The concentration of Nitric Acid and its relation to Extractive Distillation.

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SUMMARY

Part I

1. Vapour-liquid equilibria in the systems HNO₃ - H₂O and H₂SO₄ - HNO₃ - H₂O have been examined.
2. Vapour-liquid equilibria in the system Mg(NO₃)₂ - HNO₃ - H₂O have been briefly examined.

Part II

The concentration of nitric acid by means of concentrated sulphuric acid in a packed column has been examined.

1. Theoretical plate by plate calculations on concentration columns have been carried out.
2. Ideal conditions in a concentration column have thus been compared with the actual results.
3. The position of the W.N.A. feed (in the cold) to the column has been examined.
4. Heat balances have been carried out at the W.N.A. feed points.
5. The use of reflux in a concentration column, operated with combined feed, has been considered.
6. The effect of preheating the W.N.A. feed has been discussed.
7. H.T.U.s. have been evaluated in the column and an attempt made to calculate the individual liquid and gas film coefficients.
Introduction.

The first great demand for highly concentrated nitric acid originated in 1862 with the discovery of nitroglycerine, and with the later developments of nitrated products.

At that time highly concentrated nitric acid was obtained by treating sodium nitrate with concentrated sulphuric acid. This method, which dates back to the sixteenth century, was employed up to comparatively recent times. At the present day, nitric acid is mainly produced from the oxidation of ammonia, and absorption of the oxides of nitrogen in water which results in the production of an acid of 50 – 60\% concentration.

Up to the time of the first World War, dilute nitric acid solutions were concentrated by two methods –

(1) by the neutralisation of the acid with soda ash, evaporation and recovery as a nitrate, from which concentrated nitric acid was liberated by treatment with concentrated sulphuric acid.

(2) by distillation.

The first method involves the consumption of large quantities of materials, and, when compared to distillation methods, the cost becomes economically prohibitive. From about 1918 onwards, dilute nitric acid solutions have, therefore, been concentrated almost solely by distillation methods.

Nitric /
Nitric acid forms a constant boiling mixture with water at approximately 68% nitric acid by weight, so that the limit of concentration of a dilute solution by ordinary fractionation is 68%. Distillation in the presence of a suitable third substance, however, alters the composition of the vapour phase and the azeotrope may be broken. The third substance normally used is concentrated sulphuric acid, and its presence in the liquid phase increases the volatility of the nitric acid relative to the water so that the concentration of nitric acid in the vapour increases.

The best known and most efficient of the original methods for concentrating nitric acid are those of Pauling and Zeisberg.

In the Pauling method, the concentration is accomplished by passing weak nitric acid "mixed with a dehydrating agent, against a countercurrent stream of hot gaseous medium composed largely of steam".

Zeisberg claims that concentrated nitric acid may be obtained by subjecting a mixture of nitric and sulphuric acids, "containing not less than 64% sulphuric acid and from 3-25% of nitric acid, to a hot gaseous current".

The original type of tower used in the concentration process consisted of a stoneware lined column, filled with a contact mass, down which the mixed acids flowed and up which steam was blown.

A review of the patent literature shows that a vast amount has been published on the concentration process, but most
most of it is concerned with modifications and improvements to the above original plant.

(3) Probably the most important is an American design, in which the liquid flowing down the column is heated at an intermediate point by external means. This will reduce the amount of steam required, and also the amount of concentrated sulphuric acid required. It will, however, complicate the construction of the plant.

Another suggestion is that the mixture of dilute nitric acid and dehydrating agent be heated in a series of externally heated, horizontal pipes, the concentrated nitric acid vapour being obtained from the top pipe.

There are many other modifications.

In recent years, bubble cap columns in ferro-silicon have been adopted for concentration columns in many countries.

(5)(6) An entirely different method for concentrating dilute nitric solutions has been developed in recent years on the Continent — mainly in Germany — in which, a mixture of dilute nitric acid and nitrogen tetroxide is treated with oxygen under pressure.

Both in this country and in America, however, it would appear that the main method for concentrating nitric acid is distillation in the presence of concentrated sulphuric acid, using a simple packed tower, or bubble cap column, into the top of which the concentrated sulphuric and weak nitric acids are fed, and into the bottom of which steam is blown.
Most plants use open steam heating but some use external heating with steam or molten metal, in order to economise in the use of sulphuric acid. Apparently, however, external heating plants have mainly been failures.
Separate feeding of the acids into the column is normally used, so that the heat of mixing is developed inside the tower. When the acids are premixed, the mixture is usually preheated by means of the hot dilute sulphuric acid leaving the bottom of the column.

The column is usually operated so that the dilute sulphuric acid (W.O.V.) leaving the bottom of the column has a concentration of 65 - 70%, and has a very low nitric acid content (approximately 0.01%) in order to prevent corrosion difficulties in the sulphuric acid concentration. The sulphuric to nitric acid ratio in the feeds is usually about 2.5 to 3 or higher.

The patent literature contains suggestions that the weak nitric acid (W.N.A.) be fed in at a lower point than the concentrated sulphuric acid (C.O.V.), in order that the vapours should have a final scrubbing with the C.O.V. (7),(8),(9) and (10) that reflux be added to the column though this latter suggestion does not seem to have received any attention. In the main, the acids are both fed at the top of the column.

Other Dehydrating Agents

Sulphuric acid is the dehydrating agent almost universally used in the concentration process, but other substances have been suggested. (11)

Boetters proposed as dehydrating agents, salts which form hydrates, such as calcium and magnesium chlorides, sodium and /
and calcium sulphates, and various nitrates. Creighton and Smith (12) studied the effect of potassium acid sulphate, and of sulphuric acid, on dilute solutions of nitric acid. They found that with the addition of potassium hydrogen sulphate, the maximum boiling point of the nitric acid-water mixtures was raised, but the composition of the mixture of maximum boiling point was unchanged, indicating that the composition of the equilibrium vapours was unchanged, and that potassium hydrogen sulphate would be of no use in concentrating nitric acid solutions.

Frischer (13) proposed the use of concentrated phosphoric, sulphuric or arsenic acids, or their mixtures and solutions of salts not affected by nitric acid.

A countercurrent stream of phosphorus pentoxides has been used to distill off strong nitric vapours in a packed column, the nitric acid being vaporised by the heat of hydration of the pentoxide.

Sulphur trioxide obtained by heating oleum, and fed into the bottom of the column, has been used in the same way (14), (15). A recent American patent (16) indicates that magnesium nitrate is at present being used instead of sulphuric acid in the concentration process. The weak nitric acid solution is fractionally distilled with a 76% solution of magnesium nitrate, the product containing the major part of the nitric acid as 90 - 98% acid. The still bottoms is distilled under reduced pressure until it is free of the remaining nitric acid.
acid, and until the residue contains 78% magnesium nitrate, the weak acid so obtained being then concentrated to about 64% by fractionation, and then further concentrated by the use of magnesium nitrate.

In general, however, sulphuric acid is still being used because of its ready availability, low cost and the existence, generally, of sulphuric acid concentration plants for the concentration of spent acid, on the sites of nitric acid concentration plants.

Very little has been published which makes any attempt to analyse the actual distillation in the concentration process from a chemical engineering point of view. Because of this lack of information of a scientific nature, it could probably be said that the concentration of nitric acid is largely a "traditionally empirical" process.

(18) Gallo investigated the preliminary concentration of weak nitric acid solutions with the object of economising in the use of sulphuric acid. He showed that it was possible to "preconcentrate" the weak nitric acid up to about 65% by fractionation without the use of sulphuric acid, the 65% acid then being "superconcentrated" with sulphuric acid.

(19) Carpenter and Babor also investigated the "preconcentration" to 55 - 65%, but point out that it has proved more practical to add the dehydrating agent right away to the dilute solution.
It seems that "preconcentration" without the use of a third substance is now being used in connection with the use of magnesium nitrate in the concentration process. (20)

Sillick describes methods for predicting the operation of columns for fractionating the mixture water-nitric acid-sulphuric acid when external heating is used without the use of open steam. He points out that it is impossible by simple fractionation to separate continuously 95% nitric acid from a ternary mixture and remove less than 70% sulphuric acid at the bottom of the column.

(21)

Stephenson describes a partly graphical method applicable to denitrating columns - which are essentially similar to concentration columns, with the acid feeds combined before entering - for determining:

(a) the possibility of obtaining a given product from a given strength of feed.

(b) the heat efficiency of a denitrating column

(c) the possibility of denitrating successfully a given feed.

No other method of examination of denitration or concentration columns appears to have been published. (22)

In an unpublished paper, Professor J. Cathala discusses at some length theoretical and experimental investigations on the nitric acid concentration process. He has worked out ideal mass and thermal balances with external and internal steam heating and discusses the influence of various /
various factors on the cost of concentration. He points out that to be efficient thermally the plant should operate with the weakest W.O.V. compatible with the desired C.N.A. to be produced, and points out that the column performance is accurately predicted by means of the sulphuric to nitric acid ratio, and by the strength of the W.O.V.

He gives a review of theoretical considerations affecting the separation of nitric acid and water in the presence of sulphuric acid and concludes that the columns should be operated with split feed - i.e. with the W.N.A. fed in at a lower point than the C.O.V. feed.

Experimental results were obtained on a glass column and on actual plants, operated with split feed, and information was obtained about temperature conditions inside the column, on the location of the W.N.A. feed and on the introduction of multiple W.N.A. feed to the column.

He points out that effective acid ratios as low as 1.6 in external heating stills and 1.7 in live steam plants are compatible with the production of nitric acid of nearly 100% concentration, and that W.O.V. as low as 53 - 55% was obtained in the case of the live steam plant when operated with split feed.
Extractive distillation was only developed on a large scale during the recent war when it was employed for the separation of toluene from associated hydrocarbons using phenol as solvent and for separating butadiene from associated butenes.

It is applied to systems which exhibit azotropism, or in which the boiling points of the components are not far apart. The mixture containing the two components to be separated is fed at some intermediate point in the fractionating column and a high boiling relatively non-volatile "solvent" is fed near the top. The presence of the solvent at all points below the solvent feed alters the relative volatilities in such a way that the concentration of the required component in the vapour increases as it passes up the column and it is effectively separated.

It may be said that extractive distillation depends on the increase in non-ideality in already non-ideal solutions. The system $H_2SO_4 - HNO_3 - H_2O$ is very far from an ideal one, and the concentration of nitric acid by distillation in the presence of sulphuric acid may be regarded as an extreme case of extractive distillation.

In the general case the solvent is obtained from the bottom of the column mixed with the other component of the feed, from which it is separated and re-introduced to the tower.
The length of column above the solvent feed serves to fractionate the solvent out of the vapour and its length will vary according to the volatility of the solvent.

The similarity of the process to the nitric acid concentration process can be seen at once. The use of sulphuric acid is exactly similar to the use of a "solvent" in extractive distillation.

It is apparently universal procedure to feed the C.O.V. and W.N.A. into the top of the column, though it has been pointed out above that suggestions have been made that the feeds.
feeds be split, which would make the concentration process similar to extractive distillation procedure.

When both acids are fed into the top, the very large heats of mixing are developed at the top of the column, where, as the concentration of water is high, it will probably cause vaporisation of water and consequent weakening of the product. By lowering the position of the W.N.A. feed to the column, so that the feeding arrangements correspond to those of extractive distillation, the heat of mixing will be developed at a lower point in the column. Moreover, the rectifying effect of the vapours above the W.N.A. feed meeting the strong sulphuric acid, should, presumably, reduce the amount of sulphuric acid required for a given concentration.

Since the economy of the process depends to a large extent on the amount of sulphuric acid used, the cost of concentration of the nitric acid should be decreased with the use of split feed.

It, therefore, seems worthwhile to consider and examine the concentration of nitric acid by sulphuric acid with regard to its relation to extractive distillation.

This might have two consequences:

(1) The application of such modern ideas and methods of calculation might lead to fresh developments in the concentration process.

(2) The study of this ternary system where conditions are extremely non-ideal might throw light on the more normal process of extractive distillation.
Vapour - Liquid Equilibria

(1) In the binary system HNO₃ - H₂O.

Carpenter and Babor, Berl and Saenger and Pascal have examined the vapour-liquid equilibria at the boiling point. Of the three Carpenter and Babors' data are probably the best, as they took greater care to eliminate fractionation in their apparatus than the others. It is pointed out by Carpenter and Babor that Pascal's values are very erratic.

The partial pressures of nitric acid over nitric acid solutions at temperatures lower than the boiling point have been investigated by many workers. Burdick and Freed calculated the partial pressure of nitric acid over acid solutions, from the vapour absorbed by an air stream blown through the acid. They covered the range 24% to 70% nitric acid at 25°C, 50°C and 75°C. Sproesser and Taylor covered the same range as the latter workers using the same method.

Klemenc measured the partial pressure of nitric acid over acids of 10% - 100% strength mainly at 12.5°C. Saposchnikow gives some data at 15°C ranging from 65 - 98% acid.

Taylor has collected and re-calculated all the above data. Wilson and Miles point out that Taylor's values do not agree with values obtained by Berl and Saenger and Klemenc and Rupp who deal mainly with 100% nitric acid.

Wilson and Miles found the partial pressures of nitric acid.
acid over solutions from 50% to 100% in strength at 20° and 0°.

Forsyth and Giauque have examined the data of many of
the above workers by means of the Gibbs-Duhem equation, and
have shown quite large errors in much of the data.

The data obtained at the boiling point in the binary
system by the three workers mentioned above are in the form-
weight per cent. nitric acid in the liquid in equilibrium
with weight per cent. nitric acid in the vapour. It is
probably worthy of note that a set of data is given in The
Chemical Engineers Handbook (Perry) for the binary HNO₃ - H₂O
system, in the more usual form of mol fraction nitric acid in
the liquid in equilibrium with mol fraction nitric acid in
the vapour. It is supposed to have been calculated from
Carpenter and Babors' data in the International Critical
Tables, but the points given in no way form a smooth curve.

(2) The Ternary System H₂SO₄ - HNO₃ - H₂O

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Vapour-liquid equilibria at the boiling point in the
ternary system have been examined by Carpenter and Babor
by Berl and Sambrook and by Pascal.

Saposchukow investigated the partial pressures of
nitric acid above ternary solutions containing increasing
amounts of sulphuric acid at 25°C. Pascal, besides
obtaining vapour-liquid equilibrium data at the boiling point
at standard atmospheric pressure, also obtained data at total
pressures /
pressures of 300, 440, 550 and 760 m.m. of mercury.

Of the data on the ternary system those of Carpenter and Babor are probably the most accurate and most extensive, as, again, there was less danger of fractionation in their apparatus.

None of the workers found the composition of a vapour in equilibrium with a particular liquid directly, but took successive fractions of distillate from a batch of liquid in the equilibrium still, and subsequently calculated the equilibrium data. This seems to involve much smoothing of curves and extensive interpolation, with the possible consequent introduction of errors.

Carpenter and Babor compare their data with those of Berl and Samtleben and there are quite considerable differences. Carpenter and Babor's method of evaluation of the equilibrium vapour includes the plotting of the ratio of $\frac{H_2SO_4}{H_2SO_4 + H_2O}$ against the ratio of $\frac{HNO_3}{HNO_3 + H_2O}$ in the liquid in the still as distillation proceeds, the vapour in equilibrium with a particular liquid being evaluated from these curves, making use of the fact that the sulphuric acid does not distill over. Such a set of curves, given by Carpenter and Babor, is reproduced here to illustrate the differences between the data of the latter workers and those of Berl and Samtleben. (The solid curves are those of Carpenter and Babor and the dotted curves those of Berl and Samtleben.)
The International Critical Tables give all the data on the ternary system in the form of a triangular diagram, which illustrates the discrepancies in the different sets of data. The triangular co-ordinates, however, do not bring out the differences as well as rectangular co-ordinates.

Further, Cathala in the unpublished paper already mentioned, and in a private communication has pointed out that the vapour-liquid equilibrium data available are unreliable in the ranges encountered in concentration columns, the result of excessive interpolation.

It was considered, therefore, worthwhile to examine the vapour liquid equilibria in this system.
Object

The object of this work is thus:

1. To examine the vapour-liquid equilibria in the system H₂SO₄ - HNO₃ - H₂O

2. To consider the concentration of nitric acid with respect to its relation to extractive distillation.
PART I
PART I.

Experimental

Vapour - Liquid Equilibria in the System $\text{H}_2\text{SO}_4 - \text{HNO}_3 - \text{H}_2\text{O}$

Apparatus

Previous Workers' Apparatus

A diagram of the apparatus used by Carpenter and Babor (a), by Pascal (b) and by Berl and Sauterendon (c) in their work on this system is shown.

Carpenter and Babor immersed the distilling flask and delivery tube in a well-stirred bath of calcium chloride solution.
solution. Pascal and Berl and Santleben both used an air bath heated by means of a bunsen burner. Two thermometers are suspended in the neck of the flask in Pascal's apparatus, while Berl and Santleben use one. Carpenter and Babor have left out the thermometer in their apparatus.

Because of the use of a liquid bath instead of an air bath, and by the elimination of thermometers from the neck of the distilling flask, Carpenter and Babor seem to have taken greater precautions than the others against the danger of fractionation in their apparatus. They point out that since they have taken successive fractions of distillate from the one batch of liquid in the still, any fractionation error would be cumulative and, therefore, must be avoided.

**Modern Methods and Apparatus employed in Equilibrium Distillation.**

In all methods nowadays the composition of a vapour in equilibrium with a liquid is found directly. This is most usually effected in a recycling type of apparatus, in which the vapour evolved from the boiling liquid in the still is condensed into a condensate trap, from which it is recycled to the boiler until equilibrium is attained.

(36)

Fowler gives a complete review of equilibrium distillation and indicates the great advances made in technique. A great variety of equilibrium stills have been proposed for the examination of vapour-liquid equilibria, all of which are reputed to have their advantages, though it would seem /
seem that no one type of apparatus is entirely free from the possibility of error.

The greatest difficulties that have to be encountered in equilibrium distillation are:

(1) The danger of fractionation.

Two main methods have been adopted to prevent fractionation in equilibrium stills.

(a) Jacketing of the vapour line to the still head by the same vapour Gillespie [37] points out that this method when used alone does not seem to be fully effective in the prevention of fractionation especially when dealing with high boiling liquids.

(b) External heating of the vapour line to compensate for heat losses from the upper parts of the still.

Cary and Lewis [38], using an Othmer still, surrounded the whole boiler with an accurately heated jacket. Their results on the ethanol-water system agree closely with those of Jones, Schoenborn and Colburn [39] who used an entirely different type of still in which the vapour line was heated electrically. It would seem that this method of supplying heat externally to prevent heat losses and subsequent fractionation can give concordant results in different apparatus provided suitable precautions are taken.

In the system $\text{H}_2\text{SO}_4 - \text{HNO}_3 - \text{H}_2\text{O}$ vapours from boiling solutions apparently consist wholly of nitric acid and water (and in some regions, oxides of nitrogen), except in regions of
of high sulphuric concentration in the liquid when sulphuric acid appears in the vapour.

The boiling point curve of the binary $\text{HNO}_3 - \text{H}_2\text{O}$ system is as shown.

![Boiling Point Curve](image)

It is apparent, that, if there is fractionation of a binary vapour with consequent enrichment of the more volatile component in the vapour, then, if the composition is weaker than that of the azeotrope ($68\%$), the concentration of nitric acid in the vapour will decrease, and if the concentration of the vapour is higher than the azeotrope, fractionation will cause the vapour to increase in strength.

If, however, sulphuric acid is present in the vapour, the danger of fractionation becomes even more important. The equilibrium diagram for the system $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ is shown, plotted /
plotted for the more volatile component in the usual way.

![Graph showing mol. fr. H₂O in vapor vs. mol. fr. H₂O in liquid.]

It is obvious that a very small amount of fractionation will be sufficient to change the composition of a sulphuric acid vapour to a great extent.

(2) Vapours evolved from the surface of the boiling liquid may not be in equilibrium with the bulk of the liquid.

(3) In recycling type stills there may be bad mixing of the returning condensate with the liquid in the boiler. If mixing is not instantaneous the condensate may flash vaporise.
Apparatus employed in this work

1. The Othmer Still (40)

A modified form of the Othmer Still, as shown in the diagram, was available and initial experiments were carried out on it.
To prevent heat loss and consequent fractionation in the neck, the still was fitted into a cylindrical box packed with asbestos wool, so that only the charging port, condenser, condensate trap and thermometer projected from the box.

The still was heated electrically by a small heater wound on the central leg of the U on the bottom of the flask, and operated from the 100 volts D.C. supply.

It was felt that there was a grave danger of fractionation in the long unheated neck of this still.

It was found that the ternary acid mixtures had a tendency to superheat and sometimes the liquid in the still would "bump" so violently that the liquid was forced into the condensate trap, contaminating the distillate. It was found that the nitric acid caused leaks at the stopcock on the condensate trap. The stopcock - the boiler was dispensed with because of this.

Because of these drawbacks this still was discarded.
2. The Gillespie Still (37).

The Gillespie still is an electrically heated still fitted with a Gottrell pump, a vapour-liquid separator and a condensate trap. Both the boiling liquid and the condensate circulate within the apparatus until equilibrium is reached. The original design is shown -

![Diagram of Vapor-Liquid Equilibrium Apparatus](image-url)
The liquid level in the boiler is arranged so that the vapour evolved causes a froth of liquid and vapour to pass up the Cottrell tube to the vapour-liquid separator. The liquid returns to the boiler and the vapour passes to the condensate trap whence it is recycled to the boiler.

The internal heater is included in order to provide small bubbles of vapour to carry the liquid up the Cottrell tube.

The still is designed:

(a) To eliminate fractionation. There is obviously little or no danger of fractionation in the vapour-liquid separator.

(b) To ensure that the vapour is actually in equilibrium with the liquid. Gillespie points out that the assumption that a vapour leaving a boiling liquid is in equilibrium with it, is not confirmed by ebullioscopic measurements, and indicates that it is unlikely that vapours produced by normal boiling in a flask after only a short passage through the liquid are in equilibrium with the bulk of the liquid.

The fact that in this still the vapour is in intimate contact with the liquid in the Cottrell tube until they separate should ensure that they are in equilibrium.

(c) /
SIDE ELEV. OF LIQUID SAMPLING RESERVOIR

SIDE ELEV. OF CONDENSATE TRAP

MODIFIED GILLESPIE STILL
(c) To eliminate bad mixing of the returning condensate with the liquid in the boiler. A capillary return line is used so that volume fluctuations in the return line are small, and the returning condensate is mixed with the liquid before it enters the boiler.

(d) To ensure of good boiling point data. The temperature is measured at the point of separation of the liquid and vapour and should be the true equilibrium temperature.

The main fault with this still is that, if the Carrell tube is to justify its presence, the vapour is in equilibrium with the liquid leaving the separator and there is no provision for sampling this liquid.

A still of this type was built as shown in the diagram opposite.

A liquid sampling reservoir is included below the vapour-liquid separator, into which the liquid leaving the separator flows, subsequently overflowing back to the boiler.

Stopcocks are omitted from the boiler and from the condensate trap, because of the danger of leaks, samples of condensate being removed by suction through the tube shown. Samples of liquid from the liquid sampling trap are also removed by suction.

A small reflux condenser is fitted to the condensate trap to prevent the escape of any condensable vapours.

Connection /
1. Connection is made from the top of this condenser to a pressure control device.

2. An external heater only, is used, wound on the small projecting tube at the bottom of the boiler. The boiler, Cottrell tube, and vapour-liquid separator are lagged with asbestos cord.

3. This still eliminates the danger of fractionation but goes to the other extreme and makes very imminent the danger of entrainment of the liquid phase in the vapour.

4. This is a drawback with any system but is probably even more important in the one under examination.

5. Sulphuric acid is so non-volatile that it apparently only appears in the vapour when its concentration in the liquid is high. It has already been pointed out how very slight fractionation is sufficient to change a $\text{H}_2\text{SO}_4 = \text{H}_2\text{O}$ vapour to a considerable extent. Thus, if sulphuric acid is detected in the distillate of ternary solutions when the Gillespie still is used, it may be due to the elimination of fractionation in the apparatus or simply due to entrainment.

6. Because of this the vapour-liquid separator was very carefully designed to prevent any splashing of the liquid.

Operation of the Gillespie still.

When this still was operated it was found difficult to prevent large "slugs" of liquid being carried up the Cottrell tube by the vapour as the liquid was beginning to boil, increasing considerably the danger of carry over. This tended /
tended to happen, mainly when the still was not properly heated up, and when there was cold liquid in the liquid sampling trap, and was due to the absence of an internal heater to provide small vapour bubbles. Long capillaries inserted into the boiler through the charging port helped to reduce this bumping and to provide an even froth up the Cottrell tube.

To attempt to provide an even steadier froth an internal heater was tried - a platinum wire coil working from a Variac transformer from the A.C. mains. As expected, however, the solution was electrolysed, and a greater amount of decomposition took place.

The internal heater was thus discarded and it was found, that by using a high heating rate with the external heater (\( \frac{1}{2} \) Kilowatt) quite a steady frothing effect could be obtained.

Operation of this still, however, requires careful supervision and control, the danger of entrainment, at least in the present case where an external heater only is used, being always present.
Disadvantages of the Gillespie Still with this System.

A considerable disadvantage of the Gillespie still and of most other equilibrium stills is that the composition of the vapour in equilibrium with a liquid of particular composition cannot be found directly, because of the definite amount of material retained in the condensate trap. Thus, only more or less random vapour-liquid equilibrium can be determined in a system. This is not a great disadvantage in a binary system but in a ternary system, in order to represent the data in the form of smooth curves, interpolation must be used and errors may be introduced unless an extraordinarily large amount of data is collected.

Moreover, the recycling type of still may not be satisfactory in this system because of the decomposition of nitric acid to oxides of nitrogen. When the concentration of nitric acid in the liquid is high, there may be oxides of nitrogen in the vapour. Since the decomposition of nitric acid increases with time of heating, as the condensate is recycled so will the oxides of nitrogen in the condensate increase. If the liquid is continually decomposing the composition of the vapour should keep changing as distillation proceeds.

Because of these considerations it was decided to study this system by means of the following still.
3. Batch Equilibrium Still

The composition of the vapour in equilibrium with a liquid of desired composition may be found by using a very large amount of liquid and removing only a small amount of distillate, so that the change in composition of the residual liquid is negligible.

This type of still has been developed for use for determining vapour-liquid equilibria in systems in which extractive distillation is applied (44), the equilibria being readily evaluated at fixed mol fractions of solvent in the liquid.

With this method, by using large enough volumes of liquid, the error involved could be made smaller than the errors involved in interpolation between random points in a ternary diagram.

The H₂SO₄- HNO₃ - H₂O system lends itself readily to this method, on account of the ready availability and cheapness of the materials involved, and the ease with which a ternary mixture can be accurately made up to a desired composition.

The still consists, as shown on the following page of a five litre flask, having a B 24 ground glass socket fitted to its neck, through which the still is charged with the liquid to be examined, and into which the vapour line to the condenser is fitted by means of a ground glass cone.
ILLUSTRATION
OF
HEATER & POSITION OF THERMOCOUPLES
ON NECK OF FLASK.
A 400 watt heater of Brightray tape, operated from 100 volts D.C., is wound on the tube at the bottom of the still. The still is fitted into a nest of asbestos wool in a box, provided with windows, so that the liquid surface can be observed. A thermometer pocket is fitted on the side of the flask, positioned so that it is only partly in the vapour space and mainly in the liquid.

The neck of the flask is heated by two heaters wound on a glass former surrounding the neck of the flask, as shown in the diagram opposite, so that a graded heat can be applied to the neck of the flask. The heaters are operated from 100 volts D.C. and are capable of being very carefully controlled by large resistance rheostats. Three iron-constantan thermocouples are tied closely to the neck of the flask at the top middle and bottom, as shown.

A moulded asbestos nest fits over the neck of the flask on top of the heaters and the vapour delivery tube to the condenser is well-lagged with asbestos cord.

Samples of condensate are collected in tubes fitted to the bottom of the condenser by ground glass joints. The side-arm at the bottom of the condenser is connected to a pressure control device.

Operation of the Still

Approximately 3½ litres of liquid, made up to the desired composition, are charged to the still. One or two long capillaries /
capillaries are placed inside to prevent superheating and
bumping.

2. As the liquid in the still is heated the heaters on the
neck are accurately controlled so that the thermocouples on
the neck register about 1° higher at the bottom of the neck,
about 3° higher in the middle, and about 5° higher at the top,
than the temperature of the liquid in the still.

3. A direct-reading Integra potentiometer is used to
measure the temperatures as recorded by the thermocouples.

4. The liquid is heated until it begins to boil, at which
time, the heating rate is cut down so that the distillation
rate is slow and bubbles of vapour rising to the surface are
small. When the temperature of the liquid becomes steady, as
indicated by the thermometer, the distillate collecting tube is
replaced quickly by a clean one and a sample of 3-4 m.l.
collected.

5. When the concentration of nitric acid in the distillate
is high, ice water is circulated through the condenser.

6. **Preparation of the Acid Mixtures**

   The acids used were the "pure" brands of sulphuric acid
   (approximately 95%) and nitric acid (approximately 95% and
   68%).

7. The acid mixtures were made up with the above carefully
   analysed acids and freshly distilled water to the required
calculated.
calculated composition. The acids were carefully weighed on a large beam balance and mixed slowly in an ice bath to prevent loss of vapour, then charged to the still.

After each determination the still was emptied, in the case of the ternary mixtures, by syphoning out the acid, and was then rinsed and dried.

In the case of the determinations in the HNO$_3$ - H$_2$O system, highly concentrated nitric acid was charged initially to the still and was progressively diluted with freshly distilled water after each equilibrium determination.

The liquid samples for analysis in this case were withdrawn by suction after each determination.

It was not, of course, possible to cover the entire range of concentration with the strengths of acid available. In the range of concentrations in which equilibrium data were obtained in the ternary system, a mol fraction of HNO$_3$ of 0.60 in the liquid, on a H$_2$SO$_4$ - free basis, was about the maximum that could be attained.
Analytical Procedure

Total Acid Content: Mixtures of mixed acids and distillate samples were analysed for total acidity by weighing out samples into small \( \frac{1}{4} \)" x \( \frac{1}{2} \)" glass bottles having ground glass stoppers, transferring bottle and contents to a wide-necked conical flask containing about 25 m.l. of fresh distilled water, and titrating with IN or 0.1N sodium hydroxide, depending on the concentration of the acid. Bromophenol blue was used as indicator. Large weighing pipettes of the type shown were used.

Samples of distillate of high nitric acid content were added quickly to the conical flask, cooled in ice, to prevent loss of vapour. The mouth of the flask was then covered with a watch glass, sealed with water, and allowed to stand for five minutes with frequent shaking before titration.

Nitric acid in Mixed Acids: The determination of nitric acid in the presence of sulphuric acid was at first attempted by 

(1) the Bowman-Scott method of titration with ferrous ammonium sulphate in the presence of concentrated sulphuric acid. This titration, however, was found to be difficult,
the end-point being very poor. Even though considerable
time was spent on this method, because of the convenience of
the straight titration, it was found impossible to get
accurate results with it.

It was found that an excellent method (43) was the
determination of sulphuric acid in a mixed acid, by the
repeated evaporation (three times) of the sample almost to
"dryness" in a wide-necked conical flask on a steam bath,
approximately 25 ml. of water being added before each
evaporation. The sample is weighed directly into the flask
from the weighing pipette. The sulphuric acid content is
obtained by titration with sodium hydroxide and the nitric
acid by subtraction from the total acidity of the sample.

**Oxides of Nitrogen**: They were determined by the following
method. The bottle containing the weighed sample of acid
is added to an ice-cooled, known excess of 0.1 N potassium
permanganate solution in a conical flask, covering with a
watch glass and sealing with water, and leaving to stand for
about five minutes with frequent shaking. 10 ml. of dilute
sulphuric acid and 2-3 gm. of potassium iodide are then
added and the iodine liberated is titrated with 0.1 N sodium
thiosulphate solution. The oxides of nitrogen are reported
as nitrogen peroxide NO₂.

**Test for H₂SO₃, in the distillates:**

The distillates were continually tested for sulphuric acid
in all the Runs on the Gillespie still and in those Runs on
the /
the batch still in which the mol fraction of H₂SO₄ in the liquid was over 0.15.

This was done by evaporating a sample of the distillate several times on the steam bath and titrating the residue with 0.05 N sodium hydroxide.
Pressure Control Device

All the vapour-liquid equilibria determinations were carried out at standard atmospheric pressure with the aid of the following control device.

It is similar in principle to the Cartesian Manostat and consists, as shown in the diagram, of a small glass bell floating on a pool of mercury inside a larger bell. A rubber bung in the outer bell carries three tubes, one leading to an evacuating pump - a water jet pump, one to a supply of compressed air and one to the system being controlled and to a barometer. The end of the suction tube - ground flat - is positioned a little above the floating bell, on the top of which a rubber patch is fixed.

It /
It is operated as follows:— the pressures above and below the floating bell are equalised by opening stopcock A. A small flow of air into the system and a small withdrawal of air through the suction tube are arranged until the pressure registered on the barometer is 760 m.m. The position of the bell is then such that the distance between the end of the evacuating tube and the top of the bell is sufficient to provide a throttling effect on the air being drawn out, to cause the pressure above the bell to remain at 760 m.m.

The bottle $V_1$ is included to make the effective volume under the bell greater, so that it will be more sensitive in reacting to changes in pressure above the bell, e.g. If the pressure falls above the bell, the fractional increase in volume under the bell will be the same as if $V_1$ were not included but the actual volume change will be greater and the bell will move a correspondingly greater distance.

The bottle $V_2$ serves to damp out any fluctuations in pressure that may occur in the system being controlled.

If the pressure in the system rises or falls because of leaks in or out, then the floating bell will fall or rise as the case may be, in order, on the one hand, to decrease the pressure and on the other to increase it. When the original demand is restored the bell will return to its original position and the pressure will again be 760 m.m. If, however, a permanent leak develops in the system, the device will
will not control at 760 m.m. as there is only one position of the bell with respect to the suction tube, that corresponds to 760 m.m. inside the system, with fixed air flows in and out, i.e. the device has no reset control.

The apparatus, however, provides a convenient means of keeping the pressure at standard atmospheric, and works well, provided steady flows of air in and out are assured.
The Ternary System Mg(NO$_3$)$_2$ - HNO$_3$ - H$_2$O

It has been pointed out in the Introduction that a concentrated solution of magnesium nitrate is at present being used in place of sulphuric acid in the concentration of nitric acid.

Sidgwick (44) points out that magnesium nitrate is a very stable and soluble salt. Its "affinity" for water, therefore, suggests its use as a dehydrating agent in the concentration process.

In order to find out the relative effect of magnesium nitrate and sulphuric acid on vapour-liquid equilibria in the nitric acid system, and in order to illustrate the relative selectivities of these substances in the extractive distillation of nitric acid, some vapour-liquid equilibrium data were obtained in the system Mg(NO$_3$)$_2$ - HNO$_3$ - H$_2$O. The data were obtained at a constant mol fraction of 0.05 of Mg(NO$_3$)$_2$ in the liquid using the Batch Equilibrium still.

Crystals of the hexahydrate Mg(NO$_3$)$_2$.6H$_2$O were used for making up the mixtures.

Analysis of ternary mixtures in this system presents a greater difficulty than in the previous ternary system.

The following method was devised and was found very convenient for analysing such solutions.

The nitric acid present in the ternary mixture is determined /
determined by titration with sodium hydroxide. The magnesium nitrate is determined by reacting the solution with known excess of sulphuric acid and driving off the nitric acid so liberated and that present originally, by evaporation on a steam bath.

The sulphuric acid reacts with the magnesium nitrate according to the equation:

\[ \text{Mg(NO}_3\text{)}_2 + \text{H}_2\text{SO}_4 = \text{Mg} \text{SO}_4 + 2\text{HNO}_3 \]

This reaction probably takes place on the steam bath as the solution becomes more concentrated.

25 ml. of a 2% solution of sulphuric acid are added to the weighed sample of magnesium nitrate solution contained in a conical flask, (it was found more accurate to use a dilute solution of sulphuric acid rather than to add the concentrated acid to the sample by means of a weighing pipette). The solution is then evaporated to near dryness on a steam bath, 25 ml. of water added and the evaporation repeated three times. The sulphuric acid not used up is then determined by titration with 0.5 N sodium hydroxide and the amount used up determined. The magnesium nitrate content is then found from the amount of sulphuric acid used up.

Experiments showed that two to three evaporations of the solution on the steam bath were necessary, so four are used. Very concordant results can be obtained with this method.

The solubility of Mg(NO3)2·6H2O in nitric acid solutions decreases /
decreases as the nitric acid content increases. When dealing with solutions containing 0.05 mol fraction of \( \text{Mg(NO}_3\text{)}_2 \) and especially in the region of higher nitric acid content, it was found that crystals of \( \text{Mg(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \) readily separate. The solutions must be maintained at moderately high temperatures to prevent crystallisation.

This is awkward when such solutions are to be analysed. It was done by pipetting a few ml's of the hot solution into a small glass bottle of known weight, having a ground glass stopper, allowing to cool and reweighing. The contents of the bottle were then washed into a wide-necked conical flask and the analysis carried out.

The crystals of \( \text{Mg(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \) with which the solutions were made up were slightly wet and they were analysed by the above method, an average sample being taken. They were found to contain 98.65% of \( \text{Mg(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \).

In order to economise in the use of \( \text{Mg(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \) crystals, a batch of ternary mixture was made up in the more concentrated region of nitric acid concentration and this was progressively altered to a more dilute, desired concentration after each equilibrium determination. The weights of \( \text{Mg(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \) and of water to be added to a particular residue were calculated to give a certain weight of mixture of desired composition.

This method was found to be quite accurate. For instance, the following table gives the original composition of /
of a mixture to be altered to the desired composition shown. The third column gives the actual composition obtained after such an alteration.

<table>
<thead>
<tr>
<th></th>
<th>Original Comp.</th>
<th>Desired Comp.</th>
<th>Actual Comp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WT. %</td>
<td>Mol Fr.</td>
<td>WT. %</td>
</tr>
<tr>
<td>Mg(NO₃)₂</td>
<td>18.45</td>
<td>.0505</td>
<td>20.84</td>
</tr>
<tr>
<td>HNO₃</td>
<td>55.08</td>
<td>.3730</td>
<td>43.67</td>
</tr>
<tr>
<td>H₂O</td>
<td>26.47</td>
<td>.3550</td>
<td>35.50</td>
</tr>
</tbody>
</table>

Experimental Results:

The vapour-liquid equilibria were obtained at a mol fraction of Mg(NO₃)₂ in the liquid of 0.05. The results have been evaluated on a NO₂-free basis, both in the condensate and in the "vapour" as already described. They are given in Table 10.
Experimental Results.

1. **Gillespie Still.**

In order to test the still for possible entrainment a few runs were carried out on the system $\text{H}_2\text{SO}_4-\text{H}_2\text{O}$. The results, calculated in terms of the partial pressure of sulphuric acid over the boiling solution are given in Table 1. They seem to indicate that there is no entrainment.

The binary system $\text{HNO}_3-\text{H}_2\text{O}$ was investigated and the results are given in Table 2.

Some results were obtained on the ternary system $\text{H}_2\text{SO}_4-\text{HNO}_3-\text{H}_2\text{O}$ and are given in Table 3. They were obtained by making up acid mixtures more or less at random compositions and finding the equilibria in the still.

Some of the distillates from the ternary solutions were found to contain sulphuric acid. However, as other runs, in which the strength of sulphuric acid in the liquid was higher, gave no indication of sulphuric acid in the distillates, this was regarded as being due to entrainment and the runs regarded as worthless, and are not recorded.

2. **Batch Still.**

The binary system $\text{HNO}_3-\text{H}_2\text{O}$ was examined and the results are given in Table 4.

In the ternary system, $\text{H}_2\text{SO}_4-\text{HNO}_3-\text{H}_2\text{O}$, all the previous data obtained is available in the form - weight per cent. $\text{H}_2\text{SO}_4$ in the vapour in equilibrium with a weight per cent. liquid / $\text{H}_2\text{O}$.
liquid composition. It was decided to obtain the equilibrium data directly, in the form more usual in extractive distillation, of mol fraction HNO₃ in the vapour in equilibrium with mol fraction HNO₃ in the liquid in the presence of different mol fractions of H₂SO₄. The data can thus be plotted on rectangular coordinates on a H₂SO₄-free basis, in the form of smooth curves having the mol fraction of H₂SO₄ in the liquid as parameter.

Results were obtained for 0.05, 0.10, 0.15, 0.20 and 0.30 mol fraction of H₂SO₄ in the liquid and are recorded in Tables 5, 6, 7, 8 and 9 respectively.

The temperatures recorded in the tables are the observed boiling points of the mixtures in the stills. Since no special precautions were taken in the measurement of these temperatures, they are probably not accurate values of the boiling points.
<table>
<thead>
<tr>
<th>%$\text{H}_2\text{SO}_4$ in Liquid</th>
<th>Partial Pressure of $\text{H}_2\text{SO}_4$ in Vapour (m.m. Hg.)</th>
<th>Observed Boiling Point ($^\circ$C.)</th>
<th>Partial Pressure from Data in I.C.T.</th>
<th>Temp. from I.C.T.</th>
</tr>
</thead>
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<tr>
<td>23.72</td>
<td>-</td>
<td>114</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>35.48</td>
<td>&lt; 0.01</td>
<td>111</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>67.80</td>
<td>0.09196</td>
<td>159</td>
<td>-</td>
<td>-</td>
</tr>
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<td>75.88</td>
<td>0.2394</td>
<td>187</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>82.94</td>
<td>1.578</td>
<td>215</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>91.24</td>
<td>16.48</td>
<td>250-260</td>
<td>16.3</td>
<td>262.5</td>
</tr>
<tr>
<td>B.P. °C</td>
<td>HNO₃</td>
<td>NO₂-Free Basis</td>
<td>Mol Fraction HNO₃ (NO₂-Free Basis)</td>
<td>% Total Acid as HNO₃ in Condensate</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>108.7</td>
<td>35.62</td>
<td>-</td>
<td>0.1365</td>
<td>7.042</td>
</tr>
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<td>55.10</td>
<td>-</td>
<td>0.166</td>
<td>18.42</td>
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<tr>
<td>119</td>
<td>62.07</td>
<td>-</td>
<td>0.187</td>
<td>32.65</td>
</tr>
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<td>128.5</td>
<td>62.07</td>
<td>-</td>
<td>0.187</td>
<td>52.99</td>
</tr>
<tr>
<td>118.5</td>
<td>64.62</td>
<td>-</td>
<td>0.1411</td>
<td>58.30</td>
</tr>
<tr>
<td>121.5</td>
<td>65.75</td>
<td>-</td>
<td>0.1244</td>
<td>62.20</td>
</tr>
<tr>
<td>119</td>
<td>72.16</td>
<td>-</td>
<td>0.1255</td>
<td>78.05</td>
</tr>
<tr>
<td>119</td>
<td>72.16</td>
<td>-</td>
<td>0.1255</td>
<td>78.05</td>
</tr>
<tr>
<td>117.6</td>
<td>74.67</td>
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<tr>
<td>115</td>
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<td>0.5368</td>
<td>91.51</td>
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<tr>
<td>116</td>
<td>80.37</td>
<td>0.00931</td>
<td>0.5368</td>
<td>92.30</td>
</tr>
<tr>
<td>108</td>
<td>85.57</td>
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<td>0.0288</td>
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<tr>
<td>96</td>
<td>93.67</td>
<td>0.00401</td>
<td>0.8099</td>
<td>100.8</td>
</tr>
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</table>
### Table 3

\[ \text{H}_2\text{SO}_4 - \text{HNO}_3 - \text{H}_2\text{O (Gillespie Still)} \]

<table>
<thead>
<tr>
<th>B.P. °C.</th>
<th>(%\text{H}_2\text{SO}_4)</th>
<th>(%\text{HNO}_3)</th>
<th>% Total Acid as (\text{HNO}_3)</th>
<th>(%\text{NO}_2)</th>
<th>(%\text{HNO}_3)</th>
<th>(%\text{HNO}_3) ((\text{NO}_2)-Free Basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>6.581</td>
<td>11.40</td>
<td>1.272</td>
<td>-</td>
<td>1.272</td>
<td>1.272</td>
</tr>
<tr>
<td>105.5</td>
<td>16.35</td>
<td>11.05</td>
<td>1.82</td>
<td>-</td>
<td>1.82</td>
<td>1.82</td>
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<tr>
<td>107</td>
<td>6.880</td>
<td>20.40</td>
<td>3.382</td>
<td>-</td>
<td>3.382</td>
<td>3.382</td>
</tr>
<tr>
<td>118</td>
<td>28.89</td>
<td>21.68</td>
<td>24.80</td>
<td>-</td>
<td>24.80</td>
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<tr>
<td>117</td>
<td>20.73</td>
<td>28.16</td>
<td>28.64</td>
<td>-</td>
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<tr>
<td>119.5</td>
<td>30.05</td>
<td>22.29</td>
<td>30.27</td>
<td>-</td>
<td>30.27</td>
<td>30.27</td>
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<tr>
<td>123.5</td>
<td>37.64</td>
<td>18.39</td>
<td>36.58</td>
<td>-</td>
<td>36.58</td>
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</tr>
<tr>
<td>130.7</td>
<td>50.46</td>
<td>9.957</td>
<td>42.94</td>
<td>-</td>
<td>42.94</td>
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<tr>
<td>118.5</td>
<td>8.14</td>
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<td>47.70</td>
<td>-</td>
<td>47.70</td>
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<td>-</td>
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<td>45.77</td>
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<td>-</td>
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<td>70.30</td>
</tr>
<tr>
<td>133</td>
<td>52.11</td>
<td>14.75</td>
<td>70.40</td>
<td>-</td>
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<tr>
<td>131</td>
<td>53.64</td>
<td>19.56</td>
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<td>0.068</td>
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<tr>
<td>118</td>
<td>31.14</td>
<td>45.00</td>
<td>92.51</td>
<td>0.10%</td>
<td>92.37</td>
<td>92.50</td>
</tr>
<tr>
<td>118</td>
<td>51.99</td>
<td>26.94</td>
<td>97.00</td>
<td>0.6293</td>
<td>96.14</td>
<td>96.89</td>
</tr>
<tr>
<td>112.3</td>
<td>60.72</td>
<td>41.44</td>
<td>98.21</td>
<td>0.7000</td>
<td>97.25</td>
<td>98.00</td>
</tr>
<tr>
<td>104.5</td>
<td>35.04</td>
<td>52.15</td>
<td>99.59</td>
<td>0.764</td>
<td>98.54</td>
<td>99.30</td>
</tr>
<tr>
<td>B.P.</td>
<td>% HNO₃</td>
<td>Mol Fraction NO₂</td>
<td>% Total Acid as HNO₃</td>
<td>%NO₂</td>
<td>%NO₃ in Condensate</td>
<td>%NO₃ in Condensate (NO₂-Free Basis)</td>
</tr>
<tr>
<td>------</td>
<td>-------</td>
<td>------------------</td>
<td>----------------------</td>
<td>------</td>
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<td>98.62</td>
<td>2.44</td>
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</tr>
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TABLE 4
HNO₃ - H₂O (Batch Still)
<table>
<thead>
<tr>
<th>B.P. O°C</th>
<th>Mol Fraction HNO₃ (H₂SO₄-Free Basis)</th>
<th>% Total Acid in Condensate as HNO₃</th>
<th>% HNO₂ in Condensate</th>
<th>% HNO₃ in Condensate (NO₂-Free Basis)</th>
<th>% HNO₃ in &quot;Vapour&quot; (NO₂-Free Basis)</th>
<th>Mol Fraction HNO₃ in &quot;Vapour&quot; (NO₂-Free Basis)</th>
<th>Mol Fraction HNO₃ in Condensate</th>
</tr>
</thead>
<tbody>
<tr>
<td>104.5</td>
<td>0.10</td>
<td>6.634</td>
<td>-</td>
<td>6.634</td>
<td>6.634</td>
<td>0.01989</td>
<td>0.01989</td>
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<tr>
<td>119.7</td>
<td>0.20</td>
<td>34.13</td>
<td>-</td>
<td>34.13</td>
<td>34.13</td>
<td>0.1290</td>
<td>0.1290</td>
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<tr>
<td>121.6</td>
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<td>78.08</td>
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<td>0.5098</td>
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<td>93.90</td>
<td>97.52</td>
<td>(&gt;1.00)</td>
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</tbody>
</table>
\[ \text{TABLE 6} \]

\[ \text{H}_2\text{SO}_4 - \text{HNO}_3 - \text{H}_2\text{O} \]

0.10 MOL FRACTION H\textsubscript{2}SO\textsubscript{4}

<table>
<thead>
<tr>
<th>B.P. (°C)</th>
<th>Mol Fraction HNO\textsubscript{3} (H\textsubscript{2}SO\textsubscript{4}-Free Basis)</th>
<th>% Total Acid in Condensate as HNO\textsubscript{3}</th>
<th>% NO\textsubscript{2} in Condensate</th>
<th>% HNO\textsubscript{3} in Condensate (NO\textsubscript{2}-Free Basis)</th>
<th>% HNO\textsubscript{3} in &quot;Vapour&quot; (NO\textsubscript{2}-Free Basis)</th>
<th>Mol Fraction HNO\textsubscript{3} in Condensate (NO\textsubscript{2}-Free Basis)</th>
<th>Mol Fraction HNO\textsubscript{3} in &quot;Vapour&quot; (NO\textsubscript{2}-Free Basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>118</td>
<td>0.06</td>
<td>9.568</td>
<td>-</td>
<td>9.568</td>
<td>9.568</td>
<td>0.02935</td>
<td>0.02935</td>
</tr>
<tr>
<td>119.8</td>
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<td>19.50</td>
<td>-</td>
<td>19.50</td>
<td>19.50</td>
<td>0.06473</td>
<td>0.06473</td>
</tr>
<tr>
<td>122.6</td>
<td>0.14</td>
<td>33.36</td>
<td>-</td>
<td>33.36</td>
<td>33.36</td>
<td>0.1251</td>
<td>0.1251</td>
</tr>
<tr>
<td>122</td>
<td>0.20</td>
<td>58.09</td>
<td>-</td>
<td>58.09</td>
<td>59.09</td>
<td>0.2836</td>
<td>0.2836</td>
</tr>
<tr>
<td>121</td>
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<td>80.34</td>
<td>Negligible</td>
<td>80.34</td>
<td>80.34</td>
<td>0.5387</td>
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</tr>
<tr>
<td>116</td>
<td>0.40</td>
<td>94.06</td>
<td>1.789</td>
<td>91.61</td>
<td>93.28</td>
<td>0.7984</td>
<td>0.7780</td>
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<td>105.5</td>
<td>0.50</td>
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<td>2.280</td>
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<td>97.86</td>
<td>0.9283</td>
<td>0.8990</td>
</tr>
<tr>
<td>100.3</td>
<td>0.60</td>
<td>100.05</td>
<td>1.226</td>
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<td>0.9860</td>
<td>0.9700</td>
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</table>
### Table 7
**H₂SO₄ - HNO₃ - H₂O**

0.15 MOL FRACTION H₂SO₄

<table>
<thead>
<tr>
<th>LIQUID</th>
<th>VAPOUR</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.P. °C</td>
<td>Mol Fraction HNO₃ (H₂SO₄-Free Basis)</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>125.3</td>
<td>0.03</td>
</tr>
<tr>
<td>127.2</td>
<td>0.06</td>
</tr>
<tr>
<td>129.0</td>
<td>0.10</td>
</tr>
<tr>
<td>127.0</td>
<td>0.20</td>
</tr>
<tr>
<td>121.2</td>
<td>0.30</td>
</tr>
<tr>
<td>110.5</td>
<td>0.40</td>
</tr>
<tr>
<td>107.7</td>
<td>0.55</td>
</tr>
<tr>
<td>102.7</td>
<td>0.50</td>
</tr>
<tr>
<td>B.F. °C</td>
<td>Mol Fraction HNO₃ (H₂SO₄-Free Basis)</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>137.5</td>
<td>0.05</td>
</tr>
<tr>
<td>135</td>
<td>0.10</td>
</tr>
<tr>
<td>125</td>
<td>0.20</td>
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<tr>
<td>118.2</td>
<td>0.30</td>
</tr>
<tr>
<td>96</td>
<td>0.50</td>
</tr>
<tr>
<td>B.F.</td>
<td>Mol Fraction HNO₃ (H₂SO₄-Free Basis)</td>
</tr>
<tr>
<td>------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>157</td>
<td>0.025</td>
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<tr>
<td>153.5</td>
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<td>0.10</td>
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<td>133.5</td>
<td>0.15</td>
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<tr>
<td>122</td>
<td>0.22</td>
</tr>
<tr>
<td>109</td>
<td>0.30</td>
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</tbody>
</table>
TABLE 10

\( \text{Mg(NO}_3\text{)}_2 - \text{HNO}_3 - \text{H}_2\text{O} \)

0.05 Mol Fr. Mg(NO\textsubscript{3})\textsubscript{2} in the Liquid

<table>
<thead>
<tr>
<th>B.P. (^{0}\text{C.})</th>
<th>Liq Fr. HNO\textsubscript{3} in Liquid (Mg(NO\textsubscript{3})\textsubscript{2} - Free)</th>
<th>% T.A. in Condensate</th>
<th>% NO\textsubscript{2} in Condensate</th>
<th>% HNO\textsubscript{3} in Condensate</th>
<th>% HNO\textsubscript{3} in &quot;Vapour&quot; (NO\textsubscript{2} - Free)</th>
<th>Mol Fr. HNO\textsubscript{3} in Condensate (NO\textsubscript{2} - Free)</th>
<th>Mol Fr. HNO\textsubscript{3} in &quot;Vapour&quot; (NO\textsubscript{2} - Free)</th>
</tr>
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<tbody>
<tr>
<td>116</td>
<td>0.12</td>
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<td>-</td>
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<td>21.98</td>
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<td>-</td>
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<td>-0.3816</td>
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<td>1.220</td>
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<td>0.7372</td>
</tr>
<tr>
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<td>1.394</td>
<td>96.65</td>
<td>98.02</td>
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<td>97.51</td>
<td>99.04</td>
<td>0.9674</td>
<td>0.9674</td>
</tr>
</tbody>
</table>
Discussion on the Vapour-Liquid Equilibria.

In this system, besides the normal difficulties encountered in equilibrium distillation, there is the added difficulty of decomposition of the nitric acid to oxides of nitrogen.

Nitric acid decomposes under the action of heat or sunlight according to the equation (46):

\[ 4 \text{HNO}_3 = 2 \text{H}_2\text{O} + 4 \text{NO}_2 + \text{O}_2 \]

Because they noticed that the vapour over a nitric acid solution turned brown when the solution was exposed to sunlight, Veley and Manley (47) suggest that the above reaction takes place in the vapour phase under the action of sunlight. There is no other indication in the literature as to whether the decomposition of nitric acid in boiling solutions of the acid, takes place in the vapour or in the liquid phase. It would appear, however, (48) that the decomposition takes place, at least predominantly, in the liquid phase, the amount of nitrogen peroxide in the vapour not being a fixed value at a given acid strength, but depending on the temperature and on the time of heating.

The presence of nitrogen peroxide in the vapour is a complicating factor in the evaluation of the vapour-liquid equilibrium data. If the decomposition of the acid takes place in the liquid phase, the nitrogen peroxide can be considered as a diluent gas, simply reducing the partial pressures of the nitric acid and of the water in the vapour -
in effect reducing the total pressure in the system.

The vapour-liquid equilibrium data should, therefore, be evaluated on a nitrogen peroxide-free basis.

It has been pointed out that the nitrogen peroxide in the vapour is determined experimentally by adding a weighed sample of the acid to a known excess of potassium permanganate, addition of potassium iodide and titration of the liberated iodine by sodium thiosulphate solution.

When nitrogen peroxide is dissolved in water a reversible reaction takes place, forming products of a higher and lower degree of oxidation (49)(50) thus:

\[
2\text{H}_2\text{O} + 2\text{NO}_2 \rightarrow \text{HNO}_2 + \text{HNO}_3
\]

When nitrogen peroxide is present in the vapour from the distillation of a nitric acid solution, and the vapour is condensed, the above reaction should take place with the water in the condensate. The composition of the condensate will, therefore, be different from that of the vapour.

When the sample of condensate to be analysed is added to the aqueous permanganate solution, this reaction will probably go still further to completion. If the reaction went to completion entirely, all the nitrogen peroxide would be determined as HNO\(_2\), and would be equivalent to only half of the actual amount of NO\(_2\) present in the vapour.

This effect of change in the oxides of nitrogen content on condensation of a vapour and subsequent analysis was probably recognised by Pascal (25) in his work on the nitric acid.
acid system. In his results he gives the composition of
the condensate, and mentions that the nitrogen peroxide
content may not be the same as that in "the atmosphere of the
apparatus".

The Binary System HNO₃ - H₂O.

The data obtained in the Gillespie still and in the
Batch still are presented in Tables 2 and 4. The data has
been calculated in the two forms - mol fraction HNO₃ in the
condensate and mol fraction HNO₃ in the "vapour", assuming
the above reaction goes to completion, in equilibrium with
mol fraction HNO₃, in the liquid, all on a NO₂ - free basis.

The results show that the concentration of nitrogen
peroxide in the condensate or "vapour" from the Batch still
is much higher than that from the Gillespie still, in the same
regions of nitric acid concentration. This is because of
the greater actual amount of acid being boiled in the Batch
still, and serves to indicate that the decomposition takes
place, at least mainly, in the liquid phase. If the
decomposition took place in the vapour phase, there would be
no reason why the NO₂ concentration should be higher in the
Batch still than in the Gillespie, with the slow distillation
rates used.

This increase in the decomposition is one of the draw-
backs of this still. However, if the NO₂ merely acts as a
diluent gas, reducing, in effect, the total pressure on the
system.
FIG. 1

$\text{HNO}_3 - \text{H}_2\text{O}$

- ○ BATCH STILL DATA
- Δ GILLESPIE STILL DATA

MOL FRACTION $\text{HNO}_3$ IN LIQUID

MOL FRACTION $\text{HNO}_3$ IN CONDENSATE
FIG. 2

HNO$_3$ - H$_2$O

- - - O - BATCH STILL DATA
- - - A - GILLESPIE STILL DATA.
system, the error may not be large provided the results are calculated on a NO₂-free basis. Pascal (25) has examined the binary system at total pressures of 870, 760, 570, 458, 317, 116 and 40 mm of mercury. It is obvious from his work that pressure has little effect on the vapour-liquid equilibria. Even at 317 mm. the binary boiling point curve is practically identical with that at 760 mm.

The data from the Batch still indicate that there is a maximum in the amount of NO₂ produced, at a concentration of nitric acid in the liquid of 92 - 93%. There is no apparent reason why this should be so.

The experimental data from both the Gillespie and the Batch stills have been plotted in Figures 1 and 2 in terms of mol fractions HNO₃ on a NO₂-free basis. In Figure 1 the mol fraction HNO₃ in the condensate is plotted against mol fraction HNO₃ in the liquid, and in Figure 2 the mol fraction HNO₃ in the "vapour" is plotted against mol fraction HNO₃ in the liquid. The correct curve giving the vapour-liquid equilibria should lie between the condensate curve and the "vapour" curve, its position depending on the extent to which the reaction already mentioned takes place on condensation of the vapour and subsequent analysis.

Some of the condensate analyses in the Batch still results, and one in the Gillespie still results, show an apparent concentration /
concentration of nitric acid in the condensate of over 100%. This must be due to the presence of a higher oxide of nitrogen than nitrogen peroxide. When these results, however, are calculated as $\% \text{NO}_3$ and mol fraction $\text{HNO}_3$ in the "vapour", as already described, the points so obtained lie on a smooth curve as indicated in Figures 2 and 4.

The data are compared on a weight per cent basis with those of Carpenter and Babor and Berl and Samtleben in Figures 3 and 4 respectively. Neither of these workers, of course, give their data on a $\text{NO}_2$ - free basis, so in both Figures 3 and 4, their data are plotted as $\% \text{NO}_3$ in the condensate. In Figure 3 the Batch and Gillespie still data are plotted in terms of $\% \text{NO}_3$ in the condensate against $\% \text{NO}_3$ in the liquid, on a $\text{NO}_2$ - free basis. In Figure 4 the Batch and Gillespie still data are given as $\% \text{NO}_3$ in the "vapour" on a $\text{NO}_2$ - free basis.

Because of the difficulty of the presence of $\text{NO}_2$, and the different methods of evaluating the vapour-liquid equilibria, it is impossible to compare all the data on the system over the whole concentration range.

However, comparison of the data in Figures 3 and 4 in the more dilute regions - below the azeotrope - would seem to indicate that there is a small amount of fractionation in the Batch still, the Batch still data lying slightly below the other data.

In the more concentrated region - above the azeotrope - the /
the Batch still data lie above the other data in Figure 3 when plotted as mol fraction HNO₃ in the condensate. In Figure 4, when plotted as mol fraction HNO₃ in the "vapour", the Batch still data more nearly resemble the other data. In both figures 3 and 4 if Carpenter and Babors' and Berl and Samtleben's data had been evaluated and plotted on a NO₂ - free basis the curves of their data in the region above the azeotrope would have been higher than they actually are, resembling more closely the Batch still data.

The Gillespie still data do not coincide exactly with the other data, lying noticeably below (or further to the right of) Carpenter and Babors' data in the region below the azeotrope. This can not be explained by fractionation in the Gillespie still, as the danger of fractionation is practically negligible.

Even though the recycling nature of the Gillespie still may lead to a continual increase in the NO₂ content of the vapours as distillation proceeds, because of the prolonged heating of the liquid, examination of the results shows that this is not a very obvious drawback, the NO₂ content of the condensate never being very large.

The data obtained in the Gillespie still probably represents the best available data in this binary system.

In Figure 5 Carpenter and Babors' data, plotted in terms of mol fractions, are compared with the Batch still, in the dilute /
dilute region. The data given in The Chemical Engineers' Handbook (Perry) as mol fraction HNO₃ in the liquid in equilibrium with mol fraction HNO₃ in the vapour are also plotted in Figure 5. It is evident that the latter data are very far out.

A comparison of the weight per cent. and mol fraction methods of plotting the data indicates that the latter method opens out the upper regions of the curve to a considerable extent, because of the quite different molecular weights of nitric acid and water. For the same reason, in the dilute region, the mol fraction method of plotting the data tends to "compress" the curve.
FIG. 5

- Batch Still Data
- Carpenter & Babor Data
- Data from Perry

Mol Fraction HNO₃ in Liquid

Mol Fraction HNO₃ in Vapour
Examination of the Binary data by the Van Lear Equation.

The consistency of experimental vapour-liquid equilibrium data may be checked by the application of the Gibbs-Duhem equation, or integrated forms, such as the Van Lear or Margules equations.

It was decided to apply such equations to the system HNO₃ - H₂O in order to indicate which set of data was most accurate.

In a binary system where the vapours are perfect gases the Gibbs-Duhem equation can be written in the form:

\[
X_1 \left( \frac{\partial \log \gamma_1}{\partial X_1} \right)_{P.T.} = X_2 \left( \frac{\partial \log \gamma_2}{\partial X_2} \right)_{P.T.}
\]

where \(X_1\) = mol fraction of component 1 in the liquid and \(X_2\) = mol fraction of component 2.

\(\gamma_1\) = activity coefficient of component 1

\(\gamma_2\) = activity coefficient of component 2

The empirically derived Van Lear equation (51), can be written in the form:

\[
\log \gamma_1 = \frac{A}{\left(1 + \frac{A}{B} \cdot X_1 \right)^2} \quad \text{and} \quad \log \gamma_2 = \frac{B}{\left(1 + \frac{B}{A} \cdot X_2 \right)^2}
\]

This is a re-arranged form by Carlson and Colburn (52), so that the arbitrary constants \(A\) and \(B\) represent the terminal values of the \(\log\) of the activity coefficients of the two components.

i.e. at \(X_1 = 0\), \(\log \gamma_1 = A\) and at \(X_2 = 0\), \(\log \gamma_2 = B\).
The Margules equation (53) is:

\[ \log \gamma_1 = (2B - A) X_2^2 + 2(A - B) X_2^3 \] ........................ (3)

and \[ \log \gamma_2 = (2A - B) X_1^2 + 2(B - A) X_1^3 \]

again re-arranged by Carlson and Colburn so that \( A \) and \( B \) represent the end values of \( \log \gamma \).

Scatchard and Hamer (54) present an equation which brings in the molar volumes (\( V_1 \) and \( V_2 \)) of the components. When the molar volumes are equal the equation reduces to Margules' equation, and when the ratio \( V_1 : V_2 = A : B \), the equation reduces to the Van Lear equation.

The Gibbs-Duhem equation and its above integrated forms, only apply at constant temperature and pressure. Since the data to be calculated is not isothermal, a correction for temperature will have to be applied.

The activity coefficient changes with temperature and is related to the relative partial molal enthalpy of the particular component by the equation:

\[ \frac{d \log \gamma_1}{dT} = \frac{-L_1}{RT^2} \] ............................... (4)

\( L_1 \) is the partial molal enthalpy of component 1 in solution minus the enthalpy of the pure liquid at the same temperature. It is the heat absorbed or evolved on adding a mol of component 1 to an infinite quantity of solution.

If it is assumed that \( L_1 \) does not vary with temperature, integration of the above equation gives

\[ \log \gamma_{1_{T_2}} = \log \gamma_{1_{T_1}} - \frac{L_1}{R} \left[ \frac{T_2}{T_1} - 1 \right] \] ........................ (5)
It was decided to apply either the Van Laar or Margules' equations to the system.

Carlson and Colburn (52) indicate that when the ratio of molar volumes \( V_1 : V_2 \approx 1 \), Margules' equation should be used, and when the ratio \( V_1 : V_2 = A : B \) (\( A \) & \( B \) being the constants in the Van Laar equation) then the Van Laar equation should represent the data more closely.

The molar volume, \( V_N \), of nitric acid = \( \frac{63.03}{1.5125} = 41.65 \) c.c., and the molar volume, \( V_W \), of water = 18 c.c.

Thus \( V_N : V_W = 41.65 : 18 = 2.36 \).

The constants in the Van Laar equation may be obtained by solving the equation for \( A \) & \( B \) and we have

\[
A = \log \gamma_1 \left( 1 + \frac{X_2 \log \gamma_2}{X_1 \log \gamma_1} \right)^2 \]

and

\[
B = \log \gamma_2 \left( 1 + \frac{X_1 \log \gamma_1}{X_2 \log \gamma_2} \right)^2
\]

\( A \) and \( B \) were calculated at the point where the Carpenter and Babor curve crosses the curve of the Batch still data, so that it may be seen how the calculated curve compares with either. Thus \( A \) and \( B \) were evaluated at the common point \( X_N = 0.4285 \) and \( y_N = 0.5207 \), where \( X_N \) = mol fraction \( \text{H}_2\text{O}_3 \) in the liquid and \( y_N \) = mol fraction \( \text{H}_2\text{O}_3 \) in the vapour.

\[
\gamma_N = \frac{P \cdot y_N}{P_N \cdot X_N} \quad \text{and} \quad \gamma_W = \frac{P \cdot y_W}{P_W \cdot X_W}
\]

where \( P = \) total pressure = 760 m.m.

\( p = \) vapour pressure of the pure component at the particular temperature.

Subscripts /
Subscripts $N$ and $W$ refer to nitric acid and water respectively.

The boiling point data for the system were obtained from the values of Creighton and Githens (55). The vapour pressure of pure nitric acid was obtained from the data in the International Critical Tables by plotting $\frac{P_N}{2}$ vs. $\frac{1}{T}$ on semilogarithmic paper in order to get an approximately straight line. The vapour pressure of water was also obtained from the International Critical Tables.

The values of $A$ and $B$ in the Van Leer equation were found to be $-2.23$ and $-0.808$ respectively. The ratio $A : B = 2.76$ which compares with the ratio of $V_N : V_W = 2.54$. Thus the Van Leer equation should fit the system better than Margules' equation.

Values of the activity coefficients of both $\text{HNO}_3$ and $\text{H}_2\text{O}$ at the same liquid composition were calculated by means of the Van Leer equations over the whole composition range.

The effect of temperature on the activity coefficient was calculated by means of equation 5. Values of the relative partial molal enthalpy $L$ were obtained from a plot of the data of Wilson and Miles (31).

The vapour compositions were calculated from the activity coefficients, using the aforementioned vapour pressure and boiling point data.

The following table gives the calculated values both for the $\text{HNO}_3$ and for the $\text{H}_2\text{O}$. 
The fact that the values of $\gamma_N + \gamma_W$ do not equal 1, indicates that the equation does not apply rigidly to this system. It applies more or less in the region $x_N = 0.3$ to $x_N = 0.5$ because the constants were evaluated in this region.

The inability of the Van Laar equation to represent this system, or to indicate the accuracy of the experimental vapour-liquid equilibria is most likely due to its inapplicability to systems of electrolytes of this type, but may also be due to -

1. Errors in L. Wilson and Miles (31) obtained values for the differential heats of solution (the differential heat of solution is identical with the relative partial molal enthalpy) of HNO₃ and H₂O at concentrations of 90, 80, 70, 60 and 50% HNO₃ and point out that the value for 50% is doubtful.

2. Changes in L with temperature.

Carlson /
Carlson and Colburn (52) point out that there are indications that changes rapidly with temperature.

(3) Deviations of the vapour from a perfect gas.

It is pointed out, however, by Forsyth and Giauque (54) that no appreciable association exists in the vapour over nitric acid solutions.

(4) Inaccurate vapour pressure data: Taylor's set of data was used because it is the most extensive, but it is pointed out in the Introduction that other workers have found discrepancies in it.
The Ternary System H₂SO₄ - HNO₃ - H₂O

The results are calculated on a NO₂ - free basis both in the condensate and in the "vapour", as already described in the binary system.

It has already been pointed out that the maximum mol fraction of HNO₃ obtainable in ternary mixtures, with the strengths of acid available is about 0.6. Because of the consequently lower concentrations of HNO₃ in ternary solutions the NO₂ content of the condensate is not as high as with binary solutions. The problem of NO₂ is, therefore, not as difficult in the ternary system.

The data are plotted in Figure 6 as mol fraction HNO₃ in the condensate and in Fig. 7 as mol fraction HNO₃ in the "vapour", against mol fraction HNO₃ in the liquid on a H₂SO₄ - free basis. The correct curves of the vapour - liquid equilibria should, presumably, lie between the corresponding curves of Figures 6 and 7, their position depending on the extent to which the reaction between NO₂ and H₂O takes place on condensation of the vapour and subsequent analysis.

Smooth, regular curves are obtained in Figures 6 and 7, but it is evident that the curves of mol fraction HNO₃ in the "vapour" (Figure 7) are more regular than the curves of mol fraction HNO₃ in the condensate (Figure 6), in the concentrated region (above a mol fraction of HNO₃ of 0.90).

The evaluation and plotting of the data in terms of mol fractions /
FIG. 7

$H_2SO_4 - HNO_3 - H_2O$

$0.05, 0.10, 0.15, 0.20, 0.30$, MOL FR. $H_2SO_4$

MOL FRACTION $HNO_3$ IN "VAPOUR"

MOL FRACTION $HNO_3$ IN LIQUID
fractions is a very rigorous method in this system, in the
region of high HNO₃ concentration in the vapour. A value
for the mol fraction of HNO₃ in the condensate (or vapour) of
0.90 corresponds to a weight %HNO₃ of 97%. Because of the
quite different molecular weights of HNO₃ and of H₂O, a small
change in the weight %HNO₃ in this region can alter the mol
fraction to a large extent. For instance a %HNO₃ of 97%
corresponds to a mol fraction of 0.899, but a %HNO₃ of 97.86%
corresponds to a mol fraction of 0.928. Similarly a change
from 98% to 99% HNO₃ corresponds to a change in mol fraction
from 0.9345 to 0.966.

Since quite a large part of the curve exists above a mol
fraction of 0.90, and because of the difficulty of handling
and analysing accurately those highly concentrated, fuming
acids, it is very difficult to obtain smooth curves on such a
rigorous plot as a mol fraction plot.

In fig.8, in order to illustrate the above effect, the
data are plotted in terms of weight %HNO₃ in the condensate
on a NO₂ - free basis against mol fraction HNO₃ in the liquid
on a H₂SO₄- free basis. It is evident that smooth curves can
be obtained in this less rigorous method.

It is impossible to compare the data obtained in the
Batch still, directly with the data of Carpenter and Babor or
of Berl and Samtleben, over the whole composition range, as
their data is not evaluated on a NO₂ - free basis.
FIG. 8.

$\text{HSO}_4^{-} + \text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$

$0.05 \ 0.10 \ 0.15 \ 0.20 \ 0.30 \text{ MOL FR. H}_2\text{SO}_4$

$\% \text{ HNO}_3 \text{ IN CONDENSATE}$

$\text{MOL FRACTION HNO}_3 \text{ IN LIQUID}$
FIG. 9

\( H_2SO_4 - HNO_3 - H_2O \)

0.05, 0.10, 0.15, 0.20 mol fr. \( H_2SO_4 \)

Comparison with
Carpenter & Babors' Data

Mol Fraction \( HNO_3 \) in Liquid vs. Mol Fraction \( HNO_3 \) in Vapour

FIG. 10

\( H_2SO_4 - HNO_3 - H_2O \)

0.05 0.10 0.15 0.20 mol fr. \( H_2SO_4 \)

Comparison with
Berl & Samtleben's Data

Mol Fraction \( HNO_3 \) in Liquid vs. Mol Fraction \( HNO_3 \) in Vapour
In the dilute region of HNO₃ concentration the Batch still data (dotted curves) are compared with the data of Carpenter and Babor and of Berl and Santleben (solid curves) in Figures 9 and 10 respectively. Carpenter and Babor's data have been evaluated in terms of mol fractions from values interpolated from the original values, and given in convenient form by Smith and Cairns (56). Berl and Santleben's data have been evaluated in terms of mol fractions from the diagrams given by Stephenson (21). The curves for 0.05, 0.10, 0.15 and 0.20 are compared.

The Batch still curves would seem to be more regular than those of the other workers, and differ from those of Carpenter and Babor, and those of Berl and Santleben, though the curves show that the Batch still data resemble the former workers' data more closely than those of the latter workers.

It is apparent from Figures 9 and 10, that the Batch still curve corresponding to 0.05 mol fraction of H₂SO₄ lies below those of the other workers and that as the mol fraction of H₂SO₄ is increased, the Batch still curves tend to lie above the corresponding curves of the other workers.

These differences can not be explained by a consistent error due to fractionation in any of the data.

Fractionation in a HNO₃ - H₂O vapour evolved from a ternary solution will have the same effect as in the case of a binary solution the vapour strength decreasing if below
68%, and increasing if above 68%.

In the case of a ternary solution, however, there should possibly be less danger of fractionation in the vapour, than in the vapour evolved from a binary solution, because of the raising of the boiling point by the sulphuric acid. The following graph, Figure 11, shows the effect on the temperature of the vapour, of the presence of H2SO4 in the liquid.

The consequent superheating of the vapour should probably tend to offset any heat loss that may occur in the vapour, reducing the possibility of fractionation.
The vapour-liquid equilibria at any desired mol fraction of $\text{H}_2\text{SO}_4$ in the liquid can be obtained by interpolation from the curves of the Batch still data. This can be done as in Figure 12 in which smooth curves are obtained by plotting mol fraction $\text{H}_2\text{SO}_4$ in the liquid against mol fraction $\text{HNO}_3$ in the liquid, with mol fraction $\text{HNO}_3$ in the condensate as parameter. The equilibrium data at any mol fraction of $\text{H}_2\text{SO}_4$ up to 0.30 can be readily obtained.

The equilibrium data obtained in the Gillespie still in the ternary system are compared in Figure 13 with the data of Berl and Sartleben. The data are plotted as $\%\text{HNO}_3$ in the condensate in equilibrium with ternary mixtures. The series of curves give Berl and Sartleben's data in the form of $\%\text{HNO}_3$ in the vapour in equilibrium with ternary mixtures. They are reproduced from the diagrams given by Stephenson (21).

Figure 13 would seem to indicate that the Gillespie still values for the strengths of the vapour in equilibrium with ternary solutions are generally higher than the corresponding values of Berl and Sartleben.
FIG. 12

INTERPOLATED VAPOUR-LIQUID EQUILIBRIA

MOL FR. HNO₃ IN VAPOUR AS PARAMETER
GILLESPIE STILL DATA
COMPARSED WITH
BERL & SAMTLEBENS' DATA

FIG. 13
The data obtained are given in Table 10 and are plotted in Figure 14 as mol fraction HNO₃ in the condensate on a NO₂-free basis vs. mol fraction HNO₃ in the liquid on a Mg(NO₃)₂-free basis. The corresponding curve for 0.05 mol fraction H₂SO₄ in the liquid is plotted on the same graph.

Figure 14 shows that 0.05 mol fraction of Mg(NO₃)₂ in the liquid has a greater effect in increasing the volatility of the nitric acid than a similar amount of H₂SO₄, i.e. the selectivity of Mg(NO₃)₂ is greater than that of H₂SO₄.
FIG. 14

\[ \text{MOL FRACTION HNO}_3 \text{ IN CONDENSATE} \]

\[ \text{MOL FRACTION HNO}_3 \text{ IN LIQUID} \]

- O - 0.05 MOL FR. H_2SO_4 IN LIQUID

+ - 0.05 MOL FR. Mg(NO_3)_2 IN LIQUID
Conclusions

The results obtained above and the comparisons made between them and the other data illustrate the discrepancies that exist in the vapour-liquid equilibrium data in the systems HNO₃ - H₂O and H₂SO₄ - HNO₃ - H₂O, particularly, in the ternary system.

The importance of the presence of oxides of nitrogen in the vapour on the evaluation of the equilibrium data has been indicated and results have been calculated on a nitrogen peroxide - free basis. It would appear that this importance of the oxides of nitrogen has not been completely realised previously.

Since the decomposition of nitric acid increases with time of heating, the ideal equilibrium still for use with this system would be one which reduces the time of heating of the acid to a minimum.

The main part of the work has been carried out in the Batch Equilibrium still. It would seem, from the results on the system HNO₃ - H₂O that there is a slight fractionation effect in this still, and that it may not give results as rigorous as those obtained with the Gillespie still. However, the desirability of obtaining the data in the predictable form described above, probably outweighs any slight inaccuracies in the method. As it is, the results obtained would seem to indicate possible errors in the existing /
existing data, in the important region 0.15 to 0.30 mol fraction H₂SO₄ in the liquid.

The inability of the Van Laar equation to apply closely to the system HNO₃ - H₂O is to be expected in a system of this type, in which, besides the customary forms of "non-ideality", there must exist strong ionic forces.

The results obtained in the system Mg(NO₃)₂ - HNO₃ - H₂O indicate that, mol for mol, the Mg(NO₃)₂ has a greater effect than H₂SO₄ in increasing the volatility of nitric acid from nitric acid solutions. In that respect, therefore, Mg(NO₃)₂ should be more efficient than H₂SO₄ in the concentration of nitric acid.
PART II
Fractionating Column for Concentrating Nitric Acid

The column is a 2" diameter glass column containing five feet of quartz packing. It is diabatically controlled in order to prevent heat loss and provision is made for sampling the liquid and vapour streams inside the column.

The column is built between two wooden platforms eight feet apart, the lower one being seven feet from the floor.

The concentrated sulphuric and weak nitric acids are pumped by a diaphragm pump to the top platform whence they are fed into the column. Open steam from an electrically heated steam generator is fed into the bottom of the column.

The column consists basically of five 18" long sections of 2" diameter Pyrex glass pipe with flanged ends as shown. Each section has four side outlets of standard ½" pipe; outlets A and B are for vapour and liquid sampling respectively, C is for a thermocouple pocket and D for providing an entry for feed if required.
Metal flanges fit around the ends of the pipe, graphited asbestos inserts fitting between the metal and the glass. The sections are joined by butting the ends together on a compressed asbestos gasket and bolting the flanges together.
THERMOCOUPLE POCKET for LIQUID SAMPLING DEVICE

ILLUSTRATION OF VAPOUR & LIQUID SAMPLERS & THERMOCOUPLE
Sampling Devices inside the Column

In order to sample the liquid and vapour streams inside the column, sampling devices were made to fit inside each section except the bottom one, in order to bring the liquid and vapour streams leaving and entering each section respectively, to convenient points for samples to be withdrawn through the outlets mentioned above.

The sample devices are made in glass in one piece as shown in diagram. They rest on four indentations in the wall of the section. The device consists of an inverted cone at the top with four grooves ground in its rim so that the device can be pushed up from the bottom of the section past the indentations, turned and lowered so that it rests on them. This cone serves to support the packing in the section. It has several holes in its surface to allow the vapour to pass up and the liquid down. Holes in the wall of the central tube connected to this cone allow the vapour coming from the section below to pass on up the column. Liquid flowing down from the packing in the section collects in the annular tray, leaving by means of the downpipe. This downpipe is bent so that a pool of liquid is always present on the tray, and is provided with a siphon breaker to prevent the liquid from syphoning over. The annular tray is made from tubing slightly larger in diameter than the inside diameter of the section and the walls of the tray are ground down so that a comparatively tight fit is obtained when the device is pushed into the section.

Each /
Each sampling unit was individually made to fit inside a particular section.

**Vapour Sampling.**

A sample of vapour entering a particular section is obtained through a tube as shown which projects through the side outlet on the section and into the vapour stream through a hole in the wall of the central tube of the sampling device. This hole is provided with a large lip in order to prevent liquid from falling down on to the sampling tube and probably contaminating the vapour sample. For the same reason the end of the vapour sampling tube is slightly bent up.

Because of the mixing of the vapours induced by their passing up the narrower central tube the sample should be representative of the vapour passing this point in the column.

**Liquid Sampling.**

A sample of liquid leaving a particular section is obtained through a narrow bore glass tube bent as shown dipping into the pool of liquid on the annular tray. The sampling tube dips into the liquid just above the downpipe so that a sample of liquid leaving the tray is taken by which time it should be well mixed and be representative of the liquid leaving the section.

The wall of the tray partially blocks the side outlet on the section and a groove is ground in the wall of the tray to allow/
allow the sampling tube to enter and to dip into the liquid.

The vapour and liquid sampling tubes are sealed into $\frac{3}{8}$" pipeline ends which are bolted to the appropriate $\frac{1}{8}$" side outlet. The sampling lines outside the column are of thick walled capillary.

The liquid and vapour sampling tubes were made individually for each section before the sections were packed or built into the column so that proper fitting would be assured.

Small coil condensers were then added to the sampling lines for the condensation and cooling of the samples. These arrangements will be described later.
Heat Insulation Arrangements of the Column

Each section before being packed and fitted into the column was fitted with a device to prevent heat loss from the section and to ensure that the column could be operated adiabatically.

The essentials are:-

Two coils of resistance wire of the same length are wound on each section - one on the glass itself and one outside a layer of lagging. These two coils form two arms of a Wheatstone Network. Two standard coils form the other two arms. An electric heater is wound on outside the outer coil of resistance wire. The heater is controlled until the galvanometer in the Network indicates that the bridge is balanced at which time the resistances and, therefore, the temperatures of the two resistance coils on the section are the same. The normal heat loss from the section is then balanced by the heat supplied by the heater.

Details of the arrangements are:-

125 feet of 28 S.W.G. enamelled copper wire are non-inductively wound on each section by means of a lathe, the wound length on the section being approximately 11 inches. The ends of the wire are insulated by sleeving and clamped to the glass. 125 feet were used in order to get a considerable length of wire on the section and still allow reasonable spacing between the turns (18 per inch). The resistance of the coil is approximately 5.8 ohms.
A \( \frac{1}{2} \)" thick layer of moulded glass wool lagging is clamped around the section on top of this coil, fitting around the side-arms and having \( 1" \) holes for sight glasses in front and back opposite the vapour sampling tube.

On top of this layer of lagging the second resistance coil is wound, of the same length as the first, and again non-inductively wound on the lathe.

It was at first thought that magnetic amplifiers could be used to amplify the unbalanced current of the Wheatstone Network and operate the heater which would be a wire of larger resistance taking a small current. It was found, however, that the amplifiers necessary would be unduly expensive.

It was thus decided to use Sunvic Simmertats operated by 250 volts A.C. to operate the heaters on each section.

Some experiments were carried out to determine what size of heater was required to balance the bridge when the column was working.

No data was available on glass wool lagging but it was found from the literature that with magnesia lagging (2"), and overall diameter 5", surrounding a pipe carrying steam, the heat loss was approximately 70 B.T.U. per hour per \( \frac{1}{2} \) foot length - roughly equivalent to 25 watts. Thus it was decided to allow for at least 50 watts of heat input to each section. One section was rigged up to test the arrangement. The two resistance coils were wound on. A heater coil /
coil was wound on, also by means of a lathe, insulated from
the outer resistance coil by asbestos paper and a sheet of
micas. A heating coil of 70 feet of 30 S.W.G. Brightray
heating wire, having a total resistance of 300 ohms, and
taking a current of 0.8 amps, was tried. It was controlled
by a simmerstat. A 4" thick layer of glass wool lagging was
clamped on top of the heater coil. The Wheatstone Network
was completed by making up two coils of manganin wire of
1.0 ohms each as the other two arms, and connecting in a
1.2 volt battery and a centre zero milliammeter as
galvanometer.

Steam was used to heat up the section and when passed
in the galvanometer needle was very quickly deflected to the
end of the scale. When the heater was switched on, by
means of the simmerstat, it was found that in order to get
approximately zero deflection on the galvanometer the on-off
control had to be on for only a comparatively short time.
This short time of heating caused the galvanometer needle to
hunt about the zero rather than come to rest.

Thus a higher resistance was required in the heating
circuit to reduce the current and the heating effect and
ensure that the on-off control would be on for a greater part
of the time so that temperature fluctuations would be
smaller.

Bearing in mind that approximately 50 watts of heat
input are required for each section, and assuming that the
simmerstat /
simerstat would now be on for at least 50% of the time in order to give ample heating capacity when the temperature is higher inside and the heat loss proportionally greater than when steam at 100° is inside the section - a heater which could supply 100 watts was required. Thus 40 yards of 30 S.W.G. Brightray heating wire of total resistance 480 ohms, taking a current of 0.5 amperes, were used.

To lessen further the temperature fluctuations arising from the intermittent heat supply, a sheet of 18 gauge aluminium was shaped to fit around the section. For ease of fitting it was cut lengthwise in two halves. Holes were cut in it so that it would fit around the side outlets on the section. This sheet was interposed between the heater and the outer resistance coil, insulated from the latter by asbestos paper, and from the heater by a sheet of mica.

The aluminium will serve to damp and even out the heat supply.

When this arrangement was tried out by passing steam into the test section, it was found to work perfectly, the galvanometer needle being quickly brought to zero by the action of the heater, without any hunting of the needle.

Each section is, therefore, fitted with this method of adiabatic control.

On operation of the column it was found that the heaters were of adequate size to cater for any heat loss, and were never on for more than 75% of the time even in those sections where the temperature was very high.
Column Packing

Quartz-chip packing is used, very carefully sieved and graded between 1/8" and 3/16" sieves.

Several larger chips of quartz placed on the packing support of the sampling device prevent the small chips from falling through.

About 1/4" layer of smaller chips are spread on top of the packing in each section in order to help distribute the liquid flow coming from the section above.

Details of packing:

- Height of packing in each section = 12"
- Weight " " " " = 750 gm.
- Volume " " " " = 320 m.l.
- Free volume in the packed length of each section = 293 m.l.

The five sections of the column wound and packed in the above way are built into a column between two platforms 8 feet apart the lower one being 7 feet from the floor.

PHOTOGRAPH
OF
PACKED SECTION.
Column Supports

The column is supported at the top and bottom of the five superimposed sections.

Top Support (See diagram)

The top of the column is reduced from 2" diameter to 1" diameter by a 2" to 1" reducer having three side-arms of \( \frac{5}{8} \)" pipe-line ends as shown in diagram.

The top of the column projects through a hole cut in the top platform, wide enough to let the lagged column through. Two pieces of 1" thick wood of the shape shown are bolted to steel straps on each side of the hole. Screwed to the wood and having the same shape are two pieces of \( \frac{1}{8} \)" aluminium sheet. The two halves of the support are butted together around the top section so that the heads of the bolts in the flange on the top section rest on the aluminium. This forms the top support of the column.

Bottom Support (See diagram)

The bottom of the column is reduced from 2" diameter to \( \frac{5}{8} \)" diameter by a 2" to \( \frac{5}{8} \)" reducer.

The bottom support consists of an \( \frac{1}{8} \)" aluminium sheet slung from 1" steel straps bent in the shape shown. The reducer on the bottom of the column fits through a \( \frac{5}{8} \)" hole in the centre of the aluminium sheet and the heads of the bolts in the flange on the reducer rest on the aluminium.

The position of the support is adjustable by means of
ADJUSTING SCREWS

FRONT VIEW

8'

SIDE VIEW

7'

BOTTOM SUPPORT
OF
COLUMN
the adjusting nuts and bolts.

**Erection of the Column**

The column was built section by section from the top downwards. The nuts and bolts in the flanges on each section had to be tightened very carefully and evenly to ensure that the column was vertical. When the bottom section of the column was added the adjustable support was raised to meet the heads of the bolts in the flange and to take part of the weight of the column.

**SECTION WOUND**

**WITH**

**WHEATSTONE NETWORK & HEATER COILS**
Top of the Column

The 2" to 1" reducer at the top of the column is provided with three \( \frac{3}{8} " \) outlets. These are for feed entry ports and for a thermocouple pocket.

The reducer is connected to a 30" length of 1" pipe. This length of pipe is wound with resistance coils and heater coil in exactly the same way as the packed sections of the column in order to prevent heat loss and condensation in this pipe of the vapour, leaving the top of the column.

A standard 1" T piece is connected to the top of this pipe. A resistance thermometer pocket made from a 1" blank pipe-line end, is bolted to the top of the T and provides a means of measuring the temperature of the vapour. A 1" right angle bend leads from the T to a condenser. The condenser is a triple coil condenser having a 1" pipeline end at the top and a \( \frac{3}{8} " \) end at the bottom, the overall length being 12".

The bottom of the condenser is 18" from the inlet to the head of the column, providing adequate height for a reflux control device if required.

The condenser is supported by an adjustable aluminium bracket fixed to the wall, the flange at the top of the condenser resting on the bracket.

The bottom of the condenser is connected by a 14" length of \( \frac{3}{8} " \) pipe, provided with a vent to atmosphere, to a 11 mm. Fyrex glass line leading to the product receivers.
The product line is clamped to a 4" cable plate screwed to the wall at the side of the column. Two stopcocks in a T at the bottom of the line enable the product receivers to be switched.

To prevent contamination of the atmosphere with nitrous fumes with bare tubing leading to a fume duct is placed conveniently near the vent below the condenser and at the product receivers.
SUPPORTING PLATE

PLATFORM

SYPHON BREAKER

COOLER JACKETS

SPRING CLIP

THERMOCOUPLE POCKET

SCALE INS.

SWIVEL DEVICE

LEAD TRAY

WOOD SUPPORT

TO RECEIVERS

BOTTOM OF COLUMN
Bottom of the Column

The column is reduced at the bottom to \( \frac{3}{8} \)" pipe by a 2" - \( \frac{3}{8} \)" reducer as described and connected to a cooler as shown using standard \( \frac{3}{8} \)" right angle and U return bends. Two water jackets surrounding the \( \frac{3}{8} \)" pipes serve to cool the liquid leaving the bottom of the column. The cooler provides a liquid seal at the bottom of the column. A syphon breaker as shown prevents the liquid from syphoning over.

The liquid flowing from the cooler enters a swivelling device which enables the bottoms to be switched from one receiver to another. This device consists, as shown, of a lead tray supported on wood on steel brackets from the wall. A B14 ground glass socket joined to the pipe ab in the diagram fits through a hole beaten in the centre of the tray. A B14 cone fitting into this socket can be swivelled to direct the acid flow from the column into either of three funnel shaped holes beaten in the tray and so into either of three lines leading to the bottoms receivers.

When the column was operated it was found that the acid lying in the cooler tended to seep through the compressed asbestos gaskets at the pipeline joints. The asbestos gaskets in the colder part of the cooler were, therefore, replaced by polythene gaskets cut from \( \frac{1}{16} \)" polythene sheet.
ILLUSTRATION
OF
THE SAMPLE CONDENSERS
The sampling lines between the column and condenser are in capillary, partly for strength, and also to ensure that the hold-up in the line is small.

Each line is provided with a stopcock and a B14 cone is fitted at the bottom of the condenser so that sampling bottles may be fitted.

The condensers are supported by clamps bolted to a 6" cable plate fixed rigidly beside the column behind the condensers. The cable plate is fixed at top and bottom to the platforms and in between by brackets from the wall.

Water is supplied to the sampling condensers and to the product condenser through ½" copper tubing, having suitable branches brazed on, fixed behind the cable plate.

When the column was operated, it was found, as expected, that the pressure inside the column was sufficient to blow out the samples of liquid and vapour without any suction being applied.

In the first few runs it was found that the sampling could upset the column equilibrium. The composition of the vapour entering each section was calculated from a mass balance across each section, making use of the constant flow of sulphuric acid down the column, and compared with the sampled value. The calculated and sampled values agreed quite well when the strength of the vapour was high but not so well in the dilute regions at the bottom of the column. This was mainly due to bad sampling. When a greater amount of manipulative skill had been acquired in the operation of the column /
When the column proper had been built as above the arrangements for the sampling of the liquid and vapour were completed and the thermocouples added.

Cooling and Collection of Samples.

It has already been described how the samples are obtained from inside the column. When withdrawn from the column the samples must be condensed and cooled respectively. This is done by small coil condensers on each line as shown.
column it was found that, with a little care, the stopcocks in the sample lines could be adjusted to deliver a sample dropwise at a very slow rate (less than one drop a minute), slow enough not to disturb the column equilibrium. A quick sample could also be easily obtained, by opening the stopcock fully for a short time, with apparently little effect on conditions inside the column.

In all the runs after the first few the liquid stream only was sampled, and the vapour composition at the corresponding point calculated by a mass balance.
**Thermocouple pockets**

Thermocouple pockets sealed to ¾" blank ends are fitted into each section as shown in the diagram. (p. 94)

The pocket protrudes into the column and just enters a hole in the central tube of the sampling device so that it should be at least partly in the stream of liquid flowing down from the packing.

When the sampling condensers and the thermocouples had been fitted an outer layer of 1" moulded glass wool lagging was clamped on each section on top of the heater coil.

This lagging does not cover the flanges at the ends of the sections, which can thus be examined for leaks and tightened if necessary without removing the section lagging. Specially cut pieces of lagging cover the flanges.

**Section heater and resistance coil leads**

The leads from the heaters and resistance coils on each section, insulated by sleeving, are led through the outer lagging and into a five way connector strip bolted to a lagging band.

The heater leads are connected to a two-core cable and the three resistance coil leads to a three-core cable which are carried on a 4" cable plate fixed beside the column between the two platforms. It also carries woven-glass insulated iron constantan thermocouple wire. The cables and thermocouple wires are led down the cable plate to an instrument panel standing on the floor in front of the column.
Instrument Panel

The instrument panel consists of a $6\frac{1}{2}' \times 2' \times \frac{1}{6}''$ aluminium sheet screwed to the front of a $6\frac{1}{2}' \times 2' \times 15''$ framework of $1\frac{1}{2}''$ angle iron. The sides back and top of the box so formed are covered with hardboard screwed to the angle iron.

This structure stands on the floor in front of the column. To make it rigid, the top of the framework is screwed to the bottom platform on which the column stands.

The aluminium panel itself is made in three parts. The simmerstats operating the heaters on the sections are fitted into one part at the top of the panel, the controls for the Wheatstone Network arrangements on a second part, and the main part contains the controls for the steam generator and the acid pump, the mains simmerstat switch, fuses and a manometer. The panel also has a Cambridge Thread Recorder fitted into it.

Section Heater Controls.

The simmerstats controlling the heaters on the sections are mounted in the detachable top section of the panel. Small panel bulbs (0.5 amps) are connected in series with each heater and are mounted above the corresponding simmerstat on the panel. These bulbs indicate when the heater is working and act as simple fuses. The leads from the heaters on the column are led into a connector strip behind this part of the panel.

Overhead /
Overhead Vapours Temperature Recorder.

Below the above section of the panel a Cambridge Thread Recorder is fitted to record the temperature of the overhead vapour by means of a resistance thermometer arrangement.

A 10 ohm resistance coil of manganin wire fits in the pocket already mentioned in the T at the top of the column. Three standard 10 ohm coils are fitted behind the instrument. A dry battery (1.2 volts) is used in the circuit. A rheostat fitted behind the recorder provides a means of adjusting the p.d. applied to the network in order to standardise the instrument. As the battery voltage varies this has to be done occasionally. It is done by adjusting the rheostat until the instrument reads the correct temperature as indicated by a thermometer placed in the resistance coil pocket or by placing the resistance coil in a beaker of hot water and adjusting the rheostat until the instrument reads the correct temperature.

The arrangement is:

---

![Circuit Diagram]

S - STANDARD RESISTANCE
S' - RESISTANCE COIL IN POCKET
R - RHEOSTAT
G - GALVANOMETER
Wheatstone Network Controls

To the right of the recorder a small detachable section of the panel (9½" x 13½") contains the controls for the Wheatstone Network Arrangements.

Twelve-contact switches are used to make and break the various circuits. One switch operates the networks on two sections, four of the contacts being used for each section circuit. By one throw of a switch the network on a particular section can be broken in two places as shown.

Thus when the battery is on and when all the network switches are off no current flows through the galvanometer. It flows only through the two standard coils. When the network /
THE INSTRUMENT PANEL.
WIRING DIAGRAM
FOR
TEMPERATURE CONTROL
ON
EACH SECTION

B. BATTERY
C. CONNECTOR
R. RESISTANCE COILS
S. SWITCHES
network on one section is switched on, current is only
flowing through the coils on that section and no other.
This is a much better and safer arrangement than one in
which the circuit is broken in one place only, in which case,
current flows through the galvanometer and through one of
the coils on each section all the time.

A centre-zero milliammeter with a low internal
resistance (6 ohms) is used as a galvanometer. Two 10 ohm
resistance coils forming the two standard arms of the
Wheatstone Networks are fixed behind the panel. A 1.2 volt
battery and switch completes the circuit. The three-core
cable leads from each section of the column are led into a
connector strip fixed behind the panel.

The wiring diagram is as shown.

Bottom Section of the Panel.

On the large bottom section of the panel are fitted an
ammeter, rheostat, rotary switch and fuses to operate the
steam generator; thermocouple switches; a rotary switch
and circuit breaker for the acid feed pump; a fuse and main
switch for the air heater; mains fuse, and a manometer to
measure the pressure drop across the column.

Thermocouple Controls.

Iron-constantan thermocouples are fitted into the
pockets in the five sections at the positions already
indicated, in one of the outlets in the reducer at the top of
the /
the column, projecting into the product vapour stream, and in a pocket in the 8" line at the bottom of the column, measuring the temperature of the liquid stream before it enters the cooler.

The thermocouple leads are connected directly into twelve-contact, double throw switches mounted in the bottom part of the instrument panel. Both leads of each thermocouple are broken across a switch. One switch operates two thermocouples. This method is more foolproof, there being less danger of leakages, than in the use of a common lead for all the thermocouples.

The temperatures are measured by a direct-reading Integra potentiometer, having a compensating cold junction.

All the thermocouples were checked by calibration on this instrument, the limits of accuracy of which should be considerably less than ± 0.5 °C.

**Manometer**

The manometer consists of a U-tube filled with mercury mounted on the panel as shown in the diagram.

The manometer line is connected to the top of an 8" reflux condenser fitted with a 3" pipeline end and connected to one of the outlets on the bottom section of the column. A small bleed of air from the compressed air supply is fed through a bubbler, fitted on the instrument panel, and blown up the manometer line to prevent any nitric acid vapour coming down the line. The reflux condenser also helps to prevent this.
The bubbler enables the flow of air to be adjusted to a very small bleed. Water was used at first in the bubbler, but it was found that water vapour carried up, condensed and blocked the line. To get over this difficulty, concentrated sulphuric acid is used in the bubbler.
CONC. SULPHURIC & WEAK NITRIC ACID PUMPS
The two push rods are driven by one cam on a shaft mounted in the middle of the angle iron framework. The cam-shaft is driven directly through a rubber coupling by a ½ H.P. electric gear motor.

The above assembly is mounted on a strong support fixed to the wall 2½ feet above the floor.

Standard ¾" T's are connected to the reducers ½" pipeline bent to the required shape leads from the bottom of the T's to the acid carboys on the floor - one of concentrated sulphuric acid and one of weak nitric acid - and from the tops of the T's to the feed lines clamped to the wall.

Glass valves are built into the lines above and below the reducers. They consist of 3" glass tubes joined to solid glass beads which are ground into constrictions in the pipeline wall. The hollow tubes of the valves are partly filled with mercury. Indentations in the pipeline wall act as guides to keep the valves vertical.

The mercury is used to make the valves heavier and to cause them to return to their seats quickly. This was found necessary especially in the sulphuric line where the acid is so viscous and dense that a solid glass valve returned so slowly to its seat that the pump made no headway.

**Feed Lines**

The two acid feed lines are clamped to a 6" cable plate screwed to the wall. The acids pumped up the lines are fed into constant head tubes on the top platform, the overflow from/
Sulphuric and Nitric Acid Feeds to the Column

The concentrated sulphuric and weak nitric acids are pumped through 3⁄8" glass pipeline from the floor level up to the top platform.

Feed Pumps

The pumps are diaphragm pumps. Two 2" to 3⁄8" pipeline reducers are bolted at either side of a 3⁄8" angle iron framework measuring 5" x 7" x 6". The diaphragms are of polythene and are clamped between the 2" end of the reducer and two thicknesses of hardboard, having 2" diameter holes corresponding to the 2" end of the reducer. The flanges on the reducer is bolted to a brass plate on the side of the framework.

The diaphragms are made up as shown. A sheet of polythene, 0.01" thick, and two thicknesses of filter cloth, are rivetted between a 3⁄8" thick, 13⁄8" diameter, polythene disc and a 13⁄8" diameter steel disc. The rivets are of aluminium and are countersunk in the polythene disc and welded over with polythene.

The diaphragms in each of the reducers are actuated by push rods which are supported by bushes on the brass plates. The end of the push rod is held as shown to the steel disc. The lengths of the push rods are adjustable to vary the pumping capacity as required. They are provided with strong restoring springs to supply the pulling action on the diaphragm.

The /
from which passes down 2\textquotesingle\textquotesingle pipe, clamped to the same cable plate, and back to the carboys. The constant head tubes are made as shown.

Acid Feed to the Column

Acid is syphoned from the constant head tubes into tubes leading to the column. These feed lines are sealed to pipeline ends and project through the appropriate outlet into the centre of the column so that the acid is delivered in the centre of the packing.

The syphons are held in spring clips in syphon adjusters by means of which the syphon can be raised or lowered to alter the amount of feed. The adjuster is screwed to the platform.

This method of feeding ensures a very steady feed rate to the column.

The acid pump is controlled from the instrument panel. As the motor takes a high starting current, a circuit breaker is included in the circuit rather than a fuse.

The pump is primed by removing the length of pipeline connecting the T in the line to the feed lines, and filling the reducer with water, the air being removed by suction through a small rubber tube pushed into the reducer.

It was found that leaks at the diaphragms in the pumps caused some trouble, either by the acids seeping through between the 4\textquotesingle\textquotesingle polythene disc and the diaphragm (see the diagram) and attacking the rivets, or by the diaphragms bursting. The polythene diaphragm was welded to the 4\textquotesingle\textquotesingle disc.
disc in order to get over this, tighter rivetting was used and double thicknesses of diaphragm were employed. This continued to give more or less consistent trouble, however. Otherwise the pump was found to work well.

Compressed asbestos gaskets were at first used in the feed lines and it was found, mainly in the W.N.A. feed line, that the acid seeped through and attacked the brass bolts joining the flanges. For this reason the gaskets in both lines were replaced by polythene gaskets cut from 1/16" polythene sheet, and the brass nuts and bolts in the nitric line were replaced by stainless steel nuts and bolts.
Steam Generator

Steam is fed into the bottom of the column from a steam generator. This consists of 1½ feet of 1" steel pipe as shown:

A 1½ Kilowatt heater coil is wound on asbestos paper on the pipe - 50 feet of 22 S.W.G. Dullray heating wire of resistance 0.8 ohms/foot are used and operated from the 240 volts A.C.

The pipe is fixed on brackets from the wall and its level is adjustable.

It is reduced at the water entrance and to ¹⁄₄" and at the other end to ¹⁄₂". A ½" brass union joins this end to a glass connecting piece which is fitted with a ¾" glass pipeline end and joined to the outlet at the back of the bottom section of the column. The connecting piece is also provided with a thermometer pocket and a steam poker to project into the column.

Water /
Water is fed into the generator from a constant head tube by a syphon. A syphon adjusting device is used similar to those described for the acid feeds.

This method of generating steam is used in order to eliminate any reservoir of water so that the amount of steam produced can be controlled more or less directly by the water input rather than by the heat input, as the former can probably be altered and controlled more easily.

It was calculated that approximately 500 watts should be sufficient to evaporate the necessary amount of water for the concentration column. With the above method, however, this amount of heat supply is not nearly enough and it was found quite difficult to generate steam by feeding water into a hot tube so that the water feed would be the controlling factor.

Various methods were tried before the above method was adopted. It was found necessary to have the tube sloping down towards the water entrance end so that a small pool of water is always present.

The rheostat in the heater circuit is adjusted until all the water fed in is vaporized, as indicated by the tap at the end of the generator, the temperature of the steam being maintained at 100°C.
PHOTOGRAPH OF COLUMN.
Experimental Procedure

The distillation column was first employed to fractionate an ethyl alcohol-water mixture in order to determine the equivalent number of plates in the column.

The alcohol-water system, though not well suited for such a determination in a column in which the number of plates is large, because of the shape of the equilibrium curve and the existence of an azeotrope, should be of use in this column where, it was presumed, the equivalent number of plates is not large.

The reducer and the ½” pipeline leg on the bottom of the column were removed and a 4 litre flask, clamped to a retort stand, connected to the bottom of the column by means of a rubber bung. The flask was provided with a bottom outlet and stopcock.

A dilute alcohol solution was boiled in the flask by a gas burner. The column was operated at total reflux by feeding the distillate into one of the ½” side-arms in the reducer at the top of the column. The column was allowed to run for about 6 hours in order to ensure that equilibrium was reached. After this time a sample of distillate was collected and a sample of the bottoms run off from the flask.

The samples were analysed by density determinations for which extensive data are available in the International Critical Tables.
The equivalent number of plates was determined graphically by the McCabe-Thiele method, the vapour-liquid equilibrium data of Jones Schoenbom and Colburn (39) being used. The number of plates was found to be 8.3 and the H.E.T.P. is therefore \( \frac{5 \times 12}{8.3} = 7.2\). 

Though this figure will probably give little indication of the equivalent number of plates when the column is used to concentrate nitric acid, it serves as a comparison for columns used for more normal distillations.

Operation of the column as a Concentration Column.

Experiments were carried out with water flowing down the column and air blown up to determine the approximate flooding point in the column. They indicated that this corresponded to rather a low liquid flow rate compared for instance to the flooding rate of 10-12 litres per hour of a column of similar diameter packed with 5/32" steel helices (57).

When the column was used to concentrate nitric acid it was found that a liquid flow rate corresponding to approximately /
approximately 5 litres an hour of acid feed corresponded to a pressure drop across the column of about 1 foot of water.

This was considered to be rather high so the flow rate was lowered to 3 - 4 litres an hour and was maintained at approximately this value throughout the whole series of runs, corresponding to a pressure drop of a little over 6\" of water.

From the start the column worked well. No leaks could be observed at the gaskets in the column at the start of operation, but it was found eventually that the acid tended to seep through. This happened mainly with the gaskets in the \( \frac{3}{8} \)" side-arms on the sections, the acid seeping through and eventually attacking the brass bolts and, in the top part of the column where the nitric strength was high, attacking the plastic flanges. Stainless steel bolts were used, tightened as much as possible and this solved the trouble to a considerable extent.

It was realised that this difficulty could only be solved completely by the use of an impervious, resistant material such as poly-tetrafluoroethylene.

In the main, however, the column stood up well to the rigorous conditions under which it was used.

**Adiabatic Controls**

The simmerstats operating the heaters on the sections...
were adjusted so that the heat supplied was very slightly less than that required, as indicated by the Wheatstone Network controls.

**Liquid and Vapour Sampling.**

As already mentioned after the preliminary runs, only the liquid stream was sampled. This was done by adjusting the stop-cock in the sampling line so that a slight bleed of liquid was delivered all the time that the column was running (less than one drop per minute), and collecting it only when the column had come to equilibrium. When equilibrium was reached a snap sample could easily be obtained by opening the stop-cock fully for a short time. This was sometimes done, only after the product and bottoms had been collected over a period, however.

**Collection of Product and Bottoms.**

When it was considered that equilibrium had been attained in the column, as indicated by the steady state of the temperatures at the various points, and after running for an hour at these steady conditions, the product and bottoms streams were switched into tared vessels and collected over ½ to ½ hour. This served to give accurate values of the feed rates of both concentrated sulphuric and weak nitric acids.

It was found that the time to reach equilibrium varied according to the conditions, varying from about one hour to about six.

The /
The feed rates of both acids were usually adjusted approximately to the desired values by timing the flow from the feed syphon and adjusting it accordingly, before a particular run.

Analysis.

The acids were handled in weighing pipettes and analysed as described in the section on vapour-liquid equilibria.

(a) Product: Total acidity was determined by titration with sodium hydroxide. Oxides of nitrogen were determined by the addition of a known excess of potassium permanganate, addition of potassium iodide and back titration of the liberated iodine by sodium thiosulphate. The oxides of nitrogen are reported as NO₂.

Since 1 mol of NO₂ is obtained from the decomposition of 1 mol of HNO₃, the value for the total acidity (as HNO₃) of the product is a measure of the HNO₃ present assuming no decomposition has taken place. It is the value of total acidity that has been used, therefore, in the material balances in order to find the F.M.A. feed rate.

(b) Ternary liquid mixtures: Total acidity was determined by titration with sodium hydroxide. The H₂SO₄ content was determined by evaporating the /
the mixture on a steam bath to drive off the HNO₃, as already described, and titration of the remaining H₂SO₄ with sodium hydroxide.

In order to analyse accurately those liquids containing very small amounts of HNO₃, they were analysed by weighing 4 - 5 gm. of the mixture directly into a 500 ml. standard flask and analysing 25 ml. portions of the diluted mixture in the above manner, using N/10 sodium hydroxide.

The column was run at first with the feeding arrangements of normal extractive distillation, the W.N.A. being fed in at the bottom of the second section (numbering the sections from the top downwards), through the ½" outlet for the purpose, at the back of the section, and on to the tray of the sampling device inside the section. The C.O.V. was fed into the top of the column through one of the outlets in the reductor at the top of the column.

This method of feeding the W.N.A. meant that a sample of L₂ (the liquid leaving the second section) could not be obtained, but a sample of the mixture of L₂ and the W.N.A. feed was obtained. It was found, however, that a representative sample of this mixture could not be obtained, presumably because of poor mixing of the two streams on the tray of the sampling device. This was shown by carrying out material balances across sections 2 and 3, calculating the composition of V₃, (the vapour leaving the third section) assuming the sampled value of (L₂ + W.N.A.) to be correct, and comparing the /
the calculated value of $V_3$ with the sampled value of $V_3$. They did not agree. It has already been mentioned that in the upper parts of the column where the vapour strength was high, the calculated values of vapour strength agreed well with the sampled values in the early runs. Thus, the sampled value of $V_3$ was probably correct and the calculated value wrong. As the sampling technique had not yet been expertly acquired, this was probably due to "over" sampling in the lower part of the column, besides being due to poor mixing of $L_2$ and the W.N.A. on the tray.

The correct value of the composition of $L_2$ could be determined by a heat and material balance across sections 2 and 3, and this was attempted. However, because of the poor quality of the early runs (1 and 2), and the tedious nature of the calculations involved, it was not considered worth while to complete them.

Because of this difficulty of finding the composition of $L_2$, the method of feeding the W.N.A. was changed. It was fed in at the side of the section, through the side-arm normally occupied by the thermocouple pocket. The feed tube projected into the central tube of the sampling device, as shown in the diagram, on the following page, so that the W.N.A. did not mix with $L_2$ on the sampling tray, but fell down into the top of section 3.
A sample of L2 can thus be directly obtained. This method of feeding the W.N.A. was used in all the runs with split feed except Runs 1 and 2.
Experimental Results

The results obtained in the concentration column are tabulated in the following tables.

As mentioned above, the column was first run with the feeding arrangements of a normal extractive distillation unit, the W.N.A. in Runs 1, 2 and 3 being fed at the bottom of the second section and the C.O.V. at the top of the column.

In Runs 4 to 12 the column was run in the normal concentration column manner with both feeds entering at the top of the column.

In Runs 13 and 14 the column was again run with the W.N.A. entering at the bottom of the second section, and in Runs 15 and 16 the W.N.A. was fed in at the bottom of the first section.

In all the runs material balances have been carried out over each section using the sampled values of the liquid composition entering and leaving the section. The vapour compositions given have, thus, been calculated. A basis of 100 mols H_2SO_4 flowing down the column has been used.

The tables of results are constructed so that the amount and composition of the liquid and vapour streams leaving and entering each section respectively are horizontally opposite each other. The values of the temperature given opposite these values in the tables are the mean values of the temperatures registered by the corresponding thermocouple at that
that point, when equilibrium had been attained.

That value of the temperature given opposite the
P and S\textsubscript{p} values in the table corresponds to the temperature
registered at the top of the column by the thermocouple in
the product vapour stream and is, therefore, the temperature
of the product vapours as they leave the packing.

The value of the temperature given opposite the steam
and Bottoms values in the tables is the temperature given by
the thermocouple at the bottom of section 5. Since it is
positioned just where the steam enters the column its value
is probably not indicative of the temperature of the liquid
stream at that point, but is probably a mean value between
the liquid temperature and the steam inlet temperature of
100\degree C.
Nomenclature in the Tables of Results.

Sections numbered 1 to 5 from the top downwards.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_f$</td>
<td>Sulphuric acid feed</td>
</tr>
<tr>
<td>$N_f$</td>
<td>Nitric acid feed</td>
</tr>
<tr>
<td>$S$</td>
<td>$\text{H}_2\text{SO}_4$</td>
</tr>
<tr>
<td>$N$</td>
<td>$\text{HNO}_3$</td>
</tr>
<tr>
<td>$W$</td>
<td>$\text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

$N(S)$ - Equivalent nitric acid = $\text{HNO}_3 + \text{NO}_2$

Since 1 mol $\text{NO}_2$ is obtained from 1 mol $\text{HNO}_3$ and since

1 mol $\text{NO}_2$ = 1 mol $\text{HNO}_3$

the value of the total acidity (reported as $\text{HNO}_3$) in the analysis is a measure of the $\text{HNO}_3$ present assuming no decomposition has taken place.

Thus mols $N(S)$ = mols ($\text{HNO}_3 + \text{NO}_2$)

and $\% N(S) = \%$ total acidity (as $\text{HNO}_3$)

$L_1, L_2, L_3, L_4$ - Liquid leaving 1st, 2nd, 3rd and 4th sections respectively, numbering from the top downwards.

$B$ or $L_5$ - Bottoms, i.e. liquid leaving section 5.

$V_2, V_3, V_4, V_5$ - Vapour leaving 2nd, 3rd, 4th and 5th sections respectively, numbering from the top downwards.

$P$ or $V_1$ - Product i.e. vapour leaving 1st section.
**Run 1**

**Split Feed:** W.N.A. \((N_p)\) fed at bottom of section 2.

**Feed Temperatures = 13^\circ\text{C}.$$  Acid ratio = 2.954$$

**Time of flow of 100 moles \(H_2S\)O\(_4\) = 3.2 hrs.**

**Note:** Not a good run. Stripping is poor. Values of the vapour compositions given are the sampled values.

<table>
<thead>
<tr>
<th>T. ^\circ\text{C}.</th>
<th>VAPOUR</th>
<th></th>
<th></th>
<th>LIQUID</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MOLS</td>
<td>MOL FR.</td>
<td>WT %</td>
<td>MOLS</td>
<td>MOL FR.</td>
<td>MOL FR. (S-FREE)</td>
</tr>
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<td></td>
<td></td>
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</table>
### Run 2

**Split Feed**: W.N.A. fed at bottom of section 2.

- **Feed Temperatures**: 13°C, **Acid ratio**: 2.565
- **Time of flow of 100 moles H₂SO₄**: 3.35 hrs.

**Note**: Improved stripping with greater steam supply than in Run 1.

See comparison of calculated and sampled values of V on following page. The difference is due to "oversampling" of the liquid.

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<tr>
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<th>LIQUID</th>
</tr>
</thead>
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<td>MOL FR.</td>
</tr>
<tr>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>60.56</td>
<td>100</td>
</tr>
<tr>
<td>W</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NO₂)</td>
<td>-</td>
<td>(1.456)</td>
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<td>000606</td>
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<td></td>
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<tr>
<td>120.6</td>
<td>STEAM</td>
<td>155.2</td>
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<tr>
<td>W</td>
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<td>000231</td>
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</table>
Comparison of the sampled values of the vapour compositions inside the column and the values calculated by material balance.

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<tr>
<th></th>
<th>Sampled Values</th>
<th>Calculated Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_2$</td>
<td>77.65% HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>78.25% HNO&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>$V_3$</td>
<td>79.52% HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>/</td>
</tr>
<tr>
<td>$V_4$</td>
<td>1.695% HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.86% HNO&lt;sub&gt;3&lt;/sub&gt;</td>
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<tr>
<td>$V_5$</td>
<td>0.076% HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.212% HNO&lt;sub&gt;3&lt;/sub&gt;</td>
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</tbody>
</table>

All the vapour compositions in the following tables have been calculated by material balance.
Run 3

Split Feed: W.N.A. fed at bottom of section 2.
Feed Temperatures = 171°C. Acid ratio = 1.903.
Time of flow of 100 mols H₂SO₄ = 3.09 hrs.

Note: NO₃ undetectable in the bottoms. Lower acid ratio used than in Run 2. Note the constant mol fraction overflow in the stripping section.

<table>
<thead>
<tr>
<th>T. °C</th>
<th>VAPOUR</th>
<th>LIQUID</th>
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<tr>
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<td>MOL FR.</td>
</tr>
<tr>
<td></td>
<td>N(E)</td>
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</tr>
<tr>
<td></td>
<td>W</td>
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</tr>
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<td>86.2</td>
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<td>88.18</td>
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<td>3.30</td>
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<td>121.2</td>
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<tr>
<td>114.7</td>
<td>V₂ N</td>
<td>78.18</td>
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<td>W</td>
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<td>V₃ N</td>
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</tr>
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</tr>
<tr>
<td></td>
<td>W</td>
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</tr>
<tr>
<td>125.5</td>
<td>V₅ N</td>
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</tr>
<tr>
<td></td>
<td>W</td>
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<td>122.8</td>
<td>STEAM</td>
<td>100</td>
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</tbody>
</table>

TOTAL | 424.2 |
### Run 4

**Combined Feed.**

Feed Temperatures = 15°C.  
Acid ratio = 1.966.

Time of flow of 100 mols H₂SO₄ = 3.29 hrs.

Note: The column is not being fully utilised. It should, therefore, be possible to decrease the acid ratio.

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<th>LIQUID</th>
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<tr>
<td></td>
<td>N(?)</td>
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<tr>
<td></td>
<td>W</td>
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<td>10.6</td>
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</tr>
<tr>
<td></td>
<td>TOTAL</td>
<td>137.8</td>
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<tr>
<td>92.9</td>
<td>V₃</td>
<td>136.5</td>
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<tr>
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<td>19.5</td>
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<td>V₄</td>
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</tr>
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</tr>
<tr>
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<tr>
<td></td>
<td>TOTAL</td>
<td>419.7</td>
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</tbody>
</table>
Combined Feed

Feed Temperatures = 18°C. Acid ratio = 1.954
Time of flow of 100 mols H₂SO₄ = 3.45 hrs.

Note: Excess steam has been used and a dilute product obtained. The mol fr. H₂SO₄ in the column is lower than in Run 4, even though the acid ratio is approximately the same, because of the weaker C.O.V. used.

Run 5

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</table>
Combined Feed.

Feed Temperatures = 17°C. Acid ratio = 1.68.

Time of flow of 100 mols H₂SO₄ = 3.84 hrs.

Note: Low acid ratio and stripping is still reasonably good.

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Run 7

Combined Feed.

Feed Temperatures = 1710°C, Acid ratio = 1.716.

Time of flow of 100 mole H₂SO₄ = 3.82 hrs.

Note: Steam supply is slightly less than in Run 6, giving slightly poorer stripping and stronger product.

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Combined Feed.

Feed Temperatures z 17 1/2°C. Acid ratio = 1.83
Time of flow of 100 mols H2SO4 = 3.82 hrs.

Note: Higher acid ratio than in Run 7 and consequently stronger product.

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### Run 9

**Combined Feed.**

Feed Temperatures = 15°C. Acid ratio = 1.601

Time of flow of 100 mols H₂SO₄ = 4.10 hrs.

**Note:** Inadequate steam supply and column is not being wholly used.

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<tr>
<td>114</td>
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Combined Feed.

Feed Temperatures = 14°C. Acid ratio = 1.676.

Time of flow of 100 mols $H_2SO_4$ = 4.25 hrs.

Note: The column is now being fully utilised.

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<tr>
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<tr>
<td>S+F</td>
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<td>F</td>
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<td>L</td>
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</table>
Run 11

Combined Feed:

Feed Temperatures = 144.0°C. Acid ratio = 1.609

Time of flow of 100 mols H₂SO₄ = 4.26 hrs.

Note: Steam supply is greater than in Run 10. The product is consequently weaker and stripping better.

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<td>132</td>
<td>V₂</td>
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<tr>
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<tr>
<td>116.6</td>
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</table>

Note: Total mass for each run is 100 moles.
Run 12

Combined Feed.

Feed Temperatures = 14°C. Acid ratio = 1.57

Time of flow of 100 mole H₂SO₄ = 4.62 hrs.

Note: The acid ratio and the mol fraction H₂SO₄ in the liquid in the column are low. The stripping is consequently poorer than in Run 11.

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<td>P(N)</td>
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<tr>
<td>132.8</td>
<td>V_2(N)</td>
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</table>
Run 13

Split Feed: W.N.A. fed at bottom of section 2.

Feed Temperatures = 151°C. Acid ratio = 1.645

Time of flow of 100 moles H$_2$SO$_4$ = 4.20 hrs.

Note: The stripping is poorer than in the runs with combined feed and product strength is not much higher.

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<td></td>
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Run 14

Split Feed: N.N.A. fed at bottom of section 2.

Feed Temperatures = 17.5°C. Acid ratio = 1.658.

Time of flow of 100 mols H₂SO₄ = 4.17 hrs.

Note: Steam supply increased over than in Run 13. Consequently, stripping is better and the product slightly weaker.

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</tr>
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Run 15

Split Feed: W.N.A. fed at bottom of section 1.

Feed Temperatures = 14°C. Acid ratio = 1.695.

Time of flow of 100 mols H₂SO₄ = 4.08 hrs.

Note: Stripping is better than in Runs 13 and 14 because of higher position of the W.N.A. feed.

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<tr>
<td>P</td>
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<tr>
<td>W</td>
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<tr>
<td>(NO₂)</td>
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<tr>
<td>153</td>
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<tr>
<td>V</td>
<td>111.77</td>
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<tr>
<td>W</td>
<td>94.33</td>
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<td>135.5</td>
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<td>113.3</td>
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</tbody>
</table>

136.
Run 16

Split Feed: W.N.A. fed at bottom of section 1.

Feed Temperatures = 14°C. Acid ratio = 1.625.

Time of flow of 100 moles H₂SO₄ = 4.14 hours.

Note: Slightly poorer stripping and stronger product than in Run 15 because of smaller steam supply.

<table>
<thead>
<tr>
<th>T °C</th>
<th>VAPOUR</th>
<th>LIQUID</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MOLS</td>
<td>MOL FR.</td>
</tr>
<tr>
<td>118</td>
<td></td>
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<tr>
<td></td>
<td>P N</td>
<td>95.1</td>
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<tr>
<td></td>
<td>W (NO₂)</td>
<td>19.14</td>
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<td></td>
<td>TOTAL</td>
<td>114.2</td>
</tr>
<tr>
<td>154</td>
<td>V₂ N</td>
<td>98.03</td>
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<tr>
<td></td>
<td>W</td>
<td>98.47</td>
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<td>TOTAL</td>
<td>195.8</td>
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<td></td>
<td>N F</td>
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<td></td>
<td>W</td>
<td>190.86</td>
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<td></td>
<td>L₁ N</td>
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<td></td>
<td>W</td>
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<td>TOTAL</td>
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<tr>
<td>132</td>
<td>V₃ N</td>
<td>5.276</td>
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<tr>
<td></td>
<td>W</td>
<td>197.92</td>
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<td>V₅ N</td>
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<td>V₆ N</td>
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<td></td>
<td>W</td>
<td>123.6</td>
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<td></td>
<td>TOTAL</td>
<td>524.2</td>
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</tbody>
</table>
Discussion

In order to compare the actual column results with the theoretical conditions that should exist in the concentration column, plate by plate calculations were carried out based on the terminal conditions existing in the actual runs on the column.

The methods used in these theoretical calculations and the results obtained from them are given in the following pages.
Theoretical Plate by Plate Calculations

Data.

Extensive data on the thermal properties of the systems HNO₃ - H₂O and H₂SO₄ - HNO₃ - H₂O are available. The data was obtained in a very convenient form from the unpublished paper of Smith and Cairns (56) of the Ministry of Supply. They have collected and tabulated all the available data on the systems.

In the binary system HNO₃ - H₂O they have computed heats of dilutions from the data of Forsyth and Giaquinto (34), Wilson and Miles (31) Berthelot (58) and Thomsen (59), boiling point data have been obtained from the data of Greigton and Githens; specific heats have been evaluated from the data of Morgan, Bender and Capell (60).

In the ternary system, the heat contents of ternary mixtures relative to the pure components at 25°C, are given. They have been evaluated from McDavid's data (61) and the heats of mixing recalculated using mean specific heats from the values of Morgan, Bender and Capell (60). Boiling points have been interpolated from the data of Berl and Semtibin (35). Specific heats have been evaluated from the data of Morgan, Bender and Capell (60). At t°C the specific heat = a + bt. Tables give the values of a and b at 5% intervals of H₂SO₄ and HNO₃ concentration. The heat contents of mixtures at temperatures other than 25°C can be obtained from the equation:

\[ H_t / \]
\[ H_t = H_{25} + (t - 25) \left( a + b \frac{(t + 25)}{2} \right) \]

where \( H_t \) = heat content at \( t^\circ C \) in cals./gm.
and \( H_{25} = " " 250 " " \)
both referred to the pure components at \( 25^\circ C \).

Values of the heat contents of nitric acid vapour are
given from 80°C to 150°C at 5°C intervals of concentration,
relative to the pure components at \( 25^\circ C \). These values have
been calculated from the equation -

\[ Q_t = \frac{p}{100} \cdot V_N + \frac{100 - p}{100} \cdot V_W + H_t. \]

where \( Q_t \) = Total heat of nitric acid vapour at \( t^\circ C \) in cals/gm.
\( p = \%\text{HNO}_3 \) in the vapour
\( V_N = \) Latent heat of vaporisation of \text{HNO}_3
\( V_W = " " " " " " \text{H}_2\text{O} \)
\( H_t = \) heat content of liquid of the same composition
as the vapour at \( t^\circ C \).

It would seem, however, that there is an error in this
method of evaluation of \( Q_t \).

This method assumes that there is no heat of separation
of the nitric acid and the water at the boiling point of the
mixture.

The heat content of the vapour should be given by the
equation -

\[ Q_t = \frac{p}{100} \cdot V_N + \frac{100 - p}{100} \cdot V_W + H_t + \text{heat of separation of the components at } t^\circ . \]

The heat of separation, \( \Delta S \), at any temperature will be
the/
the same as the heat of mixing of the components, \( \Delta M \), at
that temperature, and opposite in sign.

The variation of the heat of separation with
temperature will be given by Kirchoff's Equation -
\[
\frac{d(\Delta S)}{dt} = C_pN + C_pW - C_{P\text{mix}}
\]
where \( \Delta S \) = heat of separation at the datum temperature (25°)
\( C_pN \) = mean heat capacity of HNO\(_3\) over the temperature range
\( C_pW \) = " " " " H\(_2\)O " " " "
\( C_{P\text{mix}} \) = " " " " " mixture " " " "

Thus, the heat of separation at temperature \( t^o \) is -
\[
\Delta S_t = \Delta S_{25} + (t-25) \left( C_pN + C_pW - C_{P\text{mix}} \right)
\]
The value of \( H_t \) in the above equations can be written as:-
\[
H_t = H_{25} + (t-25) \left\{ a + b \frac{(t+25)}{2} \right\}
\]
\[= \Delta M_{25} + (t - 25). \ C_{P\text{mix}} \]
where \( \Delta M_{25} \) = heat of mixing at 25°.

Thus, the heat content of the vapour at \( t^o \) is:
\[
Q_t = \frac{\rho}{100} \cdot \ V_N \ + \ \frac{(100 - \rho)}{100} \cdot \ V_W \ + \ \Delta M_{25} \ + \ (t-25). \ C_{P\text{mix}}
\]
\[+ \ \Delta S_{25} \ + \ (t - 25) \left\{ C_pN + C_pW - C_{P\text{mix}} \right\}
\]

Since \( \Delta M_{25} = - \Delta S_{25} \)
\[
Q_t = \frac{\rho}{100} \cdot \ V_N \ + \ \frac{(100 - \rho)}{100} \cdot \ V_W \ + \ (t - 25)(C_pN + C_pW)
\]

The values of \( Q_t \) in the tables of Smith and Cairns are,
therefore, wrong.

The correct value of \( Q_t \) is given by the last equation and-
\[
Q_t = \text{Value in table} \ + \ \Delta S_{25} \ + \ (t - 25)(C_pN + C_pW - C_{P\text{mix}})
\]
\[= \text{Value in table} \ + \ H_{25} \ + \ (t - 25)(C_pN + C_pW - C_{P\text{mix}}) \]

Such /
Such a calculation in order to find $Q_t$ would be tedious. However, if it is assumed that the heat of mixing (or the heat of separation) varies but little with temperature, the last term in the above equation can be ignored.

Since $H_{25}$ is negative the corrected value of the heat content of the vapours may be obtained by adding the numerical value of $H_{25}$ to the corresponding value of $Q_t$ given in the tables of Smith and Cairns.

In the following calculations, this was done in the evaluation of the heat contents of the nitric acid vapours.
Calculation based on the terminal conditions of Run 4.

Terminal conditions in Run 4:

Basis 100 mole H₂SO₄

<table>
<thead>
<tr>
<th></th>
<th>Wt. gm</th>
<th>H₂SO₄ Cal/gm</th>
<th>Sensible heat cal/gm</th>
<th>Total heat content</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄ Feed</td>
<td>10.130</td>
<td>-13.83</td>
<td>-2.7</td>
<td>-167,450</td>
</tr>
<tr>
<td>(% = 96.8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₃ Feed</td>
<td>7.475</td>
<td>-47.54</td>
<td>-3.79</td>
<td>-385,850</td>
</tr>
<tr>
<td>(% = 66.8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam</td>
<td>3110</td>
<td>-</td>
<td>-</td>
<td>1,910,000</td>
</tr>
<tr>
<td>Product</td>
<td>5135</td>
<td>-</td>
<td>-</td>
<td>913,200</td>
</tr>
<tr>
<td>(% = 97)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bottoms</td>
<td>15380</td>
<td>-76.7</td>
<td>64.8</td>
<td>185,300</td>
</tr>
</tbody>
</table>

Acid ratio = 1.966

Heat Balance:

Heat in = Heat in Steam + Heat in Feeds
= 1,910,000 - 167,450 - 383,850
= 1,358,700 cal.

Heat out = Heat in Bottoms + Heat in Product
= -185,300 + 913,200
= 727,900 cal.

Heat loss = 630,800 cal.

The balance is out and must be due to heat loss from the column, which must be larger than would have been anticipated.

However, experiments with hot water flowing down the column from the top, indicated that by far the greater part of the heat loss was from the ends of the column, with very little /
little heat loss in between.

The heat loss at the bottom of the column is noticeable in all the runs, by the difference between the moles of steam input and the moles of $V_5$. This reduction is also partly due to the fact that the steam is supplied at $100^\circ$, part of it, therefore, being condensed to raise the temperature of the remainder to that of the boiling dilute $H_2SO_4$ at a temperature of $150^\circ - 160^\circ C$.

In order to make the heat quantities balance for the purpose of the theoretical plate by plate calculation, the amounts of steam and the composition of the bottoms were altered from the existing values of Run 4. In evaluating the new values it was assumed there was no heat loss from the column.

For simplicity the calculation was based on 100 gm $H_2SO_4$ flowing down the column instead of 100 mole $H_2SO_4$, the thermal data being available in terms of weight units.

The altered quantities based on 100 gm $H_2SO_4$ are thus:

- $H_2SO_4$ Feed: 96.80% Wt. = 103.3 gm.
- $HNO_3$ " : 66.80% Wt. = 76.18 gm.
- Product: 97% Wt. = 52.48
- Steam: Wt. = 22.40 gm.
- Bottoms: % $H_2SO_4$ = 66.9  
  % $HNO_3$ = 0.01 Wt. = 149.4 gm.

The % $HNO_3$ in the bottoms was taken as 0.01% for the purposes /
purposes of the calculation, as this is the value aimed at in commercial columns.

Heat quantities (referred to pure components at 25°C):

Heat content of the Bottoms = -1185 cals.
" " " " Feed = -5617 "
" " " " Product = 9318 "
" " " " Steam = 13750 "

The calculations were started at the bottom of the column, working upwards.

The Batch still vapour-liquid equilibrium data were used in the interpolated form of Figure 12.

In the dilute regions of HNO₃ concentration, at the bottom of the column, it can be assumed that the equilibrium curves are straight from about y = 0.1 to the origin (with the H₂SO₄ strength of the liquid as high as it is in the present case). The vapour in equilibrium with a liquid was, thus, found by converting the composition of the liquid to a mol fraction basis and drawing an equilibrium curve for the particular mol fraction of H₂SO₄ in the liquid and then finding the slope of the line; or, simply by taking the value of X (the mol fraction of HNO₃ in the liquid on a H₂SO₄-free basis) at y = 0.1 for the particular mol fraction of H₂SO₄, the slope of the equilibrium line in the dilute region then being \( m = \frac{0.1}{X} \). The mol fraction of HNO₃ in the vapour was then found from the equation \( y = mx \).
The procedure across a plate, e.g. plate 3, was thus:

1. The liquid composition leaving the plate L₃ was converted to a mol fraction basis.

2. The slope of the equilibrium curve was found at a mol fraction of H₂SO₄ equal to that in L₃, and hence the composition of the vapour, V₃, leaving the plate.

3. The heat content of the vapour V₃ was found, assuming it is at the same temperature as L₃.

4. A value for the weight of V₃ was assumed.

5. The weight and composition of L₄ was then found by means of a material balance around the plate.

6. A heat balance was then carried out over the plate to see if the assumption for the quantity of V₃ was correct. If the heat balance was out, another value of V₃ was assumed and the calculation repeated.

In order to avoid the tedious nature of the trial and error calculations involved in a plate by plate calculation, Sherwin (62) has put forward a method of calculation applicable to systems in which there is variable molal overflow. It depends on the approximation that the molar enthalpy

Hereafter the term "molal" will refer to the properties of a number of moles. The term "molar" will refer to a particular property of one mol of a substance.
enthalpy of the liquid falling on to a given tray is not greatly affected by the different trial assumptions for the vapour rate from the tray. A trial assumption for the vapour rate can be made to converge rapidly to the correct value, and the number of trials required to evaluate the plate is reduced.

By heat and material balances around m plates in a column (numbering from the bottom upwards) Sherwin develops the equation:

\[ V_m = Q - B h_m \frac{h_{m+1}}{h_m} + \frac{B h_m}{h_{m+1}} - h_m \]

where \( V_m \) = Vapour leaving mth plate; \( h_m \) = heat content of \( V_m \)

\( Q \) = reboiler heat duty

\( B \) = Bottoms; \( h_B \) = heat content of B.

\( L_{m+1} \) = liquid leaving plate \((m+1)\); \( h_{m+1} \) = heat content of \( L_{m+1} \)

In the evaluation of plate m, the only variables in the above equation are \( V_m \) and \( h_m \). By assuming a value for \( V_m \), as in the normal trial and error method, \( h_m + 1 \) can be found. If it is assumed that \( h_m + 1 \) does not change much with change in \( V_m \), then by substitution of the value of \( h_m + 1 \) in the above equation a new value of \( V_m \) can be found. Sherwin indicates that this second value of \( V_m \) can be very near to the correct value even though the original assumption is /
is very far out. If a still more accurate value of $V_m$ is required the value of $h_{im} + 1$ can be corrected using the second value of $V_m$ and the process repeated to give a third value of $V_m$.

An equation of the above type was developed for use in the plate by plate calculations in the present case.

Consider a part of the column containing $m$ plates.

A material balance gives:

$$St. + L_m + 1 = B + V_m$$

A heat balance gives:

$$St. h_{St.} - Bh_{B} = V_m \cdot h_{V_m} - L_m + 1 \cdot h_{im} + 1$$

$$\therefore \frac{V_m = St. h_{St.} - Bh_{B} + h_{im} + 1 (B-St.)}{h_{V_m} - h_{im} + 1}$$

Sherwin assumes that the molar heat content of $L_m + 1$ does not vary much with change in $V_m$, but the above equation was found to apply equally well to the present case with the quantities on a more convenient weight basis.

e.g. Sample calculation around plate 5.

From /
From the calculation around plate 4 it was found that the composition of L5 was

\[ \text{mol fraction} \]

\[
\begin{array}{ccc}
\text{H}_2\text{SO}_4 & 65.88 & 0.2753 \\
\text{HNO}_3 & 3.199 & 0.02869 \\
\text{H}_2\text{O} & 30.92 & \text{(H}_2\text{SO}_4 \text{ free)}
\end{array}
\]

and wt. of L5 was 151.8 gm.

From the data, the slope of the equilibrium curve at a mol fraction of H$_2$SO$_4$ of 0.2753 equals 9.09.

Thus \( y = 9.09 \times 0.02869 \)

\[ = 0.2603 \]

\[ = \text{mol fraction of HNO}_3 \text{ in V5} \]

\[ = 55.26\% \text{ HNO}_3 \text{ (by weight)} \]

Temperature of V5 = Temperature of L5

\[ = 155^\circ C \]

Heat content of V5 = 377.4 cal/s/gm.

Assume V5 is 36 gm.

\[ \therefore \text{By material balance L6 = B - St + V5} \]

\[ = 163 \text{ gm.} \]

H$_2$SO$_4$ in L6 = 100 gm. \( \therefore \text{H}_2\text{SO}_4 = 61.35 \)

HNO$_3$ in L6 = HNO$_3$ in V5 + HNO$_3$ in B = 19.90 gm. \( \therefore \text{HNO}_3 = 12.21 \)

Heat content of L6:

From the tables \( \text{H}_2\text{O} = -71.5 \text{ cal/s/gm.} \)

Sensible /
Sensible heat at the B.P. of 159°C. = 53.9 cals./gm.

\[ H_{L_6} = -17.6 \text{ cals./gm.} \]

Heat Balance across the 5 plates:

Heat in = Heat in Steam + Heat in L_6
\[ = 13750 - (17.6 \times 163) \]
\[ = 10,884 \text{ cals.} \]

Heat out = Heat in V_5 + Heat in Bottoms
\[ = (377.4 \times 36) - 1185 \]
\[ = 12,401 \text{ cals.} \]

The heat balance is out because of a wrong assumption for V_5.

Apply the Sherwin equation:

\[ V_5 = \frac{13750 + 1185 - 17.6}{377.4 + 17.6} \]
\[ = 32.15 \text{ say 32.2 gm.} \]

Repeat the evaluation of L_6:

The new wt. of L_6 = 159.2 gm.

\[ \text{H}_2\text{SO}_4 \text{ in L_6} = 62.62 \]
\[ \text{HNO}_3 \text{ in L_6} = 11.19 \]

Heat content of L_6, \[ H_{L_6} = -17.9 \text{ cals./gm.} \]

This value of \[ H_{L_6} \] compares with the value of -17.6 cals./gm. from the first assumption of V_5 and indicates that \[ H_{L_6} \] does not change much with change in V_5.

New Heat Balance:

Heat in = 13750 - (17.9 \times 159.2)
\[ = 10,905 \text{ cals.} \]
Heat out = (32.2 x 377.4) - 1185
= 10,968 cals.

Thus the heat quantities converge rapidly to balance point by the use of the above equation.

The equation could be applied a second time to evaluate $V_5$. This time the change in $h_{16}$ would be so small as not to make it worth while to evaluate $h_{16}$ again.

Thus $V_5 = \frac{13750 + 1185 - 17.9 (149.4 - 22.4)}{377.4 + 17.9}
= 32.04$ gm.

The calculations were carried out in this way right up the column. It was found that seven plates were required with this particular set of operating conditions.

The following tables give the liquid and vapour compositions, heat contents and molal overflows in the column in the above calculation.

### TABLE 41

<table>
<thead>
<tr>
<th>Liquid and Vapour Leaving Plate Number</th>
<th>Liquid</th>
<th>Vapour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mol Fr.</td>
<td>Mol Fr.</td>
</tr>
<tr>
<td></td>
<td>H₂SO₄</td>
<td>HN₃</td>
</tr>
<tr>
<td></td>
<td>(S-Free)</td>
<td>(S-Free)</td>
</tr>
<tr>
<td>1</td>
<td>.2785</td>
<td>.0000863</td>
</tr>
<tr>
<td>2</td>
<td>.275</td>
<td>.006571</td>
</tr>
<tr>
<td>3</td>
<td>.2743</td>
<td>.001725</td>
</tr>
<tr>
<td>4</td>
<td>.2728</td>
<td>.007425</td>
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<tr>
<td>5</td>
<td>.2752</td>
<td>.023669</td>
</tr>
<tr>
<td>6</td>
<td>.2837</td>
<td>.1091</td>
</tr>
<tr>
<td>7</td>
<td>.2856</td>
<td>.2578</td>
</tr>
</tbody>
</table>
The enthalpies of the liquid and vapour are given in terms of:

### TABLE 12

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Mols Flowing</th>
<th>H25 Cal/mol</th>
<th>Sensible heat Cal/mol</th>
<th>B.P. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>B or L1</td>
<td>3.765</td>
<td>-3.050</td>
<td>2759</td>
<td>157</td>
</tr>
<tr>
<td>L2</td>
<td>3.70</td>
<td>-3080</td>
<td>2787</td>
<td>159</td>
</tr>
<tr>
<td>L3</td>
<td>3.72</td>
<td>-3076</td>
<td>2770</td>
<td>159</td>
</tr>
<tr>
<td>L4</td>
<td>3.74</td>
<td>-3061</td>
<td>2780</td>
<td>157</td>
</tr>
<tr>
<td>L5</td>
<td>3.70</td>
<td>-3080</td>
<td>2680</td>
<td>155</td>
</tr>
<tr>
<td>L6</td>
<td>3.60</td>
<td>-3165</td>
<td>2376</td>
<td>141</td>
</tr>
<tr>
<td>L7</td>
<td>3.57</td>
<td>-3010</td>
<td>2040</td>
<td>117</td>
</tr>
</tbody>
</table>

### TABLE 13

<table>
<thead>
<tr>
<th>Vapour</th>
<th>Mols flowing</th>
<th>Latent Heat Cal/mol</th>
<th>Sensible heat Cal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam</td>
<td>1.244</td>
<td>9700</td>
<td>1350</td>
</tr>
<tr>
<td>V1</td>
<td>1.19</td>
<td>9170</td>
<td>2390</td>
</tr>
<tr>
<td>V2</td>
<td>1.20</td>
<td>9110</td>
<td>2415</td>
</tr>
<tr>
<td>V3</td>
<td>1.22</td>
<td>8950</td>
<td>2510</td>
</tr>
<tr>
<td>V4</td>
<td>1.19</td>
<td>8850</td>
<td>2510</td>
</tr>
<tr>
<td>V5</td>
<td>1.08</td>
<td>8720</td>
<td>2570</td>
</tr>
<tr>
<td>V6</td>
<td>1.05</td>
<td>8360</td>
<td>2570</td>
</tr>
<tr>
<td>V7 or P</td>
<td>0.894</td>
<td>8440</td>
<td>2040</td>
</tr>
</tbody>
</table>
terms of cals./mol relative to the pure components at 25°C,
calculated from the values in weight units obtained in the
calculation, and are still based on a flow of 100 gm. of
H₂SO₄ down the column.

The plate by plate calculation indicates that the molar
overflow is approximately constant, only slightly increasing
as the liquid flows down the column. This can be seen in
Table 12.

This means that, theoretically, the mol fraction of
H₂SO₄ in the liquid as it flows down the column is
approximately constant, and that, as there will be an
approximately linear relation between the mols of liquid and
vapour flowing, the operating lines will be approximately
straight. The system can be represented, therefore, on
rectangular coordinates and it should be possible to apply
McCabe - Thiele type calculations in the determination of the
number of plates.

This theoretical approximate constancy of molar over-
flow in this system can only be explained by the constancy
of the molar heat content of the liquid as it flows down the
column (see Table 12), combined with the fact that the molar
latent heats of vaporisation of H₂O₃ and H₂O are not very
different = 9355 cals./mol and 9729 cals./mol respectively.

The fact that the molar heat content at 25°C (H₂₅)
of the liquid flowing down the column is constant, must mean
that the molar heat of mixing at 25°C of the liquid on a plate
with /
with the liquid coming from the plate above, is negligible. This does not necessarily mean, however, that the heats of mixing of these liquids are negligible at the temperature existing inside the column. The heat of mixing may vary with temperature, the variation being given by Kirchoff's equation:

\[
\frac{d(\Delta H_{A \rightarrow B})}{dT} = (C_P)_B - (C_P)_A
\]

where \( \Delta H_{A \rightarrow B} \) = heat of mixing generated by mixing components A to give mixture B.

\( (C_P)_B \) = Heat capacity of mixture B.

\( (C_P)_A \) = " " " initial components.

Thus the heat of mixing at temperature \( T^0 \) is given by:

\[
\Delta H_T = \Delta H_{25} + (T - 25) \left\{ (C_P)_B - (C_P)_A \right\}
\]

It is difficult to show whether or not the heat of mixing of the liquids is negligible at the temperature existing inside the column. Since the molar heat of mixing is apparently negligible at \( 25^0 \), however, it is probably reasonable to assume that this is also the case at the higher temperatures inside the column.

Any change in heat of mixing with temperature will not, of course, affect the compositions or molal overflows already worked out in the above calculation, as the total enthalpy of any liquid at a particular temperature will still be the same, any change in heat of mixing with temperature merely resulting in a compensating increase or decrease in the value for the sensible /
sensible heat of the liquid, depending on the datum temperature used.

In the plate by plate calculation it is apparent that the sensible heat content of the liquid increases as the liquid flows down the column (see Table 12). The sensible heat content of the vapour, on the other hand, (Table 13) shows very little change - apart from the end values - and shows, if anything, an increase as it passes up the column. The molar latent heat of the vapour shows a decrease as the vapour passes up the column.

Thus it would seem that the gain in sensible heat of the liquid as it flows down the column is being balanced by the decrease in latent heat of the vapour as it flows up the column.

Because of the constancy of the sensible heat of the vapour and the assumed absence of heat of mixing, it is possible to balance the heat quantities across a plate, ignoring these factors and only taking into account the sensible heats of the liquids and the latent heat of in the vapours.

* e.g. Plate 4 in the calculation.

\[
L_4 h_{l4} + V_4 h_{v4} = L_5 h_{l5} + V_3 h_{v3}
\]

From Tables

\[
\begin{align*}
\text{L.H.S.} & = 2780 + 8850 = 11630 \\
\text{R.H.S.} & = 2680 + 8950 = 11630
\end{align*}
\]
also /
In Figure 15 the operating line of the above theoretical concentration is plotted - the mol fraction of HNO₃ in the vapour entering a plate is plotted against the mol fraction of HNO₃ in the liquid leaving the plate on a H₂SO₄ - free basis. A straight line is obtained.

The number of plates required for this concentration was evaluated graphically by the McCabe-Thiele method, in order to see how it compared with the plate by plate calculation.

The equilibrium curve was drawn by taking the mean value of the mol fraction of H₂SO₄ in the liquid over the column and interpolating from the Batch still data (Figure 12).

The operating line was drawn by taking the mean values of liquid and vapour flow over the column.

The mean number of mols of liquid = 3.67
" " " " " vapour = 1.16

The operating line has to be evaluated on a H₂SO₄ - free basis also, and as there are 100 gm. = 1.02 mols of H₂SO₄ flowing, the slope of the operating line is:

\[
\text{Slope} = \frac{1.56}{1.16}
\]
FIG. 15

PLOT OF OPERATING LINE
Slope \( \frac{L}{V} = \frac{3.67 - 1.02}{1.16} = 2.29 \)

Because of the fact that over the bottom plate there is a decrease in vapour flow, because steam at 100° is fed in, the bottom plate was not included in the graphical calculation, and the calculation started from the second plate upwards. The operating line was thus drawn of slope 2.29, and passing through the point \( (Y_N, V_1, X_N, L_2) \).

This McCabe - Thiele calculation is shown in Figure 16.

The number of plates was found to be 6.9, comparing well with the plate by plate calculation value of 7.

**Calculation at a lower acid ratio.**

In order to indicate if the approximate constancy of overflow is also to be found in runs in which the acid ratio is lower than in the above case (and in which the mol fraction \( H_2SO_4 \) in the liquid is lower, another plate by plate calculation was carried out.

The calculation was again carried out on a basis of 100 gm. of \( H_2SO_4 \) fed to the column by fixing on a composition for the bottoms (having approximately a mol fraction of \( H_2SO_4 \) = 0.18), the feeds and the product, the only unknown then is the amount of steam and the weight of the W.N.A. feed. These values can then be found by an overall heat and material balance.

**Basis 100 gm. \( H_2SO_4 \).**

<table>
<thead>
<tr>
<th>Bottoms</th>
<th>( % )</th>
<th>Mol Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2 )</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
FIG. 16

EQUILIBRIUM CURVE

OPERATING LINE

MOL FRACTION HNO₃ IN VAPOUR

MOL FRACTION HNO₃ IN LIQUID

0.01 0.02 0.03

0.01 0.02 0.03

PRODuct STRENGTH

0.0 0.1 0.2

0.3 0.4 0.5

0.6 0.7 0.8 0.9 1.0

0.01 0.02 0.03 0.04 0.05

0.1 0.2 0.3 0.4 0.5

MOL FRACTION HNO₃ IN LIQUID

0.0 0.1 0.2 0.3 0.4 0.5

0.6 0.7 0.8 0.9 1.0

0.01 0.02 0.03 0.04 0.05

0.1 0.2 0.3 0.4 0.5
<table>
<thead>
<tr>
<th>Bottoms</th>
<th>%</th>
<th>Mol Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄</td>
<td>54.3</td>
<td>0.1791 (\text{H}_2\text{SO}_4)</td>
</tr>
<tr>
<td>HNO₃</td>
<td>0.01</td>
<td>0.0000625 (\text{free basis})</td>
</tr>
<tr>
<td>H₂O</td>
<td>45.69</td>
<td></td>
</tr>
</tbody>
</table>

Wt. = 184 gm.

Product: 97% HNO₃  Wt. = 94.7 gm (found by heat and material balance)

H₂SO₄ feed: 96.80%  Wt. = 103.3 gm

HNO₃ feed: 66.80%  Wt. = 137.5 gm (found by heat and material balance)

Steam:  Wt. = 38 gm.

Acid ratio = 1.09

With this lower mol fraction of H₂SO₄ in the liquid, because of the lower slope of the equilibrium curve, a greater number of plates is required and the change in concentration across a plate in the dilute region is very small, with consequent small changes in enthalpies. Thus, even though there is not constancy of molal overflow in the upper parts of a column operated under such conditions, there will be approximately constant overflow in the bottom part of the column. The McCabe - Thiele method can, therefore, be applied to the bottom part of the column at least.

Since the steam is assumed to be entering the column at 100⁰, in the calculation, and the vapour leaving the bottom plate is regarded as being at the temperature of the bottoms /
bottoms (150°), the mols of vapour leaving the bottom plate will be less than the mols of steam entering because of the change in enthalpy.

In order to get the proper liquid and vapour quantities to calculate the slope of the operating line, a heat and material balance was carried out over the bottom plate and the slope of the operating line taken as \( \frac{L_2}{V_1} \) where \( L_2 \) is the mols of liquid leaving the second plate and \( V_1 \) is the mols of vapour leaving the first plate. The slope was found to be 2.24, and the line passes through the point \((x_1, L_2, y_1, V_1)\) where \( x_1 \) = mol fraction HNO₃ in \( L_2 \) on \( H_2SO_4 \) - free basis

\[
x_1 = \frac{M}{2.24} \quad V_1
\]

The equation of the operating line was thus found to be \( y = 2.24x - 0.0001623 \).

The equilibrium curve corresponding to the mol fraction of \( H_2SO_4 \) in \( L_2 \) was found from the vapour-liquid equilibrium data of Figure 12. The curve can be regarded as a straight line up to a mol fraction of HNO₃ in the vapour of about 0.1. The equation of the line was found to be \( y = 2.5x \).

The first 25 plates in the column were then determined analytically by the McCabe-Thiele method using the above equations of equilibrium and operating lines. Heat balances were carried out periodically to ensure that the method was sound, but even over this large number of plates the changes in heat contents of the liquid are small.
The plates from this point onwards were determined by heat and material balances, though it was found necessary to apply heat balances only in the upper parts of the column (after 35 plates), because of the very small change in the enthalpy of the liquid.

An equation on the lines of Sherwin's (62) was again developed to reduce the trial and error nature of the calculations in the upper part of the column.

It was found that between 48 and 49 plates were required in this theoretical concentration.

The following tables give the values of liquid and vapour compositions, amounts and heat contents evaluated in the calculation.

**TABLE 14**

<table>
<thead>
<tr>
<th>Liquid &amp; Vapour Leaving Plate No.</th>
<th>LIQUID</th>
<th>VAPOUR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mol Fr. H₂SO₄</td>
<td>Mol Fr. HNO₃ (S-Free)</td>
</tr>
<tr>
<td>1</td>
<td>.1791</td>
<td>.00000625</td>
</tr>
<tr>
<td>2</td>
<td>.1808</td>
<td>.00001328</td>
</tr>
<tr>
<td>5</td>
<td>.1808</td>
<td>.0004301</td>
</tr>
<tr>
<td>10</td>
<td>.1808</td>
<td>.001208</td>
</tr>
<tr>
<td>15</td>
<td>.1808</td>
<td>.00235</td>
</tr>
<tr>
<td>20</td>
<td>.1808</td>
<td>.004385</td>
</tr>
<tr>
<td>25</td>
<td>.1808</td>
<td>.009</td>
</tr>
<tr>
<td>29</td>
<td>.1801</td>
<td>.01445</td>
</tr>
<tr>
<td>31</td>
<td>.1802</td>
<td>.0185</td>
</tr>
<tr>
<td>35</td>
<td>.1803</td>
<td>.02378</td>
</tr>
<tr>
<td>39</td>
<td>.1804</td>
<td>.05105</td>
</tr>
<tr>
<td>41</td>
<td>.1805</td>
<td>.07425</td>
</tr>
<tr>
<td>45</td>
<td>.1810</td>
<td>.2164</td>
</tr>
<tr>
<td>46</td>
<td>.1824</td>
<td>.2807</td>
</tr>
<tr>
<td>47</td>
<td>.1818</td>
<td>.345</td>
</tr>
<tr>
<td>48</td>
<td>.1814</td>
<td>.3925</td>
</tr>
<tr>
<td>49</td>
<td>.1829</td>
<td>.407</td>
</tr>
</tbody>
</table>
TABLE 15

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Mols flowing</th>
<th>H₂O cal/mol</th>
<th>Sensible heat cal/mol</th>
<th>B.P. °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Up to 20₂₄</td>
<td>5.66</td>
<td>-2392</td>
<td>1956</td>
<td>130</td>
</tr>
<tr>
<td>20₂₄</td>
<td>5.66</td>
<td>-2334</td>
<td>1985</td>
<td>131</td>
</tr>
<tr>
<td>2O₂₅</td>
<td>5.66</td>
<td>-2350</td>
<td>1990</td>
<td>132</td>
</tr>
<tr>
<td>2O₂₆</td>
<td>5.65</td>
<td>-2480</td>
<td>2000</td>
<td>133</td>
</tr>
<tr>
<td>2O₂₇</td>
<td>5.66</td>
<td>-2185</td>
<td>2010</td>
<td>133</td>
</tr>
<tr>
<td>2O₂₈</td>
<td>5.65</td>
<td>-2510</td>
<td>2012</td>
<td>134</td>
</tr>
<tr>
<td>2O₂₉</td>
<td>5.65</td>
<td>-2540</td>
<td>2030</td>
<td>134.5</td>
</tr>
<tr>
<td>2O₂₁₀</td>
<td>5.65</td>
<td>-2554</td>
<td>2061</td>
<td>135</td>
</tr>
<tr>
<td>2O₂₁₁</td>
<td>5.64</td>
<td>-2607</td>
<td>2053</td>
<td>132</td>
</tr>
<tr>
<td>2O₂₁₂</td>
<td>5.60</td>
<td>-2680</td>
<td>2005</td>
<td>127.5</td>
</tr>
<tr>
<td>2O₂₁₃</td>
<td>5.60</td>
<td>-2687</td>
<td>1970</td>
<td>124</td>
</tr>
<tr>
<td>2O₂₁₄</td>
<td>5.59</td>
<td>-2648</td>
<td>1900</td>
<td>119</td>
</tr>
<tr>
<td>2O₂₁₅</td>
<td>5.61</td>
<td>-2594</td>
<td>1851</td>
<td>115</td>
</tr>
<tr>
<td>2O₂₁₆</td>
<td>5.62</td>
<td>-2560</td>
<td>1880</td>
<td>112</td>
</tr>
<tr>
<td>2O₂₁₇</td>
<td>5.74</td>
<td>-2470</td>
<td>1840</td>
<td>111</td>
</tr>
</tbody>
</table>

TABLE 16

<table>
<thead>
<tr>
<th>Vapour</th>
<th>Mols flowing</th>
<th>Latent heat cal/mol</th>
<th>Sensible heat cal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>V₁</td>
<td>2.062</td>
<td>11,300</td>
<td></td>
</tr>
<tr>
<td>V₂₇</td>
<td>2.08</td>
<td>9,300</td>
<td>1911</td>
</tr>
<tr>
<td>V₃₁</td>
<td>2.087</td>
<td>9,240</td>
<td>1923</td>
</tr>
<tr>
<td>V₃₄</td>
<td>2.08</td>
<td>9210</td>
<td>1986</td>
</tr>
<tr>
<td>V₃₈</td>
<td>2.086</td>
<td>900</td>
<td>2068</td>
</tr>
<tr>
<td>V₄₂</td>
<td>2.065</td>
<td>8880</td>
<td>2116</td>
</tr>
<tr>
<td>V₄₅</td>
<td>2.014</td>
<td>8575</td>
<td>2130</td>
</tr>
<tr>
<td>V₄₇</td>
<td>2.084</td>
<td>8300</td>
<td>2226</td>
</tr>
<tr>
<td>V₄₈</td>
<td>2.120</td>
<td>8250</td>
<td>2210</td>
</tr>
<tr>
<td>V₄₉</td>
<td>1.613</td>
<td>8220</td>
<td>2220</td>
</tr>
</tbody>
</table>

These results have been calculated, as before, in terms of mol fractions, and in heat contents per mol. Sufficient
of the results are given to show the trend in the quantities over the column.

As in the first calculation, it is evident that the molal overflow can be regarded as constant (see Table 15).

The value of H_{25}, in Table 15, in this calculation is not so constant as in the first one, indicating that there is heat of mixing at 25^\circ C at least, though the change in the value of H_{25} across one plate is not high, being 3% from plates 43-44, all the other values being well below this figure.

The sensible heat content of the liquid (Table 15) shows an overall increase as the liquid passes down the column, rising to a maximum value at about plate 42, corresponding roughly to the maximum shown in the value of the temperature of the liquid.

The heat quantities of the vapour in Table 16 show as before a decrease in latent heat and an increase in sensible heat as the vapour flows up the column.

The approximate constancy of the molal overflow in this theoretical concentration must be due, again, to the comparatively small changes in the values of the enthalpies and to the counterbalancing of the various heat effects as mentioned in the first plate by plate calculation.

---

Evaluation of the number of plates required at a different acid ratio by the McCabe - Thiele method.

It /
It has been shown that the McCabe-Thiele graphical method can give results comparable with those obtained in the first plate by plate calculation. The second plate by plate calculation has shown that approximately constant molar overflow also holds at a lower acid ratio. Thus the McCabe-Thiele method should apply at least within the range of operating conditions with which we have been concerned in the above calculations.

The number of plates required in a concentration in which the mol fraction H₂SO₄ in the liquid in the column was 0.20 were calculated by the McCabe-Thiele graphical method. This was done, as before, by assuming the same compositions for the feeds and the product as in the first two calculations, and by assuming an appropriate composition for the bottoms (again having 0.01% HNO₃). The quantities were then calculated by heat and material balance.

**Basis 100 gm. H₂SO₄:**

<table>
<thead>
<tr>
<th></th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bottoms</strong></td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>57.5</td>
</tr>
<tr>
<td>HNO₃</td>
<td>0.91</td>
</tr>
<tr>
<td>H₂O</td>
<td>42.49</td>
</tr>
<tr>
<td><strong>W.N.A. Feed.</strong></td>
<td>% = 66.80; Wt. = 135.4 gm.</td>
</tr>
<tr>
<td><strong>Steam</strong></td>
<td>Wt. = 28.42 gm.</td>
</tr>
<tr>
<td><strong>Acid ratio</strong></td>
<td>1.105</td>
</tr>
</tbody>
</table>

Because it was again assumed that steam at 100° was used, a /
a heat and material balance was carried out over the bottom plate in order to calculate the mole of \( L_2 \) and the mol of \( V_1 \) in order to evaluate the operating line. It was found that \( L_2 = 4.07 \) mol (H\( _2 \)SO\(_4\)-free) and \( V_1 = 1.54 \) mol, the slope of the operating, therefore, being \( \frac{4.07}{1.54} = 2.64 \). The mol fraction HNO\(_3\) (H\( _2 \)SO\(_4\)-free basis) in \( L_2 \) was found to be 0.0001569 and the mol fraction HNO\(_3\) in \( V_1 \) was found to be 0.0002353. The operating line has a slope of 2.64 and passes through the point (0.0001569, 0.0002353).

The equilibrium curve at a mol fraction of 0.20 mol fraction H\( _2 \)SO\(_4\) in the liquid has a slope of 3.52 (up to 0.20 mol fraction HNO\(_3\) in the vapour).

The number of plates required for this case was found to be 29 by the McCabe - Thiele graphical method.

Thus we have the following theoretical relationship between the acid ratio or mol fraction H\( _2 \)SO\(_4\) in the liquid and the number of plates required in the concentration.

<table>
<thead>
<tr>
<th>Acid Ratio</th>
<th>Mol fr. H(_2)SO(_4) in liquid</th>
<th>No. of Plates</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.966</td>
<td>0.279</td>
<td>7</td>
</tr>
<tr>
<td>1.105</td>
<td>0.20</td>
<td>29</td>
</tr>
<tr>
<td>1.09</td>
<td>0.18</td>
<td>49</td>
</tr>
</tbody>
</table>

If the mol fraction H\(_2\)SO\(_4\) in the liquid is plotted against the number of plates theoretically required, a curve is obtained as in Figure 17 similar in shape to the curve obtained in a plot of reflux ratio against number of plates in /
FIG. 17

MOL FR. $H_2SO_4$ vs. NO. OF PLATES

MOL FR. $H_2SO_4$

NO. OF PLATES
in normal distillation.

It is apparent that the number of plates required increases rapidly as the mol fraction of $\text{H}_2\text{SO}_4$ in the liquid is reduced, i.e., as the amount of $\text{H}_2\text{SO}_4$ used in the concentration is reduced.

This is mainly due to the change in position and slope of the equilibrium curve as the mol fraction of $\text{H}_2\text{SO}_4$ in the liquid is reduced.
Discussion of the actual column results in the light of the above theoretical calculations.

1. Molal overflow in the Runs.

The actual column results verify the fact that there is approximately constant molal overflow in the stripping section of the column, the analysis of the liquid stream samples indicating an approximately constant mol fraction of H₂SO₄ and, therefore, approximately constant molal overflow in the column. Consequently the operating lines are straight. In Figure 18 the operating lines of Runs 4, 9 and 11 are plotted. Straight lines are obtained.

Those runs with split feed, however, such as Runs 3, 13 and 14 indicate that there is constant molal overflow in the stripping section as above, but not constant overflow in the rectifying section. In those runs mentioned, however, only two sampling points are available in the rectifying section, one of them being just above the W.N.A. feed point at which point there is probably considerable disturbance of the column conditions.

2. Position of the W.N.A. Feed.

The results obtained on the column seem to indicate that there is no advantage to be gained by lowering the position of the W.N.A. feed to the column. It is apparent that when the W.N.A. is fed in at the bottom of the first section or at the bottom of the second section rather than at the top of the column, the nitric content of the bottom increases and the strength /
FIG. 18

MOL FRACTION HNO₃ IN VAPOUR

MOL FRACTION HNO₃ IN LIQUID (H₂SO₄-FREE)

RUN 4

RUN 9

RUN 11
strength of the product is not increased much, if at all.

The following values of product (total acid) and bottoms strengths from comparable runs with combined and split feeds bear this out.

**Run 10** Combined Feed

$\% \text{HNO}_3$ in $P = 94.55$

$\% \text{HNO}_3$ in $B = 0.2954$

Mean mol fraction $\text{H}_2\text{SO}_4$ in the liquid = 0.20

Ratio of acids = 1.676

**Run 11** Combined Feed

$\% \text{HNO}_3$ in $P = 90.35$

$\% \text{HNO}_3$ in $B = 0.0642$

Mean mol fraction $\text{H}_2\text{SO}_4$ = 0.197

Ratio of acids = 1.609

**Run 12** Combined Feed

$\% \text{HNO}_3$ in $P = 93.42$

$\% \text{HNO}_3$ in $B = 0.2055$

Mean mol fraction $\text{H}_2\text{SO}_4$ = 0.187

Ratio of acids = 1.57

**Run 13** Split Feed: W.N.A. at bottom of section 2

$\% \text{HNO}_3$ in $P = 96.89$

$\% \text{HNO}_3$ in $B = 0.4368$

Mean mol fraction $\text{H}_2\text{SO}_4$ = 0.193 in the stripping section.

Ratio of acids = 1.645
Run 14  Split Feed: W.N.A. at bottom of Section 2

\[ \% \text{HNO}_3 \text{ in } P = 91.90 \]
\[ \% \text{HNO}_3 \text{ in } B = 0.2184 \]

Mean mol fraction \( \text{H}_2\text{SO}_4 \) in stripping section

\[ = 0.198. \]

Ratio of acids = 1.658

Run 15  Split Feed: W.N.A. at bottom of Section 1

\[ \% \text{HNO}_3 \text{ in } P = 93.40 \]
\[ \% \text{HNO}_3 \text{ in } B = 0.1141 \]

Mean mol fraction \( \text{H}_2\text{SO}_4 \) in stripping section

\[ = 0.207 \]

Ratio of acids = 1.695

Run 16  Split Feed: W.N.A. at bottom of Section 1

\[ \% \text{HNO}_3 \text{ in } P = 94.13 \]
\[ \% \text{HNO}_3 \text{ in } B = 0.2056 \]

Mean mol fraction \( \text{H}_2\text{SO}_4 \) in stripping section

\[ = 0.202 \]

Ratio of acids = 1.625

Though a rigid comparison of the above runs would only be effective if the mol fractions of \( \text{H}_2\text{SO}_4 \) in the liquid in the column, and the ratio of acids, had been the same in each of the runs, a consideration of the product strength, \( \text{HNO}_3 \) content of the bottoms and the mean mol fraction of \( \text{H}_2\text{SO}_4 \) in the liquid indicates that when the W.N.A. is fed at section 2, as in Runs 13 and 14, there is poor stripping, when /
when at section 4, as in Runs 15 and 16, the stripping is better but is probably still not as good as when combined feed is in use.

In the runs with split feed the product strength is not as high as would be expected considering the high strength of H₂SO₄ in the liquid in the rectifying section.

The fact that efficient concentration can be carried out in columns operated with combined feed is also indicated by the theoretical plate by plate calculations carried out previously.

Normally in extractive distillation the mol fraction of more volatile component in the liquid on the feed plate (on a solvent-free basis) equals the mol fraction in the binary feed.

In the plate by plate calculations carried out earlier in this discussion plate compositions were evaluated by working up the column from the bottom. It was found in the first calculation that the desired product strength was obtained long before the mol fraction of HNO₃ in the liquid on any plate was equal to the mol fraction of HNO₃ in the W.N.A. feed.

In the second calculation with a much larger number of plates required, the mol fraction of HNO₃ in the liquid in the column on a H₂SO₄-free basis became equal to the mol fraction in the W.N.A. feed at less than two plates from the top, in a column of 49 plates:

Thus /
Thus, these calculations show that there is no need of a rectifying section at the particular acid ratios and mol fractions of $\text{H}_2\text{SO}_4$ met with in the runs actually carried out on the column. This is due to the very steep nature of the equilibrium curves, a high strength of product being obtained at a comparatively low mol fraction of $\text{HNO}_3$ in the liquid. It would seem that only if there are more than 48 plates in a column will it be desirable to operate the column with split feed in order to achieve maximum efficiency.

The runs carried out on the column indicate that the stripping is so important that in a column operating to its maximum capacity (i.e. all its height being utilised) with combined feeds, there is no advantage to be gained by lowering the position of the W.N.A. feed. This is borne out by the results of the theoretical plate by plate calculations.

In those runs with combined feed in which the whole column is not being utilised e.g. Run 4 and Run 9, the material balances indicate that the product is weaker than the vapour strength at a lower point in the column, e.g. in Run 4 $\% \text{HNO}_3$ in $P = 96.98$ and $\% \text{HNO}_3$ in $V_2 = 97.68$. In Run 9 $\% \text{HNO}_3$ in $P = 95.0$, $\% \text{HNO}_3$ in $V_2 = 97.97$ and $\% \text{HNO}_3$ in $V_3 = 98.96$. This might be due to vaporisation of water at the top of the column at the feed inlet, with consequent weakening of the product. This is not substantiated, however.
however, by those runs with split feed.

It has been mentioned above, that in the runs with split feed, the product strength is not as high as might be expected considering the high sulphuric strength in the rectifying section. A possible explanation of this may be that there is "channelling" in the rectifying section.

The liquid flow in the rectifying section is much lower than that in the stripping section. The vapour flow is also less, but it is not reduced so much, relatively, as the liquid flow. This decreased liquid flow increases the possibility of "channelling" of the liquid and may be partly the reason for the apparent poor rectifying power of the column in those runs with split feed.

Another disadvantage of the lowering of the W.N.A. feed is that there is a greater amount of decomposition of the HNO₃ and consequently a greater amount of NO₂ in the product. This is because of the high temperatures existing in the rectifying section – see Runs 2, 13, 14, 15 and 16 – owing to the high sulphuric content of the liquid.
Heat Balances at the Feed Points

1. Combined Feed at the top of the column.

In all the runs the material balances indicate that the number of moles of product is considerably less than the moles of vapour entering the first section ($V_1$). This must be due to condensation of the vapours in order to heat up the cold feeds. This "equivalent refluxing" of the vapour is apparent also in the runs with combined feed, indicating that the heat of mixing of the C.O.V. with the W.N.A. is not sufficient to raise the temperature of the mixture to boiling point.

Heat Balance at the Feed inlet in Run 4.

The heat of mixing of the C.O.V. with the W.N.A. was calculated and it was shown that it was not sufficient to raise the temperature of the mixture to boiling point.

Basis 100 moles $H_2SO_4$:

$S_F: Wt = 10,130$ gm.

$H_25 = -4383$ cal/gm.

Sensible heat = $-2.7$ cal/gm.

$N_F: Wt = 7475$ gm.

$H_25 = -47.54$ cal/gm.

Sensible heat = $3.79$ cal/gm.

$(S_F + N_F): Wt = 17,605$ gm.

$H_25 = -55.05$ cal/gm.

Sensible heat at B.P. = $38.35$ cal/gm.

Thus /
Thus, heat of mixing of $S_p$ with $N_p$ at $25^oC$

\[ H_{25} S_p + H_{25} N_p - H_{25} (S_p + N_p) = 474,400 \text{ cals.} \]

Actual sensible heat of $(S_p + N_p) = (\text{Sensible heats of } S_p \text{ and } N_p) + (\text{heat of mixing of } S_p \text{ and } N_p) = 418,700 \text{ cals.} \]

Sensible heat of $(S_p + N_p)$ at the B.P. = 675,000 cals.

Thus the heat of mixing (at $25^oC$) is not sufficient to raise the temperature of the mixture of the feeds to boiling point.

By applying Kirchoff's Equation it can be shown how the heat of mixing varies with temperature.

The heat capacities are found to be:

- $C_p$ of $S_p = 3480$ cals.
- $C_p$ of $N_p = 3650$ cals.
- $C_p$ of $(S_p + N_p) = 7720$ cals.

\[
\frac{\Delta H}{\Delta T} = 0_{p(S_p + N_p)} - (0_{pS_p} + 0_{pN_p}) = 7720 - 7130 = + 590
\]

Thus the actual heat of mixing is given by

\[
\Delta H_{\text{actual}} = -474,400 + 590 (T - 25)
\]

where $T$ is the actual temperature attained on mixing.

The heat evolved on mixing the feeds thus decreases as the temperature rises, the heat required to raise the temperature /
temperature of the mixture to boiling point being consequent-
ly greater than the amount indicated in the above balance.

This heat "deficiency" at the top of the column is the
reason for the refluxing of the vapours.

Similarly in Run 10, for example:

Heat of mixing of the feeds at $25^\circ\text{C} = 454,000$ cals.
and sensible heat of $(S_P + N_P)$ at its B.P. = 822,000 cals.
Application of Kirchoff's Equation again shows that the
heat of mixing decreases with increase in temperature. The
heat "deficiency" in this case is greater relatively than in
Run 4 in which the acid ratio is higher.

The equivalent internal reflux ratio due to this
condensation of vapour at the feed inlet, can be calculated
by taking the reflux as the difference between the moles of
product and the mean number of moles of vapour flowing in the
main part of the column.

Thus, the equivalent reflux ratio in Run 4 is $60/90 = 0.66$, and in Run 10 is $83/110 = 0.76$. The greater amount of
reflux in Run 10 is also indicated by the greater amount of
heat required to raise the temperature of the feed mixture
to boiling point.

It was mentioned previously that experiments with hot
water flowing down the column indicated that there was heat
loss.
loss at the column ends. This refluxing at the top of the column may also be due to heat loss at this point.

Thus the heat of mixing of the feeds when combined feed is used is not sufficient to boil the mixture, and even though heat evolution at the top of the column may not be desirable, it is not an argument for lowering the position of the W.N.A. feed as in more normal extractive distillations.

2. Heat balances at the W.N.A. feed point in those Runs with split feed.

The heat of mixing at the W.N.A. feed point can be examined if it is assumed that the W.N.A. mixes with the liquid flowing from the section above without receiving heat from the vapour flowing up.

Run 14. Basis 100 mols H₂SO₄ flowing.

\[ \text{L₂: Wt.} = 12,213 \text{ gm.} \]
\[ H_{25} = -63.35 \text{ cals/gm.} \]

Sensible heat = 79.5 cals/gm. at the boiling point.

\[ \text{W.N.A.: Wt.} = 9235 \text{ gm.} \]
\[ H_{25} = -43.34 \text{ cals/gm.} \]

Sensible heat = -3.74 cals/gm.

\[ (\text{L₂ + W.N.A.): Wt.} = 21,448 \text{ gm.} \]
\[ H_{25} = -65.1 \text{ cals/gm.} \]

Sensible heat = 46.05 cals/gm. at the boiling point.

**Heat of mixing at 25°C of L₂ with the W.N.A. feed**

\[ H_{25,\text{L₂ + W.N.A.}} - H_{25}(\text{L₂ + W.N.A.}) \]

By /
By applying Kirchhoff's law it can be shown that the heat of mixing in this case does not vary much with temperature.

\[
\frac{d(\Delta H)}{dT} = C_p(L_2 + W.N.A.) - (C_{pL_2} + C_{pW.N.A.})
\]

This means that the heat of mixing shows a very slight increase with rise in temperature, but is so small that the effect can possibly be ignored.

Heat Balance at the Feed point:

Heat in = (Sensible heat in L_2) + 
(Sensible heat in W.N.A.) + 
(heat of mixing)

= 1,110,950 cals.

Heat out = Sensible heat in 
(L_2 + W.N.A.) assumed to be at boiling point.
= 988,000 cals.

Thus, there is an excess of heat at the W.N.A. feed point. This heat should be used up in vaporizing some of the liquid, the assumption that all the material remains in the liquid state being wrong. The result should be an increase in the mols of vapour passing up the column at this point.

This /
This is not noticeably the case, however, in the results from Run 14,

\[ \text{mol} (L_2 + \text{W.N.A.}) = 504.8 \]

and \[ \text{mol} L_3 = 504 \]

The molal overflow of liquid is the same lower down the column as it is at the W.N.A. feed point, indicating that there is apparently no vaporisation at this point, the heat of mixing of the streams simply being sufficient to raise the temperature of the mixture to boiling point.

This discrepancy could be due to bad sampling of \( L_2 \) causing errors in the material and heat balances, but in the majority of the Runs with split feed e.g. Runs 3 and 16 it is apparent that the molal overflow at the W.N.A. feed point is the same as that in the stripping section.

In Run 16, the W.N.A. is fed at the bottom of section 1, and again a heat balance shows that there should be vaporisation at the feed point. Run 15, similar in conditions to Run 16, does show an increased vapour flow at the W.N.A. feed point.

In Run 13, however, in which the sampling must be faulty the molal vapour flow at the feed point is less than that in the stripping section.
Temperature conditions inside the Column.

(a) Combined Feed. The runs in which the whole height of the column is being utilised indicate that there is no great variation in temperature over the column. In every case except in Run 5 the temperature at the bottom of section 4 corresponds to the lowest value in the column. There is no indication in the theoretical plate by plate calculations that there should be a minimum in temperature at approximately this point, however.

In all runs the temperature recorded at the bottom of section 5 is probably a mean value between the temperature of the liquid at that point and the temperature of the steam.

(b) Split Feed. The runs with split feed indicate that the temperature is high in the rectifying section, e.g. in Runs 2, 13 and and 14. Runs 2, 15 and 16 indicate that the temperature at the W.N.A. feed point is higher than the temperatures in the stripping section, but not as high as the temperature in the main part of the rectifying section.

It is apparent in all the runs that as the acid ratio is lowered, the temperatures in the column decrease.

In the operation of the column it was apparent that the conditions of temperature inside the column were very susceptible to comparatively small changes in operating conditions. This could be seen, for instance, whenever the temperature of the steam fed in rose above 100°C. Even a superheating /
superheating of 5° for a few minutes could cause changes in the temperatures at the bottom of the column. Sometimes it was found that this caused changes in temperature quite high up in the column some time afterwards. Partly because of this, presumably, it was found that the temperature in the column took quite a long time to steady out. Depending on the operating conditions it was found possible to observe a "wave" of temperature change passing up or down the column before equilibrium was reached. This could be noticed with the Wheatstone Network and heater controls as well as with the thermocouples.

The time required to come to equilibrium was, thus, quite long varying from a little over an hour in those runs in which the whole column was not being utilised to sometimes as much as six or seven hours.
Discussion on the feeding of reflux to the column.

It is pointed out in the Introduction that it has been suggested that reflux be fed back to the concentration column, though there is no indication that the suggestion has been adopted. Although external reflux has not been fed in any of the runs here, it is probably worth while considering its effect on the concentration process in the light of the fact that normal distillation conditions, such as constant molal overflow are approximate properties of this system.

In normal binary distillations the addition of reflux to the column changes the slope of the operating lines, thereby decreasing the number of plates required for the separation. In the concentration of nitric acid, however, besides having a similar effect to this, the addition of reflux means that the mol fraction of H₂SO₄ present in the liquid in the column will be reduced. Since the overflow is approximately constant, this effect will be felt right down the column. By altering the position and decreasing the slope of the equilibrium curve this will have the effect of increasing the number of plates required, since it has already been shown that the number of plates required increases rapidly as the mol fraction of H₂SO₄ in the liquid is reduced.

Thus the addition of reflux to the concentration column should have two effects, the one tending to decrease the number of plates required by altering the slope of the operating /
operating line(s), and the other tending to increase the number of plates required by reducing the slope of the equilibrium curve.

It should, thus, be possible by finding out the rate of change of the slopes of the operating lines and equilibrium curves, caused by the addition of reflux, to find which effect is greater and whether the number of plates required decreases or increases as the reflux ratio is increased.

The increase in the number of plates as the mol fraction H₂SO₄ is reduced, is mainly due to the approach to the 45° diagonal of the equilibrium curve, in the very dilute region (of HNO₃ concentration), the extra number of plates being required mainly for stripping off the traces of HNO₃. The slope of the equilibrium curve in this region, therefore, is the critical value, as far as its effect on the number of plates required is concerned.

In the following calculations the slope of the operating line and the critical slope of the equilibrium curve have been found at different reflux ratios, for a particular set of operating conditions. The slope of the equilibrium curve has been found by evaluating the mol fraction H₂SO₄ in the liquid, drawing the corresponding equilibrium curve from the vapour-liquid equilibrium data in Figure 12, and taking the slope of the curve at the origin.

Consider a run in which 100 mol H₂SO₄ are fed (assume for simplicity that 2H₂SO₄ in the feed = 100%) and (90 mol HNO₃)
HNO₃ + 180 mls H₂O) in the W.N.A. feed (approximately 64% HNO₃). These conditions are approximately representative of those obtained in the actual column results.

Consider that combined feed at the top of the column is used. Assume that the product strength is 100% HNO₃ and that to all intents and purposes stripping of the HNO₃ from the W.O.V. is complete.

It has already been pointed out that there is internal reflux in the column - if cold feeds are used - because of the fact that the heat of mixing does not raise the temperature to boiling point, the reflux ratio being approximately 0.7 to 1.0 in the cases examined.

Assume various values of the reflux ratio.

1. Zero external reflux and zero internal reflux.

This may be brought about by preheating the feeds sufficiently, so that when mixed the temperature is at boiling point and there is no condensation of vapour.

Since there is constant molar overflow in the column -

Mols vapour flowing up the column = 90

" liquid " down " = 270 (W.N.A.)

+ 100 (H₂SO₄)

= 370

\[ \text{Slope of operating line (H₂SO₄ - free basis)} = \frac{270}{90} = 3 \]
Mol fraction H₂SO₄ in the liquid = 100/370

From the equilibrium data, slope of equilibrium curve at this mol fraction H₂SO₄ = 9.1

2. Reflux ratio = 1:1

Mols vapour flowing up the column = 180

" liquid " down " = 270 + 90 + 100

= 460

... Slope of operating line = 360/180

= 2

Mol fraction H₂SO₄ in the liquid = 100/460

= 0.2175

... Slope of equilibrium curve = 4.1

This was also done at reflux ratios of 2:1, 3:1 and 5:1, giving the following values of the slope of the operating line (mₐ) and the slope of the equilibrium curve (mₕ).

<table>
<thead>
<tr>
<th>Reflux Ratio</th>
<th>m₀</th>
<th>mₐ</th>
<th>mₕ</th>
<th>Mol fr. H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3</td>
<td>9.1</td>
<td>3.03</td>
<td>0.27</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>4.1</td>
<td>2.05</td>
<td>0.2175</td>
</tr>
<tr>
<td>2</td>
<td>1.667</td>
<td>2.4</td>
<td>1.44</td>
<td>0.182</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>1.5</td>
<td>1.0</td>
<td>0.156</td>
</tr>
<tr>
<td>5</td>
<td>1.333</td>
<td>0.8</td>
<td>0.6</td>
<td>0.122</td>
</tr>
</tbody>
</table>

In Figure 19, m₀ and mₐ are plotted against the reflux ratio, and in Figure 20 mₕ is plotted against the reflux ratio.
FIG. 19

FIG. 20
It is apparent that the slope of the equilibrium curve decreases at a much faster rate than the slope of the operating line as the reflux ratio is increased. This should be the case at any value of the acid ratio.

At a reflux ratio of 3:1, the slopes are equal, an infinite number of plates, therefore, being required at any reflux ratio greater than 3:1. It is, of course, impossible to carry out the concentration and get the stripping required above, when \( n_n \) is less than 1, as the equilibrium curve is then crossing the 45° diagonal.

Thus, it would seem that the number of plates required for this separation will increase as the reflux ratio is increased, and that for optimum conditions, the column should be operated with no reflux. This applies also to the internal reflux, and would seem to indicate that the feeds should be preheated, at least sufficient to allow the mixture to boil when the acids are mixed, thereby eliminating internal reflux.

This effect of increase in the number of plates required on the addition of reflux is due to the nature of the equilibrium curves and to the fact that good stripping is essential in the concentration process.

In general, in extractive distillation, the addition of reflux should reduce the fraction of solvent present in the liquid and, depending on the nature of the equilibrium curves and on the operating conditions, it is conceivable that the number of plates required for a particular separation will
Dunn, Miller et al. (63), in the extractive distillation of toluene found that when the ratio of solvent to feed rate was plotted against the hydrocarbon internal reflux rate, with the number of plates required as parameter, the curves obtained went through a minimum. Thus, for a particular number of plates there is a certain value of the reflux ratio which corresponds to a minimum amount of solvent required, any further increase in reflux requiring an increase in the amount of solvent as well.

The effect of reflux in the concentration of nitric acid (with combined feed in the cold) differs from this case in that, as pointed out above, it would appear that the optimum case is the one in which no reflux is fed.
Preheating the W.N.A. Feed.

The calculation of the effect of reflux on the concentration has indicated the importance of the amount of nitric acid and water in the liquid inside the column. The calculation showed that any decrease in this "sulphuric-free" internal reflux gave rise to a corresponding increase in efficiency by reducing the number of plates required for the separation.

In all the runs on the column cold feed was used and all of the previous discussion has been concerned with cold feed. It is worth while considering the effect of preheating the W.N.A. feed, and feeding it as vaporised or partly vaporised feed in order to examine the consequent decrease in internal nitric acid and water reflux and the possible decrease in the number of plates required.

The direct effect of feeding preheated W.N.A. will be to decrease the steam required, the sulphuric acid, therefore, not being used to remove the water of the steam. The internal water reflux will, therefore, be reduced.

Vaporised W.N.A. feed could not, of course, be fed at the top of a column in the same way as cold W.N.A. feed. The W.N.A. feed position would have to be lowered to correspond to more normal extractive distillation procedure. However, in this case, the increase in the fraction of $\text{H}_2\text{SO}_4$ present, by reduction of the internal ($\text{H}_2\text{O}$ and $\text{HNO}_3$) reflux, should decrease.
decrease the number of plates required in the stripping section. Thus, the lowering of the preheated W.N.A. feed will not have such a bad effect on the stripping as it does when cold W.N.A. feed is used. The rectifying section will have to rectify the W.N.A. feed vapour up to the required product composition.

Consider a run similar to the one considered in the calculation of the effect of reflux on the efficiency.

i.e. Assume 100 mols (100%) H_2SO_4 are fed to the column and (90 mols HNO_3 + 180 mols H_2O) of W.N.A. feed, 90 mols of 100% HNO_3 being obtained as product.

All the water in the W.N.A. feed is not vaporised inside the column, no matter what conditions are employed, so if the W.N.A. were fed completely vaporised, it is most likely that the heat supply would be excessive and that a dilute product would be obtained. Since the number of mols of product is 90 and there will be constant molal flow of vapour, and since the latent heat of vaporisation per mol of HNO_3 is approximately the same as that of H_2O, it should only be necessary to have about 90 mols of the W.N.A. feed to be vaporised. Assume also, for this case, that there is no condensation of vapour in order to heat up the H_2SO_4 feed.

If it is assumed that there is no heat loss from the column, this amount of W.N.A. feed vapour - 90 mols - should be
be approximately the maximum heat requirement of this concentration. In actual fact some of this heat should be supplied at the bottom of the column in the form of steam in order to strip off the traces of nitric acid.

Thus, assume that 90 mols of the W.N.A. are vapour, or at least, assume that the liquid is fed at such a temperature that when fed into the column the heat of mixing is sufficient to vaporise an amount equivalent to 90 mols of the feed.

Thus, at the W.N.A. feed point we have:

Because of the decreased amounts of HNO₃ and H₂O in the liquid by the preheating of the W.N.A., the strength of H₂SO₄ in the liquid at the W.N.A. feed point will be high. This will be the case over all the stripping section. The number of plates required in the stripping section will, therefore, be small.

The amount of steam required for stripping in this case will
will be small. Thus, the liquid flow at the W.N.A. feed point may be assumed to consist of 100 mols H_2SO_4 and approximately 180 mols (H_2O + HNO_3).

The mol fraction of H_2SO_4 in the liquid in the stripping section will, therefore, be 100/280 = 0.357. The number of plates required at such a mol fraction H_2SO_4 in the liquid in the stripping section will obviously be small.

The number of plates required for this concentration when cold feeds are fed at the top of the column can be approximately found. If the internal reflux ratio is assumed to be approximately 1:1, the calculation of the effect of reflux, carried out previously (see Fig. 183), showed that the mol fraction of H_2SO_4 in the liquid was 0.2175.

An examination of Figure 17 shows that at this mol fraction of H_2SO_4 in the liquid the number of plates required is 20.

It is possible that the total number of plates required if partly vaporised W.N.A. feed were used, would be smaller than 20 because of the factors discussed above.

Thus, because of the decrease in the number of plates required on reduction of the nitric acid and water reflux in the column, it may still be more efficient to adopt normal extractive distillation procedure in the concentration of nitric acid, the W.N.A. being fed at some point in the column below the top, provided the W.N.A. is fed as a partly vaporised feed.
Evaluation of H.T.U. in the Concentration Column.

It has been shown that the molal overflow in the concentration column is approximately constant. This fact, by reducing the number of variables enables the equilibrium curves and operating lines to be plotted on rectangular coordinates, and means that the height equivalent to a transfer unit can be worked out, as in normal distillations, with relative ease.

The H.T.U. concept was first put forward by Chilton and Colburn (64) in 1935, who suggested that the difficulty of a given separation in a packed column be expressed as the number of transfer units, given by

\[ N = \int_{y_1}^{y_2} \frac{dy}{y^2 - y} \]

in which \( y_1 \) and \( y_2 \) are the compositions of the vapours entering and leaving the column respectively; \( y \) is the actual vapour composition at any point in the column, and \( y^* \) the equilibrium composition corresponding to \( y \).
Up to that time, the concept of H.E.T.P. (height equivalent to a theoretical plate) had been used as a basis of comparison of fractionating powers of different heights of column, and different sizes and types of packing. This method, however, is based on the stepwise countercurrent process encountered in bubble cap columns, whereas the enrichment of a vapour by distillation in a packed column is a differential process.

The above concept of a transfer unit was developed to apply to cases where the gas film is the controlling factor in the resistance to transfer of material from one phase to another.

In general, however, both in distillation and absorption, both gas and liquid films must be considered.

Colburn (65) thus introduced the idea of individual film, and overall transfer units. If \( y_i = \) equilibrium composition of the vapour at the interface, then the number of gas film transfer units is:

\[
N_g = / \]
Similarly the number of liquid film transfer units is

\[ N_L = \int_{z_1}^{z_2} \frac{dx}{x - x_i} \]

where \( x_i \) is equilibrium composition in the liquid at the interface.

Rather than use these individual film values of the number of transfer units, it is more convenient to use values of the number of overall transfer units, similar to the use of overall mass transfer coefficients, based on the change in gas concentration \( (N_{0,G}) \), or based in the change in liquid concentration \( (N_{0,L}) \).

\[ N_{0,G} = \int_{y_1}^{y_2} \frac{dy}{y - y^*} \quad \text{and} \quad N_{0,L} = \int_{z_1}^{z_2} \frac{dx}{x - x^*} \]

where \( y^* \) and \( x^* \) both refer to mean body concentrations.

The height equivalent to one transfer unit is given by:

\[ \text{H.T.U.} = \frac{Z}{N} \]

where \( Z \) is the height of the column.

The following relationship exists between the heights of gas and liquid film transfer units \( (H.T.U.)_G \) and \( (H.T.U.)_L \), respectively, and the heights of overall gas and liquid transfer units \( (H.T.U.)_{0,G} \) and \( (H.T.U.)_{0,L} \), respectively.

\[ (H.T.U.)_G \]
\[ (H.T.U)_{0.G.} = (H.T.U)_G + \frac{m \cdot G}{L} (H.T.U)_L \]

and \[ (H.T.U)_{0.L.} = (H.T.U)_L + \frac{L}{m \cdot G} (H.T.U)_G \]

where \( \frac{L}{G} \) = molar liquid to vapour ratio.

and \( m = \frac{dy}{dx} \) = slope of equilibrium curve.

Packed columns have been designed using the overall values of H.T.U. rather than the individual film values.

In the present case, values of \( (H.T.U)_{0.G.} \) were calculated from the results of the runs on the column.

Many methods have been put forward both analytical and graphical, for the evaluation of H.T.U. Probably the simplest and most accurate is the evaluation of the integral graphically,

\[ N_{0.G.} = \int_{y_1}^{y_2} \frac{dy}{y^m - y} \]

by plotting values of \( y \) between \( y_1 \) and \( y_2 \) against \( \frac{1}{y^m - y} \) and finding the area under the curve.

Values of \( N_{0.G.} \) and \( H.T.U_{0.G.} \) were found over convenient sections of the column in this way, using the data obtained from the sampling of the liquid stream.

\( y_1 \) and \( y_2 \) in the above integral refer to the vapour compositions entering and leaving the section in question, \( y \) representing the vapour composition at any point in the section and \( y \) being the equilibrium vapour composition corresponding to \( y \). Values of \( y \) between \( y_1 \) and \( y_2 \) were obtained/
obtained by plotting the operating line from the actual column results and reading off the appropriate value of y. Values of y were obtained from the equilibrium curve interpolated from the Batch still data at the appropriate mol fraction of H₂SO₄.

\[ e.g. \quad \text{Run 10, Section 2.} \]

\[ L_1 \quad V_1 \quad V_2 \]
\[ \text{SECTION 2} \]
\[ V_3 \quad L_2 \]

\begin{align*}
\text{mean mol fraction } & \text{H₂SO₄ over the column} = 0.20 \\
\text{mol fraction } HNO₃ \text{ in } V_2 & = 0.3374 \\
\text{mol fraction } HNO₃ \text{ in } V_3 & = 0.01374 \\
\text{mol fraction } HNO₃ \text{ in } L_4 & = 0.1648 \\
& (\text{H₂SO₄ - free basis}) \\
\text{mol fraction } HNO₃ \text{ in } L_2 & = 0.008758 \\
& (\text{H₂SO₄ - free basis})
\end{align*}

\[
\begin{array}{|c|c|c|c|c|}
\hline
x & y & y^\# & y^\# - y & \frac{1}{y^\# - y} \\
\hline
0.1618 & 0.3374 & 0.574 & 0.2366 & 3.91 \\
0.18 & 0.269 & 0.534 & 0.269 & 4.823 \\
0.10 & 0.201 & 0.358 & 0.150 & 6.29 \\
0.08 & 0.188 & 0.288 & 0.150 & 7.70 \\
0.05 & 0.097 & 0.18 & 0.093 & 12.05 \\
0.03 & 0.057 & 0.108 & 0.051 & 19.6 \\
0.02 & 0.0365 & 0.072 & 0.0355 & 28.2 \\
0.015 & 0.026 & 0.054 & 0.028 & 35.7 \\
0.012 & 0.022 & 0.0432 & 0.0212 & 47.2 \\
0.008758 & 0.01374 & 0.05154 & 0.0178 & 58.2 \\
\hline
\end{array}
\]

\[ \text{Area under curve} = 3.23 \text{ units} \]
\[ \text{i.e.} \quad \text{H.T.U.} \cdot \text{O.G.} = 3.23 \]

Height of packing in 1 section = 1 foot.
\[ \therefore \quad \text{H.T.U.} \cdot \text{O.G.} = \frac{1}{3.23} \]

\[ \text{The} / = 0.3095 \text{ ft.} \]
The values of $N_0G$, and $(H.T.U.)_0G$, obtained in the various runs are listed in Table 17.

**TABLE 17**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1</td>
<td>.252</td>
<td>1.80</td>
<td>0.56</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>.245</td>
<td>1.67</td>
<td>0.60</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>.245</td>
<td>2.015</td>
<td>0.496</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>.217</td>
<td>2.245</td>
<td>0.445</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>.217</td>
<td>2.83</td>
<td>0.324</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>.205</td>
<td>5.6</td>
<td>0.1785</td>
</tr>
<tr>
<td>9</td>
<td>4</td>
<td>.200</td>
<td>3.968</td>
<td>0.252</td>
</tr>
<tr>
<td>15</td>
<td>2</td>
<td>.205</td>
<td>5.58</td>
<td>0.28</td>
</tr>
<tr>
<td>15</td>
<td>(3 &amp; 4)</td>
<td>.205</td>
<td>1.12</td>
<td>1.786</td>
</tr>
<tr>
<td>16</td>
<td>2</td>
<td>.202</td>
<td>3.82</td>
<td>0.262</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>.20</td>
<td>3.23</td>
<td>0.3095</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>.20</td>
<td>0.549</td>
<td>1.82</td>
</tr>
<tr>
<td>14</td>
<td>3</td>
<td>.1982</td>
<td>3.24</td>
<td>0.3085</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>.198</td>
<td>2.834</td>
<td>0.353</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>.198</td>
<td>1.291</td>
<td>0.775</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>.195</td>
<td>3.188</td>
<td>0.313</td>
</tr>
<tr>
<td>13</td>
<td>4</td>
<td>.193</td>
<td>3.005</td>
<td>0.333</td>
</tr>
<tr>
<td>12</td>
<td>2</td>
<td>.187</td>
<td>4.72</td>
<td>0.212</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>.187</td>
<td>1.48</td>
<td>0.675</td>
</tr>
</tbody>
</table>

The values are arranged in the table in descending order of the mean mol fraction H$_2$SO$_4$ in the liquid.

The effect of various factors on $(H.T.U.)_0G$.

The values obtained above are not very consistent. This may be due to the following factors.

1. Errors involved in sampling and analysis.

One difficulty in the evaluation of H.T.U. in this system arises from the nature of the equilibrium curve.
The slope is so steep that changes in composition are rapid over a short height of column. Thus, it is difficult to get a run in which the compositions of the ingoing and outgoing streams in a particular section are high in nitric content. Most of the sections are utilized in removing small amounts of nitric acid from the liquid. A small error in sampling or in analysis of these liquids can cause quite a large error in the integration and in the resultant value of \( (H.T.U.)_{O.G.} \).

It is noticeable that values of \( (H.T.U.)_{O.G.} \) obtained at the bottom of the column in these dilute regions, are higher than those values obtained higher up in the column. The difference may be partly due to such errors.

(2) Change in the value of \( m \).

(a) By departure of the equilibrium curve from a straight line.

\( (H.T.U.)_{O.G.} \) may vary if the slope of the equilibrium curve is not constant, because of the effect of \( m \) in the equation:

\[
(H.T.U.)_{O.G.} = (H.T.U.)_G + \frac{mG}{L} (H.T.U.)_L
\]

Simon and Rau (66) point out that when both liquid and gas films have to be taken into account

\[
(H.T.U.)_G = \frac{1}{k_G} \left( \frac{\mu}{k_G a} + \frac{1}{k_G a} \right)
\]

Thus, even the film value of \( H.T.U. - (H.T.U.)_G \) is a function /
function of the slope of the operating line.

In all the cases in the table, however, except the values in the sections where the vapour strength is high, the equilibrium curves vary but slightly from straight lines. This effect, therefore, should be small in different runs with similar flow conditions.

(b) By change in the amount of H₂SO₄ flowing down the column in different runs. The direct effect of this is that the mol fraction of H₂SO₄ will vary, thereby altering the position and slope of the equilibrium curve. As the mol fraction of H₂SO₄ is increased, m increases. If (H.T.U.)₀, and (H.T.U.)₀, remain constant with increasing amounts of H₂SO₄ flowing, then the value of (H.T.U.)₀, will increase because of the effect of m in the equation.

\[(H.T.U.)₀, = (H.T.U.)₀, + \frac{m'G}{L} (H.T.U.)₀,\]

It is interesting to note that the values of (H.T.U.)₀, in Table 17 (see also Table 18) are higher in those runs with higher mol fractions of H₂SO₄ in the liquid.

(c) Another likely effect of change in the amount of H₂SO₄ flowing is the effect on the individual film coefficients and consequently on the values of (H.T.U.)₀, and (H.T.U.)₀,.

(3) Change in film resistances over the distillation range.

(This is also mentioned in part (c) above.)

In the evaluation of H.T.U. it is assumed that the individual /
individual film coefficients are constant over the distillation range, where the liquid and vapour velocities are constant.

The value of $k_L a$ and $k_G a$ vary greatly with change in the rate of flow of liquid and vapour.

\[
(H.T.U.)_G = \frac{G}{K_G a} = G\left(\frac{1}{k_G a} + \frac{m}{k_L a}\right)
\]

Thus, if $k_G a$ and $k_L a$ vary, the value of $(H.T.U.)_G$ and $(H.T.U.)_L$ will vary, and consequently the value of $(H.T.U.)_{OL}$.

In all the runs the liquid and vapour velocities are not much different, the film resistances, therefore, should not change much on this account.

The film coefficients, however, may change over the distillation range. Pratt (67) indicates that variations from below 1 foot to above 20 ft. in values of H.T.U. have been found in columns using commercial sizes of packing, and indicates that this may have been partly due to change in the liquid film resistance with composition.

In the concentration of nitric acid, where the composition of a ternary solution is changing over the column, it is quite possible that the film coefficients do vary over the column.

The following table, Table 18, gives values of $(H.T.U.)_{OL}$ selected from Table 17 which represent values obtained over similar ranges of nitric acid concentration in the vapour. Values in the dilute region have been omitted.

The /
The values seem to indicate a decrease in \((\text{H.T.U.})_{\text{O.G.}}\) as the mol fraction \(\text{H}_2\text{SO}_4\) in the liquid is reduced.

**TABLE 18**

<table>
<thead>
<tr>
<th>Run</th>
<th>Section</th>
<th>Mol fr. \text{H}_2\text{SO}_4</th>
<th>N.O.G.</th>
<th>(H.T.U.)_{O.G.}</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>4</td>
<td>0.252</td>
<td>1.80</td>
<td>0.56</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>0.245</td>
<td>1.67</td>
<td>0.60</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>0.235</td>
<td>2.015</td>
<td>0.50</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>0.217</td>
<td>2.245</td>
<td>0.445</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>0.217</td>
<td>2.83</td>
<td>0.354</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>0.205</td>
<td>3.966</td>
<td>0.252</td>
</tr>
<tr>
<td>15</td>
<td>2</td>
<td>0.205</td>
<td>3.98</td>
<td>0.28</td>
</tr>
<tr>
<td>16</td>
<td>2</td>
<td>0.202</td>
<td>3.82</td>
<td>0.262</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0.20</td>
<td>3.23</td>
<td>0.3095</td>
</tr>
<tr>
<td>14</td>
<td>3</td>
<td>0.1882</td>
<td>3.24</td>
<td>0.3085</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>0.186</td>
<td>2.834</td>
<td>0.353</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>0.195</td>
<td>3.188</td>
<td>0.313</td>
</tr>
<tr>
<td>15</td>
<td>4</td>
<td>0.193</td>
<td>3.005</td>
<td>0.333</td>
</tr>
<tr>
<td>12</td>
<td>2</td>
<td>0.187</td>
<td>4.72</td>
<td>0.212</td>
</tr>
</tbody>
</table>
Evaluation of Film Coefficients in the Concentration Column.

Drickamer and Bradford (68) have shown how, in distillation, the plate efficiency is related to the viscosity of the liquid. Garner (69) points out that it has been found that when the solvent used in extractive distillation is of high viscosity, there is a marked decrease in plate efficiency. This must be due to a high resistance to transfer of material in the liquid film.

In extractive distillation generally, therefore, where a high boiling solvent is present throughout the column, it is to be expected that the liquid film is the controlling factor in the resistance to transfer of material.

In the case of the concentration of nitric acid, relatively viscous sulphuric acid is present. In order to indicate the relative importance of the liquid and gas films in the concentration, a method evolved by Simon and Rau (66) was applied in order to evaluate the film coefficients.

Simon and Rau derive the equation -

\[
\int_0^Z \frac{dZ}{G} = \frac{G}{k_G a} \int_{y_1}^{y_2} \frac{dy}{y^2 - y} + \frac{L}{k_L a} \int_{y_1}^{y_2^*} \frac{dy^*}{y^* - y}
\]

i.e. \[ Z = \frac{G}{k_G a} \cdot N_{G_1} + \frac{L}{k_L a} \cdot N_{G_2} \]

where \[ N_{G_1} = \int_{y_1}^{y_2} \frac{dy}{y^2 - y} \] and \[ N_{G_2} = \int_{y_1}^{y_2^*} \frac{dy^*}{y^* - y} \]
The values of \( e \) are the equilibrium values corresponding to the particular value of \( y \).

When the liquid and vapour velocities are constant the values of \( k_L a \) and \( k_G a \) are assumed to be constant and for another height of column \( Z_1 \):

\[
Z_1 = \frac{G}{k_G a} N_{G_1}^1 + \frac{L}{k_L a} N_{G_2}^1
\]

Solving the two equations in \( Z \) and \( Z_1 \) for \( k_G a \) and \( k_L a \) we have:

\[
k_L a = L \left[ \frac{N_{G_1}^2 N_{G_2}^1 - N_{G_2}^1 N_{G_1}^1}{z_1 N_{G_1}^1 - z_1 N_{G_2}^1} \right]
k_G a = G \left[ \frac{N_{G_1}^1 N_{G_2}^1 - N_{G_2}^1 N_{G_1}^1}{z_1 N_{G_1}^1 - z_1 N_{G_2}^1} \right]
\]

Thus, by tapping and analyzing the liquid and vapour streams at some point in the column, sufficient data may be obtained to evaluate the film coefficients.

This method should lend itself admirably for application to the results obtained in the concentration column, where the streams inside the column are tapped at several points.

The values of the integrals \( N_{G_1} \) and \( N_{G_1}^1 \) are the numbers of transfer units, N.G.U., in the heights \( Z \) and \( Z_1 \) respectively.

The values of

\[
\int_{y_2^x}^{y_1^x} \frac{dy^x}{y^x - y}
\]

are obtained by plotting \( y^x \) against \( \frac{1}{y^x - y} \) and evaluating /
evaluating the area under the curve.

The above equations only held when \( G \) and \( L \) are constant, so the coefficients were evaluated in the same run from the data from different sections, or from different runs with similar flow conditions. \( G \) and \( L \) are in terms of lb. mols/hr./sq. ft. of tower cross section.

e.g. Evaluation of coefficients using the data from Run 11, section 2 and Run 15, section 4.

Run 11, Section 2.

\[
\begin{align*}
N_{G1} &= 2.834 ; \quad N_{G2} = 5 \\
G &= 4.785 \text{ lb. mols/hr./sq.ft.} \\
L &= 11.88 \text{ " " " " }
\end{align*}
\]

Run 13, Section 4.

\[
\begin{align*}
N_{G1} &= 3.005 ; \quad N_{G2} = 4.108 \\
G &= 4.695 \text{ lb. mols/hr./sq.ft.} \\
L &= 12.46 \text{ " " " " }
\end{align*}
\]

Thus mean value of \( G = 4.74 \text{ lb. mols/hr./sq.ft.} \)

\[
L = 12.17 \text{ " " " " }
\]

By substitution in the equations:

\[
k_{GA} = 17.99 \text{ lb. mols/hr./cu.ft./unit concentration difference.} \\
k_{LA} = 14.08 \text{ " " " " " " " " }
\]

The film coefficients have been evaluated in this way from the most reliable runs and are given in Table 19.
The results do not indicate definitely which film is controlling. The negative values for the liquid film coefficient could possibly be regarded as very small values for $k_{La}$, in which case the liquid film is controlling. On the other hand, if the negative values are regarded as being wrong and the positive values correct, then it would seem as if the gas film were controlling.

Even though the coefficients have been evaluated where the mol fraction $H_2SO_4$ is constant, the $HNO_3$ content of the liquid is changing, and, if the film coefficients vary over the composition range the method does not apply. In Run 11 section 2 and in Run 13 section 4 the change in composition is approximately the same. In such a case, even though a quantitative evaluation of each film coefficient may not be possible, if they are varying, it should /
should be possible to get some sort of comparison between them. The result shows that the gas film is controlling.

However, the fact that widely varying values of $k_{la}$ are obtained would seem to indicate that the method is at fault. This could be due to:

1. the method being highly susceptible to small errors in the data.
2. the influence of the factors discussed previously on the values of $(H.T.U.)_0$.g.
Nomenclature

General

C.O.V. - Concentrated H₂SO₄
W.O.V. - Dilute H₂SO₄
C.N.A. - Concentrated HNO₃
W.N.A. - Dilute HNO₃
Acid ratio - H₂SO₄ in C.O.V. feed: HNO₃ in W.N.A. feed (by wt.)

Section on Vapour-liquid equilibria

x - Mol fraction of a particular component in the liquid.
y - Mol fraction of a particular component in the vapour.
γ - Activity coefficient.
P - Total pressure.
P - Vapour pressure of pure component.
T - Temperature.
A - Constant in Van Leer or Margules equation.
B - " " " " " "
V - Molar volume of a particular component.
L - Relative partial molal enthalpy.

Subscripts N and W refer to HNO₃ and H₂O respectively.

Tables of column results

See page 120

Section on plate by plate calculations

H_k - Heat content of a liquid at t°C referred to pure components at 25°C, (cals/gm.)

H₂₅/.
$H_o5$ - Heat content of a liquid at $25^\circ C$. referred to pure components at $25^\circ C$. (cals./gm.)
a - specific heat at $25^\circ C$.
b - temperature correction factor for the specific heat.
$q_t$ - Total heat content of a vapour at $t^\circ C$.
referred to pure components at $25^\circ C$ (cals/gm.)
p - $\%$ HNO$_3$ in the vapour
$v_N$ - Latent heat of vaporisation of HNO$_3$.
v$_f$ - " " " "$ H_2O$
$\Delta S$ - Heat of separation of the components of a mixture.
$\Delta M$ - Heat of mixing of the components of a mixture
$\Delta H_T$ - Heat of mixing at temperature $T$
$c_p$ - Specific heat at constant pressure
$v_m$ - Vapour leaving $m$th plate
$l_m$ - Liquid " " "
h - heat content of a particular vapour or liquid
$q$ - reboiler heat duty
$b$ - mols of Bottoms
$p$ - " " Product
st or steam - Steam fed to the column

Section on calculations of effect of reflux

$mg$ - slope of equilibrium curve
$mo$ - " " operating line

Section on evaluation of H.T.U.

$y_1$ - Mol fraction of a component in the vapour at the interface.

$X_1$ /
$x_i$ - Mol fraction of a component in the liquid at
the interface.

$N_G$ - Number of gas film transfer units.

$N_L$ - " " liquid " "

$N_{O,G.}$ - " " overall transfer units based on the
gas film.

$N_{O,L.}$ - " " " " " based on the
liquid film.

$G$ - Vapour flow rate.

$Z$ - Height of column

$m$ - slope of equilibrium curve.

$k_{ga}$ & $k_{la}$ - Gas and liquid film coefficients

(lb.mols/hr./cu.ft./unit amon. difference)

\[
N_{G,1} = \int \frac{y_2}{y_1^m - y_2} \, dy
\]

\[
N_{G,2} = \int \frac{y_2}{y_1^m - y} \, dy
\]
Conclusions

The following conclusions can be drawn from the results obtained with the concentration column and from the theoretical calculations.

(1) The molal overflow in the concentration column is approximately constant. This is unexpected in a "non-ideal" system of this type. It is mainly due to the apparent absence of any "molar heat of mixing" as the liquid flows down the column, and to the fact that the molar latent heats of H2O and HNO3 are very similar.

(2) Bottoms strengths as low as 56% H2SO4 and acid ratios as low as 1.6 are possible in concentration columns, and these figures may be lowered still further. In industry, generally, the corresponding figures are 65 - 70% H2SO4 and 2.5 - 3.0 respectively. Since the economy of the concentration process depends to a large extent on the amount of H2SO4 used it is obviously possible to effect considerable economies in industrial plants.

It would appear that the equivalent number of plates in the column has not been regarded as important in this respect because the process has never been regarded as anything but a very extreme and special case of distillation. It has been regarded as a property of the system, more or less, that HNO3 can not be completely stripped from the bottoms if the strength of the bottoms is /
is less than a certain value, e.g. Kaltenbach (70) states that the concentration of $\text{H}_2\text{SO}_4$ in the bottoms from a nitric acid concentration column can not be less than 70%, otherwise the water vapour pressure over the bottoms is high enough to dilute the product.

In fact the limiting factor, as pointed out in the above discussion, is the equivalent number of plates available in the column.

(3) For a given acid ratio, when the W.N.A. is fed into the cold, combined feed the W.N.A. and C.O.V. at the top of the column should be used. If the W.N.A. is fed at a lower point, poor stripping may result. The calculations show that only if the column is equivalent to a large number of plates will it be advantageous to lower the position of the W.N.A. to the column.

(4) Reflux should not be fed back to the concentration column. It would appear on feeding back reflux, that the decrease in the number of plates required caused by the decrease in slope of the operating line is more than counterbalanced by the increase in the number of plates required caused by the change in the equilibrium curve. The result is that the number of plates required will increase if reflux is added, consequently /
consequently requiring more C.O.V. to be used for a particular concentration in a particular column and thereby causing a decrease in efficiency.

It follows that the acid feeds should be preheated, in order to prevent any internal refluxing of the vapours, so that the heat of mixing inside the column is sufficient to raise the temperature to boiling point, provided that the vapour in equilibrium with the feed mixture is of the desired product strength. When the vapour in equilibrium with the feed mixture is not of the desired strength, the internal refluxing may be an advantage.

(5) The calculations on the effect of feeding partly vaporised W.N.A. feed, using split feeds, show that fewer plates may be required by this method than by the use of combined feeds in the cold. This is because of the reduction in the number of plates required for a particular concentration on decreasing the amount of internal nitric acid and water reflux in the column. This effect is indicated in the calculations of the effect of reflux on the concentration.

(6) It is difficult to obtain accurate values of the H.T.U. in this distillation, where the greater part of the column is utilised in removing small amounts of HNO₃. The values of \( (H.T.U.)_{0.\%} \) obtained are, therefore /
therefore, very susceptible to small errors in the results, besides being affected by the other factors discussed.

It would appear, however, that the value of $(\text{H.T.U.})_{0.4}$ decreases as the fraction of $\text{H}_2\text{SO}_4$ in the liquid in the column decreases, or, as the acid ratio decreases.

No definite conclusions can be drawn from the calculated values of the film coefficients inside the column, as to which film is controlling in the concentration.

It is probably not reasonable to suppose that the film coefficients in the ternary system remain constant over the column length, even though the flow rates are approximately constant. The widely different values obtained for the coefficients would seem to indicate that the method itself is susceptible to small errors in the results and in the values of H.T.U.
Suggestions for Further Work

1. Further examination of the vapour-liquid equilibria in the systems $\text{H}_2\text{SO}_4 \rightarrow \text{HNO}_3 \rightarrow \text{H}_2\text{O}$ and $\text{Mg(NO}_3)_2 \rightarrow \text{HNO}_3 \rightarrow \text{H}_2\text{O}$

2. Investigation of the use of reflux in concentration columns.

3. Investigation of the use of partly vaporised W.N.A. feed.

4. Investigation of more efficient acid-resisting packing materials for use in concentration columns (because of the importance of the equivalent number of plates on the efficiency of nitric acid concentration columns)

5. Examination of the use of $\text{Mg(NO}_3)_2$ in nitric acid concentration columns.
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