°C) (139). Zuiderweg & Harmens (147) concluded that a foam was formed due to the reinforcement of the vapour phase bubbles. The reinforcement was due to the transfer from the vapour phase to the liquid phase of the least volatile component which had a relatively high surface tension, creating areas of high interfacial tension between the bubbles. Although the sulphuric acid remained only in the liquid phase, it would appear that the presence of the catalyst in the liquid films surrounding the vapour bubbles caused areas of high interfacial tension and subsequent reinforcement of the vapour phase bubbles.

The samples were taken in the directions opposite to the flowstream in order to minimise disturbance transmissions. The liquid samples which were taken first, were taken from the reboiler upwards whilst the vapour samples were taken from above plate 1 working downwards. The liquid sample volume was 3 ml and this together with the intial liquid removed to flush out the sample line and syringe was no more than 3 per cent of the plate holdup and in most cases was less. A similar volume was removed for the vapour sample and it was hoped that by allowing the vapour to condense slowly over a period of time so that a minimum disturbance to the column's equilibrium would be caused.

It was observed that if the boilup rate was increased for a given series i.e. all the other parameters remaining the same, that the concentration of the most volatile components decreased on a given stage whilst the concentration of the least volatile increased.

The influence of the chemical reaction on the concentration profile can be best judged by examining the formation of the product ethyl acetate. In a conventional column, ethyl acetate being the second most volatile component, the concentrations should decrease down the column. However, in Runs (1 - 4, 6 - 8, 10 - 12, 14, 16 - 17, 19) the concentration of ethyl acetate increased on Plates 5 & 6 before decreasing again. Secondly, the product butyl alcohol's concentration profile increased more rapidly below the feed plate than it would normally in a conventional column (Fig.5.8).

In a conventional column the concentration of butyl acetate (the heaviest component) would increase rapidly down the column. This was observed above the feed plate, but below the feed plate the rate of increase in concentration decreased and in some experiments (Runs 7, 11 - 12, 14, 17, 19) the concentration actually decreased or remained constant below the feed plate. For ethyl alcohol, the concentration decreased rapidly below the feed plate and in some experiments the concentration decreased above the feed plate. The latter occurred at high alcohol concentrations and it was possible to detect that an azeotrope was being formed. In some experiments the alcohol's concentration slightly increased on Plates 5 & 6 suggesting that either an inaccurate sample had been taken or the

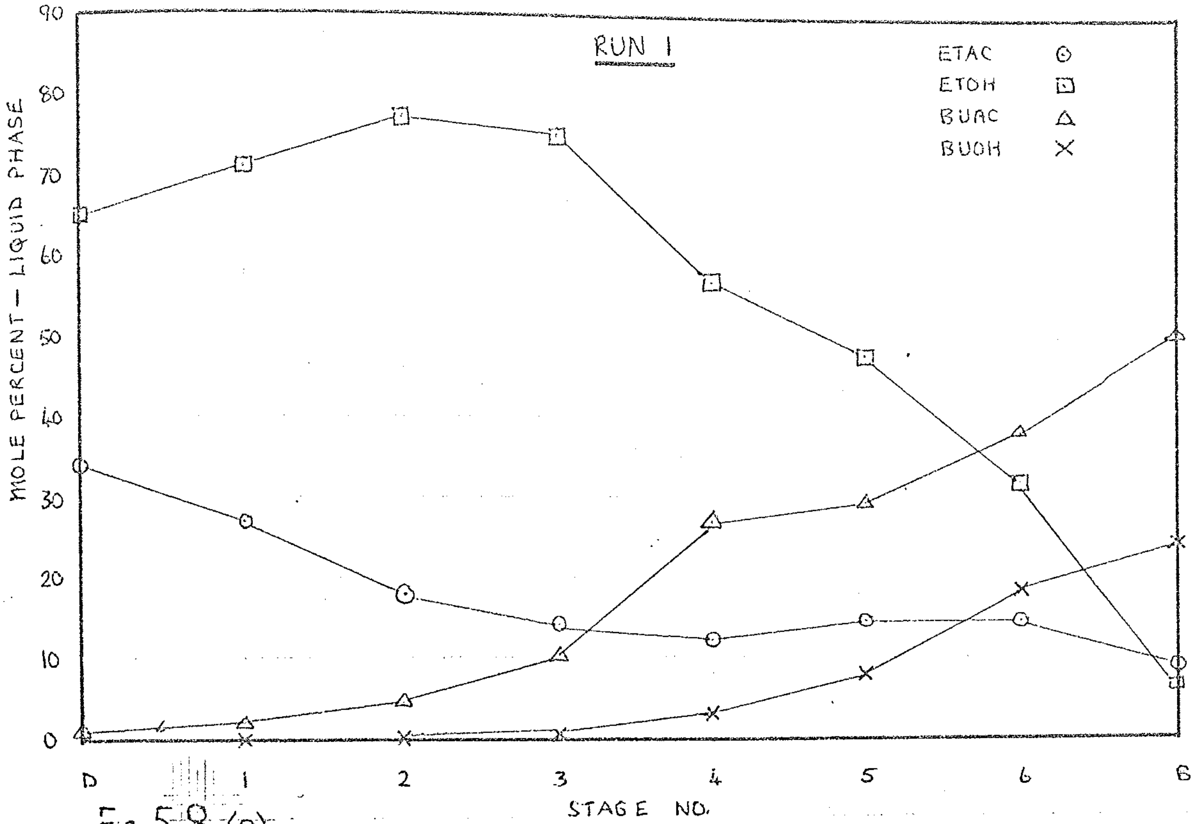


Fig 5.8 (a)

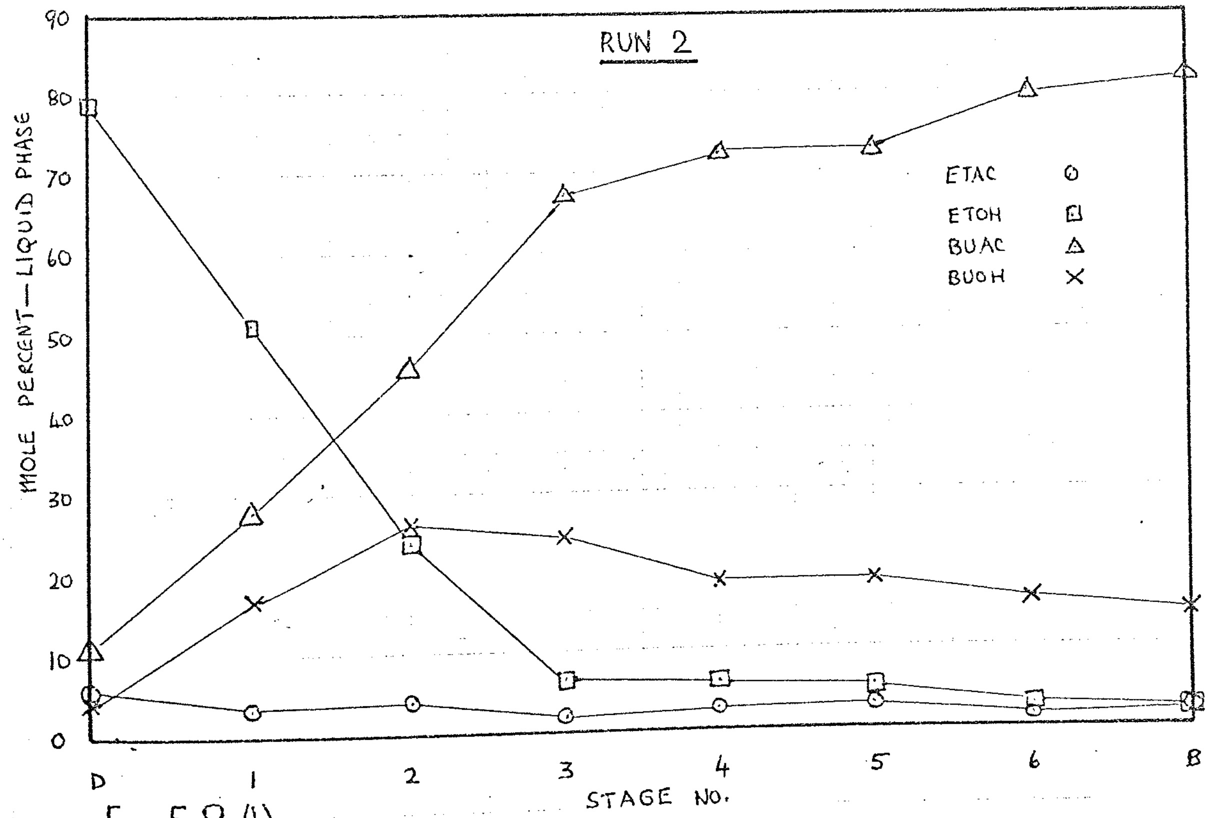


Fig 5.8 (b)

Fig 5.8 Measured Liquid Phase Compositions Runs, 1 & 2

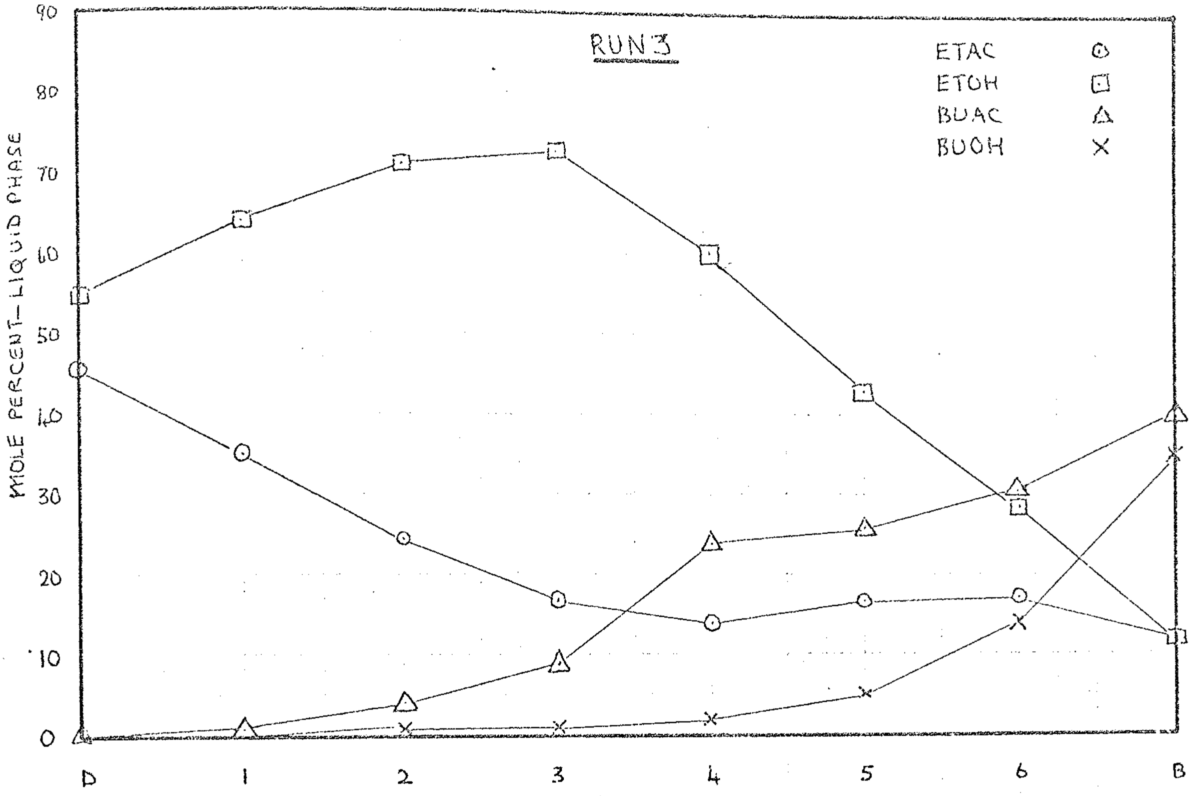


Fig 5.8 (c)

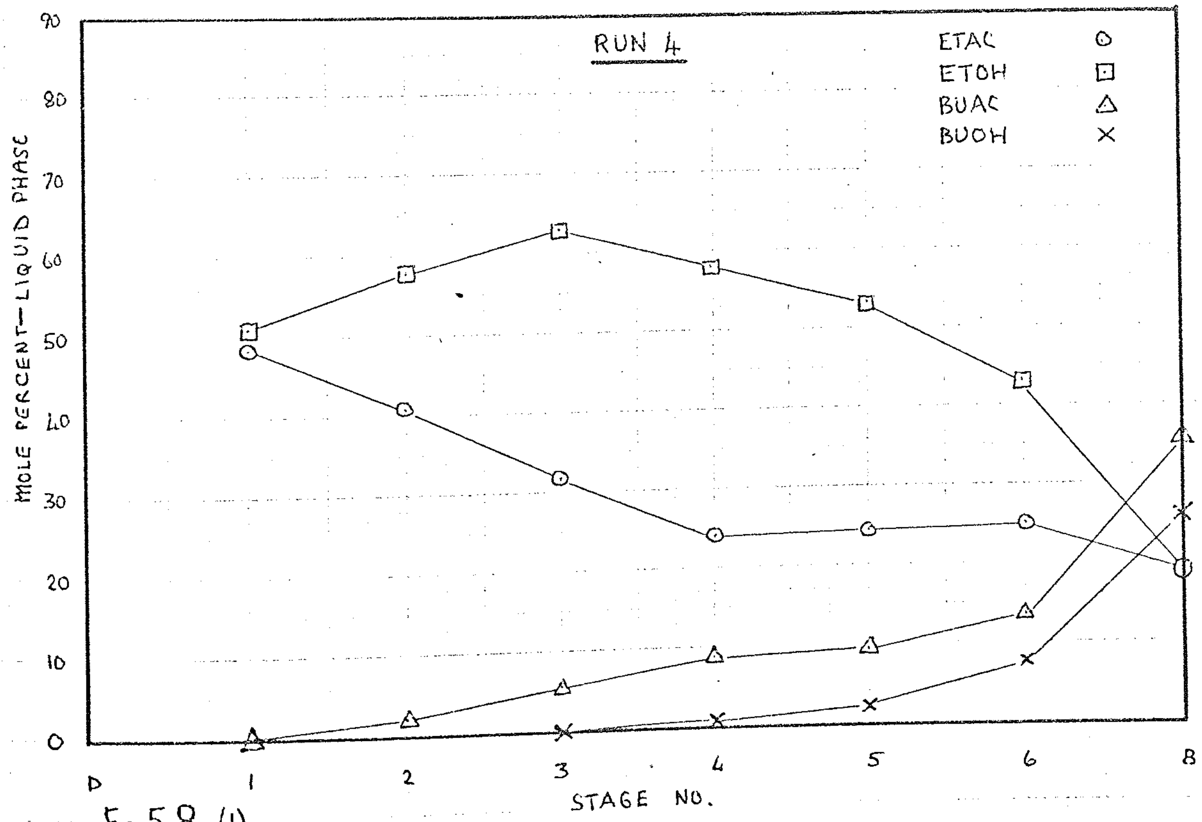


Fig 5.8 (d)

Fig 5.8 Measured Liquid Phase Compositions, Runs 3 & 4

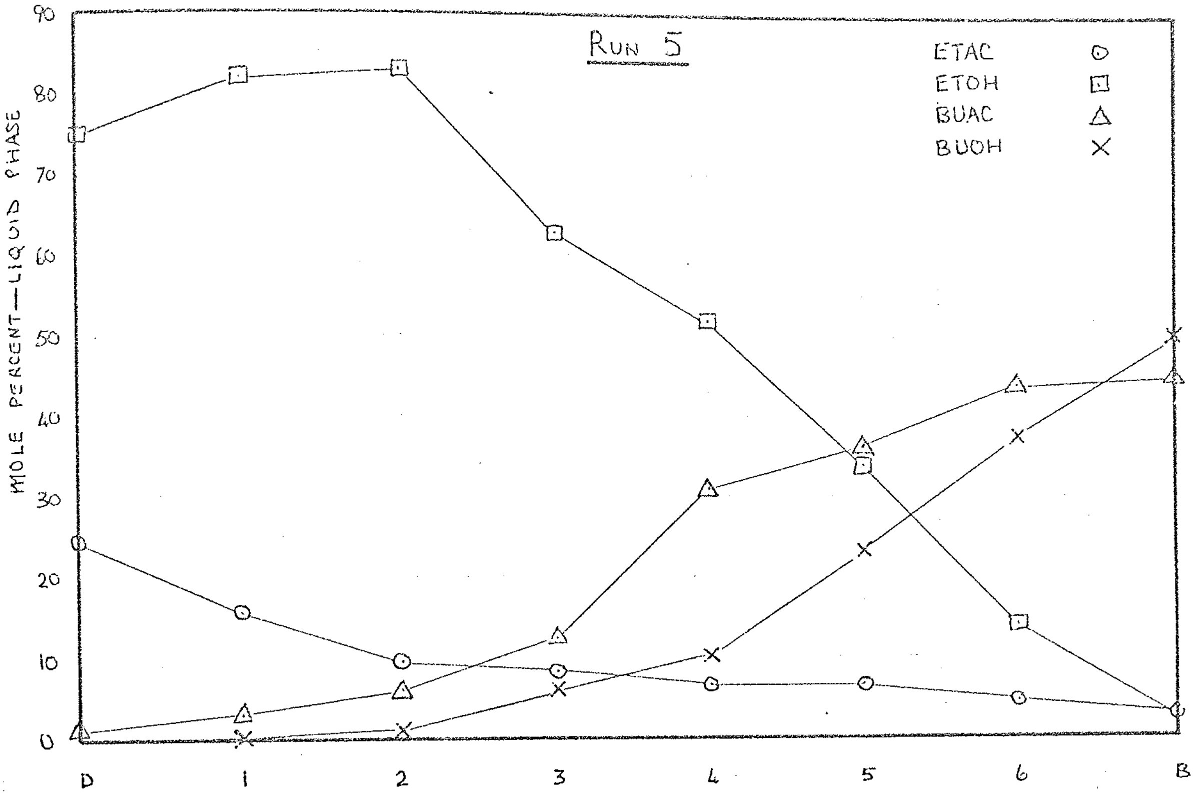


Fig 5.8 (e)

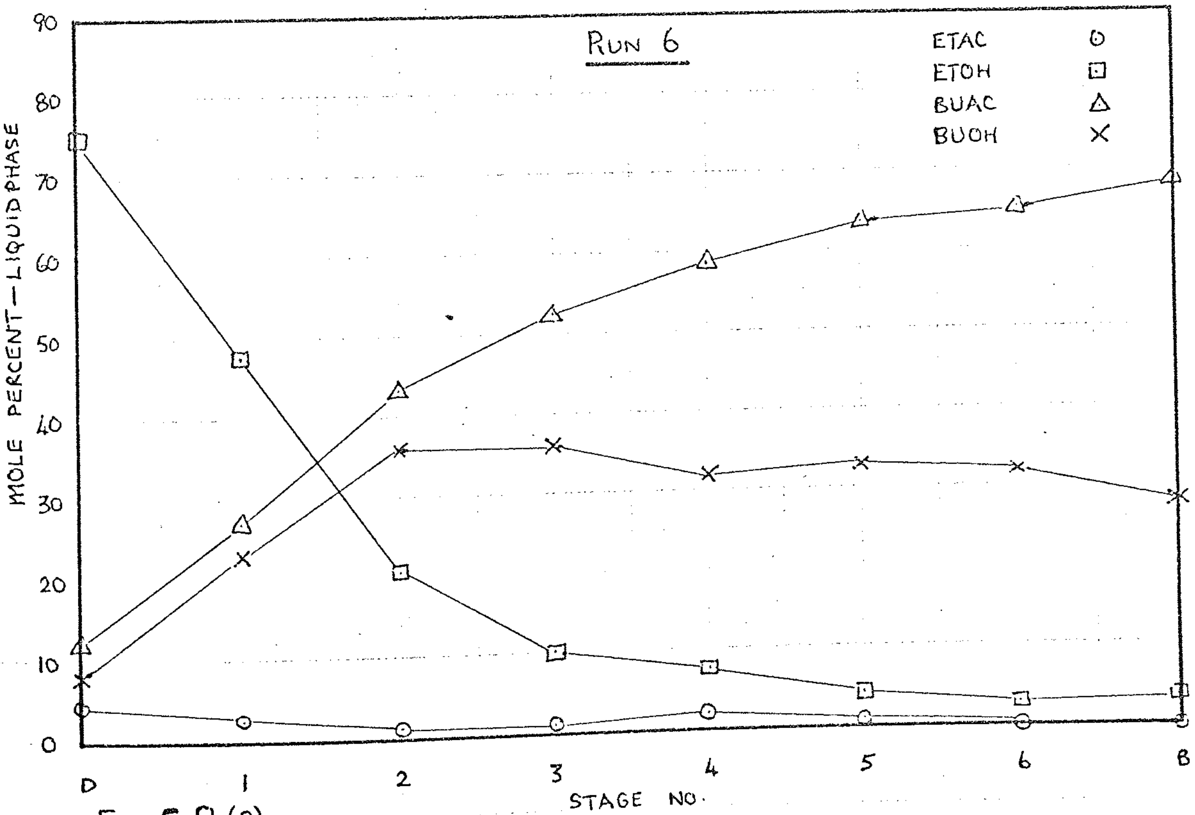


Fig 5.8 (f)

Fig 5.8 Measured Liquid Phase Compositions, Runs 5 & 6

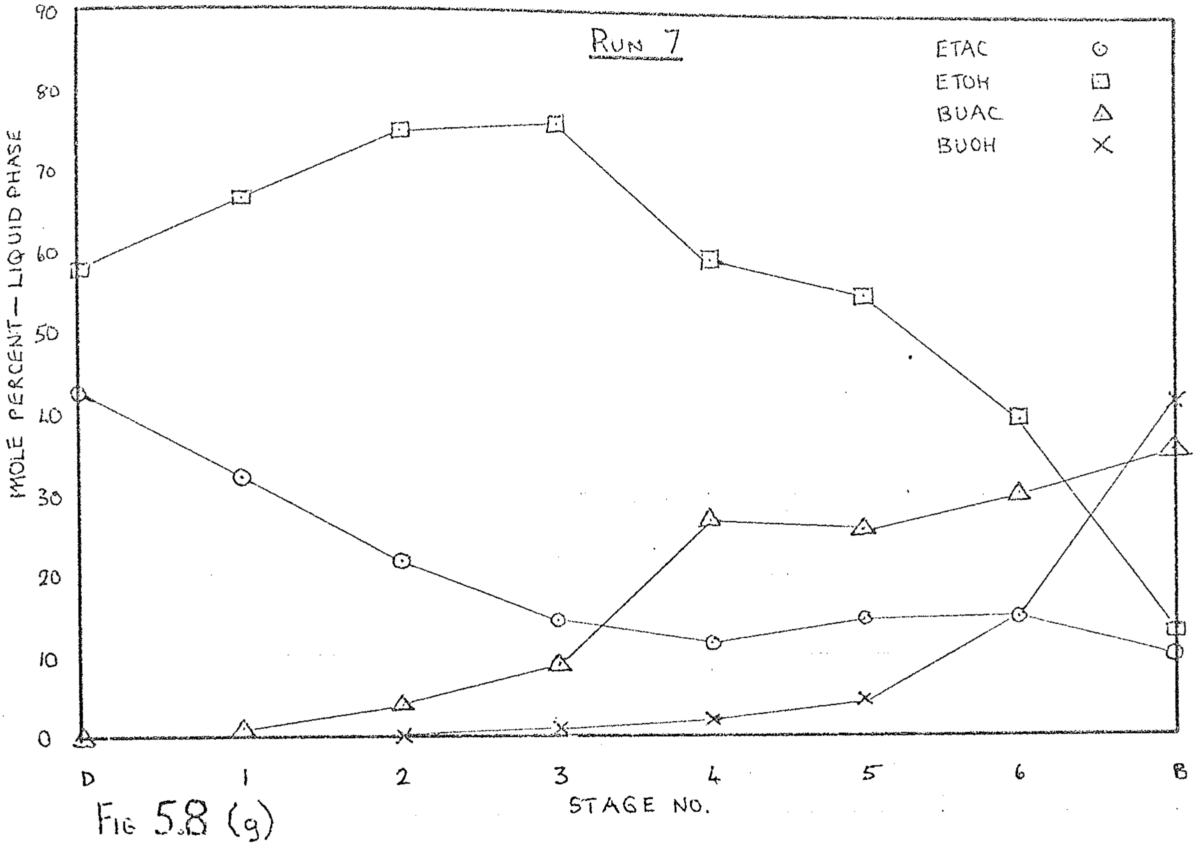


FIG 5.8 (g)

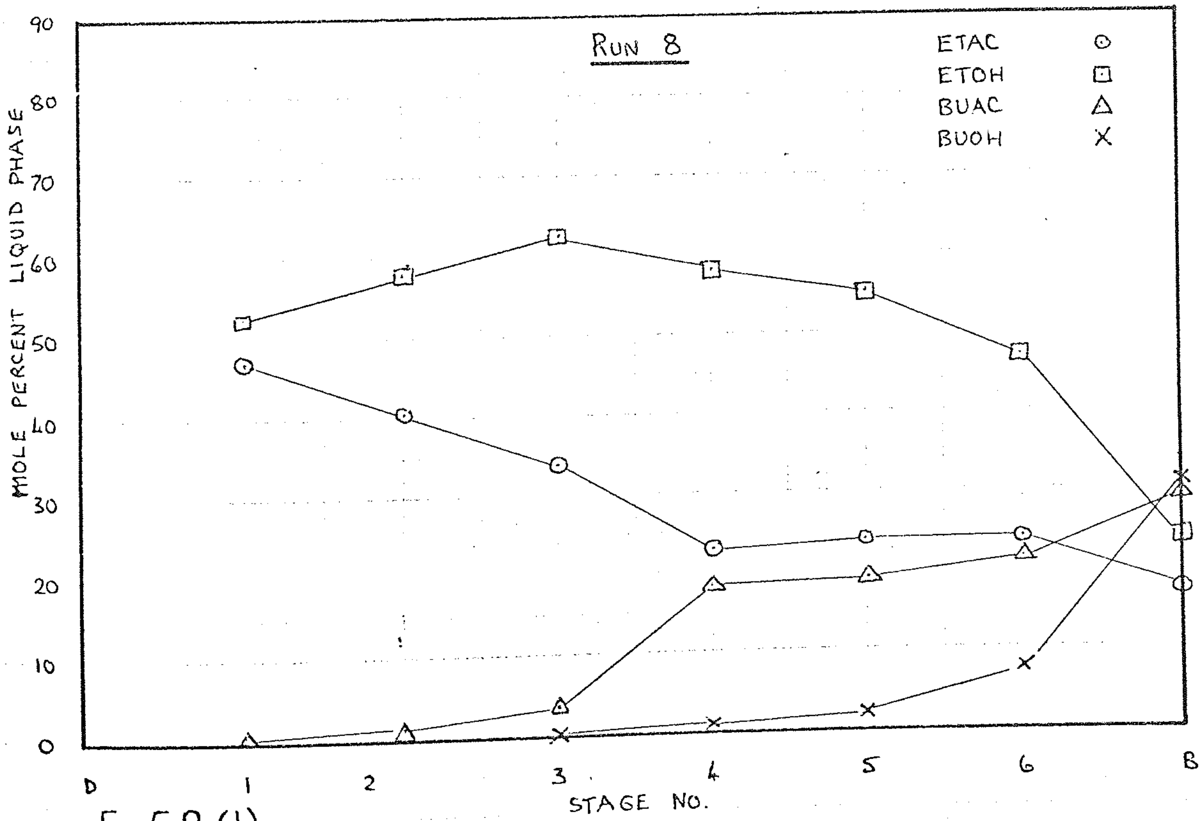


FIG 5.8 (h)

FIG 5.8 MEASURED LIQUID PHASE COMPOSITIONS, RUNS 7 & 8

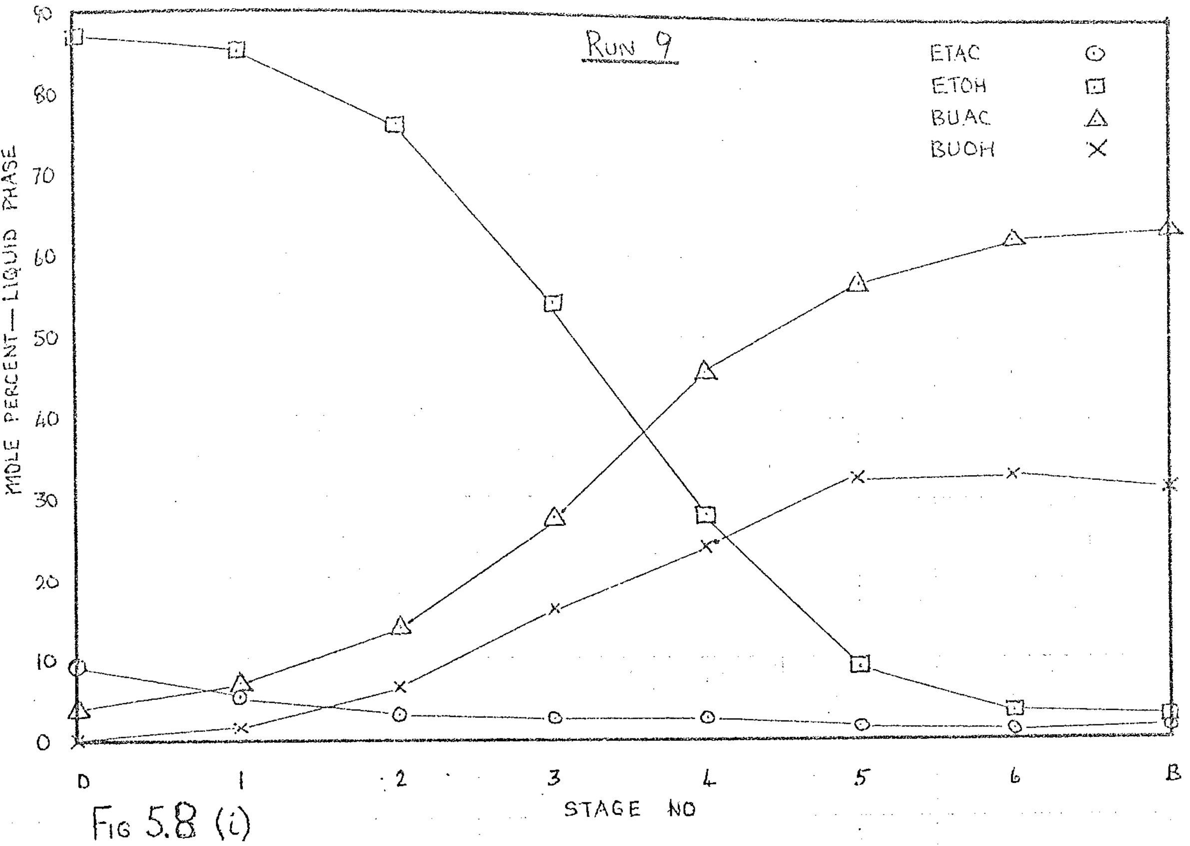


Fig 5.8 (i)

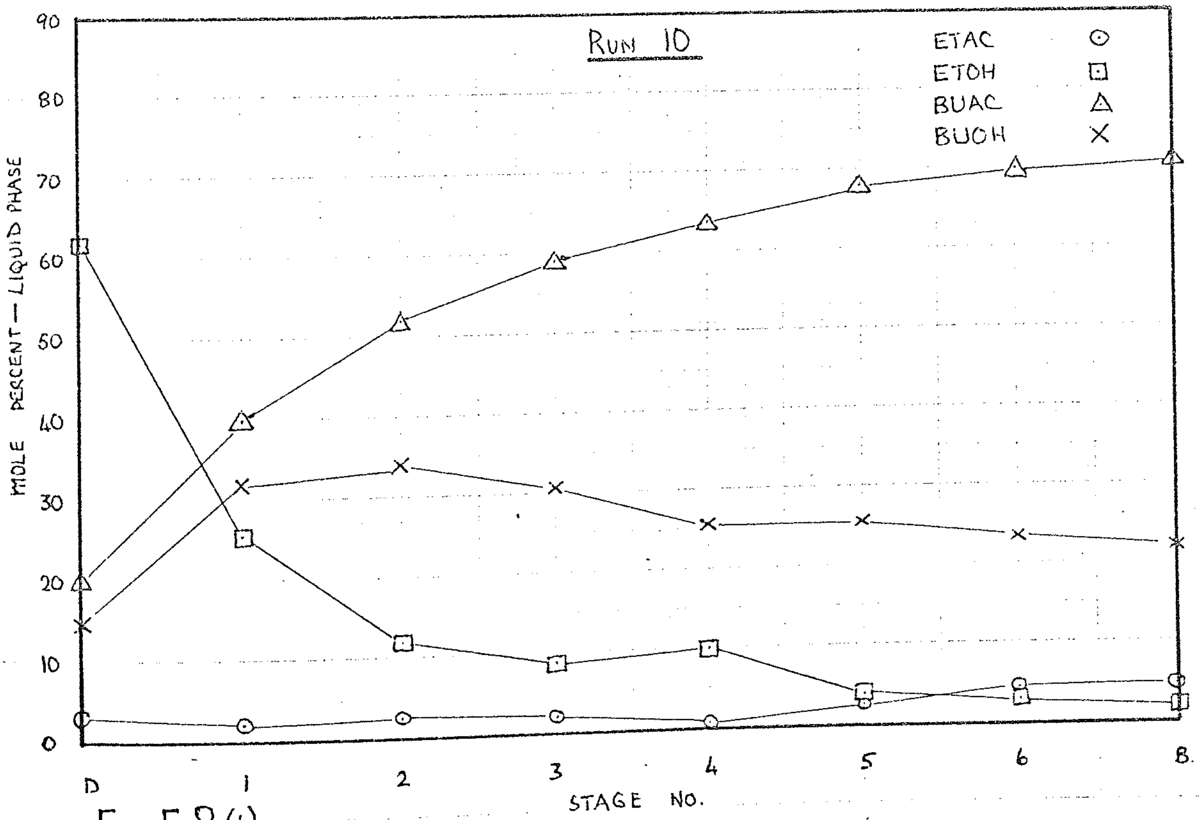


Fig 5.8 (j)

Fig 5.8 Measured Liquid Phase Compositions, Runs 9 & 10

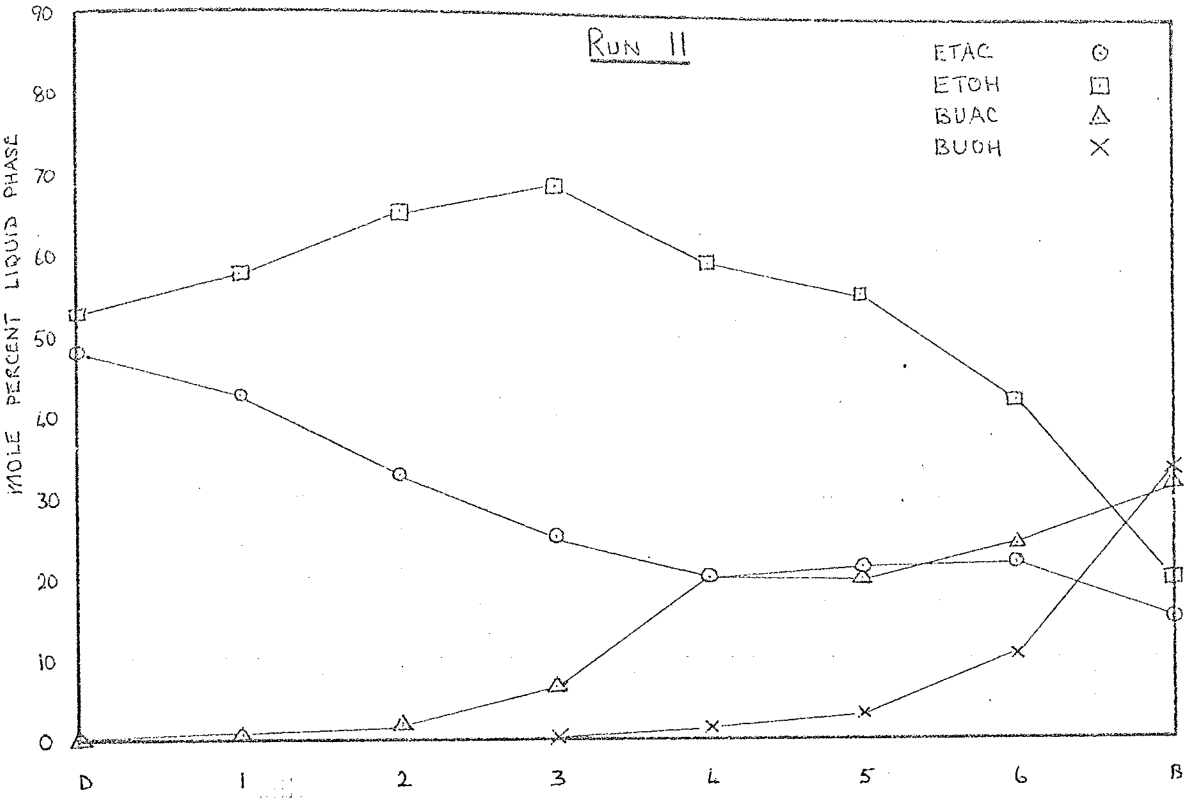


Fig 5.8 (k)

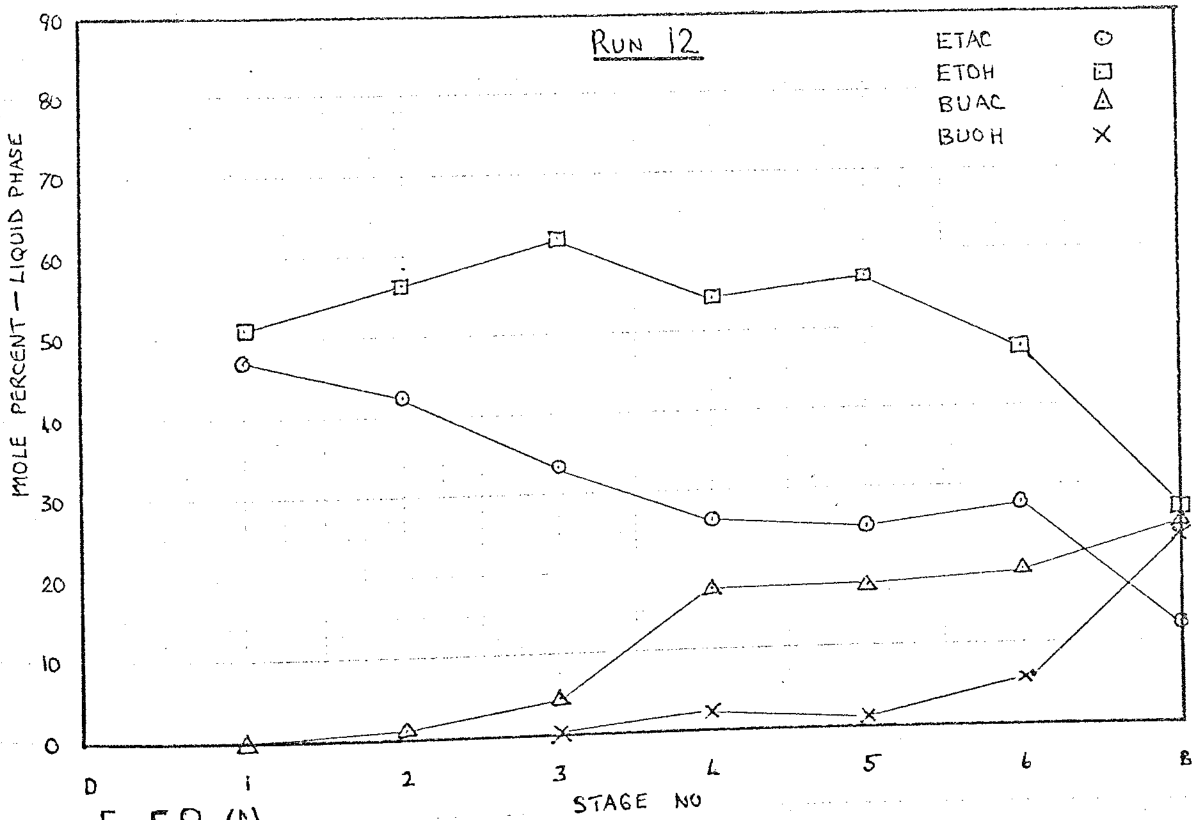


Fig 5.8 (l)

Fig 5.8 Measured Liquid Phase Compositions, Runs 11 & 12

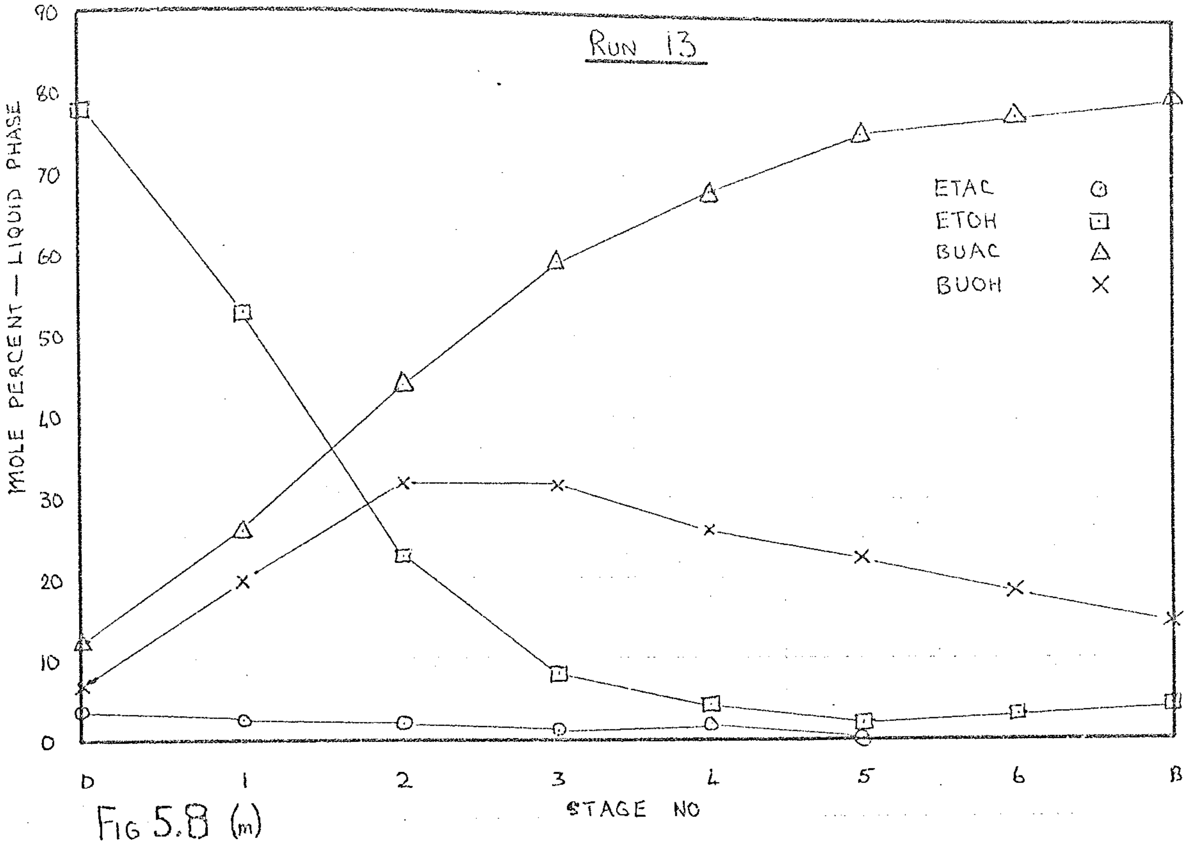


Fig 5.8 (m)

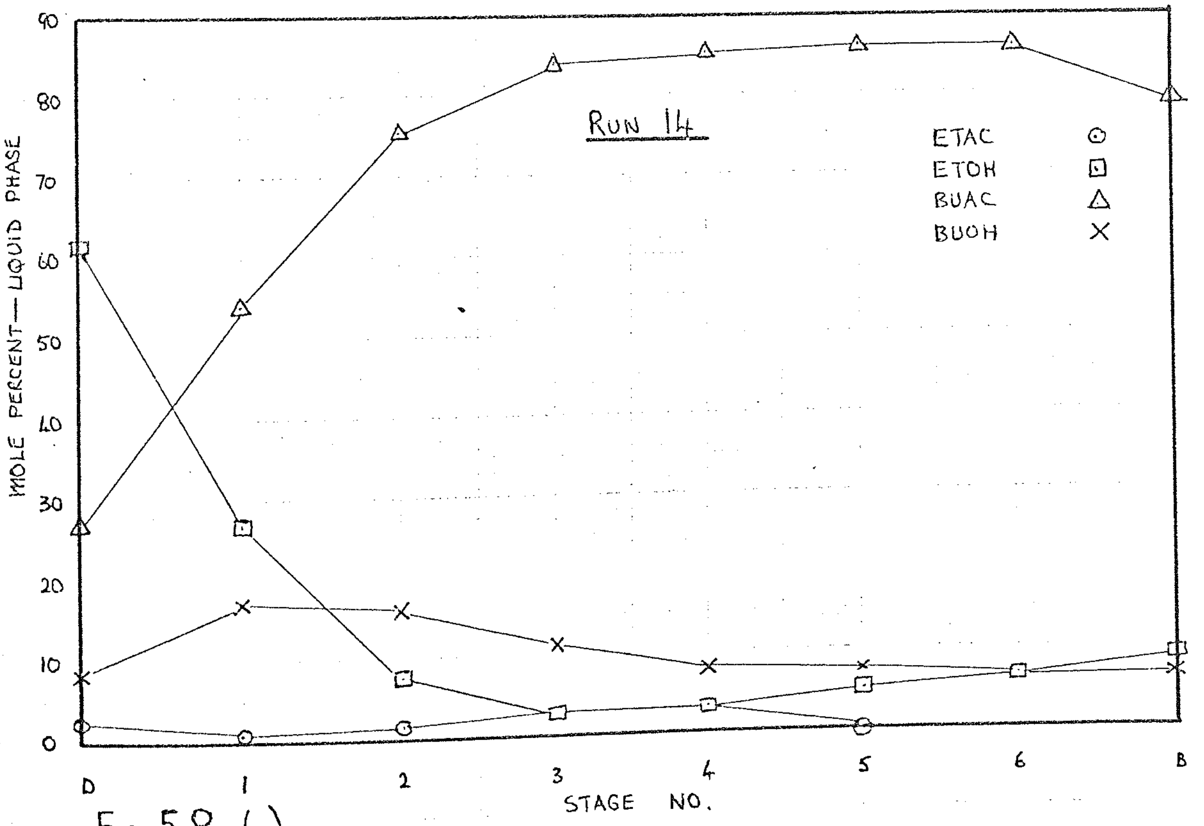


Fig 5.8 (n)

Fig 5.8 Measured Liquid Phase Compositions, Runs 13 & 14

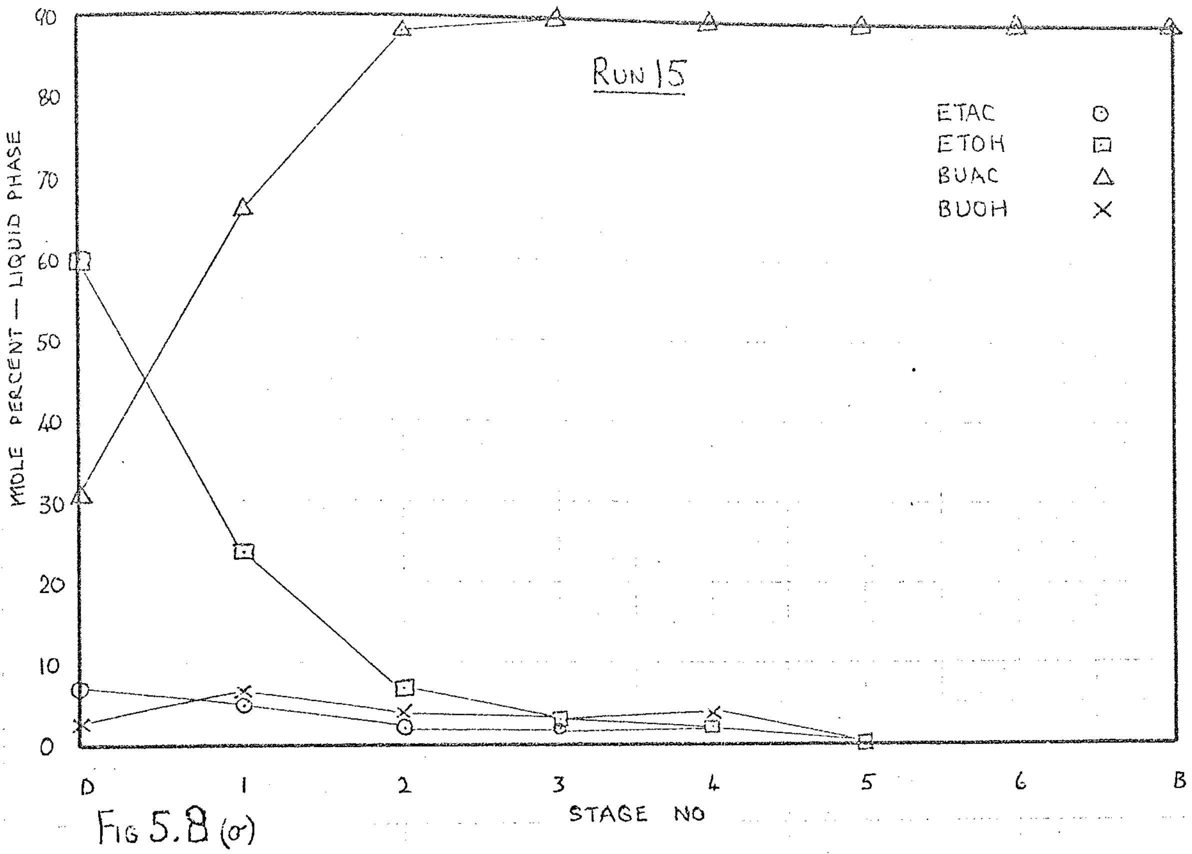


Fig 5.8 (o)

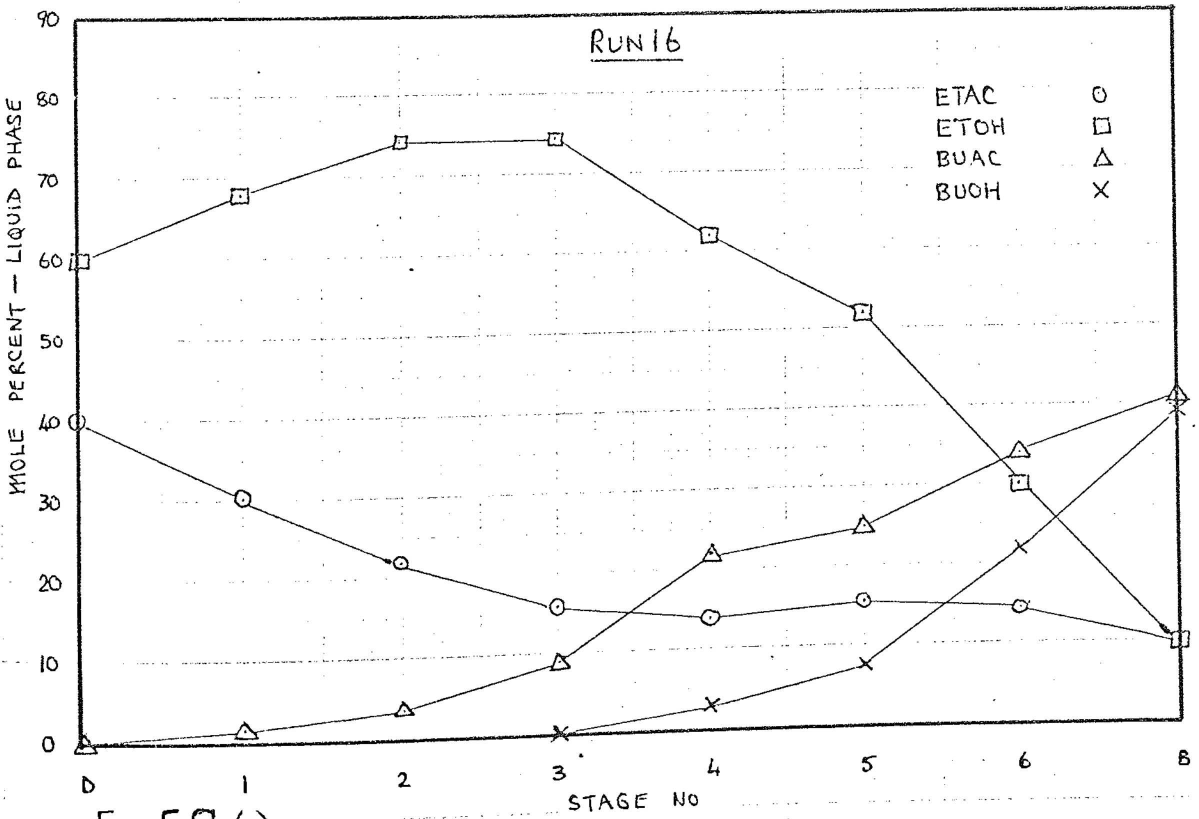


Fig 5.8 (p)

Fig 5.8 Measured Liquid Phase Compositions, Runs 15 & 16

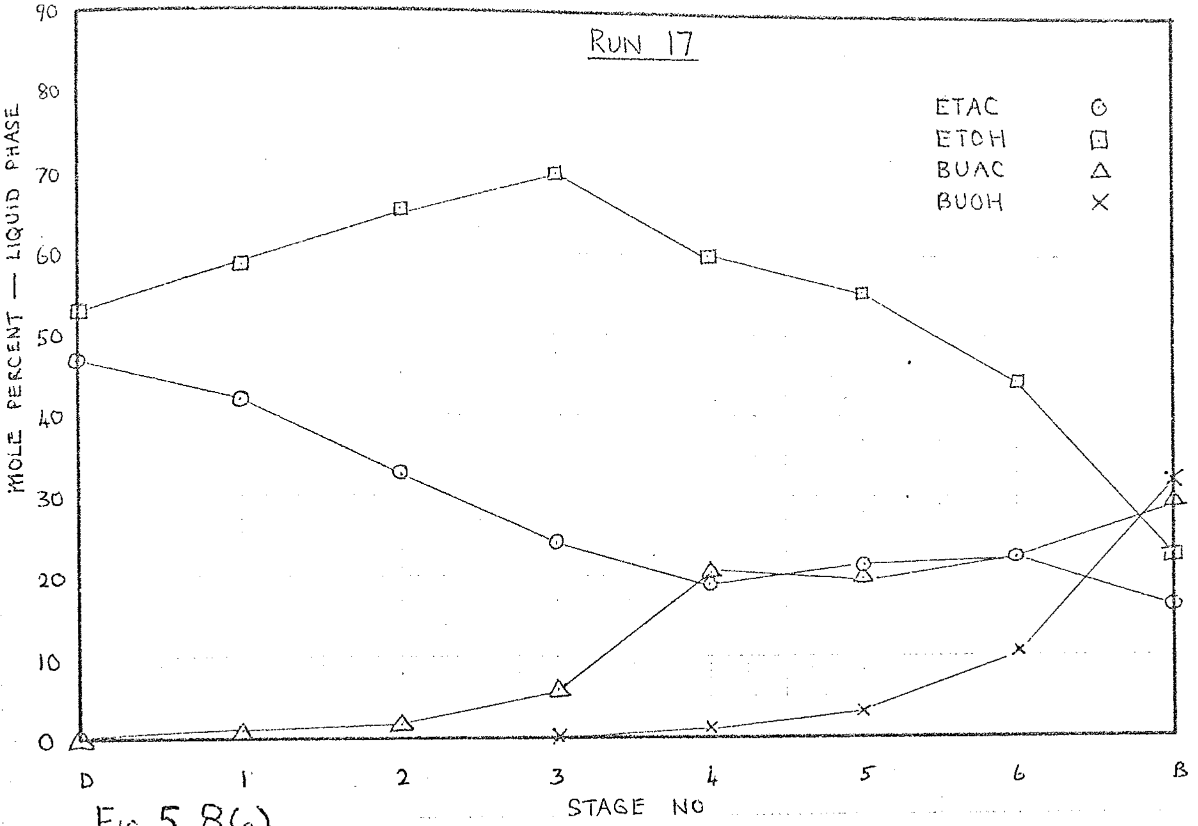


Fig 5.8(q)

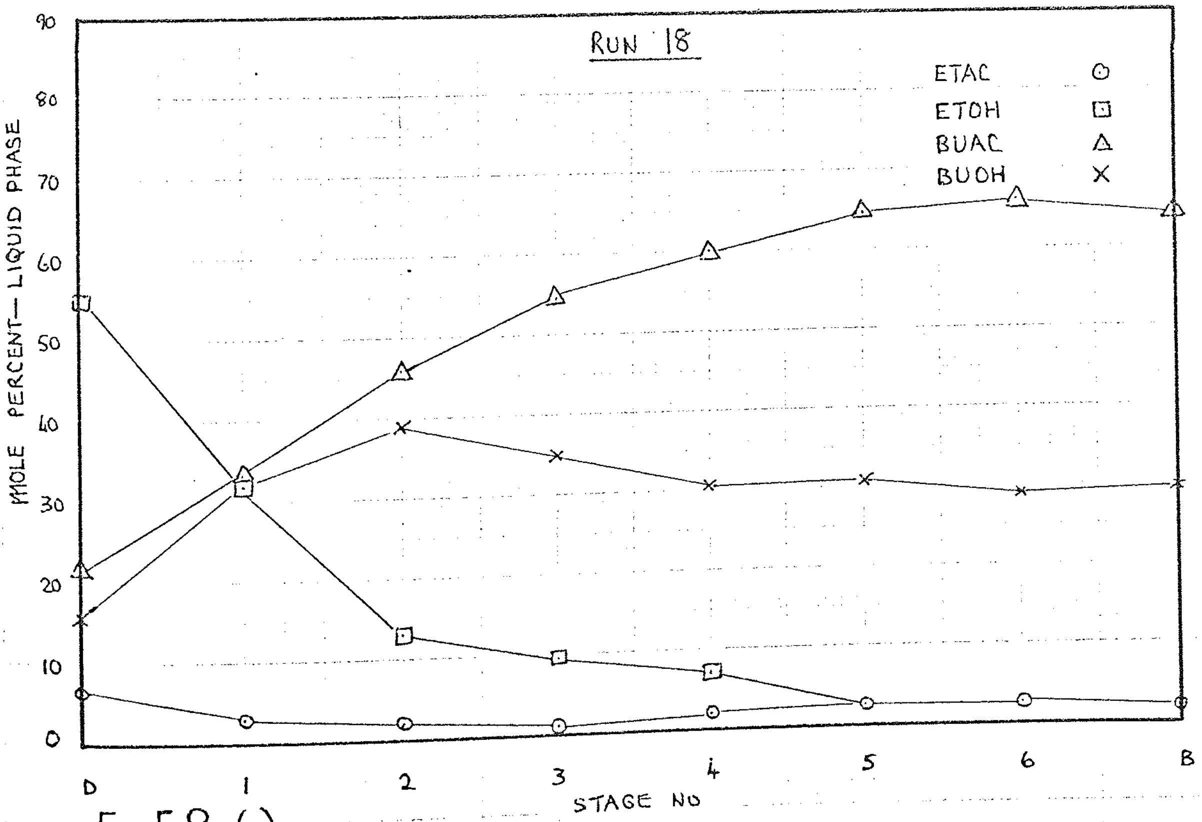


Fig 5.8 (r)

Fig 5.8 Measured Liquid Phase Compositions, Runs 17 & 18

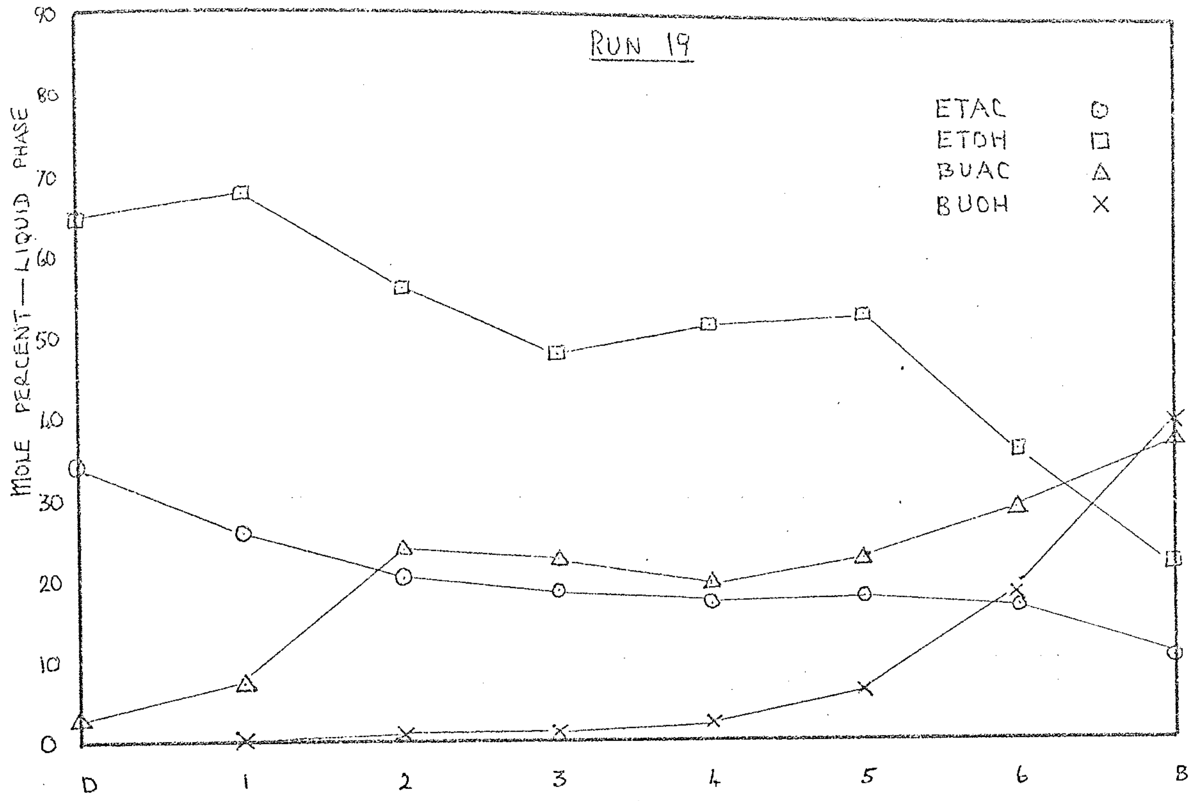


Fig 5.8 (s)

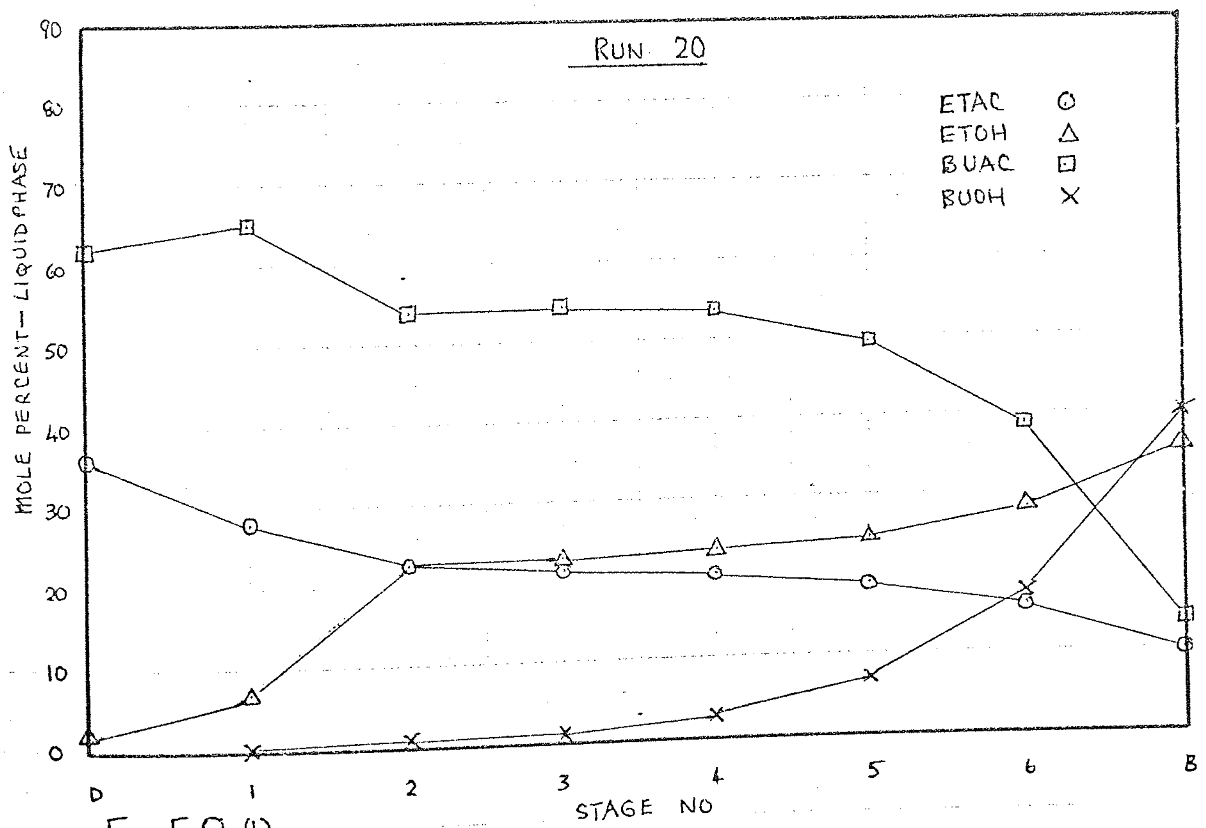


Fig 5.8 (t)

Fig 5.8 Measured Liquid Phase Compositions, Runs 19 & 20

reverse reaction was occurring (Figs. 5.8 (g),(k)-(s)).

In four component distillation, a wide variety of column concentrations are possible. Below the feed plate, the four components were present in all the experiments except two. In one run, only one component was present whilst in the remaining run a ternary of ethyl alcohol - butyl acetate was being distilled. The situation above the feed plate was a little more complex. Generally, the compositions were ethyl alcohol - ethyl acetate rich. Runs 1, 2, 6, 10, 13 - 15 has a quaternary mixture on all the plates above the feed plate (including the distillate). This would be expected for Runs 13 -15 which were carried out at the high boilup rate. The remaining concentration profiles were of ternary compositions of ethyl acetate - ethyl alcohol - butyl acetate (Runs 3 - 5, 8 - 9, 11 - 12, 16 - 17, 19 - 20) and in one experiment (Run 7) an ethyl acetate - ethyl alcohol - butyl alcohol mixture was formed. It was observed that the presence of butyl acetate (the heaviest component) continued further up the column than the second heaviest component butyl alcohol. This was probably due to the fact that butyl acetate was being fed into the column on the fourth plate and hence generally was present in much higher concentrations than butyl alcohol, rather than the volatility of butyl alcohol being suppressed (Figs.5.8(a)-(s)).

The experimental temperature profiles are tabulated in Table 5.9. The feed plate temperatures were very close to Plate 3 and this was probably due to the influence of the chemical reaction on the plate composition causing the quaternary composition to have a lower boiling point even after one separation stage.

The degree of conversion for each reactant which was calculated from the difference between the molar input and output streams has been plotted in Fig. 5.9 against boilup rate for a constant reflux ratio of 4 : 1. It can be seen that the degree of conversion decreases as the boilup rate increases for butyl acetate whilst the same trend is observed for ethyl alcohol although the conversion does begin to increase after passing through a minimum. At low boilup rates, the rate of removal of the light component ethyl alcohol from the reaction zone (Plates 4 - 6) would be slow thus giving a longer liquid residence time and a higher conversion would be expected. As the boilup rate increases, the rate of removal of ethyl alcohol would increase and the rate of reaction decreases.

It is interesting to note that in Fig. 5.9, for a boilup rate of 70 g min^{-1} the second percentage conversion of butyl acetate lies considerably below the first value which fits the general trend. The values in Fig. 5.9 were all taken at a constant reflux ratio of 4 : 1 so that a good comparison could be made. The lower percentage conversion (33.3%) at 70 g min^{-1} was due to the fact that the first series of experiments (1 - 4) were carried out with a reboiler holdup of approximately 4.5 litres whilst the remainder of the experiments (5 - 20) were carried out with a reboiler holdup of approximately 6.0 litres. Hence the increase in the conversion was due to a 33.3% increase in the reboiler holdup. A similar trend can be detected if the conversions are compared between Runs 1 - 4 and Runs 5 - 8 (Tables 5.4 & 5.5) and in all cases the butyl acetate conversion is greater at the larger reboiler holdup. An increase in component conversion due to an increase in the reboiler holdup would be anticipated because the liquid phase residence time would be increased thus increasing the extent of the reaction.

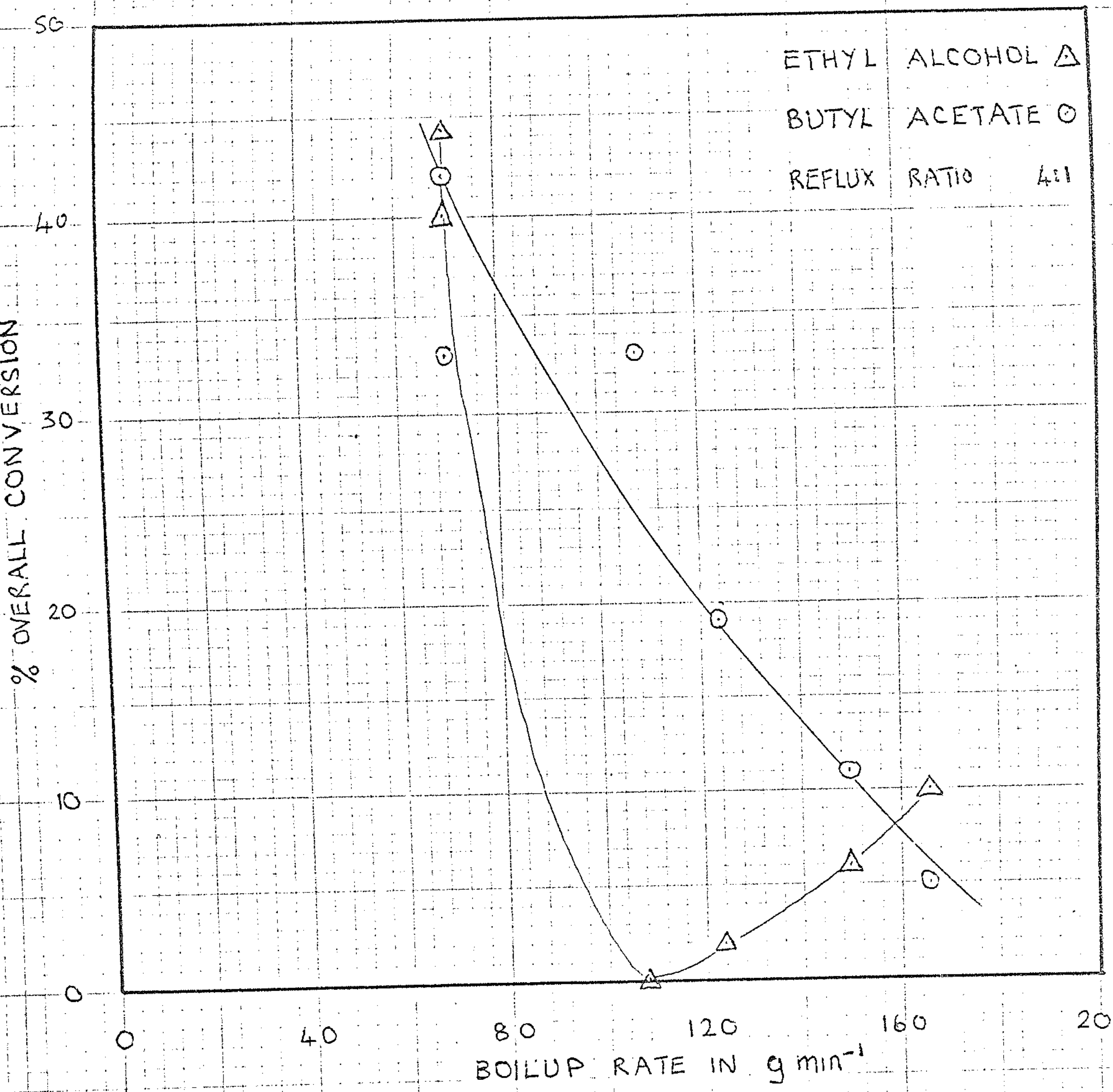


Fig 5.9 Overall Component Conversions vs Boilup Rate

The effect of varying the reflux ratio between 2:1 and total reflux can be ascertained from Tables 5.4 & 5.5 and Fig. 5.10. It can be seen that as the reflux ratio is increased, the butyl acetate conversion tends to increase to a maximum value. This would be expected as the increase of the reflux ratio would decrease the rate of removal of the lightest component from the column and in particular from the reaction zone. A similar conclusion was drawn by Mamers (66) from the comparison of only two of his experiments. At this point it is interesting to note the effect of using the solenoid reflux divider. It was thought that by using this type of divider, rather than the conventional industrial technique of pumping the reflux back to the top of the column from the distillate product tank, that an intermittent reflux might be caused which would cause "plug-flow". However, due to the timing of the reflux divider cycle, the column was only "starved" of the liquid reflux for two seconds and consequently no visible effect was observed on the performance of the column and the liquid flows. O'Leary & Bowman (148) have considered the effect of an intermittent reflux on a distillation column where fixed intervals of operation at zero and total reflux were alternated in time. They approached the problem from both an experimental and theoretical standpoint. At zero reflux, the rate of decay of the distillate composition (i.e. the heavier components would tend to "creep" up the column) and at total reflux where the growth of the distillate composition were both assumed to be an exponential function of time. The resulting model indicated that the mean distillate composition obtained under such alternating reflux conditions would be heavier than that obtained at

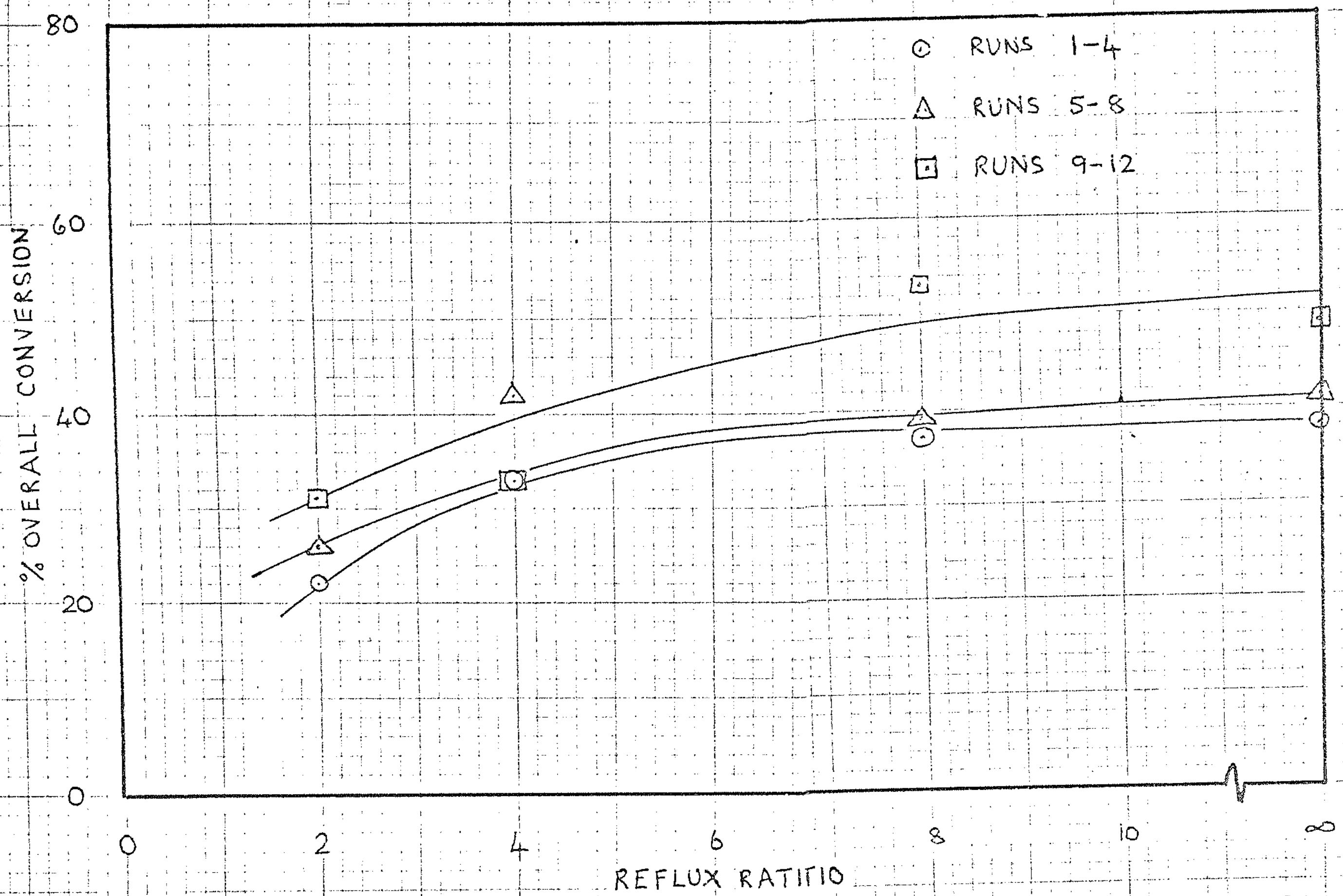


Fig 5.10 Overall Conversion vs RReflux Ratio

total reflux conditions but the difference would only be slight. To check on their prediction, they carried out an experiment in a 30 plate one inch diameter Oldershaw column using a heptane - methlcyclohexane and the experimental results confirmed their theoretical predictions. These results confirmed the conclusions of other authors whom O'Leary & Bowman (148) had reviewed.

A comparison was made between the overall conversion and the sum of the individual conversions. The second order rate equation, rate = $\left(x_{ETOH}\, x_{BUAC} - \frac{1}{K}\, x_{ETAC}\, x_{BUOH}\right) \frac{k_1 Z}{v^2}$, was used for the evaluation of the stage conversions where k_1 was calculated from the formula $\log k_1 = A - \frac{B}{T}$ for the appropriate catalyst concentration as outlined in Section 3. The equation gave the rate of disappearance of either of the reactants and was also equal to the rate of appearance of either of the reaction products. Six of the experiments gave a conversion calculated from the sum of the individual stage conversions which was to within 23 per cent of the overall conversion (Table 5.10 Runs 1, 3, 7, 11, 12, 17 & 20) whilst Run 12 was to within 3 per cent and Run 20 was to within 1 per cent (Table 5.10). Four experiments (Table 5.10 Runs 5, 7, 16 & 19) the agreement lay between 52 and 70 per cent whilst for three experiments (Table 5.10 Runs 4, 10 & 18) the agreement had dropped to 37 per cent. For the remaining experiments the agreement was less good due to the high conversion which was predicted by the rate equation for the reboiler contents. A higher conversion in the reboiler would be expected due to the large holdup of the reboiler which was between 30 and 40 times larger than that of a typical stage holdup rather than due to concentration effects.

However, it was observed that when large reboiler conversions were predicted by the rate equations, the composition of the reboiler was such that in these cases a large excess of the reactant ester, butyl acetate, was present. It was concluded in Section 3 that a different value for the forward velocity constant had been measured when an ester rich mixture was reacted. Hence it would appear that there may be some difficulty in applying the rate equation to a system where butyl acetate was in a large excess. However, it was concluded that the rate equation was able to predict the stagewise conversions when equimolar or near equimolar reactants were present. It was observed that in some of the experiments that both the reactants were present in the reboiler whilst only one of the reaction products was present (Table 5.10 Runs 6, 13 - 15). This could have been expected for Runs 6, 13 - 15 which were being carried out at the high boilup rates but even a small concentration of the products would be expected and thus the rate equation would be devoid of the reverse reaction term giving a higher value for the rate constant. Hence it could be concluded that a poor liquid phase sample had been taken particularly as in two of the experiments, the vapour phase composition leaving the reboiler contained approximately 2 mole per cent of ethyl acetate (see also Fig. 5.11).

For the experiments where a very large reboiler conversion was predicted by the rate equation, the sum of the conversions on the remaining plates (4 - 6) was still small indicating that a large proportion of the conversion occurred in the reboiler.

In general, the agreement between the totals of the stagewise conversions and the overall conversions appeared to be close enough

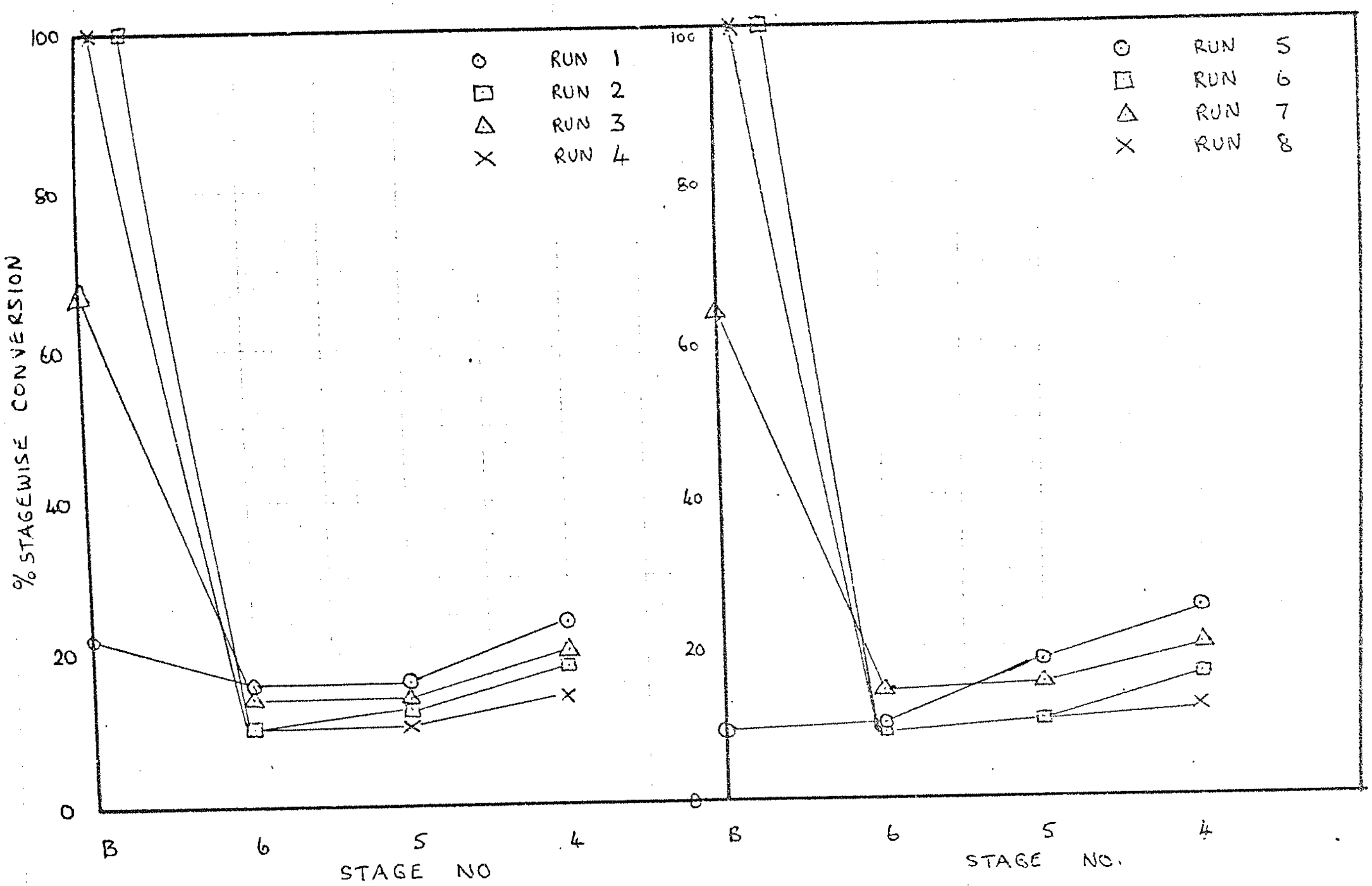


Fig 5.11 % Stagewise Conversions, Runs 1 – 8.

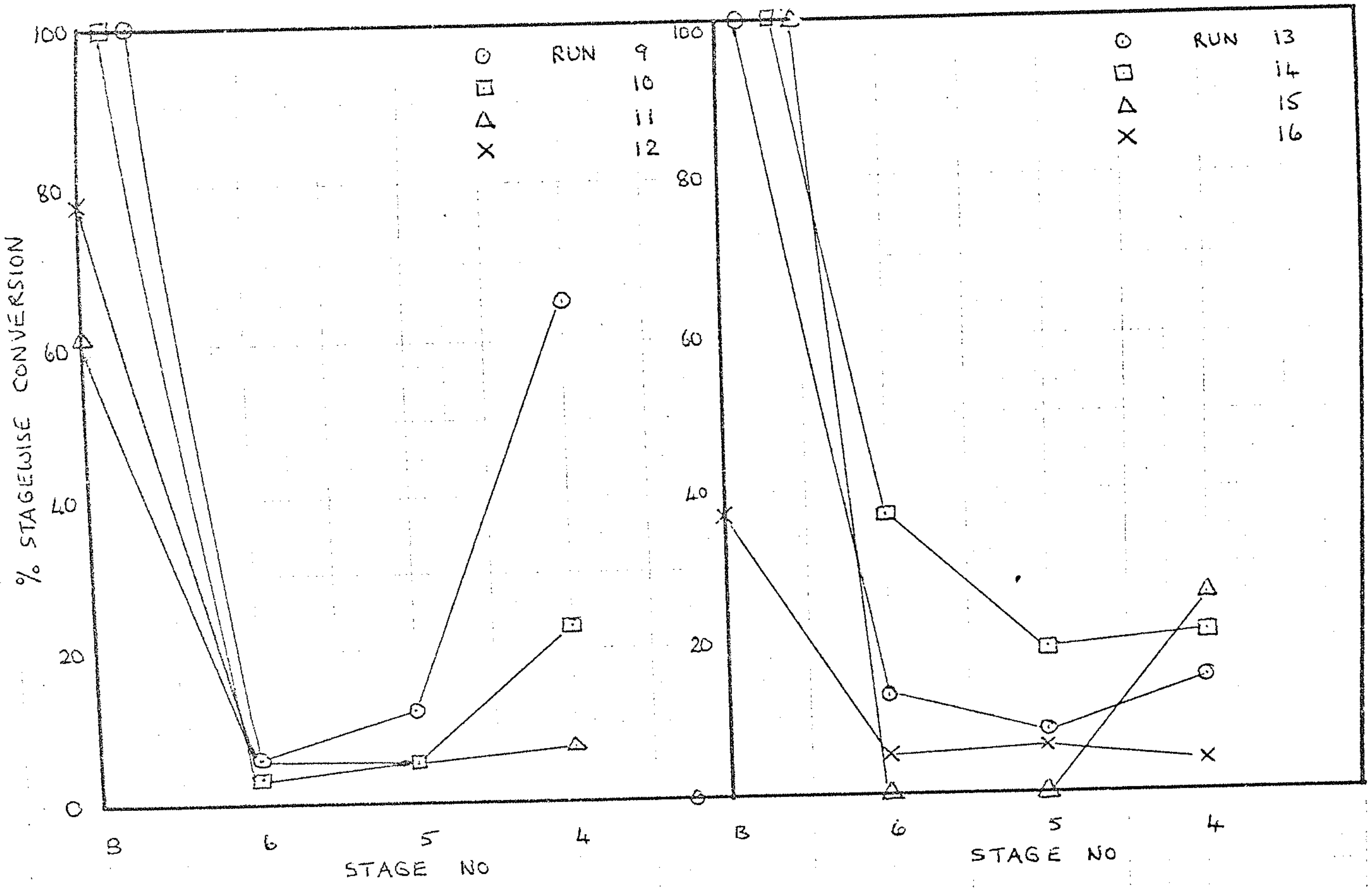


Fig 5.11 % Stagewise Conversions, Runs 9–16

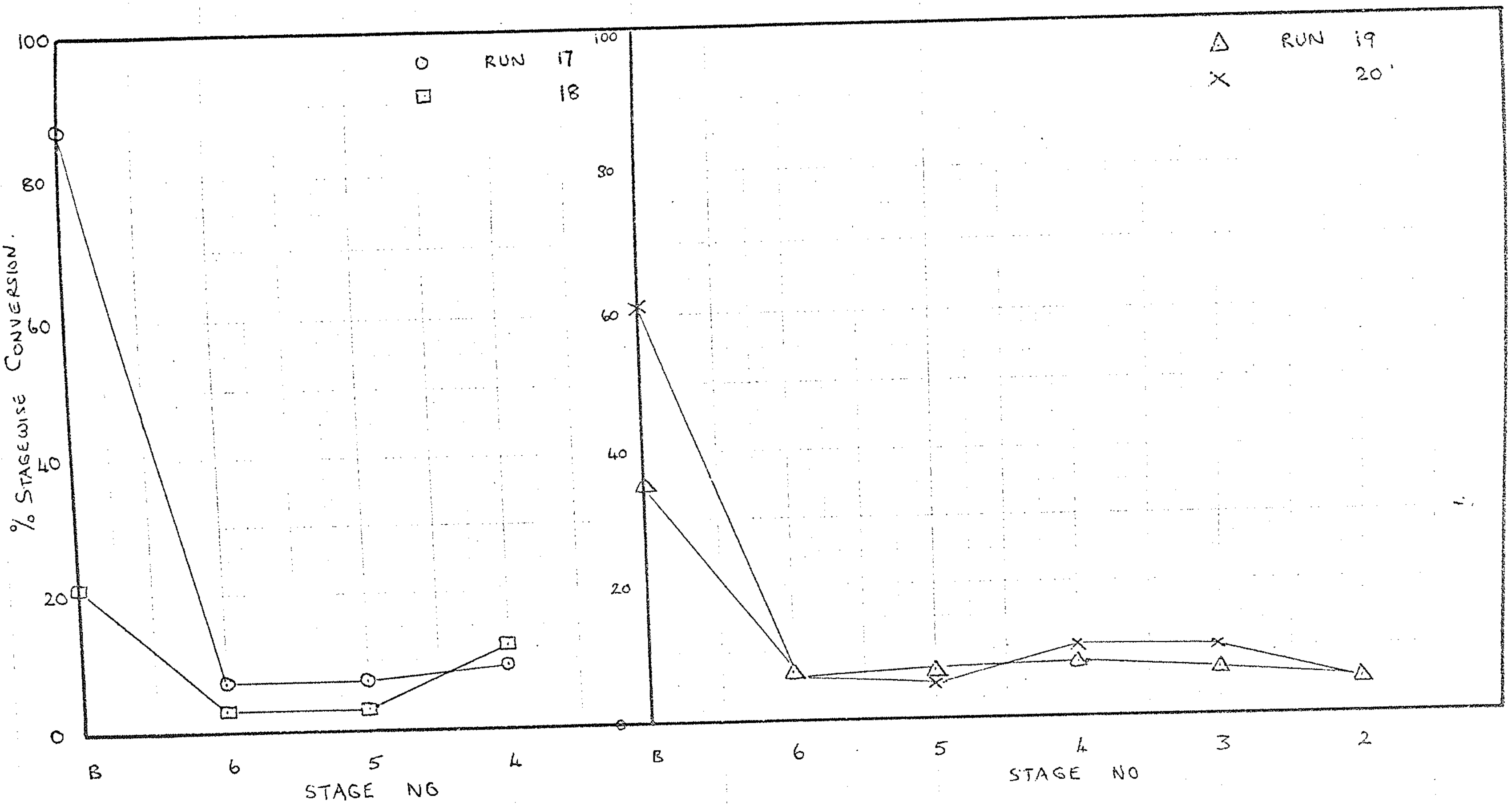


Fig 5.11 % Stagewise Conversions, Runs 17-20

for systems where the reboiler contents were approximately equimolar or near equimolar whilst for systems where the reboiler contents had a large excess of butyl acetate the agreement was less good although the sum of the remaining stage conversions (Plates 4 - 6) was in quite good agreement with the overall conversions.

An examination of the percentage stagewise conversion in greater detail revealed that in the majority of the experiments, the largest amount of the conversion occurred on the feed plate and in the reboiler (Table 5.10 Runs 1 - 13, 15, 17 & 18). This would be expected due to the large reboiler holdup and due to the higher reactant concentration on the feed plate. Also a greater conversion would be expected in the reboiler because of the higher catalyst concentration which varied between 0.98 and 3.32 weight per cent. A similar variation also occurred on the plates where the catalyst concentration varied between 0.29 and 0.52 weight per cent and thus less conversion would be expected on the plates between the reboiler and the feed plate.

In most experiments the conversion decreased below the feed plate and this demonstrates the effects of simultaneous physical separation and reaction in the column. Below the feed plate, the ethyl alcohol concentration would decrease due to the physical separation although the butyl acetate concentration would similarly increase. As the boilup rate was increased, the concentration of ethyl alcohol would decrease on the feed plate whilst the butyl acetate concentration would increase. Thus the reaction zone would tend to move up the column and the distillation and reaction effects would tend to cancel each other out and thus the percentage conversion on the feed plate remained constant within a range of 10 - 25 per cent.

The Murphree efficiency (E_m) and the Vaporisation efficiency (E_v) are two of the most used techniques for defining component plate efficiencies in a multi-component distillation column (106).

The Murphree efficiency for a component on plate n is defined by:-

$$E_m = \frac{y_n - y_{(n-1)}}{y_n^* \quad y_{(n-1)}}$$

and the Vaporisation efficiency is given by:-

$$E_v = \frac{y_n}{y_n^*}$$

where y_n^* is the vapour composition in equilibrium with the liquid on plate n.

y_n is the actual vapour composition from plate n.

$y_{(n-1)}$ is the actual vapour composition from plate (n - 1), the plate below plate n.

The Murphree plate efficiency is a measure of the change in the vapour phase composition of a particular component on passing through a stage and it is a function of the composition of the vapour phase leaving the stage below whilst the Vaporisation efficiency treats the plate as a separate unit independently of the neighbouring stages.

Column and plate efficiencies have been analysed in a number of different ways. Zuiderweg & Harmens (147) investigated the effect of surface tension gradients on the overall column efficiency and they observed that high overall efficiencies were obtained for positive surface tension gradients due to the fact that the bubble stability was reinforced thus creating a larger mass transfer area. However, for negative surface tension gradients, the overall efficiencies were reduced to about 50 per cent.

In multi-component distillation, Toor (149) has demonstrated that the efficiency of a component is proportional to the rate of diffusion to the transfer interface. In the present investigation, an additional factor is caused by the appearance and disappearance of the components due to the chemical reaction.

The experimentally obtained component plate efficiency patterns were reasonably consistent within each series of results although the patterns varied between each series of results.(see Figs.12 (a)-(j)).

The Vaporisation efficiencies have been examined first for the twenty experiments. As the Vaporisation efficiencies treat the stages as separate units, the results should reflect the diffusional effects quoted by Toor (149). The diffusion constants have been calculated for the components (see Appendix D3) and ethyl alcohol was found to have the highest constant and should therefore have the highest efficiency. On balance the vaporisation efficiencies for ethyl alcohol and ethyl acetate were approximately the same and lay in the 90 - 120 per cent range, although for three series of runs for ethyl alcohol (Runs 1 - 4, 5 - 8 & 17 - 20) the efficiency was approximately 95 per cent. The efficiency of butyl acetate tended to be slightly higher than those of ethyl acetate and ethyl alcohol whilst the efficiency of butyl alcohol was the lowest of the four components although in particular for the two least volatile components, analytical errors could have caused higher efficiencies and scattering of the data due to the error incurred in calculating

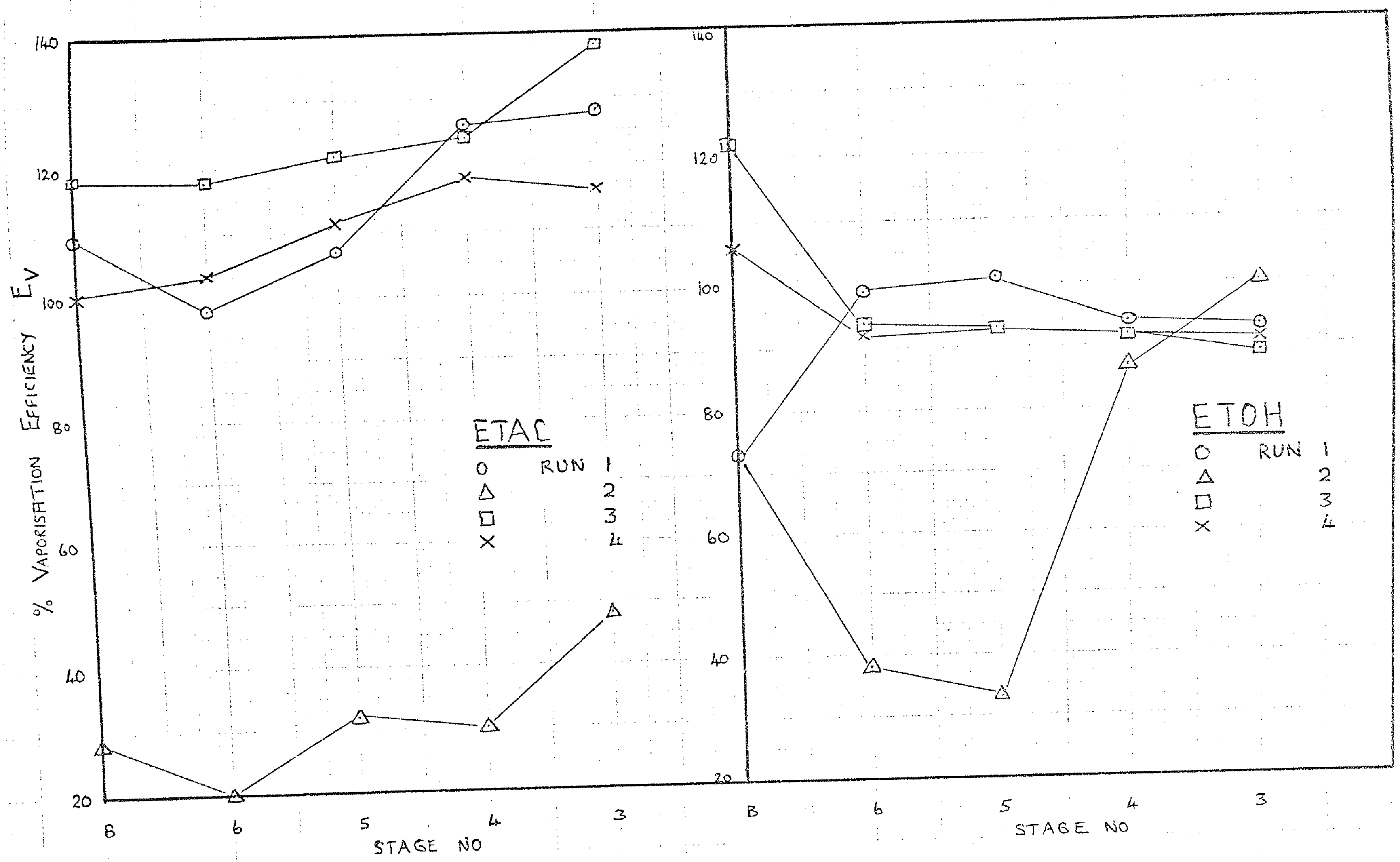


Fig 5.12 (a) Component Vaporisation Efficiencies, Runs 1–4

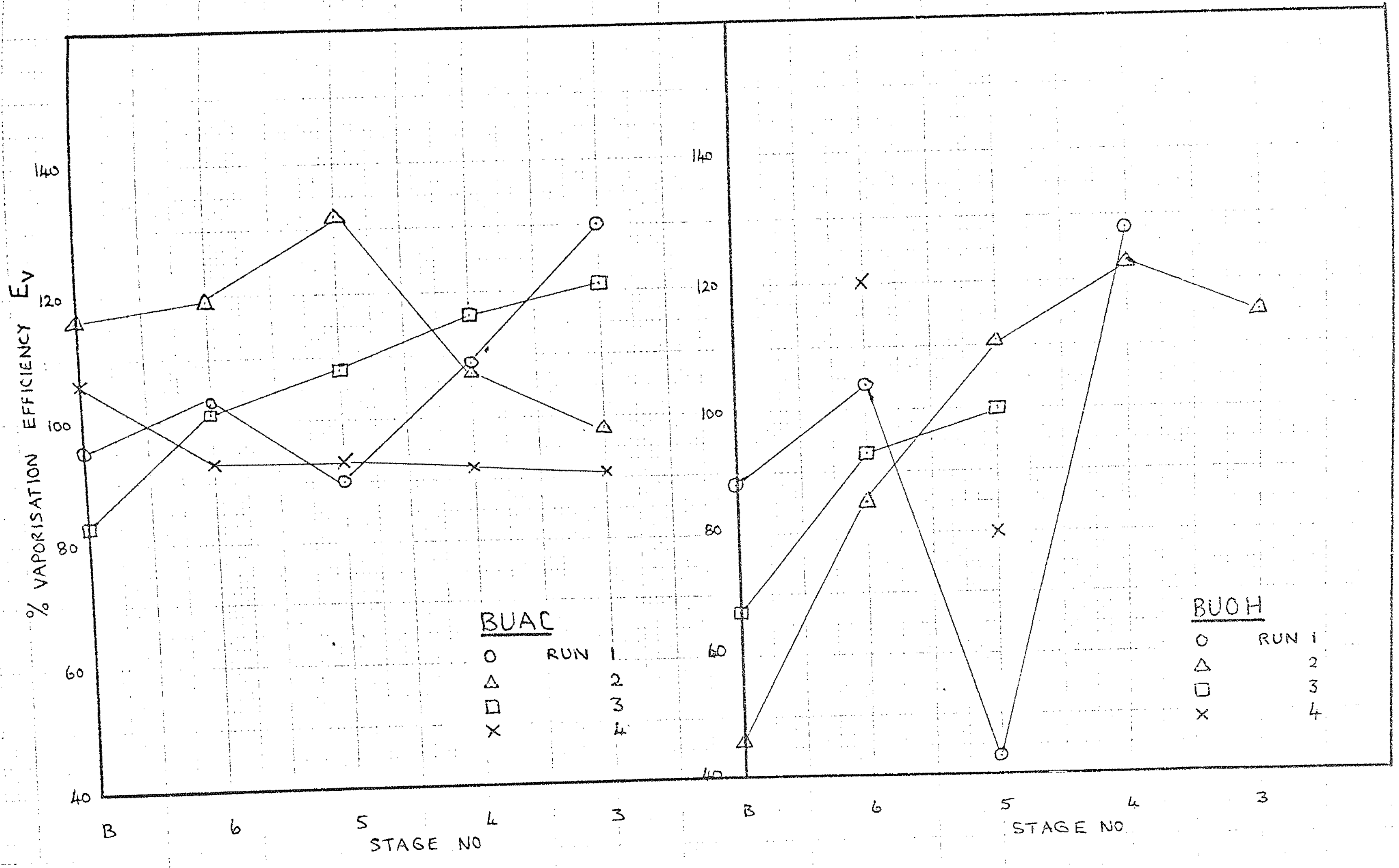


Fig 5.12 (b) Component Vaporisation Efficiencies, Runs 1-4

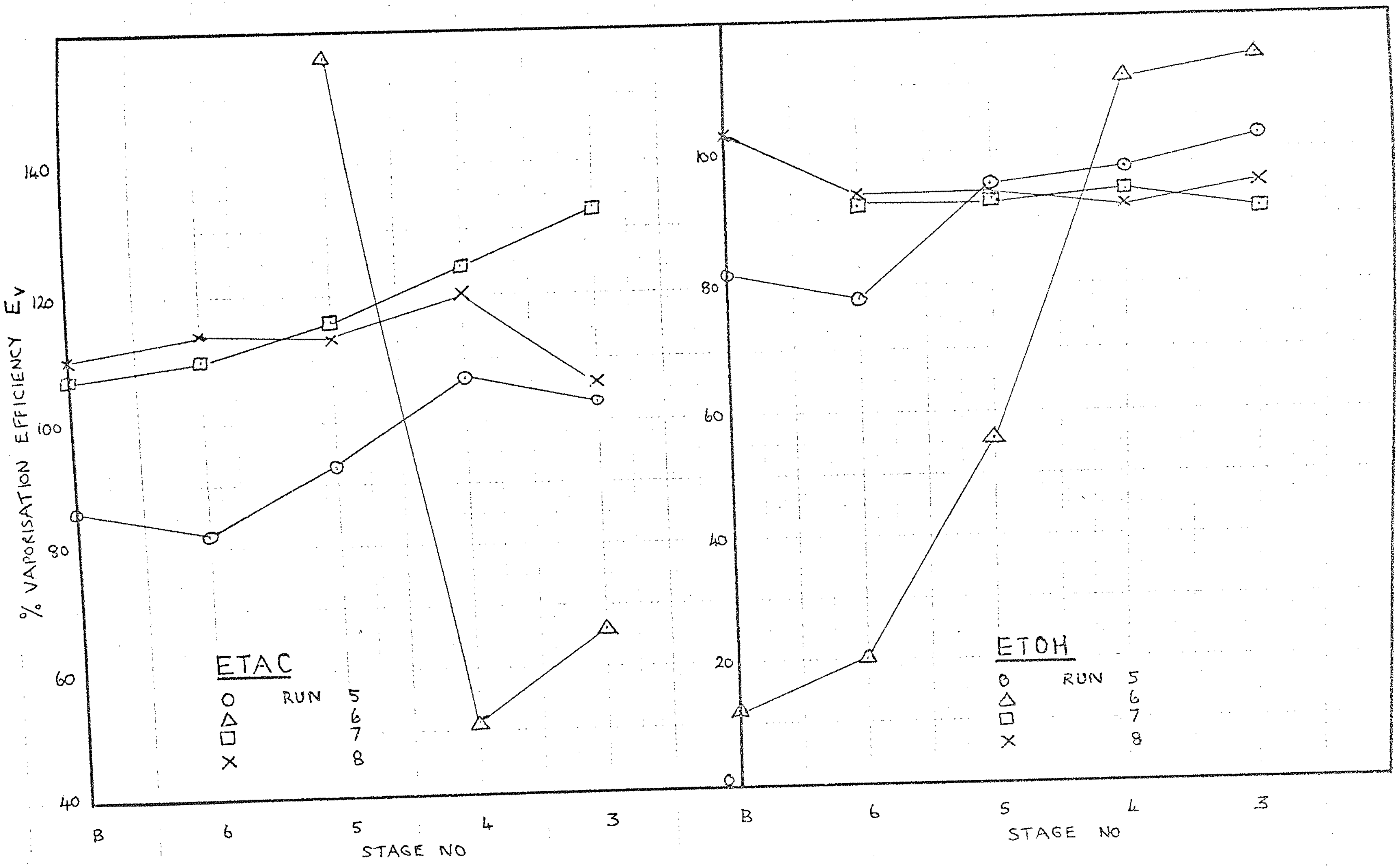


Fig 5.12 (c) Component Vaporisation Efficiencies, Runs 5–8

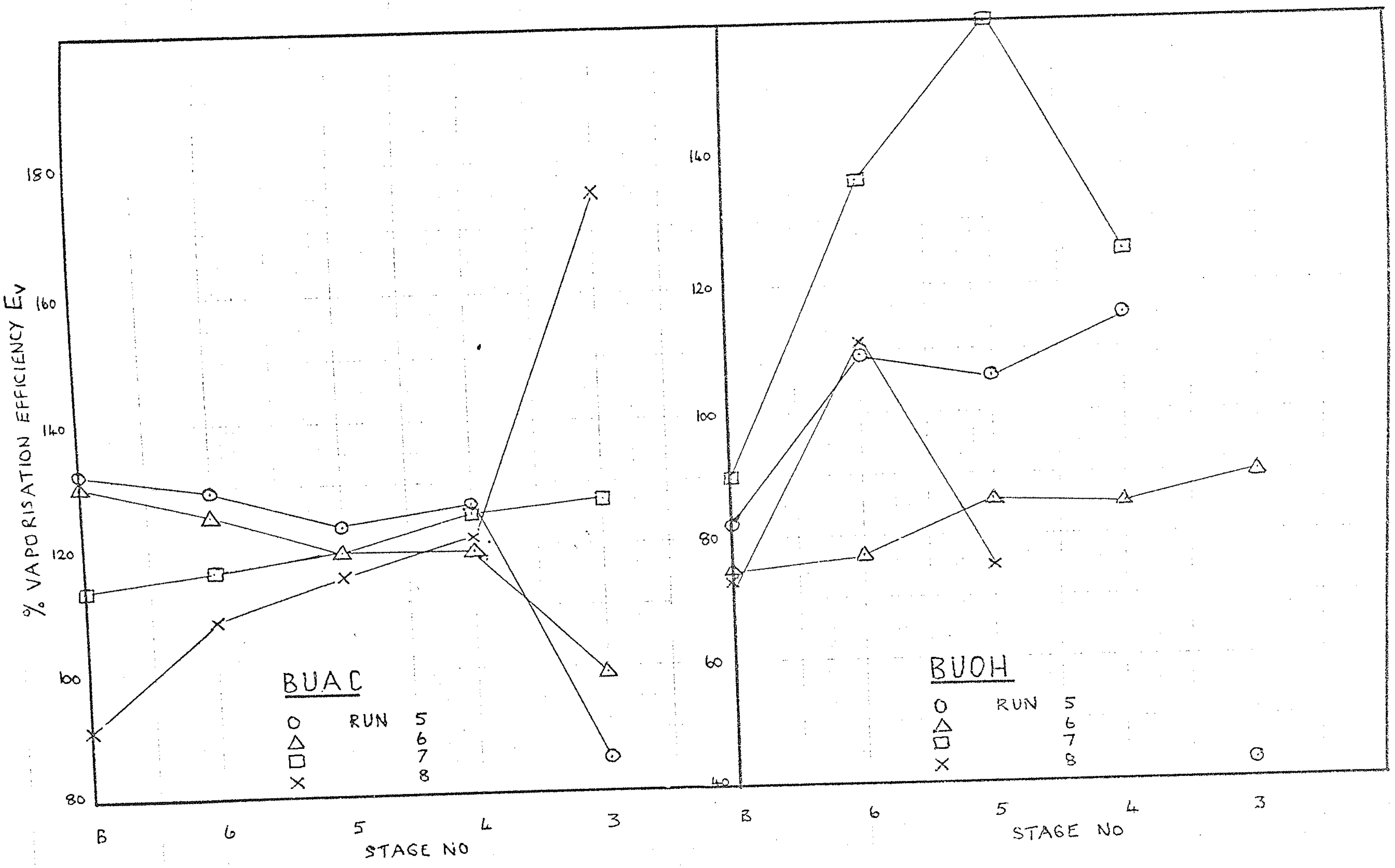


Fig 5.12 (d) Component Vaporisation Efficiencies, Runs 5 – 8

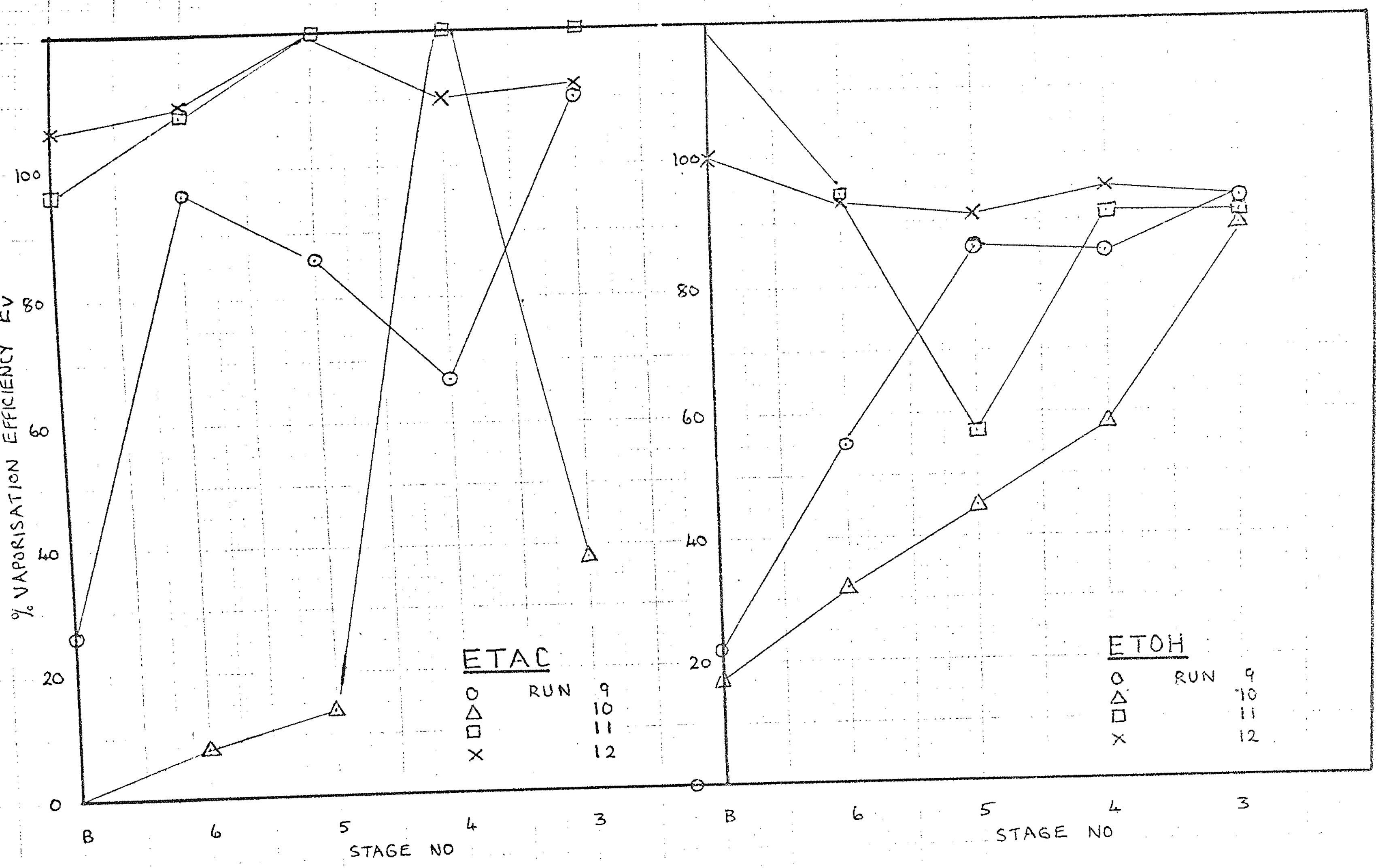


Fig 5.12 (e) Component Vaporisation Efficiencies, Runs 9–12

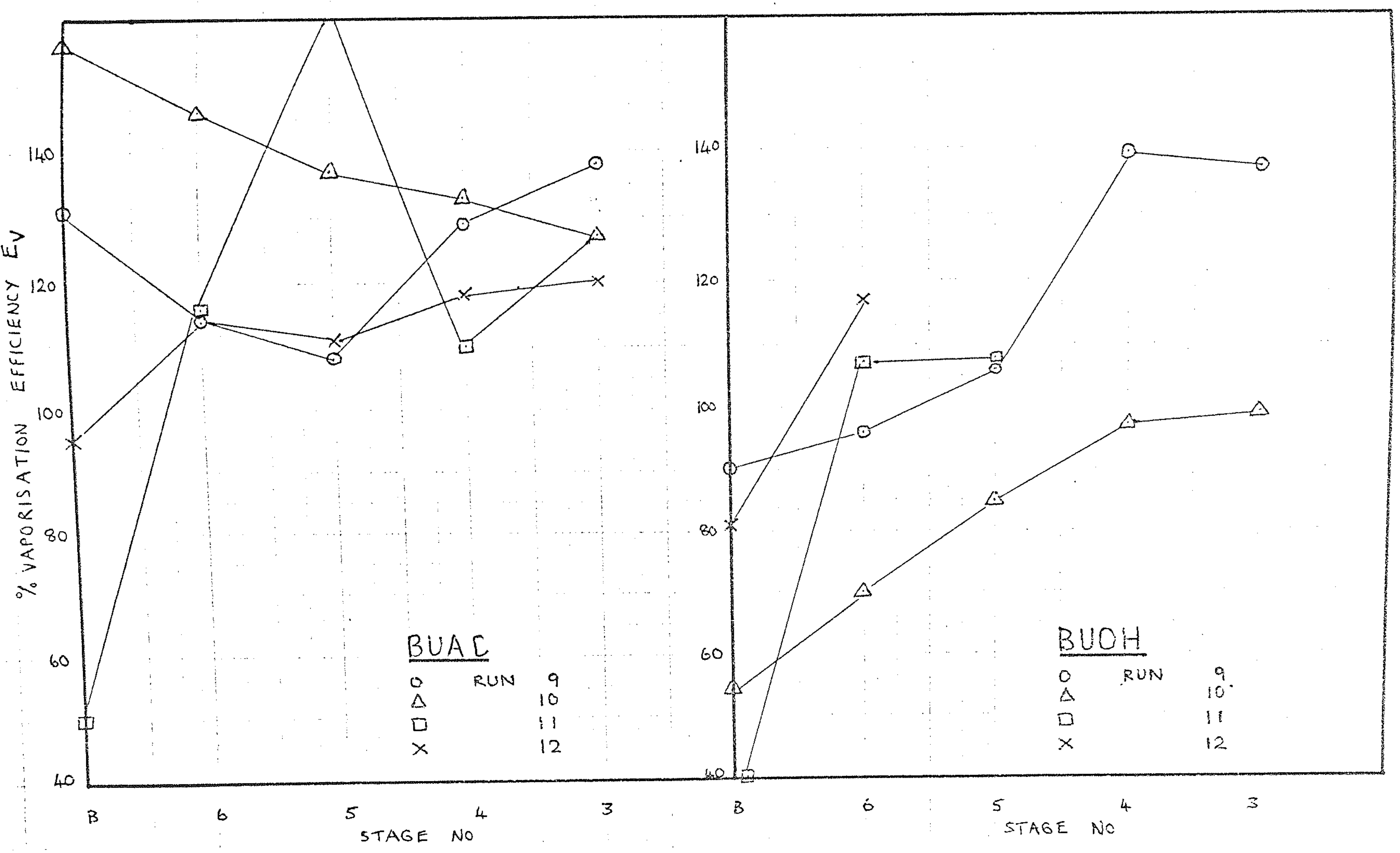


Fig 5.12 (f) Component Vaporisation Efficiencies, Runs 9–12

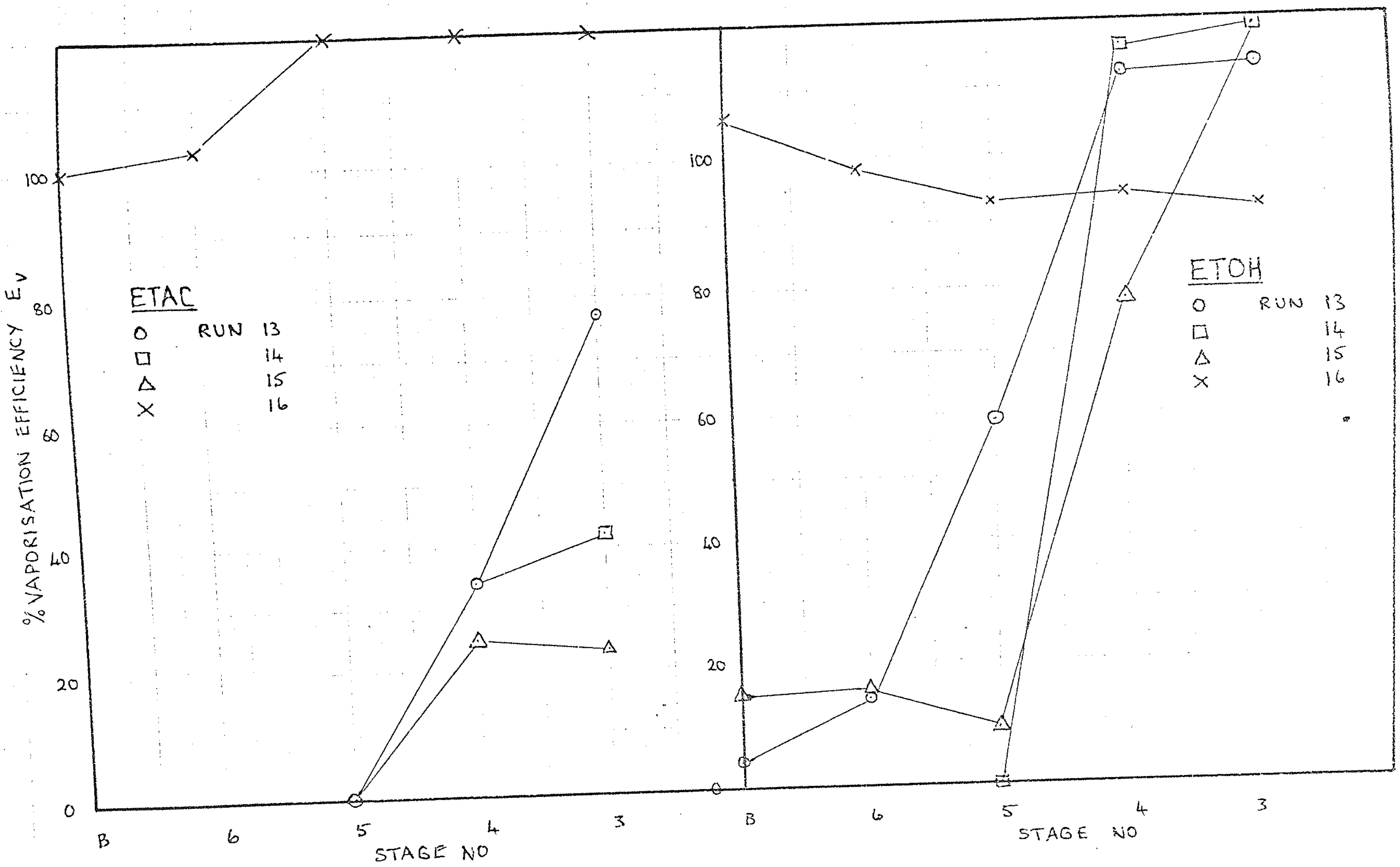


Fig 5.12 (g) Component Vaporisation Efficiencies, Runs 13–16

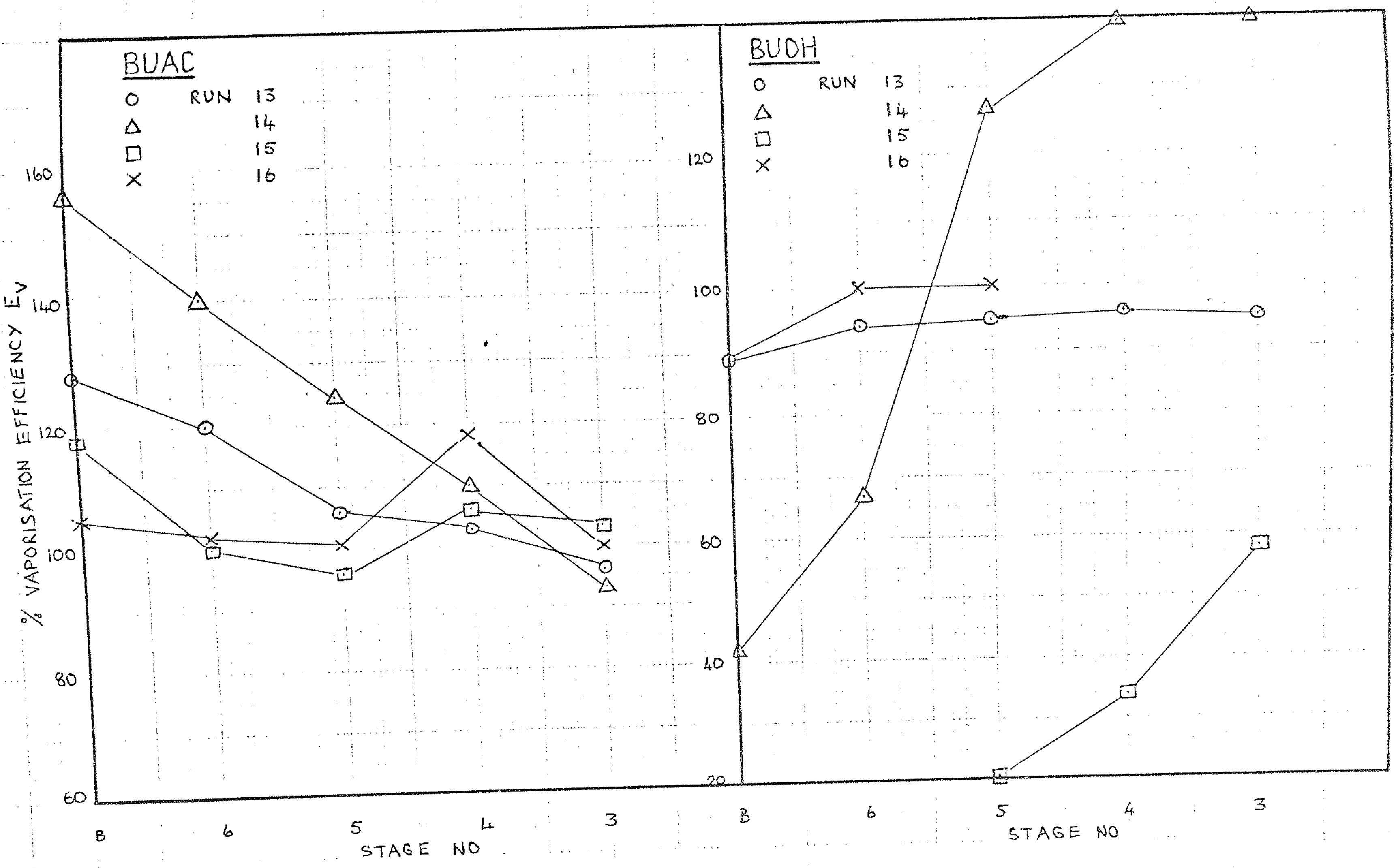


Fig 5.12(h) Component Vaporisation Efficiencies, Runs 13–16

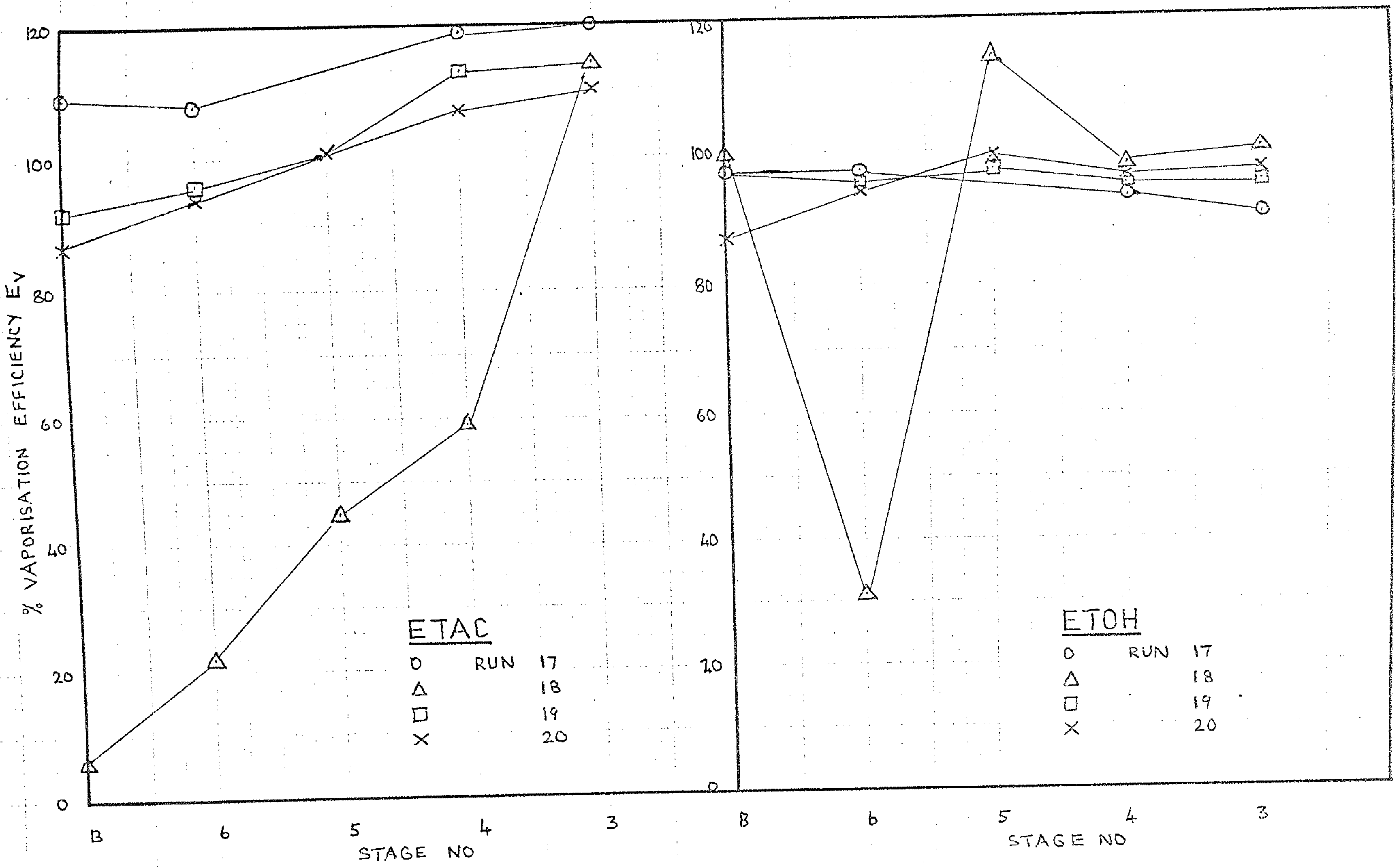


Fig 5.12(i) Component Vaporisation Efficiencies, Runs 17-20

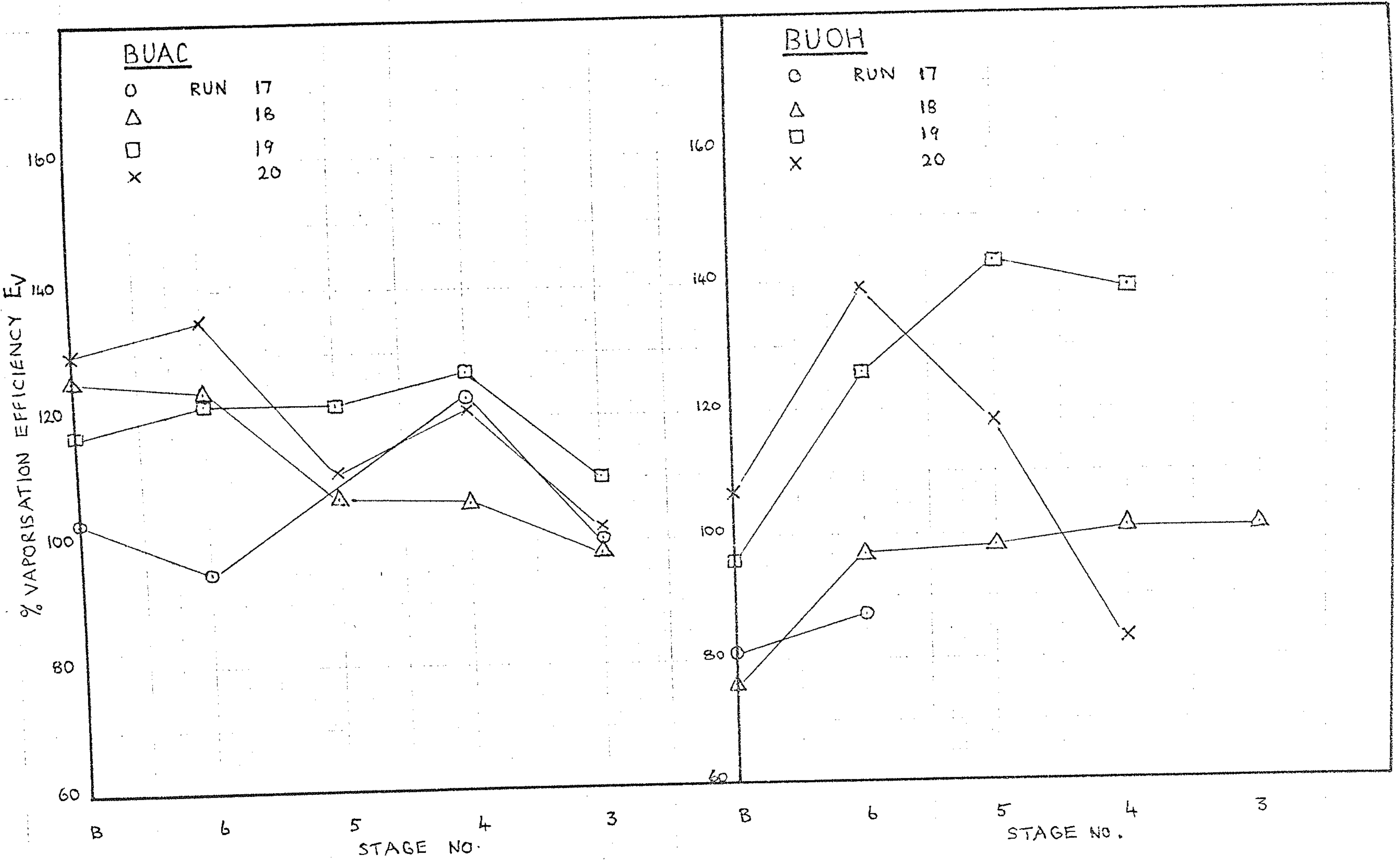


Fig 5.12 (j) Component Vaporisation Efficiencies, Runs 17-20

the ratio of small numbers. Also the slight discrepancies could well be due to the fact that the system contains four non-ideal components all of which demonstrate polar and hydrogen-bonding characteristics. It was difficult to detect any specific effect of the reflux ratio on the vaporisation efficiencies although for ethyl acetate (Runs 1 - 4) the efficiency increased as the reflux ratio increased. However, it was observed that all the experiments carried out at a reflux ratio of 2:1, the efficiency tended to be either considerably lower or to have a larger scatter.

It was anticipated that the Murphree efficiencies which involve the interactions between the stages, would clearly show the effects of carrying out a reaction in a distillation column. The four components all had lower efficiencies in the region of the feed plate than at either ends of the column, the phenomenon being most pronounced for butyl acetate. When the efficiencies are examined together with the appropriate stage conversions and stage concentrations, a clearer picture is obtained. In the case of Run 2, the overall conversion of ethyl alcohol had been calculated to be slightly negative (see Table 5.14) indicating that the reverse reaction may have dominated in the column. Belck (136) overcame this problem by removing the catalyst from the plate below the "equilibrium plate". Because of this, the concentration of butyl alcohol in the liquid phase decreased below the feed plate thus behaving as a pseudo-light component and causing the efficiencies to fluctuate between -70 & +300 per cent (Fig. 5.13 (a)).

In the remaining 3 experiments, the efficiency of ethyl alcohol (the light component) was affected by the reaction. The ethyl

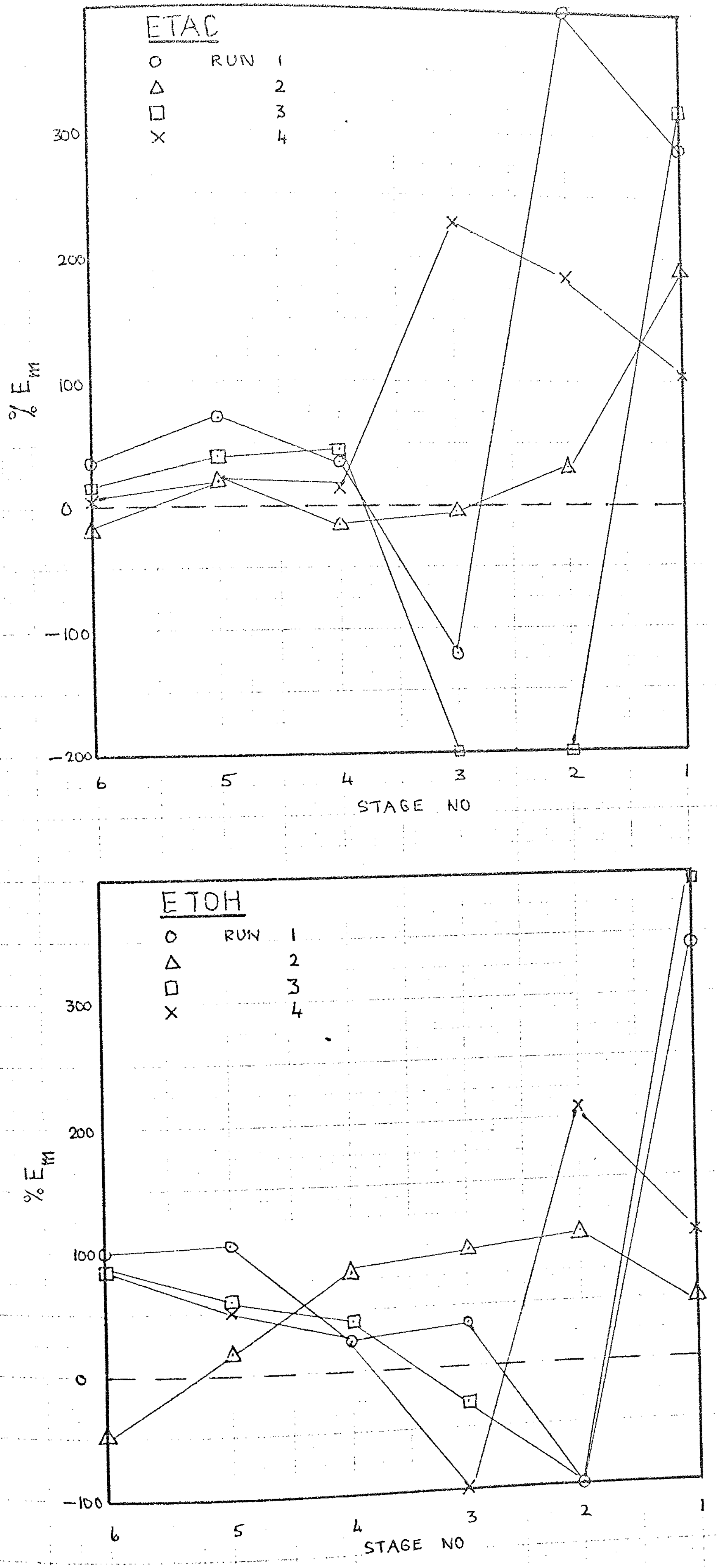


Fig 5.13 (a) Component Murphree Efficiencies, Runs 1–4

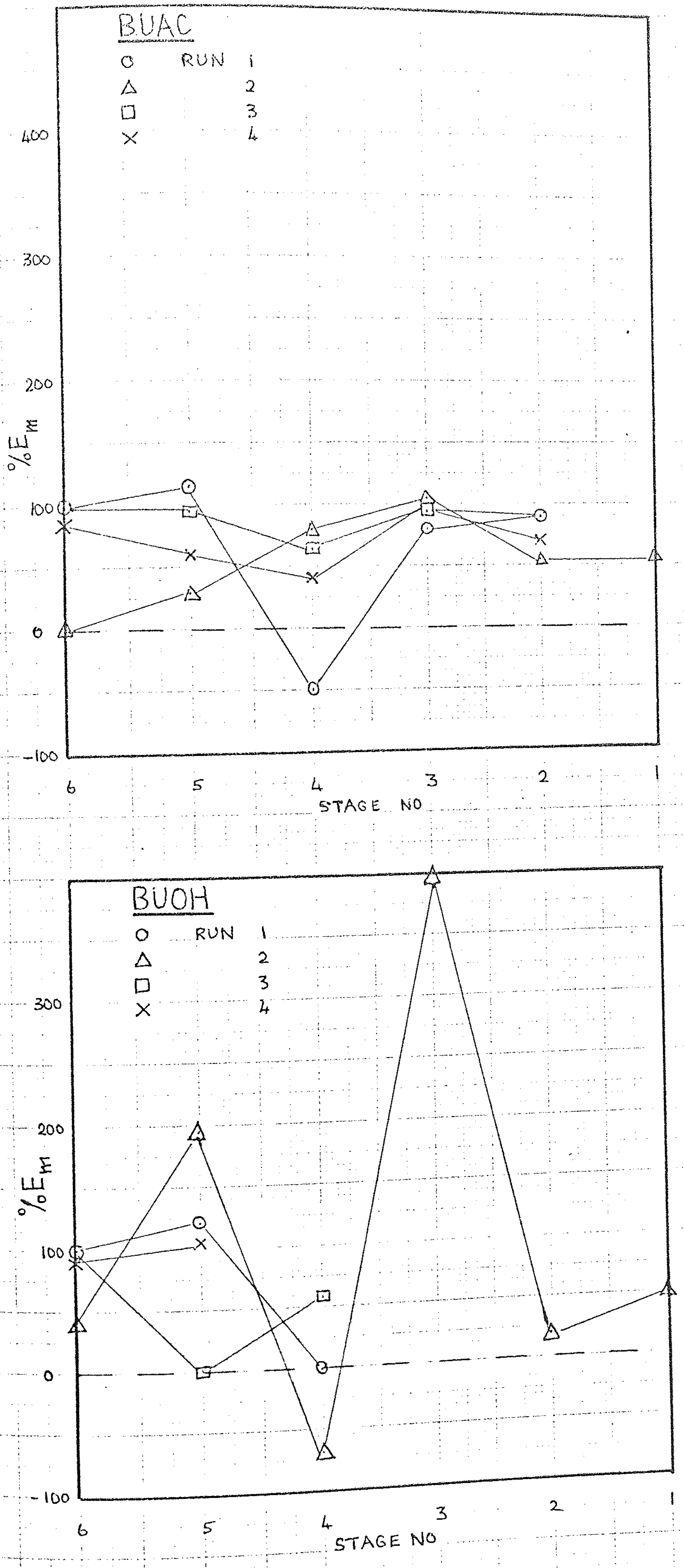


Fig 5.13(b) Component Murphree Efficiencies, Runs 1–4

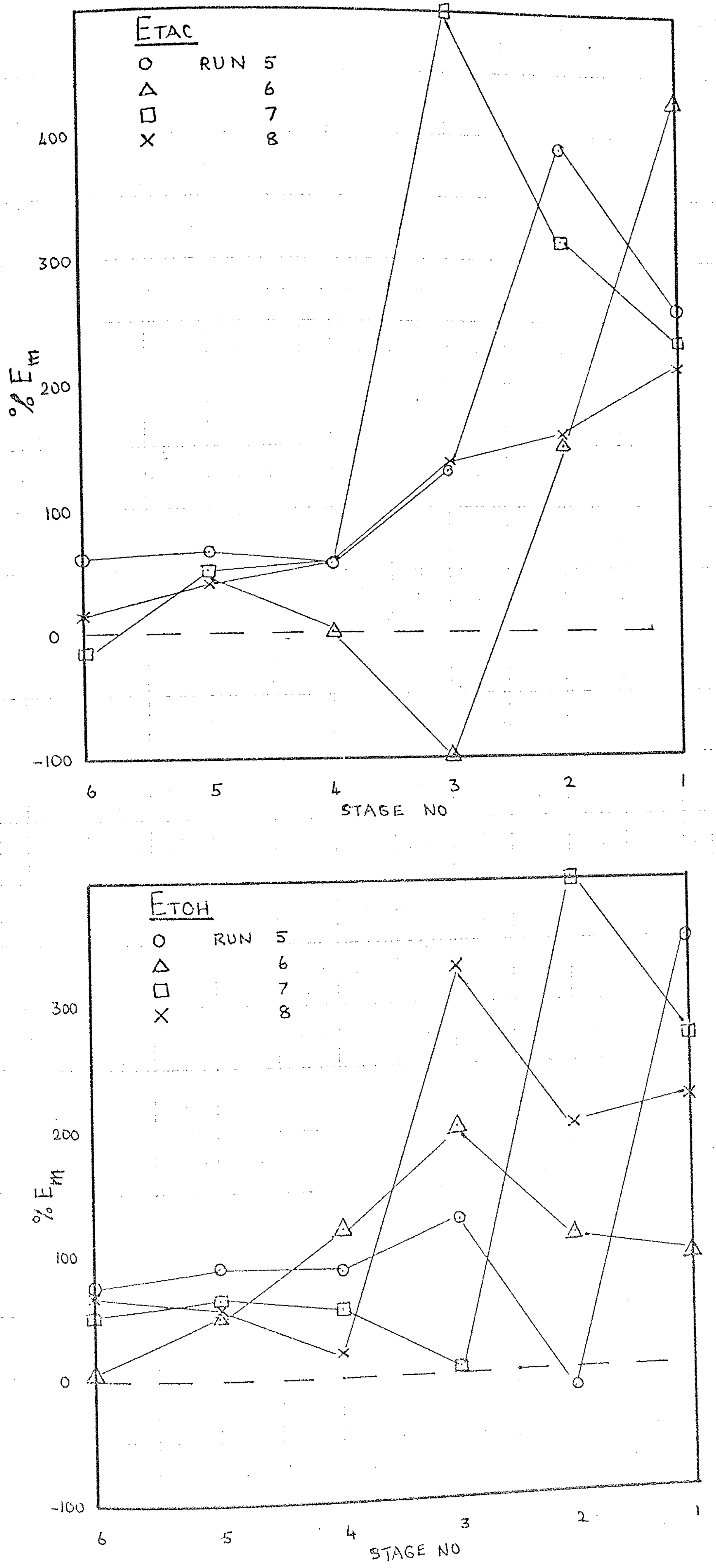


Fig 5.13 (c) Component Murphree Efficiencies, Runs 5-8

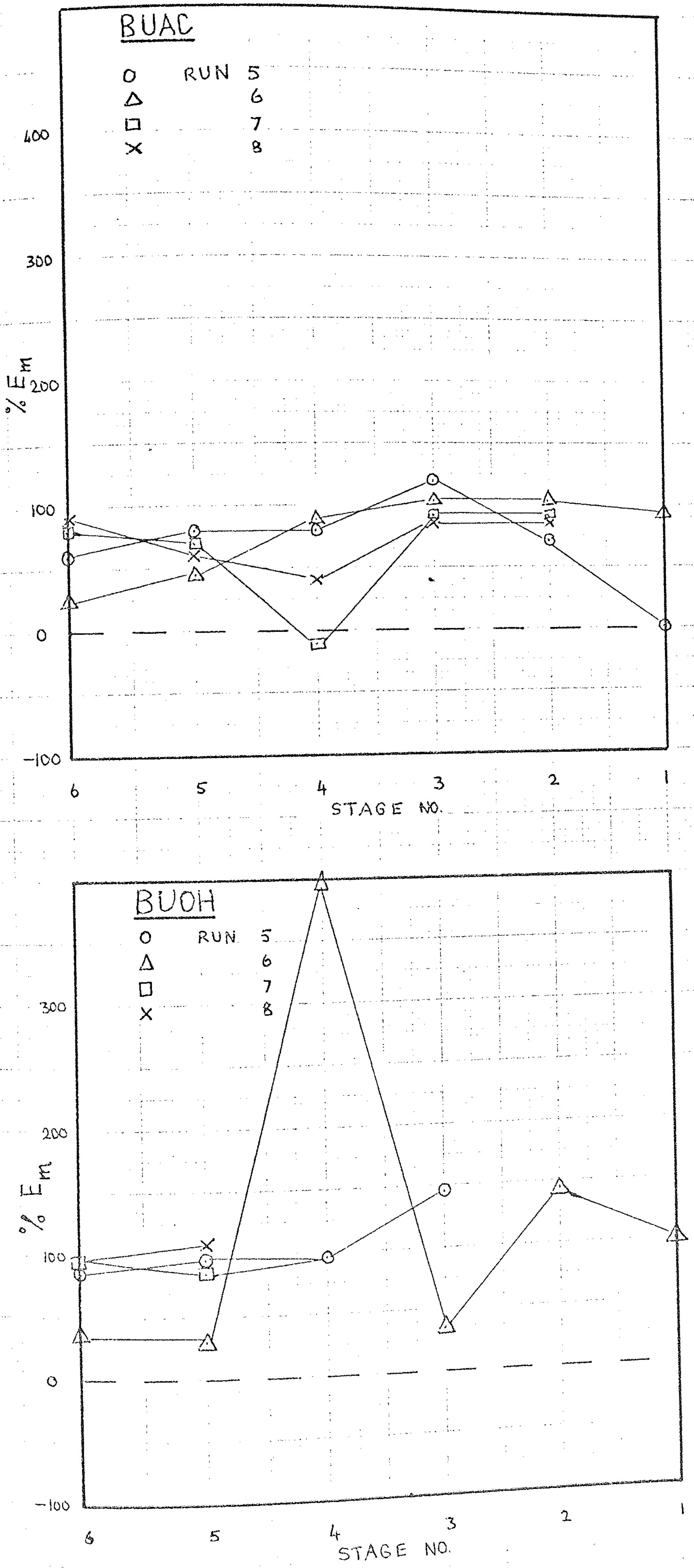


Fig 5.13 (d) Component Murphree Efficiencies, Runs 5–8

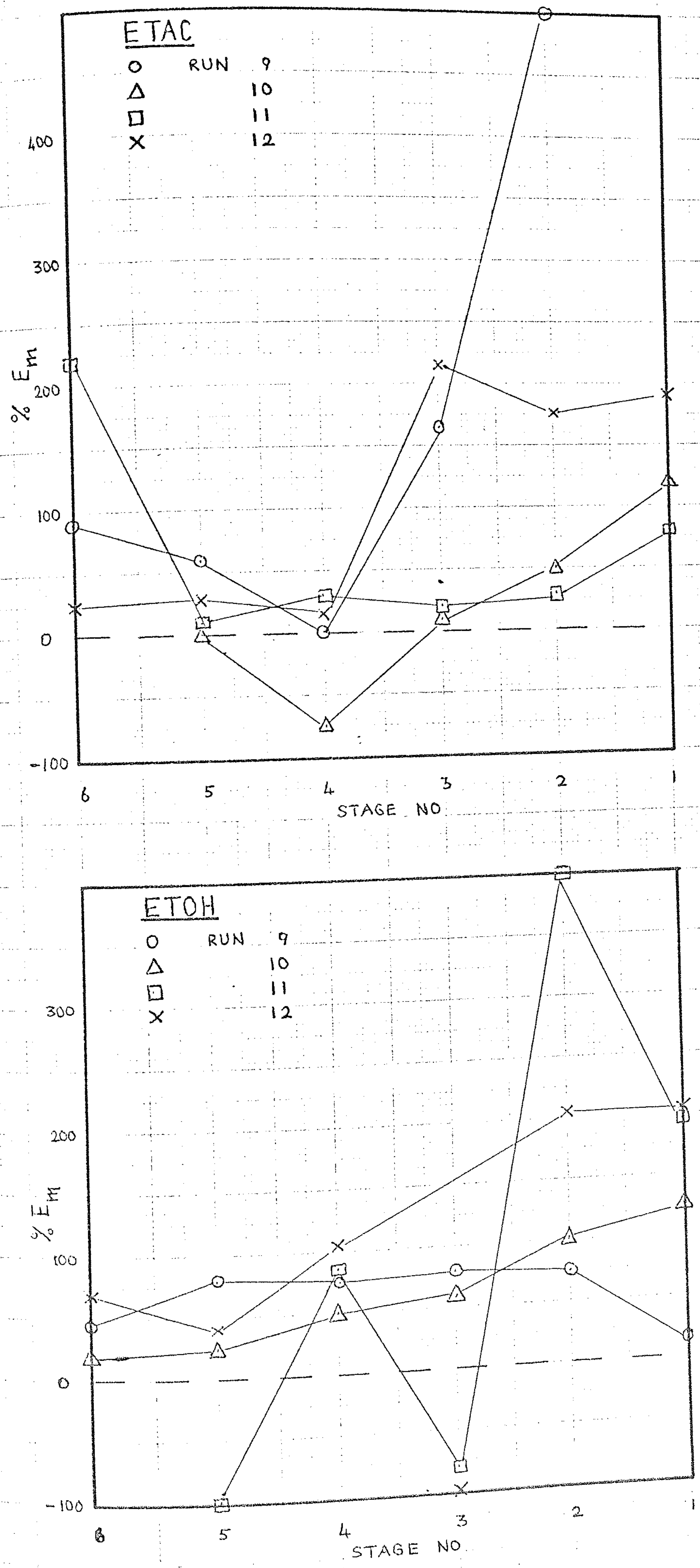
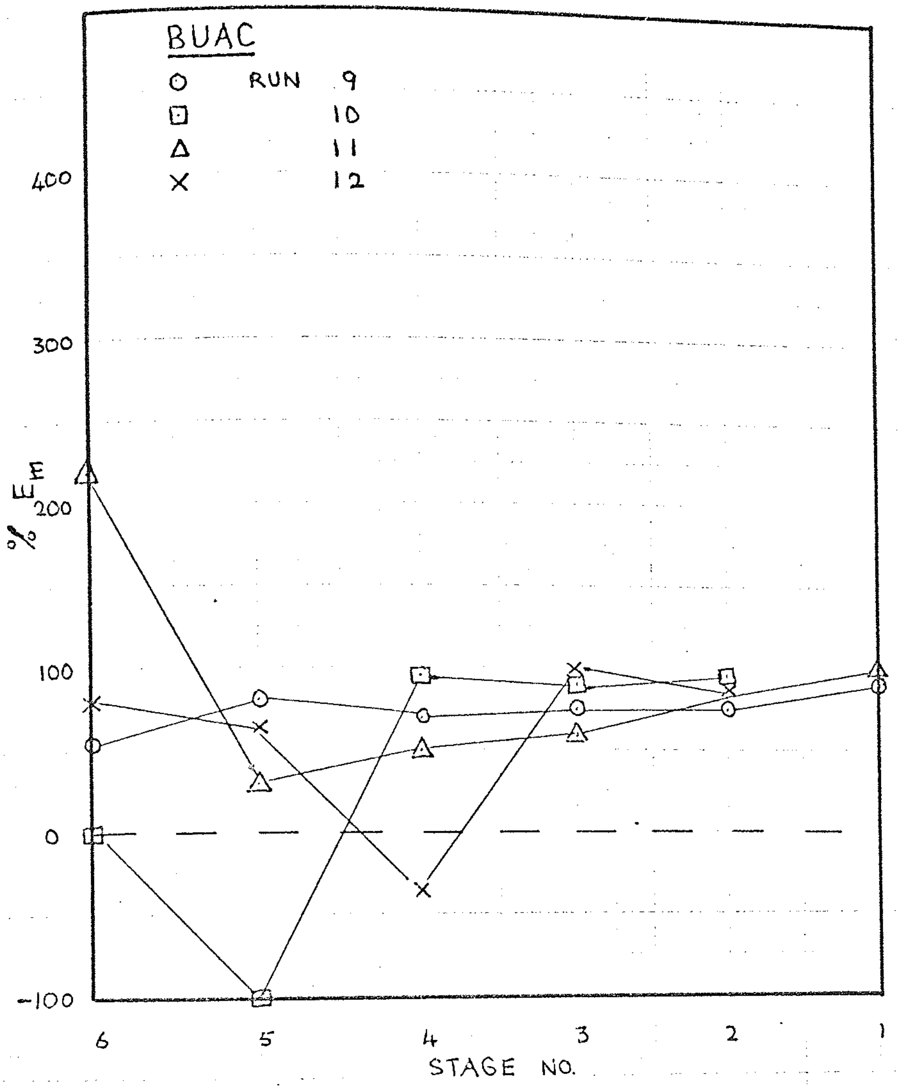


Fig 5.13 (e) Component Murphree Efficiencies, Runs 9-12



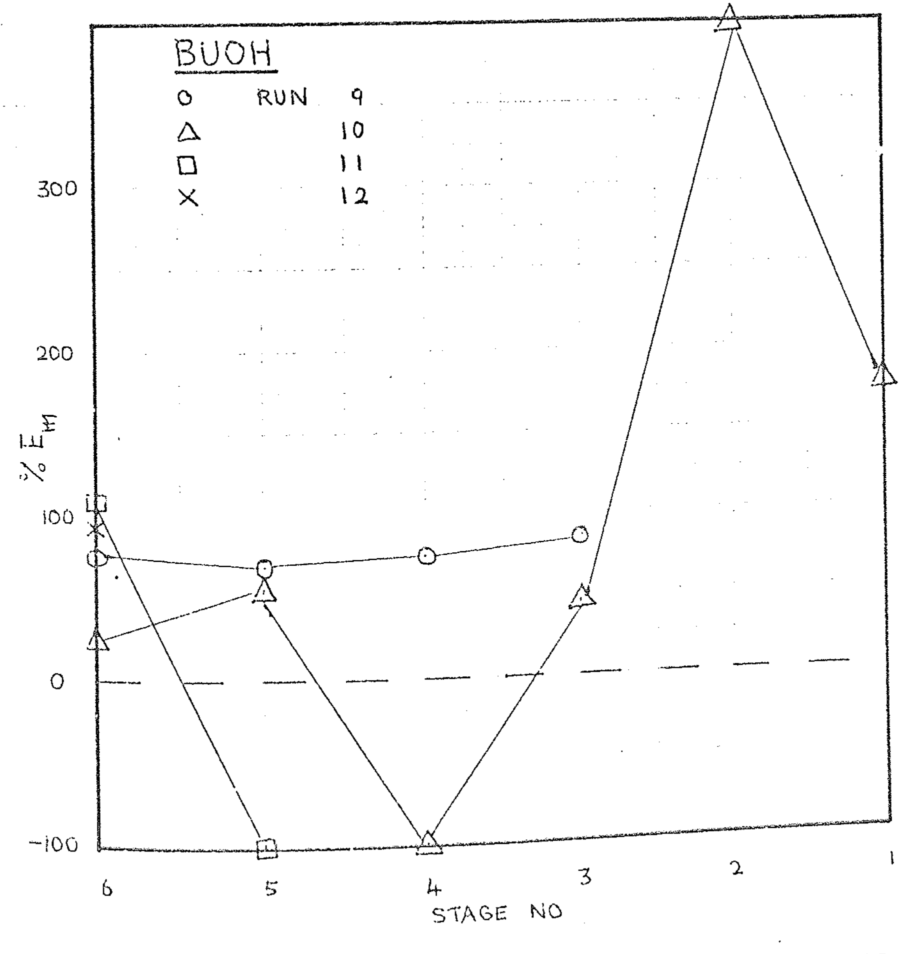


Fig 5.13 (f) Component Murphree Efficiencies, Runs 9–12

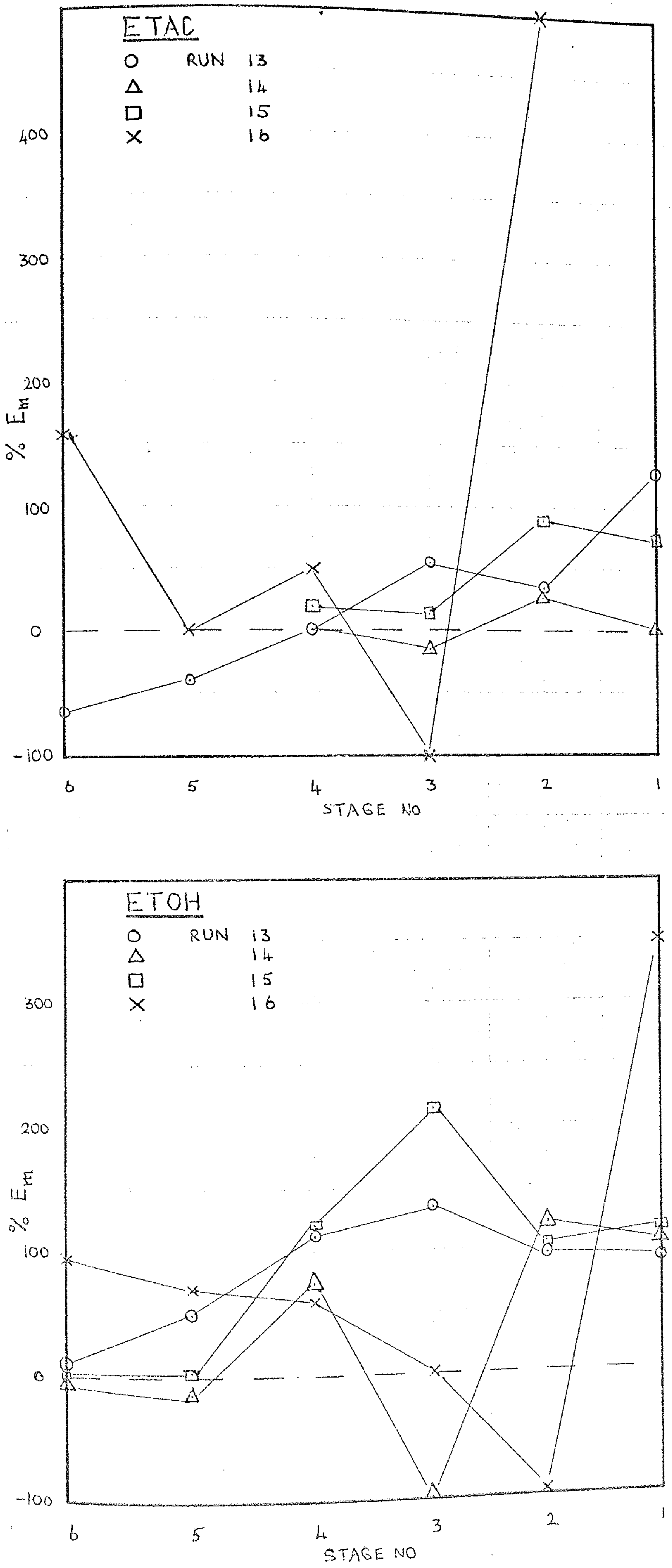


Fig 5.13 (q) Component Murphree Efficiencies, Runs 13-16

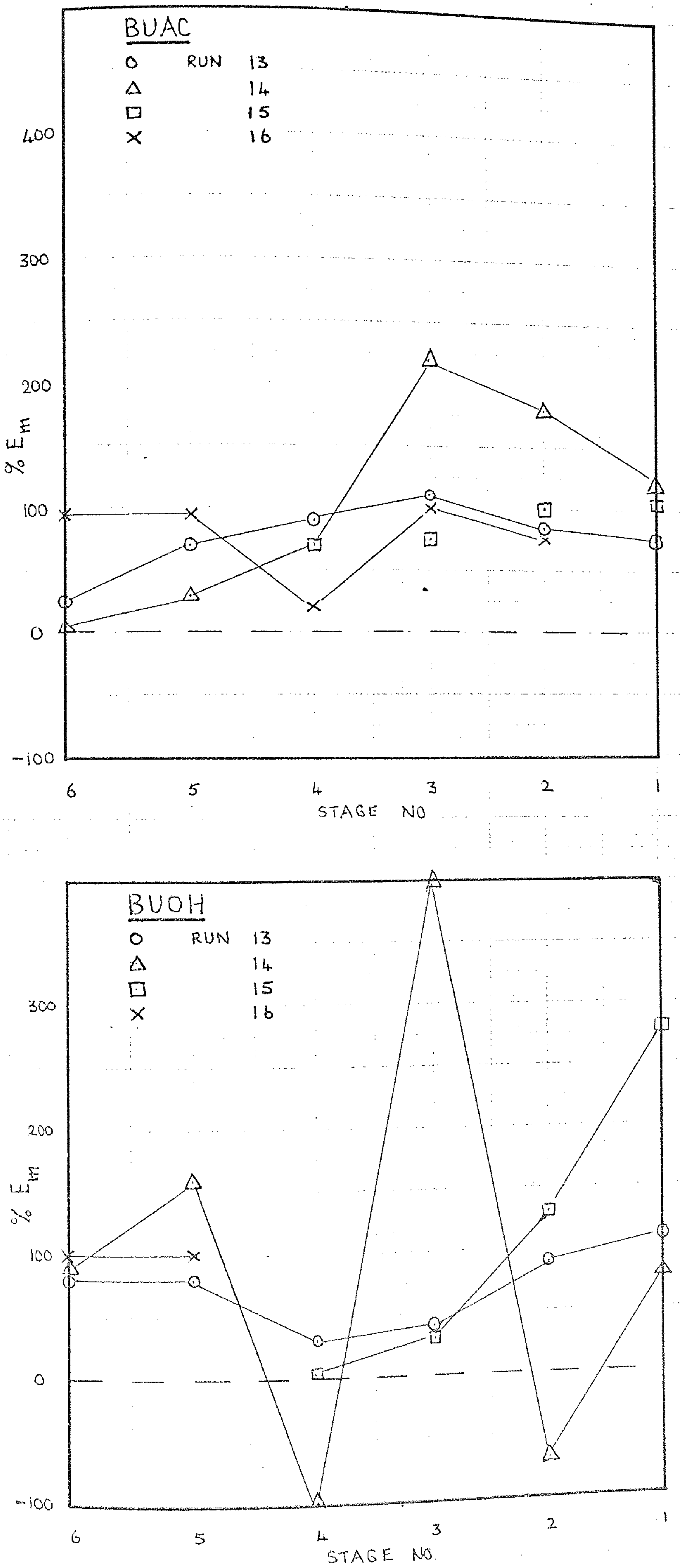


Fig 5.13 (h) Component Murphree Efficiencies, Runs 13-16

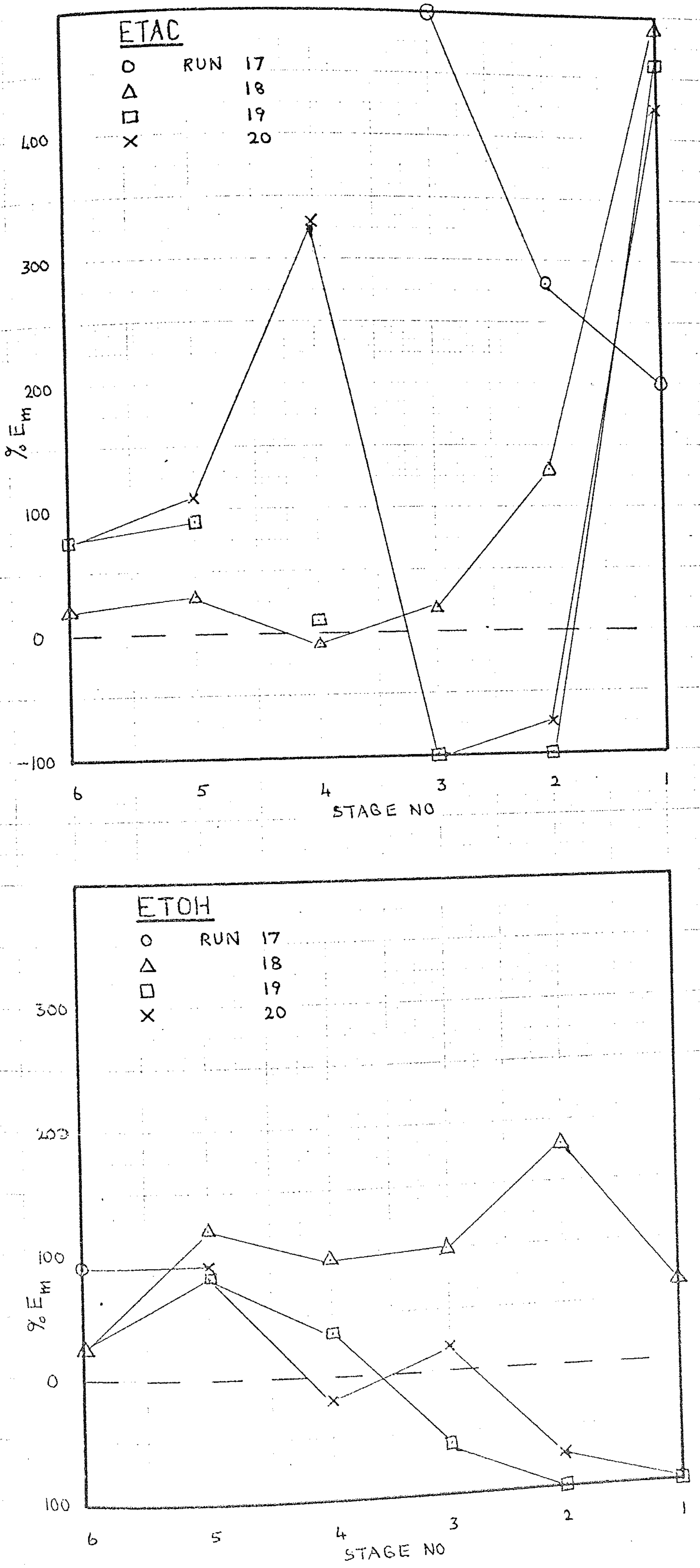
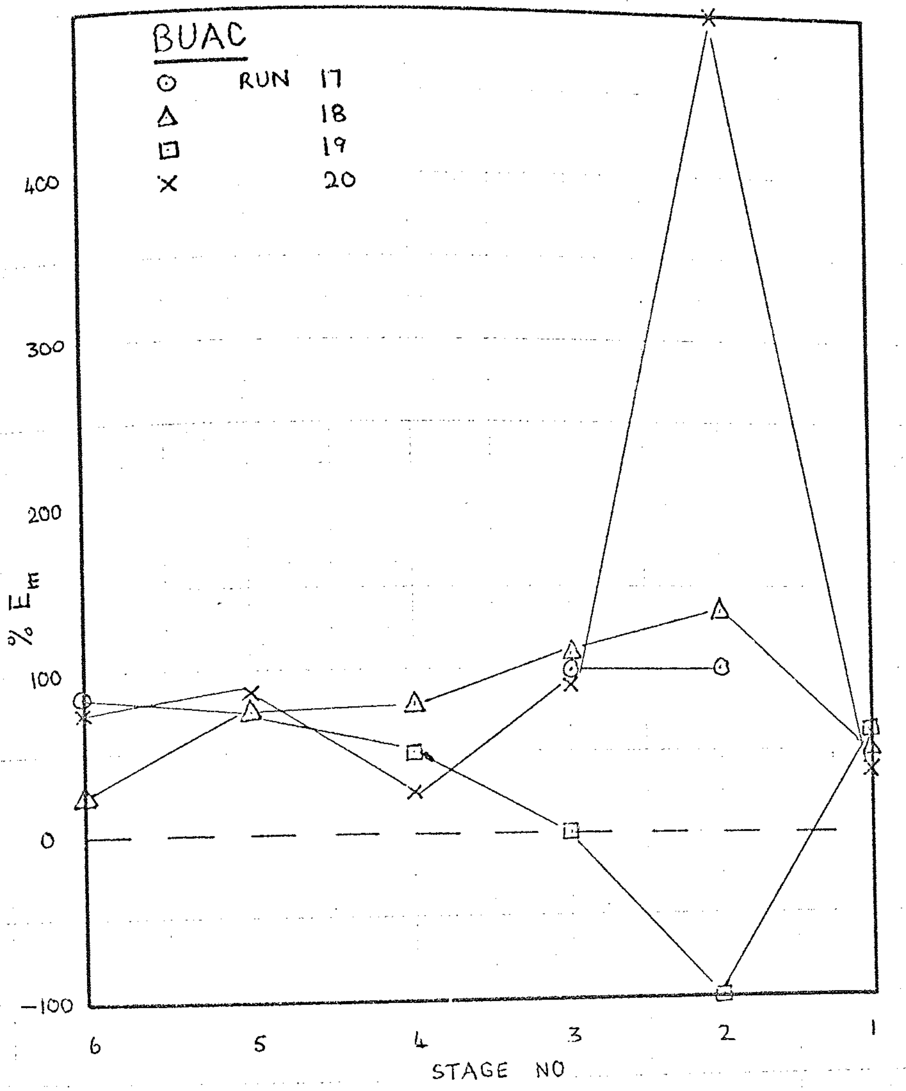


Fig 5.13 (i) Component Murphree Efficiencies, Runs 17-20



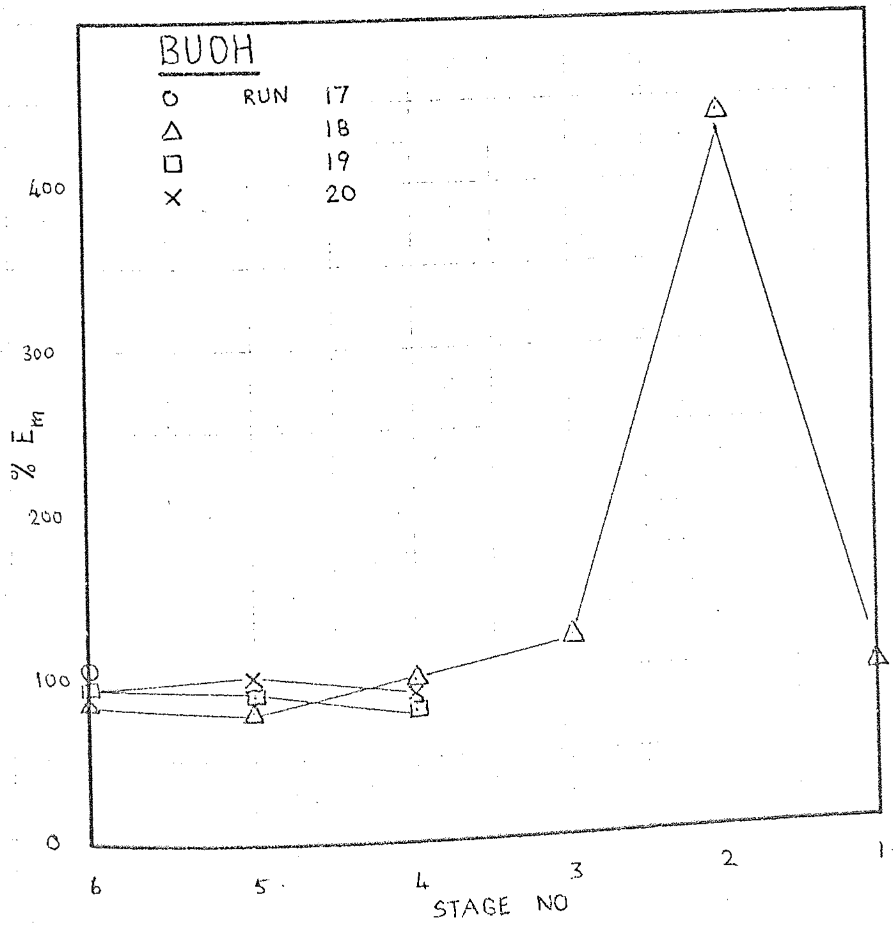


Fig 5. 13 (j) Component Murphree Efficiencies, Runs 17-20

alcohol was being constantly converted by the effect of the chemical reaction which would mean that as the light component, the concentration up the column would increase less rapidly than if no reaction was occurring. Thus the Murphree efficiencies were lower on the reactive plates than the non-reactive plates and the efficiencies were generally less on adjoining stages where the reaction was the greatest i.e. Plate 3. Similarly for butyl acetate, the other reactant, the liquid phase concentration below the feed plate increased at a slower rate than in a conventional distillation column, due to the disappearance of the component caused by the reaction and this was reflected by a low feed plate efficiency.

For ethyl acetate, the reaction product, the meaning of the Murphree efficiency is different from that of ethyl alcohol. For a plate to have a high efficiency, the concentration of the ethyl acetate should increase up the column. The natural physical separation of ethyl acetate (the light component) is aided by its formation in the reaction and thus a higher efficiency would be expected in the region of the feed plate. This was observed for two of the experiments. At the feed plate, the concentration of ethyl acetate in the liquid phase started to increase down the column for Run 2. When the situation was translated in terms of Murphree efficiencies, a negative value was obtained for three points since $y_n^* - y_{(n-1)}$ remained positive whilst $y_n - y_{(n-1)}$ became negative. For a stage to have a high butyl alcohol efficiency, the concentration should decrease as quickly as possible but the formation of the butyl alcohol by the reaction effectively contracts this process and thus diminishes the stage efficiency. Again the effect would be most noticeable where the interactions are the largest i.e. at the feed plate region. Lower plate efficiencies were obtained at the feed plate in two of the runs. (Fig.5.13 (a) & (b)).

For the second series of runs the reboiler holdup was increased but the stagewise efficiency patterns were very similar to the patterns obtained for the first four runs (Fig.5.13(a-b)) and it was difficult to detect any effect of the increased holdup in the reboiler on the efficiencies.

For the third series of runs (9 - 12) the boilup rate was increased by approximately 50 per cent. As the boilup rate had been increased, it was anticipated that the least volatile concentration profile would increase up the column tending to diminish the concentration of the most volatile components and thus decrease their effect in the reaction zone. However, the component Murphree plate efficiency patterns for the reactive plates were very similar in shape and magnitude to the previous experiments indicating that the majority of the reaction was still being carried out in the reboiler and on the feed plate. One slight anomaly was observed for Run 10, in that ethyl acetate was found to be present in the liquid phase in the reboiler but none was detected in the vapour leaving the reboiler indicating that an unrepresentative vapour sample had been taken. A further increase in the boilup rate for the fourth series of experiments (Runs 13 - 16) caused a considerable change in the liquid phase concentrations, and also the reaction zone of the column tended to move upwards with the result that the butyl acetate component efficiency did not decrease in the feed plate region. In two of the runs (13, 14) butyl alcohol acted as a pseudo-light component causing the efficiency to decrease within the reaction zone of the column. In one experiment (Run 15) the boilup rate was such that only butyl acetate was present below the feed plate although three of the components were present in the reboiler. At the high boilup rates when the concentration of the most volatile components were very small, it was observed that in Runs 13, 14 that ethyl acetate was detected in the vapour phase but not in the liquid phase for the corresponding plate (Fig.5.13 (e) - (h)).

In Runs 17, 18 the experiments were commenced using only the reactants as the reboiler feedstock and these results tended to duplicate the results observed in Runs 10 & 11. In Runs 19 & 20, a split feed technique was used. It was anticipated that the reaction conversion would be spread over the column rather than being predominantly in the reboiler and the feed plate. This was confirmed from Table 5.10. It was observed that in both runs the rate at which ethyl acetate decreased down the column was much slower than for normal distillation indicating the influence of the reaction on each stage and consequently the Murphree efficiency also reflected this by steadily decreasing from the reboiler for Run 19 and from Plate 4 for Run 20. Similar effects were noted for butyl acetate which increased slowly in concentration down the column whilst butyl alcohol increased rapidly down the column and its efficiency consequently remained high at nearly one hundred per cent (Fig.5.13 (i) - (j)).

The effect of the heat of reaction on the stage efficiencies has not been considered as yet. The heat of reaction was endothermic so considerable heat absorption on the plate could occur (see Table 5.10). The maximum heat absorption was 1517 cal min^{-1} on Plate 4 in Run 9.

It was thought that the heat of reaction could affect the plate efficiencies by impeding the vaporisation of the light components. This would occur when the heat absorption was high and the volatile component concentration was low. Under these conditions a small change in the vaporisation could cause quite a large change in the light component efficiency.

If the results are examined in this context, the vaporisation efficiency of ethyl acetate was very low on the feed plate where the concentration was 2.5 mole per cent. However, the vaporisation efficiencies for the remaining plates were much greater although the concentrations were of the same order.

It was difficult to draw any conclusions about the effect of the heat of reaction on the plate efficiencies due to the low heat absorption on the plates for the remaining experiments. However, the heat absorption was very much greater in the reboiler but any effects would be masked by the electrical heat input and thus the effect of the heat of reaction would have to be examined in further experimental work.

Section 6.

DISTILLATION WITH CHEMICAL REACTION
- THEORETICAL SOLUTION

6. DISTILLATION WITH CHEMICAL REACTION - THEORETICAL SOLUTION.

6.1 Literature Survey

The theoretical approach to distillation with chemical reaction can be divided into two categories (a) graphical technique and (b) a theoretical solution.

Costa & Canepa (129) used a graphical method to calculate the number of theoretical plates required for the separation of a ternary mixture in which a chemical reaction was taking place. The method was based on the plane projection of the enthalpy - concentration diagram and the Authors claimed that it gave a more rigorous solution than the approximation technique which had been previously used. The results from the graphical technique were compared with those from the performance of a ten plate column in which the hydrolysis of acetic anhydride was carried out and the graphical technique was found to be accurate to within 5%.

Marek (135) used a modified McCabe-Thiele construction to predict the number of plates which were required for a ternary mixture. The problem was simplified by assuming that the heat of reaction was zero, the component efficiency was 100% and that constant molal overflow conditions could be applied. Operating lines were constructed on a ternary V.L.E. diagram plotted on rectangular co-ordinates for the system $A + B \longrightarrow C$ and $A + B \longrightarrow 2C$. It was observed that by constructing steps in a similar manner to that of the McCabe-Thiele method, the number of plates could be predicted for a given conversion. The predictions were then tested against data obtained from the hydrolysis of acetic anhydride in a continuous plate distillation column and provided that the column component efficiency was of the order of 50%, a reasonable agreement was obtained.

Geelen & Wijffels (118) used a modified vapour liquid equilibrium diagram to predict the performance of a 20 plate distillation column in which vinyl stearate was being formed from vinyl acetate and stearic acid. By assuming that the system could be represented by the binary vapour liquid equilibrium data for vinyl acetate and acetic acid in which a solid of negligible vapour pressure was dissolved but which elevated the boiling point, and that there was a constant composition on each plate, a construction technique similar to a McCabe-Thiele method was used but no details of the accuracy of the method were given.

The theoretical analysis of a distillation column with a chemical reaction is based on the traditional approach to the analysis of a distillation column, i.e. the solution of a series of enthalpy and material balances. However, the equations also include a term which allows for the occurrence of a chemical reaction.

A set of equations were proposed by Marek (135) for a number of different reaction orders. The overall mass balance for a reaction - plate being:-

$$L_{m+1} + V_{m-1} = L_m + V_m + \Delta r_m Z_m \qquad \text{———} \quad 6.1$$

where the term $\Delta r_m Z_m$ is a function of the plate holdup (Z_m), the plate temperature and the type of the reaction. Δr_m is the term which takes into account the presence of a chemical reaction and it is defined as the rate of change in the number of moles due to the chemical reaction.

The following equations were quoted by Marek (135) for differing reaction orders.

Order	Reaction	Rate	Δr
1	$A \longrightarrow nP$	$\frac{kx_A}{v}$	$(n - 1)r$
2	$2A \longrightarrow nP$	$\frac{kx_A^{\,2}}{v^2}$	$(n - 2)r$
2	$A + B \longrightarrow nP$	$\frac{kx_Ax_B}{v^2}$	$(n - 2)r$
3	$3A \longrightarrow nP$	$\frac{kx_A^{\,3}}{v^3}$	$(n - 3)r$
3	$2A + B \longrightarrow nP$	$\frac{kx_A^{\,2}x_B}{v^3}$	$(n - 3)r$
3	$A + B + C \longrightarrow nP$	$\frac{kx_Ax_Bx_C}{v^3}$	$(n - 3)r$

Mamers (66) applied the above equations to a ternary system ($A + B \longrightarrow 2C$) and obtained the generalised stage mass and enthalpy balances:-

$$L_{(m+1)}\,x_{(m+1)A} + V_{(m-1)}\,y_{(m-1)A} = L_m x_{mA} + V_m y_{mA} + k_m \frac{x_{mA}\,x_{mB}}{v_m^{\,2}} Z_m \qquad 6.2$$

$$L_{(m+1)}\,h_{(m+1)} + V_{(m-1)}\,H_{(m-1)} = L_m h_m + V_m H_m + Q_R + \text{Losses} \qquad 6.3$$

Hence by using equations 6.2 & 6.3 and the overall plate balance, starting from the reboiler in one example and the condenser in a second example, the series of simultaneous equations were solved providing that the following assumptions were made:- (1) the system was at steady state (2) the column was operating under adiabatic conditions (3) there was complete mixing of the liquid on the plates and in the reboiler (4) the reboiler was equivalent to a perfect plate (5) no reaction occurred in the vapour phase or in the condenser (6) the heat of mixing was assumed to be negligible (7) the output streams left at their boiling points.

A calculation commencing from the reboiler, was made knowing the feed conditions, the bottom product conditions, the reboiler heat load, the component vaporisation efficiencies, the kinetic and the vapour liquid equilibrium data. The simultaneous equations were solved for each plate with the plate molar balance summating to 100% although the mass balance tended to be slightly in error. It was observed that the summation of the individual stage conversions always equalled the overall column conversion. It was concluded that good agreement was attained and the largest discrepancy between the predicted and measured values was not greater than 2.5% for any component.

A second calculation commencing from the top of the column was made. The material balances were accurate to 0.4% but the summation of the stage conversions was in error by about 5% compared with the experimental results. The same calculation was repeated twice - once with the plate holdups halved and once with the plate holdups doubled. In the former case, the summation of the stage conversions was in error by about 7% whilst in the latter case the error was less than 1%.

Thus the stagewise mathematical analysis closely duplicated the observed experimental conditions and if the stage holdup was increased, the conversion and the prediction accuracy also increased accordingly.

Leyes & Othmer (130) used a theoretical kinetic and vapour liquid equilibrium method to predict the number of plates required for the continuous esterification of butyl alcohol by acetic acid. For a 11
four plate column they predicted that six plates were required.

Belck (136) has studied hypothetical 2 and 3 component liquid phase reversible reactions which were carried out continuously in a distillation column. He assumed that (1) the reaction occurred in 2
the liquid phase only (2) the catalyst had a negligible vapour pressure (3) the heat of reaction; temperature effects on density, enthalpy and heat of reaction were all neglected (4) ideal liquid properties (5) adiabatic conditions (6) 100% plate efficiency.

Belck (136) has considered two examples of a two component reversible reaction. The first case was with a low boiling point product where the majority of the reaction took place in the reboiler whereas in the second example a high boiling point product was formed and the majority of the reaction occurred in the column which was operating under total reflux conditions. In the latter example, the catalyst was removed below the equilibrium plate or else the reverse reaction would have dominated. For a hypothetical $2A \rightleftharpoons B$ reaction, a design procedure was calculated for a 7 plate (plate holdup 1 litre) column of which 4 plates were reaction plates where the boiling points for A and B were 60 ^{o}C and 165 ^{o}C respectively. The throughput of B was 0.5 mole min^{-1}. The catalyst was removed between the third and fourth plate and the final calculated purity was 99%.

Belck (136) used a similar approach for a hypothetical
$2C \rightleftharpoons A + B$ reaction where the order of the boiling points was
$B > C > A$. The reaction occurred in a 7 plate column (1.6 litre
plate holdup) where the catalyst was fed in on the top plate and
removed from the bottom plate. A plate to plate calculation 11
commencing from the reboiler was carried out using vapour liquid
equilibrium data for the benzene toluene xylene system.

For the above reactions, the kinetics for the 2 and 3 component
reactions were represented by:- 12

$$2A \rightleftharpoons B$$

$$r_m = k_{m1} \frac{x_{mA}^2}{v_m^2} - k_{m2} \frac{x_{mB}}{v_m} \qquad \text{———} \; 6.4$$

13

$$2C \rightleftharpoons A + B$$

$$r_m = k_{m1} \frac{x_{mC}^2}{v_m^2} - k_{m2} \frac{x_{mA} x_{mB}}{v_m^2} \qquad \text{———} \; 6.5$$

Hence it would appear that only one example emerges from the 4
literature where the experimental results have been calculated by
a mathematical model and in this case the correlation was applied
to a column in which an irreversible reaction was continuously being
carried out. Otherwise the approaches have been either extremely 5
theoretical or the equations have been applied in non-ideal
conditions where high heat losses and poor liquid mixing have
occurred. These conditions were largely avoided in this work and
consequently it was hoped that it would be possible to apply a
stagewise calculation method which would predict the behaviour of a

distillation column in which a reversible reaction was being carried out.

6.2 The Column Equations

The column equations are now considered specifically for the reversible transesterification reaction between butyl acetate and ethyl alcohol. In the following treatment the subscripts A, H, I, J, K will stand for ACID, ETAC, ETOH, BUAC, BUOH respectively.

Overall molar balances

The reaction produces no change in molarity so that

$$C_2H_5OH + CH_3COOC_4H_9 \rightleftharpoons C_4H_9OH + CH_3COOC_2H_5$$

the overall balance may be written as:-

$$F = B + D \tag{6.6}$$

Overall component molar balances

a) Ethyl acetate (H)

The rate of formation of ethyl acetate within the column

$$= Dx_{HD} + Bx_{BH} - Fx_{HF} \tag{6.7}$$

b) Ethyl alcohol (I)

The rate of conversion of ethyl alcohol within the column

$$= Fx_{IF} - (Dx_{ID} + Bx_{IB}) \tag{6.8}$$

Overall enthalpy balance

$$Fh_F + Q_E = Dh_D + Bh_B + Q_D + Q_R\left[Dx_{HD} + Bs_{HB} - Fx_{HF}\right] \tag{6.9}$$

Stage molar balance

$$V_{(m+1)} + L_{(m-1)} = V_m + L_m \tag{6.10}$$

Stage component balance

a) Ethyl acetate (H)

$$\begin{aligned} &V_{(m+1)}\, y_{H(m+1)} + L_{(m-1)}\, x_{H(m-1)} = V_m y_{Hm} + L_m x_{Hm} \\ &-\frac{k_{1m}\, Z_m}{v_m^2} \left[\left(x_{Im}\, x_{Jm} - \frac{1}{K}\, x_{Hm}\, x_{Km}\right)\right] \end{aligned} \qquad 6.11$$

b) Ethyl alcohol (I)

$$\begin{aligned} &V_{(m+1)}\, y_{I(m+1)} + L_{(m-1)}\, x_{I(m-1)} = V_m y_{Im} + L_m x_{Im} \\ &+\frac{k_{1m}\, Z_m}{v_m^2} \left[\left(x_{Im}\, x_{Jm} - \frac{1}{K}\, x_{Hm}\, x_{Km}\right)\right] \end{aligned} \qquad 6.12$$

c) Butyl acetate (J)

$$\begin{aligned} &V_{(m+1)}\, y_{J(m+1)} + L_{(m-1)}\, x_{J(m-1)} = V_m y_{Jm} + L_m x_{Jm} \\ &+\frac{k_{1m}\, Z_m}{v_m^2} \left[\left(x_{Im}\, x_{Jm} - \frac{1}{K}\, x_{Hm}\, x_{Km}\right)\right] \end{aligned} \qquad 6.13$$

d) Butyl alcohol (K)

$$\begin{aligned} &V_{(m-1)}\, y_{K(m-1)} + L_{(m-1)}\, x_{K(m-1)} = V_m y_{Km} + L_m x_{Km} \\ &-\frac{k_{1m}\, Z_m}{v_m^2} \left[\left(x_{Im}\, x_{Jm} - \frac{1}{K}\, x_{Hm}\, x_{Km}\right)\right] \end{aligned} \qquad 6.14$$

e) Sulphuric acid (A)

$$L_m\, x_{Am} = L_{(m-1)}\, x_{A(m-1)} \qquad 6.15$$

Stage enthalpy balance

$$\begin{aligned} &V_{(m+1)}\, H_{(m+1)} + L_{(m-1)}\, h_{(m-1)} = V_m\, H_m + L_m\, h_m \\ &+\frac{k_{m1}\, Z_m}{v_m^2} \left[\left(x_{Im}\, x_{Jm} - \frac{1}{K}\, x_{Hm}\, x_{Km}\right)\right] Q_R \end{aligned} \qquad 6.16$$

When stage (m) is equal to the feed plate, an additional input term occurs on the left hand side of stage equations.

6.3 Specification of the boundary conditions

The object of the mathematical model is to predict the flowrates and compositions from a distillation column given the following parameters:-

1) A column containing a known number of plates with a reboiler and a total condenser.

2) The column characteristics including the plate holdups and efficiencies.

3) A feed of known rate, composition and temperature entering at a given position.

4) The reflux ratio and/or the reboiler heat input.

5) The physical properties of the components involved (including the kinetic and vapour-liquid equilibrium data).

In order to simplify the model, a number of assumptions have been made:-

1) The system has attained steady state.
2) The system is adiabatic.
3) There is complete mixing in the plates and in the reboiler.
4) The reboiler acts as a perfect plate.
5) There is no vapour phase reaction.
6) The heats of mixing are negligible.
7) The output streams leave at the boiling point.

6.4 Calculation 1

The first problem to be considered will be the calculation of the stream compositions and stage conversions given a column which is operating under total reflux with the following conditions:-

1) Number of plates in the column = 6.
2) Feed plate = 4th plate from the top.
3) Plate holdup = 180 ml.
4) Reboiler holdup = 6.5 litres.
5) Component vaporisation efficiencies (E_V)
    - ETAC = 110%
    - ETOH = 94%
    - BUAC = 120%
6) Reboiler efficiency = 100% for each component.
7) Reboiler heat input (Q_E) = 19430 cal min^{-1}.
8) Feed rate = 50.82 g min^{-1}
    - consisting of ETOH = 0.3170 g mole min^{-1}
    - BUAC = 0.3070 g mole min^{-1}
    - ACID = 0.0053 g mole min^{-1}
9) Feed temperature = 85 ^{o}C
10) Bottom rate = 50.82 g min^{-1}
    - whose composition x_H = 0.234
    - x_I = 0.262
    - x_J = 0.255
    - x_K = 0.241
    - x_A = 0.008
11) Colum pressure = 760 mm Hg.
12) The components' physical properties are given in sections 3, 4 & 5.

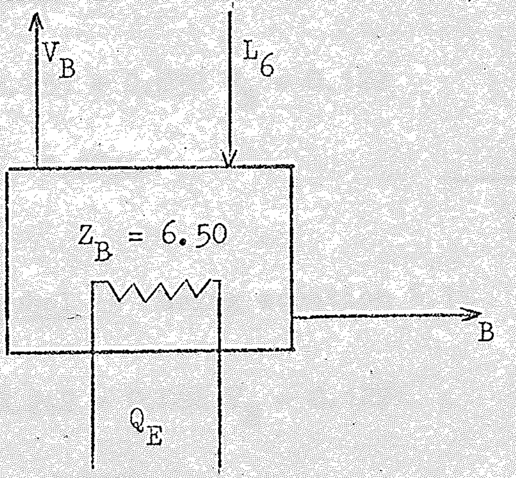
The vaporisation efficiencies rather than the Murphree efficiencies were used to calculate the equilibrium vapour compositions as they were less dependent on the effects of a reaction and they were easier to calculate. Three component efficiencies were utilised, the vapour phase concentration of the fourth (butyl alcohol) was obtained by difference.

The column characteristics which were selected, such as the plate efficiencies, stage holdups and flowrates were based upon Run 12 of the continuous distillation experiments (Section 5).

6.4.1 Stagewise Calculations

The stagewise calculations commenced from the reboiler whose temperature was 91.2 °C and the liquid phase composition was

$x_H = 0.234$, $x_I = 0.262$, $x_J = 0.255$, $x_K = 0.241$, $x_A = 0.008$.



$T_B = 91.2$ °C

The catalyst concentration in stream B = 1.0 weight per cent.

From Section 3, k_1 = 0.02409 litre $\text{mole}^{-1}\text{min}^{-1}$

From Section 4, predicted equilibrium vapour compositions

$$y_{HB} = 0.350 \qquad y_{IB} = 0.473$$

$$y_{JB} = 0.092 \qquad y_{KB} = 0.086$$

These being the vapour composition leaving the reboiler as the reboiler efficiency was assumed to be 100%.

Writing the component balances

a) <u>Ethyl acetate</u> - using equation 6.11

$$L_6\ x_{H6} = Bx_B + V_B\ y_{HB} - \frac{k_B Z_B}{v_B^2}\left[\left(x_{IB}\ x_{JB} - \frac{1}{K}\ x_{HB} x_{KB}\right)\right]$$

$$= 0.633 \times 0.234 + 0.35\ V_B - \frac{0.02409 \times 6.5}{(0.102)^2}\ 0.262 \times 0.255 - \frac{0.241 \times 0.234}{0.96}$$

$$L_6\ x_{H6} = 0.35\ V_B + 0.0261 \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_}\ 6.17$$

b) <u>Ethyl alcohol</u> - using equation 6.12

$$L_6\ x_{I6} = 0.633 \times 0.262 + 0.473\ V_B + 0.122$$

$$L_6\ x_{I6} = 0.473\ V_B + 0.2872 \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_}\ 6.18$$

c) <u>Butyl acetate</u> - using equation 6.13

$$L_6\ x_{J6} = 0.633 \times 0.255 + 0.092\ V_B + 0.122$$

$$L_6\ x_{J6} = 0.092\ V_B + 0.2834 \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_}\ 6.19$$

d) <u>Butyl alcohol</u> - using equation 6.14

$$L_6\ x_{K6} = 0.633 \times 0.242 + 0.086\ V_B - 0.122$$

$$L_6\ x_{K6} = 0.086\ V_B + 0.0312 \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_}\ 6.20$$

e) <u>Acid</u> - using equation 6.15

$$L_6\ x_{A6} = 0.0053 \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_}\ 6.21$$

Enthalpies

The datum was 0 °C

$$h_B = T_B \left(40.27 \text{ x } x_{HB} + 31.33\ x_{IB} + 71.67\ x_{JB} + 50.92\ x_{KB} + 32.85\ x_{AB}\right)$$

$$= 91.2\ (9.42 + 8.21 + 18.28 + 12.27 + 0.33)$$

$$\underline{h_B = 4424 \text{ cal g mole}^{-1}}$$

$$H_B = T_B\ \ 40.27\ y_{HB} + 31.33\ y_{IB} + 71.67\ y_{JB} + 50.92\ y_{KB}$$

$$+ 8988\ y_{HB} + 9410\ y_{IB} + 8575\ y_{JB} + 10470\ y_{KB}$$

$$= 91.2\ (14.09 + 14.82 + 6.59 + 4.38) + 3146 + 4451 + 789 + 900$$

$$\underline{H_B = 12923 \text{ cal g mole}^{-1}}$$

The heat absorbed due to the reaction

$$Q_R = 22950 \text{ x } 0.122 = \underline{2800 \text{ cal g mole}^{-1}}$$

Plate 6 was assumed to be at 82.9 °C.

Enthalpy balance

$$Q_E + L_6\ h_6 = H_B\ V_B + Bh_B + Q_R$$

$$19430 + 83.9\ L_6\left(40.27\ x_{H6} + 31.33\ x_{I6} + 71.67\ x_{J6} + 50.92 x_{K6} + 32.85\ x_{A6}\right)$$

$$= 12923\ V_B + 0.633 \text{ x } 4424 + 2800 \qquad \text{———} \quad 6.22$$

Substituting equations 6.17, 6.18, 6.19, 6.20 & 6.21 into 6.22

$$19430 + 1182\ V_B + 88 + 1244\ V_B + 755 + 553\ V_B + 1704 + 367\ V_B + 133$$

$$+ 12923\ V_B + 2800 + 2800$$

$$\text{hence } V_B = \frac{16525}{9577} = 1.725$$

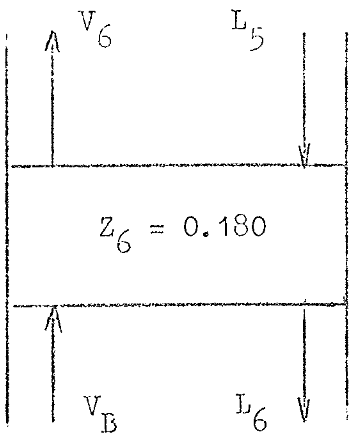
$$\text{and} \quad L_6 = V_B + B = \underline{2.358}$$

substituting back into the component equations 6.17 - 6.21

$x_{H6} = 0.267$; $x_{I6} = 0.468$; $x_{J6} = 0.187$; $x_{K6} = 0.076$; $x_{A6} = 0.0022$

Having calculated the liquid phase composition and flowrate leaving plate 6, the method is applied to the next stage.

Plate 6



Liquid phase composition

$x_{H6} = 0.267$

$x_{I6} = 0.468$

$x_{J6} = 0.187$

$x_{K6} = 0.076$

$x_{A6} = 0.002(2)$

$T_6 = 110\ ^{\circ}C$; $E_{VH} = 110\%$; $E_{VI} = 94\%$; $E_{VJ} = 120\%$

The equilibrium vapour compositions predicted from the liquid phase composition $y^*_{H6} = 0.329$; $y^*_{I6} = 0.605$; $y^*_{J6} = 0.048$; $y^*_{K6} = 0.017$

Hence $y_{H6} = 0.362$; $y_{I6} = 0.569$; $y_{J6} = 0.058$; $y_{K6} = 0.011$.

In order to calculate the stage conversion, it is necessary to determine the catalyst weight concentration in the liquid phase.

Catalyst concentration = 0.30 weight per cent.

However, it was realised that most of the stage catalyst concentrations would fall within the range of 0.1 - 1.0 weight per cent which was used in the determination of the rate constant values. It was observed that as the catalyst concentration increased so the rate constant increased and if the catalyst concentration was changed by a factor of 10 (i.e. 0.1 → 1.0) the rate constant increased approximately the same factor (see Section 3, Tables 3.1 - 3.8). Hence in the determination of the rate constant, the value for the rate constant was calculated from the equation applicable to a 0.1% catalyst concentration (equation 3.24) which in turn was multiplied by a factor equal to ten times the catalyst concentration.

$$\log k_1 = 4.9939 - \frac{2773}{T} \qquad \text{\_\_\_\_\_\_\_\_\_\_} \ 3.24$$

@ 0.1% $k_1 = 0.001685$

@ 0.3% $k_1 = 0.001685 \times 3.0 = \underline{0.00506}$ litre $\text{mole}^{-1}\,\text{min}^{-1}$

Ethyl acetate balance

$$L_5\,x_{H5} = 0.362\,V_6 + 0.0261 - \frac{0.00506 \times 0.180}{(0.0929)^2}\left[\left(0.468 \times 0.187 - \frac{0.267 \times 0.076}{0.96}\right)\right]$$

$$= 0.362\,V_6 + 0.0261 - 0.00701$$

$$L_5\,x_{H5} = 0.362\,V_6 + 0.0191 \qquad \text{\_\_\_\_\_\_\_\_\_\_} \ 6.23$$

Ethyl alcohol balance

$$L_5\,x_{I5} = 0.569\,V_6 + 0.00701 + 0.2872$$

$$L_5\,x_{I5} = 0.569\,V_6 + 0.2942 \qquad \text{\_\_\_\_\_\_\_\_\_\_} \ 6.24$$

Butyl acetate balance

$$L_5\,x_{J5} = 0.058\,V_6 + 0.00701 + 0.02834$$

$$L_5\,x_{J5} = 0.058\,V_6 + 0.2904 \qquad \text{\_\_\_\_\_\_\_\_\_\_} \ 6.25$$

Butyl alcohol balance

$$L_5\,x_{K5} = 0.011\,V_6 + 0.011\,V_6 + 0.0311 - 0.00701$$

$$L_5\,x_{K5} = 0.011\,V_6 + 0.0242 \qquad \text{\_\_\_\_\_\_\_\_\_\_} \ 6.26$$

Acid balance

$$L_5\,x_{A5} = 0.0053 \qquad \text{\_\_\_\_\_\_\_\_\_\_} \ 6.27$$

Enthalpies

$h_6 = 3587$ cal g mole^{-1}. $\qquad$ $H_6 = 12335$ cal g mole^{-1}

$Q_R = 22950 \times 0.00701 = 161$ cal g mole^{-1}

Enthalpy balance

Plate 5 assumed to be at 81.8 °C

$$1.725 \times 12923+81.8\left(40.27\, x_{H5}+31.33\, x_{I5}+71.67\, x_{J5}+50.92\, x_{K5}+32.85\, x_{A5}\right)$$

$$= 12335\, V_6 + 3587 \times 2.358 + 161 \qquad 6.28$$

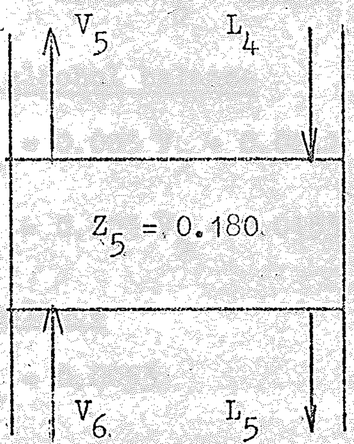
substituting equations 6.23 - 6.27 into 6.28

$$9299\, V_6 = 16307$$

$$\therefore\ V_6 = \underline{1.754} \quad \& \quad L_5 = \underline{2.387}$$

substituting these values back into equations 6.23 - 6.27.

Plate 5



Liquid phase composition

x_{H5} = 0.274
x_{I5} = 0.541
x_{J5} = 0.164
x_{K5} = 0.018
x_{A5} = 0.002(2)

T_5 = 81.8 °C; E_{VH} = 110%; E_{VI} = 94%; E_{VJ} = 120%

y^*_{H5} = 0.302; y^*_{I5} = 0.652; y^*_{J5} = 0.164; y^*_{K5} = 0.004.

y_{H5} = 0.332; y_{I5} = 0.613; y_{J5} = 0.052; y_{K5} = 0.003.

Catalyst concentration = 0.31 weight per cent

k_1 = 0.001515 x 3.1 = $\underline{0.0047}$ litre mole^{-1}min^{-1}

$$\text{Conversion} = \frac{0.0047 \times 0.18}{(0.0891)^2}\left[0.541 \times 0.164 - \frac{0.274 \times .018}{.96}\right]$$

$$= 0.00891 \text{ g mole min}^{-1}$$

Ethyl acetate balance

$L_4\ x_{H4} = 0.332\ V_5 - .00891 + 0.0191$

$= 0.332\ V_5 + 0.0102$ ——— 6.29

Ethyl alcohol balance

$L_4\ x_{I4} = 0.613\ V_5 + 0.00891 + 0.2942$

$= 0.613\ V_5 + 0.3031$ ——— 6.30

Butyl acetate balance

$L_4\ x_{J4} = 0.052\ V_5 + 0.2904 + 0.00891$

$= 0.052\ V_5 + 0.2993$ ——— 6.31

Butyl alcohol balance

$L_4\ x_{K4} = 0.003\ V_5 + 0.0242 - 0.00891$

$= 0.003\ V_5 + 0.0153$ ——— 6.32

Acid balance

$L_4\ x_{A4} = 0.0053$ ——— 6.33

Enthalpies

$h_5 = 3331$; $H_5 = 12211$; $Q_R = 204$ cal g mole^{-1}

Enthalpy balance

Plate 4 assumed to be at 81.2 °C

$1.754 \times 12335 + 81.2\left(L_4\ 40.27\ x_{H4} + 31.33\ x_{I4} + 71.67\ x_{J4} + 50.92\ x_{K4} + 32.85\ x_{A4}\right)$

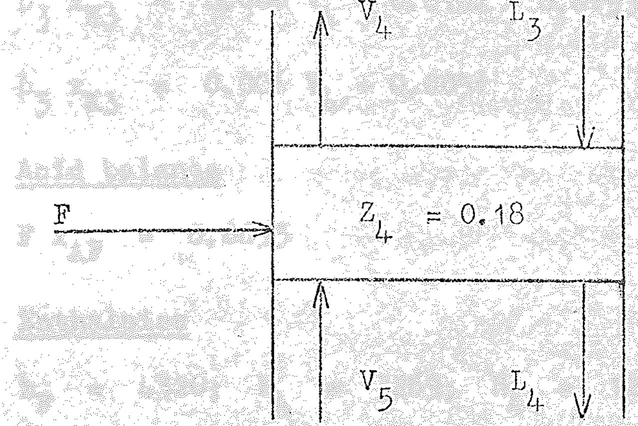
$= 12211\ V_5 + 3331 \times 2.387 + 204$ ——— 6.34

substituting equations 6.29 - 6.33 into 6.34

$9251\ V_5 = 16105$

$V_5 = \underline{1.741}$ & $L_4 = \underline{2.374}$

Plate 4 (Feed Plate)



Liquid phase composition

$x_{H4} = 0.248$

$x_{I4} = 0.577$

$x_{J4} = 0.164$

$x_{K4} = 0.008(6)$

$x_{A4} = 0.002(2)$

$y^*_{H4} = 0.284; \quad y^*_{I4} = 0.672; \quad y^*_{J4} = 0.042; \quad y^*_{K4} = 0.003$

$y_{H4} = 0.312; \quad y_{I4} = 0.632; \quad y_{J4} = 0.050; \quad y_{K4} = 0.006$

Catalyst concentration = 0.32 weight per cent.

$k_1 = 0.00146 \times 3.2 = \underline{0.004701}$

$$\text{Conversion} = \frac{0.004701 \times 0.18}{(0.08758)^2}\left[\left(0.577 \times 0.164 - \frac{0.248 \times 0.0086}{0.96}\right)\right]$$

$$= \underline{0.0102 \text{ g mole min}^{-1}}$$

Ethyl acetate balance

$L_3\, x_{H3} = 0.312\, V_4 + 0.0102 - 0.0102$

$= 0.312\, V_4$ ——— 6.35

Ethyl alcohol balance

$0.317 + L_3\, x_{H3} = 0.632\, V_4 + 0.0102 + 0.3031$

$L_3\, x_{I3} = 0.632\, V_4 - 0.0037$ ——— 6.36

Butyl acetate balance

$0.307 + L_3\, x_{J3} = 0.05\, V_4 + 0.0102 + 0.2993$

$L_3\, x_{J3} = 0.05\, V_4 + 0.0025$ ——— 6.37

Butyl alcohol balance

$$L_3\, x_{K3} = 0.006\, V_4 - 0.0102 + 0.0153$$

$$L_3\, x_{K3} = 0.006\, V_4 + 0.0051 \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_} \quad 6.38$$

Acid balance

$$F\, x_{AF} = 0.0053$$

Enthalpies

$$h_F = 4320; \quad h_4 = 3269; \quad H_4 = 12187; \quad Q_R = 234 \text{ cal g mole}^{-1}$$

Enthalpy balance

Plate 3 assumed at 77.9 °C

$$4320 \times 0.633 + 1.741 \times 12211 + L_3 \times 77.9 \left(40.27x_{H3} + 31.33x_{I3} + 71.67x_{J3} + 50.92x_{K3}\right)$$

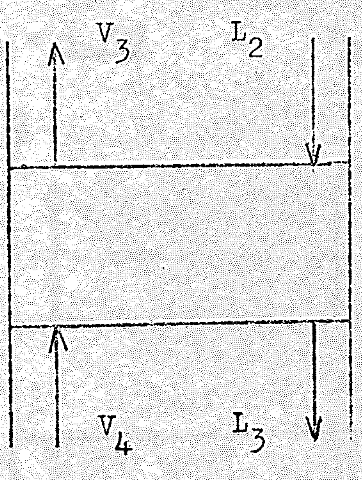
$$= 12187\, V_4 + 2.374 \times 3269 + 234 \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_} \quad 6.39$$

substituting equations 6.35 - 6.38 into 6.39

$$9362\, V_4 = 16009$$

V_4 = <u>1.710</u> & L_3 = <u>1.714</u>

Plate 3



Liquid phase composition

$x_{H3} = 0.311$

$x_{I3} = 0.628$

$x_{J3} = 0.051$

$x_{K3} = 0.009$

$y^*_{H3} = 0.359;\quad y^*_{I3} = 0.629;\quad y^*_{J3} = 0.011;\quad y^*_{K3} = 0.001.$

$y_{H3} = 0.396;\quad y_{I3} = 0.591;\quad y_{J3} = 0.013;\quad y_{K3} = 0.000.$

As there was no catalyst present on Plates 3 - 1, it was assumed that no reaction would occur and that the solution of the problem would only involve the traditional mass and enthalpy balances.

Component balances

$$L_2\, x_{H2} = 0.396\, V_3 \qquad 6.40$$

$$L_2\, x_{I2} = 0.591\, V_3 - 0.0037 \qquad 6.41$$

$$L_2\, x_{J2} = 0.013\, V_3 + 0.0025 \qquad 6.42$$

Enthalpies

$L_3 = 2829 \qquad H_3 = 11989$ cal g mole^{-1}

Enthalpy balance

Plate 2 assumed to be at 77.4 °C.

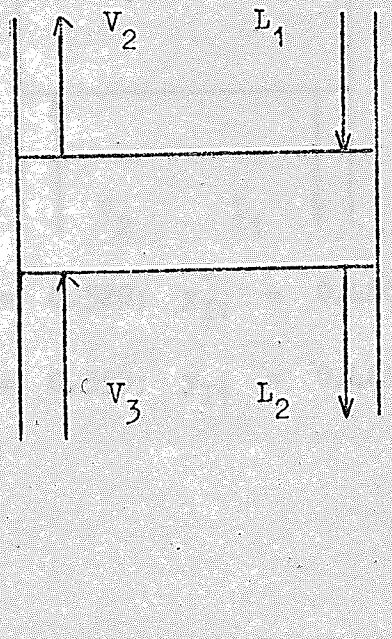
$$1.71 \times 12187 + 77.4\, L_2 \left(40.27\, x_{H2} + 31.33\, x_{I2} + 71.67\, x_{J2}\right)$$

$$= 11989\, V_3 + 1.714 \times 2829 \qquad 6.43$$

substituting equations 6.40 - 6.42 into equation 6.43

$V_3 = \underline{1.729}$ & $L_2 = \underline{1.733}$

Plate 2



Liquid phase composition

$x_{H2} = 0.396$

$x_{I2} = 0.590$

$x_{J2} = 0.014$

$y^*_{H2} = 0.432$; $y^*_{I2} = 0.530$; $y^*_{J2} = 0.005$.

$y_{H2} = 0.470$; $y_{I2} = 0.525$; $y_{J2} = 0.005$.

Component balances

$$L_1 x_{H1} = 0.470\, V_2 \qquad 6.44$$

$$L_1 x_{I1} = 0.525\, V_2 - 0.0037 \qquad 6.45$$

$$L_1 x_{J1} = 0.005\, V_2 + 0.0025 \qquad 6.46$$

Enthalpies

$h_2 = 2742$ and $H_2 = 11972$

Enthalpy balance

Plate 1 assumed to be at 72.5 °C.

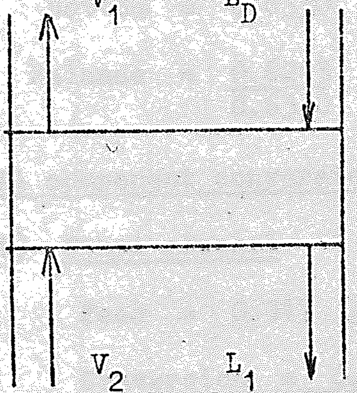
$$1.729 \times 11989 + 72.5\, L_1 \left(40.27\, x_{H1} + 31.33\, x_{I1} + 71.67_{J1}\right)$$

$$= 11972\, V_2 + 1.733 \times 2742 \qquad 6.47$$

substituting equations 6.44 - 6.46 into equation 6.47

$V_2 = \underline{1.711}$ & $L_1 = \underline{1.715}$

Plate 1



Liquid phase composition

$x_{H1} = 0.470$

$x_{I1} = 0.524$

$x_{J1} = 0.006$

$y^*_{H1} = 0.520$; $y^*_{I1} = 0.480$

$y_{H1} = 0.559$; $y_{I1} = 0.441$

Thus the composition of V_1 will also equal the composition of the reflux stream L_D.

Enthalpies

$h_D = 2634; \quad H_1 = 11808 \quad \text{cal g mole}^{-1}$.

As the column is operating under total reflux conditions, the streams V_1 and L_D will be equal and hencean enthalpy balance across Plate 1 will compute their values.

Enthalpy balance

$$1.711 \times 11972 + 2634\,L_D = 11808\,V_1 + 1.715 \times 2594$$

$$V_1 = L_D = \underline{1.748 \text{ g mole min}^{-1}}$$

The heat abstracted by the condenser = $H_1 - h_D = \underline{9174 \text{ cal min}^{-1}}$

Overall mass balance

Feed = 50.82 g min^{-1}

Bottom = 50.82 g min^{-1}

This balance is equal due to the formulation of the boundary conditions for a column operating under total reflux.

Feed = $0.6293 \text{ g mole min}^{-1}$

Bottom = $0.6330 \text{ g mole min}^{-1}$

$$\text{Balance} = \frac{0.6293}{0.6330} \times 100 = \underline{99.4\%}$$

Overall component conversions

1) Ethyl alcohol

Feed = $0.317 \text{ g mole min}^{-1}$; Bottom = $0.166 \text{ g mole min}^{-1}$

Conversion = $0.151 \text{ g mole min}^{-1}$

2) Butyl acetate

Feed = $0.307 \text{ g mole min}^{-1}$; Bottom = $0.161 \text{ g mole min}^{-1}$

Conversion = $0.146 \text{ g mole min}^{-1}$

Table 6.1 Summary of column conditions, Calculation 1.

Stage	Conversion	x				y				T
		ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	°C
T	—	—	—	—	—	—	—	—	—	—
1	—	0.470	0.524	0.006	—	0.559	0.441	—	—	72.5
2	—	0.396	0.590	0.014	—	0.470	0.525	0.005	—	77.4
3	—	0.311	0.628	0.051	0.009	0.396	0.591	0.013	—	77.9
4	0.0102	0.248	0.577	0.164	0.009	0.312	0.632	0.050	0.006	81.2
5	0.0089	0.274	0.541	0.164	0.018	0.302	0.652	0.043	0.004	81.8
6	0.0070	0.267	0.468	0.187	0.076	0.362	0.569	0.058	0.011	83.9
B	0.1220	0.234	0.262	0.255	0.241	0.350	0.473	0.092	0.086	91.2
$\sum =$	0.1481									

Table 6.2 Measured compositions, Run 12.

Stage	x				y				T °C
	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	
T	—	—	—	—	—	—	—	—	—
1	0.487	0.513	—	—	0.527	0.474	—	—	72.5
2	0.423	0.564	0.013	—	0.466	0.527	0.007	—	77.4
3	0.337	0.617	0.046	—	0.374	0.600	0.026	—	77.9
4	0.264	0.541	0.173	0.019	0.270	0.554	0.095	0.081	81.2
5	0.247	0.565	0.175	0.011	0.256	0.598	0.098	0.048	81.3
6	0.277	0.471	0.195	0.054	0.270	0.430	0.100	0.200	83.4
B	0.236	0.262	0.255	0.242	0.371	0.473	0.087	0.070	91.2

Due to the formulation of the problem a perfect mass balance occurred whilst the molar balance was 99.4%. The prediction of the conversion of the components within the column was accurate to 2.0% where the total predicted conversion was 0.148 g mole min^{-1}.

As a guide to the calculations, some difficulty was experienced in the selection of the vaporisation efficiency due to the scatter of the values obtained in the experimental runs for some of the components. It was found that if a low vaporisation efficiency was selected for butyl acetate, the liquid phase concentrations decreased more rapidly up the column than was measured and also the conversion on each stage decreased. Because of this the vapour phase compositions tended to show a larger degree of variation between the calculated and measured values. However, the liquid phase compositions which were calculated from the model, were in good agreement with the measured values, the worst discrepancy being 3.7 mole per cent whilst the majority of the compositions were well within 2.0 mole per cent.

Having applied the technique successfully to a column operating under total reflux conditions, the next stage was to apply the method to a column operating continuously in which both top and bottom products were being removed. This is done in Calculation 2.

6.5 Calculation 2

Operating conditions

1) Number of plates in the column = 6
2) Feed plate = 4th plate from the top
3) Plate holdup = 180 ml
4) Reboiler holdup = 4.5 litre

5) Component efficiencies (E_V)

ETAC = 116%

ETOH = 96%

BUAC = 115%

6) Reboiler efficiency 100, 125, 100, difference.

7) Reboiler heat input (Q_E) = 16050 cal min^{-1}

8) Feed rate = 49.02 g min^{-1}

consisting of ETOH = 0.3020 g mole min^{-1}

BUAC = 0.2980 g mole min^{-1}

ACID = 0.0053 g mole min^{-1}

9) Feed temperature 85 °C

10) Bottom rate = 40.94 g min^{-1}

whose composition was x_H = 0.111

x_I = 0.116

x_J = 0.399

x_K = 0.363

x_A = 0.001

11) Column press = 760 mm Hg.

12) The components' physical properties are given in Sections 3, 4 & 5.

A similar stage to stage analysis was applied and the results are summarised in Tables 6.3 & 6.4.

Table 6.3 Summary of column conditions, Calculation 2.

Stage	Conversion	x				y				g mole min^{-1}		T
		ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	L	V	°C
T	—	0.459	0.538	0.003	—	—	—	—	—	0.148	—	74.8
1	—	0.326	0.663	0.011	—	0.459	0.538	0.003	—	1.219	1.374	75.3
2	—	0.253	0.719	0.028	—	0.329	0.663	0.008	—	1.228	1.367	76.4
3	—	0.199	0.688	0.073	0.041	0.266	0.712	0.022	—	1.232	1.376	77.5
4	0.0157	0.170	0.586	0.207	0.034	0.227	0.708	0.063	0.002	1.916	1.380	82.0
5	0.0148	0.191	0.516	0.234	0.056	0.259	0.663	0.076	0.002	1.903	1.459	83.9
6	0.0110	0.172	0.360	0.307	0.158	0.278	0.581	0.121	0.020	1.870	1.446	89.0
B	0.0771	0.111	0.116	0.399	0.363	0.246	0.385	2.223	0.146	0.457	1.412	103.0

Weight balance

Bottom stream output = 40.94 g min^{-1}

Top stream output = $(0.459 \times 88.11 + 0.538 \times 46.07 + 0.007 \times 116.16) \times 0.148$

= 9.71 g min^{-1}

Total output = 9.71 + 40.94 = 50.65 g min^{-1}

Feed = 49.02 g min^{-1}

% mass balance = $\frac{50.65}{49.02} \times 100$ = 103.3%

Reflux ratio

$$L_D = V_1 - D$$

$$= 1.374 - 0.148 = 1.226 \text{ g mole min}^{-1}$$

$$R = \frac{L_D}{D} = \frac{1.226}{0.148}$$

$$\underline{R = 8.28 : 1}$$

Overall component conversion

In order to calculate the overall component conversion, it is necessary to take a material balance over the reacting section in the column only - i.e. between Plate 4 and the reboiler.

The overall component balance for the n^{th} component is:-

$$Fx_{nF} + L_3 x_{n3} = Bx_{nB} + V_4 y_{n4} \pm S$$

where S = component conversion.

From Table 6.3 $V_4 = 1.380$ & $L_3 = 1.232$ mole min^{-1}.

1) Ethyl acetate

$$1.232 \times 0.199 = 0.0507 + 1.380 \times 0.227 - S$$

$$0.245 = 0.0507 + 0.313 - S$$

$$\underline{S = 0.1187 \text{ mole min}^{-1}}$$

2) Ethyl alcohol

$$0.302 + 1.232 \times 0.688 = 0.053 + 1.380 \times 0.708 + S$$

$$0.302 + 0.848 = 0.053 + 0.978 + S$$

$$\underline{S = 0.1190 \text{ mole min}^{-1}}$$

3) Butyl acetate

$$0.298 + 1.232 \times 0.073 = 0.1823 + 1.380 \times 0.063 + S$$

$$\underline{S = 0.1187 \text{ mole min}^{-1}}$$

4) Butyl alcohol

$$1.232 \times 0.041 = 0.1659 + 1.380 \times 0.002 - S$$

$$\underline{S = 0.1182 \text{ mole min}^{-1}}$$

5) Stagewise conversion

$$\Sigma S = 0.0771+0.0110+0.0148+0.0157$$

$$= \underline{0.1186 \text{ g mole min}^{-1}}$$

The conditions for Calculation 2 were based upon a practical determination - Run 3. The measured concentration profile is given in Table 6.5.

In the examination of the results obtained from Calculation 2, a slightly positive mass balance was obtained. This could be partially attributed due to an insufficient quantity of ethyl alcohol in the top product and hence in the assumed reboiler composition although if the same conversion was to be maintained a reduction in the butyl acetate reboiler concentration would be required.

The conditions which were specified for Calculation 2 were based on Run 3 and it is interesting to compare the calculated and measured concentration profiles (Tables 6.3 & 6.4). In the liquid phase, the worst discrepancy between the two sets of concentrations was 3.2 mole per cent, whilst the worst discrepancy for the vapour phase was

Table 6.4 Measured concentrations - Run 3.

Stage	x				y				T
	ETAC	ETOH	BUAC	BUOH	ETAC	ETOH	BUAC	BUOH	°C
T	0.447	0.550	0.003	—	—	—	—	—	—
1	0.350	0.638	0.012	—	0.459	0.541	—	—	75.0
2	0.244	0.712	0.037	0.008	0.359	0.631	0.011	—	76.0
3	0.179	0.726	0.088	0.007	0.287	0.685	0.028	—	77.0
4	0.147	0.596	0.241	0.018	0.211	0.704	0.078	0.007	81.5
5	0.162	0.528	0.258	0.048	0.245	0.664	0.080	0.011	83.0
6	0.168	0.384	0.308	0.137	0.275	0.582	0.104	0.039	88.0
B	0.111	0.116	0.401	0.361	0.288	0.376	0.185	0.151	103.0

4.5 mole per cent although the majority of the concentrations were well within 2.0 molar per cent error for both phases. Some divergence was expected partially due to the initial assumptions which had been made and partially due to the variations in the measured vaporisation efficiencies from which a constant value was used. For ethyl alcohol, a larger reboiler vaporisation efficiency had to be used (125%) in order to obtain a reasonable concentration profile, otherwise the profile would have been considerably lower than the measured concentrations. This was borne out in the measured value of the efficiency in Run 3 where the ethyl alcohol reboiler efficiency was calculated to be 122%.

The stagewise conversions were calculated and the summation of these closely duplicated the conversion of all the components. In order to determine the overall component conversions it was necessary to take the material balance over the reacting section of the column only.

The value of the reflux ratio (8.28 :1) which was calculated from the model compares well with the value used in Run 3 (8 : 1). The calculations predicted correctly a phenomenon which is not normally used in conventional distillation i.e. an increase in concentration of one of the lighter components down the column. In both the experimental and calculated determinations, the concentration of ethyl acetate in the liquid phase increased between Plates 4 and 5.

6.6. Conclusions

Calculations 1 and 2 were selected as being typical of some of the types of column conditions which were encountered in the experimental work. Calculation was carried out at total reflux with an increased boilup rate and reboiler holdup whilst Calculation 2 was at a lower boilup rate and reboiler holdup and at a reflux ratio of 8 : 1. In both examples, (Runs 3 & 12), the concentration of ethyl acetate increased down the column in the region below the feed plate. The stagewise analysis predicted an increase in the ethyl acetate concentration between Plates 4 and 5 for both calculations whilst in Calculation 1 the decrease in concentration from Plates 5 to 6 was very small.

Constant values of component vaporisation efficiencies gave good agreement between the observed and calculated conditions despite considerable variations in component efficiencies as for instance in Run 12, where the butyl acetate efficiency varied between 95 and 146% but a value of 120% was found to be satisfactory in Calculation 1.

Some variations in the liquid and vapour molar flowrates were obtained due to differences in the component molar thermal properties. For instance, the vapour flowrate changed by six per cent. A decrease in the vapour flowrate was observed at Plates 4 and 5, partially due to the feed being fed in at slightly below its boiling point. The slightly higher reflux ratio which was obtained in Calculation 2 could be due to the fact that no allowance has been made for heat of mixing. The heat of mixing has already been reported for two binary systems (70 & 145) and it was observed in Section 3 that heat was absorbed when butyl acetate and ethyl alcohol were mixed. The main effect of the heat of mixing would be to reduce the molar vapour and liquid flowrates which would cause the reflux ratio to be reduced.

Section 7.

CONCLUSIONS.

7. CONCLUSIONS.

The following conclusions have been drawn from this investigation

1) The four components in the system were analysed on 10 weight per cent polyethylene glycol on 100 mesh celite columns in a gas liquid chromatograph. With iso-octane as the internal reference, the analysis error was found to be ± 0.73%.

2) The mechanism for the transesterification of butyl acetate by ethyl alcohol was found to be second order.

3) The transesterification reaction would not proceed in the absence of a catalyst.

4) For approximately equimolar reactants and a temperature range of 21.4-85 °C, the forward velocity constant is related to the aboslute temperature by the following equations:-

0.1 wt.% catalyst $\log k_1 = 4.9939 - \frac{2773}{T}$

0.2 " " $\log k_1 = 5.3511 - \frac{2791}{T}$

0.5 " " $\log k_1 = 5.8992 - \frac{2846}{T}$.

1.0 " " $\log k_1 = 6.1873 - \frac{2841}{T}$

5) In near equimolar conditions and for a catalyst concentration range of 0.1-1.0 weight per cent, the mean activation energy was 12.87 kcal g mole^{-1}.

6) The modified Cathala dynamic equilibrium still gave good value for the vapour liquid equilibrium of five of the six binary systems which were investigated. Consistency tests were successfully applied to four of the binary systems whilst the fifth system was in close

agreement with data previously published in the literature. Low values of the ethyl acetate activity coefficients in the ethyl acetate - butyl acetate system were determined and they were attributed to the magnification of analytical errors in the low composition range.

7) From the six binary systems, the Van Laar constants were determined and used in a computer programme which would predict the multi-component vapour liquid equilibrium.

8) The prediction accuracy of the computer programme was determined by comparing the root mean square deviation incurred between the predicted equilibrium vapour composition and the experimental vapour composition for the same liquid phase composition.

For 101 experimental quaternary points, the error was found to be 1.87 mole per cent whilst the error for the four ternary systems (totalling 151 experimental points) was between 1.70 and 2.40 mole per cent.

9) In the continuous distillation where a transesterification reaction was being carried out simultaneously, concentration profiles occurred which are not normally encountered in conventional distillation columns. For example, the concentration of ethyl acetate (one of the lighter components) increased below the feed plate.

10) The conversion of ethyl alcohol and butyl acetate was a function of:-

a) The boilup rate

At near equimolar feed ratios the conversion of both of the reactants decreased as the boilup rate increased.

b) Reflux ratio

For a given feed, reboiler holdup and heat input the conversion increased as the reflux ratio increased.

c) Reboiler holdup

For a given feed and heat input, increasing the reboiler holdup by 30 per cent caused the conversion to be increased.

11) It was observed that in the section below the feed plate, that a highly developed foam was formed. This was attributed to the interfacial tension effects of the catalyst.

12) The presence of a chemical reaction within the distillation column caused large variations in the component Murphree efficiencies. Depending on the conditions, positive, negative or zero efficiencies could be obtained.

13) The stagewise vaporisation efficiencies were much less variable than the Murphree efficiencies. The values for ethyl alcohol tended to be constant just below one hundred per cent whilst butyl acetate and ethyl acetate had efficiencies which were considerably higher.

14) If allowances are made for the presence of a chemical reaction, a stagewise mathematical model based on enthalpy and material balances, closely duplicates the experimental results obtained from a continuously operated distillation column.

Section 8.

RECOMMENDATIONS FOR FUTURE WORK.

8. RECOMMENDATIONS FOR FUTURE WORK.

An overall examination of the present work has revealed a number of areas in which a further investigation would be of use. It has been observed that in both the kinetic observations and the experimental distillation programme that when a considerable excess of ester was present in the reacting mixture the second order correlation predicted a larger value for the rate constant than under identical conditions with an equimolar feed. Thus the scope of the kinectic investigations could be enlarged.

In the determination of the vapour liquid equilibrium data it was observed that low ethyl acetate activity coefficient values were calculated in the ethyl acetate - butyl acetate system. As an analytical technique was developed to cover the whole of the research work, it was quite possible that in a binary system analytical errors could be magnified when a calculation involved low component concentrations. Thus the binary system could be further investigated using a different analytical technique which would be applicable to the two components.

With regard to the multi-component vapour liquid equilibrium computer programme it could be possible to obtain an improved prediction accuracy using Wilson parameters. These could be calculated from the present binary data.

The modified Cathala dynamic still is capable of determining the vapour liquid equilibrium of reacting systems. As an initial approach it was decided to predict the vapour liquid equilibrium of the non-reacting quaternary and thus the next step would be to obtain experimental V.L.E. data for the reacting quaternary and to test the accuracy of the prediction programme.

The distillation column could be modified to widen the scope of the work. Although it was observed that the conversion increased when the reboiler holdup increased, the effect of varying the plate holdup was not determined. The plate holdup could easily be varied by constructing different sets of the liquid downcomers which are easily changed. It would also be useful to observe whether the mathematical model would duplicate any changes which occurred in varying the plate holdup.

The effect of splitting the feed was to increase the conversion but only two experiments were carried out and it would be useful to investigate more thoroughly the effect of a split feed. In 18 experiments the catalyst was fed in with the feed on the fourth plate and it would be interesting to assess the changes incurred in the column by feeding the catalyst in on the top plate with the reflux.

It was observed that some anomalies existed in the sampling system in the column. For example, butyl alcohol was detected in the liquid phase on one plate but not in the vapour phase leaving the plate below. This occurred in the non-reaction zone of the column. Thus the vapour sampling system could be improved by utilising on-line gas chromatographic techniques.

Finally it would be advantageous to combine the vapour liquid equilibrium prediction programme with a computer programme which could be developed for the mathematical stagewise analysis.

Section 9.

NOMENCLATURE

9. NOMENCLATURE.

Symbol	Meaning	Units
A	Peak Area	
A_{AB} A_{BA}	Van Laar coefficients for a binary A - B system	
a	mole fraction of ethyl alcohol	
B	Bottom flowrate	g mole min^{-1}
b	mole fraction of butyl acetate	
C	$\left[(a+b)^2 - 4ab\left(1 - \frac{1}{K}\right)\right]$	$(\text{g mole litre}^{-1})^2$
D	Distilled flowrate	g mole min^{-1}
E	Activation energy	kcal g mole^{-1}
E_m	Murphree efficiency	
E_v	Vaporisation efficiency	
F	Feed flowrate	g mole min^{-1}
f	Response factor	
H	Vapour enthalpy	cal g mole^{-1}
(H^+)	Hydrogen ion concentration	g mole litre^{-1}
h	liquid enthalpy	cal g mole^{-1}
I J	Factors defined by the Herington consistency test	

Symbol	Meaning	Units
K	Equilibrium constant	
k_1	Forward second order velocity constant	
L	Liquid flowrate	g mole min^{-1}
M	Number of experimental points	
m	m^{th} stage	
N	Number of components	
P	Pressure	mm Hg, atm
Q_E	Heat input to the reboiler	cal min^{-1}
Q_R	Heat of reaction	cal g mole^{-1}
R	Reflux ratio	
r	Reaction rate	g mole $\mathrm{litre}^{-1}\mathrm{min}^{-1}$
S	Conversion	g mole min^{-1}
T	Temperature	^{o}C
t	Time	min
V	Vapour flowrate	g mole min^{-1}
v	Molar volume	litre g mole^{-1}
W	Weight per cent	
x	liquid composition, mole fraction	

Symbol	Meaning	Units
Y	$\frac{1}{\sqrt{C}} \ln \left[\frac{2ab - x(a + b - \sqrt{C})}{2ab - x(a + b - \sqrt{C})} \right]$	g mole litre^{-1}
y	vapour composition, mole fraction	
y^*	equilibrium vapour composition, mole fraction	
Z	Plate holdup	cm^3
γ	Activity coefficient	
Δr	Rate of change of moles	g mole litre^{-1}min^{-1}
μ	viscosity	poise
ρ	density	g cm^{-3}
σ	Surface tension	dyne cm^{-2}

Subscripts

1 - 6	Stages 1 - 6	H	Ethyl acetate
A	Sulphuric Acid	I	Ethyl alcohol
B	Bottoms	J	Butyl acetate
D	Distillate	K	Butyl alcohol
F	Feed	R	Reference compound

Section 10.

BIBLIOGRAPHY.

10. BIBLIOGRAPHY.

(1) Nagao H., Mifune M., Japanese Patent, 10,350 ('57) Dec. 1957.

(2) Dutch Patent, 6,507,842 Dec. 1966.

(3) German Patent, 1,227,653 Oct. 1966.

(4) German Patent, 1,950,553 April, 1970.

(5) Schade G., South African Patent, 6,706,258 April, 1968.

(6) British Patent, 1,130,387 1968.

(7) Hahn W.D., Griehl W., Stoll B., German Patent 1,805,071 May 1970.

(8) Vodonik J.L., British Patent, 729,803 May, 1955.

(9) Sorokin M.F., Chebotarena N.A., Tr. Mosk. Khim. Tekhnol. Inst. No.61, 103-6, 1969.

(10) Vodonik J.L., U.S. Patent, 2,681,310 June, 1954.

(11) Yoda K., Kimoto K., Todat., Kogyo Kagaku Zasshi, 67 (6), 909-14, 1964.

(12) Kudrna M., Pavelcova V., Chem Prumysl, 14 (1), 12-16, 1964.

(13) Snyder M.D., U.S. Patent, 2,744,087 May, 1956.

(14) Torraca G., Turriziani R., Chim. Ind. (Milan), 44 (5), 483-8, 1962.

(15) Price A.J., Carlson K.O., U.S. Patent, 3,420,803, Jan. 1969.

(16) Steward M.J., Michelman D., U.S. Patent, 3,511,812 May, 1970.

(17) Koch M.J., Price A.J., U.S. Patent, 3,425,998 Feb. 1969.

(18) Steward M.J.,Price A.J., U.S. Patent, 3,509,100 April, 1970.

(19) Steward M.J.,Price A.J., U.S. Patent, 3,451,973 June, 1969.

(20) Steward M.J.,Price A.J., U.S. Patent, 3,454,531 July, 1969.

(21) Sumoto M., Kogyo Kagaku Zasshi 66 (12), 1867-70, 1963.

(22) Italian Patent, 744,517 Feb. 1967.

(23) Mihail R., Acad. Rep. Populare Romine Studii Cercetari Chim., 6, 161-83, 1958.

(24) Hamilton L.A., U.S. Patent, 2,328,439 June, 1967.

(25) Holcik C., Vesely R., Czech Patent, 84,531 July, 1955.

(26) U.S. Patent, 3,142,733, 1964.

(27) Miyake T., Kogyo Kagaku Zasshi, 64 744, 1961.

(28) U.S. Patent, 3,297,651 Jan. 1967.

(29) Spanish Patent, 323,418 Seda de Barcelona, 1966.

(30) Michaelis W., German (East) Patent, 59,084 Dec. 1967.

(31) Gottfried R., German (East) Patent, 62,913 June, 1968.

(32) Hahn W.D., Swiss Patent, 492,477 August, 1970.

(33) Wilfong J., J. Polymer Sci., 54, 385-410, 1961.

(34) Fehlandt P.R., Adkins H., J. Am. Chem. Soc., 57, 193-5, 1935.

(35) Mainkar S.V., Mene P.S., Indian J. Technol., 3 (4), 134-5, 1965.

(36) Mainkar S.V., Mene P.S., Trans. Indian. Chem. Engt. 7 (3), 47-52, 1965.

(37) Bogin C.D., Ind. Eng. Chem., 16, 380-5, 1924.

(38) Barker G.E., White R.R., Chem. Eng. Prog. Symp. No.4, 48, 75-90, 1952.

(39) Farkas L., Schächter O., Vromen B.H., J. Am. Chem. Soc., 71, 1991-4, 1949.

(40) Furnas C.C., Leighton W.B., Ind. Eng. Chem., 29, 709-10, 1937.

(41) Buess-Thiernagand D., Fierens P.J.C., Bull. Soc. Chim. Belge., 61, 403-26, 1952.

(42) Shaposhnikov Yu.K., Vedeneev K.P., Vodzinskii Yu.V., Druskina E.Z, Gaz Khromatogr Akad. Nank. Sssr., Tr. Vtoroi. Vses. Konf., Moscow 265-9, 1962.

(43) Curry A.S., Walker G. W., Simpson G.S., The Analyst (London), 91, 742-3, 1966.

(44) Selwitz C.M., Walde R.A., U.S. Patent, 3,255,236, 1966.

(45) Hrivnak J., Vesela Z., Sohler E., Drabek J., Chem. Prumsyl., 15 (1), 7-9, 1965.

(46) Juvet R.S., Wachi F.M., J.Am.Chem.Soc., 81, 6110-15, 1959.

(47) Pye W.G. & Co. Ltd., Cambridge, England.

(48) Oster H., Z.Anal. Chem., 170, 264-71, 1959.

(49) Batt L., Cruickshank F., J. Chromatog., 21 (2), 296-300,1966.

(50) Knox J.H., "Gas Chromatography"

(51) Gill J.M., Tao F.J., Chem. Anlagen Verfahren, 39-40, 1967.

(52) Condal-Bosch L., J.Chem.Educ., 41 (4), A235, 1964.

(53) Girling G.W., Gigg A.R., Heley M.R., J.Chromatog., 31 (2), 525-7, 1967.

(54) Kent Instruments Ltd., Luton, England.

(55) Damm F., Pichler A., Libs., Bull. Soc. Chim. France, 3020-3, 1967.

(56) Benzole Conference, J. Chromatog., 12 (3), 293-304, 1963.

(57) Evans M.B., J. Chromatog., 12, 2-7, 1963.

(58) Germaine R.W., Haken J.K., J. Chromatog., 43 (1), 33-42, 1969.

(59) Martin J., Krchma I.J., U.S. Patent, 1,770,414, July, 1930.

(60) Haken J.K., J.Appl.Chem., 13 (4), 168-171, 1963.

(61) Haken J.K., McKay T.R., Lab. Pract., 14 (4) 460-1, 1965.

(62) Carroll M.F., J.Chem.Soc., 557-61, 1949.

(63) Kudryavtsen R.V., Kwsanov D.N., Zhur.Obshchei Khim., 21, 1686-7, 1957.

(64) Sabel A., Smidt J., Jira R., Prigge H., Chem. Berlin, 102 (9), 2939-50, 1969.

(65) Hatch G.B., Adkins H., J.Am.Chem.Soc., 59, 1694-6, 1937.

(66) Mamers H., Ph.D. Thesis, Birmingham, 1965.

(67) Moroney M.J., "Facts from Figures" Penguin Books Ltd., 1962.

(68) Kolhatkar G.B., J.Chem.Soc., 107, 921-33, 1915.

(69) Skljarenko S.J., Baranev M.K., Z.Physik.Chem. A175, 203-13, 1935.

(70) Murti P.S., Van Winkle M., Chem. & Eng. Data Ser., 3, 65-81, 1958.

(71) Mainkar S.V., Mene P.S., Indian J. Technol, 3 (7),228-9,1965.

(72) Brunjes A.S., Bogart M.J.P., Ind.Eng.Chem., 35, 255-60, 1943.

(73) Hellwig L.R., Van Winkle M., Ind.Eng.Chem., 45, 624-9, 1953.

(74) Brunjes A.S., Furnas C.C., Ind.Eng.Chem., 27, 396-400, 1935.

(75) Sheinker J.N., Persleni E.M., Zh.Fiz.Khim., 26, 1103, 1952.

(76) Taylor A.E., J. of Phys.Chem., 4, 290-305, 1900.

(77) Rayleigh J.W., Phil.Mag. VI 4, 521, 1902.

(78) Sage B. H., Lacey W.N., Ind.Eng.Chem., 32, 992-6, 1940.

(79) Hala E., et al, "Vapour Liquid Equilibrium" Pergammon Press, London 1958.

(80) Verchoyle T.T.H., Tr. Royal Society (London), A230, 189, 1931.

(81) Bloom C.H., et al, Ind.Eng.Chem., 53, 829-32, 1961.

(82) Jones C.A., Schoenborn E.M., Colburn A.P., Ind.Eng.Chem., 35, 666-72, 1943.

(83) Hipkin H., Myers H.S., Ind.Eng.Chem., 46, 2524-8, 1954.

(84) Othmer D.F., Ind.Eng.Chem., 35, 614-20, 1943.

(85) Ellis S.R.M., Trans.Inst.Chem.Eng., 30, 58-64, 1952.

(86) Gillespie D.T.C., Ind.Eng.Chem., (Anal.Ed.), 18, 575-7, 1946.

(87) Malenko Yu. I., Lutugina N.V., Bashmakova T.S., Zh.Prik.Khim., 39 (12), 2737-43, 1966.

(88) Solokov N.M., Sevryugova N.N., Zhavoronkov N.M., "International Symposium on Distillation", Brighton, England, 1969.

(89) Colburn A.P., Schoenborn E.M., Schilling D., Ind.Eng.Chem., 35, 1250-4, 1943.

(90) Vilim O., Hala E., Fried V., Rick J., Coll.Czech.Chem. Commun., 19, 1330-4, 1954.

(91) Rius A., Otero J.L., Macarron A., Chem.Eng.Sci., 10, 105-111, 1959.

(92) Cathala J., Hardie D., Leclerc R., Bull Soc.Chim. France, 17, 1129-32, 1950.

(93) Cathala J., Hardie D., Leclerc R., Industrial Chemist, 27, 565, 1951.

(94) Danckwerts P.V., Sawistowski H., Smith W., "International Symposium on Distillation", Brighton, England, 1960.

(95) Marek J., Coll.Czech.Chem.Commun., 20, 1490-1502, 1955.

(96) Marek J., Coll.Czech.Chem.Commun., 21, 269-280, 1956.

(97) Cathala J., "International Symposium on Distillation", Brighton, England, 1960.

(98) Edwards High Vacuum Ltd., Manor Royal, Crawley, Sussex.

(99) Fisher & Porter, Workington, England.

(100) "Wiggin Electrical Resistance Materials", Henry Wiggin & Co. Ltd., Birmingham.

(101) Polak J., Mertl I., Coll. Czech. Chem. Commun., 30, 3526-8, 1965.

(102) Merriman R.W., J. Chem. Soc., 103, 628-36, 1913.

(103) Perry J.H. (Ed.) "Chemical Engineers Handbook", (McGraw Hill New York).

(104) Schiopu M., Boto., Onuv., Bul.Inst. Politeh.Isai, 7 (304) 115-8, 1961.

(105) Gallant R.W., Hydrocarbon Processing, 45, 171-182, 1966.

(106) Coulson J.M., Richardson J.F., "Chemical Engineering", Vol.2, (Pergammon Press London 1962).

(107) Herington E.F.G., J. Inst. Petrol., 37, 457-70, 1951.

(108) Bogdan W., Polish Patent, 36,783, Jan. 1958.

(109) Hollo J., Lengyel T., Coll. Czech. Chem. Commun., 23, 1735-43, 1958.

(110) Suzuki I., Komoatsu H., Hirata M., J. Chem. Eng. of Japan, 3 (2), 152-7, 1970.

(111) Sabylin I.I., Aristovich Yu. V., Zh. Prik. Khim., 43 (9), 2021-8, 1970.

(112) King M.B., "Phase Equilibrium in Mixtures", Pergammon Press 1969.

(113) Hala E., "Vapour Liquid Equilibrium Data at Normal Pressures", Pergammon Press.

(114) Prausnitz J.M., Exkert C.A., Orye R.V. O'Connell J.P., "Computer Calculations for Multicomponent Vapour Liquid Equilibrium", (Prentice-Hall Inc., New York,1967).

(115) Ma K.T., McDermott C., Ellis S.R.M., "International Symposium Distillation", Brighton, England, 1969.

(116) McClellan A.L., "Tables of Experimental Dipole Moments", W.H. Freeman & Co., London 1963.

(117) D'Ans. Lax-Taschenbuch für Chemiker und Physiker, 2 Organische Verbindungen, Springer-Verlag, Berlin 1964.

(118) Geelen H., Wijffels J. B., "Third European Symposium on Chemical Reaction Engineering", (Pergammon Press Ltd., 1964).

(119) Buselli A.J., Rutledge T.F., U.S. Patent, 2,949,480, 1960.

(120) Backhaus A.A., U.S. Patent, 1,400,849, 1921.

(121) Keyes D.B., Ind.Eng.Chem., 24, 1096, 1932.

(122) Rose A.E., "Distillation Literature", 1941-1945, 1946-1952, 1953-1954, State College Pennyslvania.

(123) Bolles W.L., Fair J.R., Ind.Eng.Chem., 1962-1970.

(124) Holdsworth S.D., Chemical Process Engineering, 528-34, 1963.

(125) Parker A.S., U.S. Patent, 2,839,588, 1958.

(126) Matz G., Chem.Ing.Tech., 33, 653, 1961.

(127) Marek J., Coll,Czech.Chem.Commun. 21, 1560-8, 1956.

(128) Legg R.J., Ph.D. Thesis, Birmingham, 1962.

(129) Costa P., Canepa B., Quad.Ing.Chim.Ital., 5 (9), 113-21, 1969.

(130) Leyes C.E., Othmer D.F., Trans.A.Inst.Ch.E., 41 157-196, 1945.

(131) Berman S., Melnychuk A.A., Othmer D.F., Ind.Eng.Chem., 40, 1312, 1948.

(132) Corrigan T.E., Ferris W.R., Canadian J. of. Chem.Eng., 47 (3), 334-5, 1969.

(133) Schniepp L.E., Dunning J.W., Lathrop E.C., Ind.Eng.Chem., 37, 872-7, 1945.

(134) Corrigan T.E., Miller J.H., Ind.Eng.Chem. Process Design Development, 7, 383-4, 1968.

(135) Marek J., Coll.Czech.Chem.Commun., 19, 1055-73, 1954.

(136) Belck L.H., A.I.Ch.E.J., 1 (4), 467-470, 1955.

(137) Heating Equipment Ltd., Salisbury, England.

(138) Pyro Tenax, Birmingham, England.

(139) "International Critical Tables".

(140) Riiber C.N., Z. Elektrochem, 29, 334-8, 1923.

(141) Tavernier P., Mem Poudres, 39, 253-96, 1957.

(142) Tjebbes J., Pure Applied Chem, 2, 129-32, 1961.

(143) Chao J., Rossini F., J.Chem.Eng.Data., 10, 374-9, 1965.

(144) Green J.H., Chem. & Industry, 1215-6, 1960.

(145) Pope A.E. et al, Canadian J. of Chem.Eng., 45, 2665-74, 1967.

(146) Smith B.D., "Design of Equilibrium Stage Processes", (McGraw Hill New York).

(147) Zuiderweg F.J., Harmens A., Chem.Eng.Sci., 9, 89-103, 1958.

(148) O'Leary P.T., Bowman J.R., Ind.Eng.Chem., 43, 541-4, 1951.

(149) Toor H.L., Burchard J.K., A.I.Ch.E.J., 6, 202, 1960.

(150) Wilke C.R., Chang P., A.I.Ch.E.J., 1, 264, 1955.

Section 11.

APPENDICES

Appendix A1

Materials Specification

1) Analar grade ethyl acetate

a) The material contained not less than 99.0 weight per cent of ethyl acetate.

b) Not less than 95 per cent distilled off between 76.5 and 77.5 °C.

c) The density at 20 °C was 0.899 - 0.901 g cm^{-3}

d) The free acid was 0.005%

The non-volatile content was 0.001%

The water content was 0.05%

2) Analar grade ethyl alcohol

a) The material contained not less than 99.7 weight per cent of ethyl alcohol.

b) Not less than 95 per cent distilled off between 78.0 and 78.5 °C.

c) The density at 20 °C was not more than 0.7897 g cm^{-3}

d) The aldehyde & ketone content was 0.005%

The non-volatile content was 0.001%

Methyl alcohol content was 0.1%

Other higher alcohol content was 0.01%

The water content was 0.3%

3) Analar grade butyl alcohol

a) The material contained not less than 99.0 weight per cent of butyl alcohol.

b) Not less than 95 per cent distilled off between 116 and 118 °C.

c) The density of 20 °C was 0.808 - 0.810 g cm^{-3}

Appendix A1

(Cont'd.)

d) The free acid content was 0.003%

The aldehyde & ketone content was 0.015%

Impurities determined by G. C. was 0.5%

The non-volatile content was 0.003%

The water content was 0.3%

4) General Purpose Reagent grade butyl acetate

a) The material contained a minimum of 97 weight per cent of butyl acetate.

b) Not less than 95 per cent distilled off between 124 and 128 °C.

c) The density at 20 °C was 0.878 - 8.881 g cm^{-3}

d) The free acid content was 0.01%

The non-volatile content was 0.01%

5) General Purpose Reagent grade iso-octane

a) The material contained a minimum of 97 weight per cent of iso-octane.

b) Not less than 95 per cent distilled off between 98 and 99.5 °C.

c) The density at 20 °C was 0.69 - 0.693 g cm^{-3}

6) Commercial grade argon

Purity not less than 99.99%

Impurities

Oxygen	10	v.p.m.
Nitrogen	20	v.p.m.
Hydrogen	5	v.p.m.
Carbon dioxide	1	v.p.m.
Water vapour	5	v.p.m.

Appendix A1

(Cont'd.)

7) High purity hydrogen

Purity not less than 99.99%

Impurities

Nitrogen	500	v.p.m.
Carbon monoxide	5	v.p.m.
Carbon dioxide	5	v.p.m.
Hydro carbons	5	v.p.m.
Water vapour	6	v.p.m.
Oxygen	10	v.p.m.

8) High purity air

Purity not less than 99.995%

Impurities

Hydrocarbons	4	v.p.m.
Carbon dioxide	1	v.p.m.
Water vapour	5	v.p.m.

Appendix A2

Calculation of response factors for ETAC, ETOH, BUAC, BUOH.

	Area		f	Area		f
	ISO	ETAC		ISO	ETOH	
1	61	151	2.424	99	291	2.041
2	103	257	2.406	106	308	2.064
3	78	194	2.413	115	330	2.090
4	70	174	2.415	120	351	2.051
5	48	117	2.463	102	295	2.074
6	37	90	2.468	98	289	2.033
7	76	190	2.401	93	274	2.036
8	103	253	2.444	111	325	2.048
9	88	218	2.423	102	294	2.081
10	29	70	2.487	114	333	2.053

	Area		f	Area		f
	ISO	BUAC		ISO	BUOH	
1	116	404	1.722	134	548	1.467
2	126	437	1.729	113	465	1.458
3	106	362	1.756	110	451	1.463
4	120	418	1.722	116	474	1.467
5	113	389	1.742	116	473	1.471
6	109	373	1.753	115	477	1.446
7	93	318	1.754	123	518	1.424
8	88	308	1.714	115	470	1.468
9	143	497	1.726	114	468	1.461
10	101	351	1.727	120	494	1.457

The response factors were calculated using equation 2.2

$$f_x = \frac{A_r}{A_x} \times \frac{W_x}{W_r} \times f_r \qquad \text{———} \qquad 2.2$$

$$\frac{W_{ETAC}}{W_{REF}} = 6.003 \qquad \frac{W_{ETOH}}{W_{REF}} = 5.998$$

$$\frac{W_{BUAC}}{W_{REF}} = 5.998 \qquad \frac{W_{BUOH}}{W_{REF}} = 5.998$$

The mean values for the response factors are:-

$$f_{ETAC} = 2.434 \qquad f_{ETOH} = 2.057$$

$$f_{BUAC} = 1.735 \qquad f_{BUOH} = 1.458$$

Appendix A3

Composition of Standard Solutions.

Sample No.	Weight Per Cent			Nominal % ETAC in ETAC/ETOH mixture
	Iso-Octane	ETAC	ETOH	
1	14.29	0.00	85.71	0
2	14.29	4.40	81.31	5
3	14.28	8.71	77.01	10
4	14.29	17.64	68.07	20
5	14.29	25.95	59.79	30
6	14.29	34.29	51.42	40
7	14.28	42.87	42.85	50
8	14.29	51.35	34.36	60
9	14.29	59.80	25.91	70
10	14.29	69.32	16.39	80
11	14.29	77.18	8.53	90
12	14.29	81.28	4.64	95
13	14.28	85.72	0.00	100

Sample No.	Weight Per Cent			Nominal % BUAC in BUAC/BUOH mixture
	Iso-Octane	BUAC	BUOH	
14	14.29	0.00	85.71	0
15	14.28	4.52	81.20	5
16	14.28	8.80	76.91	10
17	14.28	17.07	68.64	20
18	14.28	25.93	59.78	30
19	14.28	34.25	51.47	40
20	14.29	42.94	42.78	50
21	14.28	51.33	34.38	60
22	14.29	59.99	25.73	70
23	14.28	68.51	17.21	80
24	14.28	77.10	8.61	90
25	14.29	81.09	4.63	95
26	14.29	85.71	0.00	100

Appendix A4

Chromatograph Calibration Results - Analysis of samples 1 - 26

Table 1

	Area			fA		ΣfA	$(fA/\Sigma fA) \times 100$		
	ISO	ETAC	ETOH	ETAC	ETOH		ISO	ETAC	ETOH
1	99	-	291	-	599	698	14.19	-	85.81
2	106	-	308	-	634	740	14.32	-	85.68
3	115	-	330	-	679	794	14.48	-	85.52
4	120	-	351	-	722	842	14.25	-	85.75
5	102	-	295	-	607	709	14.39	-	85.61
6	98	-	289	-	594	692	14.16	-	85.84
7	93	-	274	-	564	657	14.16	-	85.84
8	111	-	325	-	669	780	14.23	-	85.77
9	102	-	294	-	605	707	14.43	-	85.57
10	114	-	333	-	685	799	14.27	-	85.73

Table 2

	Area			fA		ΣfA	$(fA/\Sigma fA) \times 100$		
	ISO	ETAC	ETOH	ETAC	ETOH		ISO	ETAC	ETOH
1	121	16	346	38.9	712	872	13.88	4.46	81.65
2	93	12	267	29.2	549	671	13.86	4.35	81.81
3	106	14	293	34.1	603	743	14.27	4.59	81.16
4	108	15	305	36.5	627	772	13.99	4.73	81.22
5	79	10	227	24.3	467	570	13.86	4.26	81.93
6	110	14	305	34.1	627	771	14.27	4.42	81.32
7	98	13	280	31.6	576	706	13.89	4.48	81.59
8	102	13	291	31.6	599	733	13.92	4.31	81.72
9	121	15	335	36.5	689	847	14.29	4.31	81.35
10	115	14	328	34.1	675	824	13.96	4.14	81.92

Appendix A4

(Cont'd.)

Table 3

	Area			fA		ΣfA	$(fA/\Sigma fA) \times 100$		
	ISO	ETAC	ETOH	ETAC	ETOH		ISO	ETAC	ETOH
1	95	24	254	58.4	522	675	14.07	8.65	77.33
2	103	26	271	63.3	557	723	14.25	8.76	77.04
3	108	28	291	68.2	599	775	13.94	8.80	77.29
4	104	27	279	65.7	574	744	13.98	8.83	77.15
5	108	28	294	68.2	605	781	13.83	8.73	77.46
6	114	30	311	73.0	640	827	13.78	8.83	77.39
7	115	30	308	73.0	634	822	13.99	8.88	77.13
8	119	30	310	73.0	638	830	14.34	8.80	76.87
9	115	30	303	73.0	623	811	14.18	9.00	76.82
10	124	32	324	77.9	666	868	14.29	8.97	76.73

Table 4

	Area			fA		ΣfA	$(fA/\Sigma fA) \times 100$		
	ISO	ETAC	ETOH	ETAC	ETOH		ISO	ETAC	ETOH
1	90	47	219	114	450	654	13.76	17.43	68.81
2	99	53	246	129	506	734	13.55	17.51	68.94
3	114	60	259	146	533	793	14.38	18.41	67.21
4	116	61	270	148	555	819	14.16	18.07	67.77
5	121	62	273	151	562	834	14.50	18.11	67.39
6	109	56	266	136	547	792	13.74	17.17	69.07
7	123	65	291	158	599	880	13.98	17.95	68.07
8	113	59	268	144	551	808	13.99	17.82	68.19
9	109	58	260	141	535	785	13.89	17.96	68.15
10	106	56	256	136	527	769	13.78	17.69	68.53

Appendix A4

(Cont'd.)

Table 5

	Area			fA		ΣfA	(fA/ΣfA) x 100		
	ISO	ETAC	ETOH	ETAC	ETOH		ISO	ETAC	ETOH
1	102	79	213	192	438	732	13.93	26.33	59.84
2	97	74	197	180	405	682	14.22	26.39	58.38
3	104	81	211	197	434	735	14.15	26.80	59.05
4	93	72	198	175	407	675	13.78	25.93	60.30
5	106	81	215	197	442	745	14.23	26.44	59.33
6	126	98	255	239	525	890	14.16	26.85	58.99
7	100	78	207	190	426	716	13.97	26.54	59.50
8	100	76	202	185	416	201	14.27	26.39	59.34
9	110	85	234	207	481	298	13.78	25.94	60.23
10	105	80	209	195	430	730	14.38	26.71	58.90

Table 6

	Area			fA		ΣfA	(fA/ΣfA) x 100		
	ISO	ETAC	ETOH	ETAC	ETOH		ISO	ETAC	ETOH
1	96	98	175	239	360	695	13.81	34.39	51.80
2	95	97	169	236	348	679	13.99	34.76	51.25
3	104	105	177	256	364	724	14.36	35.36	50.28
4	102	105	186	256	383	741	13.76	34.55	51.69
5	112	114	201	277	413	802	13.96	34.54	51.50
6	99	100	179	243	368	710	13.94	34.23	51.83
7	111	112	200	273	411	795	13.96	34.34	51.70
8	124	127	224	309	461	894	13.87	34.56	51.57
9	87	86	151	209	311	607	14.33	34.43	51.24
10	107	108	190	263	391	761	14.06	34.56	51.38

Appendix A4

(Cont'd.)

Table 7

	Area			fA		ΣfA	(fA/ΣfA) x 100		
	ISO	ETAC	ETOH	ETAC	ETOH		ISO	ETAC	ETOH
1	76	97	110	236	226	538	14.13	43.87	42.01
2	101	130	146	316	300	717	14.09	44.07	41.84
3	97	126	145	307	298	702	13.82	43.73	42.45
4	111	141	165	343	339	793	14.00	43.25	42.75
5	97	123	139	299	286	682	14.22	43.84	41.94
6	102	131	151	219	311	732	13.93	43.58	42.49
7	111	142	162	346	333	790	14.05	43.80	42.15
8	73	93	109	226	224	523	13.96	43.21	42.83
9	85	107	124	260	255	600	14.17	43.33	42.50
10	109	138	162	336	333	778	14.01	43.19	42.80

Table 8

	Area			fA		Σ fA	(fA/ΣfA) x 100		
	ISO	ETAC	ETOH	ETAC	ETOH		ISO	ETAC	ETOH
1	104	156	127	380	261	745	13.96	51.01	35.03
2	97	146	116	355	239	691	14.04	51.37	34.59
3	122	183	150	445	309	876	13.93	50.80	35.27
4	104	156	124	380	255	739	14.07	51.42	34.51
5	90	133	105	324	216	630	14.28	51.43	34.29
6	102	156	128	380	263	745	13.69	51.01	35.30
7	77	115	91	280	187	544	14.15	51.47	34.38
8	109	164	132	399	272	780	13.98	51.15	34.87
9	118	175	137	426	282	826	14.29	51.57	34.14
10	88	132	107	321	220	629	13.99	51.03	34.98

Appendix A4

(Cont'd.)

Table 9

	Area			fA		Σ fA	(fA/ΣfA) x 100		
	ISO	ETAC	ETOH	ETAC	ETOH		ISO	ETAC	ETOH
1	29	54	28	131	58	218	13.49	60.09	26.42
2	67	119	58	290	119	476	14.08	60.92	25.00
3	45	81	43	197	89	331	13.74	59.52	26.74
4	79	135	65	329	134	542	14.58	60.70	24.72
5	114	200	97	489	200	803	14.19	60.90	24.91
6	113	200	101	489	208	810	13.95	60.37	25.68
7	97	170	83	414	171	682	14.23	60.70	25.07
8	97	167	82	406	169	672	14.43	60.42	25.15
9	119	211	103	514	212	845	14.08	60.83	25.09
10	103	181	87	441	179	723	14.24	61.00	24.74

Table 10

	Area			fA		Σ fA	(fA/ΣfA) x 100		
	ISO	ETAC	ETOH	ETAC	ETOH		ISO	ETAC	ETOH
1	132	204	74	497	152	781	16.90	62.64	19.46
2	50	104	28	253	58	361	13.85	70.08	16.07
3	72	147	40	358	82	512	14.06	69.92	16.02
4	72	146	41	355	84	511	14.09	69.47	16.44
5	54	109	29	265	60	379	14.25	69.92	15.83
6	80	163	45	397	93	570	14.03	69.65	16.32
7	68	140	39	341	80	489	13.91	69.73	16.36
8	126	256	71	623	146	895	14.08	69.61	16.31
9	92	185	51	450	105	647	14.22	69.55	16.23
10	75	155	42	377	86	538	13.94	70.07	15.99

Appendix A4

(Cont'd.)

Table 11

	Area			fA		$\sum$fA	(fA/$\sum$fA) x 100		
	ISO	ETAC	ETOH	ETAC	ETOH		ISO	ETAC	ETOH
1	45	106	13	258	26.7	330	13.73	78.18	8.09
2	90	204	26	497	53.5	641	14.11	77.54	8.35
3	69	156	19	380	39.1	488	14.12	77.87	8.01
4	77	179	23	436	47.3	560	13.69	77.86	8.45
5	73	166	22	404	45.3	522	13.93	77.39	8.68
6	76	171	22	416	45.3	537	14.08	77.47	8.44
7	91	206	26	501	53.5	646	14.17	77.55	8.28
8	82	189	25	460	51.4	593	13.76	77.57	8.67
9	117	264	34	643	69.9	830	14.11	77.47	8.42
10	55	126	16	307	32.9	395	13.95	77.72	8.33

Table 12

	Area			fA		$\sum$fA	(fA/$\sum$fA) x 100		
	ISO	ETAC	ETOH	ETAC	ETOH		ISO	ETAC	ETOH
1	71	169	10	411	20.6	503	14.19	81.71	4.10
2	49	119	8	290	16.5	356	13.91	81.46	4.63
3	59	138	8	338	16.5	414	14.37	81.64	3.99
4	53	129	8	314	16.5	384	13.93	81.77	4.30
5	94	225	15	548	30.9	673	13.98	81.43	4.59
6	92	227	16	553	32.9	678	14.54	80.61	4.85
7	72	165	12	402	24.7	499	13.49	81.56	4.95
8	97	231	16	562	32.9	692	14.04	81.21	4.75
9	75	181	12	441	24.7	541	13.91	81.52	4.57
10	115	275	18	669	37.0	821	14.00	81.49	4.51

Appendix A4

(Cont'd.)

Table 13

	Area			fA		∑fA	(fA/∑fA) x 100		
	ISO	ETAC	ETOH	ETAC	ETOH		ISO	ETAC	ETOH
1	61	151	-	368	-	429	14.22	85.78	-
2	103	257	-	626	-	729	14.13	85.87	-
3	78	194	-	472	-	550	14.18	85.82	-
4	70	174	-	424	-	494	14.17	85.83	-
5	48	117	-	285	-	333	14.41	85.59	-
6	37	90	-	219	-	256	14.45	85.55	-
7	76	190	-	462	-	539	14.29	85.71	-
8	103	253	-	616	-	719	14.33	85.67	-
9	88	218	-	531	-	619	14.22	85.78	-
10	29	70	-	170	-	199	14.57	85.43	-

Table 14

	Area			fA		∑fA	(fA/∑fA) x 100		
	ISO	BUAC	BUOH	BUAC	BUOH		ISO	BUAC	BUOH
1	134	-	548	-	799	933	14.36	-	85.64
2	113	-	465	-	678	791	14.29	-	85.71
3	110	-	451	-	658	768	14.32	-	85.68
4	116	-	474	-	691	807	14.37	-	85.63
5	116	-	473	-	690	806	14.39	-	85.61
6	115	-	477	-	695	810	14.20	-	85.80
7	123	-	518	-	755	878	14.01	-	85.99
8	115	-	470	-	685	800	14.37	-	85.63
9	114	-	468	-	682	796	14.32	-	85.68
10	120	-	494	-	720	840	14.29	-	85.71

Appendix A4

(Cont'd.)

Table 15

	Area			fA		ΣfA	(fA/ΣfA) x 100		
	ISO	BUAC	BUOH	BUAC	BUOH		ISO	BUAC	BUOH
1	101	19	387	33.0	564	698	14.47	4.73	80.80
2	115	21	443	36.4	646	797	14.38	4.57	81.05
3	114	22	450	38.2	656	808	14.08	4.73	81.19
4	99	18	390	31.2	569	699	14.14	4.46	81.40
5	97	17	373	29.5	544	671	14.53	4.40	81.07
6	120	22	460	38.2	671	829	14.51	4.55	80.94
7	110	19	436	33.0	636	779	14.12	4.24	81.64
8	123	24	470	41.6	685	850	14.52	4.89	80.59
9	135	25	514	43.4	749	927	14.52	4.68	80.80
10	120	23	466	39.9	679	839	14.31	4.76	80.93

Table 16

	Area			fA		ΣfA	(fA/ΣfA) x 100		
	ISO	BUAC	BUOH	BUAC	BUOH		ISO	BUAC	BUOH
1	108	37	389	64.2	567	739	14.58	8.69	76.73
2	118	45	448	78.1	653	849	13.89	9.20	76.91
3	118	45	428	78.1	624	820	14.38	9.52	76.10
4	117	42	437	72.9	637	827	14.16	8.81	77.03
5	130	48	467	83.3	681	894	14.51	9.32	76.17
6	135	49	500	85.0	729	949	14.22	8.96	76.82
7	131	47	474	81.5	691	904	14.54	9.02	76.44
8	126	45	457	78.1	666	870	14.47	8.98	76.55
9	121	44	453	76.3	660	857	13.20	8.90	77.9
10	90	32	359	55.5	523	669	13.52	8.30	78.18

Appendix A4

(Cont'd.)

Table 17

	Area			fA		ΣfA	(fA/ΣfA) x 100		
	ISO	BUAC	BUOH	BUAC	BUOH		ISO	BUAC	BUOH
1	96	67	318	116	464	676	14.20	17.16	68.64
2	117	87	400	151	583	851	13.75	17.74	68.51
3	109	76	362	132	528	767	14.17	17.17	68.66
4	115	81	379	141	553	809	14.21	17.43	68.36
5	108	75	354	130	516	754	14.32	17.24	68.44
6	117	82	386	142	563	822	14.23	17.28	68.49
7	120	83	391	144	570	834	14.38	17.27	68.35
8	113	78	372	135	542	790	14.30	17.09	68.61
9	110	73	347	127	506	743	14.81	17.09	68.10
10	112	76	365	132	532	776	14.43	17.01	68.56

Table 18

	Area			fA		ΣfA	(fA/ΣfA) x 100		
	ISO	BUAC	BUOH	BUAC	BUOH		ISO	BUAC	BUOH
1	110	118	321	205	468	783	14.05	26.18	59.77
2	119	135	348	234	507	860	13.84	27.21	58.95
3	110	115	308	200	449	759	14.49	26.35	59.16
4	113	122	334	212	487	812	13.92	26.11	59.98
5	114	123	329	213	480	807	14.13	26.39	59.48
6	128	133	365	231	532	891	14.37	25.93	59.71
7	121	129	356	224	519	864	14.00	25.93	60.07
8	112	120	327	208	477	297	14.05	26.10	59.85
9	101	107	295	186	430	717	14.09	25.94	59.97
10	125	131	360	227	525	897	14.25	25.88	59.86

Table 19

	Area			fA		ΣfA	(fA/ΣfA) x 100		
	ISO	BUAC	BUOH	BUAC	BUOH		ISO	BUAC	BUOH
1	115	160	282	278	411	804	14.30	34.58	51.12
2	123	173	307	300	448	871	14.12	34.44	51.44
3	99	137	247	238	360	697	14.20	34.15	51.65
4	122	169	298	293	434	849	14.37	34.51	51.12
5	94	130	228	226	332	652	14.42	34.66	50.92
6	109	153	269	265	392	766	14.22	34.60	51.18
7	109	149	262	259	382	750	14.54	34.53	50.93
8	114	159	282	276	411	801	14.23	34.46	51.31
9	108	154	272	267	397	772	14.18	34.59	51.43
10	114	165	291	286	424	824	13.83	34.71	51.46

Table 20

	Area			fA		ΣfA	(fA/ΣfA) x 100		
	ISO	BUAC	BUOH	BUAC	BUOH		ISO	BUAC	BUOH
1	62	109	129	189	188	439	14.12	43.05	42.83
2	113	200	233	347	340	800	14.12	43.38	42.50
3	115	198	229	344	334	793	14.50	43.38	42.12
4	119	209	245	363	357	839	14.18	43.27	42.55
5	106	187	219	324	319	749	14.15	43.26	42.59
6	126	218	254	378	370	874	14.42	43.25	42.33
7	110	194	226	337	330	771	14.16	43.37	42.47
8	111	191	223	331	325	767	14.47	43.16	42.37
9	122	216	253	375	369	866	14.09	43.30	42.61
10	28	49	56	85	81.6	195	14.35	43.59	42.06

Appendix A4

(Cont'd.)

Table 21

	Area			fA		Σ fA	(fA/ΣfA) x 100		
	ISO	BUAC	BUOH	BUAC	BUOH		ISO	BUAC	BUOH
1	106	229	178	397	260	763	13.89	52.03	34.08
2	130	286	222	496	324	950	13.68	52.21	34.11
3	103	218	170	378	248	729	14.13	51.85	34.02
4	99	208	163	361	238	698	14.18	51.72	34.10
5	115	249	197	432	287	834	13.79	51.80	34.41
6	109	225	178	390	260	759	14.36	51.38	34.24
7	104	222	177	385	258	747	13.92	51.54	34.54
8	126	269	209	467	305	898	14.03	52.00	33.97
9	103	223	175	387	255	745	13.82	51.95	34.23
10	119	247	195	429	284	832	14.31	51.56	34.13

Table 22

	Area			fA		Σ fA	(fA/ΣfA) x 100		
	ISO	BUAC	BUOH	BUAC	BUOH		ISO	BUAC	BUOH
1	93	236	119	409	174	676	13.76	60.50	25.74
2	107	262	134	455	195	757	14.13	60.11	25.76
3	108	267	136	463	198	769	14.04	60.21	25.75
4	118	293	148	508	216	842	14.02	60.33	25.65
5	106	261	131	453	191	750	14.13	60.40	25.47
6	102	250	126	434	184	720	14.14	60.28	25.56
7	112	280	142	486	207	805	13.92	60.37	25.71
8	124	305	153	529	223	876	14.15	60.39	25.46
9	99	250	130	434	190	723	13.69	60.03	26.28
10	132	325	163	564	238	934	14.13	60.39	25.48

Appendix A4

(Cont'd.)

Table 23

	Area			fA		ΣfA	(fA/ΣfA) x 100		
	ISO	BUAC	BUOH	BUAC	BUOH		ISO	BUAC	BUOH
1	103	292	89	507	130	740	13.92	68.51	17.57
2	110	309	983	536	136	782	14.07	68.54	17.39
3	124	353	106	612	155	891	13.91	68.69	17.40
4	114	312	94	541	137	792	14.39	68.31	17.30
5	128	354	106	614	155	897	14.27	68.45	17.28
6	92	257	76	446	111	649	14.18	68.72	17.10
7	132	371	111	644	162	938	14.07	68.66	17.27
8	131	376	111	652	162	945	13.86	69.00	17.14
9	107	313	95	543	139	789	13.56	68.82	17.62
10	83	238	69	413	101	597	13.90	69.18	16.92

Table 24

	Area			fA		ΣfA	(fA/ΣfA) x 100		
	ISO	BUAC	BUOH	BUAC	BUOH		ISO	BUAC	BUOH
1	103	313	42	543	61.2	707	14.54	76.80	8.66
2	99	321	44	557	64.2	720	13.75	77.36	8.89
3	95	299	40	519	58.3	672	14.14	77.23	8.63
4	107	328	48	569	70.0	746	14.35	76.27	9.38
5	115	366	49	635	71.4	821	14.01	77.34	8.65
6	104	326	44	566	64.2	734	14.17	77.17	8.72
7	139	438	59	760	86.0	985	14.11	77.16	8.73
8	108	343	45	595	65.6	769	14.05	77.37	8.58
9	84	293	39	508	56.9	649	12.84	78.38	8.78
10	109	356	48	618	70.0	797	13.68	77.54	8.78

Appendix A4

(Cont'd.)

Table 25

	Area			fA		Σ fA	(fA/ΣfA) x 100		
	ISO	BUAC	BUOH	BUAC	BUOH		ISO	BUAC	BUOH
1	100	345	23	599	33.5	733	13.64	81.72	4.64
2	109	373	27	647	39.4	795	13.71	81.38	4.91
3	107	355	25	616	36.5	760	14.08	81.05	4.87
4	110	361	24	626	35.0	771	14.27	81.19	4.54
5	102	340	22	590	32.1	724	14.09	81.49	4.42
6	88	283	20	491	29.2	608	14.47	80.76	4.77
7	101	343	23	595	33.5	730	13.83	81.51	4.66
8	168	545	41	946	59.8	1174	14.33	80.58	5.09
9	120	399	27	692	39.4	851	14.10	81.32	4.58
10	107	356	24	618	35.0	760	14.07	81.32	4.61

Table 26

	Area			fA		Σ fA	(fA/ΣfA) x 100		
	ISO	BUAC	BUOH	BUAC	BUOH		ISO	BUAC	BUOH
1	116	404	-	701	-	817	14.20	85.80	-
2	126	437	-	758	-	884	14.25	85.75	-
3	106	362	-	628	-	734	14.44	85.56	-
4	120	418	-	725	-	845	14.20	85.80	-
5	113	389	-	675	-	788	14.34	85.66	-
6	109	373	-	647	-	756	14.42	85.58	-
7	93	318	-	552	-	645	14.42	85.58	-
8	88	308	-	534	-	622	14.15	85.85	-
9	143	497	-	862	-	1005	14.23	85.77	-
10	101	351	-	609	-	710	14.23	85.77	-

Appendix A4

(Cont'd.)

Summary of the mean values of $\frac{fA}{\Sigma fA} \times 100$

Table 27

Table No.	$(fA/\Sigma fA) \times 100$			Table No.	$(fA/\Sigma fA) \times 100$		
	ISO	ETAC	ETOH		ISO	BUAC	BUOH
1	14.29	-	85.71	14	14.29	-	85.71
2	14.02	4.41	81.57	15	14.36	4.60	81.04
3	14.06	8.82	77.12	16	14.24	8.97	76.79
4	13.98	17.81	68.21	17	14.28	17.25	68.47
5	14.09	26.42	59.49	18	14.12	26.20	59.68
6	14.01	34.57	51.42	19	14.18	34.56	51.26
7	14.04	43.58	42.38	20	14.26	43.30	42.44
8	14.03	51.23	34.74	21	14.01	51.80	34.19
9	14.10	60.55	25.35	22	14.01	60.30	25.69
10	14.05	69.78	16.17	23	14.01	68.69	17.30
11	13.97	77.66	8.37	24	13.97	77.25	8.78
12	14.03	81.44	4.53	25	14.06	81.23	4.71
13	14.30	85.70	-	26	14.29	85.71	-

Appendix A4

(Cont'd.)

% Error of ETAC, ETOH

Table 28

	Weighed Per Cent			(fA/ΣfA) x 100			Error %		
	ISO	ETAC	ETOH	ISO	ETAC	ETOH	ISO	ETAC	ETOH
1	14.29	0.00	85.71	14.29	0.00	85.71	0.00	0.00	0.00
2	14.29	4.40	81.31	14.02	4.41	81.57	1.89	-0.23	-0.32
3	14.28	8.71	77.01	14.06	8.82	77.12	1.26	-1.26	-0.14
4	14.29	17.64	68.07	13.98	17.81	68.21	2.17	-0.96	-0.79
5	14.29	25.95	59.79	14.09	26.42	59.49	1.40	-1.81	0.50
6	14.29	34.29	51.42	14.01	34.57	51.42	1.96	-0.82	0.00
7	14.28	42.87	42.85	14.04	43.58	42.38	1.68	-1.67	1.14
8	14.29	51.35	34.36	14.03	51.23	34.74	1.82	0.23	-1.11
9	14.29	59.80	25.91	14.10	60.55	25.35	1.33	-1.25	2.16
10	14.29	69.32	16.39	14.05	69.78	16.17	1.68	-0.66	1.34
11	14.29	77.18	8.53	13.97	77.66	8.37	2.17	-0.62	1.88
12	14.29	81.28	4.64	14.03	81.44	4.53	1.82	-0.20	2.03
13	14.28	85.72	0.00	14.30	85.70	0.00	-0.14	0.02	0.00

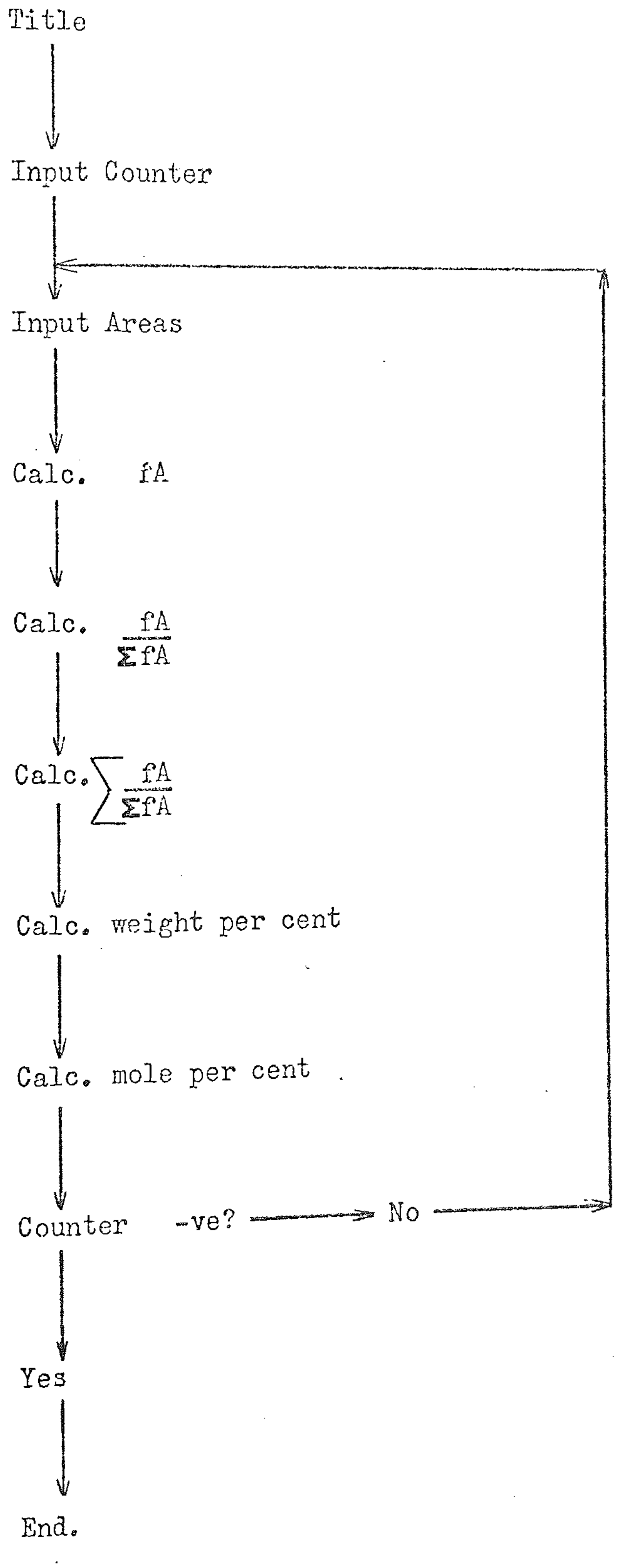
% Error of BUAC, BUOH

Table 28

	Weighed Per Cent			(fA/ΣfA) x 100			Error %		
	ISO	BUAC	BUOH	ISO	BUAC	BUOH	ISO	BUAC	BUOH
14	14.29	0.00	85.71	14.29	0.00	85.71	0.00	0.00	0.00
15	14.28	4.52	81.20	14.34	4.60	81.04	-0.56	-1.77	0.20
16	14.28	8.80	76.91	14.24	8.97	76.79	0.28	-1.93	0.16
17	14.28	17.07	68.64	14.28	17.25	68.47	0.00	-1.05	0.25
18	14.28	25.93	59.78	14.12	26.20	59.68	0.98	-1.04	0.17
19	14.28	34.25	51.47	14.18	34.56	51.26	0.70	-0.91	0.41
20	14.29	42.94	42.78	14.26	43.30	42.44	0.21	-1.02	0.79
21	14.28	51.33	34.38	14.01	51.80	34.19	1.89	-1.03	0.55
22	14.29	59.99	25.73	14.01	60.30	25.69	1.96	-0.52	0.16
23	14.28	68.51	17.21	14.01	68.69	17.30	1.89	-0.26	-0.64
24	14.28	77.10	8.61	13.97	77.25	8.78	2.17	-0.19	-1.97
25	14.29	81.09	4.63	14.06	81.23	4.71	0.91	-0.17	-1.73
26	14.29	85.71	0.00	14.29	85.71	0.00	0.00	0.00	0.00

Appendix A5

Analysis programme - flow diagram



Appendix A5

(Cont'd.)

Analysis Programme

```
    RETAIN 1+
    1-
    ANALYSIS
    RUN
    NO
    INDEX
16  INP
17  C20-
18  D+
19  INP
20  C10-
21  TYPE
22  INP
23  TYPE
24  525-
25  M6-
26  C11-
27  A10-
28  C10-
29  INP
30  TYPE
31  533-
32  M7-
33  C12-
34  A10-
35  C10-
36  INP
37  TYPE
38  540-
39  M8-
40  C13-
41  A10-
42  C10-
43  INP
44  TYPE
45  D+
46  548-
47  M9-
48  C14-
49  A10-
50  C10-
51  L11-
52  554-
53  D10-
54  C15-
55  L12-
56  558-
57  D10-
58  C16-
59  L13-
60  562-
61  D10-
62  C17-
63  L14-
64  566-
65  D10-
66  C18-
67  A17-
68  A16-
69  A15-
70  C19-
71  L15-
```

Store	Contents
0	100
1	88.11
2	46.07
3	116.16
4	74.12
5	-1.0
6	f_{ETAC}
7	f_{ETOH}
8	f_{BUAC}
9	f_{BUOH}
10	$\sum fA$
11	$(fA)_{ETAC}$
12	$(fA)_{ETOH}$
13	$(fA)_{BUAC}$
14	$(fA)_{BUOH}$
15	wt% ETAC
16	wt% ETOH
17	wt% BUAC
18	wt% BUOH
19	$\left({}^{fA}/_{\sum fA}\right)$
20	N

Appendix A5

(Cont'd.)

```
72   | 575-
73   | D19-
74   | MO-
75   | TYPE
76   | 578-
77   | D1-
78   | C15-
79   | L16-
80   | 583-
81   | D19-
82   | MO-
83   | TYPE
84   | 586-
85   | D2-
86   | C16-
87   | L17-
88   | 591-
89   | D19-
90   | MO-
91   | TYPE
92   | 594-
93   | D3-
94   | C17-
95   | L18-
96   | 599-
97   | D19-
98   | MO-
99   | TYPE
100  | 5102-
101  | D4-
102  | C18-
103  | A17-
104  | A16-
105  | A15-
106  | C19-
107  | D+
108  | L15-
109  | 5112-
110  | D19-
111  | MO-
112  | TYPE
113  | L16-
114  | 5117-
115  | D19-
116  | MO-
117  | TYPE
118  | L17-
119  | 5122-
120  | D19-
121  | MO-
122  | TYPE
123  | L18-
124  | 5127-
125  | D19-
126  | MO-
127  | TYPE
128  | D+
129  | L20-
130  | A5-
131  | C20-
132  | G134-
133  | 719-
134  | RETAIN
```

This programme was executed on the Department's PDS 1020 Computer.

Appendix B1

Typical Calculation - Reaction Rates

$$\text{Now } C = \left[(a+b)^2 - 4ab\left(1 - \frac{1}{K}\right)\right] \qquad 3.18$$

$$\text{and } Y = \frac{1}{\sqrt{C}} \ln\left[\frac{2ab - x(a+b - \sqrt{C})}{2ab - x(a+b + \sqrt{C})}\right] \qquad 3.19$$

Abstracting the data from reaction rate series K1.1

time t	mole fractions			
	ETAC (x)	ETOH (a)	BUAC (b)	BUOH (x)
0	0.0000	0.4822	0.5108	0.0062
50	0.0674	0.4281	0.4309	0.0728

The average value of x :-

$$\frac{0.0674 + (0.0728 - 0.0062)}{2} = 0.0670$$

substitute in 3.18 using mole fractions

$$C = \left[(0.4722 + 0.5108)^2 - 4 \times 0.4822 \times 0.5106 \quad 1 - \frac{1}{0.96}\right]$$

$$C = 0.986 - 4 \times 0.4822 \times 0.5106\ (-\ 0.042)$$

$$\underline{C = 1.0274}$$

Initial Concentrations

	Volume (cm^3)	Moles	Concentration (g mole litre^{-1})
ETOH	758	4	5.2742
BUAC		4	5.2742
H_2SO_4	0.4		

Substitute in 3.18 using g mole litre^{-1}

$$\text{Hence } C = \sqrt{\left[10.5484 + 5.2742 \times 5.2742 \times 4 \times \left(1 - \frac{1}{0.96}\right)\right]}$$

$$C = (10.5484 + 111.2728 \times 0.0417)^{\frac{1}{2}}$$

$$C = (15.1887)^{\frac{1}{2}}$$

$$\underline{C = 3.8973} \quad \text{g mole litre}^{-1}$$

Appendix B1

(Cont'd.)

substitute in 3.19

$$Y = \frac{1}{3.8973} \ln \left[\frac{0.4925 - 0.067\,(0.993 - 1.013)}{0.4925 - 0.067\,(0.993 + 1.013)}\right]$$

$$Y = \frac{1}{3.8973} \ln \left[\frac{0.4925 + 0.00134}{0.4925 - 0.1345}\right]$$

$$Y = \frac{1}{3.8973} \ln 1.379$$

$$\underline{Y = 0.0825}$$

This value compares favourably with the value of 0.0817 calculated by the computer.

Appendix B2

The approximate and full form of the integrated rate equation

K3.1			K3.4		
time t min	$\ln\left[\frac{2ab-x(a+b-\sqrt{C})}{2ab-x(a+b+\sqrt{C})}\right]$	$\ln\frac{ab}{ab-x}$	time t min	$\ln\left[\frac{2ab-x(a+b-\sqrt{C})}{2ab-x(a+b+\sqrt{C})}\right]$	$\ln\frac{ab}{ab-x}$
0	0.0000	0.0000	0	0.0000	0.0000
15	0.0480	0.0478	10	0.2958	0.3016
30	0.0895	0.0891	20	0.6250	0.6291
45	0.1324	0.1328	30	0.9394	0.9494
60	0.1846	0.1847	40	1.2788	1.2969
75	0.2314	0.2311	50	1.5559	1.5865
90	0.2868	0.2867	60	1.8610	1.9091
110	0.3477	0.3477	70	2.0567	2.1186
120	0.3798	0.3805	80	2.2410	2.3182
135	0.4256	0.4266	90	2.6487	2.7781
150	0.4695	0.4706	100	3.0285	3.2414
165	0.5213	0.5224	110	3.1805	3.4385
180	0.5536	0.5550	120	3.4798	3.8634

Appendix C1

Vapour Liquid Equilibrium Flowrator Calibrations

Table 1 Ethyl Acetate

Scale No.	0 - 10 Scale			0 - 16 Scale		
	C N=1143	W=51.2C g min^{-1}	V cm^{3}min^{-1}	C N=770	W=34.5C g min^{-1}	V cm^{3}min^{-1}
2	-	-	-	0.0068	0.234	0.256
3	0.0056	0.287	0.314	0.0134	0.461	0.505
4	0.0215	1.100	1.205	0.0232	0.799	0.875
5	0.0370	1.892	2.070	0.0370	1.274	1.396
6	0.0590	3.020	3.310	0.0550	1.892	2.070
7	0.0830	4.240	4.640	-	-	-
8	0.1090	5.570	6.100	0.0940	3.285	3.540
10	0.1610	8.230	9.010	0.1380	4.750	5.200
12	-	-	-	0.1860	6.410	7.010
14	-	-	-	0.2370	8.160	8.940
16	-	-	-	0.2930	10.090	11.040

Table 2 Ethyl Alcohol

Scale No.	0 - 10 Scale			0 - 16 Scale		
	C N=421	W=48.1C g min^{-1}	V cm^{3}min^{-1}	C N=285	W=32.6C g min^{-1}	V cm^{3}min^{-1}
2	-	-	-	0.0026	0.083	0.104
3	0.0018	0.088	0.110	0.0048	0.156	0.195
4	0.0070	0.336	0.419	0.0078	0.254	0.316
5	0.0124	0.596	0.713	0.0129	0.420	0.523
6	0.0200	0.962	1.200	0.0208	0.677	0.844
7	0.0300	1.442	1.797	-	-	-
8	0.0430	2.070	2.580	0.0375	1.220	1.520
10	0.0750	3.600	4.490	0.0601	1.950	2.430
12	-	-	-	0.0900	2.930	3.650
14	-	-	-	0.1180	3.840	4.790
16	-	-	-	0.1500	4.880	6.080

Appendix C1

(Cont'd.)

Table 3 Butyl Acetate

Scale No.	0 - 10 Scale			0 - 16 Scale		
	C	W=50.6C	V	C	W=34.1C	V
	N=738	$g\ min^{-1}$	$cm^3 min^{-1}$	N=531	$g\ min^{-1}$	$cm^3 min^{-1}$
2	-	-	-	0.0048	0.164	0.184
3	0.0035	0.175	0.196	0.0092	0.314	0.352
4	0.0133	0.624	0.700	0.0155	0.529	0.592
5	0.0235	1.190	1.335	0.0253	0.864	0.969
6	0.0377	1.910	2.140	0.0390	1.330	1.490
7	0.0560	2.840	3.180	-	-	-
8	0.0775	3.940	4.420	0.0700	2.390	2.680
10	0.1260	6.380	7.150	0.1070	3.650	4.090
12	-	-	-	0.1500	5.120	5.740
14	-	-	-	0.1950	6.650	7.460
16	-	-	-	0.2430	8.240	9.240

Table 4 Butyl Alcohol

Scale No.	0 - 10 Scale			0 - 16 Scale		
	C	W=48.6C	V	C	W=32.8C	V
	N=176	$g\ min^{-1}$	$cm^3 min^{-1}$	N=119	$g\ min^{-1}$	$cm^3 min^{-1}$
2	-	-	-	0.0011	0.034	0.042
3	-	-	-	0.0020	0.066	0.081
4	0.0029	0.141	0.172	0.0033	0.107	0.131
5	0.0053	0.257	0.313	0.0054	0.176	0.214
6	0.0083	0.407	0.495	0.0085	0.279	0.340
7	0.0125	0.607	0.738	-	-	-
8	0.0180	0.875	1.065	0.0158	0.519	0.631
10	0.0315	1.530	1.863	0.0243	0.797	0.970
12	-	-	-	0.0370	1.213	1.477
14	-	-	-	0.0485	1.592	1.935
16	-	-	-	0.0645	2.120	2.580

Appendix C2

The holdup time in the vaporiser and preheaters

1) The Vaporiser

The volume of the liquid retained in the weir has been calculated (66) to be 7.6 cm^3.

Assuming a liquid film of 0.5 mm on the heating surface of the vaporiser, the holdup will be:-

$$2.2 \times \pi \times 35 \times 0.05 = 12.1 \text{ cm}^3$$

Thus the total vaporiser holdup = 19.7 cm^3.

Assuming that flowrates of 8-12 g min^{-1} are employed the holdup time is approximately 2-3 minutes.

2) The Superheater

$$\text{Volume} = \pi \times (0.07)^2 \times 18$$

$$= 27.6 \text{ cm}^3$$

Allowing for the end volume, total volume $\triangleq$ 33 cm^3.

The density of ethyl alcohol vapour (105 is 1.596 g $litre^{-1}$).

Taking a mean vaporisation rate of 10 g min^{-1}.

$$\text{Holdup time} = 33 \text{ cm}^3 \times \frac{\text{min}}{10\text{g}} \times 1.596 \frac{\text{g}}{\text{litre}} \times \frac{60\text{s}}{\text{min}} \times \frac{\text{litre}}{1000 \text{ cm}^3}$$

$$= \frac{33 \times 1.596 \times 60}{10 \times 1000}$$

$$= \underline{0.32\text{s.}}$$

3) The Liquid Preheater

$$\text{Volume} = (0.4)^2 \times \pi \times 35$$

$$= 17.6 \text{ cm}^3$$

20 cm^3 allowing for end volume.

Again the liquid flowrate was in the range 8-12 ml min^{-1}, the holdup time would be 2-3 minutes, and the holdup in the two feed heating sections would be approximately the same.

Appendix C3

Droplet Diameter Entrainment

With reference to the de-entrainer, the extreme operating conditions will be with a vaporisation rate of 10 g min^{-1} of ethyl alcohol, as ethyl alcohol is the component with the lowest molecular weight and thus it will have the highest vapour velocity per unit mass. At 78.5 °C, the density of saturated ethyl alcohol vapour

$$= 1.596 \text{ g litre}^{-1}$$

Hence the vapour rate = 104.4 cm^3 s^{-1}

Viscosity of ethyl alcohol vapour (105) = 93.5 micropoise

The free cross-sectional area of the de-entrainer

$$= \frac{\pi}{4} \text{ x } (3.7)^2 - \frac{\pi}{4} (2.6)^2$$

$$= 5.45 \text{ cm}^2$$

Thus the vapour velocity = 19.2 cm s^{-1}

From Heywood's correlation (106)

$$\frac{R}{\rho u^2} \text{ x } Re^{-1} = \frac{2 \quad g}{3\rho^2 u^3} \text{ x } (\rho_s - \rho)$$

where R = shear force per unit area.

Re = Reynolds number

g = gravitational constant

μ = vapour viscosity

ρ = vapour density

ρ_s = droplet density

u = vapour velocity

Thus $$\frac{R}{\rho u^2} \text{ x } Re = \frac{2 \text{ x } 93.5 \text{ x } 10^{-6} \text{ x } 981}{3 \text{ x } (19.2)^2 \text{ x } (1.596 \text{ x } 10^{-3})^2} \text{ x } 0.77$$

$$\frac{R}{\rho u^2} \text{ x } Re = 2.47$$

Appendix C3

(Cont'd.)

From the chart (106) the value of Re corresponding to this is 2.5

$$\text{Thus Re} = \frac{\rho u d}{\mu}$$

$$d = \frac{2.5 \times 93.5 \times 10^{-6}}{1.596 \times 10^{-3} \times 19.2}$$

$$\therefore \underline{d = 0.076 \text{ mm.}}$$

This represents the largest diameter of droplet which could be entrained.

Appendix C4

Pure component data for the vapour liquid equilibrium prediction programme.

1) Critical Temperature (^{o}K)

	T_c	reference
ETOH	516.0	(114)
ETAC	523.3	
BUOH	562.9	
BUAC	573.1	(117)

2) Critical Pressure (atm)

	P_c	reference
ETOH	63.0	(114)
ETAC	37.8	
BUOH	43.6	
BUAC	30.1	(117)

3) Critical Volume (mole litre^{-1})

	v_c	reference
ETOH	161.3	(114)
ETAC	286.0	
BUOH	223.3	
BUAC	397.8	(117)

4) Acentric Factor ω

		reference
ETOH	0.637	(114)
ETAC	0.373	
BUOH	0.667	
BUAC	0.455	

Appendix C4

(Cont'd.)

5) Homomorph Acentric Factor

	ω_H	reference
ETOH	0.152	(114)
ETAC	0.278	
BUOH	0.252	
BUAC	0.400	

6) Dipole Moments (Debye)

	μ_D	reference
ETOH	1.69	(116)
ETAC	1.78	
BUOH	1.65	
BUAC	1.68	

7) Association Factor

		reference
ETOH	1.10	(114)
ETAC	0.50	
BUOH	0.45	
BUAC	0.40	(est'd)

8) Vapour Pressure Data - Antoine equation constants

where $\ln P = A + \frac{B}{C + T}$

$P = \text{atm}, \quad T = {}^{o}K.$

	A	B	C	reference
ETAC	9.7221	-2867.8	-55.24	(101)
BUOH	10.4710	-3237.7	-89.25	(103)
BUAC	9.0568	-2845.6	-84.27	(104)

for ethyl alcohol the following equation was used where

$$\ln P = C_1 + \frac{C_2}{C_3 + T} + C_4 T + C_5 T^2 + C_6 \ln T.$$

P = atm, T = °K & $C_1 \longrightarrow C_6$ are constants the values of which are tabulated by Prausnitz et al (114).

9) Molar Volume Data

See Section 5.

Appendix D1

Feed Preheater Calculations

Assume a total feed throughput of 80 g min^{-1}.

Using the highest specific heat of all the components i.e. butyl acetate 0.68 cal g^{-1} deg^{-1}.

Assume that heat is required to raise liquid from room temperature (20°C) to highest boiling point (125°C).

Heat required = 0.68 x (125 - 20) x 80

= 5720 cal min^{-1}

= 400 watts.

With a 2 amp loading, the voltage will be 200 volts.

Resistance required = $\frac{200}{2}$ = 100 ohm.

Brightray Alloy C has a resistance of 5 ohm ft^{-1}.

Thus 20 ft wire required.

The glass tube diameter = $\frac{1}{2}$ in.

Thus number of turns = $20 \times 12 \times \frac{2}{\pi}$

= 153

Allowing 8 turns per inch maximum

Length of glass tube required = 17 inches.

Appendix D2

Distillation Column Feed Flowrator Calibrations

1) Butyl Acetate:-

Using a $\frac{1}{8}$ in dia., 0-16 scale tube with a stainless steel float,

$$N_{16} = \frac{A}{\mu} \sqrt{(\rho_F - \rho)\,\rho}$$

where A = Size factor

μ = viscosity of the fluid

ρ_F = density of the float ($g\ cm^{-3}$)

ρ = density of the fluid ($g\ cm^{-3}$)

N = viscous influence number

substituting

$$N_{16} = \frac{404}{0.675} \sqrt{(8.02 - 0.879)\ 8.02}$$

$$\underline{N_{16} = 1500}$$

The mass flowrate is related to the densities:-

$$W = CB \sqrt{(\rho_F - \rho)\,\rho}$$

where W = mass flowrate ($g\ min^{-1}$)

C = flow coefficient

B = size factor

substituting

$$W = 76.8\ C\ (3.02 - 0.879)\ 8.02$$

$$\underline{W = 192\ C} \quad g\ min^{-1}$$

From Fisher & Porter's Manual (99) the values of C against N are tabulated.

Table D2.1 Flowrator scale number against flowrate

Scale No.	C @ N=1500	W=192C g min^{-1}	V $cm^3 min^{-1}$
0	0.0000	0.0	0
2	0.0065	1.3	1.4
3	0.0169	3.3	3.7
4	0.0340	6.5	7.5
5	0.0540	10.4	11.8
6	0.0730	14.0	16.0
8	0.1160	22.3	25.4
10	0.1670	32.1	36.5
12	0.2150	41.3	47.0
14	0.2650	50.9	58.0
16	0.3180	61.2	69.6

2) Ethyl Alcohol:-

Using the same calculation procedure:

$N = 806$

$W = 183.7\ C \quad g\ min^{-1}$

Table D2.2 Flowrator scale number against flowrate

Scale No.	C @ N=806	W=183.7C g min^{-1}	V $cm^3 min^{-1}$
0	0.0000	0.0	0.0
2	0.0036	0.7	0.8
3	0.0093	1.7	2.2
4	0.0189	3.5	4.4
5	0.0395	7.3	9.2
6	0.0505	9.3	11.8
8	0.0880	16.2	20.5
10	0.1340	24.7	31.2
12	0.1780	32.7	41.3
14	0.2250	41.4	52.3
16	0.2760	50.6	64.0

Appendix D2

(Cont'd.)

3) Sulphuric Acid

Using the same calculation procedure:-

$N = 50.5$

$W = 259\ C \quad g\ min^{-1}$

Table D2.3 Flowrator scale number against flowrate

Scale No.	C @ $N=50.5$	$W=259C$ $g\ min^{-1}$	V $cm^3 min^{-1}$
0	0.00000	0.000	0.00
3	0.00052	0.135	0.07
4	0.00115	0.298	0.16
5	0.00195	0.506	0.28
6	0.00305	0.792	0.43
8	0.00600	1.554	0.85

Appendix D3

Calculation of Diffusion Coefficients

Wilke & Chang (150) have demonstrated that the diffusion coefficient of a component dissolved in an associated liquid can be predicted from the equation

$$D = 7.4 \times 10^{-8} \left(x M\right)^{\frac{1}{2}} \frac{T}{\mu V^{0.6}} \qquad cm^2 s^{-1}$$

where D = diffusion coefficient

x = an association parameter

T = absolute temperature

M = molecular weight

μ = solution viscosity

V = molecular volume of the diffusion component.

However, for small concentrations of the diffusing component in a given solvent at a fixed temperature, the equation can be reduced to $D = \frac{C}{V^{0.6}} \qquad cm^2 s^1$

where C = a constant

substituting the component properties.

(a) Ethyl Alcohol $D = \frac{C}{(62.6)^{0.6}} = 0.0833C$

(b) Ethyl Acetate $D = \frac{C}{(119)^{0.6}} = 0.0569C$

(c) Butyl Alcohol $D = \frac{C}{(99.8)^{0.6}} = 0.0632C$

(d) Butyl Acetate $D = \frac{C}{(147.8)^{0.6}} = 0.0501C$