A STUDY OF THE SEPARATION OF C_2-HYDROCARBONS AND THE ASSOCIATED PHASE EQUILIBRIA

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by

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ABSTRACT

Phase equilibrium data for the C_2-hydrocarbons and the solubilities of mixtures of these gases in acetone at low temperatures have been obtained at atmospheric pressure using a flow cell. The data was shown to be thermodynamically consistent, but attempts to provide a theoretical correlation for the results were unsuccessful.

Absorption and distillation columns were designed, using the experimental data, to enable C_2-hydrocarbon feedstocks to be separated into their constituents. Sieve-plate columns were erected and trials were made to substantiate the design calculations and to permit a comparison of the proposed separation methods. For high acetylene content feedstocks, absorption was shown to be satisfactory. For low acetylene content feedstocks, distillation and distillation with a side-stream provided good solutions and a computer programme was written to permit verification and extension of the results to the desired product purities. The programme reproduced the experimental results, but failure to predict plate efficiencies in the region of the pure components and to obtain a satisfactory correlation for the experimental phase equilibrium data made a complete solution impossible. Nevertheless it is considered that sufficient data has been presented to provide an adequate foundation for the design of physical separation processes to solve the problem under consideration.

Acknowledgments

I should like to thank Professor R. W. H. Sargent for his interest, help, and encouragement during the course of this work. In particular I wish to acknowledge the amount of time that he has devoted to the development of the computer programmes described in this thesis.

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Chapter 1

INTRODUCTION

The expansion of the world's chemical industry has recently been dominated by petrochemicals. The foundations of the petrochemical industry are the olefins and of these ethylene,[19] with its wide variety of derivatives, Fig. 1:1, is the most important.

Initially ethylene was recovered from refinery off-gas streams and used for the manufacture of ethylene oxide and ethyl alcohol. During the second World War the importance of synthetic rubber, in particular the butadiene-styrene co-polymer, led to a large expansion in ethylene production. This expansion was accelerated after the war with the introduction of polyethylene. To meet the growing demand for ethylene, plants designed for thermal cracking of feedstocks ranging from ethane to crude oil have been installed.

In the separation of ethylene from by-product streams ethane and propane are recovered and used as feedstock to tubular cracking furnaces. The severity of operations necessitates the use of alloy steel tubes and the addition of steam to minimize coke formation.[20] The reactions are arrested by water quenching in spray towers.

Heavier feedstocks, such as naphtha, give complex mixtures of products with a low ethylene yield. Severe operating conditions improve the yields but increase the tendency to coke. Different cracking techniques using pebble heaters, fluidized sand beds, the Catarole process, etc.[19] overcome the inherent disadvantages of the tubular furnace and

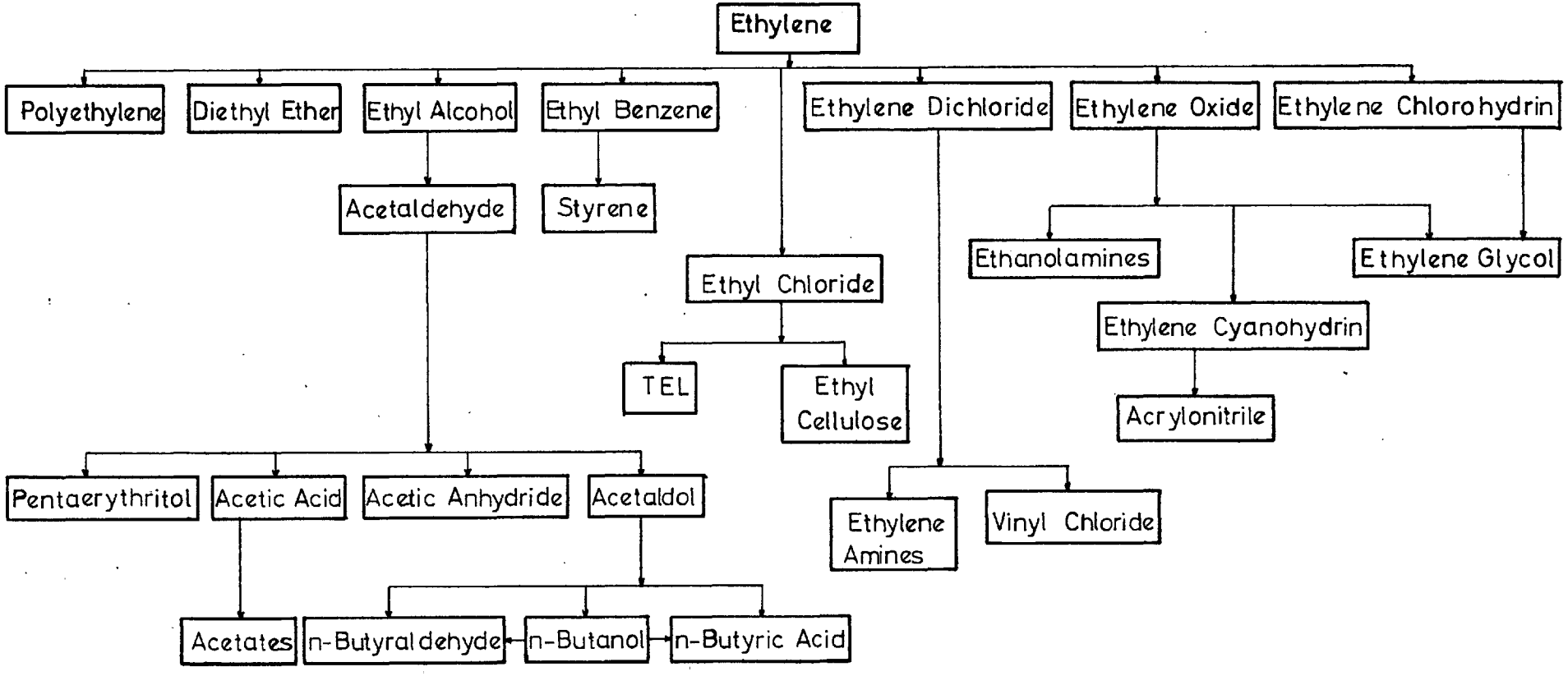


FIGURE 1:1

MAJOR DERIVATIVES OF ETHYLENE

improve the product yield.

In autothermic cracking the endothermic heat of cracking is supplied by partial combustion of the feed. Recently several processes for the simultaneous production of acetylene and ethylene, with emphasis on the former, have used this principle e.g. the S.B.A.-Kellogg process.[64]

In Fig. 2:1 a typical flowsheet for the manufacture of ethylene from refinery off-gas is given. The feedstock and cracked gas are compressed to 100-200 p.s.i.g. The heavy material in the feed, along with the bulk of the C_4 fraction, is thus condensed and removed. Acid gases and acetylene are then removed by scrubbing and catalytic hydrogenation, respectively. The gases are then compressed to 400-600 p.s.i.g., cooled and dried.

The purified gas is fed to a series of fractionators characterized by low temperature overhead conditions and elaborate heat exchange between the feed and product streams. The top product from the demethanizer is used as a fuel gas. Ethane and propane are fed to the cracking furnaces. Propylene is used for polypropylene and the C_4 stream for butadiene.

The demethanization stage has also been performed by aromatic oil absorption and by hypersorption. In the latter the light hydrocarbons are adsorbed on a moving bed of activated charcoal and selectively desorbed.[41]

About 25% of the ethylene so produced is consumed in the manufacture of polyethylene.[84] The original I.C.I. process operated

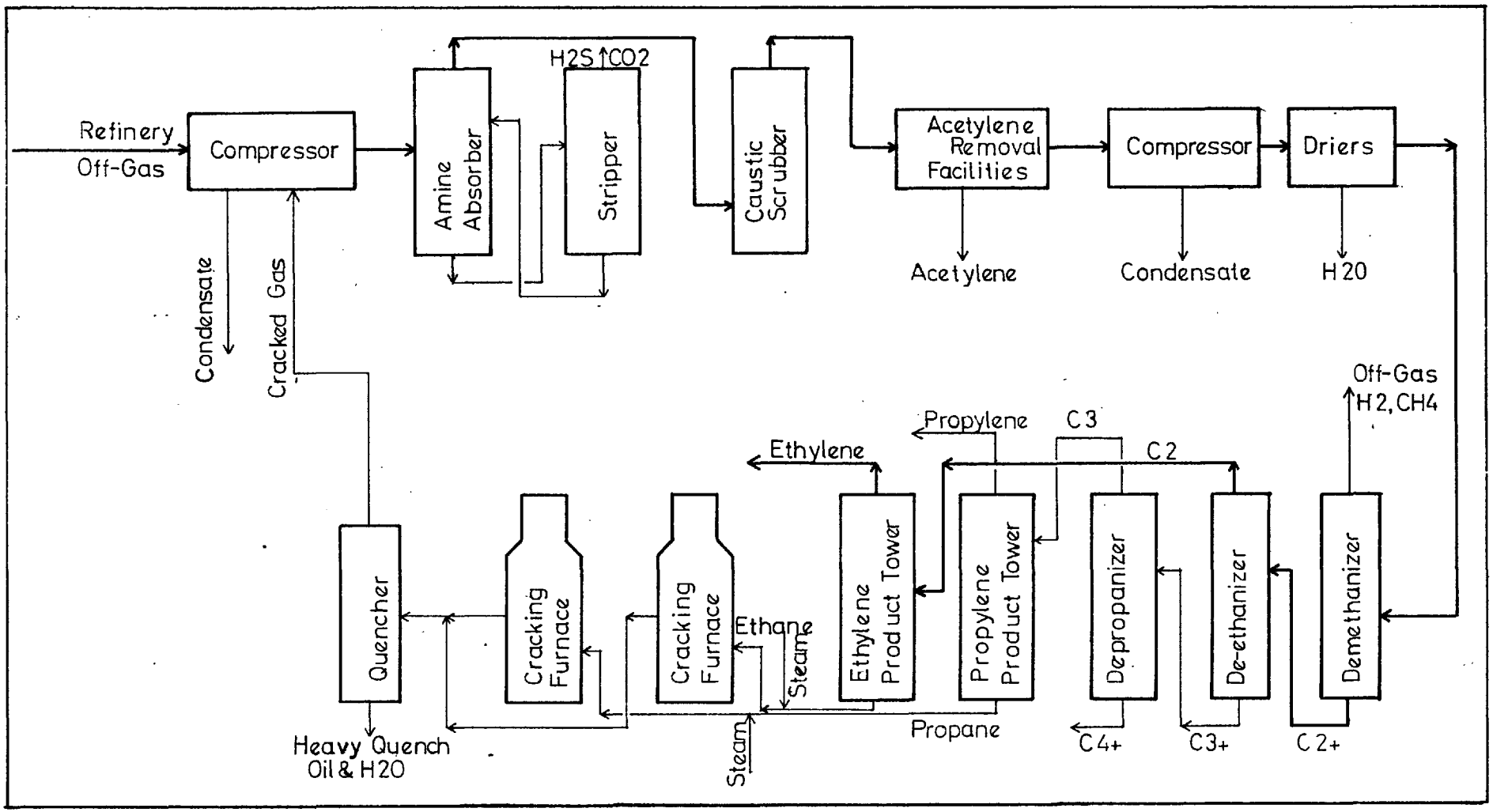


FIGURE 2:1

ETHYLENE FROM REFINERY OFF-GAS STREAMS

at 500 to 3,000 atmospheres and was used exclusively from 1943-1956. Free radical yielding catalysts such as organic peroxy compounds give a 25% conversion to the polymer at 1500 atmospheres and 375°F. The plant investment costs, however, are high and the product has a low softening temperature.

High density products, produced at lower operating pressures and characterized by more regularly ordered structures, have higher softening temperatures and greater strength and now account for about one third of the total process capacity. These low pressure processes (1-100 atm.) employ sensitive catalysts which are deactivated by impurities such as acetylenes, diolefins, and acid gases.[19, 72, 80] The ethylene stream is usually subjected to catalytic hydrogenation to reduce the acetylene concentration to 10 p.p.m. The process is applied to the crude gas early in the purification sequence to take advantage of the hydrogen present in the stream. Cobalt-molybdate or nickel-cobalt-chromium complexes are used as hydrogenation catalysts. The sensitivity of the former is enhanced by the presence of sulphur and steam and hydrogenation is carried out prior to the removal of acid gases. If butadiene is to be recovered, the nickel catalyst is used to reduce the acetylene concentration to 100 p.p.m. and final cleaning takes place from the ethylene product stream over a palladium catalyst.

Recently some interest has been shown in the possibility of acetylene removal and recovery by physical processes. Little work, however, has been done on the phase equilibria of the constituents of the furnace effluent streams. It has therefore been impossible to present either analyses or comparisons of the possible separation

processes.

Stanton[85] has compared catalytic hydrogenation with solvent extraction and arrived at the conditions of plant capacity and acetylene concentration at which acetylene recovery by extraction could profitably be undertaken.

Schutt[80] describes a plant for acetylene removal from ethylene using acetone as an absorption agent. He considers that this process would have low investment and running costs and would be economical for small ethylene plants.

In the Hoechst high temperature process and the Eastman process[64] acetylene and ethylene are produced simultaneously and selective absorption agents and hypersorption are used to recover both gases at high purities.

From the above it would seem that an experimental investigation into the separation of acetylene from ethylene and ethane would be worthwhile. The introduction of carbon dioxide etc. would needlessly complicate the problem, as these gases are adequately removed in existing plant.

There are numerous chemical compounds which exhibit a high solvent power for acetylene and a high selectivity between acetylene and ethylene.[80]

TABLE I:1

SOLVENT NAME	ATM. BOILING PT. °F	MELTING PT. °F	C_2H_2 SOLUBILITY @ 60°F NCF GAS/CF SOLVENT
METHYLAL	111.2	-156.0	27.2
ETHYL FORMATE	129.2	-110.2	21.5
ACETONE	133.7	-138.0	27.1
METHYL ACETATE	134.8	-145.5	26.8
ETHYL ACETATE	170.8	-116.4	22.7
METHYL PROPIONATE	175.4	-125.5	16.6
ACETONITRILE	178.8	- 46.0	17.8
1,4 DIOXANE	215.0	+ 53.0	19.7
MORPHOLINE	262.2	-	19.2
PROPIONIC ACID	285.8	- 7.5	26.8
DIMETHYL FORMAMIDE	307.0	- 78.0	40.5
ACETONYL ACETONE	379.4	+ 15.8	17.6
BUTYROLACTONE	402.8	- 62.0	17.1
METHYL PYRROLIDONE	395.6	- 11.5	44.2

These solvents may be classified into two groups, the more volatile compounds boiling below 100°C and the less volatile boiling above this temperature. In the first group the selection is made on economic grounds and acetone seems to be the most satisfactory. In the second group dimethyl formamide combines a low melting point with a high solvent power. For acetylene recovery the lower boiling point of acetone indicates a greater heat economy when using low temperature

processes. Acetone has therefore been used as the absorption medium where necessary.

Preliminary surveys of the available physical data for C_2-hydrocarbon equilibria (Chapter 2) indicate that low pressure separation processes would be more likely to yield satisfactory results. In addition, the increasing importance of low temperature technology has naturally led to the choice of an atmospheric pressure system for this study.

Two possible lines of attack exist for the solution of the problems outlined above.

In the first, many types of separation process would be tested experimentally in a versatile stagewise contactor. A detailed study of the more satisfactory methods could then be made.

In the second approach the phase equilibria of the C_2-hydrocarbons would be investigated. From an analysis of these results equipment could be designed and constructed to give the desired results. The former would involve many fruitless lines of research and could omit the best solution. The second procedure is more logical and was adopted.

PART I - Phase Equilibria

Chapter 2

REVIEW OF PREVIOUS WORK

2:1 Previous vapour-liquid equilibrium data

A limited amount of equilibrium data is available for the C_2-hydrocarbon systems, but previous investigators have usually worked at elevated pressures.

Kharakhorin[40] studied the ethane-ethylene system using a circulation method. The data is comprehensive between 0 and - 103.8°C corresponding to pressures from 0.5 to 40 atmospheres. Moran[55] used the dew and bubble-point method. The results were interpolated to give isobars from 0.25 to 2.0 atmospheres. The dew-point measurements are in fairly good agreement with those of Kharakhorin. The bubble-points, however, show wide random discrepancies which were not accounted for. Hanson et. al.[31] used a forced circulation equilibrium apparatus and the results are represented as isotherms at 0, -40 and -100°F.

Kuenen[42] observed azeotropic behaviour in the ethane-acetylene system. The data is of little use for quantitative calculations because of impurities which apparently entered the system.

Churchill et. al.[10] extended Kuenen's study of critical loci and border curves to the ethylene-acetylene system. These investigators used a rotating glass-windowed cell and discovered that the system is azeotropic at high pressures. The critical loci for the C_2-hydrocarbons are shown in Fig. 1:2. The critical locus and border curve, for the

68 mole % ethane mixture with acetylene, after Kuenen,[42] is given in Fig. 2:2.

McMillan[53] fractionally distilled acetylene-ethane mixtures at atmospheric pressure. He reported the existence of an azeotrope containing 40.8 mole % of acetylene boiling at - 94.5°C. Clark and Din[13] measured the vapour pressures, initial freezing points, and the condensation pressures of binary mixtures of acetylene with ethylene and ethane. From the results the phase diagrams given in Fig. 3:2 were obtained. The authors concluded that the acetylene-ethane azeotrope is suppressed at atmospheric pressure by the separation of a solid phase. Nevertheless at this pressure a vapour of constant composition would be obtained due to the invariance of a three-phase mixture in a binary system. This vapour would contain 40% acetylene at -95.8°C. No indication of azeotropic behaviour in the acetylene-ethylene system was found.

Rowlinson and Sutton used[75] the statistical thermodynamics of non-spherical molecules to predict the azeotropic compositions for these systems. By assuming that the deviations from ideality are due to a lack of balance of the central forces they obtained good agreement with empirical observation.

McCurdy and Katz[51] studied the three component system at 40 and 60°F. The static method was used and samples were analysed by gas absorption methods. The point 40°F is below

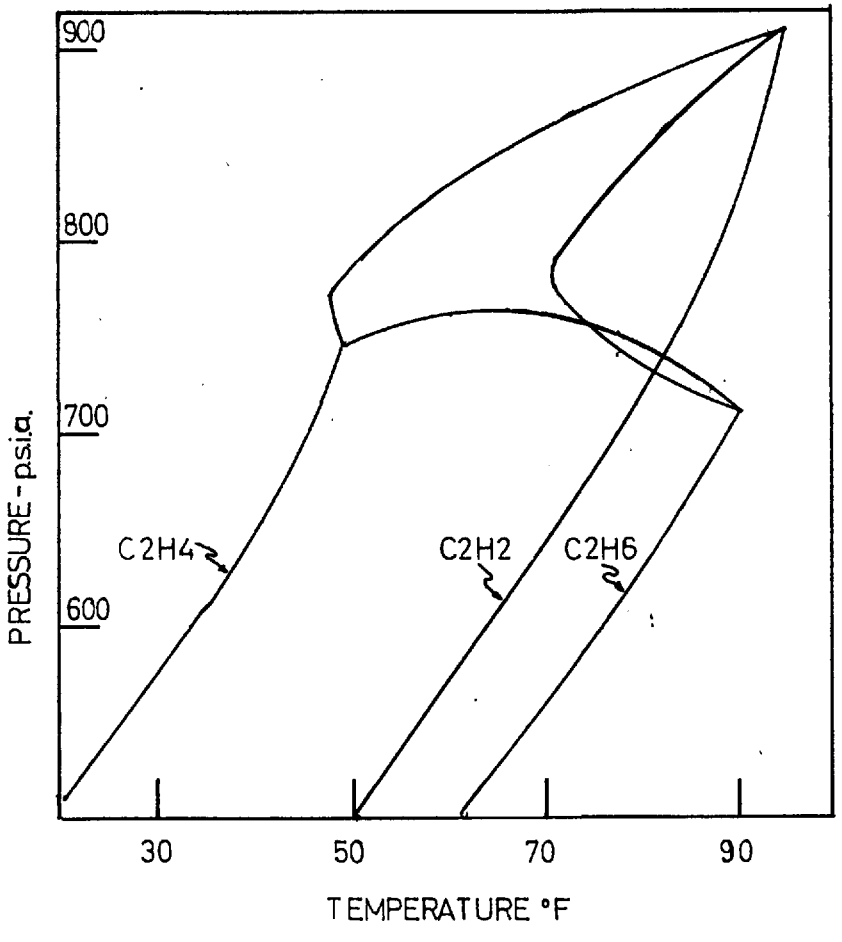


FIGURE 1:2

CRITICAL LOCI OF C2 HYDROCARBONS

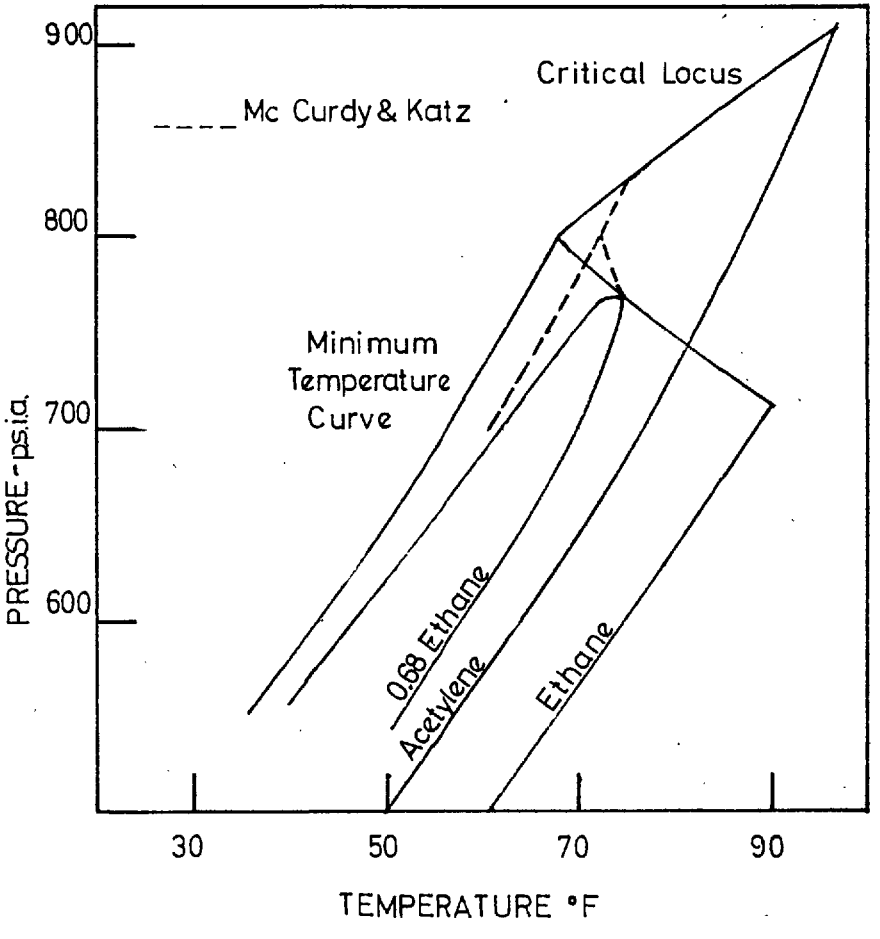
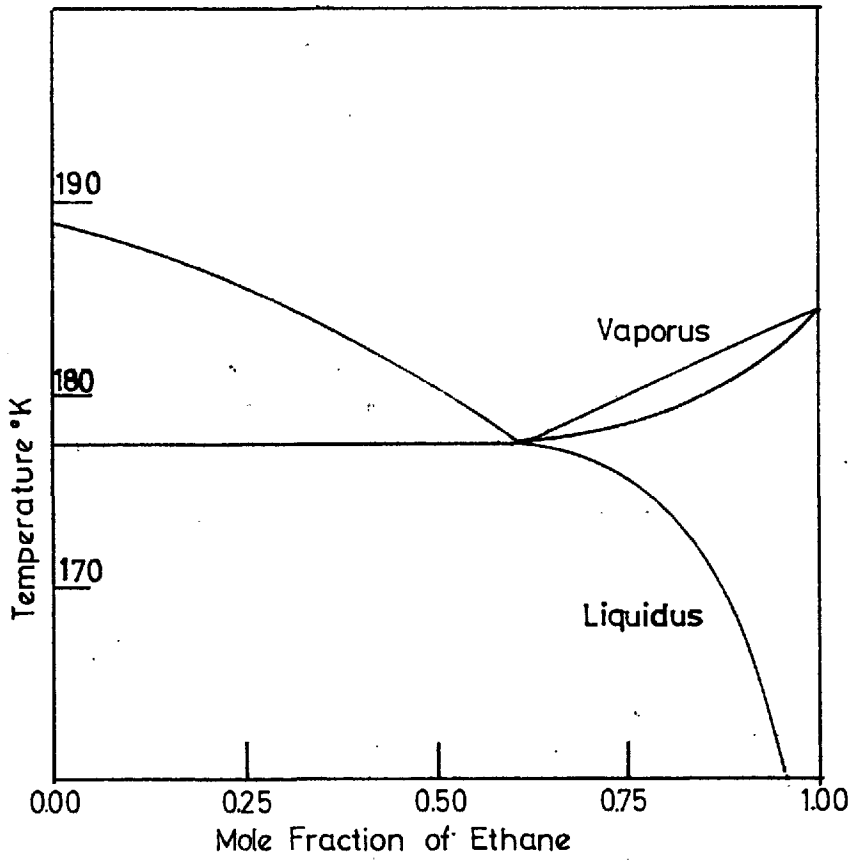


FIGURE 2:2

ACETYLENE-ETHANE SYSTEM AFTER KUENEN



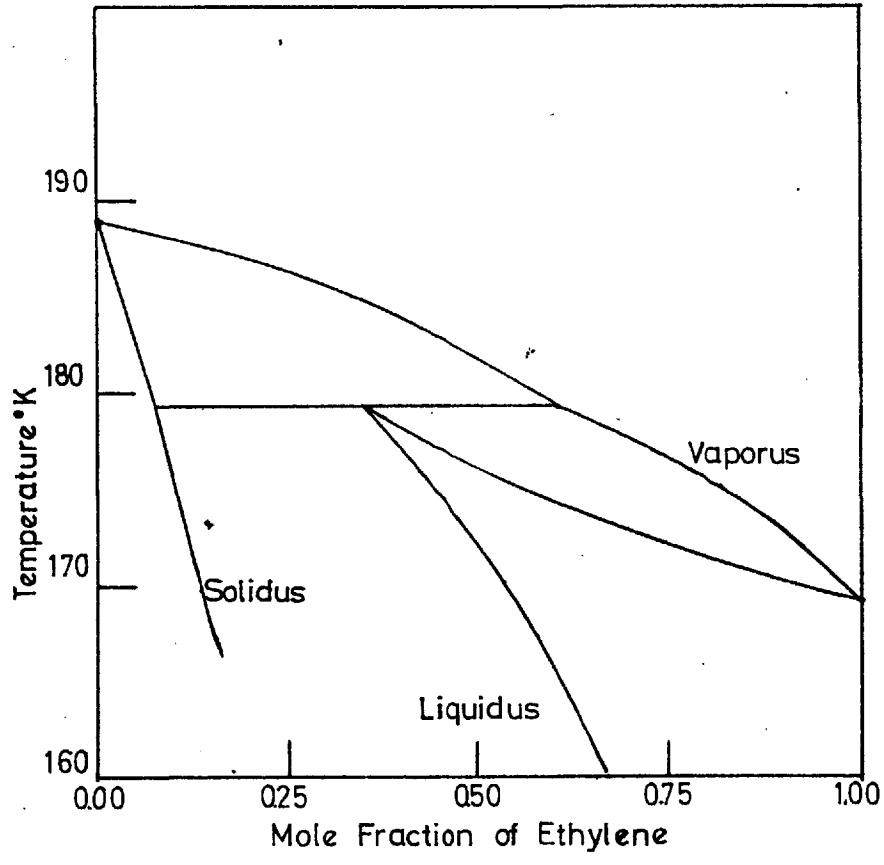


FIGURE 3:2

T-X DIAGRAMS OF ACETYLENE SYSTEMS AFTER CLARK & DIN

the critical temperature of all three pure constituents, whereas 60°F. is above the critical temperature of ethylene. At 40°F azeotropes exist in the acetylene binary systems and the authors describe "a series of ternary azeotropes" crossing the triangular diagram, Fig 4:2 (a). At 60°F the diagram is slightly complicated by the critical phenomenon, Fig 4:2 (b).

Hogan et.al.[35] obtained binary and ternary results at -35,0 and 40°F using a rocking bomb equilibrium cell. Samples were analysed by standard methods.[2,3] No azeotrope was discovered in the acetylene-ethylene system at -35°F. The ternary results at 40°F did not compare favourably with those of McCurdy and Katz.[51]

Schutt[80] has collected the available data on the solubility of C_2 - hydrocarbons in acetone. The results are expressed in terms of the Bunsen coefficient. For ethylene and ethane work has not previously been carried out below room temperature. The solubilities of acetylene in acetone are available to -75°F. No information was discovered on the solubilities of mixtures of hydrocarbons in acetone.

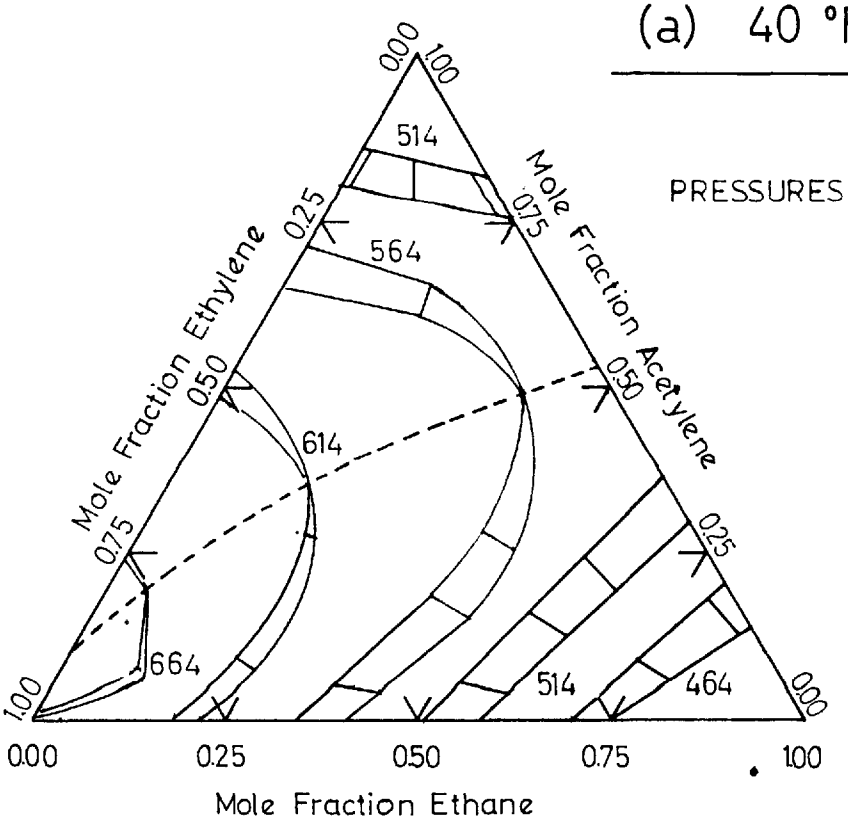
2:2 The direct experimental determination of vapour-liquid equilibrium.

In the direct determination of vapour liquid equilibrium, samples of a liquid and vapour in true equilibrium are separated and analysed.

The equilibrium curves may be measured at constant temperature or at constant pressure. The various forms of the Gibbs -Duhem equation, used for checking the thermodynamic

(a) 40 °F

PRESSURES IN P.S.I.A.



(b) 60 °F

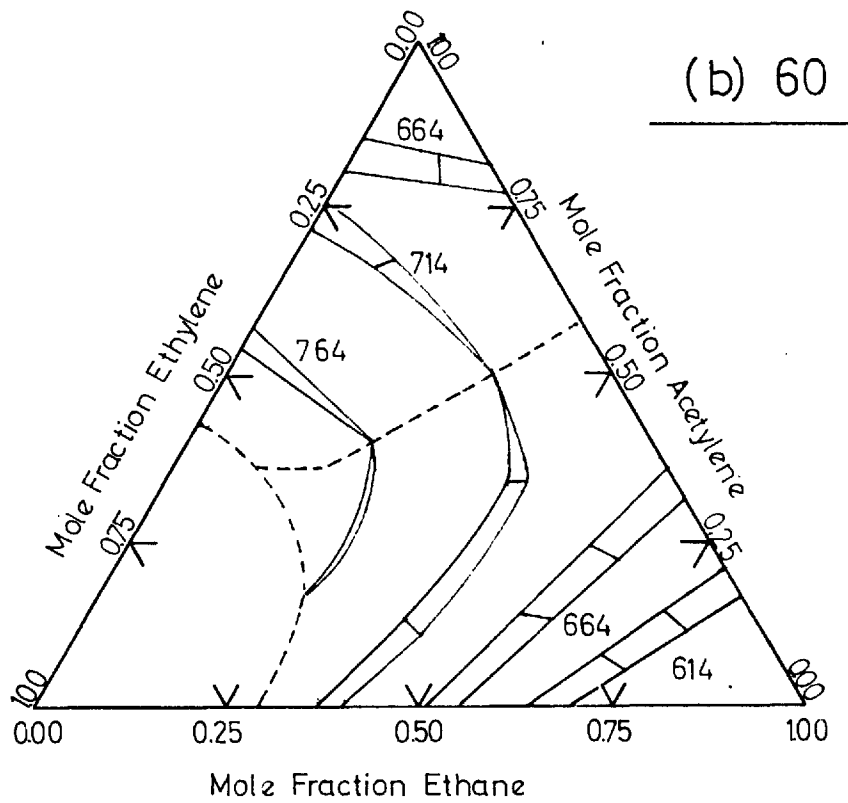


FIGURE 4:2

TERNARY DIAGRAMS AFTER McCURDY & KATZ

consistency of measured results, are more simply applied to isothermal data. The determination of isobaric equilibria is, however, simpler and of more direct use in the design of process equipment.

The experimental methods available for the determination of vapour - liquid equilibria can be classified in the following groups[30]:-

(1) Distillation Method.

(2) Circulation Method.

(3) Static Method.

(4) Dew and Bubble-Point Method.

(5) Flow Method.

(1) Distillation Method.

In this method a small amount of liquid is distilled off from a large volume of charge. Large errors may result from the condensation of vapours on the cold walls of the flask at the beginning of an experiment.

(2) The Circulation Method.

The vapours evolved from the boiling charge are completely condensed in a product receiver. When the latter has been filled the condensate is continuously recycled to the distilling flask. The steady state is achieved when the compositions of the liquids in both vessels no longer change with time. If the vapours are neither superheated nor partially condensed this state corresponds to phase equilibrium.

The Othmer still was the first to function satisfactorily and use these principles. To obtain a more precise measure of the boiling point the Gillespie[30] still was introduced. This instrument incorporates the Cottrell pump, whereby a mixture of vapour and liquid slugs is thrown onto the thermometer well. The heterogeneous mixture then flows to the separator where the vapour is separated allowing the equilibrium liquid to return to the boiling flask. The vapour is totally condensed and returned via a receiver and drop counter to the flask. Recently other stills employing circulation of both phases have been introduced, including the Ellis still.[30]

For low temperature equilibria a forced circulation technique is employed. A gaseous mixture is circulated through the liquid in the equilibrium vessel by a small pump at constant temperature and pressure. In course of time liquid and gas assumeequilibrium. Both phases are analysed from time to time until the analysis tests give constant results. This method was developed by Dodge and Dunbar in their work on oxygen-nitrogen mixtures.[22]

The circulation method may be used over a wide range of temperatures at low and medium pressures.

(3) The Static Method.

The charge is placed in a closed, evacuated vessel in a thermostat. The cell is shaken until equilibrium is

established when samples are taken.

At low and medium pressures the volume of the vapour sample required is of the same order as the volume of the vapour phase. To prevent disturbance of the equilibrium during sampling the method is, therefore, only used at high pressures.

The static method was used by Verschoyle[91] in the study of the nitrogen-hydrogen, carbon monoxide-hydrogen, and nitrogen-carbon monoxide-hydrogen systems.

(4) The Dew and Bubble-Point Method.

The equilibrium bomb is submerged in a thermostat and a gaseous mixture of known composition is compressed. The pressures at which condensation commences and finishes are observed.

Various methods have been used to detect the presence of the small quantities of liquid and vapour involved. Holland[36] and Shah[82] detected the onset of condensation by observing interference fringes. Compression was continued until a small bubble of gas remained. Clark and Din[12] cooled a gas mixture of known composition, at constant volume, and detected the dew-point as a break in the pressure-temperature plot. Bubble-points were determined as the vapour pressures of liquid mixtures of known composition in equilibrium with a small volume of vapour. Moran[55] has developed a new method for the detection of a thin film of condensate, based on the

change of dielectric constant between two plates of a condenser.

The advantages of the dew and bubble-point method are that samples of the phases at equilibrium are not required and the consumption of pure substances is small. It is, however, restricted to binary mixtures and the results are extremely sensitive to traces of impurity.

(5) The Flow Method.

A steady stream of vapour is bubbled through a volume of liquid (initially condensed) in an equilibrium chamber. At the steady state the feed and product streams have identical fixed compositions and the liquid level in the cell remains constant. Sampling is carried out at the end of the run and does not disturb equilibrium conditions.

Guter, Newitt and Ruhemann[29] determined the equilibria of light hydrocarbons at high pressures using a flow method. The authors passed the gas mixture slowly through a bundle of copper capillary tubes immersed in a cryostat. The liquid-gaseous mixture, formed in the capillaries, was separated in the liquid receiver and the two phases were analysed at the completion of a run.

2:3 Choice of experimental method.

In order that the equilibrium cell should function simply and economically whilst giving good results it must fulfil several basic requirements.[30]

To obtain consistent data, thorough agitation of the boiling charge is essential. Concentration gradients in the liquid will not only result in sampling errors but may lead to non-equilibrium vaporisation of the liquid. If the agitation is too violent, however, liquid may well be carried into the vapour receiver. To offset this and to prevent partial condensation of the equilibrium vapour, heating coils are often wound around the chamber above the liquid surface. The power dissipated from these coils must be carefully controlled to avoid superheating the vapour and the walls of the flask.

In the present application ternary and quaternary phase equilibria are to be studied at atmospheric pressure. When dealing with the solubility of hydrocarbons in acetone at low temperatures immiscible regions in the phase diagrams are likely to occur. From these considerations and the discussion of section 2.2 it is seen that the flow method involving the bubbling of vapour is the most suitable for this type of work. The flow method employing the steady fractional condensation of vapour is subject to the entrainment of liquid droplets in the effluent gas and also could not be used for solubility measurements.

A Colburn flow cell [15,30,54] was modified for these low temperature applications and it is described in Chapter 3.

Chapter 3.

EXPERIMENTAL

3:1 Apparatus - General description.

A flow diagram of the equipment is shown in Fig 1:3. The apparatus consists essentially of a modified Colburn flow cell immersed in a well-stirred cryostat bath. Pentane was circulated by a small centrifugal pump through a coil immersed in liquid nitrogen. The pentane was maintained at the desired temperature by controlling the level of the liquid nitrogen in the Dewar vessel B and by varying the power supplied to a small heater in the return line.

The feed gases were discharged from the high pressure supply bottles to the mixing chamber via potassium hydroxide drying towers and orifice boxes. The feed stream was then cooled to the operating temperature in the cryostat before entering the cell.

Samples of the liquid and vapour in equilibrium were analysed using a chromatograph.

3:2 The cryostat.

55

Previous workers in this department have employed a cooled copper block immersed in a well-stirred cryostat liquid for low temperature measurements.

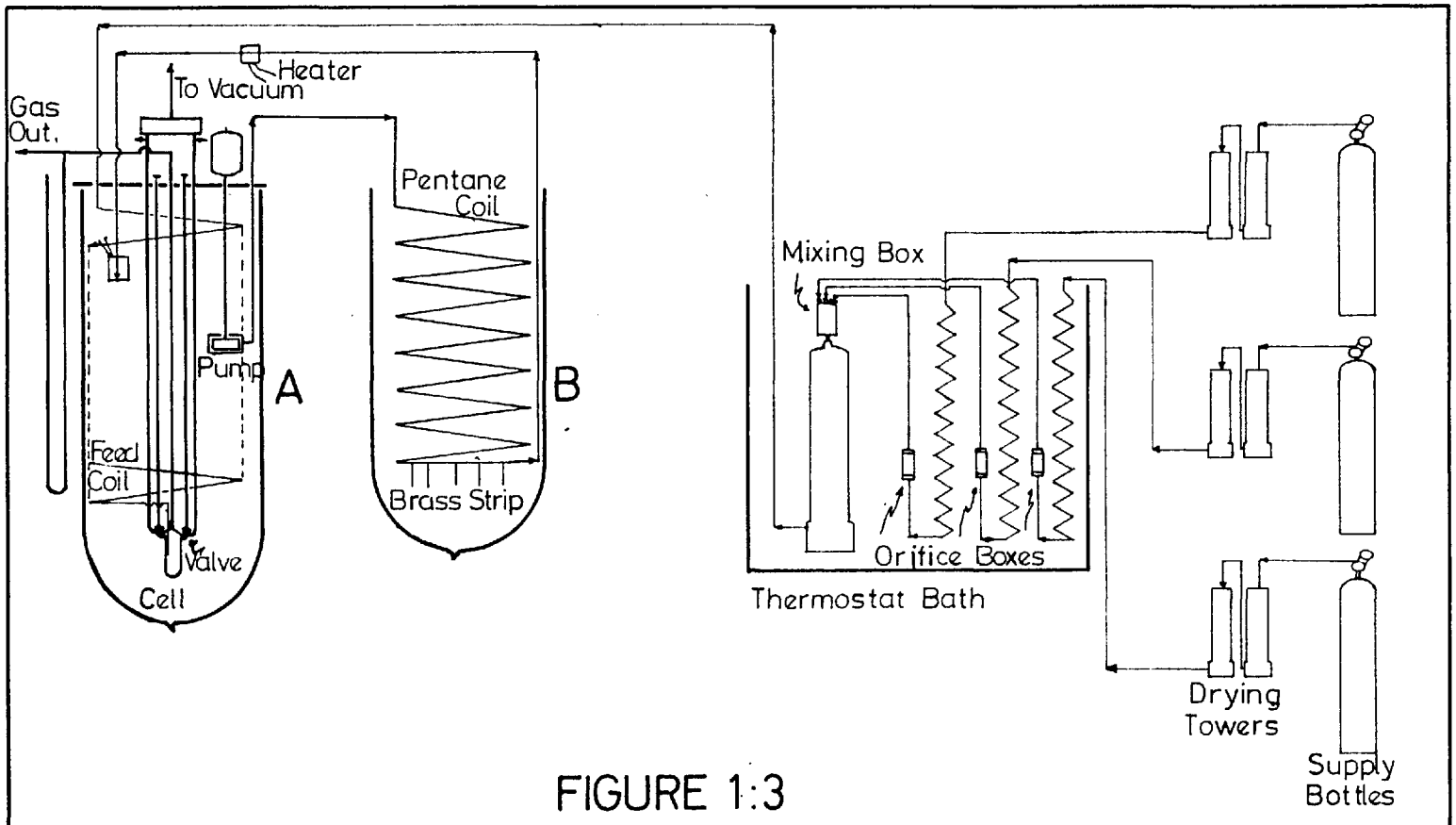


FIGURE 1:3

FLOW DIAGRAM OF PHASE EQUILIBRIUM APPARATUS

Inevitably temperature gradients in the bath result from use of this method. To overcome this disadvantage the apparatus of Fig 2:3 was developed.

Several commercial pumps were used to deliver about 4l. per min. of pentane at 150 K. In all cases leakage or seizure occurred. A simple centrifugal pump with a straight bladed impeller was therefore designed for this duty. To eliminate gears and glands, a 12 volt D.C. motor was mounted above the cryostat bath and used to drive the submerged impeller, which was positioned by a P.T.F.E. foot bearing. The joints of the motor casing were carefully sealed with P.T.F.E. tape to offset the effects of condensation. During start up severe vibrations occurred in the delivery line and P.T.F.E. bellows were fitted to overcome them.

The pump was used to circulate a mixture of normal and iso-pentane through a secondary Dewar vessel containing liquid nitrogen. The capacity of the cryostat bath was about 13l. of pentane, therefore the contents of the Dewar were circulated every 3-4 mins. The small equilibrium cell was mounted centrally at the bottom of the Dewar to enable the feed gas to attain the bath temperature. Due to the large volume of pentane used the cell was effectively maintained at a constant temperature.

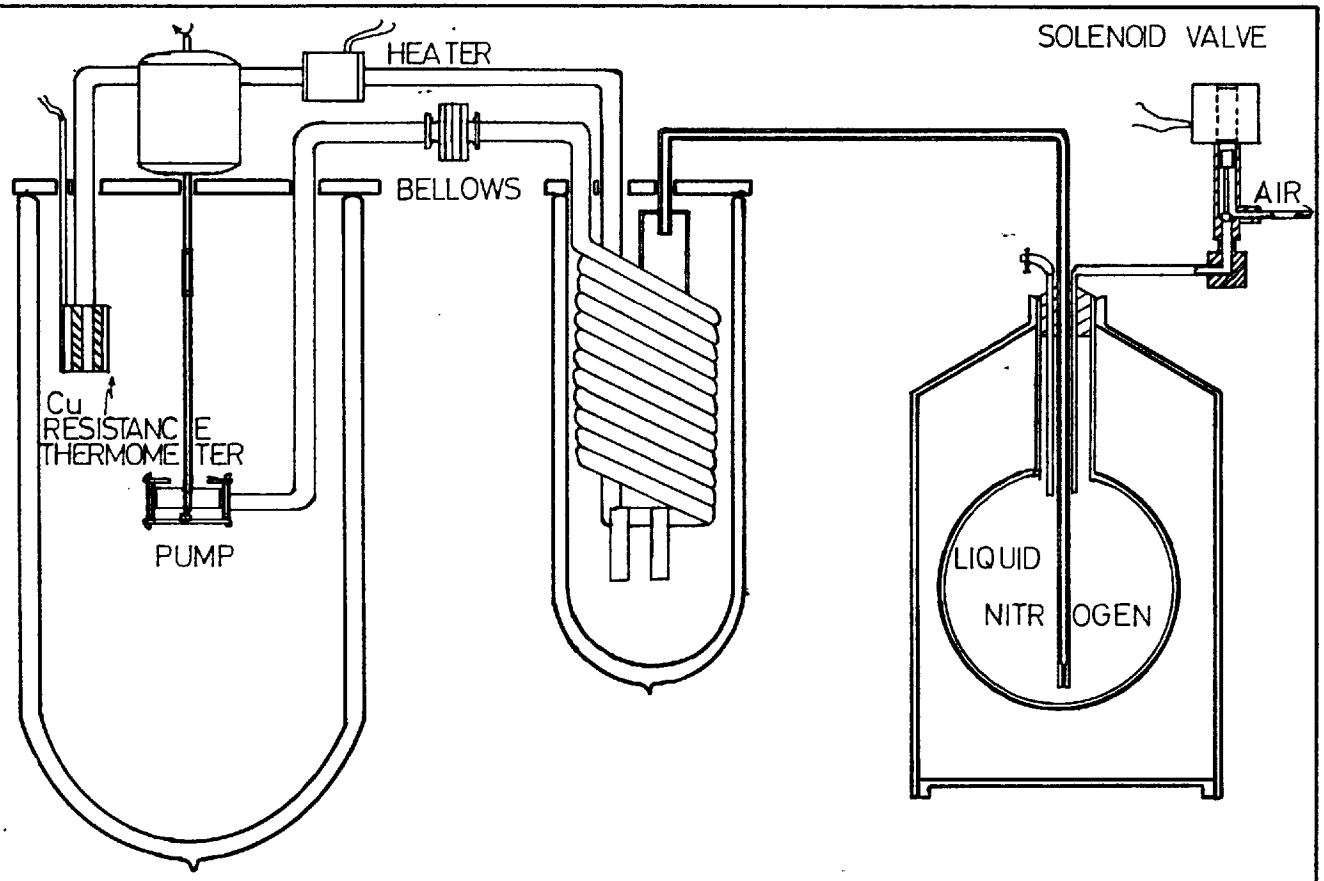


FIGURE 2.3

CRYOSTAT ARRANGEMENT

3:2:1 The Level controller

The pentane was cooled to the desired temperature, at the beginning of a run, by partially immersing the coil in the secondary Dewar in liquid nitrogen. Further cooling under these conditions results in the pentane freezing. During a run sufficient heat must be removed from the pentane to offset heat leaks into the apparatus and to cool the feed gas. Brass strips were therefore hung from the bottom of the cooling coil and the liquid nitrogen surface was maintained at such a level in contact with the strips, that thermal equilibrium was established.

The liquid nitrogen was transferred from a 5 gallon capacity storage tank to the secondary Dewar by pressurizing the container with compressed air. An electro-magnetic valve was used to control the admission of air to the vessel. An air bleed-off line, fitted to the storage tank, was constricted in such a way that delay periods associated with the build-up and let-down of air pressure were reduced to a minimum.

A level control circuit was required to operate the valve. A selected germanium diode was placed at the desired interface and a low voltage D.C. current was applied to it, Fig. 3:3. The forward current through the diode was dependent upon the temperatures of the liquid nitrogen and its vapour. This current was passed through a resistor and the resulting voltage drop was used to operate a bistable flip-flop circuit of the

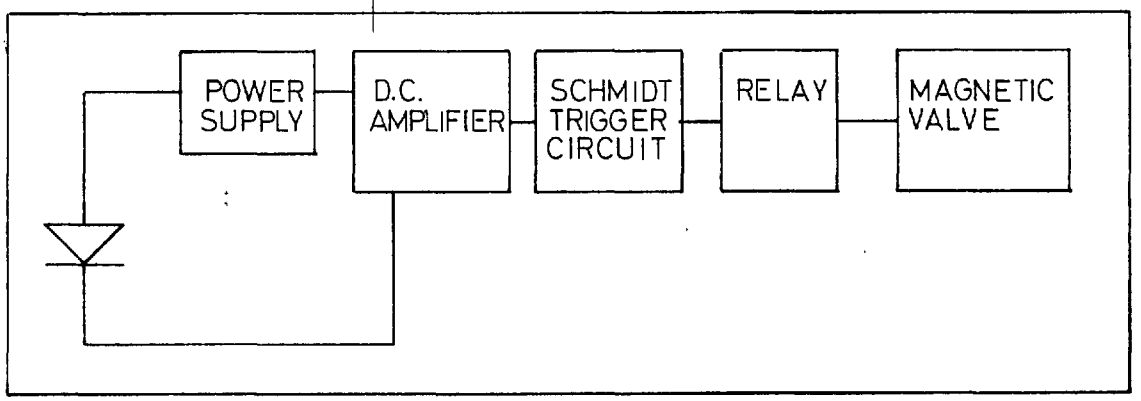


FIGURE . 3:3

LEVEL CONTROLLER

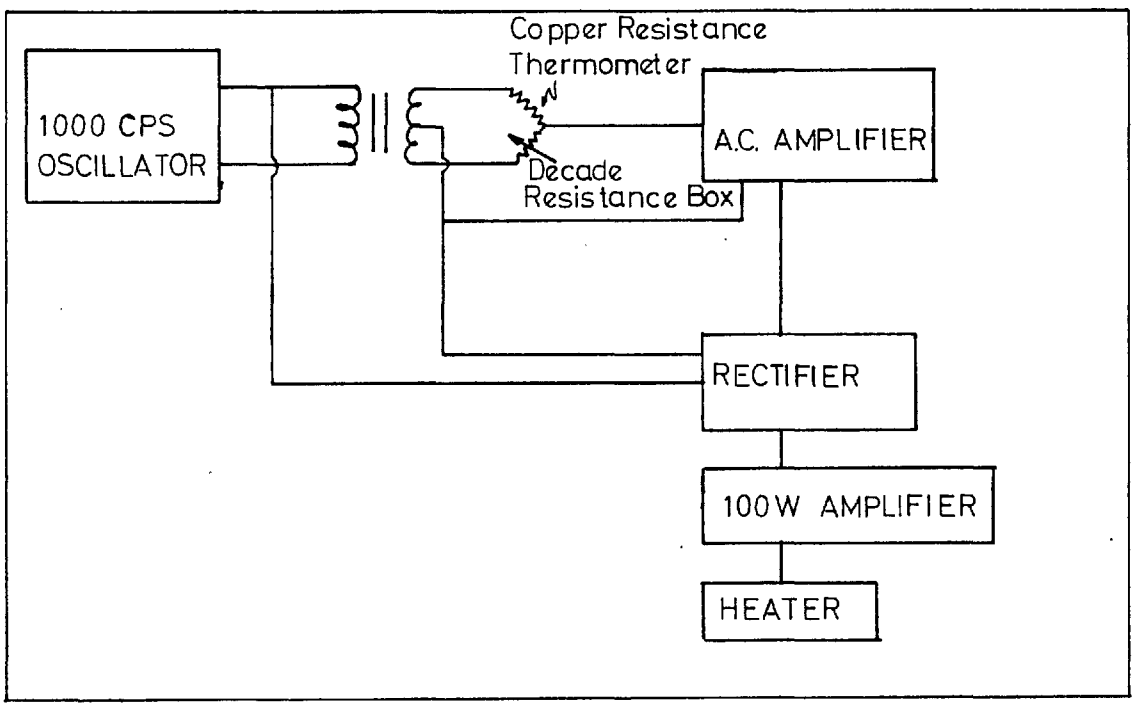


FIGURE 4:3

TEMPERATURE CONTROLLER

Schmidt trigger type. The latter activated a relay at one specific voltage and deactivated it at another. Chatter was thus eliminated and the fixed degree of hysteresis set the upper and lower limits of the operation. The relay was used to operate the electro-magnetic valve.

In practice this method of control enabled the cell temperature to be maintained to within $\pm$ 0.2°C of the desired value.

3:2:2. Fine temperature control.

The large heat capacity of the circulating pentane stream gave a stable control but the response of the system to changes in the setting of the level controller was correspondingly slow. A secondary control system was introduced to reduce the temperature variations resulting from the oscillating liquid nitrogen level and to give a more positive means of setting the level controller. A copper resistance thermometer and a 1000 ohm enamelled Eureka wire heater were therefore wound onto the pentane return line.

The temperature controller is shown diagrammatically in Fig. 4:3. A 1000 c.p.s. square wave was generated by an oscillator and fed to a transformer. The low voltage coil of the transformer, the copper resistance thermometer and a

decade resistance box were used to make up an A.C. Wheatstone bridge. The supply to the thermometer was restricted to about one volt to eliminate the heating effects of the current. The resultant square wave voltage from the bridge was amplified and fed to a phase conscious rectifier together with a reference waveform from the 1000 c.p.s. oscillator. The output of a 100 watt D.C. amplifier, used to drive the heater, was increased or decreased by the rectifier signal.

The signal produced from the unbalanced bridge was either in phase or out of phase with the reference voltage depending upon the relative magnitudes of the resistances of the thermometer and decade box. For in phase signals the temperature of the pentane stream was too low and the heater output was therefore increased. For out of phase signals the rectified voltage was decreased and the heater was effectively shut off.

During operation an ammeter was placed in series with the heater to simplify the setting of the level controller. The resistance thermometer was calibrated against a thermocouple. The temperature of the return pentane stream was therefore established by balancing the Wheatstone bridge with the aid of the ammeter. After a change in level controller setting this temperature settled more rapidly than the bulk temperature, and an estimate of the equilibrium value of the latter could be made. The position of the level controller was then altered if necessary.

3:3 The equilibrium cell.

Various forms of the flow still are described in the literature.[30,77] Of these the Colburn still,[15,54] Fig 5:3(a), is the most suitable for the present application. It is small, readily made in glass, and is easily adapted to the proposed feed system.

The cell shown in Fig 5:3(a) was developed for systems[15] boiling above room temperature. The feed constituents were vaporized in separate vessels, mixed and fed to vessel B. This vessel maintained the equilibrium cell at the desired temperature and served to even out slight variations in feed composition. Heat losses were compensated for by partial condensation of the feed. The vapour entered the cell through the bent capillary tip of the tube C, where it bubbled through the liquid, causing it to circulate through tube D. The air jacket L prevented excessive heat transfer into the cell. The vapour left the cell through tube G.

The modified cell is shown in Fig 5:3 (b). The still and its feed line were immersed in the cryostat bath. The outer chambers of the original cell were therefore not required. For partially miscible systems, two sampling capillaries were sealed into the cell at different levels. These sample lines were normally closed by remotely operated needle valves, and were connected to a vacuum system.

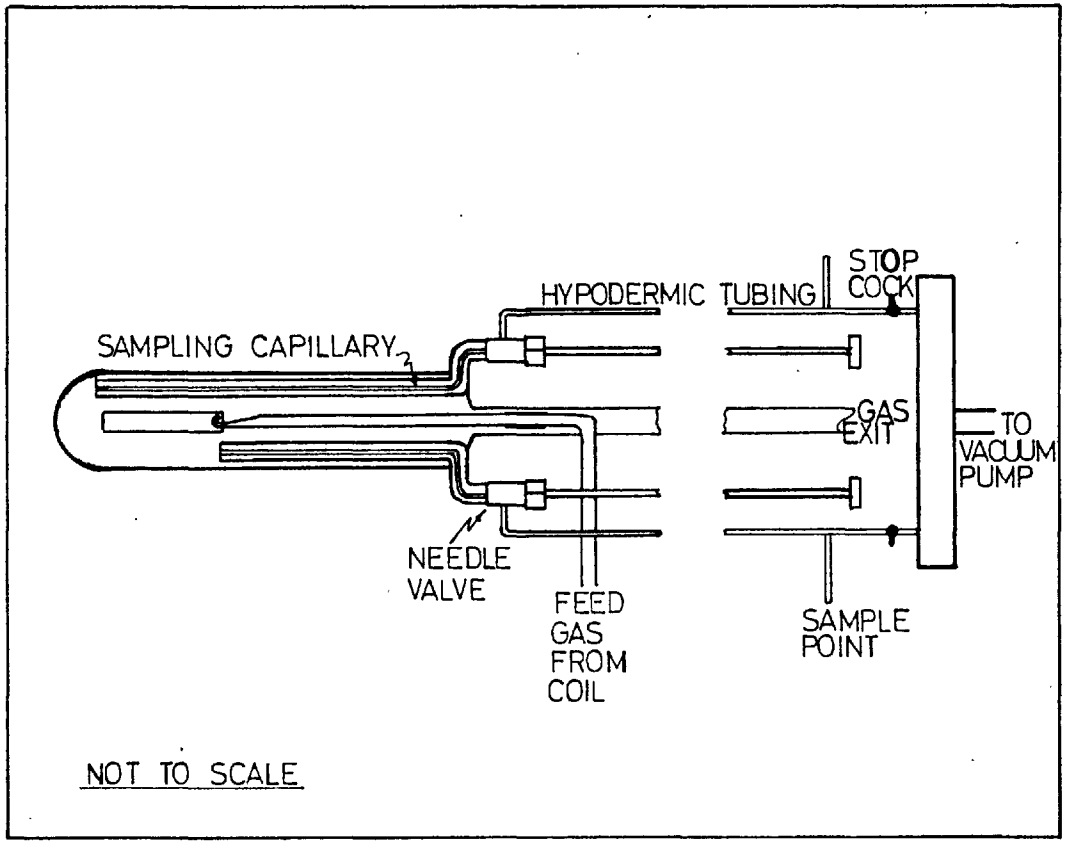


FIGURE 5:3(b)

EXPERIMENTAL FLOW STILL

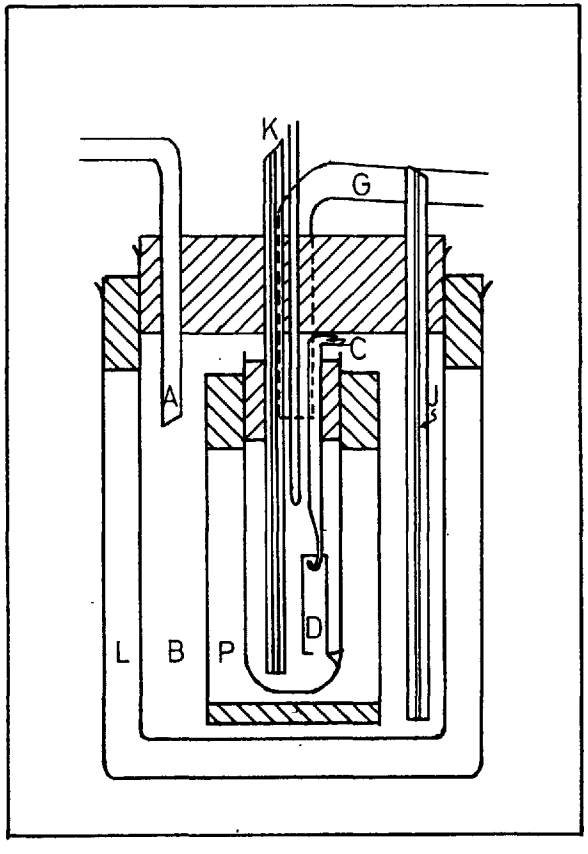


FIGURE 5:3(a)

COLBURN FLOW STILL

Initially a thermocouple was sealed into the base of the cell. The leads corroded, however, and subsequently the thermocouple was placed in the gas outlet line.

Considerable difficulty was experienced in fitting the glass cell to the copper feed coil and outlet pipe. At first copper-glass seals and soldered brass bushes were used. Due to differential contraction and vibration, however, these seals fractured on cooling. Eventually P.T.F.E. tubing was used, and this material retained sufficient flexibility at low temperatures to overcome these problems.

3:3:1 Temperature measurement.

Temperatures were measured by a single-junction copper-constantan thermocouple made from 40 S.W.G. wire. The thermocouple was introduced into the gas outlet line through a rubber bung held in one neck of a brass T-piece. The reference junction was maintained at 77.35°K [60] with boiling nitrogen. The e.m.fs. were measured on a Pye Precision Potentiometer capable of reading to 1 microvolt. The null point was indicated on a Scalamp galvanometer sensitive to 10 microvolts (1 scale division = 10μV). Calibration details are given in Appendix 1.

3:4 Feed gas preparation.

To operate the equilibrium still satisfactorily a feed gas stream of fixed composition is required. This

condition may be fulfilled by ensuring that each of the high pressure supply bottles delivers a constant flow rate of gas. By placing small orifices in the bottle delivery lines and maintaining the ratio of upstream to downstream pressures above the critical value, the theoretical velocity at the vena contracta of the orifices is the velocity of propagation of a pressure wave and hence the flow rate is independent of downstream conditions. For delivery to the atmosphere the critical pressure ratios of the process gases require an upstream pressure of at least 13 lbs/sq.in. gauge.

Preliminary work indicated that the liquid in the cell was well agitated by a total gas flow of from 10 to 20ccs/sec. The orifices were sized by the standard equations,[7] and holes of 0.002 in. to 0.015 in. were drilled in brass discs. P.T.F.E. washers were used to provide a good seal and the orifices were housed in brass unions in a thermostat bath (maintained at 25°C).

The safety regulations governing the use of acetylene restrict the delivery pressure to 10 lbs/sq.in. gauge. The velocity at the vena contracta in this case was therefore subsonic. Acetylene also forms spontaneously explosive acetylides with copper at these pressures,[61] hence brass tubing was used to deliver the gas to the mixing vessel.

Acetylene and ethane were supplied by B.O.C. Ltd. The former is dissolved under pressure in acetone and on

delivery may contain traces of acetone vapour as impurity. However, no acetone was found when the cell was carefully examined after each series of runs. The ethane supplied was analysed by a chromatograph and found to contain about 2% of propane and traces of butane. The gas was not purified further, as large quantities of gas were used to obtain the phase equilibrium data and subsequently to operate the distillation columns, and low temperature fractionation was impracticable.

Polymerisation grade ethylene containing more than 99.7% ethylene was supplied by the Societe Ethylene Plastique and required no further purification.

Standard regulators with fine adjustment needle valves were fitted to the cylinders. In conjunction with the orifices, the regulators delivered a constant flow of gas to the mixing chamber. The combined gas stream was passed through a tower packed with Raschig rings to assist mixing.

Glass wool and gauze filters were placed in the lines downstream of each drying or mixing tower to avoid blockage of the orifices and the thin walled glass capillary in the cell.

3:5 Analysis of samples.

Previous workers [35,51] have used standard methods [2,3] involving absorption techniques for the analysis of

C_2-hydrocarbon mixtures. These methods are long and tedious and alternatives were sought. Chromatography was eventually chosen as being efficient, fairly accurate and not too expensive.

Gas Chromatography Ltd. supplied a versatile unit capable of performing a variety of analyses, Fig 6:3. Hydrocarbon samples were separated in a 6 ft. column packed with 40-60 mesh silicagel. For the analysis of mixtures containing acetone the sample was divided into two. One part was passed through the silicagel column to establish the composition of the dissolved hydrocarbons. The second was passed through a column containing dinonyl phthalate supported on 60-80 mesh G-Cel. By combining the results of the analyses the complete composition of the mixture was calculated.

The samples were injected into the hydrogen carrier gas stream by hypodermic syringes and the column effluent was mixed with air and burnt in a flame ionisation detector. A constant direct potential of 100v. was applied to the flame. The resultant detector signal was amplified and recorded and the peak areas were automatically evaluated by an integrator.

The calibration of the instrument is discussed in Appendix II

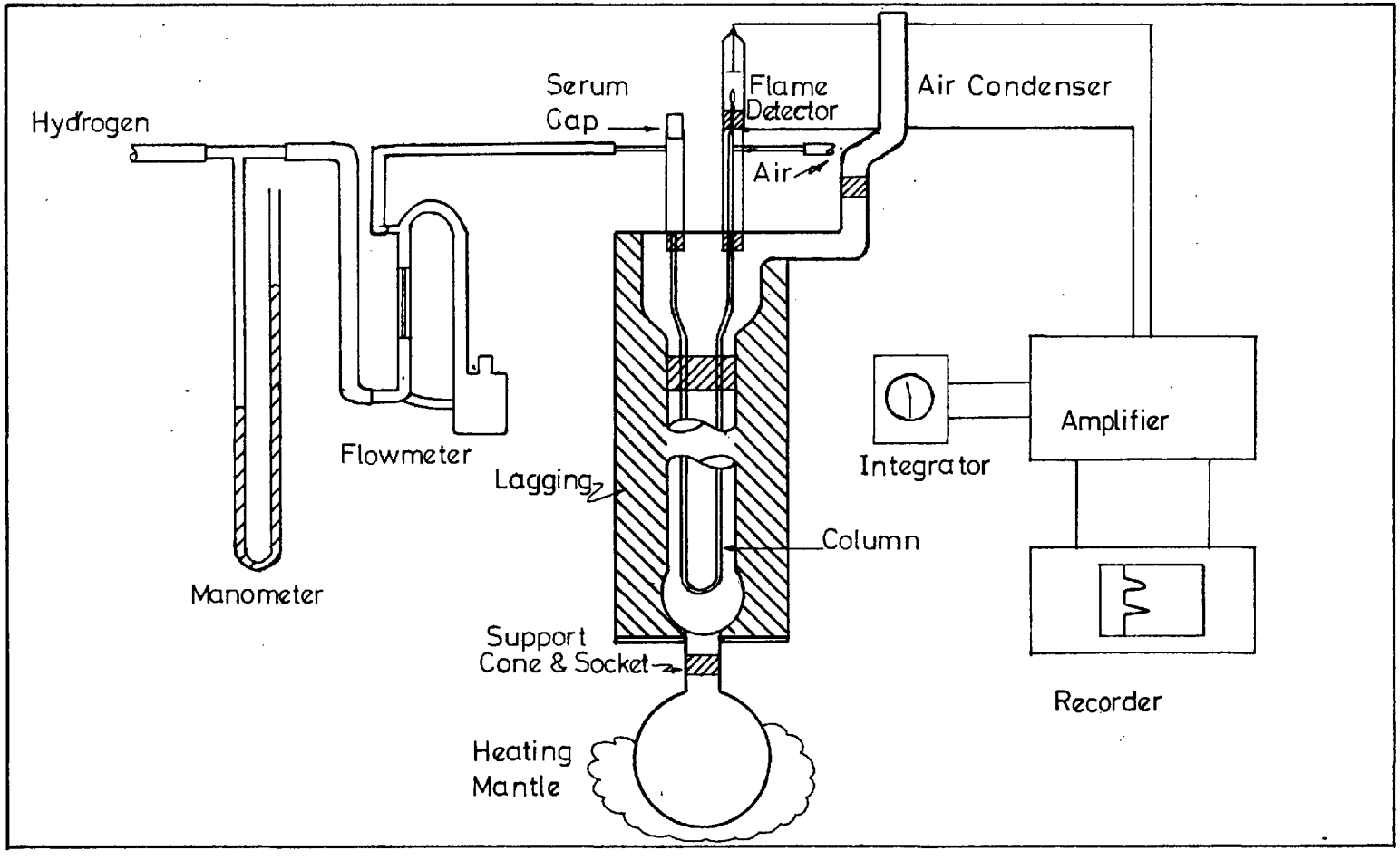


FIGURE 6:3

LAYOUT OF CHROMATOGRAPH

3:6 Experimental Procedure.

Initially several test runs were carried out to calibrate the various sections of the apparatus. The composition of the feed gas stream was measured for different supply bottle delivery pressures and orifice sizes. Several samples were taken at five minute intervals and analysed on the chromatograph. Although the compositions were observed to oscillate about a mean value (± 1 mole % at 50 mole %), the variations were considered to be too slight to make a material difference to the results.

Secondly, the equilibrium cell was cooled to the working temperature range and the level controller was set to a given position. The fine temperature controller was switched on and the bridge was balanced using the ammeter in series with the heater and the decade resistance box. Under conditions of thermal equilibrium the cell temperature and the resistance of the thermometer were recorded. The trials were repeated at several level controller positions to calibrate the thermometer. It was also established that this method of control enabled the cell temperature to be maintained to within ± 0.1°C of the desired value.

Finally a full scale test run was carried out. The effluent gas stream composition was measured at five minute intervals and compared with the fixed feed gas composition.

After a period of twenty minutes the two compositions were sensibly identical and equilibrium had been attained.

The techniques employed in the determination of vapour-liquid equilibrium data varied according to the number and nature of the components, and will be described separately.

3:6:1. Binary hydrocarbon mixtures.

Consideration of the phase rule shows that provided there is no immiscibility it is necessary to specify two properties of a binary system in order to define a particular equilibrium condition. The vapour composition was identical with the fixed feed gas composition and the cell was maintained at atmospheric pressure. It follows that the system was invariant and equilibrium could only be established at a specific temperature.

The cryostat bath was set to a temperature a few degrees below the estimated dew-point of the mixture and the gas stream was fed to the cell. Condensation occurred and the temperature of the cell was allowed to rise. The liquid level in the cell was observed through the diametrically opposed clear strips of the Dewar. After a short time this level started to fall. The temperature of the cell was then controlled so that the level remained constant. After twenty minutes at constant conditions a vapour sample was

taken with a hypodermic syringe. The vapour outlet was then closed, the needle valve opened, and liquid was forced out of the cell to be collected in a second syringe. The sampling operation was rapid and the longer capillary tube was normally used. In this manner changes in the surface composition of the liquid resulting from the increase in cell pressure did not introduce sampling errors.

The samples were then analysed on the chromatograph, and the procedure was repeated with a different feed gas mixture.

3:6:2. Ternary hydrocarbon mixture

In this case there are three degrees of freedom, but the vapour composition and the pressure were fixed and so equilibrium could only be established at a specific temperature. The experimental procedure employed was therefore identical to that for binary mixtures.

3:6:3. Solubility of pure hydrocarbons in acetone.

The cell was charged with acetone prior to a run by use of the vacuum system. The range of boiling points involved was from $+56^{\circ}C$ to $-104^{\circ}C$, and the vapour pressure of acetone in the temperature range considered was therefore very small, nevertheless trace quantities of vapour appeared in the effluent gas stream.

In the work on hydrocarbon systems, by fixing the composition of the vapour, the available degrees of freedom were reduced by one for binary mixtures and two for ternary mixtures. However, for solubility measurements in completely miscible systems the presence of acetone in the vapour reduced the available degrees of freedom by only one for ternary mixtures etc.

The hydrocarbon employed was bubbled through the acetone during cooling to facilitate the rapid attainment of saturation. When the pentane bath had reached the desired temperature, the controllers were used. Eventually the gas no longer dissolved in the acetone, the level of liquid in the cell remained constant and samples were taken, as above. It was established that the vapour stream contained negligible quantities of acetone.

For partially miscible binary systems there is only one degree of freedom available. At constant pressure therefore partial miscibility occurs at a specific temperature with fixed liquid compositions.

3:6:4. Solubility of mixtures of hydrocarbons in acetone.

The solubility of binary and ternary mixtures of hydrocarbons in acetone were also measured. In most cases the first run was carried out at the lowest temperature used.

During sample analysis the pentane bath was allowed to warm through 5°C whilst the gas mixture continued to bubble through the acetone. In this manner the consumption of liquid nitrogen was reduced and the longer analysis time was offset by the shorter period required for the attainment of equilibrium.

For the case of partially miscible systems, equilibrium could only be established at a specific temperature with a given feedstock. The procedure was therefore similar to that used for hydrocarbon mixtures.

In nearly all the runs the composition of the vapour stream was limited to 20 mol.% acetylene. Dangerous accumulations of acetylene vapour and the formation of solid acetylene were thus avoided.

The liquid samples containing acetone were difficult to handle owing to partial vaporisation. Details of the methods employed are given in Appendix II.

Chapter 4.

Theoretical.

4:1. Introduction.

The thermodynamics of solutions of non-electrolytes are discussed in detail elsewhere.[30,34,77] In this chapter a general review of the available equations for the correlation of vapour-liquid equilibrium data is given.

4:2 Basic Concepts

Although the quantitative relationships of the vapour pressures of liquid mixtures are extremely complex certain simplifications may be introduced which are valid in some important cases and may be used as a standard for the comparison of other cases.

Raoult's law states that:

$$p_i = x_i P_i^{\circ}, \qquad - (1:4)$$

and by Dalton's law $p_i = y_i P,$ $\qquad - (2:4)$

where P is the total pressure,

P_i is the partial pressure of component; i

x_i and y_i are the mole fractions of component i in the liquid and vapour phases, respectively,

and P_i° is the vapour pressure of the pure constituent at the given temperature.

It follows that the liquid-vapour equilibrium curve may be drawn, using vapour pressure data only, for any given pressure, for systems that obey these laws completely. Raoult's law applies only to mixtures which are isothermally formed from similar chemical constituents without either changes in the total volume of the solution or thermal effects.

The Gibbs-Duhem equation is of fundamental importance in dealing with the complex vapour-liquid equilibria that occur in most systems. Several presentations of the equation have been given in the literature including its derivation from basic concepts.[34,44] Ruhemann[77] proceeds to derive the Gibbs-Duhem equation by pure thermodynamic treatment and then applies equations of state to obtain the Duhem-Margules relationship. The author points out that by its nature thermodynamics cannot give quantitative information regarding the exact form of equilibrium curves and surfaces. This needs the use of equations of state, which frequently lack sufficient accuracy to give the required results and it is generally necessary to determine the (P-T-x) data for liquid mixtures in equilibrium with their vapours by experimental means.

Nevertheless, at low pressures, when the state of the vapour is not far removed from that of a perfect gas, some

theoretical conclusions can be drawn.

If a liquid and a vapour are in equilibrium then:

(1) the temperature of both phases must be identical;

(2) the pressure of both phases must be identical;

(3) the chemical potential of component i shall be the same in both phases. A basic thermodynamic relation, valid for any homogeneous phase is:

$$-SdT + VdP - \Sigma_i n_i d\mu_i = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots (3:4)$$

For the special case of isothermal changes at constant pressure this reduces to the Gibbs - Duhem equation:

$$(\Sigma_i n_i d\mu_i = 0)\ TP \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4:4)$$

At a fixed temperature, for binary mixtures and for a vapour phase which is a perfect gas:

$$d\mu_i = RT\ d\ \ln p_i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5:4)$$

since

$$\mu_i = \mu_i^{o}(T) + RT\ln p_i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (6:4)$$

The equation for one mole of a liquid phase of two components at constant temperature may be written:[11]

$$V_{liq}\ dP = x_1\ d\mu_1 + x_2\ d\mu_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (7:4)$$

Hence if this liquid is in equilibrium with a vapour for which the components have partial pressures p_1 and p_2:

$$V_{liq}\ dP = RT\ (x_1\ d\ \ln p_1 + x_2\ d\ \ln p_2) \quad \ldots\ldots\ldots (8:4)$$

For a perfect gas:

$$PV_{VAP} = RT,$$

where V_{VAP} is the molar volume of the vapour.

i.e. $$\frac{V_{liq}}{V_{VAP}} \frac{dP}{P} = x_1 \, d \ln p_1 + x_2 \, d \ln p_2 \quad \ldots\ldots (9{:}4)$$

At ordinary pressures $\frac{V_{liq}}{V_{VAP}}$ is very small and

$$(x_1 \, d \ln p_1 + x_2 \, d \ln p_2 \simeq 0)_T \quad \ldots\ldots\ldots (10{:}4)$$

This is the Duhem - Margules equation.

4:3 Real solutions.

The deviations of real binary systems from ideal phase equilibrium behaviour can be classified as follows:-

(1) departure of the vapour phase from the perfect gas law;

(2) deviations of the vapour phase from the ideal solution laws;

(3) deviations of the liquid phase from the ideal solution laws.

Raoult's law is based on kinetic considerations, it being assumed that the tendency for a molecule to escape is proportional to the pressure it exerts in the vapour phase. This itself is true only if the vapour behaves as a perfect gas. Lewis[43] introduced a term to measure the "escaping tendency " of a molecule, which was given the name fugacity, denoted by f and defined by:

$$d\mu_i = RT \, d \ln f_i \quad \ldots\ldots\ldots\ldots\ldots\ldots (11{:}4)$$

The numerical value of the fugacity is not completely determined by this equation and a further condition, that the fugacity of a perfect gas is equal to its pressure, is introduced. At low pressures the behaviour of real gases approaches that of perfect gases and the condition may be written as:

$$\lim_{P \to 0} \left(\frac{f}{P}\right) = 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12:4)$$

The activity is defined as the ratio of the fugacity of a substance to it fugacity in some arbitrarily chosen state, i.e. $f/f^o = a$ ..... (13:4)

The standard state is usually chosen as the pure substance.

The activity coefficient is defined as:

$$\gamma_i = a_i/x_i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14:4)$$

Lewis[44] defined an ideal solution by:

$$(f_i)_{LIQ} = x_i (f_i^o)_{LIQ} \quad \ldots\ldots\ldots\ldots (15:4)$$

Thus from (13:4) $a_i = x_i$ } ..... (16:4)

and from (14:4) $\gamma_i = 1$ }

At equilibrium the fugacity of any constituent is the same in the liquid and vapour phases:

$$(f_i)_{LIQ} = (f_i)_{VAP} \quad \ldots\ldots\ldots\ldots\ldots (17:4)$$

From the definitions (13:4) and 14:4) given above:-

$$y_i \gamma_{i\,VAP} (f_i^o)_{VAP} = x_i \gamma_{i\,LIQ} (f_i^o)_{LIQ} \ldots (18:4)$$

In general therefore, the gas law deviations in both the liquid and vapour phases are dealt with by fugacities, assuming the liquid to be an ideal solution, and solution deviations are dealt with by activity coefficients, assuming the vapour to be a perfect gas.

All the work in this thesis was performed at low pressures and gas law deviations have been assumed negligible. The activity coefficient has been used to account for deviations from the ideal solution laws and was calculated from:-

$$p_i = y_i P = \gamma_i x_i P_i^{o} \quad \text{.....(19:4)}$$

By differentiation and substitution the Gibbs-Duhem equation is readily obtained in the form:-

$$\left[\frac{d \ln \gamma_1}{d \ln \gamma_2}\right]_T = \frac{-x_2}{x_1} \quad \text{.....(20:4)}$$

4:4 Correlation of experimental data in binary systems

Vapour - liquid equilibrium data may be readily correlated in terms of activity coefficients. A number of attempts have been made to integrate the Gibbs-Duhem equation[27] and the equations obtained by this procedure are reviewed in the following pages.

Wohl[94] derived the change of free energy on mixing pure liquid constituents as:-

$$\Delta G_{mix} = \Sigma_i n_i RT \ln x_i + \Sigma_i n_i RT \ln \gamma_i \quad \text{.....(21:4)}$$

For an ideal solution:-

$$\Delta G^*_{mix} = \Sigma_i n_i RT \ln x_i \quad \text{.....(22:4)}$$

The excess free energy on mixing is therefore:-

$$\Delta G_E = \Delta G_{mix} - \Delta G^*_{mix} = \Sigma_i n_i RT \ln \gamma_i \quad \text{.....(23:4)}$$

On differentiating (23:4) with respect to the number

or moles of any constituent i, and applying the generalised form of (20:4), Wohl obtained the following expression for the excess partial-molar free energy change on mixing:-

$$\left(\frac{\partial \Delta G_E}{\partial n_i}\right)_{T,P,n_j \neq i} = RT \ln \gamma_i \quad \ldots\ldots\ldots\ldots\ldots\ldots (24:4)$$

Wohl also expressed the dependence of the molar excess free energy on the composition of the liquid phase by the expansion:

$$\frac{\Delta G'_E}{2.303\ RT \Sigma_i q_i x_i} = \Sigma_{ij} z_i z_j a_{ij} + \Sigma_{ijk} z_i z_j z_k a_{ijk} + \ldots (25:4)$$

where $\Delta G'_E = \dfrac{\Delta G_E}{\Sigma n_i}$

q_i, q_j, q_k, .. are constants which Wohl called the effective molar volumes of the constituents,

z_i, z_j, z_k ... are the effective volumetric fractions of the constituents, e.g. $z_i = \dfrac{q_i x_i}{\Sigma_j q_j x_j}$

and a_{ij}, a_{ijk}, .. are empirical constants measuring the interactions in various groups of molecules ij, ijk, etc.

The first summation of (25:4) therefore takes into account the force interations between each pair of dissimilar constituents. The more summations that there are in an equation, the better it will represent the behaviour of the given system, but the more constants will need to be determined from experimental data. Practically

equations of the third and fourth order are used. Partial differentiation of (25:4) with respect to n_i, and substitution in (24:4) gives relationships between the activity coefficient and the composition of the solution. This procedure gives equations that automatically satisfy the Gibbs-Duhem equation.

By making special choices of the coefficients, the equations for binary systems derived by this method reduce to the corresponding semi-empirical Van Laar,[90] Margules[49] and Scatchard-Hamer[78] equations. In view of the possible molecular interactions it is impossible to produce one simple general equation. All that can be expected is to have a general equation which permits simplification for special cases.

Wohl extended the previous work of Carlson and Colburn,[9] who had summarized the utilisation of theoretical methods to extend data up to 1942.

Redlich and Kister[70] have proposed equations for the dependence of the ratio of the activity coefficients of the components on the composition of the liquid phase. It has been shown that these equations are equivalent to the Margules equations.[30]

Recently various authors have proposed a series of

empirical equations which express the mutual dependence of the equilibrium compositions of the vapour and liquid phases. In this group the correlations of Clark,[11] Scheibel and Friedland[79] etc. are to be found.

Bourne and Ellis[5] have reviewed the methods for the thermodynamic analysis of vapour-liquid equilibria. For isothermal conditions they use the following form of the Gibbs-Duhem equation:-

$$\Sigma_i x_i \, d \ln \gamma_i = \frac{VE}{RT} \, dP \quad \ldots\ldots\ldots\ldots\ldots\ldots (26:4)$$

and for isobaric conditions:-

$$\Sigma x_i \, d \ln \gamma_i = \frac{HE}{RT^2} \, dT \quad \ldots\ldots\ldots\ldots\ldots\ldots (27:4)$$

The authors show that the right-hand side of (26:4) is generally very small in comparison with any term on the left-hand side, whereas the right-hand side of (27:4) is generally comparable with the terms on the left-hand side. Solutions of the isothermal, isobaric Gibbs-Duhem equation, described above are therefore often applicable to isothermal vapour-liquid equilibrium data. The experimental findings of Razavipour and Ellis[69] suggest that in accurate calculations the Van Laar and Margules equations should not be applied to isobaric data where the boiling range exceeds $10^{\circ}C$, or even less than this in azeotropic systems.

To correct for the effect of temperature on the activity coefficient the rule $T \log \gamma_i$ = constant at constant composition has been widely applied.[14] White,[93] Li and Coull,[46] and Yu and Coull[95] have developed isobaric forms of the Van Laar equation including similar temperature correction factors. Li and Coull derived an expression for the change in internal energy resulting from molecular collisions of two species when mixed. They neglected volume changes on mixing and also assumed that in the absence of orienting and chemical effects random distribution existed and the entropy change was idential with that for an ideal solution. They obtained:-

$$(T \log \gamma_1)^{-1/2} = \left(\frac{b_1}{b_2}\right)\left(\frac{b_2}{k_{12}}\right) \frac{{}^{1/2}x_1}{x_2} + \left(\frac{b_2}{k_{12}}\right)^{1/2} \quad \ldots(28:4)$$

$$\text{and } (T \log \gamma_2)^{-1/2} = \left(\frac{b_2}{b_1}\right)\left(\frac{b_1}{k_{12}}\right) \frac{{}^{1/2}x_2}{x_1} + \left(\frac{b_1}{k_{12}}\right)^{1/2} \quad \ldots(29:4)$$

Li and Coull considered b_1 and b_2 to be the partial molar volumes of species 1 and 2, and as such they are functions of the composition of the mixture. The authors presented values of the b-ratio obtained by different methods from (28:4) and (29:4), for a variety of systems. Although variations in the values of the ratio resulted from this treatment, the authors have found that any of the values may be used in the development of ternary correlations without introducing

great discrepancies. Application of the equations to the correlation of isobaric data requires the additional assumptions that the constants k and b remain unchanged over the temperature range considered. Nevertheless, the form of the Li-Coull equations makes them more applicable to isobaric data than the developments of Wohl described previously.

4:5 Correlation of experimental results in ternary systems.

Because of analytical difficulties the experimental determination of ternary equilibrium data is likely to give less reliable results than reasonable predictions from binary data.

Colburn,[14] Scheibel[79] etc. have obtained ternary activity coefficients by interpolation from binary data and for systems of similar components this method is successful.

Wohl[94] extended his work to deal with ternary systems in a comprehensive manner. The resultant second order equations employ only constants derived from the binary systems. Third and fourth order equations also use constants derived from ternary data. The ternary second order Van Laar equation, as developed by Wohl, is restricted by a relationship between the constants, such that only five independent values of the six binary variables are

required. White[93] uses an equation which is identical in form to Van Laar's[90] equation in the case of binary systems. The extension of these equations to ternary systems, however, results in a $\pm$ sign in the numerator. This ambiguity can only be resolved by the introduction of a relationship between the constants, which causes White's ternary correlations to become identical with the thermodynamically correct equations of the Van Laar type. The general validity of this relationship is not accepted by Wohl,[94] who points out that the examples quoted by White[93] do not necessarily satisfy the condition.

Li and Coull[46] extend their binary equations to deal with ternary data by ignoring the energy change resulting from ternary collisions. The equations are of the type:-

$$T\log\gamma_1 = \left\{\left(\frac{k_{12}}{b_1}\right)\left(\frac{b_2}{b_1}\right) x_2^2 + \left(\frac{k_{13}}{b_1}\right)\left(\frac{b_3}{b_1}\right) x_3^2 + \left[\left(\frac{k_{12}}{b_1}\right)\left(\frac{b_3}{b_1}\right) + \left(\frac{k_{13}}{b_1}\right)\left(\frac{b_2}{b_1}\right) - \left(\frac{k_{23}}{b_1}\right)\right] x_2 x_3 \right\} \Big/ \left\{ x_1 + \left(\frac{b_2}{b_1}\right) x_2 + \left(\frac{b_3}{b_1}\right) x_3 \right\}^2 \quad \ldots\ldots\ldots (30:4)$$

4:6 Consistency of measured data.

Experimental data may be subject to systematic errors which do not show up as a scattering of the measured points and a simple method of checking the consistency of the data prior to correlation is required.

Herington,[33] Coulson, Hales and Herington,[17] and Redlich and Kister[70,71] integrated an equation for the partial-molar excess free energy and obtained for a miscible binary system at constant temperature:-

$$\int_{x_1=0}^{x_1=1} \log\frac{\gamma_1}{\gamma_2}\, dx_1 = \frac{1}{2.303RT}\int_{P=P_2^o}^{P=P_1^o} V_E\, dP \simeq 0 \quad \ldots(31:4)$$

Herington[32] generalised this procedure to include isobaric data and proved that, $\int_0^{1.0} \log \gamma_1/\gamma_2 \, dx = \int_0^{1.0} \frac{HE}{2.303\,RT^2}\frac{dT}{dx}\, dx$

$$= I \quad \ldots\ldots\ldots\ldots\ldots\ldots(32:4)$$

The logarithm of γ_1/γ_2 is plotted against x_1 and the sum of the magnitudes of the areas beneath the curve is denoted by Σ. The percentage deviation is given by,

$$D = \frac{100\,|I|}{\Sigma} \quad \ldots\ldots\ldots\ldots\ldots\ldots(33:4)$$

where $|I|$ is the numerical value of the

algebraic sum of the areas.

A further factor, J, is defined as,

$$J = \frac{150|\theta|}{T \text{ min}} \qquad \text{.....(34:4)}$$

where θ is the overall range of boiling points of the system, and T min is the lowest measured boiling point in ^{O}K.

Herington[32] derived a maximum probable value for the ratio $\left|\frac{\Delta Hm}{\Delta G_{mE}}\right|$, where the suffix m indicates the maximum. values of the functions in the concentration range, by examining systems for which these parameters had been measured. In this manner the author showed that D should be less than J for consistent data. He also stated that if $D - J < 10$ the data could still be considered correct.

Chapter 5.

Results and Discussion.

5:1:1 The Phase equilibria of C_2 - hydrocarbon systems

The experimental results for the binary systems ethylene-ethane, acetylene-ethane and acetylene-ethylene, are given in Appendix III. The temperature-composition and vapour-liquid composition diagrams are shown in Graphs 1:5 to 6:5. The results of other workers are superimposed on these diagrams. The results for the ternary system are also given in Appendix III. The experimental temperature composition diagram is shown in Graph 7:5.

The equilibrium temperatures have been corrected, for variations in ambient pressure, by a combination of the Clausius-Clapeyron equation and Trouton's rule:[60]

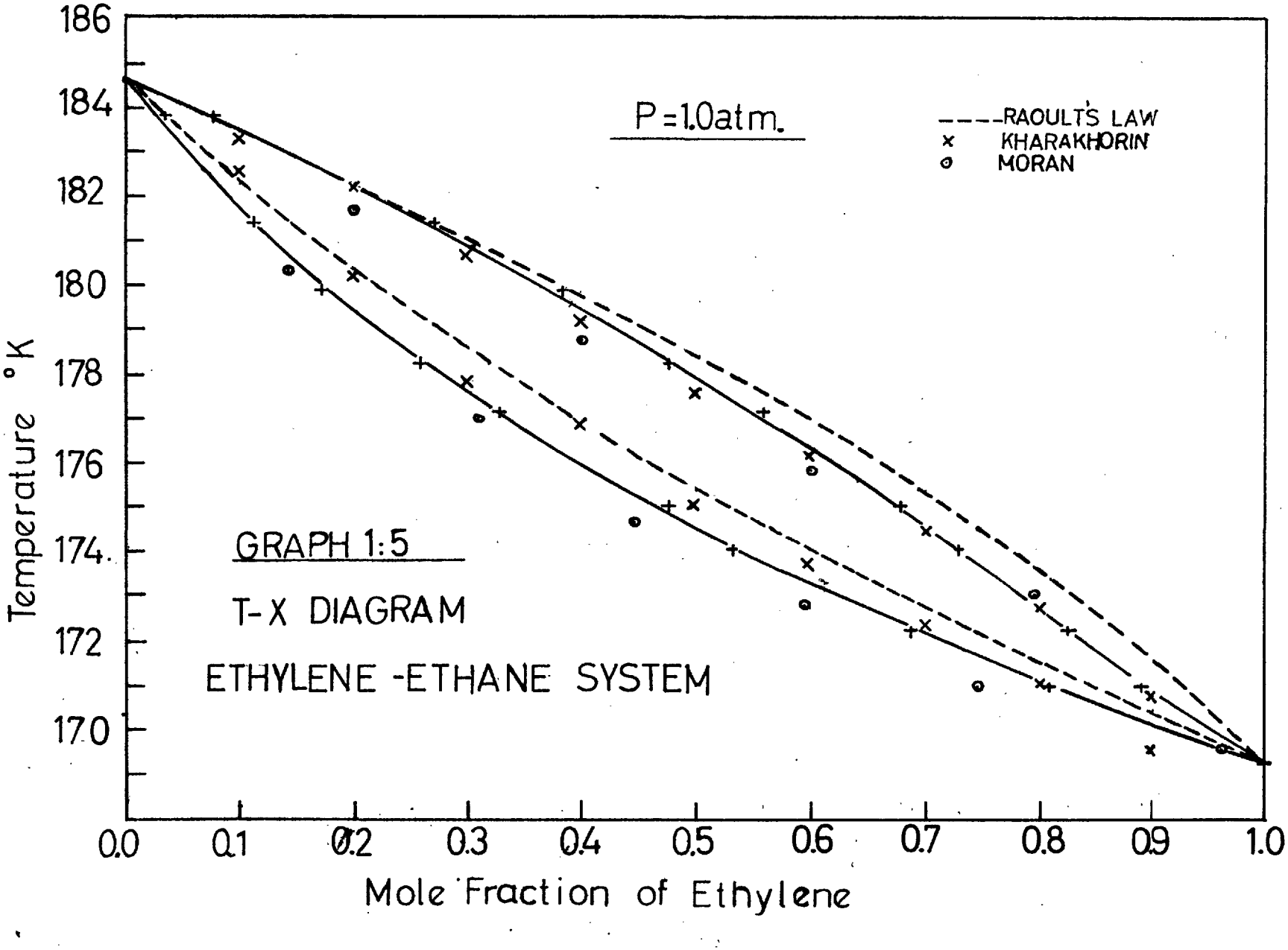
$$\Delta T_b = 0.00012 \; T_b \Delta p \quad \text{.....(1: 5)}$$

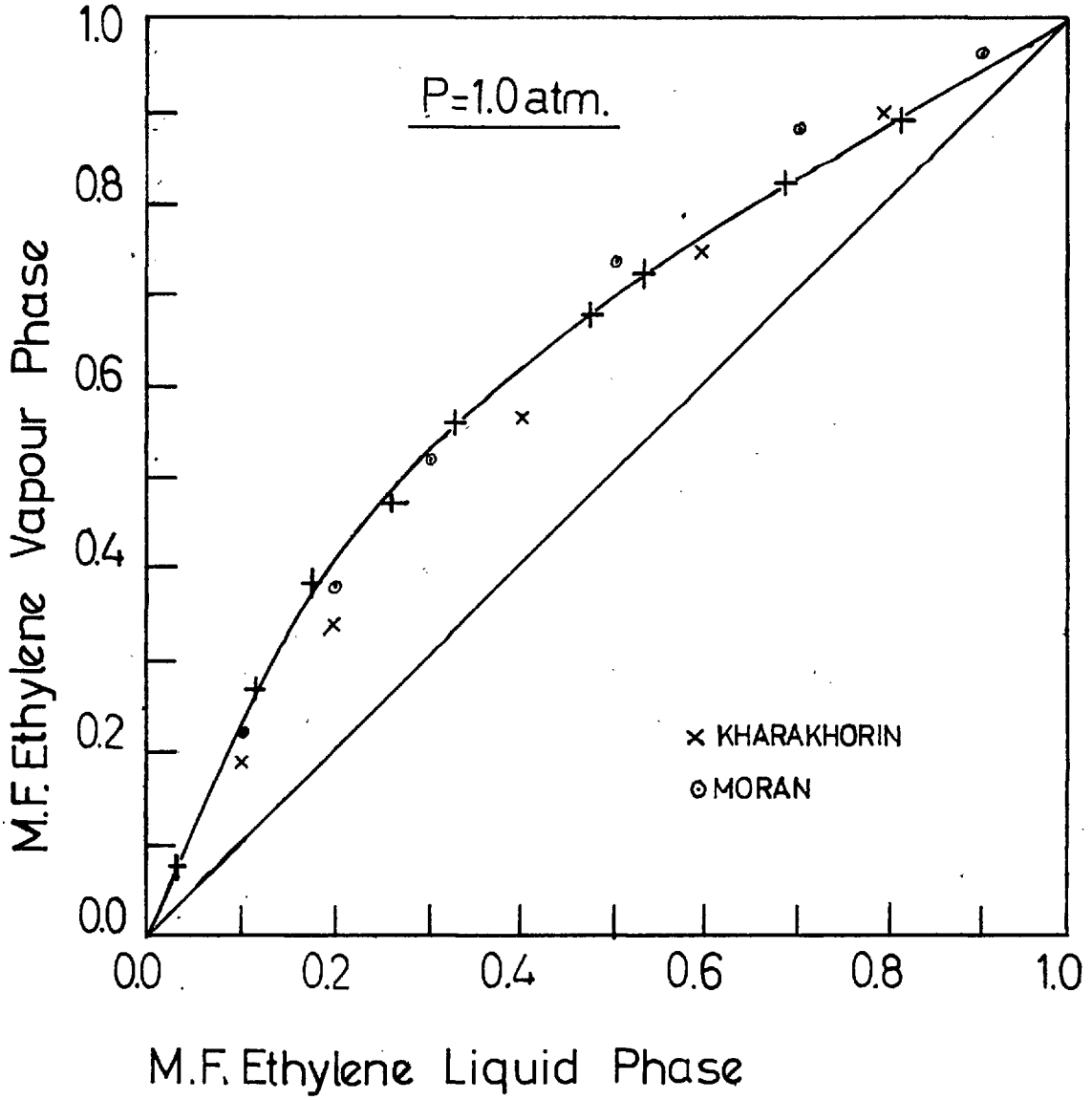
where T_b is the normal boiling point,

and ΔT_b is the change in the normal boiling point corresponding to a change in pressure of Δp mm. of Hg. No corrections have been made for the impurities present in the ethane feedstock.

5:1:2 Vapour-pressure data.

The vapour pressure data, used for the correlation of the phase equilibrium results, was obtained from a variety

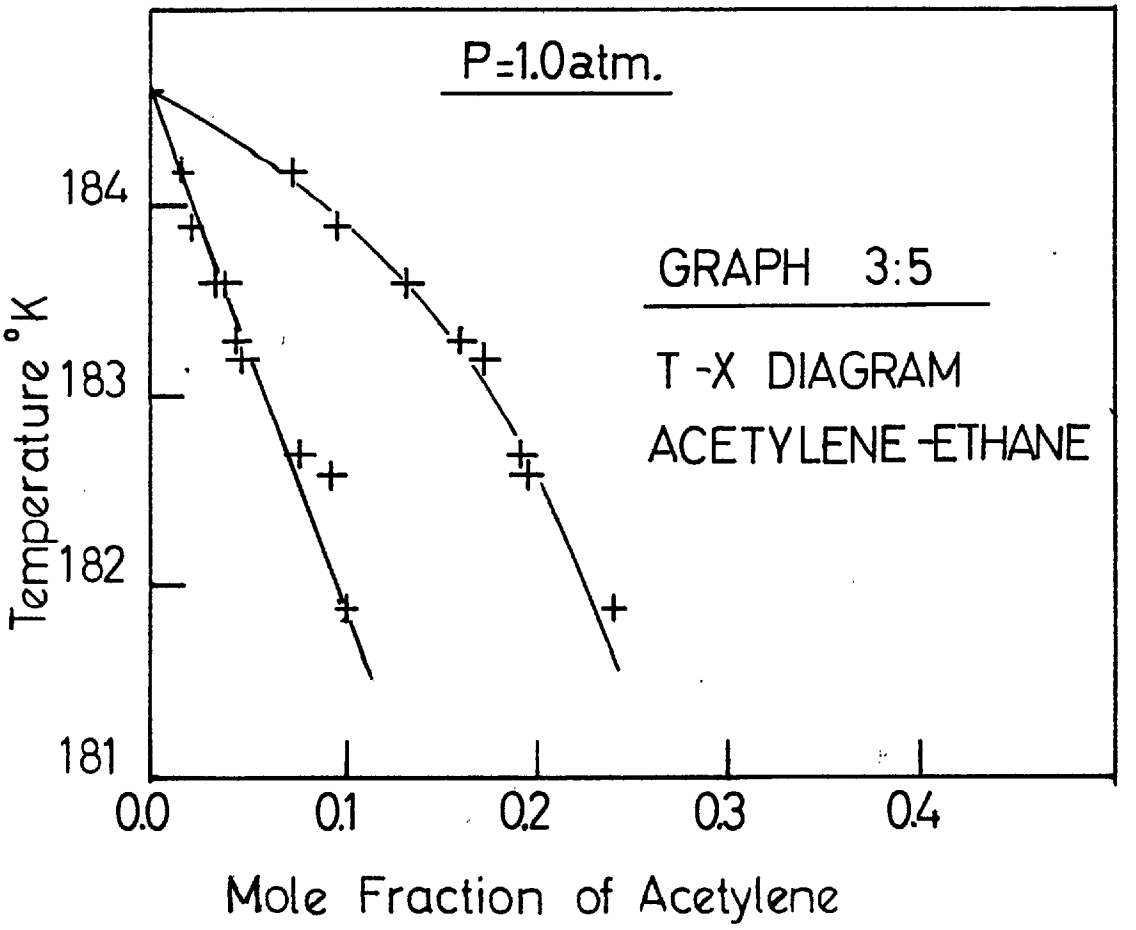

P=1.0atm.
----RAOULT'S LAW
× KHARAKHORIN
o MORAN
GRAPH 1:5
T-X DIAGRAM
ETHYLENE -ETHANE SYSTEM
Temperature °K
186
184
182
180
178
176
174
172
170
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Mole Fraction of Ethylene

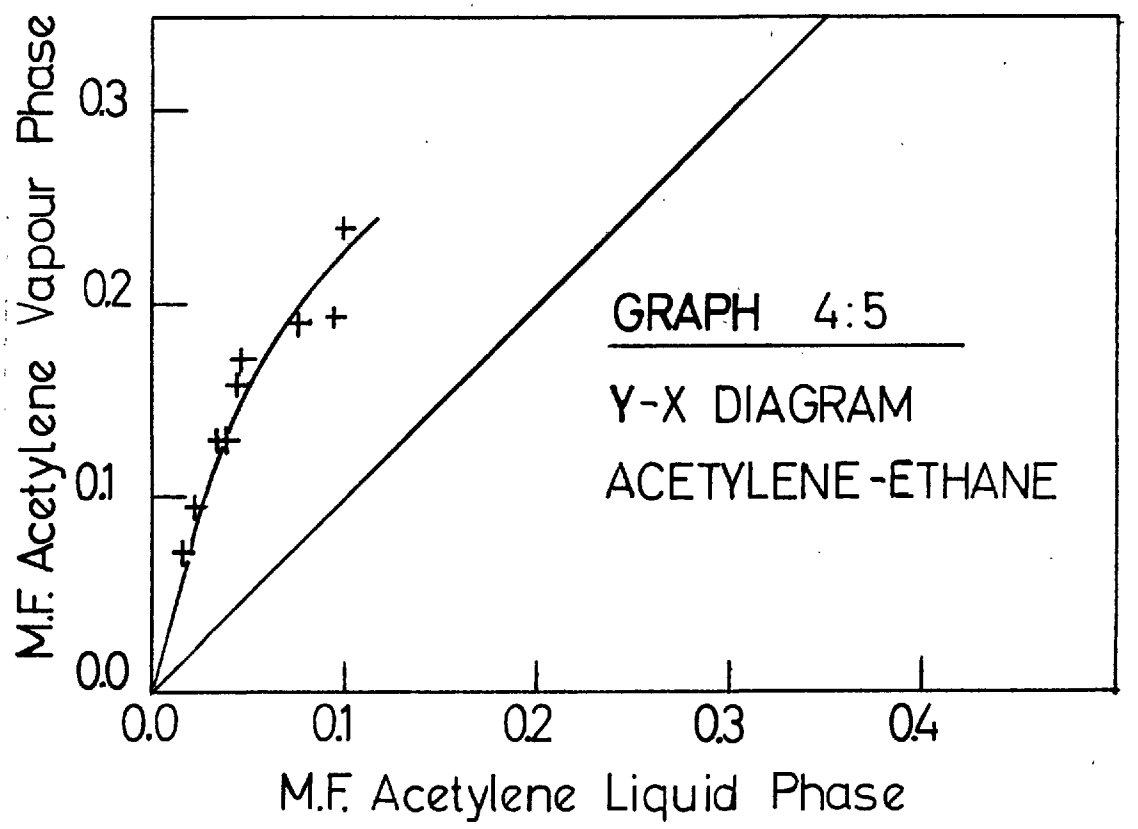


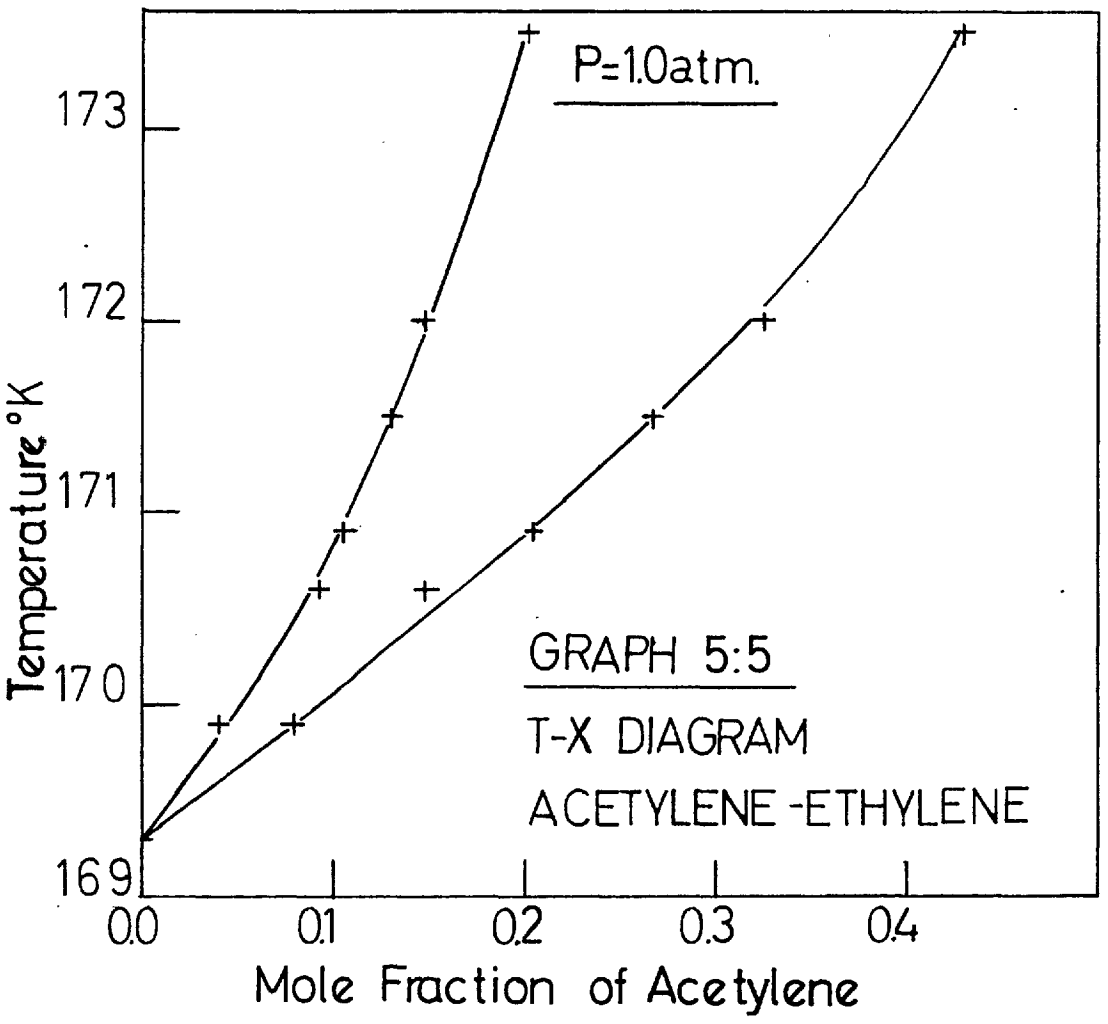
GRAPH 2:5

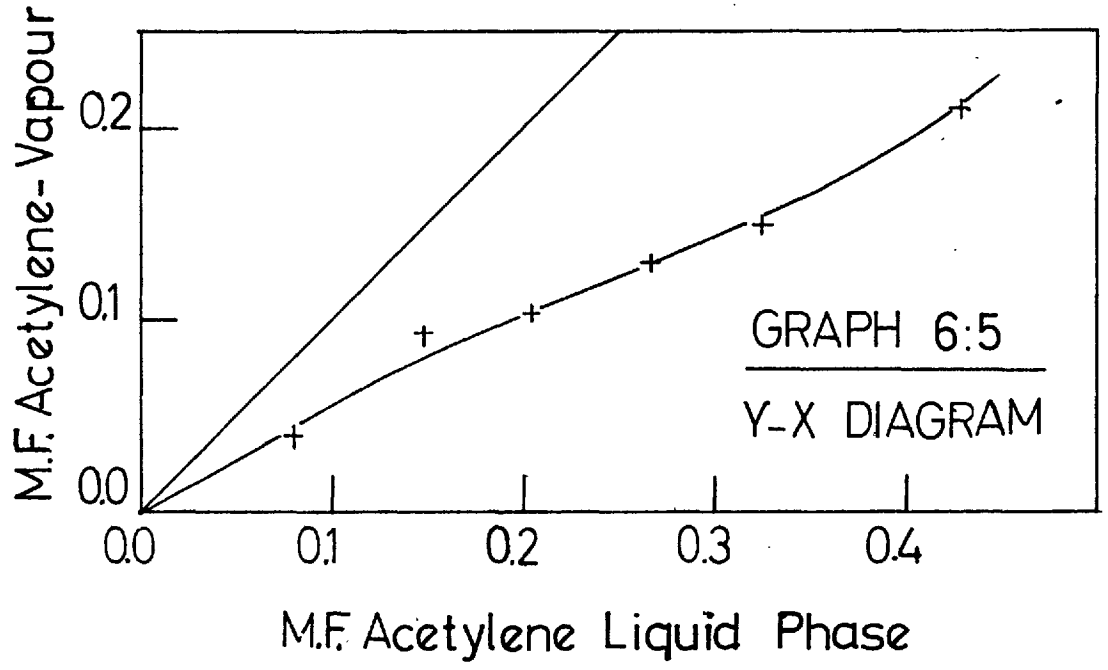
Y -X DIAGRAM

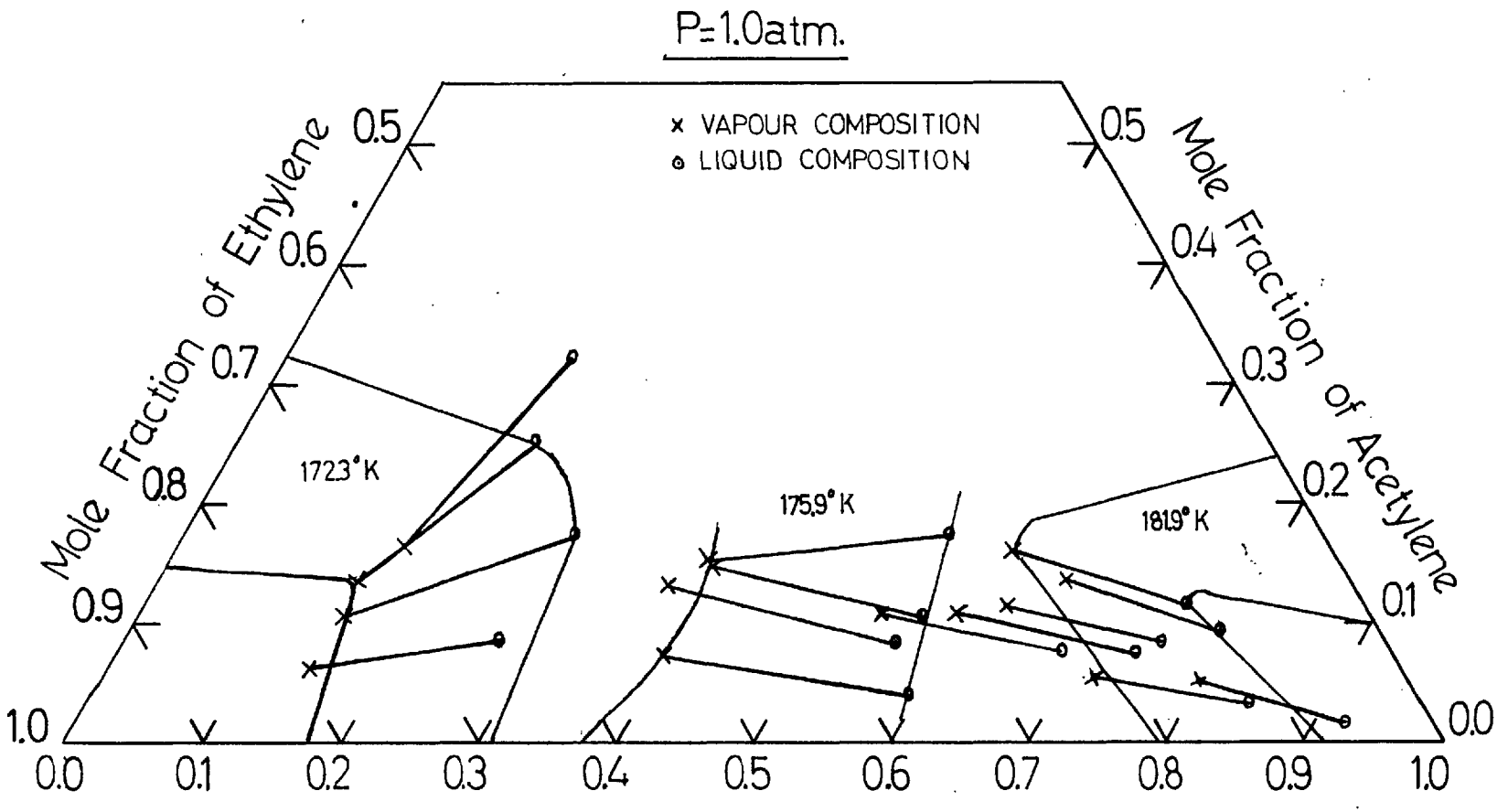
ETHYLENE -ETHANE SYSTEM


P=1.0atm.
GRAPH 3:5
T -X DIAGRAM
ACETYLENE -ETHANE
Temperature °K
184
183
182
181
0.0
0.1
0.2
0.3
0.4
Mole Fraction of Acetylene


GRAPH 4:5
Y-X DIAGRAM
ACETYLENE-ETHANE
M.F. Acetylene Vapour Phase
0.3
0.2
0.1
0.0
0.0
0.1
0.2
0.3
0.4
M.F. Acetylene Liquid Phase


P=1.0atm.
173
172
171
170
169
Temperature °K
0.0
0.1
0.2
0.3
0.4
Mole Fraction of Acetylene
GRAPH 5:5
T-X DIAGRAM
ACETYLENE -ETHYLENE


M.F. Acetylene- Vapour
0.2
0.1
0.0
0.0
0.1
0.2
0.3
0.4
M.F. Acetylene Liquid Phase
GRAPH 6:5
Y-X DIAGRAM



GRAPH 7:5

PHASE EQUILIBRIA OF TERNARY SYSTEM

of sources[8,38,47,86] and fitted to a straight line plot of the form: $\log_{10} P = A - \frac{B}{T}$ .....(2:5)

where P is measured in m.m. Hg, and T in $^{\circ}K$

The resulting equation for ethylene was:-

$$\log_{10} P = 7.322 - \frac{754.7}{T} \quad .....(3:5)$$

and for ethane: $\log_{10} P = 7.308 - \frac{819.1}{T}$ .....,(4:5)

The triple point of acetylene is at - 81.0°C and 1.25 ats. At atmospheric pressure solid acetylene sublimes at -84.0°C. For the calculation of activity coefficients the vapour pressure curve of liquid acetylene should be extrapolated to sub-atmospheric pressures.[63] The resulting equation was

$$\log_{10} \frac{P}{760} = 4.588 - \frac{865.4}{T} \quad .....(5:5)$$

The simple forms of vapour pressure equation obtained above do not give a complete representation of the data. Correction graphs to be used in conjunction with (3:5) and (4:5) were therefore plotted.

5:1:3 Consistency of measured data

Neglecting gas law deviations, and using the experimental values of atmospheric pressure and equilibrium temperature, activity coefficients were calculated from (19:4)

$$y_i P = \gamma_i x_i P_i^{\circ}$$

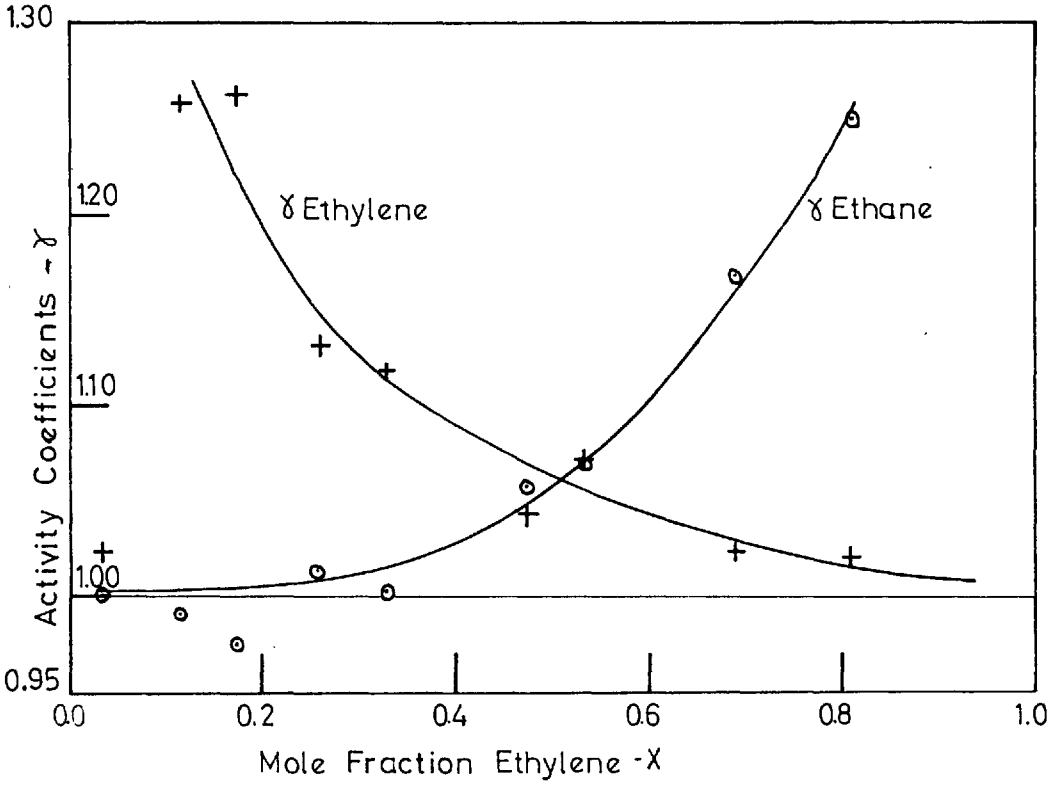
For the ethylene-ethane system the Herington consistency test was applied.[32] The data required for this test is given in Table III 1.5. In graph 8:5 the activity coefficients for this system are plotted and in graph 9:5 the Herington plot is given. At this stage it may be noted that one of the experimental points for a low ethylene concentration is seriously in error. Neglecting this point, the Herington test shows that the results, although subject to considerable experimental scatter, are consistent.

The test could not be applied to the other binary systems as the results did not cover the full composition range.

5:1:4 Correlation of results

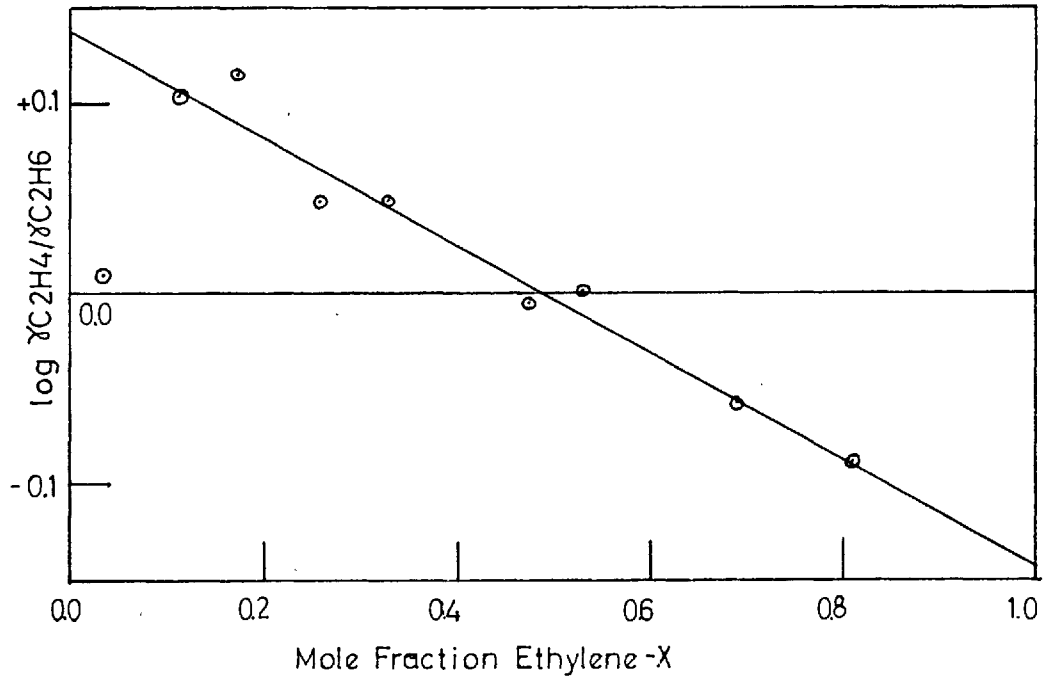
The Li-Coull equation[46] was chosen to obtain a correlation of the experimental data and initially its application to the ethylene-ethane system was considered. In table III 1.6 the parameters required for the correlation are given. In graph 10:5 the Li-Coull correlation plots, $(T \log \gamma_1)^{-\frac{1}{2}}$ v. x_{1/x_2} and $(T \log \gamma_2)^{-\frac{1}{2}}$ v. x_{2/x_1}, are given.

The emphasis placed on the points used for the correlation depends upon their reliability. For x-x ratios below 0.1, small errors in analysis become greatly magnified, and for ratios above 1.0, experimental values of γ lie close to unity, causing $(T \log \gamma)^{-\frac{1}{2}}$ to become very large, and



GRAPH 8:5

EXPERIMENTAL ACTIVITY COEFFICIENTS

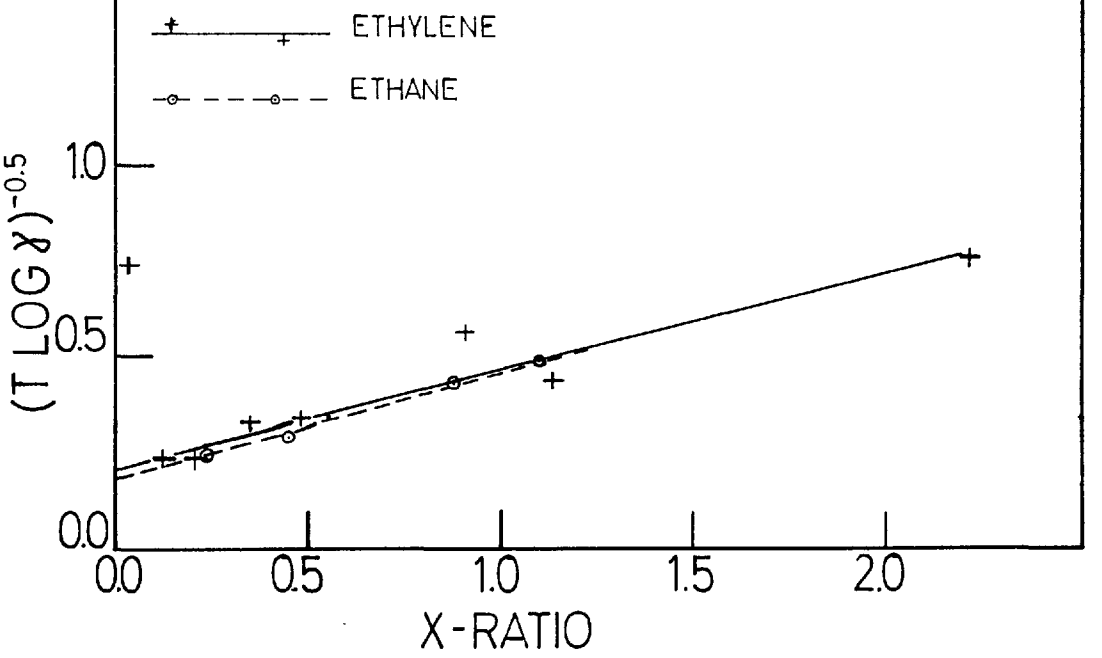


GRAPH 9:5

HERINGTON TEST - ETHYLENE ETHANE SYSTEM

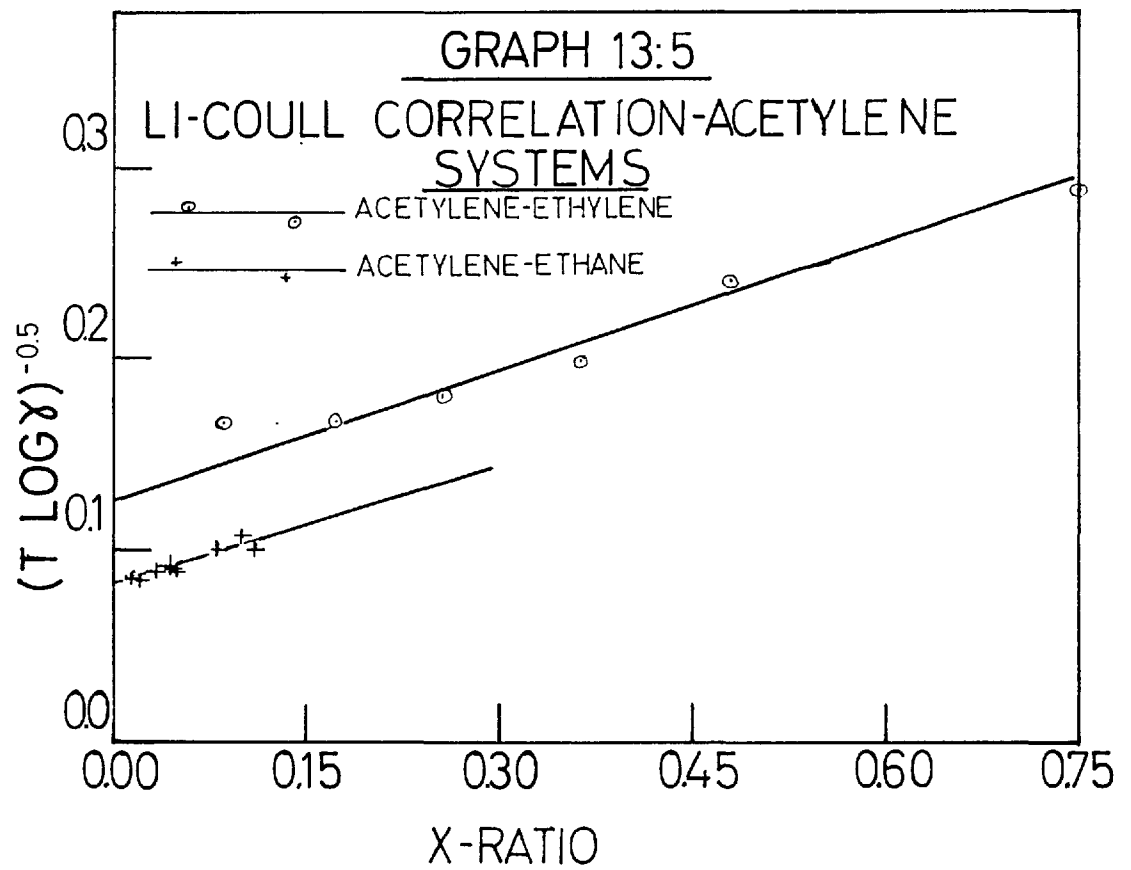
GRAPH 10:5

LI-COULL CORRELATION -ETHYLENE-ETHANE



GRAPH 13:5

LI-COULL CORRELATION-ACETYLENE SYSTEMS



again subject to considerable error.

The resultant equations were:-

$$(T \log \gamma_{C_2H_4})^{-\frac{1}{2}} = \frac{x_{C_2H_4} + 0.8\, x_{C_2H_6}}{3.9\, x_{C_2H_6}} \quad \ldots\ldots(6:5)$$

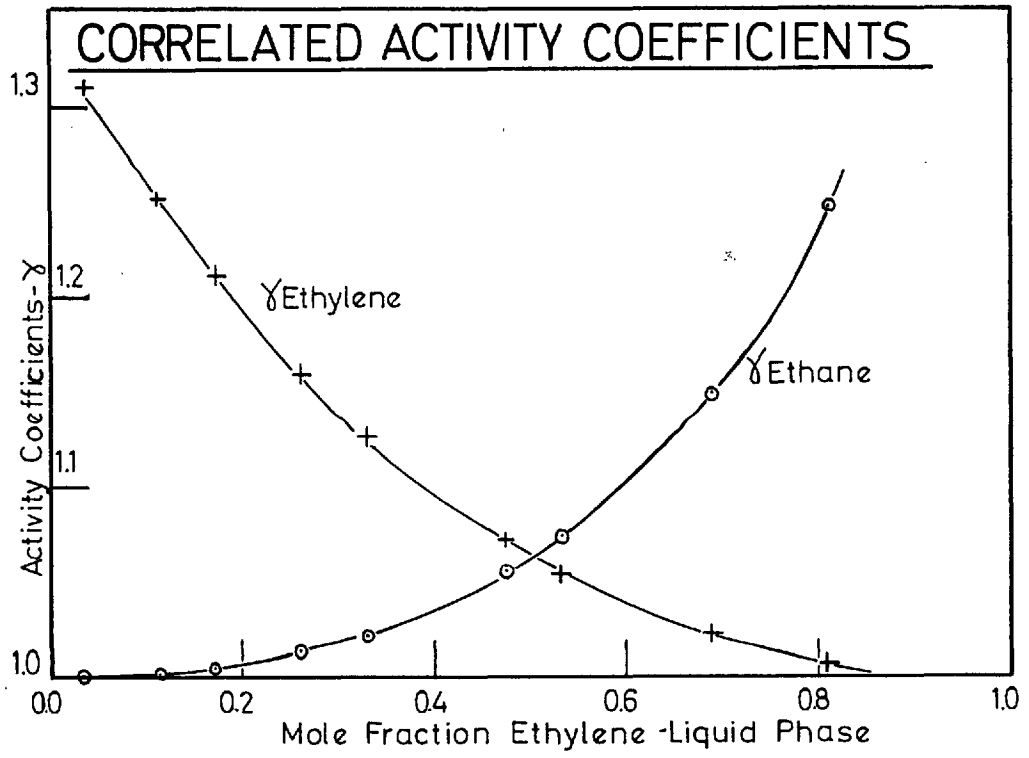
and

$$(T \log \gamma_{C_2H_6})^{-\frac{1}{2}} = \frac{x_{C_2H_6} + 0.63\, x_{C_2H_4}}{3.5\, x_{C_2H_4}} \quad \ldots(7:5)$$

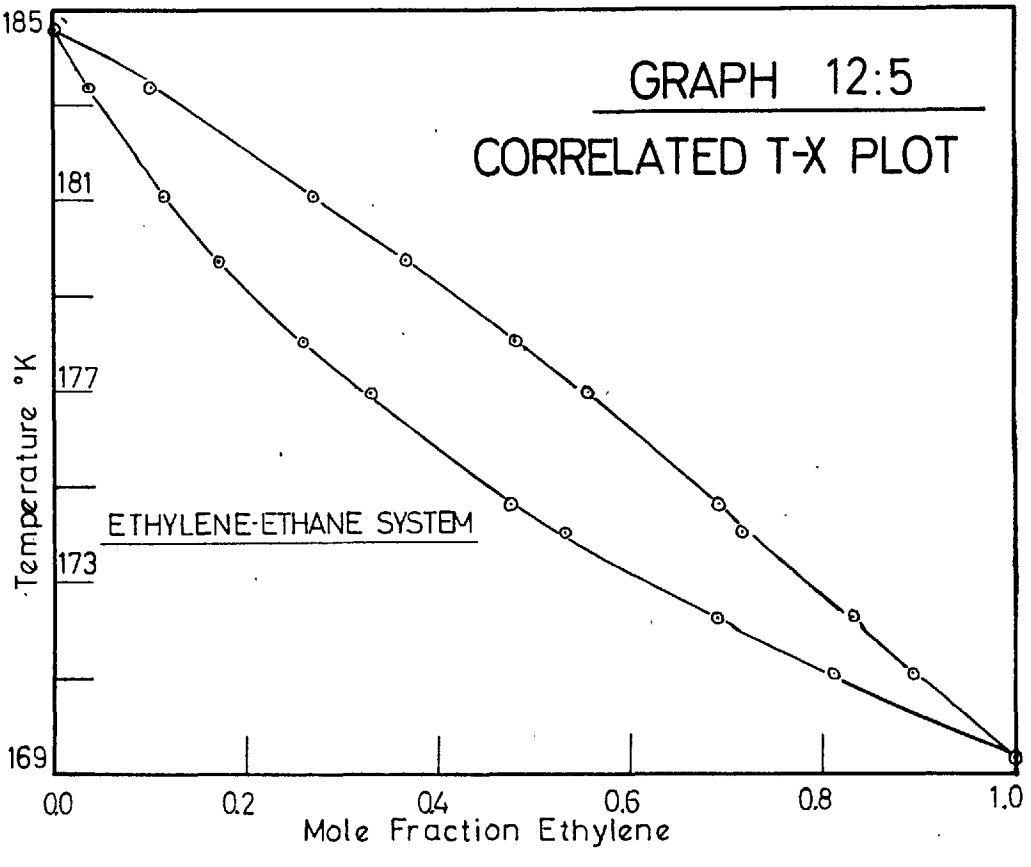
A comparison of the experimental and correlated data was obtained by calculating activity coefficients from (6:5) and (7:5) using the experimental values of liquid composition and assuming equilibrium temperatures. The vapour composition was calculated for each component from these activity coefficients and the vapour pressure data. An iterative procedure was then used to determine the equilibrium temperature which made the sum of the vapour compositions unity.

In Table III 1.7 the calculated equilibrium data is given. In graphs 11:5 and 12:5 the correlated activity coefficients and temperature-composition diagram are plotted.

The Li-Coull correlation is not strictly applicable to the acetylene binary systems, since in both cases part of the composition range cannot be studied owing to the separation


CORRELATED ACTIVITY COEFFICIENTS
1.3
1.2
1.1
1.0
Activity Coefficients-γ
γEthylene
γEthane
0.0
0.2
0.4
0.6
0.8
1.0
Mole Fraction Ethylene -Liquid Phase

GRAPH 11:5


GRAPH 12:5
CORRELATED T-X PLOT
185
181
177
173
169
Temperature °K
ETHYLENE-ETHANE SYSTEM
0.0
0.2
0.4
0.6
0.8
1.0
Mole Fraction Ethylene

of solid acetylene. To synthesize a ternary correlation, however, all the binary constants are necessary.

In tables III 1.8 and III 1.9 the activity coefficients for acetylene in the systems acetylene-ethane and acetylene-ethylene are presented. The activity coefficients for the second component of these binaries range from 0.95 to 1.10 and are not included.

In graph 13:5 the Li-Coull plots for acetylene in the respective binary systems are given.

The resulting equation for the acetylene-ethane binary is:

$$\left(T \log \gamma_{C_2 H_2}\right)^{-\frac{1}{2}} = 0.203 \frac{x_{C_2H_2}}{x_{C_2H_6}} + 0.081 \quad \ldots\ldots(8:5)$$

and for the acetylene-ethylene binary:

$$\left(T \log \gamma_{C_2 H_2}\right)^{-\frac{1}{2}} = 0.224 \frac{x_{C_2H_2}}{x_{C_2H_4}} + 0.125 \quad \ldots\ldots(9:5)$$

The plots for the second component were not satisfactory and this was attributed to the magnification of experimental errors caused by calculating activity coefficients in composition regions approaching the pure component. Equations for these constituents were therefore calculated from (8:5) and (9:5). The Li-Coull equations for a binary system, 1-2 ((28:4) and (29:4)) are:[46]

$$\left(T \log \gamma_1\right)^{-\frac{1}{2}} = \left(\frac{b_1}{b_2}\right)\left(\frac{b_2}{k_{12}}\right)^{\frac{1}{2}}\left(\frac{x_1}{x_2}\right) + \left(\frac{b_2}{k_{12}}\right)^{\frac{1}{2}}$$

and $$\left(T \log \gamma_2\right)^{-\frac{1}{2}} = \left(\frac{b_2}{b_1}\right)\left(\frac{b_1}{k_{12}}\right)^{\frac{1}{2}}\left(\frac{x_2}{x_1}\right) + \left(\frac{b_1}{k_{12}}\right)^{\frac{1}{2}}$$

whence $$\frac{b_1}{b_2} = \frac{\text{Slope of constituent 1 plot}}{\text{Intercept of constituent 1 plot}} = \left(\frac{S_1}{I_1}\right) \quad \text{.(10:5)}$$

$$= \left(\frac{I_2}{I_1}\right)^2 \quad \text{.....(11:5)}$$

$$= \left(\frac{I_2}{S_2}\right) \quad \text{.....(12:5)}$$

For the acetylene-ethane system therefore:

$$\left(T \log \gamma_{C_2H_6}\right)^{-\frac{1}{2}} = 0.051\, x_{C_2H_6} / x_{C_2H_2} + 0.129 \quad \text{...(13:5)}$$

and for the acetylene-ethylene system

$$\left(T \log \gamma_{C_2H_4}\right)^{-\frac{1}{2}} = 0.093\, x_{C_2H_4} / x_{C_2H_2} + 0.167 \quad \text{...(14:5)}$$

The equations for the acetylene-ethane system were satisfactory but the agreement between the exprimental data and the correlated data, calculated from (8:5) and (13:5), as described above for the ethylene-ethane system, was not good enough to justify the use of these equations for purposes other than as a step in the development of a ternary

correlation. The majority of the x-x ratios for this system were less than 0.1 and so the partial success of the correlation does not reflect upon the applicability of the method. Equilibrium data calculated from (9:5) and (14:5) for the acetylene-ethylene system is recorded in Table III. 1. 10. The results in this case compare favourably with the experimental data.

The ternary Li-Coull equations[46] involve only binary constants. The constants k_{12} etc., are assumed to be dependent only upon binary molecular collisions, ternary collisions being neglected. For a system with components 1-2-3 the equation (30:4) for component 1 is:-

$$(T \log \gamma_1) = \frac{\left\{\left(\frac{k_{12}}{b_1}\right)\left(\frac{b_2}{b_1}\right) x_2^2 + \left(\frac{k_{13}}{b_1}\right)\left(\frac{b_3}{b_1}\right) x_3^2 + \left[\left(\frac{k_{12}}{b_1}\right)\left(\frac{b_3}{b_1}\right) + \left(\frac{k_{13}}{b_1}\right)\left(\frac{b_2}{b_1}\right) - \left(\frac{k_{23}}{b_1}\right)\right] x_2 x_3\right\}}{\left\{x_1 + \left(\frac{b_2}{b_1}\right) x_2 + \left(\frac{b_3}{b_1}\right) x_3\right\}^2}$$

The constants are obtained from the binary equations with the aid of the relationships (10:5) to (12:5). The constant $\frac{k_{23}}{b_1}$ is evaluated from $\frac{(k_{23}/b_2)_{23}}{(b_1/b_2)_{12}}$

The resultant ternary equations are:-

$$\left(T \log \gamma_{C_2H_2}\right) = \frac{\left[20.15x_{C_2H_4}^2 + 23.75x_{C_2H_6}^2 + 30.75x_{C_2H_4}x_{C_2H_6}\right]}{\left[x_{C_2H_2} + 0.563x_{C_2H_4} + 0.395x_{C_2H_6}\right]^2} \quad ..(15:5)$$

$$\left(T \log \gamma_{C_2H_4}\right) = \frac{\left[114.5x_{C_2H_2}^2 + 49.0x_{C_2H_6}^2 - 85.0x_{C_2H_2}x_{C_2H_6}\right]}{\left[x_{C_2H_4} + 1.79x_{C_2H_2} + 1.59x_{C_2H_6}\right]^2} \quad ...(16:5)$$

$$\left(T \log \gamma_{C_2H_6}\right) = \frac{\left[383.0x_{C_2H_2}^2 + 29.8x_{C_2H_4}^2 + 170.3x_{C_2H_2}x_{C_2H_4}\right]}{\left[x_{C_2H_6} + 2.51x_{C_2H_2} + 1.25x_{C_2H_4}\right]^2} \quad ...(17:5)$$

These equations are not unique results of the binary data, since the constants of the ethylene-ethane system do not satisfy relationships (10:5) to (12:5). Although Li and Coull state that[46] the b_1/b_2 ratio may vary within consistent binary data and any of the calculated values may be used to develop the ternary relationships, it would appear that failure of the results to satisfy the inter-relationships of the constants of the Li-Coull equations would represent a failure to satisfy the Gibbs-Duhem equation. These conflicting statements may be resolved as the Li-Coull equations are only strictly applicable

to isobaric data if the constants b and k do not vary with temperature and b is independent of composition, it would appear that Li and Coull recognised that these conditions would not always be obeyed but found them to be of small practical importance.

Equation (16:5) could therefore have been obtained as:-

$$\left(T \log \gamma_{C_2H_4}\right) = \frac{\left[114.5x^2_{C_2H_2} + 24.7x^2_{C_2H_6} - 15.4x_{C_2H_2}x_{C_2H_6}\right]}{\left[x_{C_2H_4} + 1.79x_{C_2H_2} + 0.8x_{C_2H_6}\right]^2} \quad \ldots(18:5)$$

To determine the value of the correlation, experimental values of temperature and liquid composition were substituted in (15:5) to (17:5) and the corresponding vapour compositions were calculated, Table III.1.11.

The Li-Coull equations do not give an adequate representation of the ternary data. In Table III.1.12 (18:5) has been used instead of (16:5). The change of equation increases the mole fraction of ethylene in the vapour by about 2 mole%. The deviations from the experimental results, obtained in the first instance, were random, being either positive or negative, and the use of (18:5) did not, therefore, improve the correlation.

It would appear that the experimental system is too complex to be analysed by the Li-Coull equations, and a further

investigation of other equations was temporarily abandoned in favour of obtaining an empirical correlation from the London University Mercury Computer for use with the multi-component distillation studies.

A surface fitting programme, R.A.E. 194/A, written and developed by Dr. J.H. Cadwell of R.A.E. (Farnborough), was used to fit bivariate polynomials to the data. For n triplets of values $(z_i, x_i, y_i,)$ the resultant equation is of the form:-

$$z = g(x,y) = \sum_{i=o}^{l} \sum_{j=o}^{l-i} a_{ij} (x')^i (y')^j \quad \ldots\ldots(19:5)$$

where $x' = x - \bar{x}$ and $y' = y - \bar{y}$, $\bar{x}$ and $\bar{y}$ being the mean values of the n x-values and the n y-values, respectively.

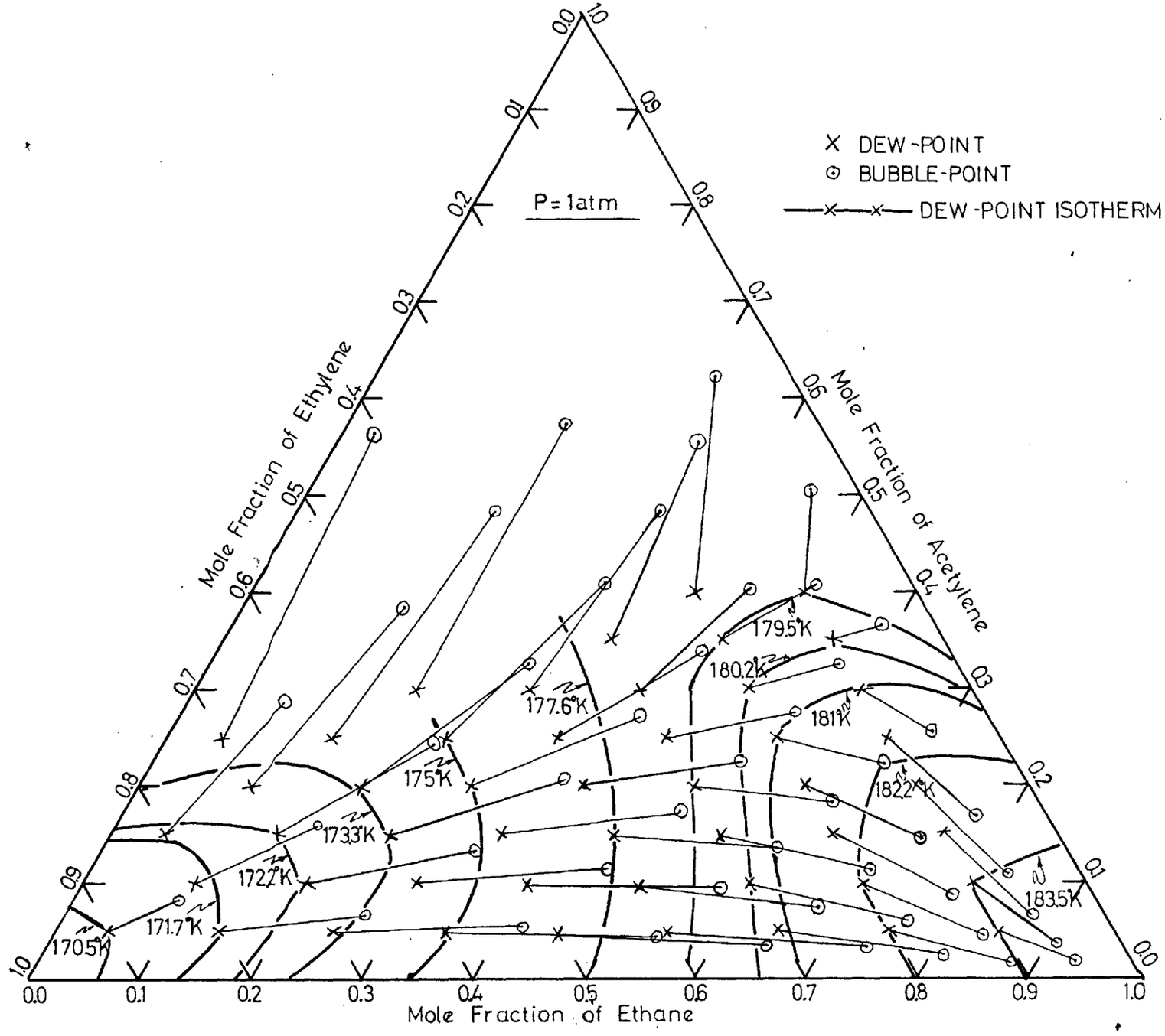
Initially four polynomials of the form:

$$\begin{aligned} T &= f(y_1', y_2') \\ x_1 &= f(y_1', y_2') \\ x_2 &= f(y_1', y_2') \\ x_3 &= f(y_1', y_2') \end{aligned} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(20:5)$$

were fitted to the data. The pure component points and the acetylene-ethane azeotrope point, given by Din and Clark,[13] were slightly weighted so that the equations always satisfied these values. When using equations of the sixth degree the maximum

residual of temperature (experimental value - fitted value) was 0.37°K and of composition was 0.025 mole fraction. The average residuals, however, indicated that equations of a lower degree would describe the data adequately. In consequence a polynomial of degree 4 was used to obtain $T = f(y_1', y_2')$ and polynomials of degree 3 were used to obtain $x = f(y_1', y_2',)$. In Tables III.1.13 to III.1.16 the polynomial coefficients are given. In the determination of these, correlated data was used for the ethylene-ethane binary system, but the original experimental results were used for the other points. In Table III.1.17 all residuals are given. The results are given in the 'floating-point form', i.e. 3.01, 2 $\bar{=}$ 3.01×10^2. The experimental results are represented satisfactorily by these polynomials. The average temperature residual is about 0.2°K and the average composition residual is about 1.5 mole%. A short programme was written to obtain values of temperature and liquid composition, at 5 mole % intervals of acetylene vapour composition and 10 mole % intervals of ethylene and ethane composition, from the polynomials. The results are given in Table III.1.18 and plotted in graph 14:5.

Programme R.A.E. 194/A was also used to obtain correlations for $K_i = f(x_1', x_2')$, $K_i = f(y_1', y_2')$ and $T = f(x_1', x_2')$. The polynomials are presented in Tables III.1.19 to III.1.25 and all residuals are given in Table III.1.17.



GRAPH 14:5

CORRELATED TERNARY DATA FROM SURFACE FITTING PROGRAMME

A second theoretical correlation for ternary vapour-liquid equilibrium data was developed and used in a further attempt to test the consistency of the experimental work and to provide a satisfactory correlation for it. In Section 3 of Appendix III a detailed derivation of the relevant equations and the calculation techniques employed is given. The method in essence is similar to Wohl's developments[94] of the excess free energy equations but it uses the rule (strictly applicable only to regular solutions) $T \log \gamma_i$ = constant at constant composition to correct for the effect of temperature on the activity coefficients. Initially, as is shown in Appendix III, the values of the function $T \sum_i x_i \log_e \gamma_i$ derived from the experimental phase equilibrium data were correlated with the experimental liquid compositions using the surface fitting programme R.A.E. 194/A. It was found that the summation, $\sum x_i \log_e \gamma_i$, was very sensitive to the introduction of activity coefficients whose magnitude was less than one and this led to a poor correlation for the excess free energy of mixing and subsequent failure of the method. It was decided to set the negative values of $\log_e \gamma_i$ to zero and repeat the calculations. This procedure was considered to be justified as experimental errors are magnified at high concentrations of a given component and are particularly noticeable when the results are expressed in terms of the activity coefficients. Although this technique produced some improvement in the correlation

the average residuals of the excess free energy of mixing were only reduced from about 14% to about 11% of the average experimental value when using a polynomial of degree 3. For the correlation of isobaric data of non-ideal systems it would appear that the excess free energy of mixing is a function of both temperature and liquid composition and in consequence the coefficients of the polynomials developed above are temperature dependent and therefore are not true constants.

The free energy correlation, vapour pressure equations experimental pressure, and either two compositions or a temperature and a composition were used as data in a computer programme written to calculate the equilibrium conditions that satisfy the equations described in Appendix III. To obtain a direct measure of the value of the method the experimental values of firstly $x_{C_2H_2}$ and $x_{C_2H_4}$, secondly, $y_{C_2H_2}$ and $y_{C_2H_4}$ and finally T and $x_{C_2H_2}$ were fed as data to the computer. The most satisfactory results were obtained when using vapour compositions as initial conditions but the differences between the calculated and the experimental values were too great to attribute them to experimental errors. The computed results are given in Table III.3.1.

5:1:5 Discussion of results

The phase equilibria of the ethylene-ethane system have been previously studied by Moran[55] and Kharakhorin.[40]

Moran measured the dew and bubble-points of mixtures of known composition over a pressure range of 0.25 to 2 atms. He fitted equations of the form $\log_{10} P = A + B/T$ to the results and interpolated to give vapour-liquid isobars at 0.25, 0.50, 1.00, and 2.00 atms. Kharakhorin used the circulation method[77] to obtain a series of isotherms in the temperature range 0 to -103.8°C.

Moran[55] considered that the effect of the deviations of the vapour from perfect gas behaviour was negligibly small. He demonstrated that the maximum deviation in the equilibrium constant resulting from this cause was 10%. To establish the thermodynamic consistency of his measured data he used the general phase boundary equations.[87] He measured the slope of the dew-point curves of two isotherms at 176°K and 182°K and compared them with calculated values. Good agreement was obtained at sub-atmospheric pressures but the deviations were considerable at higher pressures. The reliability of the bubble-point curves was not established.

The dew-point curves of Moran and Kharakhorin show quite good agreement at atmospheric pressure. The bubble-point curves, however, exhibit wide random discrepancies which were not accounted for. Moran considered that his results at 0.961 mole fraction of ethylene were unreliable, due to the presence of a small amount of non-condensible impurity present at the

beginning of the run.

The experimental data obtained in the present work satisfied Herington's consistency test.[32] The straight line relationship obtained indicates that the mixture is almost regular.[76] The results were correlated satisfactorily by the Li-Coull method,[46] the predicted compositions agreeing well with the experimental values although in two cases the experimental temperatures were in error by 0.5°C. The iteration method employed was relatively insensitive to temperature change and the experimental errors were therefore accumulated within this variable. The data is compared with the results of other workers in Graphs 1:5 and 2:5. The dew-point curve approximates to the curves obtained by Moran[55] and Kharakhorin.[40] The bubble-point curve agrees with Kharakhorin's results at low temperatures and with Moran's results at high temperatures. The presence of small quantities of propane and butane in the ethane feedstock should reduce the positive deviations from Raoult's law at the ethane (high temperature) end of the diagram, although errors in the boiling point of the pure constituent were in fact negligible.

Quantitative data for the comparison of the results of the acetylene binary systems and the ternary systems were not available. Din and Clark[13] studied the binary systems, but they were principally concerned with solid-liquid equilibria. In the present work, no azeotrope was discovered in the acetylene-

ethylene system, although the shape of the phase boundary curves was indicative of azeotrope formation at higher pressures.

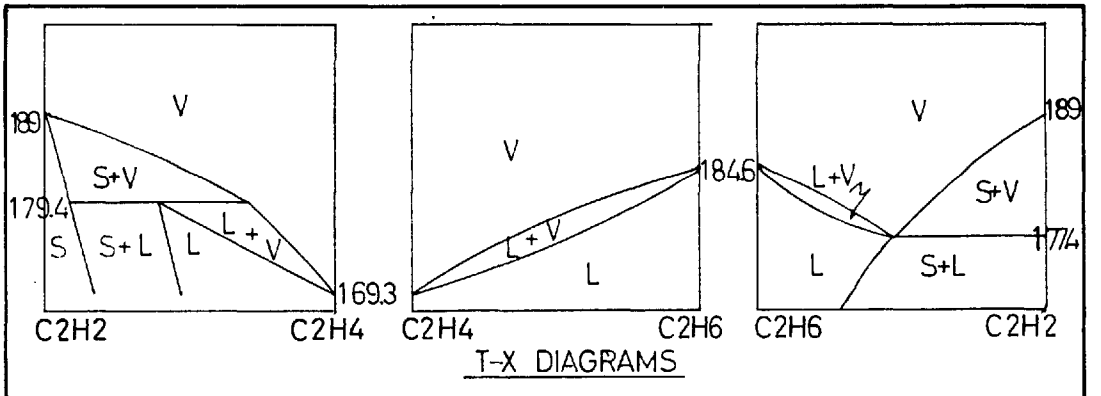
Prigogine and Defay[68] consider binary azeotropes to be a special case of a family of thermodynamic states, which they term indifferent states. The authors generalize the Gibbs-Konovalow theorems to deal with polyvariant systems and show that for any isobaric or isothermal equilibrium displacement in which a system passes through an indifferent state then the temperature or pressure passes through an extreme value. McCurdy and Katz[51] studied the ternary phase equilibria of the C_2 - hydrocarbons at 40°F and 60°F. They described "a series of ternary azeotropes" traversing the diagram from the acetylene-ethane azeotrope to the acetylene-ethylene azeotrope at 40°F, and from the acetylene-ethane azeotrope to the critical locus at 60°F. It seems likely that the dew and bubble-point curves make a close approach to each other along these lines, due to the critical phenomena. However, it would appear that the authors were mistaken in attributing their results to a series of ternary azeotropes.

Hogan et.al.[35] also obtained some ternary data at -35°, 0° and 40°F. At 40°F their results do not compare favourably with the values of McCurdy and Katz.[51] The authors also considered the ethylene-acetylene binary system. At 0°F

an azeotrope containing between 3 and 8 mole % acetylene was observed. At -35°F any azeotrope present contained less than 2 mole % acetylene. Hogan et. al. also quoted the work of Spessard, "at -133°F either an azeotrope is not formed or, if formed, is of low acetylene content, about 0.1%".

Owing to the formation of solid acetylene, the binary phase equilibrium diagrams and hence the ternary diagram, at atmospheric pressure, are quite complex. In Fig. 1:5 a qualitative picture of the expected variation in the ternary diagram with temperature is given. The acetylene binary system diagrams of Din and Clark[13] were used in the synthesis of these figures.

The Li-Coull equations were used to correlate the equilibrium data of the three binary systems. For the ethane-acetylene system the only available experimental results were for liquids containing less than 10% of acetylene, and as the x-x ratios were less than 0.1 for acetylene and greater than 1.0 for ethane, any experimental errors were magnified and the use of the method was not justified. A satisfactory correlation was obtained for the ethylene-ethane system, but the constants in the equations did not satisfy the inter-relationships required by the Gibbs-Duhem equation. Li and Coull considered[46] that the conditions could be disobeyed when developing a ternary correlation. Nevertheless the effectiveness of the correlation in predicting the experimental results does not prove the thermodynamic consistency of the data in this case. For the acetylene-ethylene system the correlation was developed by obtaining the equation for acetylene



T-X DIAGRAMS

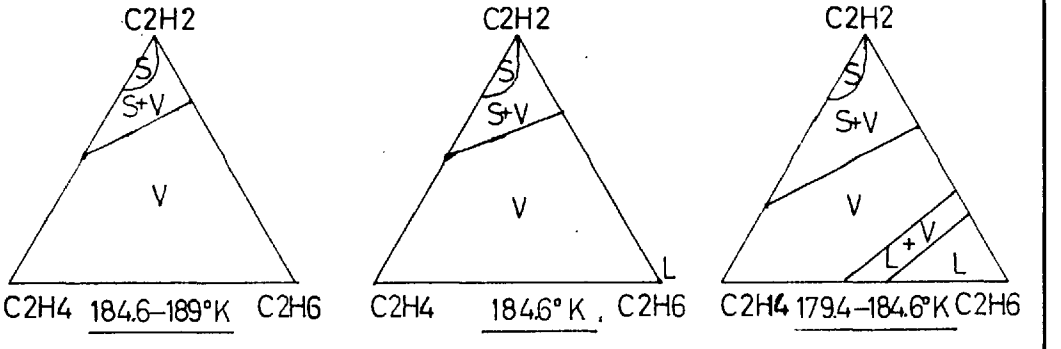


FIGURE 1:5

PHASE DIAGRAMS FOR TERNARY SYSTEM

and using the relationships between the constants to produce the equation for the component ethylene. The equations were then used to predict the experimental data and the good agreement between the calculated and experimental values was taken as proof of the consistency of the results. The Li-Coull ternary correlation is developed entirely from binary constants[46] and its failure to predict the experimental results was considered to be due to the non-ideality of the systems involved.

The ternary equilibrium correlation developed in Appendix III uses all the data and therefore ternary molecular interactions are taken into account and the equations should be more applicable for non-ideal systems. However, as has been seen above the correlation for excess free energy would appear to be dependent on temperature and the rule $T \log \gamma$ = constant at constant composition is not sufficient to take into account the variations of activity coefficients with temperature. Although the results obtained were better than those generated by the ternary Li-Coull equation, they were not completely satisfactory and it must be concluded that there are no available methods that will correlate non-ideal isobaric phase equilibrium data. Although there is no thermodynamic justification for the use of bivariate polynomials to express the equilibrium results,

there appeared to be no alternative, and the experimental data were correlated satisfactorily by the use of third and fourth degree equations. The validity of the expressions in the regions outside those covered by experimental work cannot be commented on at this stage.

Although the equipment and particularly the chromatograph were not capable of giving extremely precise results, it has been established that the results for the ethylene-ethane and acetylene-ethylene systems are thermodynamically consistent. In spite of a certain degree of scatter of the results it therefore seems reasonable to assume that the rest of the data is satisfactory for use in design calculations.

The phase equilibria of the C_2-hydrocarbons, at atmospheric pressure, has been measured more extensively than has been recorded in the past. There is still scope, however, for more refined work.

5:2 The Solubility of C_2-hydrocarbons in Acetone

5:2:1 General

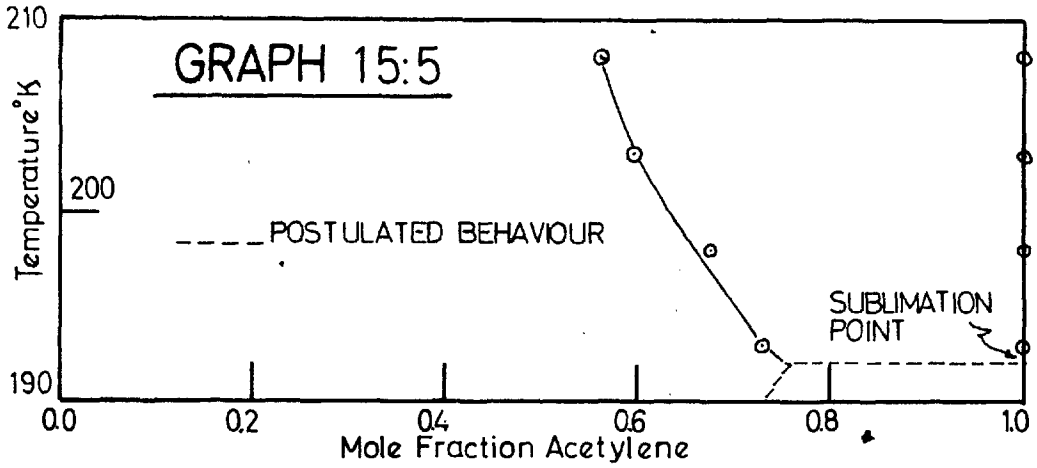
The solubilities of the three hydrocarbons in acetone are

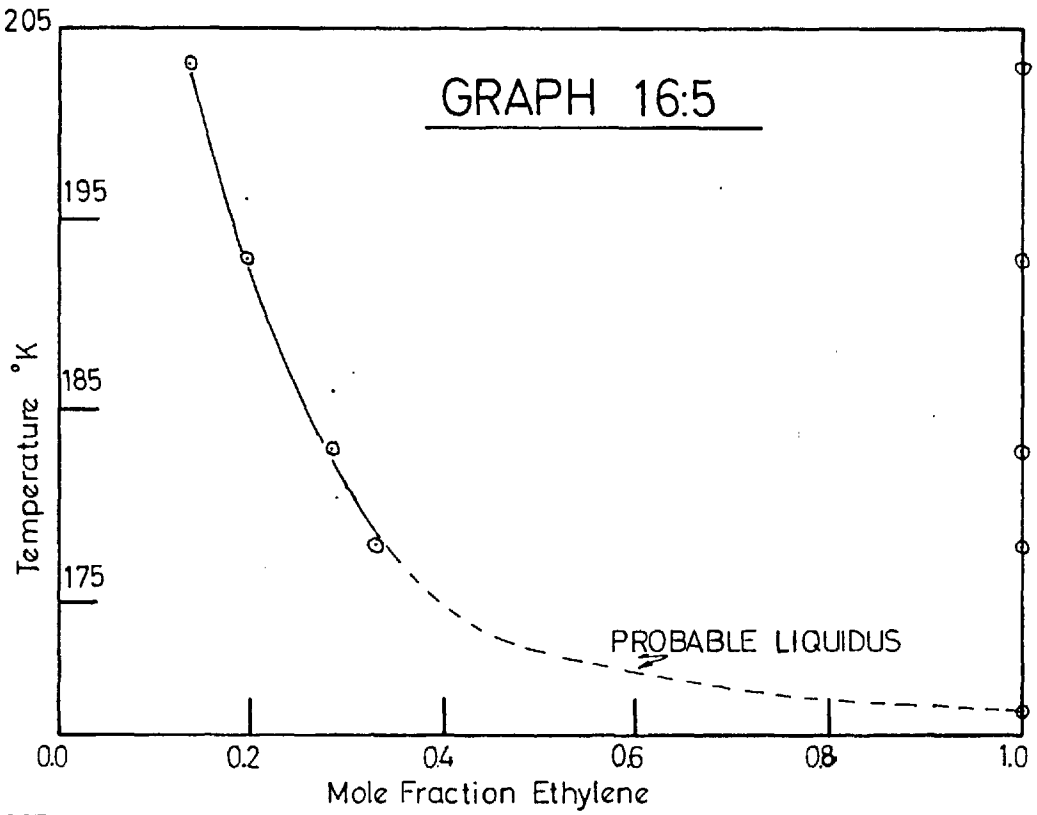
recorded in Tables III:2:1 to III:2:3. Temperature composition diagrams are given in graphs 15:5 to 17:5. The solubilities of pairs of hydrocarbons in acetone are given in Tables III:2:4 to III:2:6. Isotherms for each system are plotted in graphs 18:5 to 20:5 and the results are plotted on an acetone-free basis, with temperature as a parameter, in graph 21:5 to 23:5. Finally results for the quaternary system at -80°C are recorded in Table III:2:7 and represented in graph 24:5.

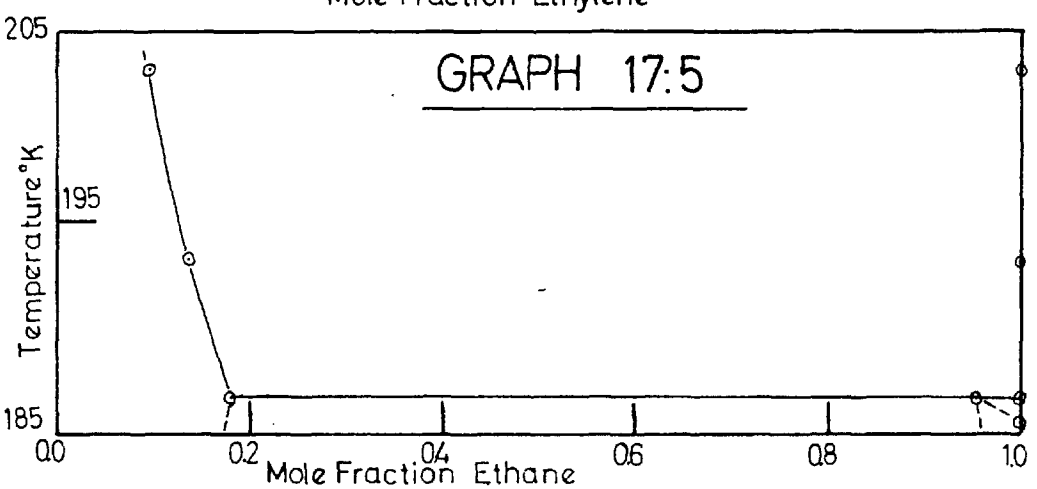
The results were not corrected for variations in ambient pressure.

5:2:2 Previous Work

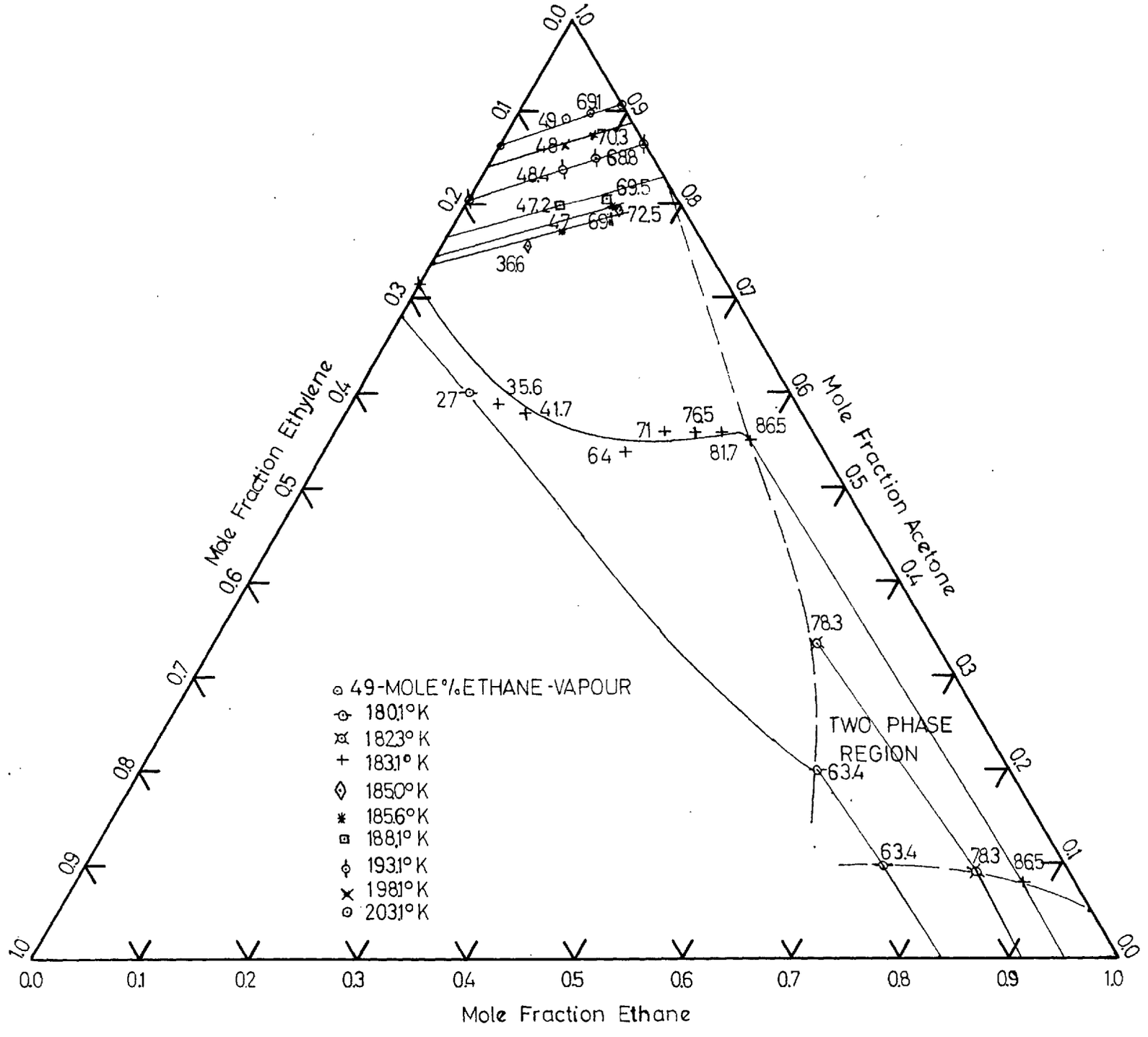
The solubility data of hydrocarbons in acetone has been expressed in a variety of forms in the literature. Schutt[80] has collected this data and expressed it in terms of the Bunsen coefficient, defined as: the volume of solute (measured at N.T.P.) that is dissolved in one





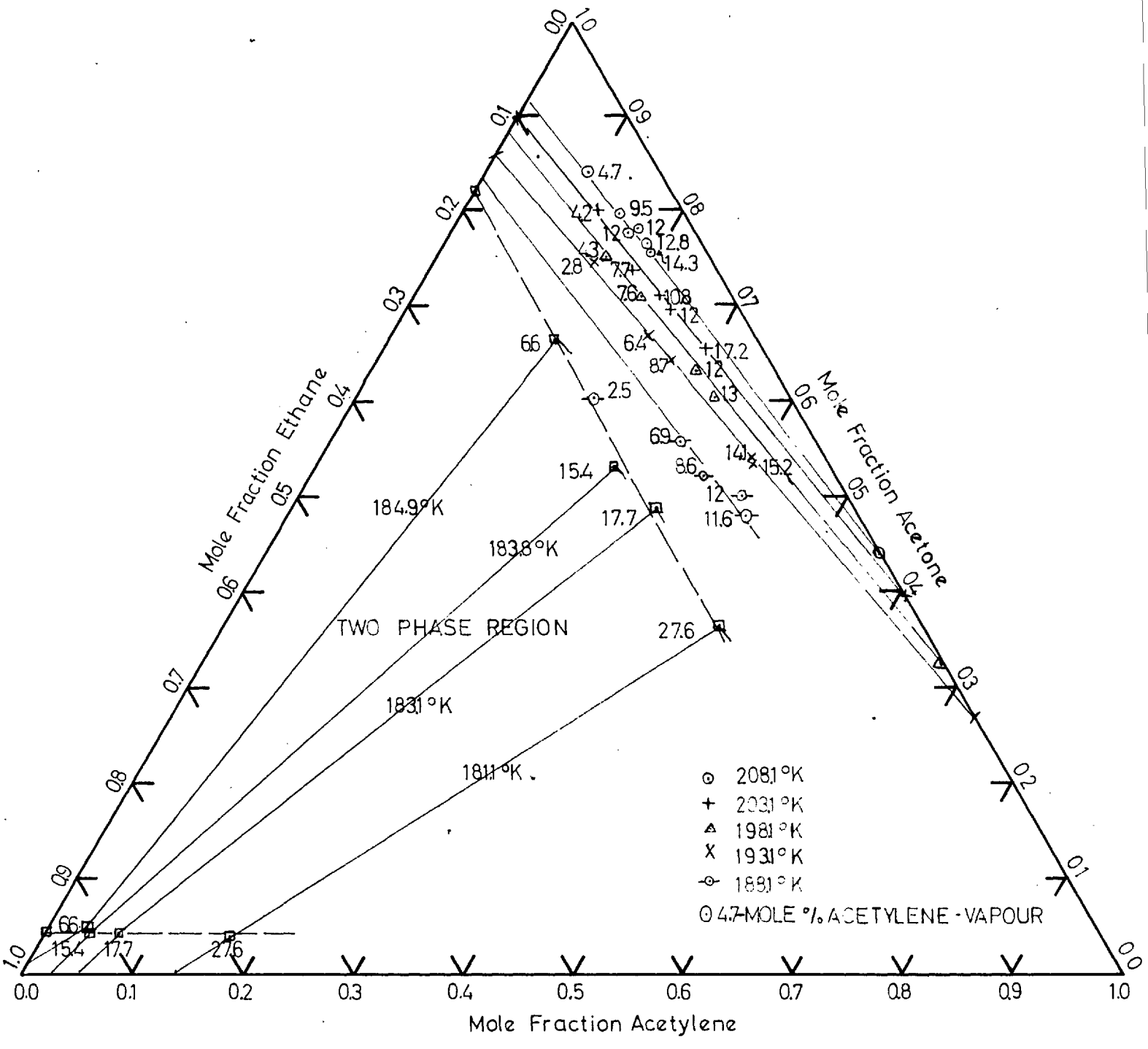


T-X DIAGRAMS - HYDROCARBONS IN ACETONE



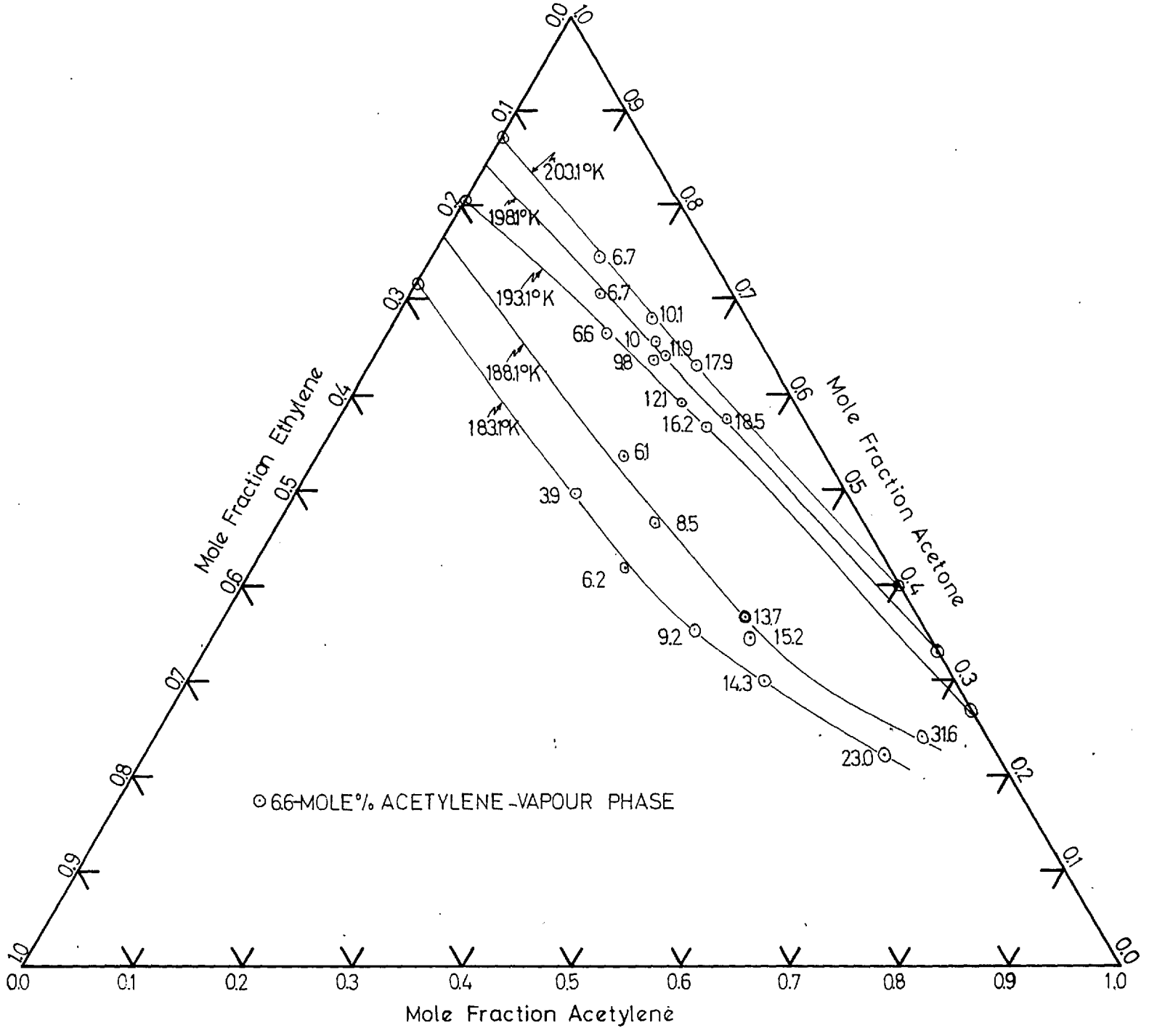
GRAPH 18:5

T-X DIAGRAM FOR ETHYLENE ETHANE ACETONE SYSTEM



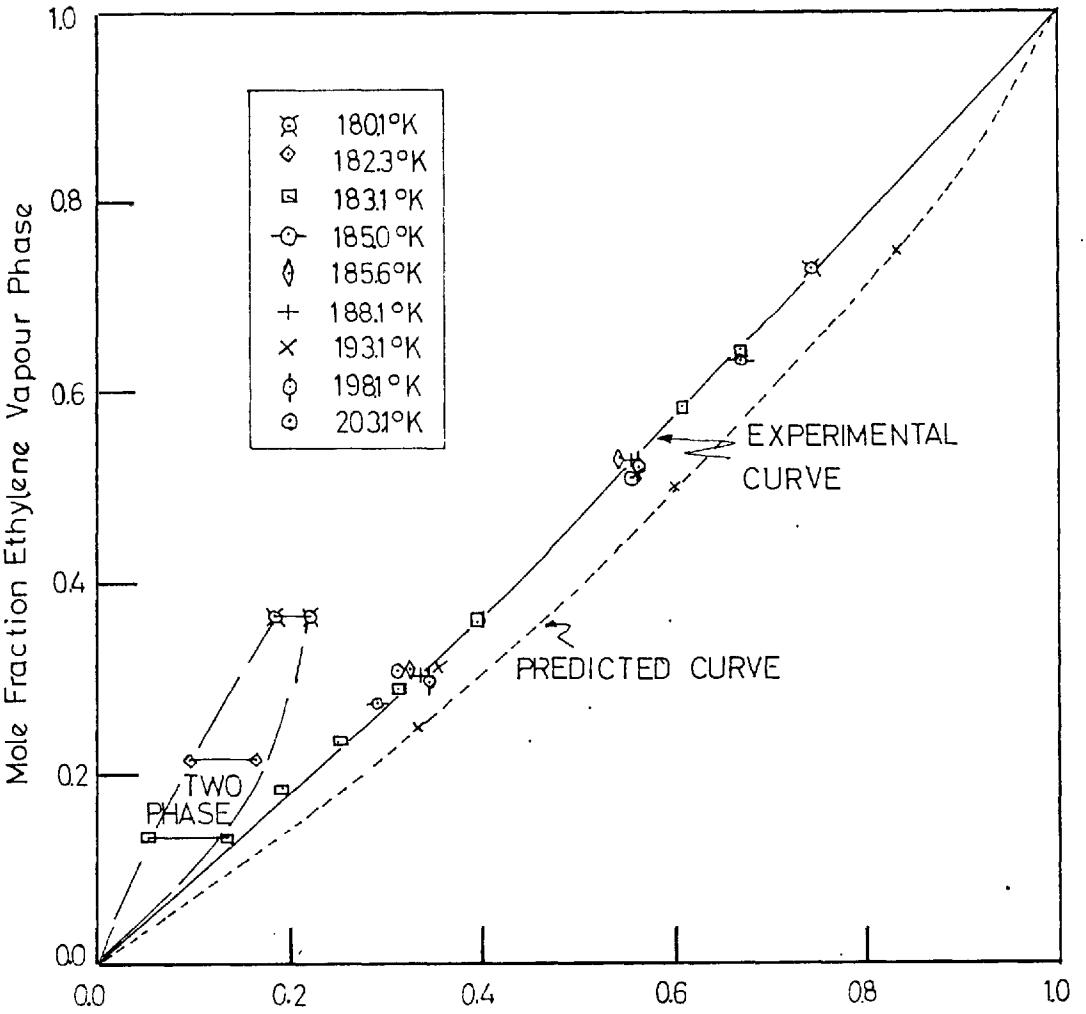
GRAPH 19:5

T-X DIAGRAM FOR ETHANE ACETYLENE ACETONE SYSTEM



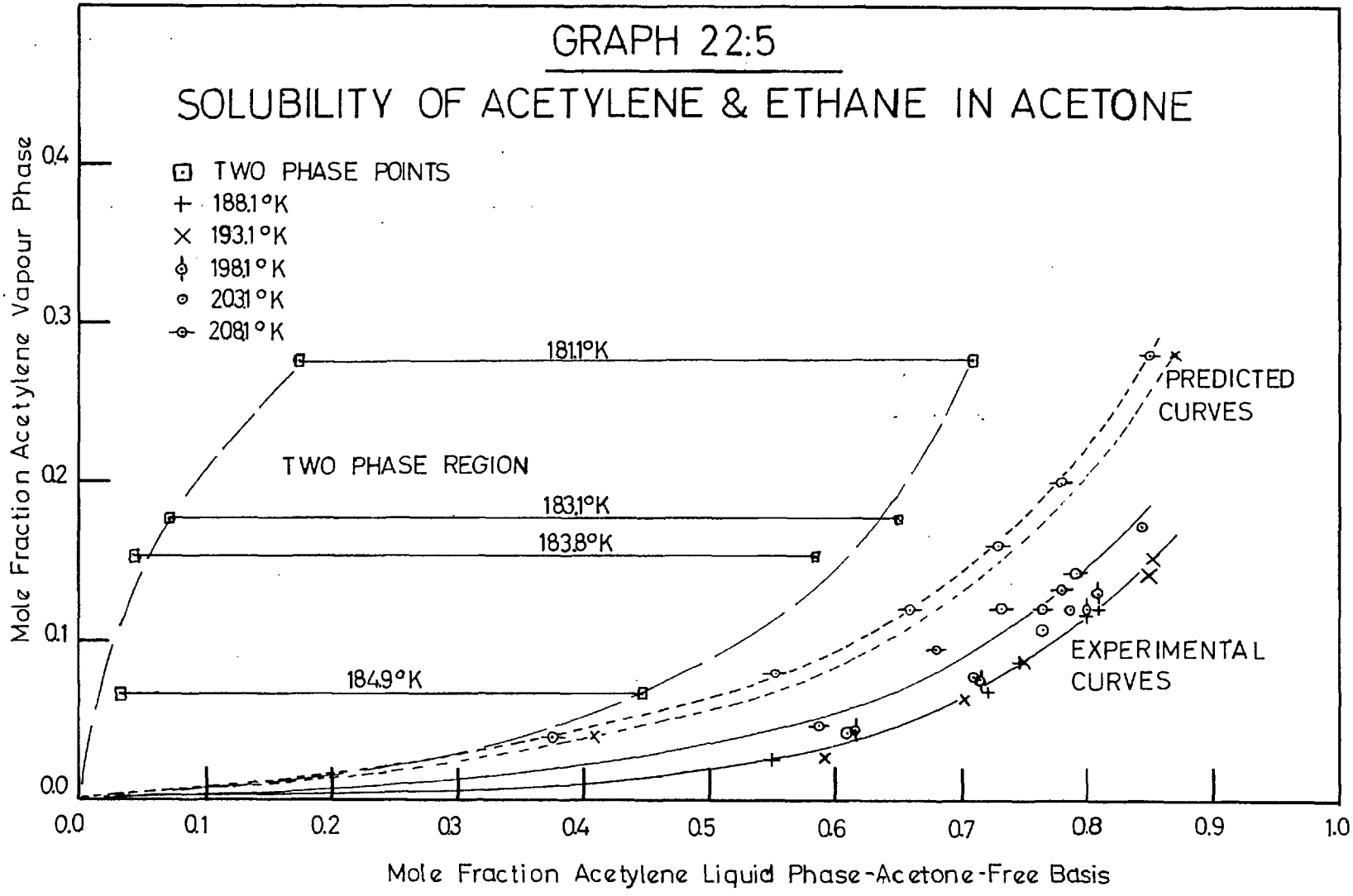
GRAPH 20:5

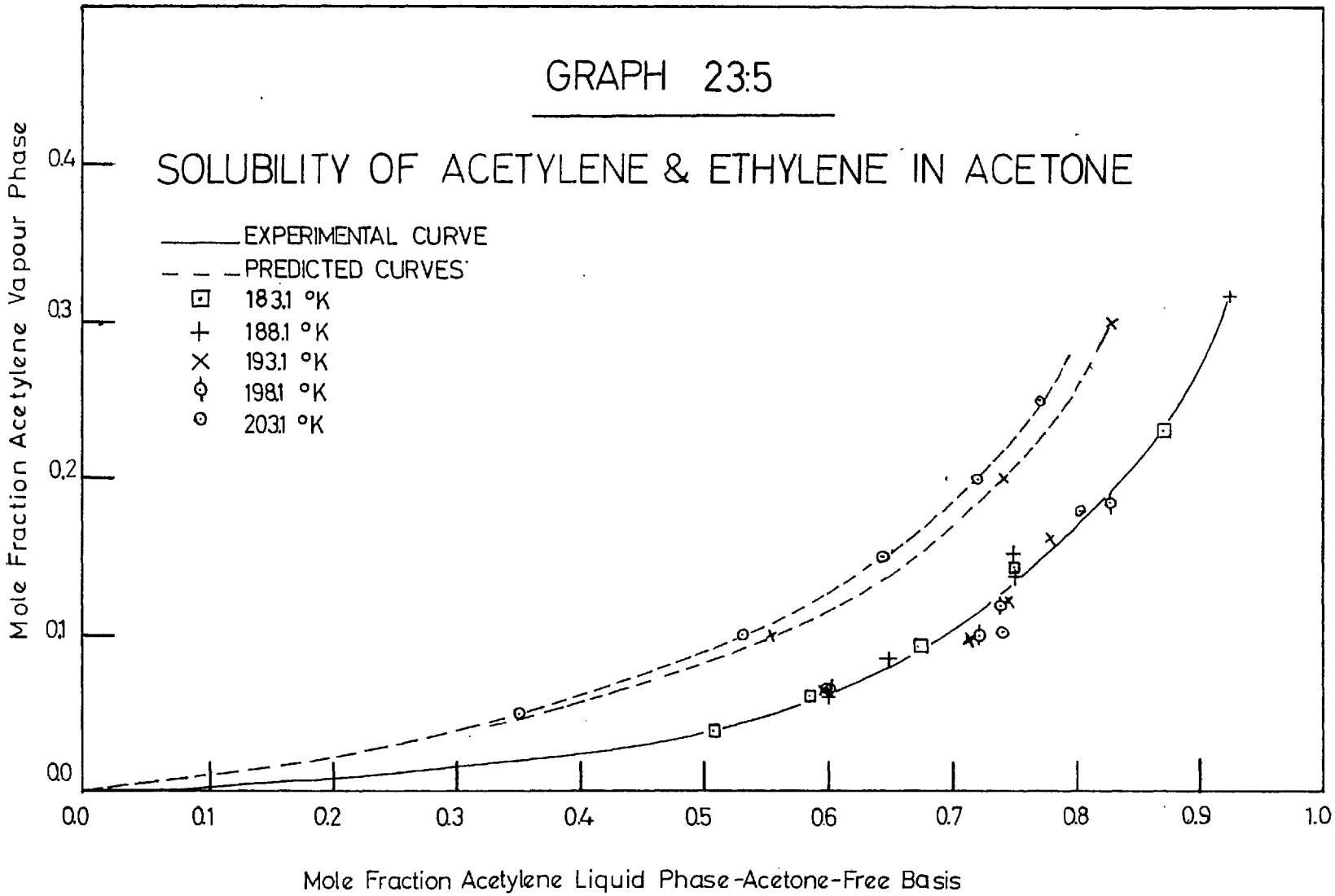
TEMPERATURE V. LIQUID COMPOSITION-ETHYLENE ACETYLENE ACETONE

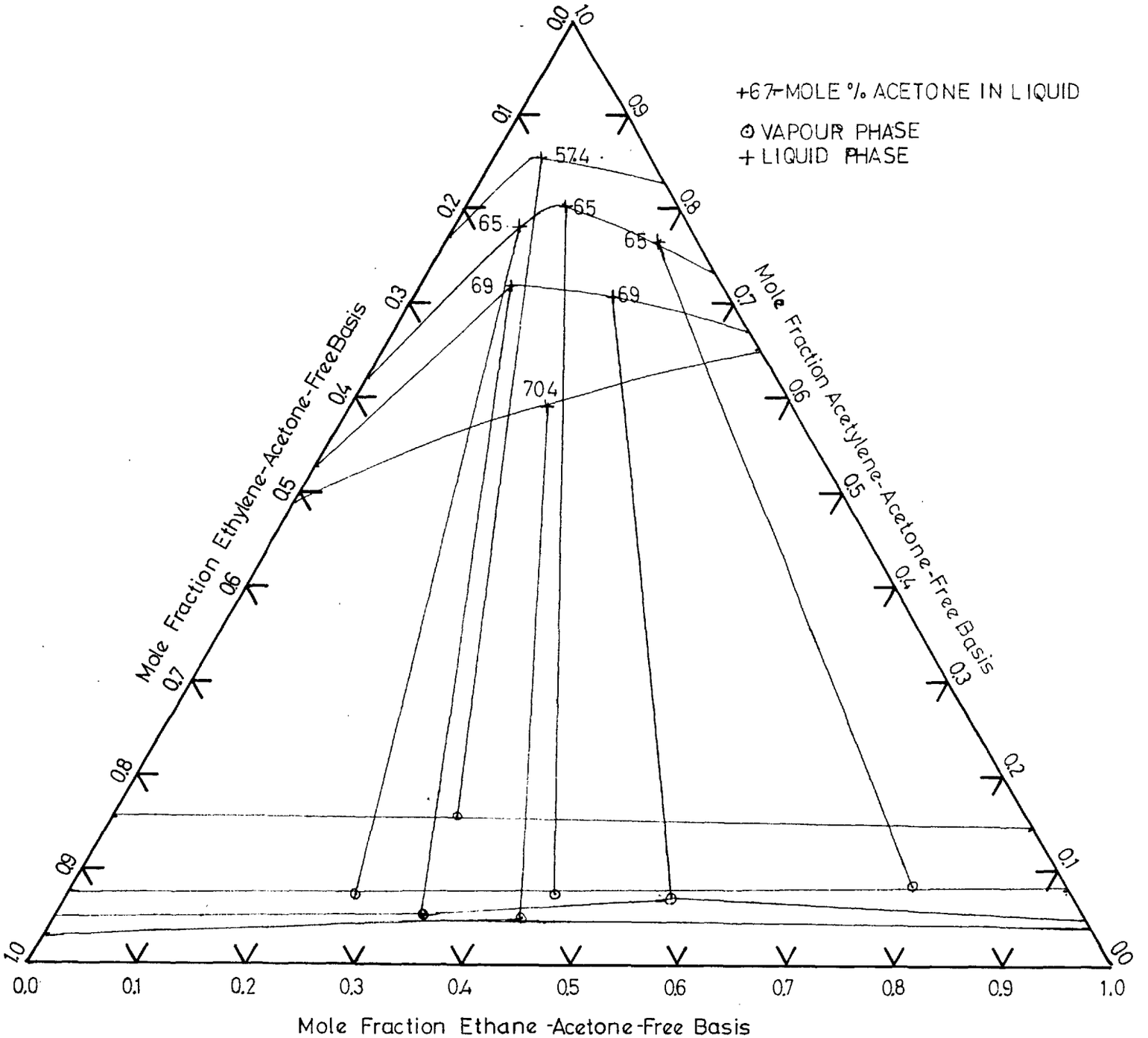


GRAPH 21:5

SOLUBILITY OF ETHYLENE & ETHANE IN ACETONE


GRAPH 22:5
SOLUBILITY OF ACETYLENE & ETHANE IN ACETONE
TWO PHASE POINTS
188.1°K
193.1°K
198.1°K
203.1°K
208.1°K
181.1°K
183.1°K
183.8°K
184.9°K
TWO PHASE REGION
PREDICTED CURVES
EXPERIMENTAL CURVES
Mole Fraction Acetylene Vapour Phase
Mole Fraction Acetylene Liquid Phase-Acetone-Free Basis
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0


GRAPH 23:5
SOLUBILITY OF ACETYLENE & ETHYLENE IN ACETONE
EXPERIMENTAL CURVE
PREDICTED CURVES
183.1 °K
188.1 °K
193.1 °K
198.1 °K
203.1 °K
Mole Fraction Acetylene Vapour Phase
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Mole Fraction Acetylene Liquid Phase-Acetone-Free Basis



GRAPH 24:5

EQUILIBRIUM DIAGRAM FOR QUATERNARY SYSTEM AT 193.1 °K

volume of the solvent (measured at the temperature and pressure of the experiment) when the partial pressure of the solute is 1 atm.abs.

Brameld and Clark[6] measured the solubility of acetylene in acetone over a range of temperature from -70°C to 40°C. Their results were given in terms of the weight of acetylene dissolved by unit weight of acetone.

Horiuti [37] measured the solubilities of the C_2-hydrocarbons in acetone over a range of temperature from 0°C to 40°C. The author expressed his results as modified Ostwald coefficients. The Ostwald coefficient is defined as: the volume of gas dissolved in unit volume of the solvent, both volumes being measured under experimental conditions. Horiuti [37] replaced the unit volume of solvent by the unit volume of solution, thus taking the incremental volume of the absorbed constituents or a factor of dilation into consideration.

Seidell[81] records the results of these and other workers in his 'Solubilities of Organic compounds.'

Friend and Adler[25] have formulated the relationships between the various solubility concepts. In Figure 2:5 Schutt's plot has been reproduced.

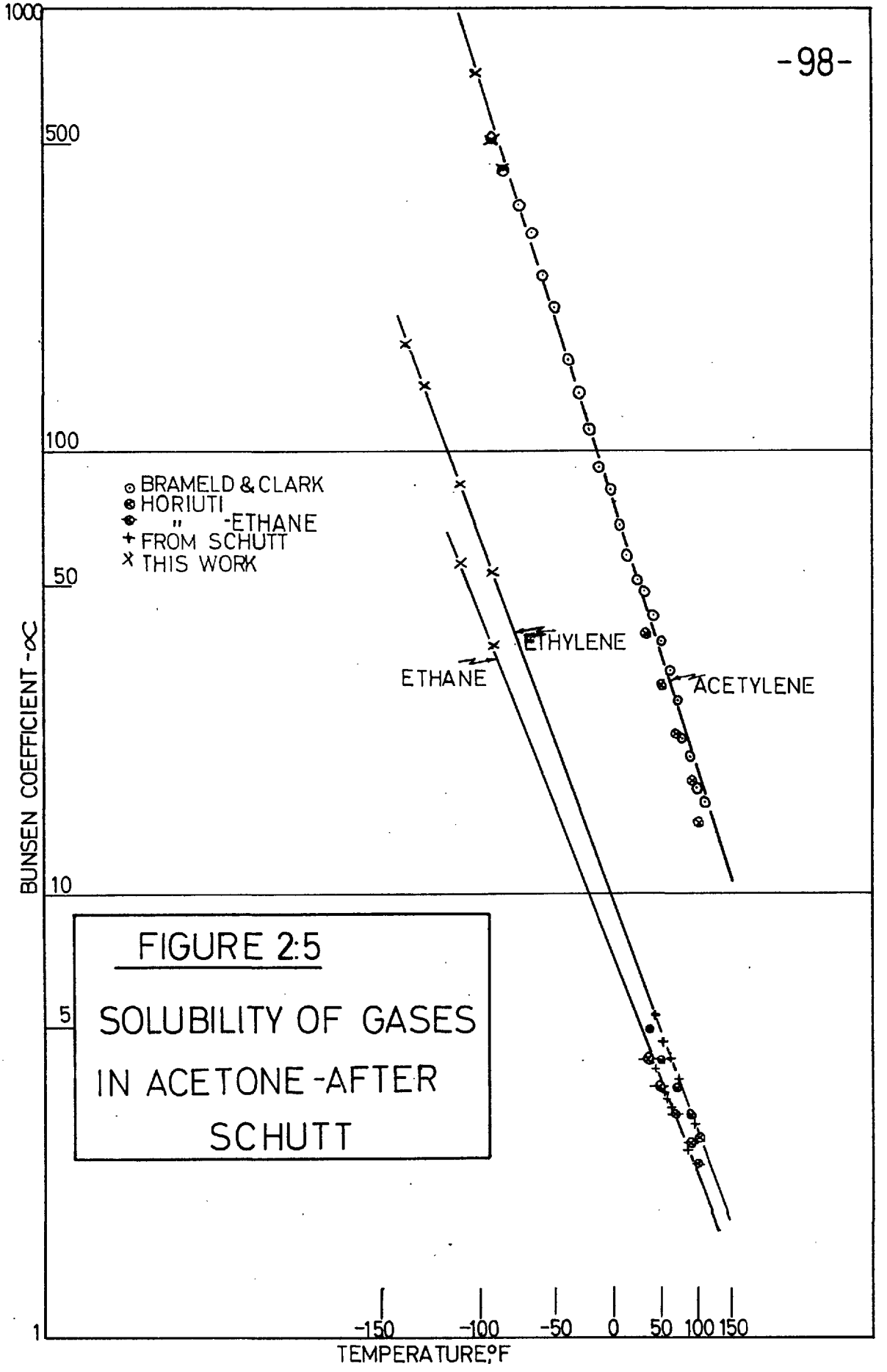


FIGURE 2:5

SOLUBILITY OF GASES IN ACETONE -AFTER SCHUTT

5:2:3 Correlation of data

It has been seen that the developments of Wohl[94] and other workers, for the direct correlation of log γ with x, may be applied to isobaric data if the term $\frac{HE_2}{RT^2}\,dT$ in (27:4), where HE is the integral heat of mixing per mole of solution, may be neglected. To correct for the effect of temperature on the activity coefficient the rule $T\log \gamma_i$ = constant at constant composition has been used to modify Wohl's equations as described in Appendix III and to develop the Li-Coull equations.[46] In both sets of equations the coefficients used are assumed to remain constant over the temperature range considered. The physical significance of these coefficients is generally obscure but for the case of the Li-Coull equations their variation with temperature has been demonstrated above. In general therefore, no satisfactory method for the correlation of isobaric data exists, particularly, as in the present case, for non-ideal systems covering a wide temperature range.

From the definition of the Bunsen coefficient it follows that:

$$Xi = \frac{pi \alpha i\, Ms}{22{,}400 \rho s} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (21:5)$$

where, Xi is the mole ratio of solute i to solvent,

αi is the Bunsen coefficient,

Ms and ρs are the molecular weight and density of the solvent, respectively,

and pi is the partial pressure of solute i in atm.

For a C_2 hydrocarbon vapour phase of fixed composition at a fixed temperature, Xi can be evaluated from (21:5) for each

component, and the composition of the liquid phase can be calculated assuming that each gas dissolves independently of all others. These results are plotted and compared with experimental data on graphs 21:5 to 23:5.

A qualitative approach was used to develop the form of the ternary phase diagrams from a knowledge of the behaviour of binary systems. In figures 3:5 to 5:5 the expected variations of the ternary diagrams with temperature are given. For the C_2-hydrocarbon binaries the phase diagrams of Din and Clark[13] have been used. For the remaining binaries the differences in chemical structure that exist between acetone and the hydrocarbons indicate that eutectic formations would be more probable than solution behaviour in the solid phase.

5:2:4. Heats of solution.

In the design of separation equipment a knowledge of the heats of solution is essential. Solubility data themselves are the best source for the heats of absorption of hydrocarbons in acetone which can be determined by an equation analogous to the Clausius Clapeyron equation:[80]

$$\ln \frac{\alpha_1}{\alpha_2} = \frac{M\,Hs}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \ldots\ldots\ldots\ldots \quad (22:5)$$

where α_1 is the Bunsen coefficient at temperature T_1,

Hs is the heat of solution per unit mass of solute,

R is the gas Constant,

and M the molecular weight of the solute.

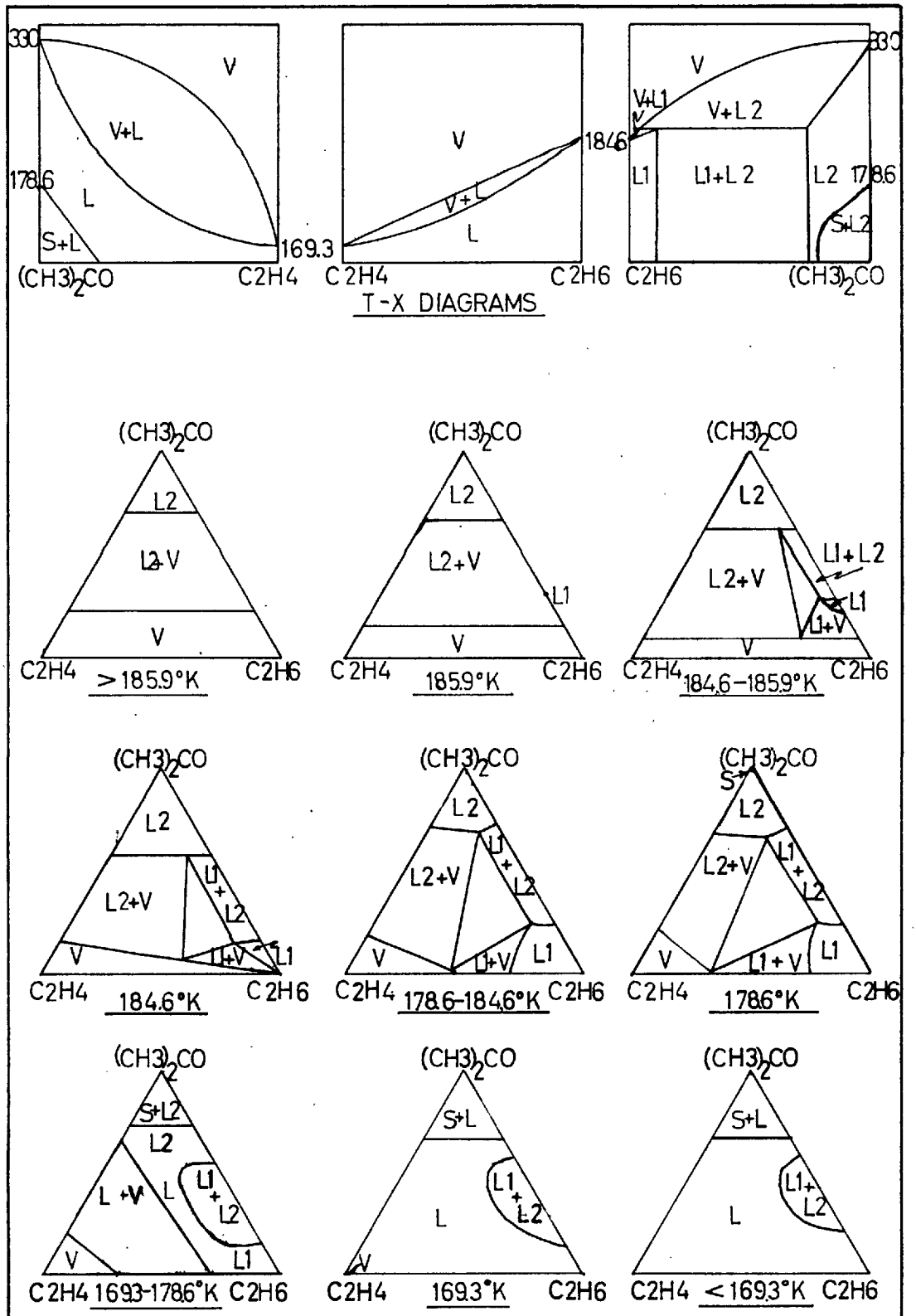
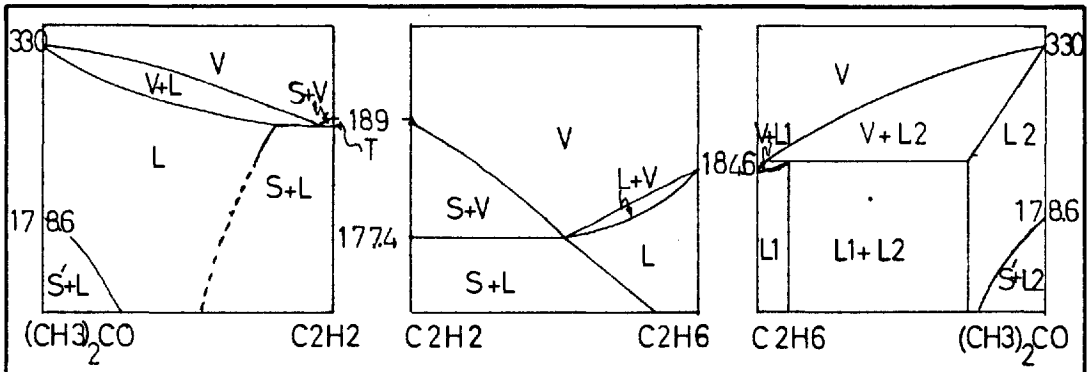
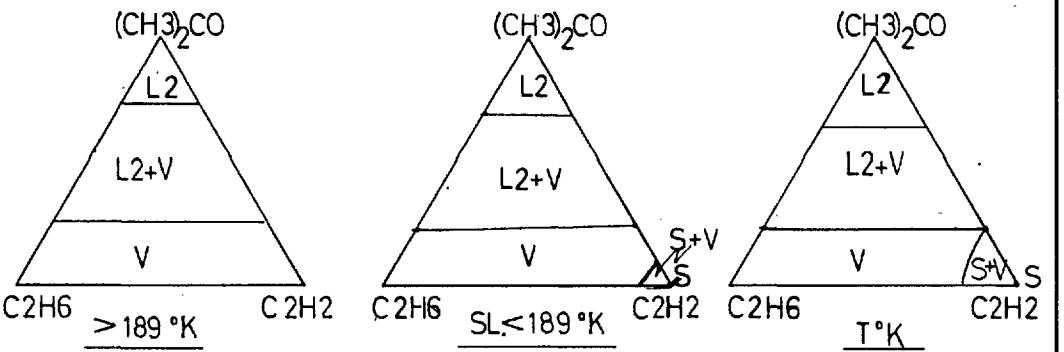


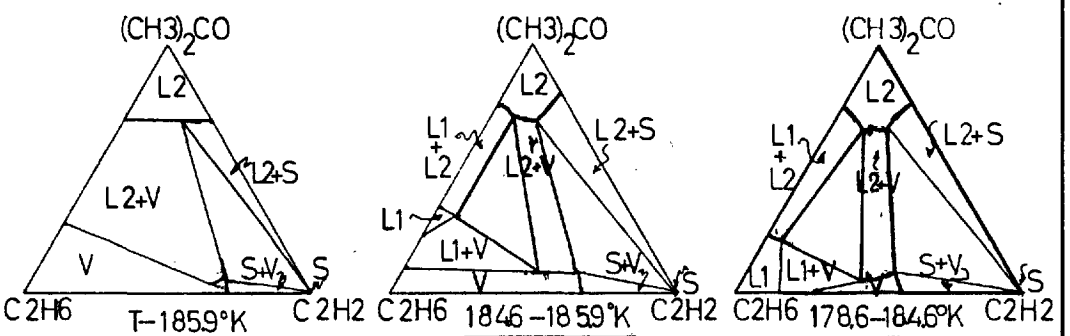
FIGURE 3:5

PHASE DIAGRAMS FOR TERNARY SYSTEM



T-X DIAGRAMS





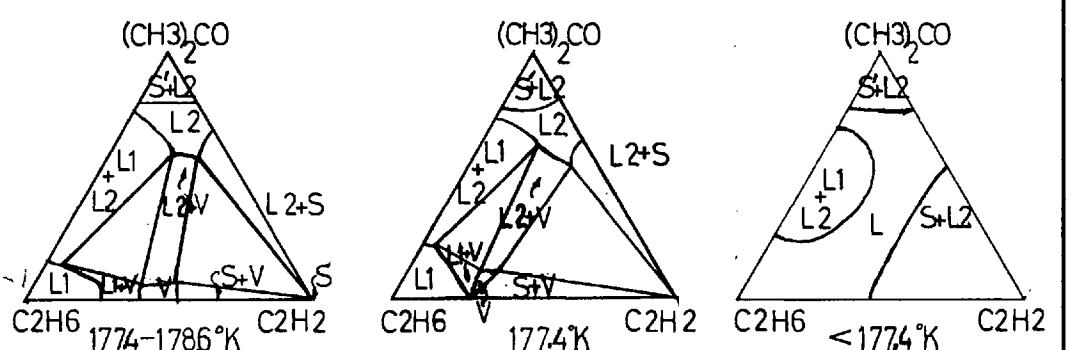
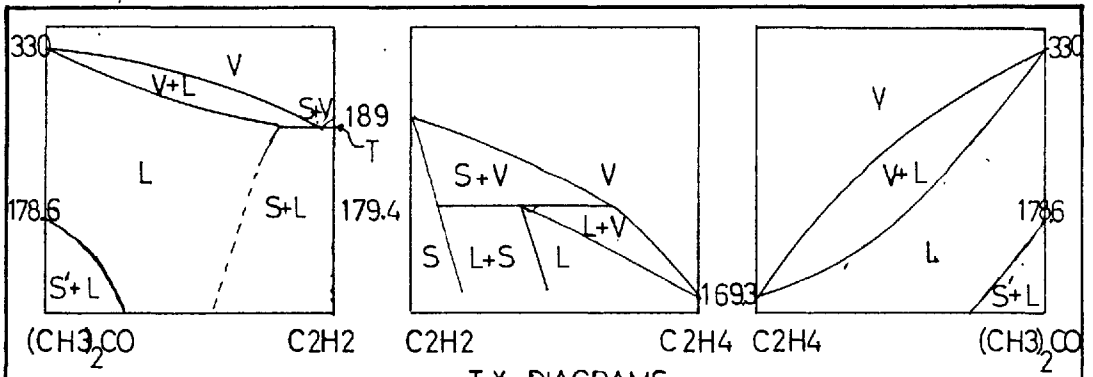
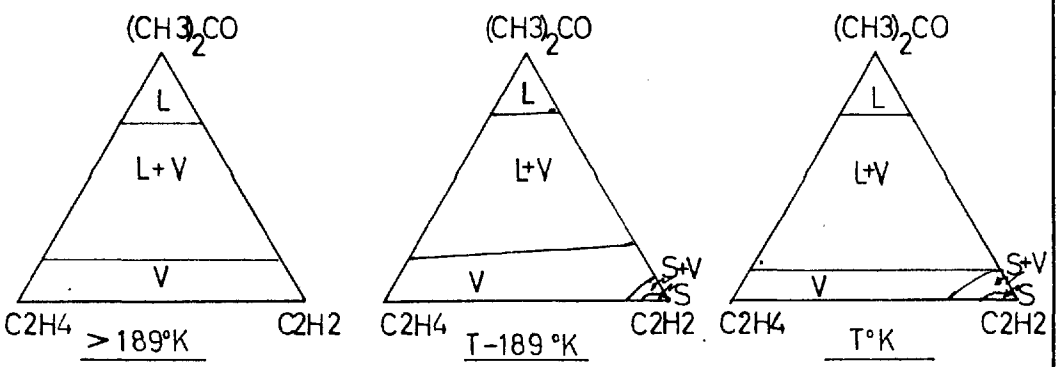


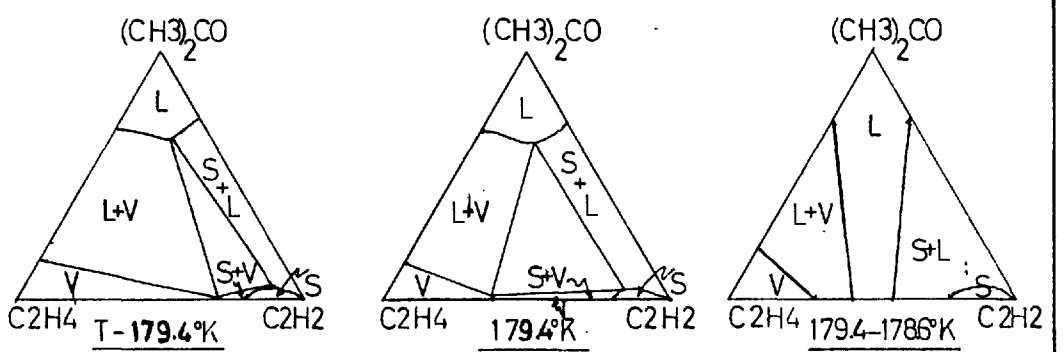
FIGURE 4:5

PHASE DIAGRAMS FOR TERNARY SYSTEM



T-X DIAGRAMS





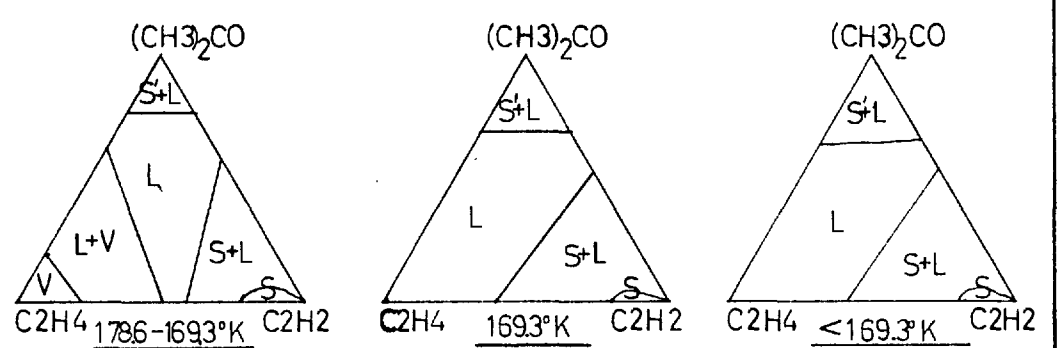


FIGURE 5:5

PHASE DIAGRAMS FOR TERNARY SYSTEM

From Figure 2:5: Hs acetylene over the experimental range is 283.5 BTU/lb and for ethylene and ethane 215.0 and 195.5 BTU/lb, respectively.

5:2:5 Discussion.

The solubility of acetylene in acetone was measured at -65 and -70°C and could therefore be compared directly with the results of Brameld and Clark.[6] The concentrations of aceylene agreed to within ± 1 mole%. The remainder of the experimental data was completely original.

Partial miscibility was observed in the ethane-acetone system; ethylene and acetone were miscible in all proportions over the complete temperature range, although solubilities were only measured to -95°C. All the experimental solubility data agreed well with values taken from the extrapolated log α v. $1/T$ curves of Schutt.[80]

In graphs 21:5 to 23:5 the ternary results are plotted on an acetone-free basis. The predicted results, assuming additive solubilities of the gases, are also plotted on these graphs. For the systems containing acetylene, the experimental values indicated a greater solubility of acetylene relative to ethylene and ethane than predicted. For the ethylene-ethane-acetone system, the solubility of ethylene relative to ethane was less than predicted. The predicted results also showed little variation with temperature on an acetone-free basis.

In the ethane-acetylene-acetone system the solubility of acetylene relative to ethane increased slightly with decrease in temperature, but in the remaining systems little variation was observed. The obvious conclusion that can be drawn from these results in that for the C_2-hydrocarbon systems mutual solubility effects are present.

A few results were taken for the quaternary system at $-80^{\circ}C$. The results are plotted on an acetone-free basis using the acetone concentration as a parameter in graph 24:5. Once again the liquids contain more acetylene than could be predicted from the ternary data.

The general form of the ternary diagrams is explained in Figures 3:5 to 5:5. Qualitative experiments showed that at about $-96^{\circ}C$ the system ethylene-ethane-acetone was miscible for the complete range of vapour compositions. This does not however lead to any definite conclusions regarding the extent of the partially miscible region of the ethane-acetone binary.

Finally it must be remembered that the solubilities were measured principally to facilitate the design of separation equipment in this and other work. For this reason few results were taken at temperature below $-90^{\circ}C$, because acetone freezes at $-94.6^{\circ}C$. It is felt that correlation of the results would be impossible at the present state of knowledge; nevertheless interesting work could still be done on the solid-liquid equilibria involved.

PART II - The separation of C_2-hydrocarbons.

Chapter 6

The available methods of separation.

6:1. Separation without the use of an absorption medium.

There has been a general tendency in the separation of cracked gases to work at fairly high pressures and temperatures. This is partly due to the fact that the processes have been developed for the oil industry which is not accustomed to the use of low temperatures. Under these conditions a minimum boiling azeotrope exists in the ethylene-acetylene system.

Zernike[96] discusses the change in composition of a ternary liquid on being distilled at constant pressure and develops a series of residue and distillate curves for varying reflux ratios. In general the greater the reflux ratio the greater is the curvature of the distillation line. He also considers ternary systems in which the binary subsystems possess invariant extremes. In this case groups of residue curves are obtained separated by physical ridges or valleys in the vapour and liquid surfaces. These boundary lines are generally curved and as they are made up of straight tie lines they lose the impassable character previously attributed to them by Ostwald et.al.[96]

Ewell and Welch[23] studied ternary systems having binary azeotropes by rectification analysis. They discovered a saddle-point azeotrope in the methanol-acetone-chloroform system and showed that the boundary ridges separating rectification regions could be crossed when approached from the concave side of the ridge.

The 'azeotrope' line described by McCurdy and Katz[51] for the C_2-hydrocarbon system at elevated pressures was curved as shown in Fig.4:2. At lower pressures, away from the critical region, tie lines of finite length joining the ethane-acetylene azeotrope either to the second minimum azeotrope or to the ethylene vertex would describe this boundary curve. For economic values of the reflux ratio the distillation path would almost certainly lie within the boundary curve. At low pressures therefore separation to give either pure ethane or pure ethylene is feasible. The acetylene concentration within the column should describe a curve with a well-developed maximum and the removal of a sidestream at this point should facilitate the separation.

6:2 Separation employing an absorption medium.

6:2:1 General.

The solubility of acetylene in acetone increases more rapidly with decrease in temperature than the solubilities of ethylene and ethane. A low temperature absorption column, using cooling to offset the heat liberated by solution of acetylene, should therefore be capable of completely scrubbing acetylene from C_2-hydrocarbon mixtures, without appreciable dissolution of ethylene in the solvent.

The top product from such a column, consisting only of ethylene and ethane, could be separated in a conventional fractionator. The contaminated acetone could be recovered by boiling off the dissolved hydrocarbons. The disadvantages of this method are the loss of the dissolved ethylene in the product gas from the acetone recovery column and the poor heat economy of a plant requiring refrigeration at $-100^{\circ}C$ and reboil at $+ 60^{\circ}C$.

6:2:2. Stripping

In Fig. 1:6 a hypothetical plant designed to overcome these disadvantages is shown. Ethane from the overhead splitter is passed into the base of the absorption column. By using a high gas flow ethane could replace some of the acetylene dissolved in the acetone and strip the rest from solution. A gaseous side stream of ethane and acetylene could

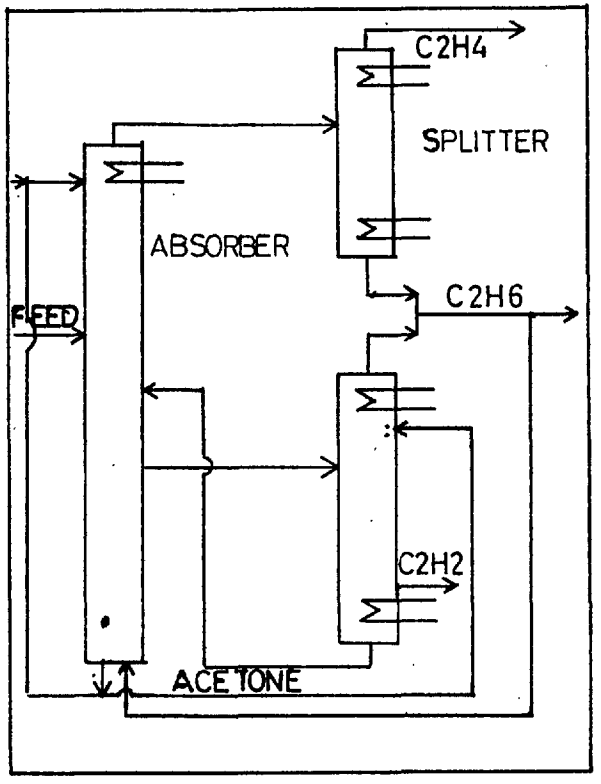


FIGURE 1:6

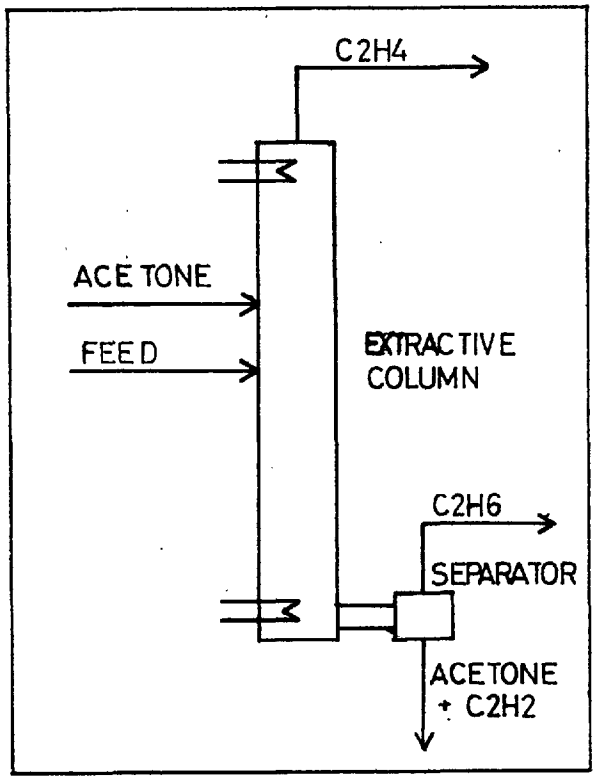


FIGURE 2:6

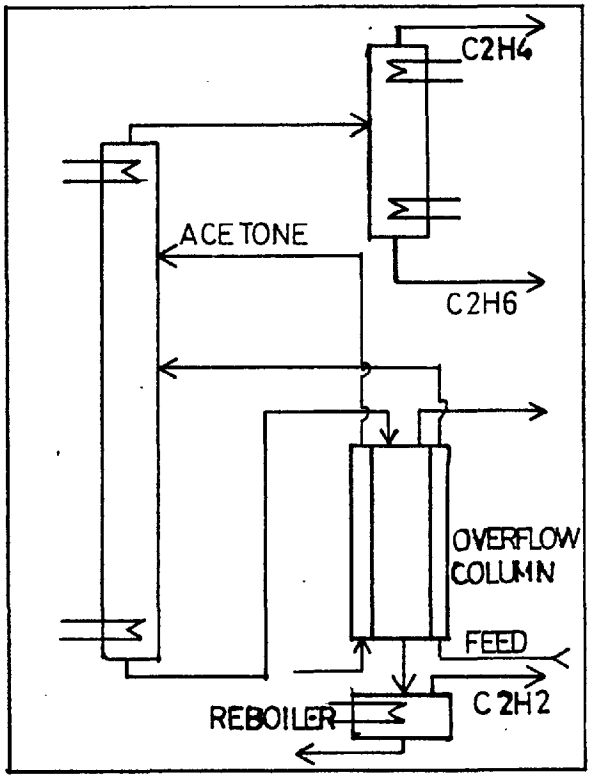


FIGURE 3:6

POSSIBLE SEPARATION METHODS USING ACETONE

be removed from the main column and separated in an extractive distillation column, using acetone as the extractive agent. The overhead, ethane, could be used for stripping and pure acetylene could be withdrawn from the base of the column.

As is seen from Graph 22:5, however, the vapour to liquid ratio required at the base of the absorption column would be prohibitively high. The use of an inert gas, such as nitrogen, would also be impracticable as in this case no substitution of acetylene by nitrogen in solution could be expected.

6:2:3. Use of overflow packing

From the above it would appear that there is no alternative to reboil for the complete regeneration of acetone.

Platt[65] and Wahhab[92] have studied the use of overflow packing for non-adiabatic fractionation. The packing is oriented and possesses good heat and mass transfer properties. The packed column is surrounded by plate-fin heat exchange sections. By replacing the rectifying section of a column with its condenser by a partial condenser, and similarly in replacing the stripping section plus reboiler by a partial evaporator, a closer approach to thermodynamic reversibility is achieved.

In this case, the acetone stream from the base of the absorption column could be warmed to room temperature by heat exchange with the feed gas and feed acetone. Final removal of acetylene from the acetone would require a reboiler. A stream of pure acetylene would thus be produced but the majority of the acetylene together with the degassed ethylene and ethane would require further treatment.

6:2:4 Extractive distillation.

An improved separation could be achieved by the arrangement of Fig 3:6. The absorption column described above has been replaced by a reboiled absorber. In this way, it is hoped that the concentration of dissolved ethylene in the acetone stream could be reduced without contaminating the top product with degassed acetylene.

To improve the recovery of ethylene still further, the extractive distillation column of Fig. 2:6 could be used. In the upper section of the column ethylene is separated from ethane. The ethane is therefore forced down the column and is removed with acetylene and acetone in the bottom product. In this case, it seems likely that the distillation path will cross the partially miscible regions of the phase diagrams described above.

6:3 Conclusions.

Distillation with and without a sidestream was studied as the principal method of separation. The columns were designed by plate to plate methods, using graphical extrapolations of the phase equilibrium data. A simple absorption column, a section of overflow packing, and an ethylene-ethane fractionator were also designed. The designs were not rigorous and were attempted merely to give an estimate of the size and amount of equipment needed. Distillation columns were ordered as simple units e.g. 10 and 15 plate sections, to retain a degree of flexibility in the final choice of the methods of separation to be tested.

Chapter 7.

Experimental.

7:1 The distillation column.

It was desired that the mechanism of the liquid-vapour contacting process should approximate to industrial methods, to give the results a more general significance and to allow them to be directly scaled-up for use with large columns. The Oldershaw column[57] uses the principles of sieve plate contacting and it is considered that the results obtained are widely applicable for non-foaming mixtures.[26]

The design calculations, mentioned above, for a hydrocarbon separation column, indicated that at least forty theoretical plates would be required. The total available headroom of the laboratory was about 9' and therefore, a requirement of the column was that it should have a low H.E.T.P. The average temperature of the separation was about $-90^{\circ}C$, so that efficient lagging was necessary. As dangerous mixtures were to be separated it was also desired to observe the behaviour of the liquid on the plates. The only possible method of insulation that would satisfy both these requirements was a partially silvered Dewar vessel.

7:1:1 The Oldershaw column.

In Fig 1:7 a section of a column and a plate are

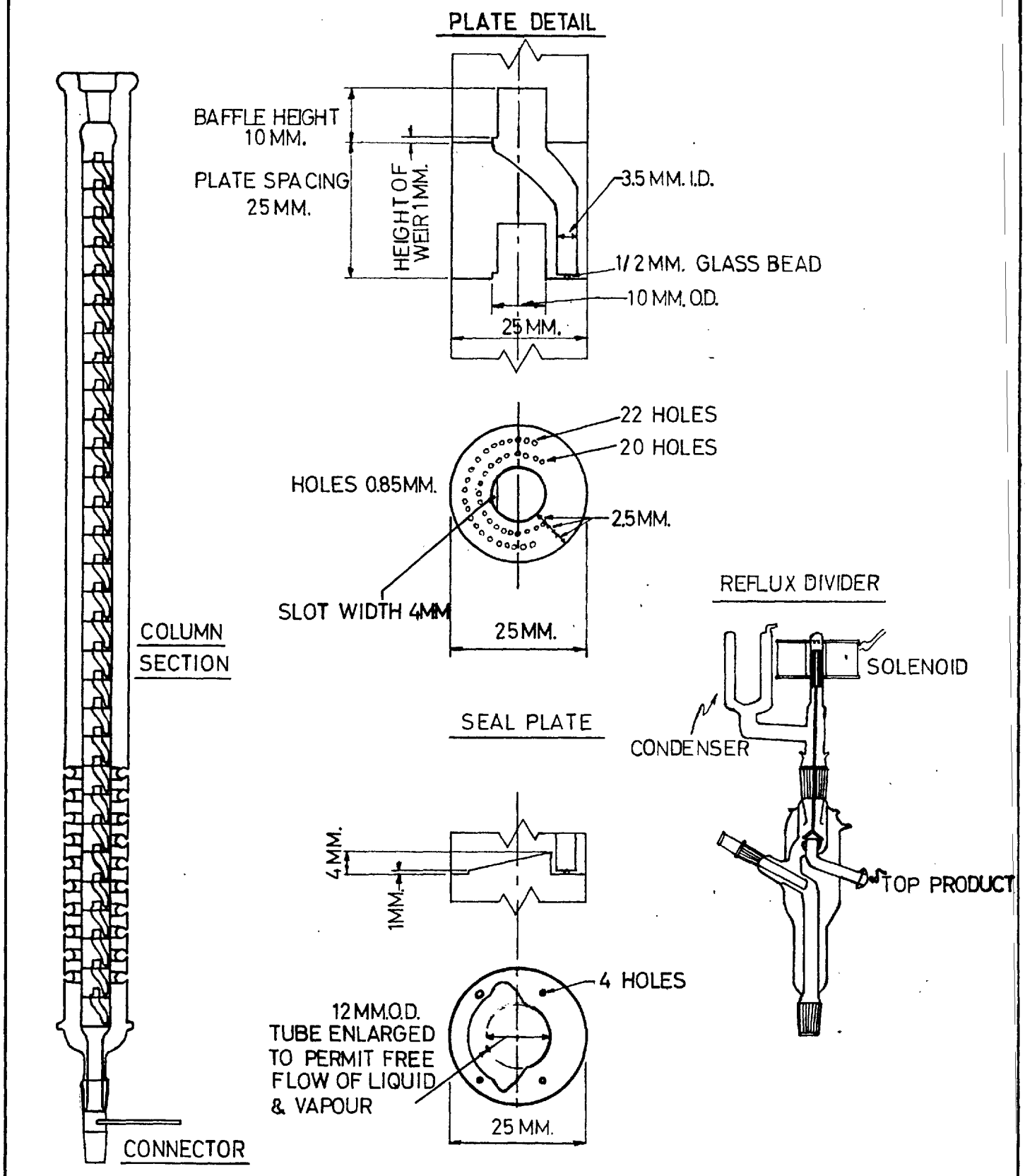


FIGURE 1:7

OLDERSHAW COLUMN DETAILS

shown. The mode of operation of the equipment is essentially that of a sieve plate column with a central downcomer. It consists of a series of perforated glass plates sealed into a tube. Each plate is equipped with a baffle to direct the flow of liquid, a weir to maintain the proper liquid level on the plate, and a reflux return tube. The ascending vapour stream flows through the holes in the plates and bubbles through the liquid reflux. The bottom plate in the column serves as a small reservoir which is necessary to maintain a liquid seal for the drain tube from the first regular plate. The column is provided with an integral Dewar jacket with bellows, permitting its use over a wide range of temperature. The details of the method of construction have been described by Oldershaw.[57]

The column sections were made by the Loughborough Glass Co. Ltd., To reduce the consumption of raw materials the smallest column of the available range was chosen. The column diameter and plate spacing were each 25 m.m., and the plates contained 42 perforations of 0.85 m.m. diameter in two concentric rings. Five column sections were obtained viz: two 15 plate sections and one each of 5, 10, and 30 plates.

7:1:2. Ancillary column equipment.

To make the equipment as versatile as possible

standard B24 cones and sockets were used throughout. To enable feeds to be introduced and products to be removed from the column several sections of the type shown in Fig 1:7, were used to connect the individual plate sections.

Reflux was provided to the column by the use of an automatic vapour-dividing stillhead, Fig 1:7. Vapour rising from the top plate of the column was directed by a glass valve plunger either to the product line or to a total condenser. Liquid nitrogen was used as a convenient source of refrigeration for the latter. A 240 V A.C. solenoid was used to operate the plunger at timed intervals. A micro-switch operated by a leaf spring was connected to the solenoid and rigidly mounted so that the spring was in continuous contact with the circumference of a perspex disc. The disc was driven at about 2 RPM by a small constant-speed motor. Brass cams were fitted to the circumference of the disc, so that they operated the micro-switch and hence the solenoid on passing the leaf spring. By varying the size of cam segment nominal reflux ratios of from 2.0 to 12.0 were obtained.

The microswitch was initially connected to an Airmec counter for calibration purposes. The duration of the applied current for each segment was consistent to within $\pm$ 0.02 sec This variation would result in negligible errors in the operating reflux ratio.

A simple glass reboiler with a side-neck for product removal and a 'hot-finger' heater was used. It was considered that this method of providing reboil allowed the heat to be uniformly and completely transferred to the liquid and overcame the dangers associated with the use of immersion heaters.

The inductance of the heating coil was measured directly as 8 mH. The resistance of the coil under operating conditions was about 280 Ω. The inductive reactance of the coil could therefore be neglected when considering the power dissipation of the heater. The coil was calibrated, using standardised instruments, whilst heating a mixture of solid carbon dioxide and industrial spirit. During operation the coil was connected in series to a rheostat, an AVO-meter and the A C mains. From the calibration the heat dissipation was obtained directly from the current reading. The reboiler was mounted on a bed of Perlox (a granular insulating material) in a small partially silvered Dewar. The top of the Dewar was packed with expanded polystyrene to provide rigidity and minimize heat leaks.

7:1:3 Column support.

The Oldershaw columns were fragile and considerable care was needed in the design of the supports. The columns were protected from accidental knocks by enclosing them in

hardboard boxes which were mounted on a framework of 'handy-angle' and screwed to the floor. Lengths of galvanised iron-pipe were rigidly attached to the boxes and key-clamps fitted to the pipes were used to hold the column supports. Loose-fitting split ring clamps made from 3" square sections of aluminium bar were used to prevent sideways movement of the column sections and the whole column was supported in a wooden cup of the same shape as the column base. The A.C. solenoid was glued to a steel plate and clamped to the galvanised pipe. Strips of foam rubber were glued to the contact surfaces of all the clamps.

Prior to setting up the column the positions of all the supports were adjusted by the use of shims until the centre line of the clamps was vertical. The reboiler was positioned under the botton clamp and the first column section was lowered into its wooden support cup. Owing to the rigidity of the reboiler in its Dewar, it was found to be impossible to obtain a true fit between the ground glass cone and socket of the column and reboiler, respectively. A small PTFE bellows was therefore connected to a B 24 cone and socket by Araldite, to provide a flexible connection between the reboiler and the column.

Considerable care was always exercised in setting up the column to prevent stresses from accumulating on the vacuum-jacketed cones at the base of each section.

7:1:4 Insulation.

Podbielniak,[66] in his work on laboratory distillation equipment, considered the efficiency of various modes of insulation. He measured the heat leak from a partially silvered vacuum jacket, of 9 m.m. I D and 35 m.m. OD, 3' long, as 27 BTU / hr. ft.^{2} of surface, for a column temperature of 110°C above ambient conditions. This result implies that the outside wall of the Dewar vessel would be about 10°C above ambient temperature.

In all the experimental work on Oldershaw columns the estimated temperature difference between the walls of the column and the atmosphere was of the order of 2-3°C. This would result in a maximum overall heat leak of about 20 BTU/hr for the distillation columns. Calculations based on the radiant heat transfer across the vacuum jacket appeared to substantiate this result. Podbielniak's work was done thirty years ago and the improvement in high vacuum techniques may well account for the discrepancies in the results.

Heat transfer from the atmesphere at the total condenser was unimportant as the consumption of liquid nitrogen could not be measured accurately. The joints at the ends of the column sections were lagged with expanded polystyrene.

The minimum reboiler duty used was about 200 BTU/ hr and so the probable maximum heat leak was about 10% of the reboiler duty. This value is quite large but the inaccuracies resulting from this cause were considered to be insufficient to justify lagging the column with powder insulation. The heat flux across the walls of the column is low and it is due to the small scale of the experimental work that it is an appreciable percentage of the column heat load. The ability to observe the behaviour of the liquid on the plates was considered to be of major importance owing to the dangerous nature of the mixtures treated.

7:2 Feed introduction and product removal.

7:2:1 Feed Introduction.

The gases were delivered from cylinders to orifice boxes and the mixing chamber as described previously. The caustic potash drying towers were replaced by towers containing self-indicating silica gel to reduce the possibility of blocking the column with ice. Larger orifices were used to cope with the increased gas consumption.

The use of polymerisation grade ethylene was discontinued owing to the difficulties associated with its import from France. Although several alternative sources were sought in this country none were suitable and the gas was purchased from B.O.C. Ltd. The ethylene was about 98% pure,

impurities were principally non-condensible gases, which were vented from the condenser. Carbon dioxide was initially scrubbed from the ethylene by concentrated caustic potash solution. The method was unsuitable, however, owing to the possibilities of water entrainment, incomplete drying and subsequent column blockage. Duplicate runs with and without the use of the potash solution indicated that carbon dioxide did not affect the separations. Ethane and acetylene were also supplied by B.O.C. Ltd., as described above.

Initially it was intended to feed the gas into the column at its dew-point. The feed gas was passed through the equilibrium cell, which was maintained at -90°C by the bath of iso-pentane, and then through 2' 6" of copper pipe, lagged by 3" of expanded polystyrene to the column. The gas temperature at the entrance to the column was + 10°C. This heat leak was attributed to the low feed flow rate of 3l./min. It seemed likely that an improvement could only be achieved by the use of very narrow bore, low conductivity tubing and the increased pressure drop in this section would then require high delivery pressures from the cylinders to maintain the correct flow conditions in the orifices. To reduce the temperature of the feed gas from ambient conditions to its dew-point required the abstraction of about 40 BTU/hr from it. The additional load on the condenser was not excessive and as this factor could be introduced into any subsequent calculations, it was decided

to feed the superheated stream directly to the column.

The feed gas from the mixing chamber was therefore passed through a rotameter into the column.

7:2:2 Product removal.

To simplify column operation gaseous products were always taken from the column in distillation experiments. The gases were passed from the column to a fume cupboard via stop-valves, rotameters, manometers and Ermeto fine adjustment needle-valves. At the measuring position all the gases had returned to atmospheric pressure and the rotameters were calibrated under operating conditions by the use of a wet gas-meter.

To allow the top-product to flow to waste, via the rotameter and manometer system, the condenser pressure was increased slightly by partially closing the vent. The top-product flow-rate as measured by the rotameter, however, was not satisfactory, owing to the intermittent action of the vapour dividing still-head. The flow oscillations were only partly damped by the introduction of a surge vessel in the line.

The vapour flows within the column could be calculated from the heat input to the reboiler. It was found that the achievement of steady state, as measured by the stability of the reboiler liquid level, was very sensitive to the reboiler

heat input and therefore, the flow of top-product could be obtained by overall material balance, from an average rotameter position, or by a calculation based on the heat load on the reboiler. Generally the three results agreed very well and in subsequent runs the condenser was maintained at atmospheric pressure and the top-product flow was calculated.

Temperatures within the column were measured by copper-constantan thermocouples. Each thermocouple was threaded through a rubber bung held in one junction of a brass Tee-piece and passed through the gas line to the column. The top product temperature was recorded by a thermocouple placed in the thermometer-well of the reflux divider. The still-head was vacuum jacketed but owing to the thermal resistance of the glass the measured temperatures were consistently in error. All gas streams were analyzed and temperatures were used principally as an indication of the achievement of equilibrium. Consistent inaccurate temperature measurements were therefore unimportant.

The distillation column was connected by flexible PVC tubing to the copper tubing of the feed and product lines. Although PVC hardens on cooling, the heat transfer from the air was usually sufficient to warm the product lines to room temperature within a few inches of the column. In this manner the column was isolated from accidental knocks to the rest of the apparatus.

Chapter 8

The operating characteristics of Oldershaw columns.

The operating characteristics of Oldershaw columns were determined for the separation of mixtures of ethylene and ethane, so that these values could be applied later to multicomponent separations. It was also hoped that any unforeseen dangers could be eliminated before acetylene was introduced into the feedstock.

8:1 Previous Work.

Oldershaw[57] measured the plate efficiency, operating hold up and pressure drop of several different column sections, for the distillation of carbon tetrachloride- benzene mixtures. Collins and Lantz[16] increased the number of perforations on each plate and measured the operating characteristics of the columns, with a variety of mixtures, under conditions approximating to actual operation, rather than under ideal conditions for maximum separation.

8:1:1. Choice of operating conditions.

A comparison of the equilibrium data for the ethylene-ethane system, obtained in this work, by Moran,[55] and by Kharakhorin[40] gives rise to divergencies in the expected behaviour of a C_2-splitter. Thus for a feed containing 33.3% ethylene at its dew point, the minimum reflux ratio required to

obtain a top product of 99% ethylene is 3.67 by this work, 4.00 according to Moran and 4.95 according to Kharakhorin. A column designed to separate this feed into a top product of 99% ethylene and a bottom product of 99% ethane, with a reflux ratio of 5, would require 9 theoretical plates in the rectifying section and 7 in the stripping section, according to this work, and 7 plates in the rectifying section and 9 in the splitting section, according to Moran. The differences between the author's work and that of Kharakhorin are greatest at the high temperature (ethane) end of the diagram, whilst Moran's work disagrees more noticeably at the low temperature (ethylene) end of the diagram.

The available sections of column were of 5,10,15,15 and 30 plates. By choosing a feedstock of about 35% ethylene, varying the reflux ratio from 3.8 to 6.9 and by using 5 plates in the rectifying section and 10 in the stripping section and vice-versa, it should be possible to differentiate between the three available sets of data.

The plates used had 42 perforations of 0.85 m.m. diameter and the area of perforation per plate was therefore 0.238cm.^{2} Oldershaw [57] used vapour rates of 0.065 -0.417 gm.moles/min. in a column of these dimensions. His values corresponded to gas flow rates of 1460-9350 ml./min. measured at N.T.P. or vapour hole velocities of 133-850 cm/sec under column conditions.

The superficial vapour velocities in the column ranged from 6.5 -41 cm/sec.

Collins and Lantz[16] measured the maximum vapour rate for several columns having 0.508 $cm.^2$ area of perforations per plate. The values ranged from 14,500 -17,800 ml/min measured under column conditions. The equivalent vapour hole velocities were therefore 475-585 cm/sec. The experimental range of vapour flow rates for the present work, measured under column conditions, would therefore appear to be 1,900 - 6,800 or 12,100 ml/min. For the separation outlined above, with a reflux ratio of 5, these values correspond to a feed flow rate of 3,000 -9,600 ml/min at 20°C and 1atm.

Collins and Lantz[16] also measured the heat leak from the columns for a temperature difference of 80°C between the plates and the surroundings. The minimum value obtained was 5% of the column heat load, which would seem to agree well with the value quoted above for this work.

8:2 Run procedure

The column was assembled as described above. The gas delivery pressures were adjusted to give a feedstock containing 35% ethylene at a flow rate of 4,000 ml.min. The appropriate cam segment for the required reflux ratio was fitted to the perspex disc and the timing mechanism was started. The feed was liquefied by filling the condenser

cup with liquid nitrogen. Flooding of individual plates often occurred at this stage, owing to the evaporation of the liquid when cooling the column. Under these circumstances, normal operation was resumed by allowing gas to escape through the bottom product line.

After about an hour the liquid level in the reboiler was sufficient to cover the heating coil. A pre-calculated amount of current was then supplied to the reboiler to give the desired vapour rates within the column. From a knowledge of the reflux ratio and these vapour rates, the flow rate of the top product and hence the flow rate of the bottom product were calculated. The control valve on the bottom product line was then opened to give the calculated flow rate and adjusted until the liquid level in the reboiler remained constant. The temperatures at the top, bottom and feed position of the column settled to steady values after about twenty minutes and the steady state was then considered to have been attained. Samples of the feed and products were then taken by hypodermic syringe and analysed on the chromatograph, and column pressures, temperatures and flow rates were also recorded.

Trials were performed with constant feed flow rate and composition for various reflux ratios and reboiler heat duties. Initially 10 plates were used in the stripping section with 5 plates in the rectifying section. A second series of runs was then performed with the position of the column sections

reversed.

The reflux ratio divider was kept in operation throughout the start-up period in order to prevent the glass plunger from freezing in the closed position.

8:2:1. Difficulties encountered during operation.

The perforations on the plates were only 0.85 m.m. in diameter, so that any moisture or particles of dirt that entered the column partially blocked the holes and reduced the vapour rate required for the onset of flooding. No complete solution to the problem was found, although column sections were always cleaned and dried before the commencement of each day's work.

After about an hour of operation severe pressure oscillations often built up in the column and the instability frequently led to the loss of manometer fluid (dibutyl phthalate). The cause of this behaviour was traced to blockages of the condenser vent. The condenser was filled manually with liquid nitrogen and this procedure resulted in the condenser experiencing slight (1"-2" w.g.) positive and negative pressure oscillations. Whilst the condenser operated under vacuum small quantities of atmospheric air were sucked in and a deposit of ice accumulated at the vent. The instability was overcome by connecting the vent to a Drechsel bottle, immersed in liquid nitrogen, and a drying tower, containing anhydrous calcium chloride and self-

indicating silica gel. It was established that the loss of hydrocarbons from the vent, during the positive pressure part of the condenser cycle, was too small to affect the results. Infrequently instability occurred after the above precautions had been taken. It was established that this was due to the formation of solid ethylene in the vent. Ethylene melts at -169°C and nitrogen boils at -196°C. A large temperature head was necessary to transfer sufficient heat through the glass walls of the condenser. The use of liquid oxygen under these circumstances could not be considered due to its explosive combinations with hydrocarbons. The problem occurred rarely and was readily overcome, by allowing the nitrogen level in the condenser to fall, thus permitting the vent to warm up sufficiently to melt the ethylene.

8:3 Results.

The experimental results are given in Appendix IV. The latent heat of vaporisation of ethylene at atmospheric pressure is 5,810 BTU/lb mole and of ethane 6,300 BTU/lb mole. These values were judged to be sufficiently close to one another to justify the use of the Mc Cabe-Thiele method,[50] with its simplifying assumptions, for the analysis of the results. Plate efficiencies were calculated using the three available sets of equilibrium data and are presented in Appendix IV as a function of vapour rate. Deviations

of the feedstock from the condition of a saturated vapour were accounted for by use of the 'q-factor.' In Figure 1:8 the Mc Cabe - Thiele diagram for a typical run is given.

8:4 Discussion

The maximum vapour rate, achieved before the onset of flooding, was 7,000 ml/min, measured at column conditions. This result indicates that the high capcity of Oldershaw's column was due to the care taken by him to obtain plate uniformity. The maximum vapour rate is determined by the poorest plate and any slight imperfections in construction can result in a considerable decrease of throughput.

Collins and Lantz[16] measured the variation of plate pressure drop with vapour rate and obtained values of 0.5 - 0.8 m.m. Hg./plate. In the present work only an accurate value for the rectifying section could be obtained. The manometer in the bottom product line gave low values owing to the pressure drop resulting from the flow of gas in this line. Allowances were made for the dry plate pressure drop and the resulting value was 0.6 m.m.Hg/plate.

Collins and Lantz[16] measured the plate efficiency of the Oldershaw column for a variety of vapour rates and reflux ratios using the system n.heptane-methylcyclohexane. They observed only slight variations of efficiency and a value of

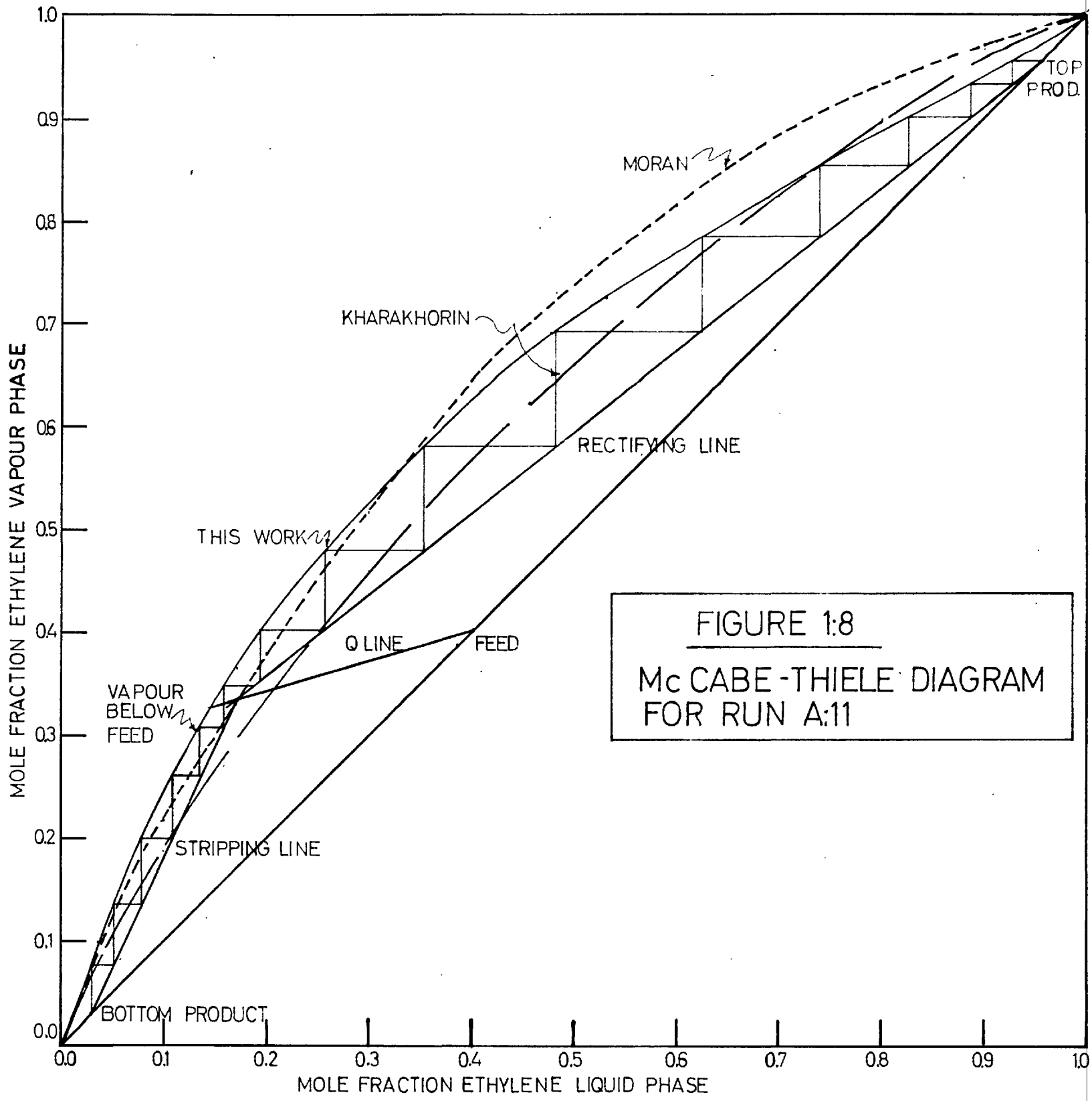


FIGURE 1:8

Mc CABE-THIELE DIAGRAM FOR RUN A:11

60% is representative of their measurements. Oldershaw[57] measured the plate efficiency of several columns having varying numbers and sizes of perforations at different vapour rates. He concluded that at a constant vapour rate the efficiency decreases with an increase in the size of the perforation, and that with perforations of a given size the efficiency varies inversely as the vapour rate. For 0.85m.m. perforations he observed variations in efficiency of from 81% to 100%.

Zuiderweg and Harmens[97] measured the plate efficiencies of Oldershaw columns for a variety of systems. They established that for neutral or negative mixtures i.e. those in which the reflux either has no surface tension gradients or decreases in surface tension as it flows down the column, the plate efficiency was about 50%. For positive systems, in which the less volatile constituent has the greater surface tension, plate efficiencies of 90% were recorded. The recorded efficiencies were not sensitive to vapour rates but varied considerably with the average composition of the plate section. The authors did not describe the size and nature of the perforated plates employed.

In the present study samples could only be taken at the condenser and the reboiler, and efficiencies for the rectifying and stripping sections of the column were determined by

establishing the feed-plate composition, using measurements of the temperature of the vapour leaving the top plate of the stripping section. Thus overall plate efficiencies were measured and the scatter of the results made it impossible to establish any systematic variation of efficiency with operating variables.

The experimental results were analysed by the three available sets of equilibrium data. Kharakhorin's equilibrium curve[40] did not give a satisfactory representation for any of the distillation results. The bottom operating line either intersected the equilibrium curve at positions below the feed plate composition or the plate efficiencies required to give the experimental separation were about 150-200%. In consequence the majority of the estimated efficiencies in this case have not been recorded in Table LV.2. Secondly the minimum reflux ratio for the experimental separation as predicted by Kharakhorin's data was about 4.5-5.0. The desired results were achieved with reflux ratios as low as 3.8.

When using 10 plates in the stripping section and 5 plates in the rectifying section, the bottom operating line usually intersected the experimental equilibrium curve at the feed plate temperature; owing to this pinch condition only a few efficiencies could be measured in the stripping section. The plate efficiencies obtained, using the experimental data, were

about 100% for both sections, and, using Moran's data,[55] about 70% in the rectifying section and 40% in the stripping section. The anomalous results for run A:4 cannot be explained.

When using 5 plates in the stripping section and 10 plates in the rectifying section very good separations were obtained. The efficiencies for both sections were about 88-100%, when usuing the experimental data. According to Moran's data, however, the runs were impossible, as the top operating line usually intersected the equilibrium curve at positions above those representing the vapour leaving the first plate of the rectifying section.

The set of equilibrium data obtained in this investigation was the only one capable of giving a satisfactory explanation to all the results. The recorded efficiencies of 88-100% showed no systematic variation with vapour rate, in general agreement with previous work on Oldershaw columns.

Zuiderweg and Harmens[97] attributed the high efficiencies of positive systems to the formation of a high stable foam and the low efficiencies of neutral and negative systems to the formation of a relatively small spray bed. Observation of the conditions on the experimental trays indicated an intermediate condition between the extremes described by Zuiderweg and Harmens. No satisfactory surface tension data could be found for the system and the high plate efficiencies were attributed to the

small size of the perforations. The values obtained, however, were greater than the efficiencies recorded by Oldershaw.[57] The shape of the liquidus equilibrium curve differs markedly from the results of Moran[55] and Kharakhorin[40] at the low temperature end of the diagram. Slight errors in this region would account for high efficiencies in the rectifying section of the column.

The vapour rates recorded in Table IV.2 were calculated from the reboiler heat input, the degree of superheat of the feed and the known bottom product flow rate. The reflux ratios calculated from these vapour rates agreed quite well with the experimental values. The material balances on the components of the feed were also satisfactory, although 5% errors based on the flow rate of ethylene to the column were accepted, owing to the inaccuracies associated with the measurement of flow-rates by rotameter.

Distillation in the Oldershaw column would therefore appear to be a valuable method for the evaluation of conflicting sets of equilibrium data.

CHAPTER 9

The separation of C_2-hydrocarbons by distillation

9:1 Introduction

The ultimate aim of this phase of the work was the establishment of the optimum conditions for the separation of the hydrocarbons by distillation. The variables investigated were reflux ratio, the total number of plates, the number of plates in each section and the position and magnitude of a sidestream. The reboil rate was adjusted so that satisfactory bubbling was observed in each section of the column, but no systematic study of the variation of performance with vapour-rate was considered owing to the conclusions of the previous section. The feed rate and feed composition were maintained at about 3,000 ml/min, measured at 20°C and 1 atm., and 10 mole % acetylene and 25 mole % ethylene, respectively. By using large amounts of acetylene in the feed the product compositions were more accurately determined, as the chromatograph is insensitive to small amounts of impurity.

9:2 Equipment and procedure

The equipment and run procedure were identical to those described in the previous chapters and the introduction of a sidestream did not present any additional problems.

9:3 Results

The experimental results are recorded in Tables 1 and 2

of Appendix V

9:4 Discussion

From the experimental results it is seen that the separation of the C_2-hydrocarbons presents a difficult problem which could not be solved to give the desired product specifications with the limited numbers of plates available. In addition the large number of possible combinations of operating variables and the restricted amount of information that could be obtained from any given trial made simple analyses, comparison and subsequent extension of the results impossible. A computer programme, using the equilibrium data obtained in the present study, was therefore written to permit verification and extension of the experimental results and the development of this programme is described in Chapter 11 The evolution of a programme of this complexity, however, required so much computing time that only a limited period remained for the treatment of the results and in consequence a semi-quantitative discussion of the experimental work is still necessary.

The majority of the work was performed at reflux ratios of from 6.9 to 12.1 and under otherwise comparable conditions the separations did not improve significantly with increasing reflux ratio. It has been seen that the minimum reflux ratio for the separation of an ethylene-ethane mixture containing 33% of ethylene

to give a top-product containing 99% of ethylene is 3.8 and it would appear from the results that this value is not appreciably altered for ternary separations. In runs B:55 to B:62 low reflux ratios were used and a comparison of B:59 and B:24 shows that a marked reduction in separating power occurred on reducing the reflux ratio from 6.9 to 4.7. In some cases, e.g. B:54, the reduction in separation may be attributed to the decrease in vapour-rates with decrease in reflux-ratio leading eventually to weeping in the stripping section of the column, but generally it is considered to be due to the approach of the operating reflux-ratio to the minimum value for the given separation.

The ratios of acetylene to ethane concentrations in the top-product and of acetylene to ethylene concentrations in the bottom product were generally greater than one, whereas in runs B:55 to B:62 performed with low acetylene content feedstocks at low reflux ratios these concentration ratios were less than one. The change in slope of the distillation path is attributed solely to the reduction of the reflux ratio, because in trials B:52 and B:53 low acetylene content feedstocks and high reflux ratios were used and sidestreams were obtained comparable in acetylene content with the results for high content feedstocks.

Some tentative conclusions may therefore be drawn at this stage. It would appear that little advantage is gained by using reflux-ratios in excess of 7.0 and at this level a sidestream containing between 25

and 33 mole % acetylene may be withdrawn from a suitable point in the column. In addition this conclusion should not be drastically modified by the reduction of the feedstock acetylene content. At lower reflux-ratios the reduction in the curvature of the distillation path would result in a sidestream of less than 25 mole % acetylene and an economic analysis comparing the large number of plates required in one case and the high refrigeration load and good by-product purity of the other case would be necessary before a final decision could be made as to the optimum value of the reflux ratio.

In order to estimate the number of plates required to achieve the desired separation it is necessary to be able to compare the experimental separations obtained with differing column lengths. It was decided to use the ratio of the ethylene recovery achieved to the maximum possible recovery for the given trial. This factor is not completely satisfactory as may be seen by comparing B:13 and B:14. In both cases 793 ml/min of ethylene are fed to the column and as the top product flow rates are 1050 and 950 ml/min, respectively, the maximum recovery for each trial is 100%; therefore the ratio for B:14 is apparently too low. The method suffers from the additional restriction that a good component material balance is required. It has already been shown that the use of rotameters to measure flow-rates frequently introduces considerable errors into these material balances.

When using a total of 15 plates the recovery ratio varied from

80% to 90%. For column sections containing 15 plates in the rectifying section and either 5 or 10 plates in the stripping section the ratio varied from 89% to 98%. For a 35 plate column at high reflux ratios the recovery ratio ranged from 95% to 100% and at lower reflux ratios this value fell to 85% to 98%. In runs B:22 and B:23 a very good separation was obtained and it would appear that removal of acetylene to the desired level from the top product could probably be achieved with a column containing about 10 plates in the stripping section and 40 plates in the rectifying section. The recovery of ethylene under these circumstances should be in excess of 90%. At low reflux-ratios insufficient experimental data was available and a reasonably reliable estimate of the number of plates required could not be made.

In trials B:30 to B:34, B:41 to B:44 and B:50 and B:51 sidestreams were removed from the column at points 5, 10, and 15 plates, respectively, above the feed entry position. The average composition of this stream was about 30 mole % acetylene, 45 mole % ethane and 25 mole % ethylene. Sidestreams were also taken at positions 5 and 10 plates below the feed plate in runs B:35 to B:40 and B:52 to B:54 and B:45 to B:49, respectively. The average sidestream composition in these cases was about 30 mole % acetylene, 50-55 mole % ethane, and 15-20 mole % ethylene. In general therefore, for the separation under consideration greater recoveries of ethylene in the overhead product should be obtained by taking the sidestream at a position about 8 plates below

the feed plate. In trial B:53 a good separation was achieved with an ethylene recovery of 78%. The desired reduction in top product acetylene content should be obtained by the addition of 10 theoretical plates to the rectifying section of the column.

Further tentative conclusions may now be drawn. For feedstocks of high acetylene content little advantage is to be gained from the removal of a sidestream and in general the overall recovery of pure ethylene would probably be less than that for distillation without sidestream. However, for low acetylene feedstocks the loss of ethylene in the sidestream would be small and the advantages of a reduced number of plates and a sidestream containing about 30% acetylene should make this the most satisfactory solution.

The computer programme described in Chapter 11 was used to calculate the product compositions for runs B:12, B:23 and B:53. A constant value of 95% was assumed for the plate efficiencies and run B:12 was recalculated using an efficiency of 85%.

The programme was arranged so that the computer printed the complete composition and flow profiles after every five iterations and a forcing parameter was used whose magnitude at any given time gave a measure of the stability of the calculation procedures. The initial value of the parameter was $\frac{1}{4}$ and after every iteration the value was halved if the calculations were satisfactory and doubled if they were not. The theoretical justification of this parameter is given in

Chapter 11 but at this stage it is only necessary to appreciate that a high value of the parameter automatically infers that the overall material balance equations are not satisfied. The magnitude of the parameter should therefore be continuously reduced in satisfactory calculations until it becomes insignificant when the results should reproduce the experimental values.

For run B:12 the forcing parameter was reduced to 1.5625×10^{-2} and 7.8125×10^{-3} for plate efficiencies of 95% and 85%, respectively, after 10 iterations. Subsequently, instability was observed in the calculations for the base of the column, for the reasons given in Chapter 11, which caused the parameter to increase to 3.125×10^{-2} after 30 iterations. For an efficiency of 95% the top product composition after 10 iterations was 2.2 mole % acetylene, 1.4 mole % ethane and 96.4 mole % ethylene and the corresponding bottom product composition was 14.9 mole % acetylene, 5.0 mole % ethylene and 80.1 mole % ethane. The corresponding values for run B:12 with a plate efficiency of 85% were a top product containing 4.5 mole % acetylene, 1.6 mole % ethane and 93.9 mole % ethylene and a bottom product of 13.2 mole % acetylene, 4.1 mole % ethylene and 82.7 mole % ethane. The maximum concentration of acetylene obtained within the column was 24 mole % in both cases. It will be seen from the operating variables given for run B:12 in Appendix V that the results do not satisfy the overall balances owing to the high value of the forcing parameter. In spite of the subsequent instabilities observed for the calculations

at the base of the column, however, the composition profiles in the rectifying section of the column became increasingly stable and a very good estimate of the eventual top product composition could be made. From these values the true bottom product composition could be calculated by an overall material balance. With a plate efficiency of 95% the resultant top product composition was 7.5 mole % acetylene, 3.3 mole % ethane and 89.2 mole % ethylene and for the bottom product 10.4 mole % acetylene, 11.8 mole % ethylene and 77.8 mole % ethane. With a plate efficiency of 85% the corresponding top product composition was 9.8 mole % acetylene, 5.6 mole % ethane and 84.6 mole % ethylene and the bottom product 9.8 mole % acetylene, 13.0 mole % ethylene and 77.3 mole % ethane.

The values obtained with a plate efficiency of 95% compare favourably with the experimental values of the product compositions, and for the trial considered this result justifies the distillation techniques, the use of the experimental plate efficiency data for the binary system in the ternary separation and the empirical correlation of the phase equilibrium data.

The calculated results for run B:23 did not lead to the satisfactory conclusions obtained for run B:12, and the variety of possible explanations for this behaviour made a complete analysis impossible.

The forcing parameter attained a maximum value of 0.5 after 15 iterations and thereafter decreased regularly to a final value of 1.562×10^{-2} after 30 iterations. At this time the top product

composition was 0.7 p.p.m. of acetylene and 30 p.p.m. of ethane and the corresponding bottom product composition was 19.4 mole % acetylene, 1.2 mole % ethylene and 79.4 mole % ethane. An overall material balance based on the assumption of a correct calculated top product composition yields a bottom product of 14.8 mole % acetylene, 6.2 mole % ethylene and 79.0 mole % ethane. These discrepancies may once again be attributed to the high value of the forcing parameter. The top product compositions do not compare favourably with the experimental values and consideration of the composition profiles shows that the experimental top product composition was achieved in 25 plates. The computed results may have been affected by the restriction placed upon the equilibrium constants, described in Chapter 11, which has previously resulted in instability at the base of the column, but which has not previously appeared to hinder the ultimate stability in the rectifying section of the column. Although the empirical correlations for the equilibrium constants were good enough to describe the distillation paths calculated for run B:12, the differences between the calculated and experimental values of the equilibrium constants at the pure component points, Table III:1:17, may have been sufficient to destroy the validity of the computed results. By using heavier weighting of the experimental values in these regions for the equilibrium constant correlation the importance of these errors could be ascertained. Unfortunately insufficient computing time was available to resolve this difficulty and it is suggested that this point be clarified at some future time. A third possibility for the discrepancies between the

distillation results is the reduction in the plate efficiency that may occur in regions close to the pure components. Zuiderweg and Harmens[97] observed variations in the plate efficiency of Oldershaw columns with the composition range studied and Danckwerts, Sawistowski, and Smith[98] have postulated explanations for this behaviour. The assumption of a constant efficiency throughout the column therefore cannot be fully justified. Finally errors in the measured top-product compositions could be considerable, owing to the unsuitability of the chromatograph for the detection of small amounts of impurity.

For run B:53 the forcing parameter decreased to 7.812×10^{-3} after 15 iterations and subsequently increased slightly, due to instability on the bottom plate, finally reaching a value of 3.125×10^{-2} after 30 iterations. The feed plate composition, the composition profile in the rectifying section and the top-product composition stabilized after ten iterations and the resultant value of the top-product composition was 0.036 mole % acetylene, 0.064 mole % ethane, and 99.90 mole % ethylene. At maximum stability the bottom product composition was 3.2 mole % acetylene, 0.3 mole % ethylene and 96.5 mole % ethane and the sidestream composition was 25.6 mole % acetylene, 25.7 mole % ethylene and 48.7 mole % ethane. These values compare favourably with the experimental values and also satisfy the component material balance equations. During subsequent iterations, however, the acetylene content of the sidestream decreased, whilst the bottom product composition

remained effectively constant. In addition the experimental ratio of acetylene to ethylene concentration in the bottom product was less than one and the ratio of acetylene to ethane concentration in the top product was greater than one, whereas the computed values of these ratios were greater and less than one, respectively. These changes in slope of the distillation path cannot be explained. Nevertheless, the satisfactory behaviour of the computed results again indicates the validity of the techniques and assumptions used.

Although, because of the difficulties of obtaining further computer time, it was not possible to modify the programme to overcome the instabilities observed above and to attempt an extension of the experimental results to give the number of plates required to achieve the desired product specifications, it is considered that the computer programme has provided evidence for the validity of the experimental distillation trials and the experimental phase equilibrium data. In addition the conclusions arrived at from a consideration of the experimental trials, which are given above, are regarded as being valid and sufficient to permit the design of a distillation column for the proposed separation. The final decisions regarding the choice of the operating reflux ratio and the plate efficiencies have still to be made by the designer before using the computer programme, but these considerations are usually determined by economics and company policy and it is felt that the inability of this work to provide answers to these questions does not detract from its overall value.

Chapter 10.

The separation of C_2-hyrocarbons using absorption techniques.

10:1 Introduction.

In the first section of this chapter the design, construction and operation of a simple absorption column, for the removal of acetylene from C_2-hydrocarbon mixtures by acetone scrubbing, are described.

10:1:1 Design of column.

The solubility of acetylene in acetone increases with decrease in temperature; below $-85^{\circ}C$, however, the phase diagrams are complicated by solid formation. A design temperature of $-80^{\circ}C$ was therefore chosen and quaternary phase equilibrium data was measured at this temperature.

The C_2-hydrocarbons liberate heat on solution in acetone and therefore the column must be cooled to maintain isothermal operation and thereby maintain a high solubility of acetylene in acetone. In these circumstances the normal industrial practice is to insert cooling coils on the trays, this procedure was not possible, however, with the Oldershaw column. As an alternative it was decided to supply the column with a stream of hydrocarbon reflux from a partial condenser, thus the heat of solution in acetone was balanced by the latent heat of vaporisation of the reflux.

A feed gas composition of 60 mole% ethane, 30 mole% ethylene and 10 mole% acetylene was chosen and the composition of a liquid stream in equilibrium with this feedstock was deduced from the quaternary data. The minimum circulation rate of acetone was therefore calculated and a design rate 20% in excess of the minimum rate was used. The actual top and bottom product compositions were then obtained from an overall material balance. The flow rate of hydrocarbon reflux required to maintain thermal equilibrium was then calculated from the heats of solution and the dew-point of the top product.

The number of theoretical plates needed to effect the separation was obtained by plate to plate calculations using the experimental equilibrium data. It was concluded that a column of 9 theoretical plates with an acetone circulation rate to feed rate ratio of 25% on a molar basis would be required to obtain a top product containing less than 100 ppm of acetylene and to give a 97% recovery of ethylene and ethane. The top product could then be separated in a conventional splitter to give the desired degree of ethylene purity.

10:1:2. Apparatus and Experimental Method.

The 10 plate Oldershaw Column was used and set up as described in Chapter 7. The reboiler was used solely as a bottom product reservoir and provision was made for the

withdrawal of a liquid product by connecting a swan-neck glass tube to the base of the vessel. A liquid seal was thus maintained and the feed gas was introduced above the reservoir surface.

Acetone was pumped to the top of the column, via a copper coil immersed in a mixture of solid carbon dioxide and industrial spirit, by a D.C.L. positive displacement metering pump of nominal maximum capacity of 1500 ml/hr.

A simple liquid nitrogen cup condenser was used to offset the effects of a superheated feed stream and the heat of solution of the hydrocarbons in acetone as described above. Thermocouples were introduced into the feed lines and used to measure temperatures in the reservoir and on the top plate of the absorption column.

A feed gas rate of about 4l./min was chosen and the design value for the acetone circulation rate was calculated. Three trials were made with acetone rates of 0.86, 1.75, and 4.35 times the design value. Initially the bottom reservoir was immersed in a mixture of solid carbon dioxide and industrial spirit to maintain the dissolved gases in solution. Acetone was pumped through the heat exchanger into the column and allowed to fill the reservoir before the feed gas was introduced. The temperatures within the column were continually observed and sufficient liquid nitrogen was added

to the condenser to maintain them at about -80°C. After about twenty minutes several samples of the top product, bottom product and feed were taken and analysed on the chromatograph.

Although the runs were satisfactory, the possibility that the plate temperature had increased down the column from the value recorded on the first plate could not be discounted. Owing to the construction of the Oldershaw column thermocouples could not be introduced onto plates at the centre of a section. The reservoir was therefore carefully insulated with expanded polystyrene, the cooling bath was discarded and the runs were repeated. No significant differences were observed between the two sets of results.

10:1:3 Results and Discussion.

The results of the trials are recorded in Appendix VI.

It has already been seen that the equilibrium data cannot be reduced to a simple mathematical form and so only a semi-quantitative discussion of the results is possible. In general, the predicted behaviour of the absorption column as described in 10:1:1 was shown to be correct. The chromatograph was capable of detecting the presence of acetylene at concentrations in excess of 100 p.p.m. and the

design calculations were therefore limited to an overhead product having this composition. Experimental trials performed in a column containing 10 practical plates at -80°C with acetone circulation rates of the same order as the design value gave top products containing about 100 p.p.m. of acetylene. In Chapter 8 it was seen that the efficiency of Oldershaw sieve plates when fractionating a mixture of ethylene and ethane was 95%. It would appear that this efficiency has been maintained in the absorption studies.

The ethylene recoveries ranged from 81% at high acetone rates to 98.5% at low acetone rates. The compositions of the bottom product streams were remarkable, in that the amount of ethylene present was less than would have been predicted from the equilibrium data. No satisfactory explanation could be found for this behaviour and as a result of it the experimental recoveries of ethylene were higher than the design values.

The material balances were sometimes in considerable error. In run C:4 20% errors based on the minor constituents were observed. The manual method used to condense a part of the top product is not a continuous operation and cyclic fluctuations in both the flow and composition of top product were obtained. The values of these operating variables recorded in Appendix VI are therefore averages of several determinations and in consequence the material balances were

not completely satisfactory.

It is considered that this work has provided an effective and simple method for scrubbing acetylene from hydrocarbon mixtures and obtaining a high recovery of the resultant ethylene stream. The design calculations have been justified and extension of the results to include top product compositions of 10 ppm acetylene or less should present no difficulties. Nevertheless, more refined work with provision for cooling the feed to its dew point and the introduction of an adequate condenser control system would be valuable.

The further treatment of the bottom product stream to recover acetylene at reasonably high purity and to regenerate the acetone has been discussed in Chapter 6. A Marston-Excelsior overflow packing column was designed to allow the work to be continued in this manner. The size of the column required for the low flow rates involved was impracticably small and after discussion with the manufacturers it was decided to accept an over-sized unit. Owing to this and the delay required for construction it seemed reasonable to treat this section of the work as a separate project to be completed at a future date.

10:2. Reboiled absorption.

To improve the recoveries of ethylene and ethane and thereby increase the percentage of acetylene relative to the other hydrocarbons in the acetone stream, reboil could be applied at the base of the column. At the same time the feed

should be introduced at some intermediate column position, thus introducing a stripping section, for the addition of reboil to a simple absorption column would merely add one theoretical plate below the feed and increase the heat load on the condenser.

In order to investigate the effectiveness of such an arrangement a few trials of reboiled absorption were attempted.

10:2:1. Apparatus and experimental method.

The apparatus employed was almost identical to that used in 10:1:2. A 5 plate Oldershaw column was introduced between the feed and the reboiler and the 'hot-finger' heater described in Chapter 7 was connected up to give the required reboil.

The experimental method was also identical to that described in 10:1:2. After the apparatus had been charged with acetone the reboiler was switched on at a minimum power dissipation level and sufficient liquid nitrogen was used to maintain stable column conditions.

10:2:2 Results and Discussion

The results of the runs are recorded in Appendix VI In general it may be said that the recoveries of ethylene have increased whilst the acetone rate required for satisfactory scrubbing has also increased.

The minimum reboiler duty of 57.1 BTU/hr was used and

the highest reflux rate consistent with stable column operation was employed to maintain the temperature at the column base at the lowest possible level. Under these circumstances the manual control of reflux led to large cyclic variations in top product flow and composition which frequently resulted in flooding conditions on the top plate and did not permit accurate measurements of either the flow rate or the composition of the product stream. In addition, in this case, the overall heat leak would be a considerable proportion of the reboiler duty and owing to the large solubility of acetylene in acetone, even at high temperatures, the majority of the reboiler duty went to provide sensible heat to the acetone. In consequence the vapour rate in the stripping section of the column was too small to prevent weeping and the expected improvement in ethylene recovery, due to the addition of this section, did not materialize. For low acetone circulation rates the increase in the bottom product temperature resulted in considerable losses of acetylene in the top product and high circulation rates were required to restore satisfactory operating conditions.

Although an economic evaluation of the processes should be made before a decision can be taken as to the relative merits of simple and reboiled absorption, it would appear that the nominal increase in ethylene recovery would not justify the increased acetone circulation rate and condenser duty and the

need for reboil.

Before attempting such an evaluation further trials should be performed in a modified apparatus designed to eliminate heat leak completely, to allow for feed pre-cooling and to permit the use of higher vapour rates within the column. All these modifications imply that the work should be carried out on a larger scale and so the existing apparatus could not be simply modified to fulfil these requirements.

10:3. Extractive distillation.

The logical extension of the ideas discussed in section 10:2 on reboiled absorption lead naturally to the concept of extractive distillation. By the addition of a column section above the acetone feed point, one might hope to produce pure ethylene as top-product and remove both the ethane and acetylene at the base with the acetone. Under these circumstances, regions of partial miscibility would almost certainly be crossed on the plates below the acetone entry point and a separate ethane fraction of reasonable purity could be removed. This arrangement can be considered as a superposition of the C_2-splitter on a reboiled absorption column, and since the equilibrium data indicate that ethylene and ethane have virtually the same volatility in the presence of acetone, the ethylene-ethane separation must inevitably occur in the section above the acetone feed-point. Little gain can therefore

be expected and it would seem preferable to keep the two functions separate.

Study of this system would present similar experimental difficulties to those encountered with reboiled absorption, and no experiments were carried out.

In conclusion an adequate solution to the problem of C_2 separation has been achieved by the use of a simple absorption column with a postulated regeneration cycle involving an overflow packing column. The method uses low acetone circulation rates and produces a top product of high purity with a good recovery of ethylene. Modifications of this method produced some improvements but in general they were not considered to justify the increase in complexity and running costs of the equipment.

CHAPTER 11

Computer solutions of multi-component distillation problems

11:1 Introduction

A multi-component distillation problem is completely defined when the following operating variables are specified:

1) Number of plates in each section,

2) Quantity, composition and thermal condition of the feed,

3) Column pressure,

4) Type of overhead condenser and reboiler,

5) Quantity of all but one of the product streams,

and 6) Reflux ratio or reboiler duty.

The compositions of all the product streams may then be determined by plate-to-plate calculations using reliable equilibrium, enthalpy and plate efficiency data. If it were possible to reproduce the results of the experimental ternary distillation trials in this manner, then it would follow that the measured data and the operating techniques were valid, and in addition it would be possible to justify the calculation of other column arrangements not studied experimentally. Hand calculation of distillation columns is a tedious procedure, however, and it was decided to programme the Mercury computer for this purpose.

11:2 Review of previous methods

Several attempts have been made to solve multi-component distillation problems by computer techniques and the essential

characteristics of the methods are outlined in the following.

11:2:1 Plate-to-plate calculations

The classical methods are those of Lewis and Matheson[45], and Thiele and Geddes[88]. In the first method the objective is to find the number of ideal steps for a given separation, and in the latter method the product compositions are calculated for a given number of steps. In the Lewis and Matheson procedure experience and judgment must be exercised to introduce non-distributed components in the stripping and absorbing sections, whereas in the Thiele and Geddes method all calculations are made in terms of mole-fraction ratios and the direct assumption of the products is avoided. McIntire,[52] Shelton and McIntire,[83] and Bonner[4] have adapted these methods for use with digital computers.

McIntire[52] describes a method for the design of a column with ideal stages required to make a given separation of a multi-component feed. Phase equilibrium data are fitted to the "Antoine" type of equation,

$$\ln K = A_K - B_K / (C_K + T) \quad -(1:11)$$

and enthalpy data are stored as coefficients of third-order polynomial equations. An initial estimate of the number of plates is made, overall heat and material balances are calculated at a specific reflux-ratio and temperature and vapour rate gradients are assumed. The heavy key and heavier components are calculated upwards throughout the column, introducing the vapour feed when the heavy key concentration nears that

in the feed and terminating the rectifying section when the heavy key concentration matches that required by the overall material balance. Similarly the light key and lighter components are calculated downwards throughout the column. The temperature and rate profiles are modified and successive passes up and down the column vary the lengths of first the rectifying section and then the stripping section to meet the end-product specifications. The calculations are terminated when the profiles and section lengths settle to steady values. This solution does not yield the optimum feed-entry location and a revised feed entry must be decided upon before recalculation.

McIntire and Shelton[83] modify the above procedure to determine the performance of an existing column under given conditions. Product compositions are initially assumed and in the case of non-distributed components infinitesimal amounts of these substances are specified in the products. Calculations are made downwards from the overhead product and upwards from the bottom product to the feed plate, using an iterative procedure based upon Newton's method to determine temperatures, flow rates and compositions simultaneously for each stage. For each component the ratio of the compositions on the feed plate, determined by the two sets of computations, is calculated and this ratio is used to revise the smallest assumed product composition of the given component.

Bonner[4] describes a programme using conventional short-cut techniques developed principally for exploratory work, where a large

number of cases must be examined and where approximate answers are satisfactory, Initially the minimum number of theoretical plates at total reflux is assumed and a trial separation using the Fenske equation,[24] with a reference component recovery of 50%, is calculated. The distillate purity of a desired component is calculated and compared with the specification value, the reference component recovery is then adjusted to improve the match, and the Fenske equation calculations are repeated. The minimum reflux-ratio is calculated from the Underwood equations,[89] and the actual reflux-ratio is derived from the Gilliland curves[28] and compared with the specification value. The number of plates required at total reflux is then adjusted and the calculations are repeated.

The short-cut technique may be used to provide the initial assumptions for Bonner's longer plate-to-plate programme. The author assumes a set of product compositions, a temperature profile and constant vapour rates, and calculates downwards from the top product and upwards from the bottom product to the feed plate using alternating equilibrium calculations and material balances. The calculated compositions and the mis-match at the feed plate are used to adjust the temperature and flow rate profiles and the product compositions for successive trials. Bonner[4] calculates the theoretical adjustment to be applied to the distillate flow of each component in order to secure correct overall material balances and a perfect feed plate match in the following trial, assuming that the temperature and flow rate profiles do not alter.

This technique involves applying corrections preferentially to the lightest and heaviest components and in this manner proper temperature gradients are established early in the calculation sequence.

11:2:2 Absorption and stripping factor method

Lyster, Sullivan, Billingsley and Holland[48] describe another computer technique based on the method proposed by Thiele and Geddes.[88] Initially temperature and flow rate profiles are assumed for the column. The absorption and stripping factors for each plate and component are calculated viz:

$$Ani = Ln/Kni\ Vn \qquad (2:11)$$

$$\text{and } Sni = Kni\ Vn/Ln \qquad (3:11)$$

Where "n" refers to the plate number and "i" the component. Plate-to-plate recursion formulae are then used from the condenser downwards and the reboiler upwards to generate a series of values of v_{ni}/d_i and l_{ni}/b_i for each component, where v_{ni} and l_{ni} are the molar flow rates of vapour and liquid of component "i" leaving plate "n" in the rectifying and stripping section of the column, respectively, and d_i and b_i are the molar withdrawal rates of the component "i" in the distillate and bottom product, respectively. From the material balance at the feed plate the ratio of the molar withdrawal rates b_i/d_i, for each component, is obtained and the ratios are corrected by a scaling factor so that they satisfy the overall material balance. The corrected values for the withdrawal rates and the results of the recursion formulae are then used to derive the normalised vapour and liquid compositions on all the

plates and by making dew or bubble-point calculations a new temperature profile is established. The new flow rate profile can then be calculated from enthalpy balances and the cycle is repeated until the total distillate flow matches the specified value.

Various forcing procedures are described by Lyster et. al., which reduce the number of trials required, by reducing the variations in the flow and temperature profiles calculated for successive trials.

11:2:3 Solutions involving matrices

Amundson and Pontinen[1] have developed a method for use with large digital computers which are capable of handling more complicated calculation procedures.

Initially a temperature and flow rate distribution are assumed. For each component a set of N+2 simultaneous linear algebraic equations are then written, where N is the number of plates, representing the material balances on each plate. This set of equations may be formally written as a matrix equation:

$$\bar{\bar{M}}_i \bar{X}_i = \bar{F}_i \qquad - (4:11)$$

Where $\bar{X}_i$ is a composition column vector,

$\bar{F}_i$ is a feed column vector,

and the matrix $\bar{\bar{M}}_i$ is tridiagonal and its non-zero elements are expressed, in terms of vapour rates, equilibrium 'K-values' and product rates. Solution of the matrix equation generates values for the liquid composition of component "i" on every plate. The procedure is repeated for every component, negative mole fractions are

set to zero and the liquid compositions on each plate are normalised by dividing the composition of each component by the sum of the compositions on the plate. A further matrix equation for the enthalpy balance is set up:

$$\bar{\bar{H}}\,\bar{V} = \bar{G} \qquad -(5:11)$$

where $\bar{V}$ and $\bar{G}$ are vapour rate column vectors and product enthalpy vectors, respectively, and $\bar{\bar{H}}$ is the square enthalpy matrix of N+1 th. order having only two non-zero elements. From the temperature distribution and the calculated compositions this matrix may be obtained and the equation solved to generate a new set of vapour flow rates. The normalised liquid compositions are used to develop a new temperature distribution which satisfies the bubble-point equation:

$$\Sigma_i K_{ni} X_{ni} = 1 \qquad -(6:11)$$

The calculations are repeated with the new distributions and are terminated when the desired degree of accuracy in X_{ni}, $\Sigma_i X_{ni}$ or $\Sigma_i K_{ni} X_{ni}$ has been attained.

11:3 Discussion

The plate-to-plate calculation methods described by Shelton and McIntire[83], and Bonner[4] were developed for slow Card Programmed Calculators having limited storage space. Under these circumstances the complicated iterative method for the complete solution of each stage described by Shelton and McIntire[83] is preferable to Bonner's method[4] in which temperature and flow rate profiles resulting from one iteration have to be stored for use in subsequent calculations. Bonner's method, however, is simpler and more readily translated into machine instructions and it is more

suitable for use with computers of large storage capacity. Bonner[4] considers that poor initial assumptions do not seriously affect the convergence of his technique and he obtains accurate and rapid solutions for most of the problems tested.

In both of these methods difficulties are encountered in the choice of successive trial values of the end compositions resulting from a mis-match at the feed plate. In the case of non-distributed components, minute changes in one product composition could lead to very large errors in the temperature and other product compositions, and although neither Bonner[4] nor Shelton and McIntire[83] discuss this behaviour, it would seem likely that their product composition modification procedures could lead to instability in difficult cases. In addition for the separation of C_2 hydrocarbons acetylene may be present in either large or small amounts in either the top or bottom products, and as the choice of modification procedures is dependent upon the expected behaviour of the column and needs to be completely systematized in advance in the form of programme instructions, it seems likely that further difficulties would be encountered in this case.

The methods of Amundson and Pontinen[1] and Lyster et. al.[48] are similar in that the composition profiles of each component are generated independently, the feed plate being treated in a similar fashion to the other plates. Lyster et. al.[48] then modify the end values of the compositions, so that they satisfy the overall material balance,

scale and normalize the calculated compositions, and develop new temperature and flow rate profiles from dew and bubble-point calculations and enthalpy balances. Amundson and Pontinen[1] use more refined matrix methods for their calculations and merely normalize their calculated compositions without forcing the end values to satisfy the overall material balance before completing the calculation cycle.

Lyster et. al.,[48] Amundson and Pontinen,[1] and Bonner[4] commence their calculations with an assumed temperature profile and express 'K' values as functions of temperature and pressure only. This assumption of ideality is not seriously in error for the hydrocarbon separations given as examples by these authors, but for more difficult separations the stability of the Amundson and Pontinen, and Lyster techniques is affected by the sensitivity of the 'K' values to changes in composition, and forcing procedures have to be introduced. For the separation under consideration the Amundson and Pontinen method was chosen, as a large computer was available, and certain modifications were made in the basic techniques employed to counteract the serious non-idealities that were observed in the C_2-hydrocarbon system.

11:4 Development of multi-component distillation programme

The development of a complicated computer programme is a tedious procedure and faults in formulation and logic have to be

eliminated before an assessment of the suitability of the programme can be made. In the following an outline of the various methods employed is given and the final form of the programme is recorded in Mercury Autocode in Appendix VII.

The material balance equations given by Amundson were modified by the introduction of a Murphree plate efficiency[56] to take into account the deviations of real stages from theoretical stages. The Murphree plate efficiency is defined by:

$$\eta_{i,p} = (y_{i,p} - y_{i,p-1})/(y^*_{i,p} - y_{i,p-1}) \quad -(7:11)$$

where $y^*_{i,p}$ is defined as the mole fraction of component "i" in the vapour in equilibrium with the liquid leaving plate "p", when this is brought to its boiling point; thus:

$$y^*_{i,p} = K_{i,p}\, x_{i,p} \quad -(8:11)$$

where $K_{i,p}$ is the value of theequilibrium constant under these conditions.

From (7:11) $y^*_{i,p} = \{y_{i,p} - (1 - \eta_{i,p})\, y_{i,p-1}\}/\eta_{i,p}$ -(9:11)

Thus if the compositions of the vapour for all components and stages are known, (9:11) and the equilibrium relationships may be used to determine the temperatures of each stage and the compositions of the liquid reflux at all points in the column.

For an ideal stage, p, in a column, the material balance equation, for component "i", may be written:-

$$(V_p + P_{v,p})y_{i,p} + (L_p + P_{L,p})x_{i,p} - V_{p-1}\, y_{i,p-1} - L_{p+1}\, x_{i,p+1} = f_{i,p} \qquad (10:11)$$

where the plates are numbered upwards from the reboiler,

$f_{i,p}$ is the quantity of component i in the feed to plate p,

P_v is the vapour product rate from plate p,

P_L is the liquid product rate from plate p,

L_p is the liquid rate entering stage p-1

V_p is the vapour rate entering stage p+1.

For real stages from (8:11), (9:11) and (10:11)

$$-V_{p-1}\, y_{i,p-1} + (V_p + P_{v,p})y_{i,p} + \frac{(L_p + P_{L,p})(y_{i,p} - (1-\eta_{i,p})y_{i,p-1})}{\eta_{i,p}\, K_{i,p}}$$

$$- \frac{L_{p+1}}{K_{i,p+1}\,\eta_{i,p+1}} \left(y_{i,p+1} - (1 - \eta_{i,p+1})y_{i,p}\right) = f_{i,p} \qquad (11:11)$$

Initially the experimental equilibrium data was fitted to third and fourth order polynomials of the form $T=f(y_{C_2H_2}, y_{C_2H_4})$ and $x_{C_2H_2}=f(y_{C_2H_2}, y_{C_2H_4})$ etc., as described in chapter 5. Liquid and vapour enthalpy data were fitted to simple equations of the form,

$$h_i = a + bT \qquad (12:11)$$

where a is the value of the enthalpy at $0^{\circ}K$ and b is the specific heat applicable over the experimental temperature range.

These equations are too simple to represent the true enthalpy-temperature relationships but owing to the scarcity of data they were considered adequate for the present purpose. Enthalpy data for ethylene and ethane were obtained from diagrams published by the Kamerlingh-Onnes Laboratory, Leiden, that for

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gaseous acetylene from Din whilst the values for liquid acetylene were assumed to be the same as those for liquid ethane. For the first iteration the vapour compositions throughout the column were assumed to be the same as the feed composition; the liquid composition and temperature at equilibrium were calculated from the polynomials, and enthalpy balances were used to calculate the flow rates within the column. Simple recurrence relations were used for these enthalpy balances which were equivalent to the matrix solution described by Amundson and Pontinen.[1] The material balances for each component on all stages, (11:11) were set up in the form of a matrix equation and the latter was solved to obtain revised estimates of the vapour compositions, using a routine written for tri-diagonal matrices by Mr. S. Michaelson formerly of the Mathematics Department at Imperial College. The vapour compositions were normalized and used to derive a new set of liquid compositions. This method proved to be unstable and subsequent refinements of the initial estimate of vapour compositions based on a linear interpolation between the experimental values of the end compositions did not produce any improvement.

It has been shown in Chapter 5 that the phase diagram of the ternary system is complicated at high acetylene concentrations by solid formation. In general, although the polynomials used to correlate the equilibrium data are satisfactory at low

acetylene concentrations they cannot be expected to represent the true situation when solids are present. The initial estimates of the vapour compositions, described above, were sufficiently inaccurate to cause the solutions to oscillate severely in the first few iterations and thus cause the composition profiles to pass through regions where the polynomials did not give an adequate representation of the phase diagram. Subsequently the instabilities were magnified, thus causing failure of the method.

Several refinements were introduced to eliminate the difficulties described above, and to increase the generality of the programme. The equilibrium data were therefore correlated in the form of third order polynomials for the equilibrium constants e.g. $K_{C_2H_2} = f(y_{C_2H_2}, y_{C_2H_4})$ etc., and the initial estimate of the vapour compositions in the column was made by the use of the Fenske equation[24] for total reflux, as detailed in Appendix VII.

It has been noted that the failure of the first programme resulted from the artificial oscillations in composition profiles that occurred during the first few iterations. A considerable improvement should be obtained if the equations could be modified to represent the real dynamic behaviour of the column as it passes from a given set of initial conditions to the final

steady-state. Rose, Sweeny, and Schrodt[73] adopt this technique by using the transient material balance equations:

$$\frac{x_{i,p,s+1} - x_{i,p,s}}{t_{s+1} - t_s} = \frac{1}{H_p}\left(V_{p-1}\, y_{i,p-1,s} + L_{p+1}\, x_{i,p+1,s} - (V_p + P_{vp})\, y_{i,p,s} - (L_p + P_{Lp})\, x_{i,p,s} + f_{i,p,s}\right) \quad -(13:11)$$

where t_s and t_{s+1} refer to successive times, and Hp is the total moles of hold-up on plate p, assumed constant during a transient. Providing that the behaviour of the column at time ts is known this can be used to predict the liquid composition at time ts+1. In this manner the gradual changes in plate and product composition that occur in a column from start-up may be developed. The final steady state solution is independent of starting compositions, but if the real initial compositions, hold-ups, flow rates and time lags are used the calculations describe the physical approach to the steady state.

If (13:11) is expressed as $\frac{x_{i,p,s+1} - x_{i,p,s}}{t_{s+1} - t_s} = \frac{\phi_{i,p}(s)}{Hp}$

then it represents the Euler solution[18] of the differential equation:

$$\frac{d\, x_{i,p}}{dt} = \frac{\phi_{i,p}}{Hp} \qquad -(14:11)$$

To enable us to compare the various forms of the finite difference solutions for (14:11) that may be used we shall discuss the equation:

$$\frac{d\,x_{ip}}{dt} = -\frac{L_p}{H_p}\,x_{ip} = -\lambda x_{ip} \qquad (15:11)$$

with $x_{ip} = x_{ipo}$ at time $t = 0$

The Euler solution of (15:11), with time interval h, is:

$$\frac{x_{i,p,s+1} - x_{i,p,s}}{h} = -\lambda x_{i,p,s} \qquad (16:11)$$

or $$x_{i,p,s+1} = (1-\lambda h)\, x_{i,p,s} = (1-\lambda h)^s\, x_{i,p,o}$$

Any error in $x_{i,p,o}$ will cause the error in $x_{i,p,s+1}$ to tend to infinity as s tends to infinity unless:

$$0 < \lambda h < 2 \qquad (17:11)$$

Thus the Euler solution will be unstable unless the time interval chosen is less than twice the natural time for the column. This result cannot be applied directly to Rose's solution (13:11), but it indicates that the method is liable to be unstable and indeed the examples given by Rose[73] show that the number of time-steps or iterations required to achieve the steady state solution may exceed 150, thus indicating that Rose et.al. found it necessary to use very small intervals for stability.

Rosenbrock, Storey, Tavendale and Challis[74] use a more effective method for the development of transient material balances, they replace (14:11) by:-

$$\frac{x_{i,p,s+1} - x_{i,p,s}}{t_{s+1} - t_s} = \frac{(1-\theta)\emptyset p(s) + \theta \emptyset p(s+1)}{Hp} \qquad (18:11)$$

where θ is a constant which equals zero in Rose's solution.

If $\theta = \frac{1}{2}$ the Crank-Nicholson solution results and (15:11) becomes:

$$\frac{x_{i,p,s+1} - x_{i,p,s}}{t_{s+1} - t_s} = \frac{1}{2}\left[(-\lambda x_{i,p,s}) + (-\lambda x_{i,p,s+1})\right] \qquad (19:11)$$

i.e. if $h = t_{s+1} - t_s$ $\quad x_{i,p,s+1} = \frac{1 - \lambda h/2}{1 + \lambda h/2} x_{i,p,s} = \frac{(1-\lambda h/2)^s}{(1+\lambda h/2)} x_{i,p,o}$

The true solution of (15:11) is

$$x_{i,p,s+1} = x_{i,p,o} e^{-\lambda t} = x_{i,p,} e^{-\lambda h s} \qquad (20:11)$$

and as the time interval, h, tends to infinity $x_{i,p,s+1}$ tends to 0. Although the Crank-Nicholson solution is unconditionally stable, as h tends to infinity the ratio $x_{i,p,s+1}/x_{i,p,o}$ tends to -1 and the method would therefore be liable to result in an inaccurate steady-state solution. In addition, although the method has a small truncation error and is useful for studying the dynamic behaviour of a column, Rosenbrock[62] considers that it can become unstable for non-linear distillation problems. It will also be seen from (19:11) that the use of the Crank-Nicholson solution implies that two sets of matrix elements, one for each of the limits of the time interval, have to be stored in the computer.

If $\theta = 1$ then (15:11) becomes;

$$\frac{x_{i,p,s+1} - x_{i,p,s}}{t_{s+1} - t_s} = -\lambda x_{i,p,s+1} \qquad (21:11)$$

i.e. $x_{i,p,s+1} = \frac{x_{i,p,s}}{1 + \lambda h} = (1 + \lambda h)^{-s} x_{i,p,o}$

This method has a larger truncation error and is therefore less suitable than the Crank-Nicholson solution for studying the

dynamics of the system. However, the solution is unconditionally stable and as the time interval becomes very large it tends to zero. The method has the additional advantage that only one set of matrix elements has to be stored for distillation problems. It would appear that substitution of $\Theta = 1$ in (18:11) gives the most satisfactory method for obtaining a rapid and accurate approach to the steady-state solution.

The time interval chosen for this solution of the Rosenbrock transient equation is not governed therefore by either considerations of stability or by the desired accuracy of the final steady-state solution, but by its ability to achieve this solution in as few iterations as possible, whilst still representing the dynamic solution adequately, so that the calculated distillation path does not pass into regions of the phase diagram where the experimental data cannot be satisfactorily extrapolated.

In one time step a value of $\lambda h = 4$, when substituted in (20:11), results in a value of $x_{i,p,s+1} = 0.018\ x_{i,p,o}$. Thus if no trouble is experienced with convergence a good approach to the steady-state solution is obtained in one iteration using a time interval of 4 natural time steps.

The form of the Rosenbrock transient equation when $\Theta = 1$ is:

$$\frac{x_{i,p,s+1} - x_{i,p,s}}{h} = \frac{\emptyset p\ (s+1)}{Hp} \qquad (22:11)$$

and the form of equation used in the computer programme is:

$$\phi_p(s+1) + u'L_p\, y_{i,p,s} = u'L_p\, y_{i,p,s+1} \qquad (23{:}11)$$

where u' is the forcing parameter

$$\text{Therefore } u' = H_p/L_p h\, K_{i,p} \qquad (24{:}11)$$

As the forcing parameter was to be continuously modified the equilibrium constant correction was ignored and therefore $u' = 1/\lambda h$. The value of $\lambda h = 4$ was derived in a somewhat arbitrary fashion and allowance was made for this by reducing λh if an iteration was not considered satisfactory and vice-versa. The vapour composition profiles for each component were derived independently by the solution of the matrix equations and the deviation of their sum from unity on any stage was taken as a direct measure of the accuracy of the 'K'-values. The following equations were used to modify the values of the forcing parameter:

$$\begin{aligned} (u')\text{new} &= 2(u')\text{old} \quad \text{if} \quad |1 - \textstyle\sum y| < 0.1 \\ (u')\text{new} &= \tfrac{1}{2}(u')\text{old} \quad \text{if} \quad |1 - \textstyle\sum y| > 0.3 \end{aligned} \qquad (25{:}11)$$

Finally two modifications were introduced into the routine used for the calculation of equilibrium constants to eliminate inaccuracies resulting from the form of the polynomials. Negative and zero equilibrium constants weremade slightly positive and values greater than three were set equal to three. The Fenske equations, described in Appendix VII, are liable to give initial estimates of the vapour composition profile that lie in regions inadequately described by the polynomials for the

equilibrium constants. Under these circumstances severe oscillations could still occur in the first few iterations and so a limit was set on the possible composition variation, by restricting the range of possible equilibrium constants.

11:5 Behaviour of the computer programme

The experimental values of the operating variables for runs B:12, B:23 and B:53 were fed as data to the computer. A constant plate efficiency of 95% was assumed in all cases and run B:12 was recalculated using a constant plate efficiency of 85%.

A comparison of the experimental and calculated profiles and product compositions has been given in Chapter 9. In the following the general behaviour and stability of the results are considered.

The Fenske equations gave a poor initial estimate of the vapour composition profiles. In all cases most of the ethane was considered to be removed from the ascending vapour in about six plates and the remainder of the column was used to separate the resulting ethylene-acetylene mixture. Nevertheless, for run B:12, the forcing parameter was reduced to 0.125 after five iterations and to 0.0078 after ten iterations. In subsequent iterations, however, the composition profile at the base of the column oscillated with the result that the forcing parameter had increased to 0.0312 after thirty iterations. The

cause of this unstable behaviour was traced to the restrictions placed upon the values of the equilibrium constants. The experimental values of the equilibrium constant for acetylene in the ethane-acetylene binary mixture frequently exceeded 3, and it was apparent from the computed results that the polynomials predicted values in excess of 3 for the ternary equilibrium constants in the neighbourhood of the ethane vertex on the triangular diagram. Insufficient computer time was available to repeat these sets of calculations and it was considered that the solutions had become sufficiently stable to be able to compare the experimental and calculated results.

11:6 Conclusions

The agreement between the experimental and the computed distillation results provides justification not only for the experimental data obtained in this thesis but also for the computer programme with its implicit assumptions. In particular, the rate of convergence obtained was good in spite of the poor initial estimate of the vapour composition profile and the inaccurate form of the enthalpy equations. It would seem therefore that these factors are not of prime importance for multi-component distillation calculations. The failures of the programme to attain complete stability and to reproduce the experimental results for trials containing a large number of plates can be attributed to the empirical nature of the correlations for the equilibrium data and under more favourable

circumstances it is considered that this programme supersedes all others described in the literature.

CHAPTER 12

Conclusions

The phase equilibria of binary and ternary mixtures of C_2-hydrocarbons have been measured at atmospheric pressure using a flow cell. The thermodynamic consistency of the data for the ethylene-ethane system was established by use of the Herington test,[32] and the results for the binary systems were satisfactorily correlated by the Li-Coull method.[46] Attempts were made to obtain a theoretical correlation for the ternary data from the binary Li-Coull equations and also by a modification of Wohl's equations for isothermal data.[94] The resultant correlations did not give an adequate representation of the experimental results and it was concluded that no satisfactory method exists for the correlation of non-ideal isobaric phase equilibrium data. Several empirical computed surfaces were therefore fitted to the data to provide equations for future use.

The solubilities of mixtures of the C_2-hydrocarbons in acetone were also measured, but no attempt was made to correlate the results. The data was used to design a simple absorption column for the separation of the C_2-hydrocarbons and the design was tested experimentally with a small Oldershaw sieve-plate column. Good agreement was obtained and the method was shown to be the most suitable for the complete removal of large quantities of

acetylene from a C_2-hydrocarbon feedstock.

The Oldershaw columns were calibrated with mixtures of ethylene and ethane and the resulting plate efficiencies together with the measured equilibrium data were used to design distillation columns for the production of pure ethylene from C_2-hydrocarbon mixtures. A large number of trials with sieve-plate columns was performed in an attempt to provide the best solution for the problem and sufficient data was obtained to establish most of the necessary design criteria. In order to verify these results a multi-component distillation computer programme was written and the experimental data from several runs were used with the programme to determine the values of the product compositions. For short columns the experimental results were reproduced but for a 35 plate column the predicted separation was considerably greater than the observed value. It was established that the inadequacy of the programme was due to the inability to obtain a satisfactory theoretical data correlation or to provide an empirical correlation that represented the true phase equilibrium behaviour in the regions close to the pure component points and also to the lack of knowledge regarding plate efficiencies under these circumstances. Unless arbitrary decisions are taken to resolve these difficulties it is considered that the experimental results cannot be extended to predict the number of plates required to produce a top-product of the desired purity.

In spite of the conclusions given above the computer programme gave satisfactory proof of the validity of the techniques used and the results obtained in this work and it would seem that the postulated solutions should also be valid.

For high acetylene content feedstocks (10 mole%) simple absorption and simple distillation provide satisfactory results. When using absorption a column of 10 practical plates operating at $-80^{\circ}C$ with an acetone circulation rate to feed rate ratio of 25% on a molar basis gives an ethylene top-product containing about 100 p.p.m. of acetylene at a recovery of about 98.5%. For simple distillation a column containing about 50 theoretical plates should give a top-product containing about 10 ppm. acetylene at reflux ratios in excess of 7.0. The recovery of ethylene should be greater than 95% and the bottom product should contain about 15 mole % acetylene for the feedstock considered in this work. The number of plates required at reflux ratios approaching the minimum value of about 4.0 for this separation were not estimated, but a value could be obtained by use of the computer programme.

For low acetylene content feedstocks (about 1 mole %) distillation with a sidestream appears to be a valuable method. A sidestream taken from the column at about 5-10 plates below the feed plate position should contain 25-30 mole % acetylene and the desired top-product should be obtained with a column of 40

theoretical plates. Very high recoveries of ethylene should again be achieved, but for low reflux ratios the acetylene content of the sidestream would be reduced and greater ethylene losses would result.

The final decisions regarding the method to be used and the values of the reflux-ratio etc. to be chosen must ultimately rest with the designer acting with the economics of the particular situation in mind, but it is considered that the present work would provide a good basis for such a designer.

Nomenclature

ai ... activity of component i.

fi ... fugacity of component i.

fi,p ... number of moles of component i per unit time, entering plate p in the feed to this plate.

ΔGE ... excess free energy on mixing.

h ... length of time interval.

HE ... integral heat of mixing per mole of solution.

Hp ... Total number of moles of liquid in hold-up on plate p, assumed constant during a transient.

Ki,p ... equilibrium constant of component i for the conditions on plate p.

Lp ... number of moles per unit time of liquid entering stage p-1.

ni ... number of moles of component i.

pi ... partial pressure of component i.

Pi° ... vapour pressure of component i at the given temperature.

P ... total pressure

Pv,p ... vapour product-rate taken from the vapour stream leaving plate p.

PL,p ... liquid product-rate taken from the liquid stream leaving plate p.

R ... gas constant.

S ... molar entropy

s ... no of time steps up to time t_s i.e. $t_s = hs$

t ... time variable

T ... temperature in absolute units.

u' ... forcing parameter used in multi-component distillation programmes.

V_p ... number of moles per unit time of vapour entering stage p+1.

V ... Molar volume.

Xi ... mole ratio of component i in the liquid phase.

xi ... mole fraction of component i in the liquid phase.

yi ... mole fraction of component i in the vapour phase.

α_i ... Bunsen coefficient for component i as solute used in Part I only.

$\alpha_{i,p}$ ... relative volatility of component i to a reference component on plate p. Used in part II only.

γ_i ... activity coefficient of component i referred to the pure substance as standard state.

θ ... constant in Rosenbrock transient equations.

$\eta_{i,p}$ ... Murphree plate efficiency for component i on plate p.

μ_i ... chemical potential of component i.

$\mu_i^\circ(T)$.. chemical potential of pure component i at the given temperature.

Suffixes

L or Liq, V or Vap ... liquid and vapour phases respectively

E ... excess as in excess free engergy of mixing ΔG_E

p,n ... plate number, numbered upwards with reboiler as stage 1.

i,1,2,3,C_2H_2,C_2H_4,C_2H_6.. a typical component and specific components represented either by chemical formulae or by the notation 1≡ acetylene, 2 ≡ethylene, 3≡ ethane.

r ... a reference component.

b ... boiling as in normal boiling point T_b

s, s+1 ... adjacent times with $t_{s+1} - t_s = h$, the time step on interval.

Superscripts

' ... molar value of function as in molar excess free energy $\Delta G_E'$

* ... ideal value as in change of free energy on mixing pure liquid constituents to give ideal solution ΔG^*_{mix} (Part I)
or y_i^*, p is the mole-fraction of component i in the vapour in equilibrium with the liquid leaving the plate p, in definition of Murphree place efficiency (Part II)

o ... value for pure component usually used as standard of reference e.g. f^o_i for fugacity of pure component i at the given temperature.

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A P P E N D I C E S

Appendix 1

Calibration of thermocouples

Single junction copper-constantan thermocouples were used to measure temperatures in both series of experiments. They were connected either directly or via a 10 way switch to the Pye Precision Potentiometer.

The triple points of n-heptane, toluene, hexane and trans butene -2 were used as reference standards. Sealed glass tubes, supplied by the National Chemical Laboratory, containing the pure liquids, were tied to the thermocouples and immersed in a Dewar containing iso-pentane at -110°C. The bath was allowed to warm up slowly and the e.m.f.s. generated by the thermocouples at the triple point of each component were recorded.

The results were compared with tables published by Powell et.al.[67] In this work thermocouples of commercially available alloys were calibrated against a platinum resistance thermometer. Over the range -90 to 106°C all the experimental results agreed with Powell's figures to within $\pm$ 0.1°C or $\pm$ 3μv. For higher temperatures no method of calibration was available and Powell's tables were used.

The thermocouples were made by one technician from the same reels of wire. These considerations obviously contributed to the uniformity of the results.

Appendix II

Calibration of the chromatograph

There are three stages in the development of a chromatographic technique to perform a specific analysis[39]:

(1) the effective separation of a sample into its components;

(2) the identification of these components;

(3) the estimation of the amount of each of the components in the sample.

For the analysis of gases the chromatographic column contains either an active adsorbing agent or an inert solid impregnated with a liquid. Usually the gas sample is transported through the column by a slow current of gas that is not adsorbed. The constituents of the sample are selectively adsorbed in the column and the process ultimately results in an actual separation. The effluent gas contains 'bands' of the constituents separated by zones of pure eluent.

The theory of the interaction of solute and solvent is complex, nevertheless certain generalisations may be made.[39] For the separation of similar compounds, a stationary liquid of a similar chemical nature will give a separation according to boiling point. If it is desired to separate components of about equal boiling points, but of different chemical nature, a solvent must be chosen that alters the position of one substance relative to another.

Initially dinonyl phthalate and polypropyl sebacate, supported on G-cel, were used to effect the separation of the C_2-hydrocarbons. These compounds show no pronounced selectivity and should separate solutes according to volatility. In this instance the volatilities of ethylene and ethane were too similar to obtain a separation. Keulemans suggests the use of solid adsorbing agents for the separation of components of low boiling point. In addition to reverse the order of elution of ethylene and ethane a material of a polar nature is required. Patton and Touey[59] used silica gel to analyse mixtures of hydrocarbons in cigarette smoke. A 6 ft. column packed with 40-60 mesh silica gel gave an excellent separation of the C_2 hydrocarbons. The total analysis time was reduced, from about 30 minutes at room temperature, to 8 minutes, by heating the column to 80°C with boiling benzene vapour. This procedure did not affect the degree of separation of the components. Under these conditions, however, the passage time of acetone exceeded 1½ hrs. In a dinonyl phthalate column at 80°C the hydrocarbons were separated from acetone but not from each other. The only available solution for the analysis of dissolved hydrocarbons in acetone, therefore, was the division of the sample. One part was passed through the silica gel column to determine the relative proportions of the hydrocarbons present and the second through the dinonyl phthalate column to ascertain the relative proportions of hydrocarbons to acetone.

The identification of the components involved making up a mixture of the hydrocarbons and passing it through the column. The time of elution of each of the peaks was recorded. The individual hydrocarbons were then passed and a comparison of the times identified the constituents. This procedure established that the polar nature of silica gel retarded the elution of ethylene to such an extent that ethane preceded it in the eluent.

The hydrogen leaving the column was mixed with air and burnt in a flame ionisation detector. A constant direct potential of 100V. was applied to the flame and the resultant signal was amplified and recorded. The presence of organic components in the effluent altered the temperature of the flame and therefore the ionisation current. The areas of the peaks produced on the recorder were automatically evaluated by an integrator.

Initially, the response of the instrument to the introduction of a known quantity of each of the components was required. The gases were injected into the chromatograph by an accurately made glass syringe capable of delivering 0 -1 ml. of gas to within $\pm$ 0.002 ml. Slight variations in the integrator count, for the injection of a given volume of gas, were observed. These variations were due to leakage of gas through the fine bore hypodermic needle and between the plunger and barrel. A large number of samples of each gas were introduced and a consistent series of high results was accepted. For the

introduction of the hydrocarbons into the silica gel and dinonyl phthalate column the results were the same. However, for the former the response was directly proportional to the volume introduced whilst in the latter case the response per unit volume decreased with increase of the volume of the sample. The recorder peak in this case was extremely narrow and this behaviour was probably due to saturation of the integrator.

The accepted values were:-

Acetylene	302 $\pm$ 1 counts per 0.1 ml. of gas;
Ethylene	201 $\pm$ 1 counts per 0.1 ml. of gas;
Ethane	188 $\pm$ 1 counts per 0.1 ml. of gas.

Mixtures of the three components were made up by volume in a syringe and injected into the chromatograph. Although this method of synthesis is not very accurate by treating a large number of mixtures the accuracy of the analysis could be estimated. For any given mixture containing between 10 and 90 mole% of one of the components, the chromatograph gave [illegible] the correct percentage to within $\pm$ 2 mole%. At the limits of the range and below 10 and above 90 mole% the estimated error was $\pm$ 0.5 mole%.

Mixtures of hydrocarbons injected into the dinonyl phthalate column were not separated. The total integrator count for the single peak, however, as calculated from the known composition of the mixture was satisfactory provided that the volume injected was less than 0.04 ml.

Acetone was injected into the dinonyl phthalate column by means of a Hamilton microlitre syringe. The results were found to be proportional to the volume injected provided that this volume was less than 2.0 µl. Acetone was also maintained at fixed temperatures in an enclosed space and known volumes of the vapour injected. From the vapour pressure curve for acetone, the two sets of data were reduced to the same basis. The response for acetone was recorded as 195 $\pm$ 5 counts per 0.1 ml acetone vapour. By using both chromatograph columns for the analysis of a mixture of hydrocarbons in acetone, it seemed likely that an error of the order of $\pm$ 3 mole % for the acetone concentration would result.

The sampling of the effluent gas streams from the flow cell was simple. A syringe was inserted in the line and a sample taken. As the relative proportions of the constituents were required the volume of the sample was not important.

Liquid samples were taken by momentarily pressurising the cell by closing a screw clip in the gas line. A needle valve connected to a glass capillary in the cell was opened and liquid was forced out into a syringe. For hydrocarbon liquids vaporisation occurred immediately. This process was so rapid that the possibility of differential loss of the components could be neglected. Acetone samples collected in this way would probably partially vaporize. The less soluble constituents could

be lost and during the subsequent analysis acetone would be left as a thin film on the walls of the syringe. To overcome these difficulties a very small sample was taken in a large syringe. The plunger was immediately withdrawn, large quantities of air were sucked in and vaporisation was assisted. A small sample was used for the hydrocarbon determination and a series of small samples were used to determine the acetone concentration. If the results of the second set of analyses were not consistent the run was discarded.

Keulemans[39] states that the ionisation current depends upon a molecular parameter called the ionisation cross-section of the molecule. From a knowledge of this quantity the peak area conversion factor could be calculated. Otvos and Stevenson[58] give values for these quantities. However, the predictions bore no relation to the results obtained using either a hydrogen flame ionisation detector or an argon ionisation detector. No further attempts were made to obtain a theoretical basis for the experimental results.

Appendix III

Section III.1

TABLE III.1.1.

Experimental results for system ethylene-ethane.

RUN No.	PRESSURE m.m.Hg.	CORRECTED TEMP. °K.	VAPOUR PHASE M.F. C_2H_4	VAPOUR PHASE M.F. C_2H_6	LIQUID PHASE. M.F. C_2H_4	LIQUID PHASE. M.F. C_2H_6
1:1	754.7	172.3	0.824	0.176	0.689	0.311
1:2	754.7	174.1	0.727	0.273	0.532	0.468
1:3	755.0	175.1	0.679	0.321	0.476	0.524
1:4	755.0	179.9	0.384	0.616	0.173	0.827
1:5	755.4	178.3	0.475	0.525	0.259	0.741
1:6	755.4	181.4	0.270	0.730	0.113	0.887
1:7	754.1	177.2	0.559	0.441	0.328	0.672
1:8	754.1	183.8	0.079	0.921	0.036	0.964
1:9	754.7	169.3	1.000	0.000	1.000	0.000
1:10	754.1	184.6	0.000	1.000	0.000	1.000
1:11	754.1	171.0	0.894	0.106	0.809	0.191

TABLE III.1.2.

Experimental results for system acetylene-ethane.

Run No.	PRESSURE m.m.Hg.	CORRECTED TEMP °K	VAPOUR PHASE M.F.C_2H_2	M.F.C_2H_6	LIQUID PHASE M.F.C_2H_2	M.F.C_2H_6
2:1	761.4	184.6	0.000	1.000	0.000	1.000
2:2	761.4	183.2	0.171	0.829	0.047	0.953
2:3	761.4	183.9	0.095	0.905	0.021	0.979
2:4	761.4	183.3	0.159	0.841	0.045	0.955
2:5	768.5	181.9	0.239	0.761	0.100	0.900
2:6	768.5	182.7	0.191	0.809	0.076	0.924
2:8	768.5	182.6	0.194	0.806	0.091	0.909
2:10	768.5	184.2	0.072	0.928	0.016	0.984
2:12	771.7	183.6	0.131	0.869	0.038	0.962
2:13	771.7	183.6	0.131	0.869	0.033	0.967

TABLE III.1.3.

Experimental results for system acetylene-ethylene.

RUN No.	PRESSURE m.m.Hg.	CORRECTED TEMP °K	VAPOUR PHASE M.F.C_2H_2	M.F.C_2H_4	LIQUID PHASE M.F.C_2H_2	M.F.C_2H_4
3:1	778.2	169.9	0.041	0.959	0.080	0.920
3:3	778.2	172.0	0.148	0.852	0.325	0.675
3:4	778.2	173.5	0.201	0.799	0.429	0.571
3:5	778.0	171.5	0.131	0.869	0.267	0.733
3:6	778.0	170.9	0.104	0.896	0.204	0.796
3:7	778.0	170.6	0.092	0.908	0.148	0.852

TABLE III.1.4.

Experimental Results for System Acetylene–Ethylene–Ethane.

RUN NO.	PRESSURE	CORRECTED	VAPOUR PHASE			LIQUID PHASE		
	mm.Hg.	Temp. °K.	M.F.C H 2 2	M.F.C H 2 4	M.F.C H 2 6	M.F.C H 2 2	M.F.C H 2 4	M.F.C H 2 6
4:1	768.6	182.9	0.054	0.149	0.797	0.017	0.060	0.923
4:2	768.7	182.0	0.058	0.223	0.719	0.034	0.120	0.846
4:3	764.1	175.9	0.076	0.527	0.397	0.042	0.366	0.592
4:4	764.1	180.2	0.110	0.298	0.592	0.075	0.184	0.741
4L5	764.1	178.7	0.110	0.352	0.538	0.079	0.236	0.685
4:6	764.1	181.5	0.114	0.259	0.627	0.085	0.160	0.755
4:7	764.1	175.2	0.132	0.497	0.371	0.085	0.355	0.560
4:8	764.1	171.6	0.064	0.792	0.144	0.088	0.638	0.274
4:9	764.1	182.1	0.137	0.206	0.657	0.093	0.112	0.795
4:10	764.1	175.6	0.148	0.454	0.398	0.107	0.323	0.570
4:11	764.1	181.7	0.160	0.232	0.608	0.116	0.125	0.759
4:12	764.1	172.1	0.108	0.743	0.149	0.174	0.540	0.286
4:13	764.1	176.1	0.154	0.457	0.389	0.176	0.266	0.558
4:14	764.1	172.5	0.137	0.721	0.142	0.252	0.532	0.216
4:15	764.1	172.8	0.165	0.673	0.162	0.321	0.471	0.208

TABLE III.1.5

Herington consistency test for system ethylene-ethane.

RUN No.	x C_2H_4	γC_2H_4	γC_2H_6	$\frac{\gamma C_2H_4}{\gamma C_2H_6}$	$\log_{10} \frac{\gamma C_2H_4}{\gamma C_2H_6}$
1:1	0.689	1.023	1.168	0.876	-0.057
1:2	0.532	1.072	1.070	1.002	+0.001
1:3	0.476	1.042	1.057	0.990	-0.004
1:4	0.173	1.263	0.974	1.300	+0.114
1:5	0.259	1.131	1.013	1.115	+0.048
1:6	0.113	1.259	0.990	1.272	+0.104
1:7	0.328	1.119	1.003	1.115	+0.048
1:8	0.036	1.023	1.000	1.023	+0.010
1:11	0.809	1.020	1.250	0.816	-0.088

$$J = \frac{150\,|\theta|}{T\ min}$$

$|\theta|$ = overall range of boiling points = 15.3°C

Tmin = lowest measured boiling point = 169.3°K.

$J = 13.55$

$$D = \frac{100\,|I|}{\Sigma}$$

$D = 1.46.$

TABLE III.1.6

Li-Coull correlation for the ethylene-ethane system.

RUN No.	TEMP °K	$\gamma_{C_2H_4}$	$\gamma_{C_2H_6}$	$(T \log \gamma_{C_2H_4})^{-0.5}$	$(T \log \gamma_{C_2H_6})^{-0.5}$	$\frac{xCH_{24}}{xCH_{26}}$	$\frac{x\ CH_{26}}{x\ CH_{24}}$
1:1	172.1	1.023	1.168	0.766	0.294	2.215	0.451
1:2	173.9	1.072	1.070	0.436	0.438	1.137	0.880
1:3	175.0	1.042	1.057	0.566	0.487	0.908	1.101
1:4	179.7	1.263	0.974	0.234	∞	0.209	4.785
1:5	178.2	1.131	1.013	0.324	1.000	0.350	2.857
1:6	181.2	1.259	0.990	0.235	∞	0.127	7.874
1:7	177.0	1.119	1.003	0.340	2.085	0.488	2.049
1:8	183.6	1.023	1.000	0.743	∞	0.037	26.800
1:11	170.8	1.020	1.250	0.826	0.246	4.236	0.236

Whence $(T \log \gamma_{C_2H_4})^{-0.5} = \left(\frac{x_{C_2H_4} + 0.8x_{C_2H_6}}{3.9\ x_{C_2H_6}} \right)$

and $(T \log \gamma_{C_2H_6})^{-0.5} = \left(\frac{x_{C_2H_6} + 0.63x_{C_2H_4}}{3.5\ x_{C_2H_4}} \right)$

TABLE III.1.7.

Calculated equilibrium data for the ethylene-ethane system.

RUN NO.	$x_{C_2H_4}$	$x_{C_2H_6}$	$y_{C_2H_4}$	$y_{C_2H_6}$	TEMP. CALC. °K	TEMP. CORRECTED °K	$\gamma_{C_2H_4}$	$\gamma_{C_2H_6}$
1:1	0.689	0.311	0.824	0.176	172.1	172.2	1.023	1.150
1:2	0.532	0.468	0.725	0.275	173.9	174.0	1.055	1.074
1:3	0.476	0.524	0.691	0.309	174.5	174.6	1.072	1.056
1:4	0.173	0.827	0.365	0.635	179.6	179.7	1.211	1.005
1:5	0.259	0.741	0.480	0.520	178.0	178.1	1.160	1.013
1:6	0.113	0.887	0.267	0.733	181.0	181.1	1.252	1.002
1:7	0.328	0.672	0.556	0.444	176.8	176.9	1.127	1.022
1:8	0.036	0.964	0.100	0.900	183.3	183.4	1.310	1.000
1:11	0.809	0.191	0.893	0.107	171.0	171.1	1.007	1.248

TABLE III.1.8.

Li-Coull correlation for the acetylene-ethane system.

RUN NO.	TEMP. °K	$x_{C_2H_2}$	$\gamma_{C_2H_2}$	$(T \log \gamma_{C_2H_2}) - 0.5$	$\frac{x_{C_2H_2}}{x_{C_2H_6}}$
2:2	183.2	0.047	4.975	0.088	0.049
2:3	183.9	0.021	5.960	0.084	0.022
2:4	183.3	0.045	4.815	0.090	0.047
2:5	182.1	0.100	3.520	0.100	0.111
2:6	182.9	0.076	3.510	0.100	0.082
2:8	182.8	0.091	3.015	0.107	0.100

TABLE III.1.8 (Cont'd)

RUN.No.	TEMP. °K.	$x_{C_2H_2}$	$\gamma_{C_2H_2}$	$(T \log \gamma_{C_2H_2})^{-0.5}$	$\frac{x_{C_2H_2}}{x_{C_2H_6}}$
2:10	184.4	0.016	5.790	0.084	0.016
2:12	183.9	0.038	4.600	0.091	0.040
2:13	183.9	0.033	5.300	0.087	0.034

Whence $(T \log \gamma_{C_2H_2})^{-0.5} = 0.203 \frac{x_{C_2H_2}}{x_{C_2H_6}} + 0.081$

TABLE III.1.9

Li-Coull correlation for the acetylene-ethylene system.

RUN No.	TEMP °K.	$x_{C_2H_2}$	$\gamma_{C_2H_2}$	$(T \log \gamma_{C_2H_2})^{-0.5}$	$\frac{x_{C_2H_2}}{x_{C_2H_4}}$
3:1	170.3	0.080	1.635	0.166	0.087
3:3	172.4	0.325	1.260	0.241	0.481
3:4	173.9	0.429	1.172	0.288	0.751
3:5	171.9	0.267	1.403	0.199	0.364
3:6	171.3	0.204	1.513	0.180	0.256
3:7	171.0	0.148	1.633	0.166	0.174

Whence $(T \log \gamma_{C_2H_2})^{-0.5} = 0.224 \frac{x_{C_2H_2}}{x_{C_2H_4}} + 0.125$

TABLE III.1.10.

Calculated equilibrium data for the acetylene-ethylene system

RUN NO.	$x_{C_2H_2}$	$x_{C_2H_4}$	$y_{C_2H_2}$	$y_{C_2H_4}$	TEMP. °K CALC.	TEMP. °K CORRECTED	$\gamma_{C_2H_2}$	$\gamma_{C_2H_4}$
3:1	0.080	0.920	0.048	0.952	170.4	170.0	1.909	1.009
3:3	0.325	0.675	0.148	0.852	172.2	171.8	1.279	1.109
3:4	0.429	0.571	0.192	0.808	173.3	172.9	1.167	1.169
3:5	0.267	0.733	0.127	0.873	171.7	171.3	1.367	1.078
3:6	0.204	0.796	0.101	0.899	171.2	170.8	1.500	1.049
3:7	0.148	0.852	0.080	0.920	170.8	170.4	1.650	1.028

TABLE III.1.11

Li-Coull correlation for ternary data

RUN NO.	TEMP. EXPT. °K	$x_{C_2H_2}$	$x_{C_2H_4}$	$x_{C_2H_6}$	$\gamma_{C_2H_2}$	$\gamma_{C_2H_4}$	$\gamma_{C_2H_6}$	$y_{C_2H_2}$	$y_{C_2H_4}$	$y_{C_2H_6}$	Σy
4:1	183.1	0.017	0.060	0.923	4.96	1.23	1.00	0.061	0.153	0.849	1.063
4:2	182.2	0.034	0.120	0.846	3.88	1.19	1.02	0.090	0.150	0.745	0.985
4:3	176.0	0.042	0.366	0.592	2.70	1.11	1.07	0.053	0.579	0.388	1.020
4:4	180.3	0.075	0.184	0.741	2.80	1.14	1.05	0.129	0.375	0.611	1.115
4:5	178.8	0.079	0.236	0.685	2.59	1.12	1.07	0.114	0.438	0.526	1.078
4:6	181.6	0.085	0.160	0.755	2.74	1.14	1.05	0.154	0.349	0.673	1.176
4:7	175.3	0.085	0.355	0.560	2.28	1.08	1.11	0.086	0.528	0.362	0.976
4:8	171.7	0.088	0.638	0.274	1.95	1.02	1.22	0.061	0.734	0.155	0.950
4:9	182.2	0.093	0.112	0.795	2.80	1.15	1.05	0.179	0.256	0.727	1.162
4:10	175.7	0.107	0.323	0.570	2.16	1.08	1.12	0.107	0.489	0.380	0.976
4:11	181.7	0.116	0.125	0.759	2.47	1.13	1.07	0.191	0.271	0.689	1.151
4:12	172.1	0.174	0.540	0.286	1.62	1.02	1.28	0.102	0.639	0.176	0.917
4:13	176.1	0.176	0.266	0.558	1.80	1.06	1.18	0.149	0.406	0.401	0.956
4:14	172.5	0.252	0.532	0.216	1.41	1.04	1.38	0.132	0.651	0.147	0.930
4:15	172.8	0.321	0.471	0.208	1.29	1.06	1.45	0.157	0.599	0.151	0.907

TABLE III.1.12.

Use of (18:5) in Li-Coull correlation

RUN No.	$\gamma_{C_2H_4}$	$y_{C_2H_4}$	Σy
4:1	1.46	0.181	1.091
4:2	1.35	0.170	1.005
4:3	1.14	0.595	1.036
4:4	1.23	0.404	1.144
4:5	1.19	0.464	1.104
4:6	1.23	0.376	1.203
4:7	1.12	0.548	0.996
4:8	1.03	0.741	0.957
4:9	1.26	0.280	1.186
4:10	1.12	0.507	0.994
4:11	1.23	0.295	1.175
4:12	1.05	0.654	0.932
4:13	1.13	0.431	0.981
4:14	1.08	0.676	0.955
4:15	1.11	0.627	0.935

TABLE III.1.13

Polynomial of degree 4 for $T = f(y'_{C_2H_2}, y'_{C_2H_4})$ obtained using programme R A E 194/A.

MEAN VALUES

$\bar{y}_{C_2H_2} = 1.04729166, -1$

$\bar{y}_{C_2H_4} = 4.11812496, -1$

POLYNOMIAL COEFFICIENTS.

POWER of $y'_{C_2H_4}$	POWER of $y'_{C_2H_2}$	
$y'_{C_2H_4} = y_{C_2H_4} - \bar{y}_{C_2H_4}$	$y'_{C_2H_4} = y_{C_2H_2} - \bar{y}_{C_2H_2}$	
0	0	1.77778996, 2
	1	- 1.14161791, 1
	2	7.65194226, 0
	3	6.57125060, 1
	4	2.68623644, 2
1	0	- 2.24498350, 1
	1	- 3.47428797, 1
	2	2.97786280, 2
	3	3.93114823, 2
2	0	1.94275792, 0
	1	6.03503015, 1
	2	4.43821333, 2
3	0	4.15625332, 1
	1	3.13942835, 2
4	0	- 1.93390044, 1

TABLE III.1.14.

Polynomial of degree 3 for $x_{C_2H_2} = f(y'_{C_2H_2}, y'_{C_2H_4})$ obtained using programme RAE 194/A

MEAN VALUES.

$\bar{y}_{C_2H_2} = 1.04729166, -1$

$\bar{y}_{C_2H_4} = 4.11812496, -1$

POLYNOMIAL COEFFICIENTS

POWER of $y'_{C_2H_4}$ $y'_{C_2H_4} = y_{C_2H_4} - \bar{y}_{C_2H_4}$	POWER of $y'_{C_2H_2}$ $y'_{C_2H_2} = y_{C_2H_2} - \bar{y}_{C_2H_2}$	
0	0	8.22498458, -2
	1	1.14272909, 0
	2	3.94751053, 0
	3	5.26519538, 0
1	0	1.79152920, -1
	1	2.44276461, 0
	2	5.85807161, 0
2	0	1.27419405, -1
	1	1.26359608, 0
3	0	5.21464362, -2

TABLE III.1.15.

Polynomial of degree 3 for $x_{C_2H_4} = f(y'_{C_2H_2}, y'_{C_2H_4})$

obtained using programme RAE 194/A.

MEAN VALUES

$\bar{y}_{C_2H_2} = 1.04729166, -1$

$\bar{y}_{C_2H_4} = 4.11812496, -1$

POLYNOMIAL COEFFICIENTS

POWER of $y'_{C_2H_4}$	POWER of $y'_{C_2H_2}$	
$y'_{C_2H_4} = y_{C_2H_4} - \bar{y}_{C_2H_4}$	$y'_{C_2H_2} = y_{C_2H_2} - \bar{y}_{C_2H_2}$	
0	0	2.59480391, -1
	1	1.88776342, -1
	2	- 2.86587182, 0
	3	8.37476393, -1
1	0	7.56377243, -1
	1	- 5.95714446, -1
	2	- 6.43551425, 0
2	0	4.92930607, -1
	1	- 2.62007499, 0
3	0	4.46432624, -1

TABLE III.1.16.

Polynomial of degree 3 for $x_{C_2H_6} = f(y'_{C_2H_2}, y'_{C_2H_4})$

obtained using programme RAE 194/A.

MEAN VALUES.

$\bar{y}_{C_2H_2} = 1.04729166, -1$

$\bar{y}_{C_2H_4} = 4.11812496, -1$

POLYNOMIAL COEFFICIENTS.

POWER of $y'_{C_2H_4}$	POWER of $y'_{C_2H_2}$	
$y'_{C_2H_4} = y_{C_2H_4} - \bar{y}_{C_2H_4}$	$y'_{C_2H_2} = y_{C_2H_2} - \bar{y}_{C_2H_2}$	
0	0	6.58269760, -1
	1	-1.33150544, 0
	2	-1.08163864, 0
	3	-6.10267169, 0
1	0	-9.35530143, -1
	1	-1.84705021, 0
	2	5.77442914, -1
2	0	-6.20350015, -1
	1	1.35647902, 0
3	0	-4.98579038, -1

TABLE III.1.17 - Experimental Data — Correlated Data Residuals Obtained From Surface Fitting Programme R.A.E. 194/A

CORRELATION	RUN NO.	1:8	1:6	1:4	1:5	1:7	1:3	1:2	1:1	1:11	2:10	2:3	2:13	2:12	2:4	2:2	2:6	2:8	2:5	AZ.	3:1	3:7	3:6	3:5	3:3	3:4	1:9	1:10	4:1	4:2	4:3	4:4	4:5	4:6	4:7	4:8	4:9	4:10	4:11	4:12	4:13	4:14	4:15	MAX. RES.	RUN NO.	ΣSQS RES.
T = $f(y_1', y_2')$	T°K	183.3	181.2	179.8	178.1	177.0	174.6	174.1	172.3	171.2	184.2	183.9	183.6	183.6	183.3	183.2	182.7	182.6	181.9	177.4	169.9	170.6	170.9	171.5	172.0	173.5	169.3	184.6	182.9	182.0	175.9	180.2	178.7	181.5	175.2	171.6	182.1	175.6	181.7	172.1	176.1	172.5	172.8	—	—	—
$1 \equiv G_2H_2$	RES.	-3.049_1	-1.073_{-1}	3.570_{-2}	1.708_{-1}	2.633_{-1}	-5.844_{-2}	-3.420_{-2}	-2.549_{-1}	-1.622_{-1}	5.617_{-2}	-7.664_{-2}	-3.451_{-2}	-3.451_{-2}	1.286_{-2}	8.566_{-2}	-9.313_{-2}	-1.413_{-1}	4.827_{-2}	-1.273_{-4}	7.395_{-2}	-1.529_{-1}	-1.039_{-1}	-1.183_{-1}	-4.219_{-2}	-6.073_{-2}	7.173_{-2}	7.654_{-2}	-1.640_{-1}	6.150_{-2}	1.779_{-1}	-5.659_{-2}	-3.709_{-1}	4.602_{-1}	-3.596_{-1}	-4.274_{-2}	1.953_{-1}	-7.336_{-1}	**4.567_{-1}**	**2.802_{-1}**	-1.049_{-1}	4.996_{-1}	2.905_{-1}	-7.336_{-1}	4:10	2.1970
$X_1 = f(y_1', y_2')$	X_1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.016	0.021	0.033	0.038	0.045	0.047	0.076	0.091	0.100	0.400	0.080	0.148	0.204	0.267	0.325	0.429	0.000	0.000	0.017	0.034	0.042	0.075	0.079	0.085	0.085	0.088	0.093	0.107	0.116	0.174	0.176	0.252	0.321	—	—	—
$2 \equiv G_2H_2$	RES.	-1.637_{-3}	-1.359_{-3}	-3.872_{-4}	1.032_{-3}	1.915_{-3}	2.895_{-3}	2.949_{-3}	2.481_{-3}	1.485_{-3}	-4.098_{-4}	-2.165_{-3}	-3.817_{-3}	1.183_{-3}	-5.885_{-3}	-1.098_{-2}	4.468_{-3}	1.724_{-2}	-1.400_{-2}	5.237_{-4}	7.457_{-3}	-2.805_{-2}	1.123_{-3}	2.606_{-4}	1.554_{-2}	-2.635_{-2}	-1.425_{-3}	-4.623_{-4}	-1.700_{-3}	9.669_{-3}	-2.495_{-2}	6.830_{-3}	1.643_{-3}	1.946_{-2}	-5.397_{-2}	-1.725_{-3}	1.727_{-2}	-4.533_{-2}	1.128_{-2}	9.646_{-3}	1.267_{-2}	2.931_{-2}	4.876_{-2}	-5.397_{-2}	4:7	1.2555-2
$X_2 = f(y_1', y_2')$	X_2	0.036	0.113	0.173	0.259	0.328	0.476	0532,	0.689	0.809	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.920	0.852	0.796	0.733	0.675	0.571	1.000	0.000	0.060	0.120	0.366	0.184	0.236	0.160	0.355	0.638	**0.112**	0.323	0.125	0.540	0.266	0.532	**0.471**	—	—	—
	RES.	9.065_{-4}	-7.044_{-4}	-9.241_{-4}	-3.040_{-3}	-4.484_{-3}	-9.722_{-3}	1.386_{-3}	1.166_{-2}	1.426_{-2}	-4.869_{-4}	-4.906_{-4}	-9.601_{-6}	-9.601_{-6}	6.447_{-4}	9.696_{-4}	1.538_{-3}	1.625_{-3}	2.823_{-3}	-1.473_{-4}	-6.672_{-3}	3.273_{-2}	3.537_{-3}	2.595_{-3}	-1.527_{-2}	9.602_{-3}	-3.699_{-3}	1.843_{-3}	-1.517_{-2}	2.618_{-3}	1.762_{-2}	3.764_{-3}	1.903_{-2}	4.320_{-3}	2.651_{-2}	-1.292_{-2}	-1.369_{-2}	2.963_{-2}	-1.841_{-2}	-3.925_{-2}	-2.886_{-2}	-8.897_{-3}	-2.513_{-3}	-3.925_{-2}	4:12	7.663-3
$X_3 = f(y_1', y_2')$	X_3	0.964	0.887	0.827	0.741	0.672	0.524	0.468	0.311	0.191	0.984	0.979	0.967	0.962	0.955	0.953	0.924	0.909	0.900	0.600	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.923	0.846	0.592	0.741	0.685	0.755	0.560	0.274	0.795	0.570	0.759	0.286	0.558	0.216	0208	—	—	—
$3 \equiv G_2H_2$	RES.	7.301_{-4}	2.044_{-3}	1.313_{-3}	2.009_{-3}	2.568_{-3}	6.827_{-3}	-4.335_{-3}	-1.415_{-2}	-1.575_{-2}	8.944_{-4}	2.655_{-3}	3.827_{-3}	-1.173_{-3}	5.210_{-3}	1.001_{-2}	-6.007_{-3}	-1.887_{-2}	1.117_{-2}	-3.744_{-4}	-7.848_{-4}	-4.680_{-3}	-4.661_{-3}	-2.856_{-3}	-2.665_{-4}	1.675_{-2}	5.124_{-3}	-1.380_{-3}	1.687_{-2}	-1.184_{-2}	7.328_{-3}	-1.059_{-2}	-2.067_{-2}	-2.398_{-2}	2.746_{-2}	1.464_{-2}	-3.581_{-3}	1.570_{-2}	7.134_{-3}	2.960_{-2}	1.619_{-2}	-2.062_{-2}	-4.625_{-2}	-4.625_{-2}	4:15	8.191-3
$K_1 = f(x_1', x_2')$	K_1	—	—	—	—	—	—	—	—	—	4.500	4.524	3.970	3.447	3.533	3.638	2.513	2.132	2.390	1.000	0.513	0.622	0.510	0.491	0.455	0.469	—	—	3.176	1.706	1.810	1.467	1.392	1.341	1.553	0.727	1.473	1.383	1.379	0.621	0.875	0.544	0.514	—	—	—
	RES.	—	—	—	—	—	—	—	—	—	2.855_{-1}	4.472_{-1}	2.130_{-1}	-1.811_{-1}	8.106_{-2}	2.354_{-1}	-2.197_{-1}	-2.880_{-1}	1.465_{-1}	2.893_{-3}	5.483_{-2}	4.726_{2}	-2.598_{-2}	6.083_{-2}	1.067_{-1}	4.932_{-3}	—	—	-3.366_{-1}	-9.111_{-1}	3.441_{-1}	-1.172_{-1}	2.641_{-2}	-2.009_{-1}	4.308_{-1}	-3.775_{-1}	-1.692_{-1}	4.053_{-1}	1.117_{-1}	-2.268_{-1}	3.192_{-1}	-1.510_{-1}	-1.237_{-1}	-9.111_{-1}	4:2	2.437,0
$K_2 = f(x_1', x_2')$	K_2	2.778	2.363	2.110	1.853	1.695	1.452	1.363	1.196	1.104	—	—	—	—	—	—	—	—	—	—	1.042	1.066	1.126	1.186	1.262	1.399	1.000	—	2.483	1.858	1.440	1.620	1.492	1.619	1.400	1.241	1.839	1.406	1.856	1.376	1.718	1.355	1.429	—	—	—
	RES.	8.405_{2}	3.028_{-2}	1.040_{-2}	2.245_{-2}	3.207_{-2}	3.422_{-2}	7.065_{-3}	-3.925_{-2}	-5.670_{-2}	—	—	—	—	—	—	—	—	—	—	-6.403_{-3}	-2.913_{-2}	-7.807_{-3}	4.331_{-3}	2.852_{-2}	4.277_{-2}	1.340_{-2}	—	5.002_{-2}	-2.185_{-1}	2.153_{-4}	-8.263_{-2}	-8.239_{-2}	-1.183_{-1}	2.379_{-2}	4.329_{-2}	-1.314_{-2}	8.269_{-3}	8.839_{-2}	8.847_{-2}	2.156_{-1}	-4.743_{-2}	-1.567_{-1}	2.156_{-1}	4:13	1.8751
$K_3 = f(x_1', x_2')$	K_3	0.934	0.826	0.768	0.702	0.661	0.590	0.588	0.566	0.560	0.943	0.924	0.899	0.903	0.881	0.870	0.876	0.887	0.846	1.000	—	—	—	—	—	—	—	1.000	0.863	0.850	0.671	0.799	0.785	0.830	0.663	0.526	0.826	0.698	0.801	0.521	0.697	0.657	0.779	—	—	—
	RES.	9.433_{-3}	-2.251_{-2}	-2.568_{-2}	-2.085_{-2}	-1.243_{-2}	-3.083_{-3}	1.511_{-2}	1.563_{-2}	-1.092_{-2}	-3.740_{-3}	-1.759_{-2}	-2.966_{-2}	-2.006_{-2}	-3.405_{-2}	-4.273_{-2}	-1.917_{-3}	2.743_{-2}	-2.638_{-3}	3.921_{-4}	—	—	—	—	—	—	—	3.792_{-2}	-2.775_{2}	1.759_{-2}	6.306_{-3}	2.209_{-2}	3.887_{-2}	4.247_{-2}	-1.458_{-2}	5.304_{-3}	1.758_{-2}	2.835_{-4}	9.622_{-3}	-4.434_{2}	-4.051_{-2}	4.577_{-2}	-1.332_{-2}	4.571_{-2}	4:14	2.355-2
$K_1 = f(y_1', y_2')$	K_1	—	—	—	—	—	—	—	—	—	4.500	4.524	3.970	3.447	3.533	3.638	2.513	2.132	2.390	1.000	0.513	0.622	0.510	0.491	0.455	0.469	—	—	3.176	1.706	1.810	1.467	1.392	1.341	1.553	0.727	1.473	1.383	1.379	0.621	0.875	0.544	0.514	—	—	—
	RES.	—	—	—	—	—	—	—	—	—	-1.051_{-1}	2.288_{-1}	2.126_{-1}	-3.104_{-1}	2.192_{-1}	5.166_{-1}	-2.893_{-1}	-6.224_{-1}	3.132_{-1}	-4.522_{-3}	3.561_{-2}	1.683_{-1}	6.911_{-2}	8.053_{-2}	6.114_{-2}	8.248_{-2}	—	—	3.181_{-1}	-5.151_{-1}	5.635_{-1}	-4.391_{-2}	4.533_{-2}	-3.013_{-1}	5.039_{-1}	-3.064_{-1}	-2.459_{-1}	3.856_{-1}	-4.903_{-3}	-3.318_{-1}	-9.145_{-2}	-3.188_{-1}	-3.033_{-1}	-6.229_{-1}	2:8	2.789,0
$K_2 = f(y_1', y_2')$	K_2	2.778	2.363	2.110	1.853	1.695	1.452	1.363	1.196	1.104	—	—	—	—	—	—	—	—	—	—	1.042	1.066	1.126	1.186	1.262	1.399	1.000	—	2.483	1.858	1.440	1.620	1.492	1.619	1.400	1.241	1.839	1.406	1.856	1.376	1.718	1.355	1.429	—	—	—
	RES.	-1.214_{-1}	3.960_{-2}	4.693_{-2}	3.988_{-2}	2.214_{-2}	-2.913_{-3}	-4.044_{-2}	-5.988_{-2}	-4.580_{-2}	—	—	—	—	—	—	—	—	—	—	-1.760_{-2}	-6.163_{-2}	-1.826_{-2}	-5.655_{-3}	2.941_{-2}	-5.082_{-2}	2.961_{-2}	—	2.777_{-1}	-1.296_{-1}	5.189_{-3}	-4.547_{-2}	9.739_{-2}	-1.053_{-1}	-4.945_{-2}	8.604_{-3}	1.810_{-2}	-1.108_{-1}	2.622_{-2}	1.138_{-1}	1.872_{-1}	4.812_{-2}	2.131_{-2}	2.777_{-1}	4:1	2.216-1
$K_3 = f(y_1', y_2')$	K_3	0.934	0.826	0.768	0.702	0.661	0.590	0.588	0.566	0.560	0.943	0.924	0.899	0.903	0.881	0.870	0.876	0.887	0.846	1.000	—	—	—	—	—	—	—	1.000	0.863	0.850	0.671	0.799	0.785	0.830	0.663	0.526	0.826	0.698	0.801	0.521	0.697	0.657	0.779	—	—	—
	RES.	**-9.920_{-3}**	1.754_{-2}	-1.082_{-2}	-2.569_{-3}	1.272_{-3}	-5.533_{-3}	4.433_{-3}	4.926_{-3}	1.929_{-3}	-1.075_{-2}	-1.255_{-2}	-9.098_{-3}	-5.098_{-3}	-5.790_{-3}	-8.376_{-3}	1.019_{-2}	2.289_{-2}	-6.787_{-4}	-3.076_{4}	—	—	—	—	—	—	—	9.453_{-3}	-2.123_{-2}	1.605_{-2}	4.039_{-2}	2.527_{-2}	4.246_{2}	3.357_{-2}	-2.567_{-2}	2.943_{-3}	2.029_{-4}	-3.093_{-2}	-2.218_{-2}	-5.659_{-2}	-4.065_{2}	1.304_{-2}	4.874_{-2}	-5.659_{-2}	4:12	1.744-2
T = $f(x_1', x_2')$	T°K	**183.3**	181.2	179.8	178.1	177.0	174.6	174.1	172.3	171.2	184.2	183.9	183.6	183.6	183.3	183.2	182.7	182.6	181.9	177.4	169.9	170.6	170.9	171.5	172.0	173.5	169.3	184.6	182.9	182.0	175.9	180.2	178.7	181.5	175.2	171.6	182.1	175.6	181.7	172.1	176.1	172.5	172.8	—	—	—
	RES.	-2.165_{-1}	-6.759_{-1}	-6.407_{-1}	-2.616_{-1}	1.878_{-1}	3.915_{-1}	5.739_{-1}	-6.031_{-2}	-5.546_{-1}	1.591_{-1}	-9.208_{-2}	-2.426_{-1}	-1.676_{-1}	-3.506_{-1}	-4.148_{-1}	-2.855_{-1}	9.027_{-3}	-4.369_{4}	4.845_{-3}	7.505_{-2}	2.962_{-2}	-2.082_{-1}	-7.319_{-2}	2.457_{-2}	-5.180_{-3}	4.931_{-2}	4.601_{-1}	-1.241_{-1}	2.935_{-1}	-2.321_{-2}	2.194_{-1}	-3.303_{-2}	1.093_{0}	-7.041_{-1}	2.121_{-1}	8.609_{-1}	-8.583_{1}	1.067_{0}	1.916_{-1}	-9.528_{-1}	5.972_{-1}	-1.462_{-1}	1.093_{0}	4:6	9.022,0

TABLE III.1.18

Results of surface fitting programme RAE 194/A for ternary phase equilibrium data.

$y_{C_2H_2}$	$y_{C_2H_4}$	$y_{C_2H_6}$	TEMP	$x_{C_2H_2}$	$x_{C_2H_4}$	$x_{C_2H_6}$
VAPOUR PHASE			°K.	LIQUID PHASE.		
0.00	0.00	1.00	184.5	0.000	-0.002	1.002
0.00	0.10	0.90	183.6	0.002	0.035	0.963
0.00	0.20	0.80	182.3	0.002	0.079	0.919
0.00	0.30	0.70	180.8	0.001	0.133	0.866
0.00	0.40	0.60	179.2	0.000	0.199	0.801
0.00	0.50	0.50	177.6	-0.001	0.280	0.721
0.00	0.60	0.40	176.1	-0.002	0.378	0.624
0.00	0.70	0.30	174.5	-0.003	0.497	0.506
0.00	0.80	0.20	172.9	-0.003	0.639	0.364
0.00	0.90	0.10	171.2	-0.001	0.807	0.194
0.05	0.00	0.95	184.3	0.011	0.000	0.989
0.05	0.10	0.85	183.6	0.015	0.049	0.936
0.05	0.20	0.75	182.3	0.019	0.102	0.879
0.05	0.30	0.65	180.6	0.024	0.162	0.814
0.05	0.40	0.55	178.7	0.030	0.231	0.739
0.05	0.50	0.45	176.7	0.037	0.314	0.649
0.05	0.60	0.35	174.8	0.045	0.411	0.544
0.05	0.70	0.25	173.2	0.055	0.526	0.419
0.05	0.80	0.15	171.7	0.067	0.661	0.272
0.05	0.90	0.05	170.5	0.081	0.820	0.099

TABLE III.1.18 cont.

$y_{C_2H_2}$	$y_{C_2H_4}$	$y_{C_2H_6}$	TEMP	$x_{C_2H_2}$	$x_{C_2H_4}$	$x_{C_2H_6}$
VAPOUR PHASE			°K.	LIQUID PHASE		
0.10	0.00	0.90	183.9	0.025	0.000	0.975
0.10	0.10	0.80	183.5	0.035	0.057	0.908
0.10	0.20	0.70	182.2	0.046	0.116	0.838
0.10	0.30	0.60	180.3	0.060	0.179	0.761
0.10	0.40	0.50	178.1	0.075	0.250	0.675
0.10	0.50	0.40	175.9	0.093	0.330	0.577
0.10	0.60	0.30	173.9	0.113	0.422	0.465
0.10	0.70	0.20	172.4	0.137	0.530	0.333
0.10	0.80	0.10	171.3	0.163	0.655	0.182
0.15	0.00	0.85	183.4	0.046	0.000	0.954
0.15	0.10	0.75	183.2	0.065	0.062	0.873
0.15	0.20	0.65	181.9	0.086	0.123	0.791
0.15	0.30	0.55	179.9	0.111	0.186	0.703
0.15	0.40	0.45	177.6	0.139	0.254	0.607
0.15	0.50	0.35	175.3	0.171	0.329	0.500
0.15	0.60	0.25	173.4	0.206	0.413	0.381
0.15	0.70	0.15	172.2	0.246	0.510	0.244
0.15	0.80	0.05	171.9	0.291	0.623	0.086
0.20	0.00	0.80	182.6	0.078	-0.002	0.924
0.20	0.10	0.70	182.7	0.109	0.062	0.829
0.20	0.20	0.60	181.5	0.144	0.123	0.733

TABLE III.1.18 cont.

$y_{C_2H_2}$	$y_{C_2H_4}$	$y_{C_2H_6}$	TEMP	$x_{C_2H_2}$	$x_{C_2H_4}$	$x_{C_2H_6}$
VAPOUR PHASE			°K.	LIQUID PHASE		
0.20	0.30	0.50	179.4	0.183	0.183	0.634
0.20	0.40	0.40	177.1	0.226	0.245	0.529
0.20	0.50	0.30	175.0	0.274	0.311	0.415
0.20	0.60	0.20	173.4	0.328	0.384	0.288
0.20	0.70	0.10	172.8	0.387	0.468	0.145
0.25	0.00	0.75	181.6	0.126	-0.003	0.877
0.25	0.10	0.65	182.0	0.171	0.060	0.769
0.25	0.20	0.55	180.9	0.222	0.117	0.661
0.25	0.30	0.45	179.0	0.278	0.171	0.551
0.25	0.40	0.35	176.8	0.340	0.223	0.437
0.25	0.50	0.25	175.1	0.408	0.277	0.315
0.25	0.60	0.15	174.1	0.483	0.336	0.181
0.30	0.00	0.70	180.3	0.193	-0.004	0.811
0.30	0.10	0.60	181.1	0.256	0.055	0.689
0.30	0.20	0.50	180.2	0.325	0.105	0.570
0.30	0.30	0.40	178.6	0.401	0.148	0.451
0.30	0.40	0.30	176.9	0.485	0.189	0.326
0.35	0.00	0.65	178.9	0.283	-0.003	0.720
0.35	0.10	0.55	180.1	0.366	0.048	0.586
0.35	0.20	0.45	179.7	0.457	0.088	0.455
0.35	0.30	0.35	178.6	0.557	0.118	0.325

TABLE III.1.18 cont.

$y_{C_2H_2}$	$y_{C_2H_4}$	$y_{C_2H_6}$	TEMP	$x_{C_2H_2}$	$x_{C_2H_4}$	$x_{C_2H_6}$
VAPOUR PHASE			$^{o}K.$	LIQUID PHASE		
0.40	0.00	0.60	177.4	0.399	0.000	0.601
0.40	0.10	0.50	179.2	0.506	0.040	0.454

TABLE III.1.19.

Polynomial of degree 3 for $K_{C_2H_2} = f(x'_{C_2H_2}, x'_{C_2H_4})$ obtained using programme RAE 194/A

MEAN VALUES.

$$\bar{x}_{C_2H_2} = 1.47393939, -1$$

$$\bar{x}_{C_2H_4} = 2.73787878, -1$$

POLYNOMIAL COEFFICIENTS.

POWER of $x'_{C_2H_4}$	POWER of $x'_{C_2H_4}$	
$x'_{C_2H_4} = x_{C_2H_4} - \bar{x}_{C_2H_4}$	$x'_{C_2H_2} = x_{C_2H_2} - \bar{x}_{C_2H_2}$	
0	0	7.15568491, -1
	1	-6.28801374, 0
	2	2.82857789, 1
	3	-3.33533683, 0
1	0	-1.25213576, -1
	1	2.12899734, 1
	2	-8.12600781, 1
2	0	6.27329353, 0
	1	-2.97138932, 1
3	0	-1.11911586, 1

TABLE III.1.20.

Polynomial of degree 3 for $K_{C_2H_4} = f(x'_{C_2H_2}, x'_{C_2H_4})$ obtained using programme RAE194/A.

MEAN VALUES.

$\bar{x}_{C_2H_2} = 9.68787872, -2$

$\bar{x}_{C_2H_4} = 4.68181823, -1$

POLYNOMIAL COEFFICIENTS.

POWER of $x'_{C_2H_4}$	POWER of $x'_{C_2H_2}$	
$x'_{C_2H_4} = x_{C_2H_4} - \bar{x}_{C_2H_4}$	$x'_{C_2H_2} = x_{C_2H_2} - \bar{x}_{C_2H_2}$	
0	0	1.27059120, 0
	1	-1.54214606, -1
	2	1.26907657, 1
	3	-2.51871572, 1
1	0	-6.14639142, -1
	1	3.49586932, 0
	2	-3.35615142, 1
2	0	1.66370812, 0
	1	-8.54693529, 0
3	0	-3.13247636, 0

TABLE III.1.21.

Polynomial of degree 3 for $K_{C_2H_6} = f(x'_{C_2H_2}, x'_{C_2H_4})$

obtained using programme RAE 194/A.

MEAN VALUES.

$\bar{x}_{C_2H_2} = 8.74615380, -2$

$\bar{x}_{C_2H_4} = 2.02641024, -1$

POLYNOMIAL COEFFICIENTS.

POWER of $x'_{C_2H_4}$	POWER of $x'_{C_2H_2}$	
$x'_{C_2H_4} = x_{C_2H_4} - \bar{x}_{C_2H_4}$	$x'_{C_2H_2} = x_{C_2H_2} - \bar{x}_{C_2H_2}$	
0	0	7.63823816, -1
	1	-1.79062590, -1
	2	-6,83395132, -2
	3	1.61094741, 1
1	0	-5.44911414, -1
	1	3.24680700, 0
	2	-1.65102415, 0
2	0	-1.81406299, -1
	1	-9.38921436, 0
3	0	3.48797553, -1

TABLE 111.1.22.

Polynomial of degree 3 for $K_{C_2H_2} = f\ (y'_{C_2H_2}, y'_{C_2H_4})$

obtained using programme RAE 194/A.

MEAN VALUES.

$\bar{y}_{C_2H_2} = 1.52333333, -1$

$\bar{y}_{C_2H_4} = 3.59575754, -1$

POLYNOMIAL COEFFICIENTS.

POWER of $y'_{C_2H_4}$	POWER of $y'_{C_2H_2}$	
$y'_{C_2H_4} = y_{C_2H_4} - \bar{y}_{C_2H_4}$	$y'_{C_2H_2} = y_{C_2H_2} - \bar{y}_{C_2H_2}$	
0	0	1.07556392, 0
	1	-6.13636429, 0
	2	1.38240543, 0
	3	1.22686082, 2
1	0	-1.67157679, 0
	1	1.62533096, 1
	2	1.86129285, 1
2	0	7.99868275, 0
	1	-3.08158848, 1
3	0	-1.52640518, 1

TABLE 111.1.23.

Polynomial of degree 3 for $K_{C_2H_4} = f(y'_{C_2H_2}, y'_{C_2H_4})$

obtained using programme RAE 194/A.

MEAN VALUES.

$\bar{y}_{C_2H_2} = 7.40606060, -2$

$\bar{y}_{C_2H_4} = 5.98999994, -1$

POLYNOMIAL COEFFICIENTS.

POWER of $y'_{C_2H_4}$	POWER of $y'_{C_2H_2}$	
$y'_{C_2H_4} = y_{C_2H_4} - \bar{y}_{C_2H_4}$	$y'_{C_2H_2} = y_{C_2H_2} - \bar{y}_{C_2H_2}$	
0	0	1.38272725, 0
	1	-1.54498745, 0
	2	2.20699450, 1
	3	4.48093813, 1
1	0	-8.63499316, -1
	1	6.66735015, 0
	2	-5.32606540, 1
2	0	6.65209162, -1
	1	-4.00882516, 0
3	0	-1.90592781, 0

TABLE 111.1.24

Polynomial of degree 3 for $K_{C_2H_6} = f(y'_{C_2H_2}, y'_{C_2H_4})$

obtained using programme RAE 194/A.

MEAN VALUES.

$\bar{y}_{C_2H_2} = 1.10512820, -1$

$\bar{y}_{C_2H_4} = 2.94461537, -1$

POLYNOMIAL COEFFICIENTS.

POWER of $y'_{C_2H_4}$	POWER of $y'_{C_2H_2}$	
$y'_{C_2H_4} = y_{C_2H_4} - \bar{y}_{C_2H_4}$	$y'_{C_2H_2} = y_{C_2H_2} - \bar{y}_{C_2H_2}$	
0	0	7.75856703, -1
	1	1.44909631, -1
	2	6.87413512, 0
	3	1.35199388, 1
1	0	-5.77379116, -1
	1	3.41550768, 0
	2	2.42490873, 1
2	0	-2.14031417, -2
	1	7.76024851, -1
3	0	7.70239207, -1

TABLE III.1.25.

Polynomial of degree 4 for $T = f(x'_{C_2H_2}, x'_{C_2H_4})$

obtained using programme RAE 194/A

MEAN VALUES.

$\bar{x}_{C_2H_2} = 1.01333332, -1$

$\bar{x}_{C_2H_4} = 3.21875002, -1$

POLYNOMIAL COEFFICIENTS.

POWER of $x'_{C_2H_4}$	POWER of $x'_{C_2H_2}$	
$x'_{C_2H_4} = x_{C_2H_4} - \bar{x}_{C_2H_4}$	$x'_{C_2H_2} = x_{C_2H_2} - \bar{x}_{C_2H_2}$	
0	0	1.76531114, 2
	1	-8.16306236, 0
	2	-2.32504395, 1
	3	1.71298961, 2
	4	1.42199214, 1
1	0	-2.30200750, 1
	1	1.06475679, 1
	2	1.94202200, 2
	3	-6.36394311, 2
2	0	8.63120761, 0
	1	-9.98378169, 1
	2	1.44585868, 2
3	0	5.61827162, 1
	1	2.18029536, 2
4	0	-6.18810204, 1

SECTION 111.2.

TABLE 111.2.1

Solubility of acetylene in acetone.

RUN No.	TEMP EXPT °K.	PRESSURE m.m.Hg.	VAPOUR PHASE M.F.C_2H_2	VAPOUR PHASE M.F.ACETONE	LIQUID PHASE M.F.C_2H_2	LIQUID PHASE M.F.ACETONE
5:1	208.1	761.6	1.000	0.000	0.560	0.440
5:2	203.1	761.6	1.000	0.000	0.595	0.405
5:3	198.1	762.0	1.000	0.000	0.675	0.325
5:4	193.1	762.0	1.000	0.000	0.730	0.270

TABLE 111.2.2.

Solubility of Ethylene in acetone

RUN No.	TEMP EXPT. °K.	PRESSURE m.m.Hg.	VAPOUR PHASE M.F.C_2H_4	VAPOUR PHASE M.F.ACETONE	LIQUID PHASE M.F.C_2H_4	LIQUID PHASE M.F.ACETONE
6:1	203.1	758.5	1.000	0.000	0.135	0.865
6:2	193.1	758.5	1.000	0.000	0.194	0.806
6:3	183.1	758.5	1.000	0.000	0.285	0.715
6:4	178.1	758.5	1.000	0.000	0.330	0.670

TABLE III.2.3.

Solubility of ethane in acetone.

RUN No.	TEMP EXPT. °K	PRESSURE m.m.Hg.	VAPOUR PHASE M.F.C_2H_6	VAPOUR PHASE M.F.ACETONE	LIQUID PHASE M.F.C_2H_6	LIQUID PHASE M.F. ACETONE
7:1	203.1	764.2	1.000	0.000	0.095	0.905
7:2	193.1	764.2	1.000	0.000	0.138	0.862
7:3	185.9	764,2	1.000	0.000	(0.180	0.820
					(0.955	0.045

TABLE III.2.4.

Solubility of ethane and acetylene in acetone.

RUN No.	TEMP EXPT. °K.	PRESSURE m.m.Hg.	VAPOUR PHASE M.F.C_2H_6	VAPOUR PHASE M.F.C_2H_2	LIQUID PHASE M.F.C_2H_6	LIQUID PHASE M.F.C_2H_2	LIQUID PHASE M.F.ACETONE
8:5	208.1	766.5	0.953	0.047	0.066	0.094	0.840
8:6	208.1	770.3	0.880	0.120	0.052	0.168	0.780
8:8	208.1	770.3	0.867	0.133	0.052	0.183	0.765
8:9	203.1	770.3	0.923	0.077	0.077	0.188	0.735
8:10	203.1	768.1	0.892	0.108	0.068	0.222	0.710
8:11	203.1	768.1	0.880	0.120	0.065	0.240	0.695
8:12	203.1	768.1	0.828	0.172	0.054	0.291	0.655
8.13	203.1	768.1	0.958	0.042	0.078	0.122	0.800
8.15	208.1	764.1	0.905	0.095	0.067	0.143	0.790
8.16	208.1	764.1	0.880	0.120	0.059	0.161	0.780

TABLE III.2.4. (Cont)

RUN No.	TEMP. EXPT. °K.	PRESSURE m.m.Hg.	VAPOUR PHASE M.F.C_2H_6	VAPOUR PHASE M.F.C_2H_2	LIQUID PHASE M.F.C_2H_6	LIQUID PHASE M.F.C_2H_2	LIQUID PHASE M.F. ACETONE.
8:17	208.1	764.1	0.857	0.143	0.050	0.190	0.760
8:18	198.1	762.8	0.870	0.130	0.076	0.324	0.600
8:19	193.1	762.8	0.859	0.141	0.069	0.391	0.540
8:20	193.1	762.8	0.848	0.152	0.069	0.396	0.535
8:21	198.1	748.8	0.957	0.043	0.096	0.154	0.750
8:22	198.1	748.8	0.924	0.076	0.083	0.208	0.709
8:23	198.1	748.8	0.880	0.120	0.074	0.296	0.630
8:24	193.1	763.8	0.972	0.028	0.102	0.148	0.750
8:25	193.1	763.8	0.913	0.087	0.090	0.270	0.640
8:26	193.1	763.8	0.936	0.064	0.098	0.232	0.670
8:27	188.1	757.4	0.880	0.120	0.095	0.404	0.501
8:28	188.1	757.4	0.975	0.025	0.180	0.220	0.600
8:29	188.1	757.4	0.931	0.069	0.124	0.316	0.560
8:30	188.1	757.4	0.914	0.086	0.122	0.358	0.520
8:31	188.1	757.4	0.884	0.116	0.104	0.416	0.480
8:32	184.9	771.4	0.934	0.066	(0.918 (0.185	0.032 0.150	0.050 0.665
8:33	183.1	771.4	0.823	0.177	(0.891 (0.179	0.069 0.331	0.040 0.490
8:34	183.8	771.4	0.846	0.154	(0.913 (0.195	0.041 0.275	0.046 0.530
8:35	181.1	771.4	0.724	0.276	(0.792 (0.185	0.168 0.450	0.040 0.365

TABLE III 2.5.

Solubility of ethylene and acetylene in acetone.

RUN No.	TEMP EXPT. °K.	PRESSURE m.m.Hg.	VAPOUR PHASE M.F.C_2H_4	VAPOUR PHASE M.F.C_2H_2	LIQUID PHASE M.F.C_2H_4	LIQUID PHASE M.F.C_2H_2	M.F.ACETONE.
9:2	188.1	770.3	0.863	0.137	0.159	0.476	0.365
9:3	193.1	770.3	0.879	0.121	0.105	0.305	0.590
9:4	198.1	770.3	0.881	0.119	0.095	0.268	0.637
9:5	183.1	752.0	0.938	0.062	0.240	0.340	0.420
9:6	188.1	752.0	0.915	0.085	0.187	0.346	0.467
9:7	193.1	752.0	0.902	0.098	0.103	0.259	0.638
9:8	198.1	752.0	0.900	0.100	0.096	0.249	0.655
9:9	203.1	752.0	0.899	0.101	0.083	0.237	0.680
9:10	183.1	775.0	0.961	0.039	0.249	0.255	0.496
9:11	188.1	775.0	0.939	0.061	0.185	0.279	0.536
9.12	193.1	775.0	0.934	0.066	0.135	0.200	0.665
9:13	198.1	775.0	0.933	0.067	0.117	0.178	0.705
9:14	203.1	775.0	0.934	0.066	0.102	0.153	0.745
9:16	183.1	755.8	0.857	0.143	0.175	0.525	0.300
9:17	188.1	755.8	0.848	0.152	0.165	0.490	0.345
9:18	198.1	755.8	0.815	0.185	0.073	0.352	0.575
9:19	183.1	766.4	0.908	0.092	0.212	0.436	0.352
9:20	193.1	766.4	0.838	0.162	0.096	0.340	0.564
9:21	203.1	766.4	0.821	0.179	0.073	0.299	0.628
9:22	183.1	761.1	0.770	0.230	0.102	0.678	0.220
9:23	188.1	761.1	0.684	0.316	0.056	0.704	0.240

TABLE III 2.6.

Solubility of ethylene and ethane in acetone.

RUN No.	TEMP$_{EXPT}$ K.	PRESSURE m.m.Hg.	VAPOUR PHASE M.F.C_2H_4	VAPOUR PHASE M.F.C_2H_6	LIQUID PHASE M.F.C_2H_4	LIQUID PHASE M.F.C_2H_6	M.F. ACETONE.
10:1	183.1	754.1	0.644	0.356	0.275	0.135	0.590
10:2	185.0	754.1	0.634	0.366	0.162	0.080	0.758
10:3	183.1	766.7	0.290	0.710	0.137	0.303	0.560
10:4	185.6	766.7	0.310	0.690	0.065	0.135	0.800
10:5	188.1	766.7	0.305	0.695	0.065	0.127	0.808
10:6	193.1	766.7	0.312	0.688	0.053	0.097	0.850
10:7	198.1	766.7	0.297	0.703	0.043	0.082	0.875
10:8	203.1	766,7	0.309	0.691	0.035	0.067	0.898
10:9	183.1	751.5	0.235	0.765	0.109	0.331	0.560
L0:10	183.1	751.5	0.360	0.640	0.183	0.279	0.538
10:11	183.1	751.5	0.583	0.417	0.254	0.165	0.581
10:12	185.0	751.5	0.275	0.725	0.060	0.146	0.794
10:13	185.6	751.5	0.530	0.470	0.124	0.103	0.773
10:14	188.1	751.5	0.528	0.472	0.111	0.089	0.800
10:15	193.1	763.0	0.516	0.484	0.091	0.071	0.838
10:16	198.1	763.0	0.521	0.479	0.077	0.060	0.863
10:17	203.1	763.0	0.510	0.490	0.061	0.049	0.890
10:19	183.1	768.7	0.183	0.817	0.085	0.356	0.559
10:20	180.1	761.1	0.730	0.270	0.297	0.103	0.600
10:21	183.1	761.1	0.135	0.865	(0.048 (0.061	0.872 0.389	0.080 0.550
10:22	182.3	761.1	0.217	0.783	(0.086 (0.109	0.823 0.556	0.091 0.335

TABLE III 2.6 cont.

RUN NO.	TEMP. EXPT.K°	PRESSURE m.m. Hg.	VAPOUR PHASE M.F.C H 2 4	VAPOUR PHASE M.F.C H 2 6	LIQUID PHASE M.F.C H 2 4	LIQUID PHASE M.F.C H 2 6	LIQUID PHASE M.F.ACETONE
10:23	180.1	761.1	0.366	0.634	(0.166 (0.176	0.736 0.624	0.098 0.200

TABLE III.2.7.

Solubility of ethylene, ethane and acetylene in acetone at -80°C.

RUN NO.	PRESSURE m.m. Hg.	VAPOUR PHASE M.F.C H 2 2	VAPOUR PHASE M.F.C H 2 4	VAPOUR PHASE M.F.C.H 2 6	LIQUID PHASE M.F.C H 2 2	LIQUID PHASE M.F.C.H 2 4	LIQUID PHASE M.F.C.H 2 6	LIQUID M. F. ACETONE
11:1	751.9	0.052	0.609	0.339	0.718	0.194	0.088	0.690
11:2	751.9	0.075	0.478	0.447	0.801	0.106	0.093	0.650
11:3	751.9	0.071	0.371	0.558	0.707	0.110	0.183	0.690
11:4	751.9	0.084	0.140	0.776	0.764	0.038	0.198	0.650
11:5	751.9	0.158	0.526	0.316	0.854	0.101	0.045	0.574
11:6	751.9	0.075	0.661	0.264	0.780	0.160	0.060	0.650
11:7	751.9	0.049	0.521	0.430	0.590	0.230	0.180	0.704

SECTION III.3.

EQUILIBRIUM CORRELATION FOR TERNARY MIXTURES.

From (23:4) the excess free energy of mixing is:-

$$\Delta GE = nRT \sum_i x_i \log_e \gamma_i \qquad (1:III).$$

since $n_i = n\, x_i$

In (25:4) Wohl[94] expresses the dependence of the molar excess free energy $\Delta GE/nRT$ on the composition of the liquid phase as a power series.

We adopt a similar technique by substituting experimental values of T, x_i, and γ_i in (1.III) and correlating the resulting values of $\Delta GE/nR$ with the experimental liquid compositions using the surface fitting programme R.A.E. 194/A.

The result is of the form:-

$$\frac{\Delta GE}{nR} = T \sum_i x_i \log_e \gamma_i = \sum_{p=o}^{l} \sum_{q=o}^{l-P} a_{pq}\, x'^{P}_{C_2H_2}\, x'^{q}_{C_2H_4} \qquad (2:III)$$

where $x'_{C_2H_2} = x_{C_2H_2} - \bar{x}_{C_2H_2}$

and $x'_{C_2H_4} = x_{C_2H_4} - \bar{x}_{C_2H_4}$

$\bar{x}_{C_2H_2}$ and $\bar{x}_{C_2H_4}$ being the average values of the experimental liquid compositions fed as data to the computer.

By using a similar technique to Wohl we differentiate (2.III) with respect to the number of moles of any constituent i, apply the Gibbs-Duhem equation, and obtain the following expression for the excess partial molar free energy change on mixing:-

$$\frac{1}{R}\left(\frac{\partial \Delta GE}{\partial ni}\right)_{T,P,nj\neq i} = T \log_e \gamma i = \sum_{p=0}^{l} \sum_{q=0}^{l-p} a_{pq}\, x'^{P}_{C_2H_2}\, x'^{q}_{C_2H_4} +$$

$$n \sum\sum a_{pq}\, x'^{(p-1)}_{C_2H_2}\, x'^{(q-1)}_{C_2H_4} \left(p x'_{C_2H_4} \frac{\partial x'_{C_2H_2}}{\partial n_i} + q x'_{C_2H_2} \frac{\partial x'_{C_2H_4}}{\partial ni} \right) \qquad (3:III)$$

We put: $$T \log_e \gamma_i = \sum_{p=o}^{l} \sum_{q=o}^{l-p} b^{i}_{pq}\, x'^{P}_{C_2H_2}\, x'^{q}_{C_2H_4} \qquad (4.III)$$

and note that: $$\frac{\partial ni}{\partial nj} = \delta_{ij} = x_i + n \frac{\partial xi}{\partial nj}$$

i.e. $$\frac{\partial xi}{\partial nj} = \frac{\delta_{ij} - x_i}{n}$$

From (3.III) and (4.III)

$$b^{i}_{pq} = a_{pq}\,(1-p-q) + a_{p+1,q}(\delta_{C_2H_2 i} - \bar{x}_{C_2H_2})(p+1) +$$

$$a_{p,q+1}\,(\delta_{C_2H_4 i} - \bar{x}_{C_2H_4})(q+1) \qquad (5.III)$$

where $$a_{jk} = 0 \text{ for } j>1 \text{ or } K>1 .$$

The equilibrium constant, $$K_i = \frac{y_i}{x_i} = \frac{\gamma_i\, p_i^{o}}{P} \qquad (6:III)$$

If the dependence of vapour pressure on temperature is expressed as $$\log_e pi^{o} = \frac{Ai}{T+Di} + Bi + Ci\,T \qquad (7:III)$$

then from (4:III), (6:III) and (7:III)

$$\log_e PK_i = \sum_{p=o}^{l} \sum_{q=o}^{l-p} \frac{b^{i}_{pq}\, x'^{P}_{C_2H_2}\, x'^{q}_{C_2H_4}}{T} + \frac{Ai}{T+D_i} + Bi + CiT \qquad (8:III)$$

Four iterative methods for the determination of the equilibrium are now described:-

(1) Given liquid compositions $x_{C_2H_2}$, $x_{C_2H_4}$ - to find temperature:

$$\text{Let } h_i = d\left(\frac{\log_e Ki}{dT}\right) = -\sum_i^{\prime}\sum_p^{\prime}\sum_q^{\prime} \frac{b_{pq}\, x_{C_2H_2}\, x_{C_2H_4}}{T^2} - \frac{Ai}{(T+Di)^2} + Ci$$

$$= -\frac{vi}{T} - \frac{Ai}{(T+Di)^2} + Ci$$

We put $S = \sum_i^{\prime} Ki\, xi - 1$

$$\left(\frac{dS}{dT}\right) = \sum_i^{\prime} xi \frac{dKi}{dT} = \sum^{\prime} yi \frac{d \log_e Ki}{dT}$$

Then $Tn+1 = Tn - Sn \Big/ \left(\frac{dS}{dT}\right)_n$

The initial estimate of temperature is made by:-

$$T_1 = \sum_i^{\prime} T_i^{\circ}\, xi$$

where T_i° is the boiling point of pure component i

From this temperature (8:III) and h_i may be evaluated to give Ki and $\frac{d \log_e Ki}{dT}$. Hence S_1, $\left(\frac{dS}{dT}\right)_1$ and $y_{i\,1}$ may be evaluated and a revised estimate of temperature obtained.

(2) Given vapour compositions y_1, y_2 to find temperature and liquid composition.

Put:- $x_i = y_i / K_i$

and:- $S' = \sum^{\prime} y_i / K_i - 1$

Then:- $\left(\frac{\partial S'}{\partial T}\right)_{x_i} = -\sum^{\prime} \frac{yi}{Ki^2} \frac{\partial Ki}{\partial T} = -\sum^{\prime} xi \frac{\partial \log_e Ki}{\partial T}$.

$$\text{Then:-} \qquad T_{n+1} = T_n - S'_n \Big/ \left(\frac{\partial S'}{\partial T}\right)_n$$

In this case $T_1 = \sum_i T_i^{\circ} y_i$ and intially the given vapour compositions are assumed to be the first estimate for the liquid compositions. Hence Ki and $\frac{d \log_e Ki}{dT}$ are evaluated and revised estimates of temperature and liquid composition are obtained.

(3) Given x_1 and T - to find x_2.

$$\text{Put } f_i = \frac{d \log_e Ki}{dx_2} = \frac{d\, vi}{dx_2}$$

$$= \frac{1}{T} \sum_{p=o}^{1} \sum_{q=o}^{1-p} q b_{pq}^{i} x_1^{p} x_2^{q-1}$$

$$\text{Put } S = \sum_i Kixi - 1 = K_1 x_1 + K_2 x_2 + K_3(1-x_1-x_2) - 1$$

$$\frac{dS}{dx_2} = \sum_i xi \frac{dKi}{dx_2} + K_2 - K_3$$

$$\text{Whence} \qquad (x_2)_{n+1} = (x_2)_n - Sn \Big/ \left(\frac{dS}{dx_2}\right)_n$$

For the first estimate of x_2, we use:-

$$T = \sum_i T_i^{\circ} x_i = T_1^{\circ} x_1 + T_2^{\circ} x_2 + T_3^{\circ} (1-x_1-x_2)$$

$$\text{Whence:-} \qquad x_2 = \frac{(T - T_3^{\circ}) - x_1(T_1^{\circ} - T_3^{\circ})}{(T_2^{\circ} - T_3^{\circ})}$$

Hence Ki and S may be evaluated and since

$$\frac{d \log_e Ki}{dx_2} = \frac{1}{Ki} \frac{dKi}{dx_2}$$ we may obtain $\frac{dS}{dx_2}$ and therefore a revised estimate of x_2.

(4) Given y_1 and T- to find x_1 and x_2

Put $x_1 = y_1/K_1$

Then:- $y_1 + K_2x_2 + K_3x_3 = 1$

and putting:- $x_3 = 1-x_1-x_2$:-

$$x_2 = \frac{1-K_3-y_1+K_3x_1}{K_2-K_3}$$

Then:- $x_3=1-x_1-x_2$

$y_2=K_2x_2$

and $y_3=1-y_1-y_2$

For the initial estimate we set $x_1=y_1$ and calculate x_2 from the temperature as described in (3) above.

The equilibrium constants are then calculated from (8.III) and a revised estimate of x_1 and hence of x_2 is obtained.

TABLE III.3.1.

RESULTS OF EQUILIBRIUM CORRELATION USING VAPOUR COMPOSITIONS AS DATA.

TEMP °K.	LIQUID COMPOSITIONS $x_{C_2H_2}$	$x_{C_2H_4}$	$x_{C_2H_6}$	VAPOUR COMPOSITIONS $y_{C_2H_2}$	$y_{C_2H_4}$	$y_{C_2H_6}$
183.18	0.0000	0.0449	0.9551	0.0000	0.1000	0.9000
181.16	0.0000	0.1262	0.8738	0.0000	0.2670	0.7330
179.83	0.0000	0.1806	0.8194	0.0000	0.3650	0.6350
178.10	0.0000	0.2551	0.7449	0.0000	0.4800	0.5200
176.85	0.0000	0.3141	0.6859	0.0000	0.5560	0.4440
174.39	0.0000	0.4523	0.5477	0.0000	0.6910	0.3090
173.74	0.0000	0.4974	0.5026	0.0000	0.7250	0.2750
171.81	0.0000	0.6644	0.3356	0.0000	0.8240	0.1760
170.63	0.0000	0.8078	0.1922	0.0000	0.8930	0.1070
183.67	0.0398	0.0000	0.9602	0.0720	0.0000	0.9280
183.46	0.0515	0.0000	0.9485	0.0950	0.0000	0.9050
183.11	0.0692	0.0000	0.9308	0.1310	0.0000	0.8690
183.11	0.0692	0.0000	0.9308	0.1310	0.0000	0.8690
182.83	0.0825	0.0000	0.9175	0.1590	0.0000	0.8410
182.70	0.0882	0.0000	0.9118	0.1710	0.0000	0.8290
182.49	0.0975	0.0000	0.9025	0.1910	0.0000	0.8090
182.45	0.0989	0.0000	0.9011	0.1940	0.0000	0.8060
181.94	0.1197	0.0000	0.8803	0.2390	0.0000	0.7610

TABLE III.3.1. Cont.

TEMP	LIQUID COMPOSITIONS			VAPOUR COMPOSITIONS		
$^{o}K.$	$x_{C_2H_2}$	$x_{C_2H_4}$	$x_{C_2H_6}$	$y_{C_2H_2}$	$y_{C_2H_4}$	$y_{C_2H_6}$
179.79	0.1952	0.0000	0.8048	0.4000	0.0000	0.6000
169.64	0.0634	0.9366	0.0000	0.0410	0.9590	0.0000
170.63	0.2287	0.7713	0.0000	0.0920	0.9080	0.0000
170.96	0.2614	0.7386	0.0000	0.1040	0.8960	0.0000
171.72	0.3169	0.6831	0.0000	0.1310	0.8690	0.0000
172.17	0.3433	0.6567	0.0000	0.1480	0.8520	0.0000
173.41	0.4032	0.5968	0.0000	0.2010	0.7990	0.0000
169.45	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000
184.25	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000
182.10	0.0311	0.0674	0.9015	0.0540	0.1490	0.7970
181.11	0.0341	0.1038	0.8621	0.0580	0.2230	0.7190
176.20	0.0554	0.3060	0.6386	0.0760	0.5270	0.3970
179.45	0.0669	0.1471	0.7860	0.1100	0.2980	0.5920
178.63	0.0696	0.1801	0.7502	0.1100	0.3520	0.5380
179.96	0.0677	0.1251	0.8072	0.1140	0.2590	0.6270
175.89	0.1010	0.2962	0.6028	0.1320	0.4970	0.3710
171.47	0.0792	0.6630	0.2578	0.0640	0.7920	0.1440
180.43	0.0787	0.0978	0.8236	0.1370	0.2060	0.6570
176.41	0.1084	0.2630	0.6287	0.1480	0.4540	0.3980
179.77	0.0934	0.1133	0.7933	0.1600	0.2320	0.6080

TABLE III. 3.1. cont.

TEMP °K.	LIQUID COMPOSITIONS $x_{C_2H_2}$	$x_{C_2H_4}$	$x_{C_2H_6}$	VAPOUR COMPOSITIONS $y_{C_2H_2}$	$y_{C_2H_4}$	$Y_{C_2H_6}$
171.94	0.1598	0.6052	0.2350	0.1080	0.7430	0.1490
176.27	0.1143	0.2675	0.6182	0.1540	0.4570	0.3890
172.24	0.2284	0.5842	0.1874	0.1370	0.7210	0.1420
172.79	0.2601	0.5366	0.2032	0.1650	0.6730	0.1620

APPENDIX IV

TABLE IV.1.

Experimental results for ethylene-ethane separations

RUN NO.	PLATES RECTIFYING	REFLUX RATIO	REBOILER CURRENT amps.	FEED PRESS cms. w.g.	FEED TEMP. °K	FEED FLOW ml/min	FEED Comp[n] m.f.C$_2$H$_4$	BOTTOM PRODUCT PRESS cms. w.g.	BOTTOM PRODUCT TEMP. °K	BOTTOM PRODUCT FLOW ml/min	BOTTOM PRODUCT COMP[n] m.f.C$_2$H$_4$	TOP PRODUCT PRESS m.m. Hg.	TOP PRODUCT COMP[n] m.f.C$_2$H$_4$
A:1	5	6.1	0.42	7.5	176.5	3750	0.395	11.5	182.0	2850	0.205	744.3	0.935
A:2	5	4.7	0.45	7.5	174.9	3800	0.455	11.0	183.1	2350	0.128	744.3	0.933
A:3	5	6.9	0.55	FLOODING IN COLUMN								744.3	-
A:4	5	4.7	0.48	8.0	176.1	3750	0.400	11.0	184.1	2100	0.036	755.4	0.963
A:5	5	6.1	0.42	7.0	176.9	3850	0.360	10.5	182.7	2850	0.152	755.4	0.930
A:6	5	3.8	0.42	7.0	175.4	3800	0.485	11.0	182.3	2250	0.179	755.0	0.928
A:7	5	3.8	0.42	7.0	175.0	3750	0.490	11.0	183.1	2100	0.124	755.0	0.940
A:8	5	4.7	0.48	7.5	174.3	3800	0.485	11.0	183.2	2150	0.108	755.0	0.951
A:9	5	6.1	0.50	8.0	174.9	3800	0.360	11.5	184.4	2400	0.015	755.0	0.954
A:10	5	6.1	0.48	7.0	174.7	3850	0.425	11.0	182.4	250[0]	0.175	755.0	0.957
A:11	10	3.8	0.42	12.0	180.6	3750	0.386	12.0	184.2	2200	0.030	752.2	0.955
A:12	10	4.7	0.50	12.0	183.1	3850	0.402	12.0	1845	2050	0.003	752.2	0.872
A:13	10	6.1	0.48	12.0	183.1	3600	0.361	12.5	184.5	2300	0.003	757.1	0.943
A:15	10	6.1	0.50	12.0	183.2	3650	0.370	12.5	1845	2200	0.002	757.1	0.950
A:16	10	6.1	0.50	12.0	1828	3840	0.402	12.0	1845	2250	0.003	761.4	0.981
A:17	10	4.7	0.45	12.0	1825	3650	0.370	12.0	1845	2250	0.005	761.4	0.913
A:18	10	3.8	0.42	12.0	179.5	4000	0.415	12.0	184.2	2400	0.030	761.4	0.965

TABLE IV.2

PLATE-EFFICIENCIES FOR OLDERSHAW COLUMNS.

RUN No.	VAPOUR RATE RECTIFYING ml/min 20°C	VAPOUR RATE STRIPPING 1a tm	PLATE EFFICIENCIES %. RECTIFYING DAVIES	STRIPPING DAVIES	RECTIFYING MORAN	STRIPPING MORAN	RECTIFYING KHARAKHORIN	STRIPPING KHARAKHORIN
A:1	7350	2250	100	–	70	33	125	–
A:2	8600	3500	95	100	70	50	110	–
A:3	11600	6500		FLOODING	IN	COLUMN.		
A:4	9800	4700	120	100	76	100	160	–
A.5	7500	2250	100	–	74	–	–	–
A:6	8000	2800	98	–	64	40	–	–
A:7	8100	3000	98	–	65	50	–	–
A:8	9800	4600	95	–	60	48	–	–
A.9	10000	4800	100	100	65	95	–	–
A:10	9400	4300	100	–	62	34	–	–
A.11	8000	2900	102	97	–	–	–	–
A:12	10500	5300	97	88	–	90	–	–
A:13	9250	4500	93	89	–	110	–	–
A:15	10200	5150	97	88	–	105	–	–
A:16	10300	5100	105	89	86	100	–	–
A:17	8600	3550	97	90	–	110	–	–
A:18	8100	2700	90	98	80	–	–	–

TABLE V.1

TERNARY DISTILLATION RUNS WITHOUT SIDESTREAM

RUN NO.		B:1	B:2	B:3	B:4	B:5	B:6	B:7	B:8	B:9	B:10	B:11	B:12	B:13	B:14	B:15	B:16	B:17	B:18	B:19	B:20	B:21	B:22	B:23	B:24	B:25	B:26	B:27	B:28	B:29	B:58	B:59	B:60	B:61	B:62
STRIPPING PLATES		10	10	10	10	10	10	5	5	5	5	5	5	10	10	5	5	5	5	5	5	5	5	5	5	5	10	10	10	10	5	5	5	5	5
RECTIFYING PLATES		15	15	15	5	5	5	10	10	10	10	10	10	5	5	15	15	15	15	15	15	30	30	30	30	30	15	15	15	15	30	30	30	30	30
FEED	FLOW ml/min 20°C1At.	3050	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3050	3050	3000	3100	3000	3000	3000	3000	2950	2950	2950	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000
	Mole% C_2H_2	8.5	9.8	9.8	10.3	10.3	10.1	8.8	8.8	8.8	9.5	8.5	9.8	9.4	9.4	8.1	8.1	6.9	8.1	6.9	8.1	11.0	11.0	11.0	7.2	7.4	10.4	10.4	6.0	6.0	3.0	6.8	6.1	4.0	4.0
	Mole% C_2H_4	26.0	31.7	31.7	24.1	24.1	25.3	25.5	25.5	25.5	24.5	26.6	27.3	26.0	26.0	33.5	33.5	25.0	25.0	25.0	25.0	30.1	30.1	30.1	30.0	23.8	29.6	29.6	27.7	27.7	31.0	33.2	36.0	31.0	31.0
	Mole% C_2H_6	65.5	58.5	58.5	65.6	65.6	64.6	65.7	65.7	65.7	66.0	64.9	62.9	64.6	64.6	58.4	58.4	68.1	66.9	68.1	66.9	58.9	58.9	58.9	62.8	68.8	60.0	60.0	66.3	66.3	66.0	60.0	57.9	65.0	65.0
BOTTOM PRODUCT	FLOW ml/min 20°C1At.	2200	2150	2200	2100	2200	2300	2000	2100	2200	2200	2200	2400	2000	2100	2200	2400	2400	2400	2400	2400	2150	2200	2200	2100	2200	2250	2150	2150	2300	2000	1950	1750	2050	1950
	Mole% C_2H_2	5.9	11.0	7.9	10.1	9.3	13.0	9.1	8.6	9.2	9.2	8.7	11.2	8.5	5.6	13.1	10.5	7.4	11.1	7.0	12.0	12.1	10.3	10.4	7.8	4.1	10.9	11.5	7.5	8.6	<100ppm	5.3	2.0	<100ppm	<100ppm
	Mole% C_2H_4	6.3	6.8	5.1	6.9	8.2	15.0	5.4	8.4	8.6	5.1	8.7	11.2	6.4	10.7	9.7	18.6	8.1	7.5	8.7	12.2	7.5	7.5	6.2	3.2	0.9	9.1	5.6	5.0	5.4	0.6	9.7	8.1	5.7	5.0
	Mole% C_2H_6	87.8	82.2	87.0	83.0	82.5	72.0	85.5	83.0	82.2	85.7	82.6	77.6	85.1	83.7	77.2	70.9	84.5	81.4	84.3	75.8	80.4	82.3	83.4	89.0	95.0	80.0	82.9	87.5	86.0	99.4	85.0	89.9	94.3	95.0
TOP PRODUCT	FLOW ml/min 20°C1At.	850	850	800	900	800	700	1000	900	800	800	800	600	1050	950	800	700	600	600	600	600	800	750	750	900	800	750	850	850	700	1000	1050	1250	950	1050
	Mole% C_2H_2	8.0	5.4	8.3	11.3	7.3	5.7	13.4	12.0	10.3	10.5	7.7	4.5	11.2	15.0	0.7	1.6	4.0	2.4	0.1	1.7	2.4	0.5	0.8	3.0	8.6	5.8	3.0	3.7	0.4	3.8	9.4	11.8	12.5	9.4
	Mole% C_2H_4	87.1	90.3	86.3	71.4	80.1	82.3	72.8	74.6	79.3	78.0	85.6	91.7	63.3	62.9	94.0	97.3	93.5	96.4	98.6	94.8	96.9	99.4	98.5	95.5	91.0	89.5	95.0	93.5	99.6	91.3	79.5	74.8	73.3	80.0
	Mole% C_2H_6	4.9	4.3	5.4	17.3	12.6	12.0	13.8	13.4	10.4	11.5	6.7	3.8	25.5	22.1	5.3	1.1	2.5	1.2	1.3	3.5	0.7	0.1	0.7	1.5	0.4	4.7	2.0	2.8	<100ppm	4.9	11.1	13.4	14.2	10.6
REFLUX RATIO		6.9	6.9	8.1	8.1	9.2	12.1	6.9	8.1	9.2	12.1	9.2	12.1	6.9	8.1	6.9	8.1	9.2	12.1	9.2	8.1	8.1	9.2	12.1	6.9	9.2	9.2	6.9	8.1	12.1	6.1	4.7	3.7	6.1	4.7
REBOILER DUTY BTU/hr.		172.5	172.5	200.0	200.0	200.0	249.5	200.0	200.0	200.0	249.5	200.0	200.0	200.0	200.0	160.0	160.0	160.0	200.0	160.0	160.0	200.0	200.0	249.5	200.0	200.0	200.0	160.0	200.0	249.5	172.5	135.0	135.0	160.0	135.0

TABLE V.2

TERNARY DISTILLATION RUNS WITH SIDESTREAM

RUN NO.		B:30	B:31	B:32	B:33	B:34	B:36	B:38	B:39	B:40	B:41	B:42	B:43	B:44	B:45	B:46	B:47	B:50	B:51	B:52	B:53	B:54	B:55	B:56	B:57
STRIPPING PLATES		10	10	10	10	10	10	10	10	10	5	5	5	5	5	5	5	5	5	10	10	10	5	5	5
INTERMEDIATE PLATES		5	5	5	5	5	5	5	5	5	10	10	10	10	10	10	10	15	15	5	5	5	10	10	10
RECTIFYING PLATES		15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
S/S ABOVE FEED =A		A	A	A	A	A	B	B	B	B	A	A	A	A	B	B	B	A	A	B	B	B	B	B	B
FEED	FLOW ml/min 20°C.1At	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	2900	2900	2800	2800	3000	3000	3000	3000
	Mole% C_2H_2	13.5	13.3	9.0	10.0	10.0	9.1	9.7	11.5	11.5	10.2	10.2	10.2	10.2	10.5	10.5	11.9	12.2	12.2	6.2	6.2	6.2	6.2	4.0	6.2
	Mole% C_2H_4	29.4	20.4	25.0	27.8	27.8	24.3	23.2	27.8	29.8	26.8	26.8	26.8	26.8	27.5	27.5	27.7	28.6	28.6	27.7	27.7	27.7	27.5	34.0	27.5
	Mole% C_2H_6	57.1	66.3	66.0	62.2	62.2	66.6	67.1	60.7	58.7	63.0	63.0	63.0	63.0	62.0	62.0	60.4	59.2	59.2	66.1	66.1	66.1	66.3	62.0	66.3
BOTTOM PRODUCT	FLOW ml/min 20°C.1At	1500	1600	1600	1500	1500	1500	1700	1600	1600	2000	1600	1500	1500	1500	2000	1600	1800	1800	1550	1550	1500	1750	1750	1900
	Mole% C_2H_2	5.1	2.8	0.3	2.1	2.1	2.4	4.2	5.5	7.4	7.4	2.7	<100ppm	<100ppm	1.1	1.8	6.7	8.4	6.6	0.1	<100ppm	<100ppm	<100ppm	<100ppm	0.5
	Mole% C_2H_4	8.2	<100ppm	<100ppm	<100ppm	<100ppm	4.1	6.3	4.0	7.7	5.6	2.7	1.1	0.9	3.5	11.8	6.7	7.9	7.4	2.4	0.9	0.7	2.5	2.4	7.8
	Mole% C_2H_6	86.7	97.2	99.7	97.9	97.9	93.5	89.5	90.5	84.9	87.0	94.6	98.9	99.1	95.4	86.4	86.6	83.7	86.0	97.5	99.1	99.3	97.5	97.6	91.7
SIDESTREAM	FLOW ml/min 20°C.1At	700	700	700	700	800	900	600	600	600	400	650	700	800	700	200	650	400	450	600	650	500	—	—	—
	Mole% C_2H_2	34.4	31.2	31.4	20.4	30.2	23.8	30.6	32.8	28.0	28.2	33.0	25.2	31.8	29.3	6.8	31.0	32.2	32.0	26.7	28.4	0.2	—	—	—
	Mole% C_2H_4	21.4	19.4	16.5	26.6	27.0	18.3	19.1	16.9	19.0	33.7	28.2	19.8	29.0	14.7	15.3	15.0	18.3	15.6	29.3	22.6	0.7	—	—	—
	Mole% C_2H_6	44.2	49.4	52.1	53.0	42.8	57.9	50.3	50.3	53.0	38.1	38.8	55.0	39.2	56.0	77.9	54.0	49.5	52.4	44.0	49.0	99.1	—	—	—
TOP PRODUCT	FLOW ml/min 20°C.1At	800	700	700	800	700	600	700	800	800	600	750	800	700	800	800	750	700	650	650	600	1000	1250	1250	1100
	Mole% C_2H_2	8.5	9.9	3.8	8.2	5.5	1.5	6.6	6.4	5.1	1.9	4.1	4.1	2.5	2.0	3.8	3.7	4.0	4.5	2.3	0.6	11.0	14.0	9.3	12.7
	Mole% C_2H_4	83.1	80.8	91.2	85.0	92.2	97.4	88.9	89.6	90.4	97.2	94.4	90.7	95.5	97.1	93.9	94.2	93.3	92.2	95.8	99.1	75.2	68.6	83.5	72.4
	Mole% C_2H_6	8.4	9.3	5.0	6.8	2.3	1.1	4.5	4.0	4.5	0.9	1.5	5.2	2.0	0.9	2.3	2.1	2.7	3.3	1.9	0.3	13.8	17.4	7.2	14.9
REFLUX RATIO		6.9	8.1	12.1	9.2	6.9	8.1	12.1	9.2	6.9	12.1	9.2	8.1	6.9	6.9	8.1	9.2	8.1	9.2	8.1	12.1	6.1	3.8	4.7	4.7
REBOILER DUTY B.Thu/hr		160.0	160.0	249.5	200.0	128.0	160.0	249.5	200.0	160.0	200.0	200.0	200.0	160.0	160.0	200.0	200.0	160.0	160.0	160.0	200.0	166.0	143.0	166.0	143.0

APPENDIX VI.

TABLE VI. I.

ABSORPTION RUNS.

RUN No		C:1	C:2	C:3	C:4	C:5	C:6
ACETONE RATE gm.mol/min.		0.181	0.073	0.036	0.181	0.073	0.036
GAS FEED RATE ml/min 20°C 1atm		4400	4400	4400	4000	4000	4000
FEED COMPOSITION MOL %	C_2H_2	10.0	10.0	10.0	9.1	9.1	9.2.
	C_2H_4	27.7	27.7	27.7	16.3	16.3	22.7
	C_2H_6	62.3	62.3	62.3	74.6	74.6	68.1
TOP PRODUCT COMPOSITION							
MOL %	C_2H_2	100ppm	100ppm	0.8	100ppm	100ppm	300ppm
	C_2H_4	31.8	29.3	27.6	16.0	17.5	25.0
	C_2H_6	68.2	70.7	71.6	84.0	82.5	75.0
BOTTOM PRODUCT COMPOSITION							
MOL % ACETONE		78.5	72.0	62.0	77.0	74.0	63.5
	C_2H_2	8.2	17.0	29.6	8.5	15.5	27.2
	C_2H_4	4.1	1.5	1.1	2.5	1.4	2.7
	C_2H_6	9.2	9.5	7.3	12.0	9.1	6.6
FLOW TOP PRODUCT ml./min 20°C 1 atm.		3200	3700	3800	2900	3300	3500
T_{TOP} °C		-80 ± 2	-80 ± 2	-80 ± 2	-80 ± 2	-80 ± 2	-80 ± 2
T_{BASE}°C		-75 ± 1	-75 ± 1	-75 ± 1	-75 ± 3	-75 ± 3	-75 ± 3

TABLE VI.2.

REBOILED ABSORPTION RUNS.

RUN No.		C:7	C:8	C:9
ACETONE RATE gm.mol/min.		0.181	0.073	0.036
GAS FEED RATE ml/min 20°C.latn		4000	4000	4000
FEED COMPOSITION				
MOL %	C_2H_2	9.5	9.5	9.5
	C_2H_4	17.1	17.1	17.1
	C_2H_6	73.4	73.4	73.4
TOP PRODUCT COMPOSITION				
MOL%	C_2H_2	100ppm	2%	5%
	C_2H_4		VARIABLE	
	C_2H_6			
BOTTOM PRODUCT COMPOSITION				
MOL%	ACETONE	86.0	88.0	92.0
	C_2H_2	8.8	5.6	5.8
	C_2H_4	0.5	0.9	0.2
	C_2H_6	4.7	5.5	2.0
FLOW TOP PRODUCT ml/min 20°C latn		NO RECORDED VALUE.		
	T_{TOP}°C	-80 ± 2	-80 ± 2	-80 ± 2
	T_{BASE}°C	-55	-30	-10
REBOILER HEAT LOAD BTU/hr.		57.1	57.1	57.1

APPENDIX VII

Section VII.1

Initial estimate of vapour composition profile

From the Fenske[24] equation for total reflux

$$\frac{y_{i,p}}{y_{i,1}} = \alpha_i^{p-1} \frac{y_{r,p}}{y_{r,1}} \qquad (1:VII)$$

where α is the relative volatility of component i with respect to a reference component r, assumed constant.

Summing (1:VII) for all components we have:-

$$\Sigma_i y_{i,p} = 1 = \frac{y_{r,p}}{y_{r,1}} \Sigma_i \alpha_i^{p-1} y_{i,1}$$

whence: $$y_{i,p} = \frac{\alpha_i^{p-1} y_{i,1}}{\Sigma_i \alpha_i^{p-1} y_{i,1}} \qquad (2:VII)$$

Also $$K_{i,p} = \alpha_{i,p} K_{r,p} = \alpha_i \Sigma_i \frac{y_{i,p}}{\alpha_i} = \frac{\alpha_i \Sigma_i \alpha_i^{p-2} y_{i,1}}{\Sigma_i \alpha_i^{p-1} y_{i,1}} \qquad (3:VII)$$

Division of (2:VII) by (3:VII) gives for theoretical plates:-

$$x_{i,p} = \frac{\alpha_i^{p-2} y_{i,1}}{\Sigma_i \alpha_i^{p-2} y_{i,1}} \qquad (4:VII)$$

An overall material balance for component i gives:-

$$\Sigma_p f_{i,p} = \Sigma_p P_{v,p} y_{i,p} + \Sigma_p P_{L,p} x_{i,p} \qquad (5:VII)$$

where P_{vp} and P_{Lp} are the flow rates of liquid and vapour product from plate p, respectively.

If we write $$S_p = \Sigma_i \alpha_i^{p} y_{i,1} \qquad (6:VII)$$

Then from (2:VII), (4:VII) and (5:VII)

$$\sum_p f_{i,p} = \sum_p \left(\frac{P_{v,p}\alpha_i^{p-1}}{S_{p-1}} + \frac{P_{L,p}\alpha_i^{p-2}}{S_{p-2}} \right) y_{i,1}$$

or:-

$$\frac{\sum_p f_{i,p}}{y_{i,1}} = \left\{ \sum_p \frac{i}{S_{p-1}}^{p-1} (P_{v,p} + P_{L,p} + 1) \right\} + \frac{P_{L,1}}{\alpha_i \sum_i \frac{y_{i,1}}{\alpha_i}} \qquad (7:VII)$$

The equations developed above are used to generate the initial estimate of the vapour composition profile in the following manner.

Initially the mean feed composition is calculated and the corresponding dew-point and equilibrium constants are obtained from the respective polynomials. In the expressions derived above only the ratios of the relative volatilities are involved and therefore the relative volatilities in (7:VII) may be replaced by the calculated equilibrium constants in carrying out the arithmetic. The mean feed composition is assumed to be equal to the vapour composition leaving the reboiler and Sp is computed for all plates from (6:VII). A new estimate of $y_{i,1}$ is then obtained by evaluating (7:VII) and the calculations are repeated until the solution converges. The vapour composition profile for the whole column is then generated from:-

$$y_{ip} = \frac{\alpha_i y_{ip-1}}{\sum_i \alpha_i y_{i,p-1}} \qquad -(8:VII)$$

MULTI-COMPONENT DISTILLATION COMPUTER PROGRAMME

```
title
 m/c distillation davies chem.eng. icst 26/7/63 u883q

 routine 1
          ternary dewpoint determination
 ø6(10320)e0,s
 m=0
 i=0(1)3
 l=øint pt(em+0.1)
 x=y1-e(m+1)
 y=y2-e(m+2)
 m=m+ 3
 j=0(1)1
 r'=1-j
 k=0(1)r'
 ck=em
 m=m+1
 repeat
 bj=øpoly(x)c0,r'
 repeat
 gi=øpoly(y)b0,1
 jump3,i=0
 jump1,gi≥0
 gi=0.0000000001
 1)jump2,3.01≥gi
 gi=3.00
 2)xi=yi/gi
 3)repeat
 u=g0
 x0=x1+x2+x3
 i=1(1)3
 xi=xi/x0
 repeat
 return
 psa
 **

 routine 2
          calculation of enthalpies
 ø6(10000)e0,t
 m=0

          liquid enthalpy
 h=0
 i=1(1)r
```

```
jumpdown1
h=h+xib(i-1)
repeat
          vapour enthalpy
h'=0
i=1(1)r
jumpdown1
h'=h'+yib(i-1)
repeat
return
          partial molar enthalpy
1)1=øint pt(em+0.1)
m=m+1
j=0(1)1
cj=em
m=m+1
repeat
b(i-1)=øpoly(u)c0,1
return
psa
**

routine300
          set first row
1)set((e0,e1))=0
set((e2,e3))=b1
set((e4,e5))=c1
set((e6,e7))=y1
i=2(1)n
          collect next row
set((e8,e9))=ai
set((e10,e11))=bi
set((e12,e13))=ci
set((e14,e15))=yi
jump5,i≠n
set((e12,e13))=0
          test need to interchange rows
5)a=ømod(e2)
b=ømod(e8)
jump2,a≥b
          interchange rows
j=0(1)7
ej=e(j+8)
e(j+8)=e(j+2)
repeat
((e14,e15))=((e12,e13))
set((e12,e13))=0
jump3
          shift pivotal row along to left
2)j=0(1)3
ej=e(j+2)
repeat
set((e4,e5))=0
```

```
          eliminati on form multiplier.
3)((e0,e1))=1/((e0,e1))
((e8,e9))=((e0,e1))*((e8,e9))
          combine equati ons
j=2(2)6
jump4,ej=0
((a,b))=((e8,e9))*((ej,e(j+1)))
((e(j+8),e(j+9)))=((e(j+8),e(j+9)))-((a,b))
4)repeat
          plant pivotal row
a(i-1)=e0
b(i-1)=e2
c(i-1)=e4
y(i-1)=e6
          move reduced equati ons up one row
j=2(1)7
ej=e(j+8)
repeat
set((e0,e1))=0
repeat
          back substitution
((yn,e0))=((e14,e15))/((e10,e11))
y(n-1)=-b(n-1)yn+y(n-1)
y(n-1)=a(n-1)y(n-1)
i=n-2
i=i(-1)1
yi=-ciy(i+2)-biy(i+1)+yi
yi=aiyi
repeat
return
psa
**

chapter1
b→18
c→6
e→320
x→17
y→17
g→17
u→9
z→64
          bring down product flow-rates
1)jumpdown(r1)
e0=0
p=1(1)n
k=2p-1
ø6(pk'-2r-5)ek,2
e0=e0+ek+e(k+1)
repeat
k=2n-1'
ek=f-e0
across9/0
```

```
            compute liquid compositions equilibrium and thermal data
4)v=0
c=0
p=1(1)n
ϕ6(pk'-k')zl,j'
i=1(1)r
j=r+i
jump5,p=1
jump5,p=n
yi=ϕdivide(eyi-yi+zj,e)
jump6
5)yi=zj
6)repeat
jumpdown(r1)
i=1(1)r
j=r+i
yi=zj
repeat
jumpdown(r2)
i=1(1)r
j=2r+i
zi=xi
zj=gi
repeat
z(j+1)=u
z(j+2)=h
z(j+3)=h'
ϕ7(pk'-k')zl,j
            compute flow-rates
z(j+4)=0
jump7,p=1
a=c-h
b=u2-h
w'=u4+u6
v'=ϕdivide(av-bw'-hul0+uδ+u9,u3-h)
z(j+4)=v'+w'-v-ul0
u5=v'-u7
ϕ7(pk'-7r-20)ul,5
v=u5
c=u3
7)i=1(1)10
j=3r+i
ui=zj
repeat
repeat
            compute product-rate and heat-transfer for last stage
u5=0
v'=v+ul0-u4
j=7-1'
uj=v'-u(1'+6)
w'=u4+u6
uδ=w'u2+u7u3-vc
ϕ7(nk'-2r-10)ul,8
jump8,p'=0
jump8,d>y
```

```
across1/2
8)across1/3
psa
close

chapter2
a→100
b→100
c→100
y→100
e→64
double length
11)w=2
1)u'=wu'
y=0
w=0.5
l=2r
p=1(1)n
cp=0
repeat
ø7(11000)c1,n
k=1(1)r
          compute matrix elements
m=r+k
q=2r+k+10
p=1(1)n
ø6(pk'-k'+r)e1,j'
w'=e(1+4)+e(1+6)
yp=u'ek+eq
jump2,p=1
jump2,p=n
g=ødivide(1,eem)
jump3
2)g=1/em
3)jump4,p=1
c(p-1)=-ge(1+4)
jump5,p=n
b(p-1)=ec(p-1)-c(p-1)+b(p-1)
ap=gew'-gw'+ap
4)a(p+1)=-e(1+5)
5)bp=e(1+5)+e(1+7)+gw'+u'
repeat
          compute new vapour compositions and adjust step-length
jumpdown(r300)
ø6(11000)c1,n
p=1(1)n
jump6,yp>0
yp=0.000000001
6)cp=cp+yp
jump7,k≠r
e'=ømod(cp-1)
jump11,e'>0.3
jump7,0.1>e'
w=1
```

```
7)repeat
Ø7(11000)c1,n
          scale and store vapour compositions
p=1(1)n
Ø6(pk'-k')e1,1
ek=yp
jump9,k≠r
i=1(1)r
j=r+i
ei=ei/cp
y'=Ødivide(ej-ei,ei)
y'=Ømod(y')
jump8,y≥y'
y=y'
8)ej=ei
repeat
9)Ø7(pk'-k')e1,1
repeat
repeat
n'=n'+1
p'=p'+1
jump10,p'≠m'
p'=0
10)across4/1
psa
close

chapter3
1)newline
caption
distillation column
newline
newline
caption
no. of components
t'=r
q'=70
jumpdown(r804/2)
caption
no. of stages
t'=n
jumpdown(r804/2)
caption
plate efficiency
z'=e
q'=7
r'=3
s'=4
jumpdown(r804/1)
jump2,n'=0
caption
iteration no.
t'=n'
q'=82
```

```
jumpdown(r804/2)
caption
forcing parameter=
z'=u'
q'=50
jumpdown(r804/1)
caption
maximum error=
z'=y
q'=51
jumpdown(r804/1)
2)across1/4
psa
close

chapter4
z→100
1)p=1(1)n
newline
caption
stage no.
t'=p
q'=82
jumpdown(r804/2)
caption
                          feed              liquid              vapour
newline
caption
compositions
newline
caption
   component no.
ø6(pk'-k')z1,k'
i=1(1)r
t'=i
q'=17
r'=2
s'=0
jumpdown(r804/2)
j=4r+10+i
z'=zj
jumpdown50
q'=37
z'=zi
jumpdown(r804/1)
j=r+i
q'=38
z'=zj
jumpdown(r804/1)
caption

repeat
newline
caption
```

```
internal flows
j=3r
z'=z(j+4)
q'=33
jumpdown(r804/1)
z'=z(j+5)
q'=38
jumpdown(r804/1)
jump2,z(j+10)≠0
jump2,z(j+6)≠0
jump2,z(j+7)≠0
jump3
2)caption
feed/product
newline
caption
     flow rate
z'=z(j+10)
jumpdown50
z'=z(j+6)
jumpdown50
z'=z(j+7)
jumpdown50
newline
caption
     heat content
y'=z(j+10)
z'=z(j+9)
jumpdown49
y'=z(j+6)
z'=z(j+6)z(j+2)
jumpdown49
y'=z(j+7)
z'=z(j+7)z(j+3)
jumpdown49
newline
3)newline
jump4,z(j+8)=0
caption
stage heat input
z'=z(j+8)
q'=36
jumpdown(r804/1)
4)caption
stage temperature
z'=z(j+1)
q'=39
jumpdown(r804/1)
repeat
jump5,d>y
jump5,n'>30
across1/2
5)o=o-1
jump6,o=0
```

```
acrossl/0
6)end
          routine for skipping zero values
49)jump5l,y'=0
50)jump5l,z'=0
q'=37
jumpdown(r804/1)
jump52
5l)caption

52)return
psa
close

chapter0
variablesl
read(o)
1)read(r)
          read equilibrium data into store
s=0
i=0(1)r
read(1)
es=1
s=s+1
k=1+3
k=Øint pt(0.5k1+3.1)
j=1(1)k
read(es)
s=s+1
repeat
repeat
Ø7(10320)e0,s
          read enthalpy data into store
t=0
k=2r
i=1(1)k
read(1)
et=1
t=t+ 1
j=0(1)1
read(et)
t=t+1
repeat
repeat
Ø7(10000)e0,t
          read column specifications
read(m')
read(d)
read(n)
read(e)
i'=2r+10
j'=i'+r
k'=5r+10
i=0(1)r
```

```
xi=0
repeat
k=1
2)read(p)
jump3,p=k
          set unspecified plate data to zero
i=1(1)i'
zi=0
repeat
l=p-1
i=k(1)l
ø7(ik'-k'+3r)zl,i'
repeat
          read specified plate data
3)jump4,p=n
read(z8)
read(z6)
read(z7)
jump5
4)z6=0
z7=0
read(l')
read(z(l'+6))
5)read(t')
jump6,t'=1
jump7,t'=2
          set unspecified feed to zero
z9=0
zl0=0
i=1(1)r
z(i+10)=0
l=i+r+10
zl=0
repeat
jump8
          read feed in partial quantities
6)zl0=0
i=1(1)r
read(z(i+10))
xi=xi+z(i+10)
zl0=zl0+z(i+10)
repeat
x0=x0+zl0
i=1(1)r
l=i+r+10
zl=z(i+10)/zl0
repeat
read(z9)
jump8
          read feed in mole-fractions
7)read(zl0)
x0=x0+zl0
i=1(1)r
l=i+r+10
```

```
read(z1)
z(i+10)=z1z10
xi=xi+z(i+10)
repeat
read(z9)
z9=z9z10
8)Ø7(pk'-k'+3r)z1,i'
k=p+1
jump2,p≠n
          compute mean vapour composition
i=1(1)r
yi=xi/x0
zi=xi
repeat
f=x0
across1/1
          compute initial vapour compositions
9)b=0
i=1(1)r
b=b+yi/gi
repeat
b0=0
i=1(1)r
xi=Ødivide(e1,bgi)
xi=xi+e2+e3
bi=gi
b0=b0+biyi
repeat
p=3(1)n
k=2p-2
e0=ek+e(k+1)
b=b0
b0=0
i=1(1)r
xi=e0bi/b+xi
bi=bigi
b0=b0+biyi
repeat
repeat
x=0
i=1(1)r
xi=zi/xi
x=x+xi
repeat
y=0
i=1(1)r
xi=xi/x
check(xi,yi,0.01,10)
y=1
10)yi=xi
repeat
jump9,y=1
Ø7(r)y1,r
i=1(1)r
```

```
y=y+giyi
repeat
p=2(1)n
x=0
i=1(1)r
yi=giyi/y
x=x+giyi
repeat
y=x
ø7(pk'-k'+r)y1,r
repeat
y=1
n'=0
p'=0
w=1
u'=0.25
across4/1
psa
close
→
```

PROGRAMME FOLLOWED BY DATA TAPE DESCRIBED OVERLEAF

Section VII.3.

The data tape for the above programme is prepared by inserting numerical values against the items in the same sequence as given below.

1. o : Number of sets of data to be computed. If this value exceeds 1 then o-1 etc. should be omitted from subsequent sections of the data tape.

2. r : Number of components maximum No. 18.

3. Equilibrium data, fitted to polynomials by library programme R.A.E.194/A, and read in the following order:

   (a) $T = f(y_1', y_2')$

   (b) $K_1 = f(y_1', y_2')$

   (c) $K_2 = f(y_1', y_2')$

   (d) $K_3 = f(y_1', y_2')$

   For each polynomial the order of the terms is:

   (a) Degree of polynomial, 1.

   (b) $\bar{y}_1$ mean value of data used for correlation.

   (c) $\bar{y}_2$ mean value of data used for correlation.

   (d) Coefficients of polynomials in order of the print-out of R.A.E.194/A.

4. Enthalpy data. The polynomials for the liquid enthalpies are read in the following order:

(a) Degree of polynomial (maximum 4).

(b) Coefficients a_{10}, a_{11}, a_{12} etc. for component 1.

When the polynomials for each component in the liquid phase have been read the procedure is repeated for the enthalpies of each component in the vapour phase.

5. Print-out indicator m': If m' = 5, say, then the results are only printed out for the 5th, 10th, 15th etc. iterations.

6. Allowable fractional error in vapour composition d: After each calculation cycle the maximum difference in vapour composition for all components and stages between the present and preceding iterations is calculated and compared with the specification value, d. If the difference is greater than the allowable value the calculations are continued, if not they are stopped.

7. Total number of stages (maximum 100)n.

8. Plate efficiency e.

Then for each stage with non-zero feeds or products:-

9. Stage number - numbering commences at reboiler, value 1.

10. Heat input (indirect usually only concerned with reboiler heat duty).

11. Liquid product-rate.

12. Vapour product-rate.

13. Feed indicator:- 0 no feed.
1 given as partial quantities f_i
2 given as total feed, F : then mole fractions $Z_{i,f}$.

If there is a feed:-

14. Either partial quantities or feed-rate then mole fractions.

15. Either feed total enthalpy or feed specific enthalpy.

For final stage (even if specified product is zero).

16. Stage number n.

17. Product specification indicator 0 if liquid product is specified.

1 if vapour product is specified.

18. Specified product-rate (even if zero).

19. 20. 21. as 13. 14. 15. for other stages.

If o > 1 leave blank tape and restart with No. 2 i.e. number of components.

if o = 1 data tape finishes after 21 with →