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I. INTRODUCTION

The operation of fractional distillation has only within the past half century become a true science. Although the art of distillation was known to the ancient alchemists, who used many of the modern techniques, very little was known about the theoretical aspects of the operation until the latter half of the nineteenth century, when investigations by Sorel furnished a theoretical basis for foretelling the operating characteristics of a fractionating column. Later investigations have resulted in modern distillation methods being based upon sound theoretical principles.

Actual columns, however, never approach perfect theoretical efficiency, and in most cases it is customary to express the ratio of actual results to theoretical results as a fraction known as the column "efficiency".

The efficiency of any particular fractionating assembly depends on a number of factors. Chief among these variables are those which can be controlled: reflux ratio, feed and reflux temperatures, feed composition, etc. Other factors, not as easily varied in a particular assembly, include the characteristics of the mixture being separated and the construction details of the column. The method of operation of a particular assembly is most important in determining the efficiency of a column; if conditions within

the column are made to parallel theoretical conditions, then highest efficiencies are attained. The method of operation will, of course, depend on the type and design of the column accessories.

With isopropyl alcohol gaining rapidly in importance as a solvent and as an intermediate, basic information on its fractionating characteristics is highly desirable; and since most of the experimental data found in the literature was obtained on columns having only a few plates, it is obvious that information dealing with columns of the larger types as used industrially is of considerable value.

The object of this investigation was to improve upon the overall design of a 15-plate fractionating assembly used in the separation of simple binary mixtures of water and isopropyl alcohol, to recalibrate all measuring devices used in the operation of the column, to develop an analytical method by which the composition of liquid samples from the column can be determined accurately and rapidly, and, in general, to increase the efficiency of the column and place the assembly in such condition that experimental runs can be made more easily and with a higher degree of accuracy than has previously been possible.

II. LITERATURE REVIEW

A. Definitions of Distillation Terms

Distillation is the separation of the constituents of a liquid mixture by partial vaporization of the mixture and separate recovery of the vapor and residue. The more volatile constituents of the original mixture are obtained in increased concentrations in the vapor; the less volatile in greater concentrations in the liquid residue⁽⁵⁷⁾.

To distinguish it from the process of evaporation, the term distillation is properly applied only to those operations where vaporization of the liquid mixture yields a vapor phase containing more than one constituent and it is desired to recover one or more of these constituents in a nearly pure state⁽⁵⁷⁾.

Rectification, or fractionation as it is more commonly called, is a distillation carried out in such a way that the vapor rising from a still comes in contact with a condensed portion of vapor previously evolved from the same still. The process results in a transfer of heat whereby a greater enrichment of the vapor in the more volatile components is secured than could be done with a single distillation using the same amount of heat⁽⁵⁷⁾.

B. Chronology of Distillation

Ancient Concepts of Distillation: Although the peoples of the ancient world did not define the term distillation as strictly as has been done in the past century, the operation of distillation was known and practiced as early as 350 B.C., Aristotle having recorded that at that time sea water was distilled by very crude methods to obtain solid salt and pure water⁽²³⁾. The term "distillation" having been derived from the Latin "stilla", meaning drop, and "dis", implying separation, literally means a "separation drop by drop", and it was not until the eighteenth century that the term was defined to exclude filtration, sublimation, and pulverization, terms which had been earlier classified with the process of distillation as we know it today⁽⁸²⁾.

Underwood⁽⁸²⁾ states that one of the earliest applications of distillation that may be considered as related to the modern conception of the operation was in the preparation of mercury from cinnabar and its subsequent purification by sublimation. Dioscorides first employed the principle of dephlegmation in the first century A.D.⁽²³⁾. His method of hanging flock wool in the vapor stream over boiling liquids was widely copied up until modern times. By the fourth century, Zozimus,

the Panopolitan, had added a chemical encyclopedia to his prolific writings on alchemy, and described and illustrated many types of distilling apparatus. Included in Zozimus' books were illustrations of copper still-heads with several drawoffs, side-tubes, air-cooled condensers, and heat controlling devices⁽⁸²⁾. Egloff states⁽²³⁾ that a refluxing dome similar to the domes on modern shell stills had been introduced by the fourth century.

Concepts of Fractional Distillation: Underwood found no sign of any conception of fractional distillation in any of the apparatus of the Greek alchemists, and states that after the Moslem conquests the Syrians made no fundamental changes in the Greek "alembics", or retorts. The Arabs, however, were quick to grasp the importance of distilling operations, and although they largely adopted the Greek science they clarified it and improved it by greater applications to practical studies. The Arabs used distillation for preparing many perfumery and pharmaceutical products, and in the eighth and ninth centuries their rose water was an important article of commerce. The Arabian alchemist, Geber, developed a still in the ninth century which was probably among the first to utilize the principle of fractional distillation; his was a regulated still heated by either a water bath or a bath of ashes. Egloff states that by 1000 A.D. a

column still had been placed in operation which had facilities for removing three different fractions from the starting liquor.

The Alchemist Concept of Distillation: Although it is recorded that Rhazes of Baghdad knew of alcohol in the tenth century, and fermented mare's milk was distilled by the Mongols in the next century, the earliest authentic reference to the preparation of alcohol by distillation is in a cryptogram dated in the twelfth century and of Byzantine origin⁽⁸²⁾. Distillation was introduced into France about 1300, and in 1366 the Parisian alchemist Ortholanus published a book on fractional distillation and rectification, describing the distillation of nitric acid as well as the preparation of alcohols and scents. Until the sixteenth century the alembics of the Greeks were the chief type of equipment used by the alchemists and the commercial distillers; after this period many modifications were made in the apparatus in order to achieve more efficient operation. Philiatrus used a still in 1555 which had several reboilers designed to give increased fractionation, and in 1540 Biringuccio illustrated the use of the coil (worm) for cooling the distillate. Attempts to increase the heat economy of

the distilling unit were evident by 1573⁽⁸²⁾. Libavius, in his book "Alchemia", published in 1606, described his "pentathlum" (so called from its number of streams) which made use of the operations of redistillation, fractional condensation, preheating of the feed, and controlled head temperature⁽²⁴⁾. Summarizing the contributions of the alchemists to the operation of distillation, Egloff and Lowry⁽²⁴⁾ state that "many of the principles which are fundamental in the design of present day distillation apparatus were widely employed in alchemist practice. Among these principles were:

- (1) taking several (six) streams from a tower simultaneously,
- (2) refluxing,
- (3) external regulation of still head temperature,
- (4) reboiling condensate for increased fractionation,
- (5) preheating liquid before distillation,
- (6) continuous feed of liquor to still in operation."

Egloff⁽²³⁾ further states: "It is startling to observe that the beginners in the art of coal-tar refining and later in petroleum refining of our own day did not take full advantage of the principles of distillation which had been discovered and used by the ancients.

Later Improvements in Distillation Techniques:

Glauber (1651) and Charas (1681) were among the first to make use of fractionation by partial condensation; and Lemury, by 1701, had introduced the serpentine "of sufficient height so than only the most subtle spirits reach the top". Somewhat earlier, Boyle had realized that it is possible to use fractional distillation as a general method for separating volatile substances of differing boiling points. Poissonnier's still, invented about 1770, was one of the first to make use of a large cooling surface within the condenser; this still also was among the first to utilize a countercurrent flow of cooling water in order to obtain more efficient condensing of the still vapors. Argand rediscovered the preheater in 1780, and started the general trend, evident even to the present day, of increasing the heat economy of the still unit to a maximum.

Development of the Continuous Still: The Adams still, developed at the beginning of the nineteenth century, was the first commercial still which could conceivably be used on a continuous basis. The principle introduced by Adams was the enrichment of a relatively poor vapor by contacting it with a liquid to evolve a richer vapor. Berard, in 1805, patented a process whereby the enrichment

of a relatively poor vapor was attained by a controlled partial condensation and removal of the condensate; he also introduced a primitive type of bubbler plate. The advances of Adams and Berard were combined in a still described by Dubrunfaut. The use of open steam for heating was patented by Wyatt in 1802, and the steam jacket was introduced in 1816. Perrier was granted a patent on the forerunner of the modern bubble cap in 1822⁽⁶²⁾. Nine years previous to the issuance of Perrier's patent Cellier-Blumenthal⁽¹⁾ had patented the first continuous still. The Cellier-Blumenthal still used a design which is fundamentally that of the modern continuous alcohol still; a bubbler plate was used in the rectifying section and wash plates in the remainder. Savalle's invention of the steam regulator about 1857 facilitated the operation on a continuous basis and also gave a closer control of still temperatures⁽⁶²⁾. With the application of the distillation process to petroleum refining in the latter half of the nineteenth century, improvements came rapidly; the utilization of the cracking still (1910) and the pipe still (1917) marked a series of mileposts in the history of distillation operations.

Modern Developments in Distillation: With Lewis' applications of theoretical principles to distillation

and fractionation in 1922⁽⁴³⁾ a new period in the history of distillation processes was initiated. Equipment and methods were rapidly improved from both theoretical and practical standpoints. Carey⁽¹⁶⁾, in summarizing the distillation situation in 1934, pointed out that the great progress made in increasing the efficiencies and lowering the operating costs of distillation units was largely due to the use of commercial control instruments which placed the operation on a highly scientific and factual basis.

C. Theory of Distillation

General Principles: The basic data of any distillation problem are the equilibrium conditions between the liquid and vapor phases of the system to be subjected to distillation. Tables and curves giving these equilibria are available in handbooks⁽⁵⁷⁾ and in the literature⁽⁸⁵⁾. From this data it may be seen that when the vapor above a liquid of a certain percentage composition at its boiling point is richer in the more volatile constituent than is the liquid from which it originates, a simple separation is possible. The fractional distillation operation involves the condensation of these vapors and their subsequent redistillation and furthered purification. Analysis of the equilibrium diagram shows that, in the case of a bubble-cap column, the separation is stepwise and will take a definite number of theoretical plates (steps) to obtain the desired purity of products.

Early Applications of Theory: Mathematical theory was first developed and applied to rectifying columns by Sorel⁽⁷⁵⁾, who applied energy and material balances from plate to plate to calculate the stepwise enrichment, assuming that equilibrium was attained between the liquid and the vapor leaving each plate. Although Sorel's method

is accurate in that it provides for variations in the quantities of liquid and vapor flowing from plate to plate, the computations become very involved, and it is extremely difficult to visualize exactly what is taking place within the column. The method suggested by Ponchon⁽⁶¹⁾ and applied by Savarit⁽⁶⁸⁾ and Thiele⁽⁷⁷⁾ simplified the visualization of Sorel's method by solving his equations graphically to determine the number of plates required to effect a given concentration and the composition of the liquid on each plate. By assuming constant molal reflux, Underwood constructed a simple nomographic chart⁽⁸¹⁾ which can be used for the solution of practical problems where the exact methods of Sorel are necessary.

Development of Modern Theoretical Calculations:

Because of the complexity of Sorel's method and its direct modifications, the calculations are usually moderated by making the following assumptions⁽⁶⁷⁾:

1. Heat losses from the column are negligible; i.e. the column is properly lagged.
2. The heats of mixing in the vapor and in the liquid phases are negligible relative to the latent heats of vaporization involved.
3. The components being separated are of the same class; i.e. both are associating or both are

nonassociating, such that their thermal properties are similar.

Fouche's method of calculation⁽²⁷⁾, simplified by Thorman⁽⁷⁹⁾ for use at high and low concentrations where the equilibrium curve can be considered a straight line, made use of the above assumptions and of boiling point and condensation curves. The method gives directly the temperature and composition on each plate of the column.

Rodebush⁽⁶⁵⁾ introduced the use of a modified x - y (equilibrium) diagram in his stepwise graphical method for the calculation of a continuous rectifying column with a limited number of plates. The method very closely approximates actual conditions, but is too complicated for general use despite its final extra accuracy. Baker and Stockhardt⁽⁶⁾ and Lewis and Wilde^(45a) also used modified equilibrium diagrams in their attack on the problem, altering the curve to correspond to observed plate efficiencies.

Additional Methods of Calculation: Assuming that the change in the vapor composition was infinitely small as the vapor rose in the column under consideration, and that perfect rectification was attained, Lewis⁽⁴³⁾ derived basic equations of general applicability for calculating the theoretical rate of rectification within

any column from the terminal conditions and the amount of overflow. Merely a modification of Sorel's method, Lewis' equations simplify the computations involved and make it possible to present the results in graphical form. During his work, Lewis developed the first method offered for determining at what point feed should enter a continuous column. The larger the number of plates in a column, the more accurate is Lewis' method; however, for column of but a few plates the error introduced by assuming continuous conditions for stepwise conditions is appreciable. The methods of Leslie⁽⁴⁶⁾ and Van Huys⁽⁸⁴⁾ are similar to that of Lewis, and are correspondingly limited in their use. Peters⁽⁵⁸⁾⁽⁵⁹⁾ also assumed a column with a large number of plates in his modifications of Lewis' basic equations.

The McCabe-Thiele Method of Calculation: One of the most popular methods of calculation used today is that of McCabe and Thiele⁽⁴⁹⁾. Although a graphical application of Lewis' work, it does not assume continuity of rectification from plate to plate, hence is much more accurate where columns having a limited number of plates are concerned. Assuming conditions of constant molal overflow (related to the assumptions mentioned on page 12), assuming that Raoult's law (for any particular constant temperature, the partial pressure of one component of a mixture is equal to the mol fraction of

that component multiplied by its vapor pressure in the pure state at the temperature of the liquid) holds throughout the column, and assuming that the overall column efficiency is known, McCabe and Theile succeeded in presenting a simple method of calculation from the equilibrium diagram which exhibits its results in a plain manner and is accurate enough for many practical uses. Shirk and Montonna⁽⁷¹⁾ have shown that this method was the most accurate of any in popular use in 1927. Although the original McCabe-Theile methods give results in terms of the theoretical plates required, Baker and Stockhardt⁽⁶⁾ have modified it by use of actual column data to give results in terms of the actual plates required for a given separation in a given column. Although the method is excellent for most problems met in practical column design, it does have the usual disadvantages of graphical methods in that the accuracy depends primarily on the care given to the construction of plots, and difficulties are often encountered in applying the method to a system involving a large number of theoretical plates. The method has, however, found almost universal acceptance⁽¹⁹⁾ because of its simplicity, and is usually given preference to other methods by leading teachers⁽⁴⁾⁽⁵⁷⁾. A similar graphical method had been introduced previously by Rodebush⁽⁶⁵⁾, but, as Shirk and Montonna have pointed out, was too complicated to meet with popular approval.

Murphree's Approach to Calculations: Treating distillation as a special case of absorption, Murphree derived both analytical⁽⁵²⁾ and graphical⁽⁵¹⁾ methods of calculation for application to column design. Both of Murphree's methods are somewhat tedious. Shirk and Montonna⁽⁷¹⁾ applied the graphical method to the separation of ethanol-water mixtures and concluded that despite the fact that it checked exactly with the McCabe-Thiele method, it involved a large amount of tabulations and calculations which are needless since identical results can be obtained more readily by use of the McCabe-Thiele method. Murphree's outstanding contributions to the science of distillation were his development of the so-called "Murphree plate efficiency" and his proof of the fact that if the feed to a continuous column is introduced on the plate at which the composition of the liquor is nearest the composition of the feed the number of plates is a minimum.

Later Advances in Theoretical Aspects: In his excellent article "The Theory and Practice of Testing stills"⁽⁸¹⁾, A.J.V. Underwood presented an analytical calculation of the number of plates required for the separation of a binary mixture when the products were desired in almost their pure states. The author claims that a correction can be introduced to allow for variations

from the pure product over a large range, but, in that case, the computations seem to be rather complicated. In his derivation, Underwood introduced the term "relative volatility" (the vapor pressure of the pure more volatile component divided by the vapor pressure of the pure less volatile component) and suggests that since the relative volatility is more constant over a small range at each end of the binary equilibrium curves where the graphical methods are least accurate, his method be applied at these ends of the curve with a graphical method being applied between. This use of the analytical method might be somewhat quicker than the process of enlarging both ends of the equilibrium curve, as is usually done.

Recent Advances in Theoretical Computations: During the past decade many trains of thought regarding distillation calculations have been along four lines:

1. Development and/or modification of the basic methods of Lewis and of McCabe and Thiele.
2. Treatment of diffusional processes as an entity; derivation of equations to apply in general to such processes as distillation, adsorption, absorption, evaporation, and extraction.
3. Simplification of known methods of calculation, since, in any case, an overall efficiency for the actual column must be applied and the use of

simplifying assumptions merely alters the final value of the efficiency which must be used.

4. Development of the general distillation equation, with liquid composition (x) and plate number (n) as the variables.

Methods of the First Class: Methods involving the further development and/or modification of the methods of Lewis⁽⁴³⁾⁽⁶⁶⁾⁽²⁾ and McCabe and Thiele⁽⁴⁹⁾ have received considerable attention since 1922. Hains⁽⁴⁷⁾ has extended Lewis' equations to cover partly miscible liquids and the process of continuous decantation. Dodge and Huffman⁽²⁰⁾ applied the same basic assumptions and the same primary equations as Peters⁽⁵⁸⁾⁽⁵⁹⁾, and, performing the integration faultlessly, succeeded in obtaining results which checked in close agreement with results by the McCabe-Thiele method. W.K. Lewis, Jr.⁽⁴⁴⁾ succeeded in developing modifications of the McCabe-Thiele method which allow for changes in plate efficiency resulting from various conditions of flow across the plates. Smoker⁽⁷³⁾ presented an ingenious analytical treatment of the usual stepwise graphical method for determining the number of theoretical plates in a rectifying column where the solution being separated is an ideal one. Smoker proposed that his method be used in place of the McCabe-Thiele method where

greater accuracy is desired. Baker and Lindsay⁽⁵⁾ modified the McCabe-Thiele operating line to present a graphical method lending itself to calculations involving application of such variables or operation as entrainment and more than one feed or drawoff.

Methods of the Second Type: Methods of the second class include those which involve the treatment of diffusional processes as an entity. Lewis and Chang⁽⁴⁵⁾ attempted to relate rectification to absorption, as had Murphree⁽⁵²⁾, but reached no definite conclusions. Chilton and Colburn's HTU method for diffusional processes⁽¹⁷⁾ is a general method whereby operations of a diffusional nature can be calculated on a common basis; modifications by Colburn⁽¹⁸⁾ and by Withrow, Koffelt, and Gerster⁽⁸⁸⁾ extended the method to the design and correlation of operating characteristics of plate column stills. The methods proposed by Randall and Longtin⁽⁶²⁾ and by Scheibel and Othmer⁽⁶⁹⁾ are similar to that of Chilton and Colburn in that they, too, relate distillation to the other diffusional processes.

Methods of the Third Class: Methods based on simplifying assumptions, and methods making use of quick graphical solutions are becoming more and more popular where the overall efficiencies of assemblies being tested are known or can be rapidly estimated. As Edgeworth-

Johnstone⁽²²⁾ has stated: "at present there appear to be no generally applicable methods for the calculation of plate efficiency, and precise theoretical calculations are thus vitiated by a large element of uncertainty. This fact should be remembered when one is considering the degree of accuracy necessary in calculations on fractional distillation." Dodge⁽¹⁹⁾ is of the opinion that choice of any particular method is one more of convenience or preference, and the chief use of involved calculations is to show comparative effects of changes in variables. Keyes, Soukup, and Nickols⁽³⁷⁾ developed a simplified graphical method for determining the minimum number of plates necessary for a given separation, and applied a safety factor based on the character of the equilibrium curve in order to obtain the actual number of plates required. Branden⁽⁸⁾ has applied a graphical distillation study which avoids all calculations, but the constructions necessary are too time-consuming for the final accuracy of the method. Brown and Martin⁽¹¹⁾ have developed an empirical prelationship between reflux ratio and the number of equilibrium plates, while Gilliland⁽³¹⁾ developed a correlation relating a function of the actual and minimum reflux ratios to a function of the actual and minimum number of theoretical plates for distillation problems in general. Underwood⁽⁸¹⁾ has

presented a nomograph for finding the number of theoretical plates required at total reflux for a given system. Smoker⁽⁷⁴⁾ evolved a similar nomograph and also one for finding the reflux ratio required for an infinite number of plates. Assuming that the minimum reflux ratio was known, and that the relative volatility was substantially constant throughout the column, Faassen⁽²⁸⁾ developed a chart for approximating the number of theoretical plates and corresponding reflux ratios for problems involving the distillation of binary mixtures. Edgeworth-Johnstone⁽²²⁾ has presented a nomographic chart for the computation of fractionating columns for the separation of binary mixtures in both general cases and in cases where the mixtures obey Raoult's law. Thomson and Beatty⁽⁷⁶⁾ simplified the calculation of theoretical plates for binary mixtures containing less than five mol percent of one component.

Methods of the Fourth Class: Methods of the fourth class include those involving the development of the general distillation equation, with liquid composition and plate number as the variables. Fenske⁽²⁶⁾ presented an equation of this type for distillation at total reflux, while Smoker⁽⁷³⁾ derived a similar equation to be applied to binary distillation at any reflux. The system of distillation equations presented by Herbert⁽³³⁾ is the

most complete of any yet published; included is the general equation for the case of any number of components and any reflux ratio. Advantages of the general distillation equation over other methods of column calculation are that (1) no simplifying assumptions need be involved, (2) solution of the general equation is rapid and simple, (3) time is often saved by being able to calculate directly the composition of the liquid on any plate, and (4) the method offers a means of developing distillation theory by direct algebraic analysis. A somewhat different treatment of the general subject of x vs. n equations is presented by Underwood⁽⁸³⁾.

D. Column and Plate Efficiencies

Necessity of Efficiency Measurements: In actual columns equilibrium between liquid and vapor is seldom realized, and consequently the number of plates needed to perform a given separation in actual columns is usually greater than the number calculated for an ideal column. The ratio of the number of actual plates to the number of ideal plates, or the number of actual plates equivalent to one ideal plate, is a measure of the efficiency of the column or plate, respectively. This ratio is an average value, and, in general, must be determined for the particular plate or column under consideration.

Overall Column Efficiency: Lewis⁽⁴³⁾ recognized the use of an overall column efficiency when he stated that through the use of "k", a constant depending on the type of column under consideration, the overflow, vapor rate, and plate efficiency, his equations could be used for the design of actual columns. Applied to the McCabe-Theile⁽⁴⁹⁾ diagram, the overall efficiency is defined as the ratio of the number of steps (theoretical plates) required for a given separation to the actual number of plates required for that separation. Overall efficiencies are also used extensively with nomographic calculations.

Individual Plate Efficiency: Realizing that the overall column efficiency did not give any indication of the efficiency gradient from plate to plate throughout the column, Murphree⁽⁵²⁾ derived his "Murphree plate efficiency", defined as the ratio of the actual vapor enrichment over a given plate ($Y_n - Y_{n-1}$) to the theoretical vapor enrichment over that plate under equilibrium conditions ($Y_n^* - Y_{n-1}$), where:

Y = composition of vapor leaving the plate

Y^* = composition of vapor in equilibrium with liquid on the plate

n = the plate under consideration.

In its original form, Murphree's efficiency is not very convenient for practical purposes, as its application at any plate involves the measurement of vapor compositions. It can, however, be put in a more suitable form⁽⁸¹⁾ involving liquid compositions, determination of which is easier in practice owing to the greater ease of taking liquid samples than vapor samples. Expressed in terms of liquid compositions, the Murphree efficiency is:

$$E_o = \frac{X_{n+1} - X_n}{X_{n+1}^* - X_n}$$

where: E_o = Murphree overall plate efficiency

X = Composition of liquid on the plate

X^* = Composition of liquid resulting from the

condensation of vapor in equilibrium with liquid on the plate

n - The plate under consideration.

Both forms of the Murphree efficiency are theoretically equivalent if the McCabe-Thiele operating line is considered straight.

Effect of Design Variables on Column Efficiencies:

The effect of design variables on column efficiencies has been the subject of numerous investigations within the past score years. Peters⁽⁵⁸⁾ showed that plate efficiency was dependent on the substance being fractionated, and that feed composition affected column conditions through its effect on heat consumption; while Murphree⁽⁵²⁾ demonstrated that the type of bubble-plate used was an important factor in the control of plate efficiencies. The effect of reflux ratio on overall efficiency has long been known, and may be readily visualized by inspection of the McCabe-Thiele⁽⁴⁹⁾ diagram. Such variables as vapor rate⁽⁴⁰⁾⁽¹⁶⁾⁽⁷²⁾, shape of the bubble slots⁽⁷²⁾, the nature of the vapor-liquid equilibrium⁽¹⁶⁾, plate spacing and liquid height⁽⁹⁾⁽⁵⁶⁾⁽⁷⁶⁾, the viscosity of the substance being separated⁽²¹⁾, and the degree of entrainment of liquid bubbles⁽⁹⁾⁽⁵⁶⁾⁽⁷⁶⁾ have received much attention, and the results of these and similar investigations have enabled the scientific design of plates and

columns of high efficiency⁽⁵³⁾. The Vulcan tangential opposed-type bubble cap, as used on the column under investigation in this thesis, is one of the most efficient caps yet produced in quantity⁽⁵⁴⁾.

E. Condensation of Vapors

Methods of Condensing Vapors: The methods of condensing the vapors from the top of a tower may, in general, be classified as either (1) simple condensation or (2) dephlegmation. Simple, or total, condensation refers to the process by which tower vapors are liquified in a single condenser, reflux and product being of the same composition. Dephlegmation, or partial condensation, refers to the condensation of tower vapors in a series of condensers; the condensate from the first condenser being returned to the column as reflux, and the condensate from the following condenser being removed as product. It is obvious that in partial condensation some fractionation of the vapors takes place in the first (dephlegmating) condenser, since the less volatile constituents are more readily liquified than are the more volatile constituents.

Comparison of Condenser Types: Considerable controversy has existed over the value of dephlegmators as fractionating devices. Some authors state that the dephlegmator is an important part of the fractionating assembly, while others believe that any separation which occurs in the dephlegmator is incidental to the major function of condensing the vapor and providing reflux⁽⁸⁰⁾. Very thorough investigations have been made to determine the actual efficiency of

dephlegmating condensers⁽⁸⁶⁾, and the maximum of 1.3 theoretical plates⁽⁸⁰⁾ is rather unusual. The additional cost of partial condensers over the cost of a total condenser of the same capacity is, however, much more than the cost of adding an additional plate to the column itself. Several authors⁽³⁵⁾⁽⁶⁴⁾ have pointed out the advantages of simple condensation over dephlegmation; applied to small scale experimental columns, these advantages may be listed as follows:

- (1) Control of reflux ratio is more accurate since it can be accomplished merely by changes in valve settings or by automatic proportioning devices instead of by the trial and error method of regulating cooling water flow.
- (2) Reflux and product are of the same composition, thus simplifying theoretical calculations.
- (3) Auxiliary mixing equipment is not necessary if total reflux is desired and the dephlegmating condenser is incapable of liquifying the entire amount of column vapor.
- (4) The additional expense and construction necessary with multiple condensers is usually unnecessary since purity of product is not a final aim.
- (5) The amounts of cooling water required are usually less than in the case of partial condensers.

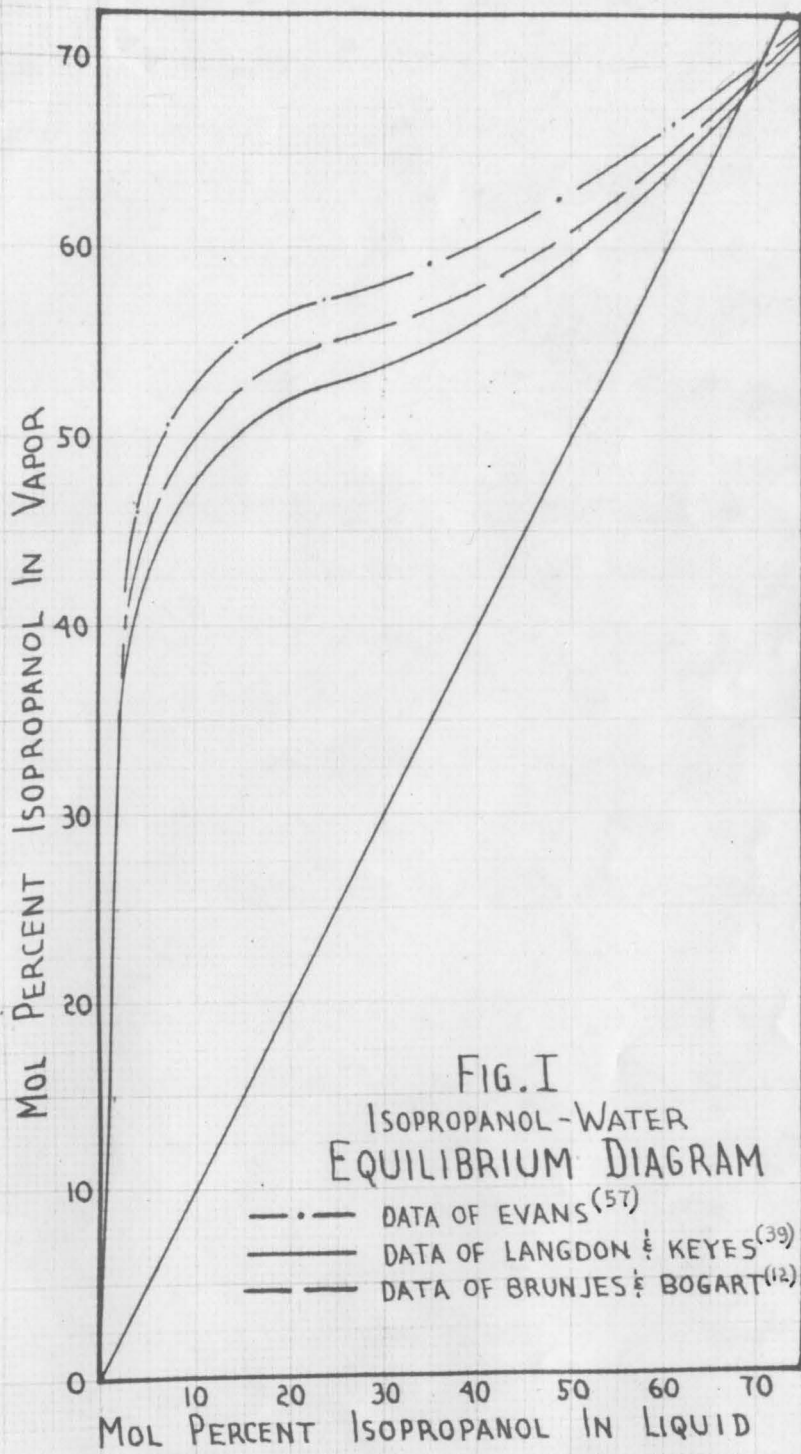
The Condenser for the Column Under Investigation:

Although a simple condenser has been used on the column to be tested in this investigation⁽³⁶⁾, no data is available for a comparison of ease of operation using the two types of condensers. Dephlegmating condensers have been used almost exclusively in previous investigations on the experimental column⁽²⁵⁾⁽³²⁾⁽⁴⁸⁾, and have been a constant source of trouble during test runs. Using a dephlegmating system, a minimum of four experimenters were necessary to hold equilibrium conditions and take samples during a run⁽⁴⁸⁾.

F. Isopropyl Alcohol

Commercial Importance of Isopropanol: Probably the only secondary alcohol with as good solvent properties as the normal alcohol⁽⁶³⁾, isopropanol has only within the past score years attained the prestige that it holds today in the fields of commercial chemicals. Initial prophecies as to its future importance were made in the mid-twenties⁽²⁹⁾⁽⁷⁰⁾, and Garlick⁽³⁰⁾ and Kirkpatrick⁽³⁸⁾ publicized its potential uses as a solvent and as a raw material. Since isopropanol is a denaturant itself, its uses are not restricted by taxes, duties, and laws as are the uses of ethanol⁽³⁾; isopropanol has, therefore, largely replaced ethanol as a solvent in many industries. Mixtures of isopropyl alcohol and water have gained rapidly in importance as a result of recent technological advances⁽³⁹⁾.

Equilibrium Data Available: Vapor-liquid equilibrium data in the literature include the results of investigations by Lebo⁽⁴²⁾, Evans⁽⁸⁷⁾, Brunjes and Bogart⁽¹²⁾, and Langdon and Keyes⁽³⁹⁾. A graphical comparison of published data is shown in Fig. I on page 31. It is obvious, as has been pointed out previously⁽⁶¹⁾, that the degree of accuracy of any theoretical calculations will depend on the accuracy of the equilibrium data



available. The data of Langdon and Keyes, having been obtained by experienced investigators using improved techniques, is probably the most accurate yet published. The exact composition of the azeotrope has long puzzled investigators, different experimenters⁽³⁸⁾⁽⁵⁰⁾ having obtained widely differing values. The most recent work, by Langdon and Keyes, indicates that the azeotrope has a composition of 68.35 mol percent alcohol at atmospheric pressure.

Analytical Procedures for Isopropanol-Water System:

Any method for use in the analysis of liquid samples taken from a column under test must fulfill two general requirements in order to be acceptable:

1. It must be accurate, rapid, and simple;
2. The removal of the necessary samples from the system must not upset equilibrium conditions within the system.

Manowitz⁽⁴⁸⁾ stated that, although density measurements were accurate when taken by Westphal balance, the amount of liquid required per analysis (50-90 cc) was so large that its removal upset equilibrium within the test column; the use of the pycnometer, as recommended by Langdon and Keyes⁽⁴¹⁾, although requiring smaller samples than necessary with the Westphal balance, still requires at least 10 cc per analysis if readily available equipment is used. The pycnometric method is, however, one of the

most accurate methods from an analytical standpoint⁽⁸⁹⁾. The use of index of refraction as a measure of the composition of aqueous isopropanol solutions, as suggested to the perfumery trade by Bennett and Garratt⁽⁷⁾, was investigated by Dorsey⁽¹³⁾ and found to be an acceptable method of analysis; further work to correlate composition and refractive index was deemed necessary, however, before the method could be used with any degree of accuracy.

Distillation Characteristics of Aqueous Isopropanol:

Continuing work initiated by Byman and Keyes⁽¹⁴⁾, Langdon and Keyes⁽⁴⁰⁾ made a detailed study of the continuous rectification of mixtures of isopropyl alcohol and water in a bubble-cap column of four plates. Their results may be summarized as follows:

1. Individual plate efficiencies showed nearly constant values over the composition range 18-55 mol percent alcohol, but decreased rapidly above 55 percent;
2. Plate efficiencies were affected very little by changes in reflux ratio and superficial vapor velocity;
3. The physical properties of the liquid being rectified had a noticeable effect on the rectification characteristics.

Manowitz⁽⁴²⁾ investigated the isopropanol-water system in a bubble-cap column of fifteen plates under conditions of continuous rectification in a closed system. Although his data is unreliable, the following general conclusions may be accepted:

1. Overall column efficiency increases with the reflux ratio;
2. The purity of the final product increases with the reflux ratio.

G. The Experimental Column

Previous Investigations: Although numerous runs have been made on the experimental column by students in the undergraduate unit operations laboratory classes, the validity of the recorded data is questionable, since all tests were made under difficult control conditions, sampling technique was poor, and equilibrium conditions were seldom, if ever, attained. Although most runs were made using ethyl alcohol-water mixtures, some classes attempted to rectify commercial anti-freeze solutions. Top overall efficiencies attained in the fractionation of ethanol-water mixtures were in the vicinity of 25%. Gross, Lucas, and McNeer⁽³²⁾, in their undergraduate thesis work, determined more specific operating characteristics of the column as used to separate ethanol-water mixtures; their data, however, was affected by incomplete attainment of equilibrium conditions, faulty analytical methods, and operational difficulties.

Rectification of Isopropanol-Water Mixtures: Manowitz⁽⁴⁸⁾ correlated the data of numerous investigations by unit operations laboratory students dealing with the rectification of isopropyl alcohol-water mixtures in the experimental column. His results show quite clearly many of the characteristics of the column; again, however, errors were

introduced by faulty analytical methods and incomplete attainment of conditions assumed in making the theoretical calculations. Manowitz' correlations may be summarized as follows:

1. The use of cold (approximately 140°F) reflux affected the temperature gradient in the column as low as the sixth plate from the bottom, lowering appreciably the degree of separation attained on the upper plates. More nearly theoretical gradients were obtained at lower reflux ratios.
2. Characteristic S-shaped concentration gradient curves were obtained, rectification taking place to a slight extent on the first few plates, sharply increasing in the center portion of the column, and decreasing gradually near the top of the column.
3. Overall McCabe-Thiele efficiency increased appreciably with reflux ratio.
4. Optimum operating conditions were found to be at a reflux ratio of from 1.0 to 1.5 with steam ^{PRESSURE} ~~temperature~~ at 6.0 psig.

Manowitz noted that there was a large inherent error in all of the column thermometers.

Difficulties in Column Operation: The chief problems encountered in the operation of the experimental column may

be listed as follows:

1. Accurate control of reflux ratio;
2. Accurate control of steam pressure;
3. Method of sampling;
4. Prevention of heat losses from column;
5. Addition of make-up liquor to system.

In addition, from the standpoint of ease of operation, too many workers (at least four) are required to make a simple test run on the column.

III. EXPERIMENTAL

A. Purpose of Investigation:

The purpose of this investigation was to improve upon the overall design of a 15-plate fractionating assembly used in the separation of simple binary mixtures of isopropyl alcohol and water, to recalibrate all measuring devices used in the operation of the column, to develop an analytical method by which the composition of liquid samples from the column could be determined accurately and quickly, and, in general, to place the assembly in such condition that experimental runs can be made more easily and with a higher degree of accuracy than has previously been possible.

B. Plan of Investigation:

The plan to be followed in conducting the investigation was divided into four main steps, as follows: (1) the investigation of previous work on the column, and the investigation of theoretical and practical methods by which the efficiency of the column could be increased; (2) the redesign of the column assembly, and the construction and piping of necessary accessories; (3) the development of a rapid, accurate analytical method for determining the composition of isopropyl alcohol-water solutions; and (4) testing of the column assembly to improve operational methods.

C. Materials:

1. The isopropyl alcohol used was obtained from the Standard Alcohol Company, Linden, New Jersey. The commercial alcohol, a petroleum product known by the trade name of "Petrohol", was shipped in 55-gallon steel drums, and was stored in these drums prior to use. A typical analysis of the isopropyl alcohol as shipped from the plant is as follows⁽⁹⁰⁾:

Specific Gravity 20/20	0.789
Purity	99.3%
Distillation- Initial °C	81.7
Final °C	82.4
Acidity as acetic acid	0.0006
Residue, gms/100	0.0002

Tests made at time of arrival showed the alcohol to be completely miscible with water in all proportions.

2. The water used throughout the investigation was obtained from the lines in the chemical engineering department of the Virginia Polytechnic Institute. Analyses of this water are on file at the VPI sanitary engineering department.

3. The 85% magnesia pipe covering and the 85% magnesia cement were obtained from the stockroom of the VPI department of chemical engineering. All insulation was a Johns-Manville product.

4. The starch paste used in applying cloth coverings to insulated equipment was made using water and a commercial grade of starch (Linit) purchased from chain stores in Blacksburg, Virginia.

5. The pipe dope used in the construction of the column assembly was made from red lead, flake graphite, and cutting oil.

6. Copper piping, tubing, and sheeting used in the construction of column accessories was obtained from the stockroom of the VPI department of chemical engineering.

7. Pyrex weir glasses, used on the two control weirs, were obtained from the Corning Glass Works, Corning, N.Y.

D. Apparatus:

1. The bubble-cap column, Figs. II, VIII, made by the Vulcan Copper and Supply Company, Cincinnati, Ohio, consisted of fifteen plates, the bottom plate enclosed in Pyrex glass and the remaining plates enclosed in bronze cylinders. The plates proper were of bronze. Each plate, as shown in Fig. III, was equipped with a Vulcan tangential opposed flow - type bubble-cap, a downcomer, a sampling outlet, provision for a vapor-space thermometer, and a provision for introducing feed above the plate (plugged). The metal cylinders were $8\frac{3}{8}$ inches i.d.; the distance between metal plates was $5\frac{7}{8}$ inches; liquid depth (at top of downcomer) was $1\frac{6}{16}$ inches; cap

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ORIGINAL LAYOUT OF LABORATORY
FRACTIONATING ASSEMBLY

DRAWN BY: CJD
 INKED BY: CJB
 APPVD BY: JWB

SCALE: $\frac{3}{4}$ " = 1'0"
 DATE: 1-30-46
 FIG. NO: II

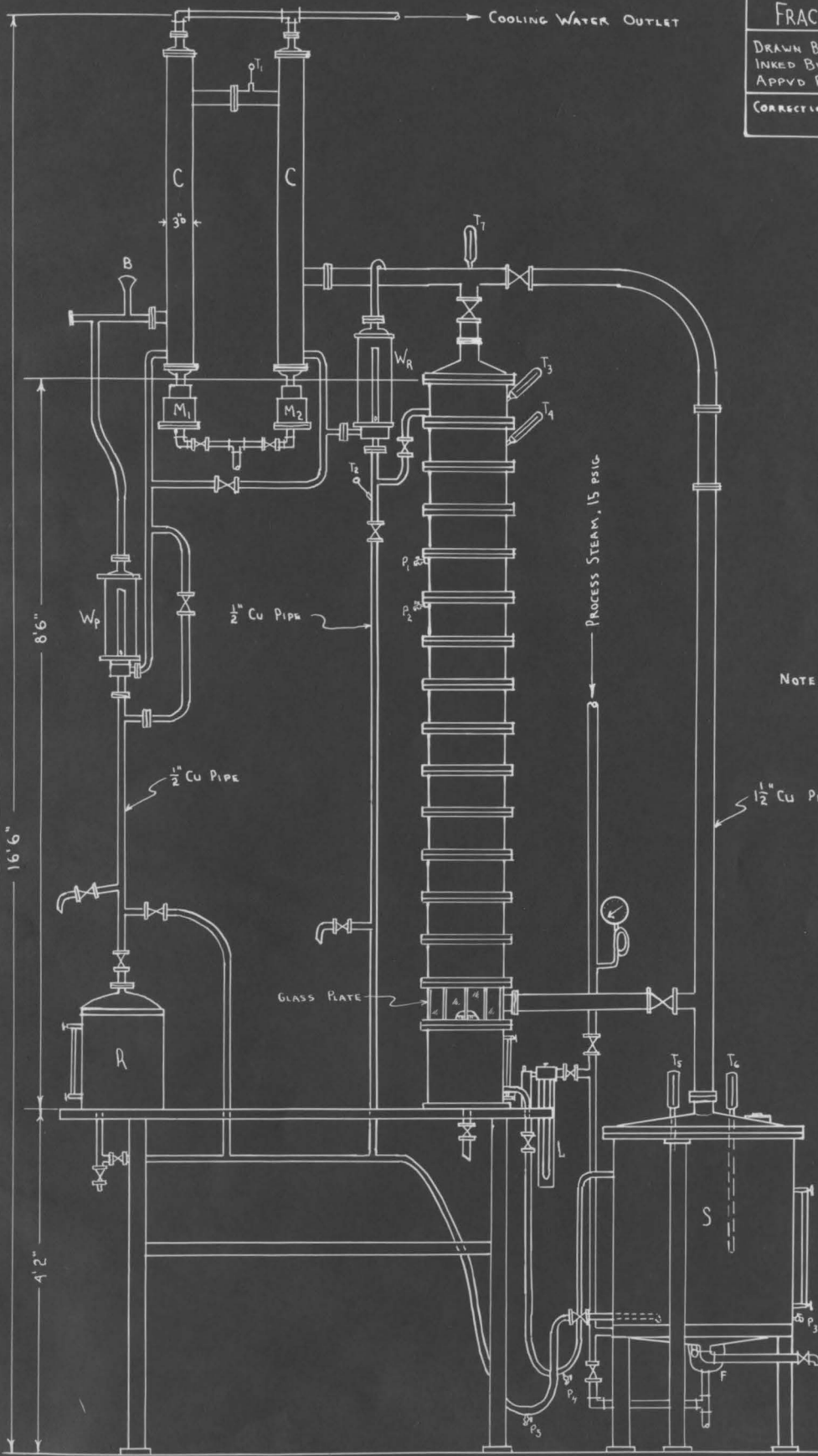
CORRECTION: VAPOR FEED FROM STILLPOT ENTERS
 BELOW GLASS PLATE, NOT AS SHOWN

LEGEND

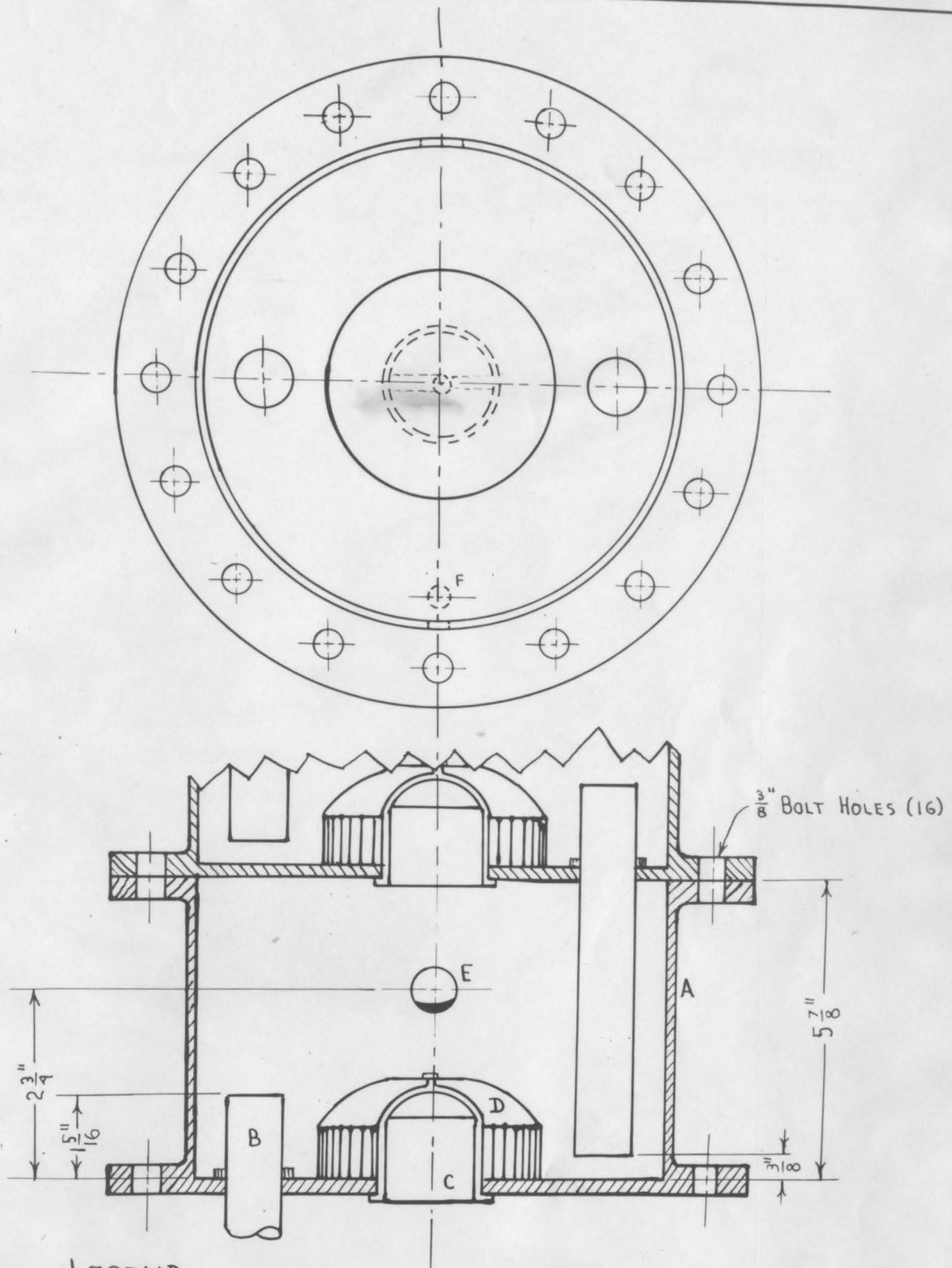
- B - BLOWHORN (VENT)
- C - CONDENSERS (2)
- F - STEAM TRAP
- L - MANOMETER
- M - WATER METER (2)
- P - PETCOCK (1 PER PLATE)
- R - PRODUCT RECEIVER
- S - STILLPOT
- T - THERMOMETER (1 PER PLATE)
- W_p - PRODUCT WEIR
- W_R - REFLUX WEIR

NOTE: FOR DETAILED DIMENSIONS
 SEE EPSTEIN⁽²⁵⁾

NOTE: STEAM COILS 36" OF
 $\frac{3}{4}$ " CU PIPE



FLOOR LINE



LEGEND

- A - BRONZE CYLINDER, $8\frac{3}{8}$ " I.D.
- B - DOWNPIPE, $1\frac{1}{16}$ " I.D.
- C - VAPOR PIPE, 2" I.D.
- D - VULCAN BUBBLE CAP, $3\frac{7}{8}$ " O.D.
- E - THERMOMETER INLET
- F - SAMPLING TUBE INLET, $\frac{5}{16}$ " D

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DETAILS OF EXPERIMENTAL PLATE

DRAWN BY: C.L.D.
 INKED BY: C.L.D.
 APPVD BY: *F.W.B.*

DATE: 1-30-46
 SCALE: $\frac{3}{8}$ " = 1'0"
 FIG. No: IV

diameter was $3\frac{7}{8}$ inches; internal diameter of the vapor riser was 2 inches; downcomers were $1\frac{1}{16}$ inches i.d. and extended to within $\frac{3}{8}$ inches of the plate below; each cap contained 32 slots $\frac{1}{8}$ inch wide by $\frac{7}{8}$ inches high to give a total slot area of 3.4 square inches per cap. Openings for vapor chamber thermometers were $3\frac{1}{2}$ inches above the plates. Glass sections were $8\frac{1}{4}$ inches i.d. and 5 inches high, the distance between the first and second plate being $5\frac{1}{8}$ inches. The cap on the glass enclosed plate was $4\frac{1}{2}$ inches in diameter; the downcomer was equipped with a copper baffle on the cap side. No downcomers were provided with baffles. Metal plates were sealed by fiber gaskets between the flanges.

2. The stillpot, manufactured by the Vulcan Copper and Supply Company, was of copper, with a capacity of fifty gallons. The enclosed heating unit in the bottom of the pot was of $\frac{3}{4}$ inch copper pipe $36\frac{1}{2}$ feet long coiled spirally.

3. The partial condensers on the original column were made by Vulcan and consisted of two 35-inch sections of $2\frac{1}{4}$ inch copper pipe in which twenty-two $\frac{1}{8}$ -inch copper tubes were inserted through tubesheets. Water circulated from top to bottom through the small tubes. Vapor to the first condenser entered through a $1\frac{1}{4}$ inch copper pipe

11- $\frac{3}{4}$ inches above the base of the condenser. Non-condensables left the system through a $\frac{3}{4}$ inch pipe 5- $\frac{1}{2}$ inches above the base of the second condenser, passing to a blowhorn vent. Condensate was removed through $\frac{1}{2}$ inch lines at the base of each condenser. The two condensers were 12- $\frac{1}{2}$ inches apart, center to center, and were joined 2- $\frac{1}{2}$ inches from their tops by a 1 inch copper pipe.

4. The simple condenser, constructed in the course of the thesis work, consisted of an 18 gage copper cylinder 6- $\frac{1}{2}$ inches o.d. with tube sheets of 18 gage copper. The condensate well at the base of the condenser, of copper, was three inches deep, 6- $\frac{1}{2}$ inches i.d., and tapered at the bottom to fit a $\frac{1}{2}$ inch copper pipe on the centerline of the condenser. Twenty-one $\frac{1}{4}$ -inch copper tubes, 27 inches long, were spaced in the tubesheets. Water flowed outside the small tubes and countercurrent to vapor flow. Overall length of the condenser was 31 inches. Vapor entered the condenser through a 1 inch copper pipe, 1 inch below the lower tube sheet, which was bronzed to the condensate well. Non-condensables were removed through a $\frac{1}{4}$ inch line to the blowhorn vent.

5. The steam pressure regulator used on the line to the stillpot was manufactured by the Fisher Governor Company, Marshalltown, Iowa. Serial number was 465400,

type 577. The high pressure side was connected to the high pressure process steam line in the laboratory.

6. The refractometer used in analytical work was a Spencer Abbe refractometer, Model 547, manufactured by the Spencer Lens Company, Buffalo, N.Y. The index of refraction range attainable was from 1.3000 to 1.7100. Temperature control was by means of water flow through the prism chambers. The instrument was adjusted before each group of determinations using a special checkglass furnished with the instrument ($n_D^{20} = 1.5108$) and using distilled water ($n_D^{20} = 1.3330$).

7. The constant temperature water flow assembly used for temperature control within the refractometer consisted of a five-gallon steel bucket with connections as a constant head tank, placed approximately three feet above the level of the instrument. Water connections were of 1/4 inch iron pipe. The tank rested on a single unit 115 volt a.c. electric heater with heating unit wound on porcelain refractory of 5 1/2 inch overall diameter. Automatic temperature control was by a Model B, 115 volt, 60 cycle, Precision Temperature Regulator, manufactured by the Eastern Engineering Company, New Haven, Conn., and controlled through an immersion bulb containing mercury. Rate of water flow was controlled by a needle valve on the supply line to the tank and by a 1/4 inch cock on the

line to the refractometer.

8. Pycnometers used in making density determinations were unadjusted Gay-Lussac specific gravity bottles of 10 and 25 milliliter capacity with ground-in perforated glass stoppers. The bottles were manufactured by the Fisher Scientific Company, Pittsburgh. Earlier density measurements, not reported in this report, were made using a standard Westphal balance, also manufactured by Fisher.

9. The soda straws used to transfer samples to the lens of the refractometer were "Sunshine" straws made by the Herz Straw Company, New York.

10. The analytical balance used in making density determinations was a Seko General Laboratory Model No. 60 with chain device, magnetic damper, and notched beam, manufactured by Seederer-Kohlbusch, Inc., Jersey City, N.J.

11. Thermometers used on the column proper included eleven "Precision" industrial mercury thermometers manufactured by the Fisher Scientific Company, and three industrial mercury thermometers (on plates 2, 3, and 4) manufactured by the United States Gage Company. The still vapor thermometer was a "Precision" thermometer, while the still liquid thermometer was a standard Taylor industrial, glass-enclosed, mercury thermometer manufactured by the

Taylor Instrument Company, Rochester, N.Y. Two Weston metal testing thermometers, manufactured by the Weston Electrical Instrument Corporation, Newark, N.J., were used to measure reflux temperatures.

12. The meter on the water line to the single condenser was a "Niagara" meter manufactured by the Buffalo Meter Company, Buffalo. Serial number was 1013790, dial 107.

E. Method of Procedure:

1. Redesign of Column Assembly: Operational difficulties encountered as a result of the inconvenient design and placement of the rectifying column accessories, coupled with the inability of the column itself to function under conditions of equilibrium, have prevented previous investigators from obtaining accurate and valid results in their work. The impossibility of reaching control valves with ease; the inconvenience of using dephlegmating condensers, often resulting in variable reflux ratios; the inability to control steam pressure accurately; the lack of accurate calibrations for measuring devices; the inability to add make-up to the system in operation; the lack of facilities for determining true feed composition; the lack of the necessary heat exchanger for preheating reflux; and the huge losses of heat from the uninsulated system all resulted in grave operational difficulties. It

was the purpose of this part of the investigation to remedy these difficulties.

a) Construction of Intermediate Level: To facilitate the convenience of operating the condensing apparatus and reflux control valves, an intermediate level was added to the original supporting platform. The frame of the new platform was constructed of $1\frac{1}{4}$ inch iron pipe, with welded joints, and was bolted to the original assembly and welded to a girder behind the platform. Three steps, 25 inches wide (width of the frame) were provided for ascending the additional platform. The new platform itself was constructed of $\frac{3}{4}$ inch angle irons, 29 inches long, placed approximately one inch apart and supported on the frame 37 inches above the original platform. Side and back rails of $1\frac{1}{4}$ inch pipe were provided 15 inches above the new platform. Details of the intermediate level are shown in Fig. IV.

b) The Sample Return System: The sample return system shown in Fig. V had been previously constructed by Bryan, Couper, and Dorsey⁽¹³⁾ to facilitate operation of a continuous sampling method and to provide a means for adding make-up to the system while in operation. The base of the main return pipe, of $\frac{3}{4}$ inch copper tubing, was inserted in a $1\frac{1}{4}$ inch copper tube attached to the product return line by a $\frac{1}{2}$ inch tee and an adapter. A $\frac{1}{4}$ inch tube about five inches long was bronzed to the

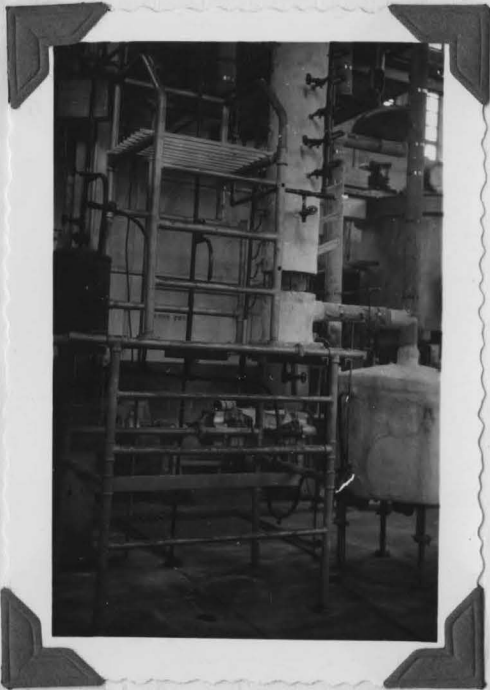


Fig. IVa

Main & Intermediate Platforms

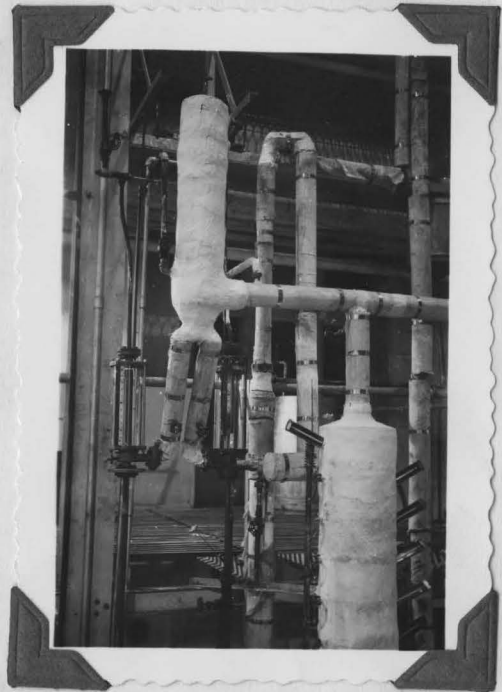


Fig. IVb

Stillhead & Control Weirs

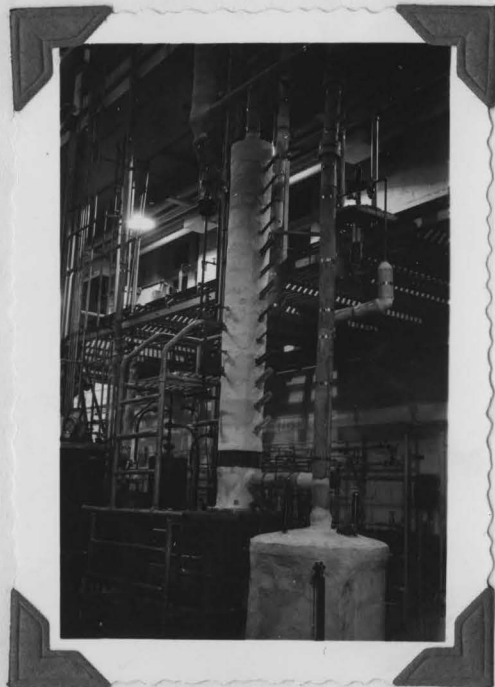
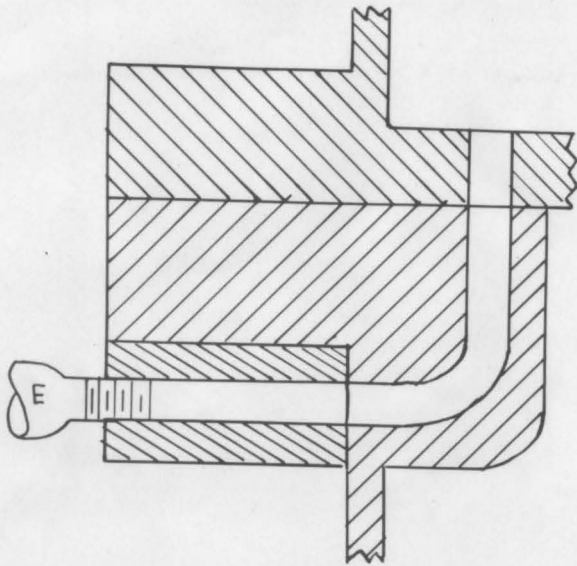


Fig. IVc

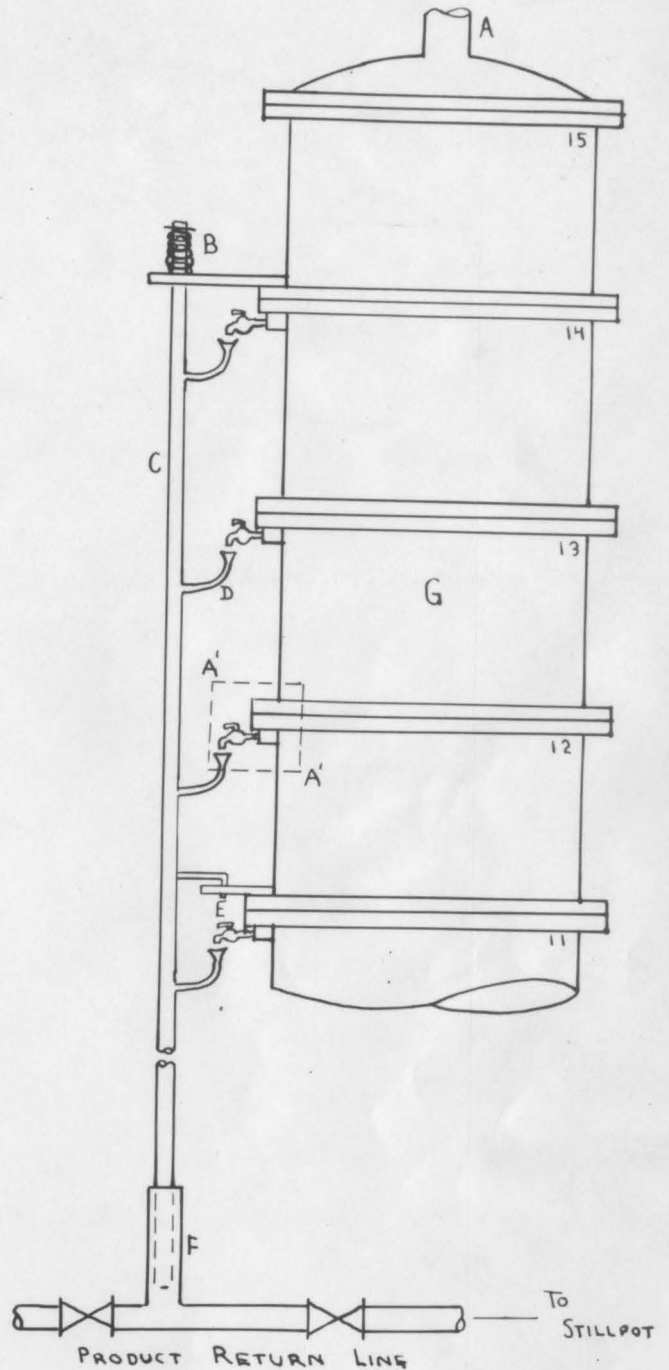
Column Assembly



SECTION A'-A'
SAMPLING PETCOCK INSTALLATION

LEGEND

- A - VAPOR LINE TO CONDENSER
- B - COIL SPRING (IN TENSION)
- C - $\frac{3}{4}$ " COPPER TUBING
- D - $\frac{1}{4}$ " COPPER TUBING (FLARED AT END)
- E - $\frac{1}{4}$ " PETCOCK
- F - 1" COPPER TUBING
- G - EXPERIMENTAL COLUMN



NOTE: COIL SPRING (B) HOLDS RECEIVING TUBES (D) AGAINST MOUTH OF PETCOCKS. RETURN TUBE (C) LOWERED WHEN SAMPLES ARE TAKEN.

NOTE: TUBE (C) SUPPORTED FROM PLATES 9, 8, 11, 14; GROOVES IN SUPPORT FROM PLATE 14 FIT KEYS ON (C) TO PREVENT TURNING.

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DETAILS OF SAMPLING SYSTEM

DRAWN BY: C.L.D.
INKED BY: C.L.D.
APPVD BY: *hwb*

DATE: 1-30-46
SCALE: NONE
FIG. NO: VI

vertical return pipe approximately three inches below the level of each petcock on the column, and each small tube was bent and enlarged to fit directly under its respective petcock when the spring assembly at the top of the vertical tube pulled the system up. Samples could be taken by pulling the vertical return tube down against the spring action, thereby uncovering the mouths of the petcocks.

c) The Simple Condenser: To facilitate more accurate control of reflux ratio, a simple condenser (Fig. VIII) was constructed to replace the original partial condensers on the column assembly. The outside cylinder and tube sheets of the simple condenser were constructed from 18 gage copper sheeting. The main cylinder was $6\frac{1}{2}$ inches o.d. The condensate well, of 24 gage copper sheeting, at the base of the condenser was 3 inches deep, $6\frac{1}{2}$ inches i.d. , and tapered at the bottom to fit a $1/2$ inch copper pipe on the centerline of the condenser. Twenty-one $1/4$ inch copper tubes, 27 inches long, were spaced in the tubesheets. The overall length of the condenser was 31 inches. Water flowed outside the small tubes and countercurrent to the direction of vapor flow. Vapor entered the condenser through a 1 inch copper pipe bronzed to the condensate well 1 inch below the lower tube sheet. Non-condensables were removed

through a 1/4 inch line at the top of the condenser above the upper tube sheet leading to a blowhorn-type vent.

d) Piping of Condenser and Control Weirs: The control weirs and the condenser were supported from steel girders immediately behind the column assembly. To facilitate ease of operation, the weirs and reflux control valves were placed immediately below the condenser at a height convenient for operation from the intermediate platform. Details of the piping are shown in Fig. VIII.

e) Construction of Reflux Heater: Since many previous investigators had recommended that the reflux be heated before being returned to the column, a small heat exchanger was constructed and placed in the reflux return line at the top of the column. The exchanger was constructed from a 2 inch copper pipe, concentric with a 1/2 inch copper tube. The ends were made of 18 gage copper sheeting. Low-pressure process steam entered and left the annular space through 1/2 inch iron pipes bronzed 1-1/2 inches from each end of the exchanger. Overall length of the accessory was 10 inches. A 1/8 inch thermometer well was inserted in the reflux line at the hot end of the exchanger. Hot reflux entered the top plate at plate level on the side opposite the downspout.

f) Feed Sampling Condenser: Details of the small condenser used to sample the vapor feed to the

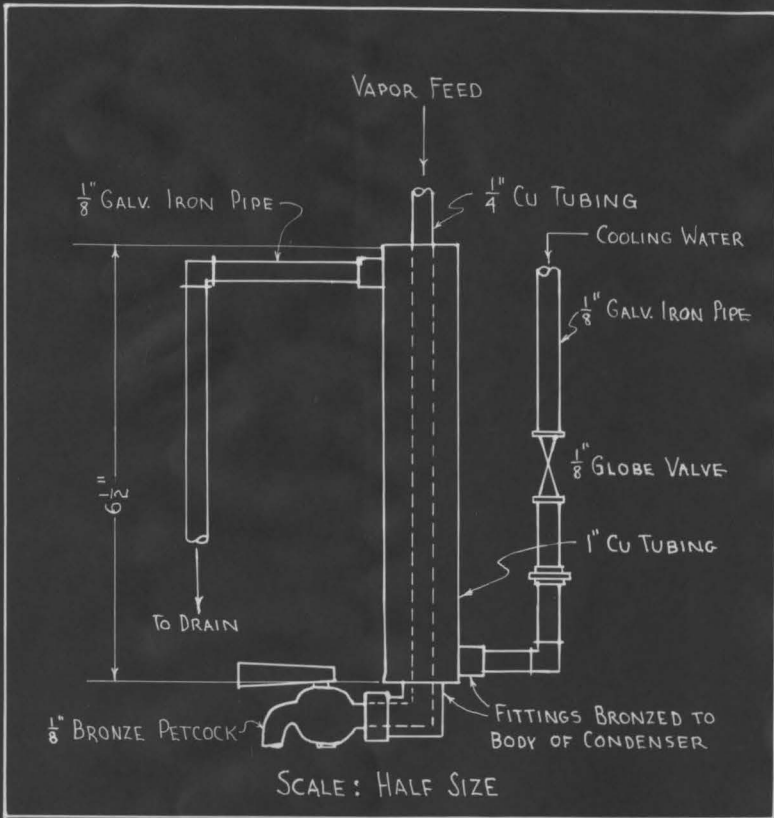
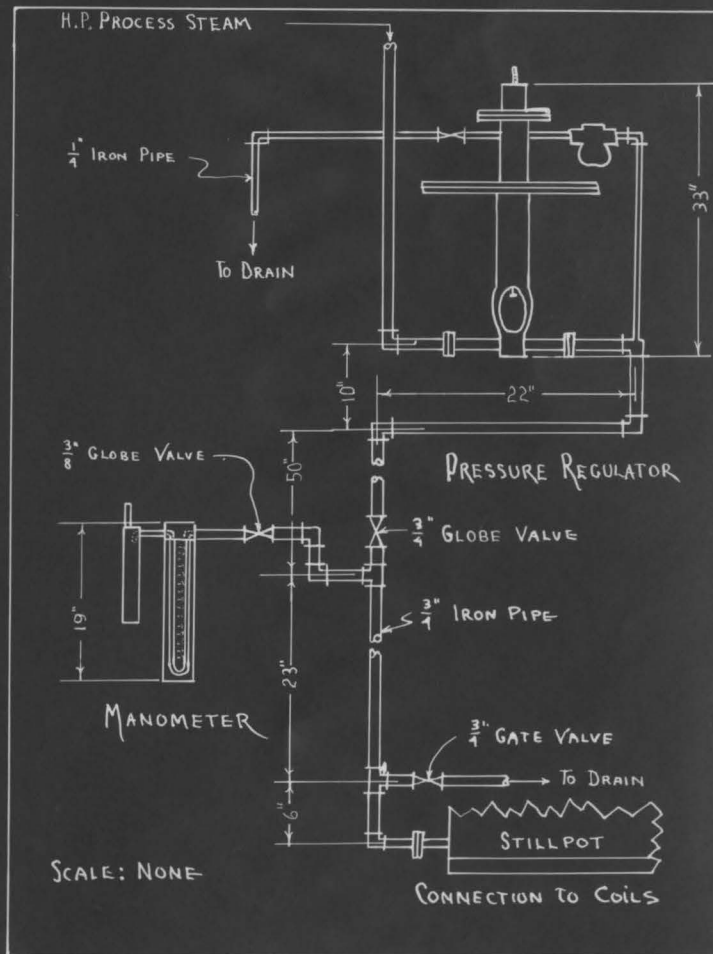


FIG. VI
FEED SAMPLING CONDENSER

FIG. VII
PIPING DETAILS
STEAM LINES TO STILLPOT



column are shown in Fig. VI. Constructed of copper, the condenser was piped so that water flow could be stopped except when samples were being taken. A 1/4 inch copper vapor pipe was bronzed to the main vapor line.

g) Steam Pressure Control: The difficulties which had been encountered in previous investigations led to the installation of a Fisher steam pressure regulator in the steam line to the stillpot. The regulator was supported from a building girder immediately behind the assembly, and the high-pressure side of the regulator was piped to the high-pressure process steam line in the laboratory. A 3/4 inch globe valve on the low-pressure side of the regulator served to increase the degree of regulation attainable. Steam pressure in the stillpot coils was measured by a mercury manometer attached immediately below the control valve mentioned above. Details of the assembly are shown in Fig. VII.

h) Cleaning of the System: The rectifying column and all lines were flushed several times with hot water and with hot isopropanol solutions. The stillpot was flushed with weak alkali and with weak acid solutions, and was cleaned with water and a wire brush. Heating coils in the pot were scraped and brushed thoroughly to remove all traces of solid sludge (see page 64).

Attention Patron:

Page 55 omitted from
numbering

i) Replacement of Fittings: All fittings and valves were checked during test runs, and any that leaked or were not in operating condition were repaired or replaced.

j) Calibration of Measuring Devices:

1. All thermometers were calibrated against a standard glass mercury thermometer by simultaneous immersion in a water bath. At least four points were determined for each thermometer, and point-to-point curves were drawn through the plotted data. Data and results are shown in Table 3 and in Figs. XI - XV.

2. Both reflux and product weirs were calibrated with the column in operation by collecting samples from the respective return lines in tared flasks. Periods of from one to five minutes were used as sampling intervals. The liquid composition at time of sampling ranged from 53 to 57 mol percent alcohol at a temperature of 156°F. Curves were drawn through the plotted data. Data is shown in Tables 1 and 2, and plotted results in Fig. IX.

3. The stillpot was calibrated with tap water at temperatures ranging from 53 to 58°F by comparison of removed weights of liquid with readings on a scale adjacent to the sightglass. Weights were converted to volumes by standard density relationships. Data is shown

in Table 4, and plotted results in Fig. XVI.

k) Insulation of the Assembly: To decrease the amount of heat loss from the system, the pot, column, reflux heater, main condenser, and all pipes carrying hot liquid, vapor, or steam were lagged with 85% magnesia insulation. The stillpot and column were lagged with a $1\frac{1}{2}$ inch layer of flattened sections of 2 inch pipe covering, wired to the metal; the column and pot were then completely covered with a 1 inch layer of 85% magnesia cement. The main condenser was lagged with a 1 inch layer of insulating cement, reinforced with wire. The straight sections of piping were lagged with standard pipe coverings, while curved fittings and valves were covered with an inch layer of cement. Cloth outer coverings were applied using starch paste and metal bands.

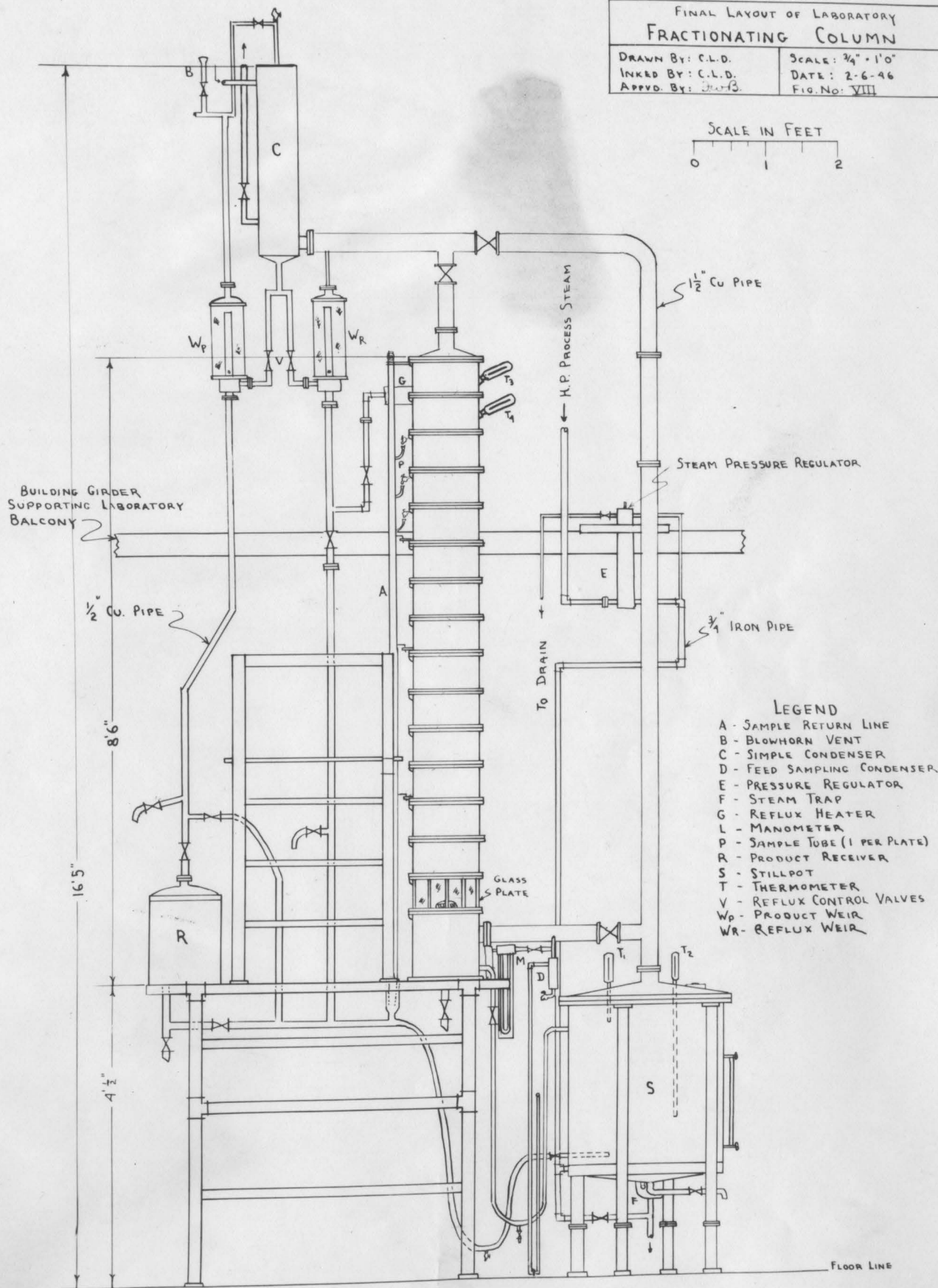
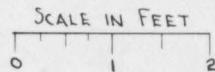
2) Method of Analysis: The problem of making accurate analyses of aqueous isopropyl alcohol solutions taken from the system in operation without disturbing the equilibrium of the system led to studies of a method of analysis more practical than that involving the use of the Westphal balance specific gravity method. The use of the refractive index of the alcohol solution as a measure of the concentration of alcohol was chosen as the most practical of several methods under consideration because of four important reasons: (1) The method allows analysis of such

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FINAL LAYOUT OF LABORATORY
 FRACTIONATING COLUMN

DRAWN BY: C.L.D.
 INKED BY: C.L.D.
 APP'D BY: [Signature]

SCALE: 3/4" = 1'0"
 DATE: 2-6-46
 FIG. No: VIII



- LEGEND
- A - SAMPLE RETURN LINE
 - B - BLOWHORN VENT
 - C - SIMPLE CONDENSER
 - D - FEED SAMPLING CONDENSER
 - E - PRESSURE REGULATOR
 - F - STEAM TRAP
 - G - REFLUX HEATER
 - L - MANOMETER
 - P - SAMPLE TUBE (1 PER PLATE)
 - R - PRODUCT RECEIVER
 - S - STILLPOT
 - T - THERMOMETER
 - V - REFLUX CONTROL VALVES
 - Wp - PRODUCT WEIR
 - WR - REFLUX WEIR

a small volume of liquid that the removal of the necessary samples from the system would not greatly upset the equilibrium conditions within the system; (2) index of refraction determinations can be made under comparatively simple temperature control, the smaller volume of liquid being analyzed reaching the desired temperature more easily and more completely than as large a volume as needed in Westphal determinations; (3) index of refraction determinations can be made readily and on the spot; (4) the equipment necessary for such determinations is readily available, and the analytical technique is readily acquired by an investigator.

a) Preliminary Investigations: Because of the rather high vapor pressure of isopropyl alcohol, it was at first assumed that a solvent would be necessary to lower the evaporation rate of the alcohol during the analytical work. The solvent chosen for this earlier work was glycerol, which had a rather high index of refraction ($n_d^{20} = 1.4729$) as compared with that of pure isopropyl alcohol ($n_d^{20} = 1.3776$). After lengthy investigation, it was discovered that the mixing and stirring procedure used caused uncontrollable amounts of the alcohol to evaporate during analysis; this, coupled with the fact that proportioning of the alcohol and solvent was a very ticklish problem in volume control, led to the discarding

of the glycerol as a solvent and to investigations along other lines.

b) Direct Analysis of Aqueous Isopropanol: After preliminary investigations showed that the index of refraction of a given solution of isopropanol and water could be duplicated without change and without the use of a solvent, the following procedure was adopted:

1. Solutions of commercial 99% isopropyl alcohol in tap water of approximate mol percentages ranging by 5% intervals from 0% to 100% isopropanol were made up and standardized by density measurements using pycnometers. Density-composition data as given in Perry's⁽⁵⁷⁾ was used in the standardizations. All measurements were at 20°C, attained by use of a water bath.

2. The Spencer Abbe refractometer was adjusted for accuracy using a special checkglass furnished with the instrument.

3. The volume and temperature of tap water flowing through the prism chambers of the refractometer were adjusted until the temperature within the prism jacket remained constant at 20°C.

4. Using droppers made of ordinary soda straws, one drop of the solution to be tested was placed directly on the lower prism of the refractometer and the prisms were rapidly closed and locked. To diminish

evaporation, the initial drop of liquid in the dropper was discarded.

5. Observation was made of the index of refraction of the solution being tested. In order to decrease any chances of a slack in the refractometer mechanism causing differences in readings, the crosshairs on the telescope were always approached with the refraction line moving down the scale.

6. Indexes were determined for each of the solutions prepared in the first step of the procedure.

c) Correlation Curves: From the data shown in Table 5 and pictured in Fig. XVII, it may be seen that the index of refraction of an isopropanol-water solution is a direct measure of the concentration of the solution.

3. Improvement in Clarity of Fractions: In test runs performed in the spring of 1945, Bryan, Couper, and Dorsey⁽¹³⁾ noted that in the distillation of isopropyl alcohol-water solutions in the experimental column the liquids on the lower plates was cloudy, as was the liquid in the stillpot; the distribution of the cloudy liquid in the column varying with the reflux ratio and the steam pressure used. Since the literature⁽⁵⁷⁾ gives data indicating that isopropanol and water are miscible in all proportions, the suspected reasons for the observed cloudiness were discussed as being due either

to vapor entrainment or to impurities in the mixture being separated. No experimental work was undertaken to learn the true reasons for the cloudiness.

1) Preliminary Investigations: A batch of 4.41 cubic feet of five molar percent isopropanol was fractionated in the experimental column and samples were taken from all plates and from the stillpot. The lean mixtures in the stillpot and on the lower plates were noted to be definitely cloudy, and remained cloudy after standing for several days; it was therefore obvious that an insoluble component, not entrainment, was responsible for the immiscibility. Correspondence⁽⁸⁹⁾⁽⁹⁰⁾ with two manufacturers of isopropyl alcohol substantiated data in Perry's⁽⁵⁷⁾ showing that the commercial product and water were miscible in all proportions; the information was checked experimentally and proved to be correct (Table 7). All indications were that a foreign substance within the column assembly was the cause of the cloudiness, since both manufacturers mentioned that any hydrocarbon present in the assembly during operation would cause a cloudiness similar to that encountered.

2) Identification of Impurity: All liquid was drained from the system, and the system was left opened to the air for 48 hours to aid in dispersing any alcohol vapors remaining; the stillpot was then filled with tap

water. A film resembling an oil film was noticed on top of the liquid; the odor of the film was like that of kerosene or a similar petroleum fraction. The fact that students working with the column in the fall of 1944 had fractionated a commercial antifreeze solution (isopropanol base) indicated that the immiscible component might be a hydrocarbon residue of these rectifications. The following steps were taken in an effort to identify the immiscible substance:

a. A 100 ml sample of the antifreeze was filtered to remove sludge and distilled in a 250 ml side-neck distilling flask fitted with a 12 inch condenser. Fractions were collected at temperature ranges of 75-84°C, 85-94°C, and 95-96°C, and the odor, color, volume collected, and solubility in aqueous isopropanol were recorded as in Tables 8 and 9. The immiscible component of the antifreeze solution was thereby identified as that fraction distilling from 75-84°C.

b. A copper distilling flask was constructed of 2 inch copper pipe 7 inches long with 1/4 inch copper tubing as a side neck, and was fitted with a 12 inch condenser. Approximately 200 ml of antifreeze solution was distilled over three times. The flask was rinsed gently with water, and 100 ml of 25% aqueous alcohol (by volume) was distilled in the flask. No cloudiness was observed in the fractions, indicating that the copper itself did not adsorb the immiscible component from the

antifreeze solution.

c. The top of the stillpot was removed, and a sample of deposit on the heating coils was taken. Approximately 5 grams of the deposit was placed in a copper flask with 100 ml of 25% (by volume) aqueous isopropanol, and the mixture was distilled. The distillate separated into two layers, the lower layer being very noticeably cloudy. Indications were that the immiscible substance had been adsorbed on the deposit on the coils and in the bottom of the stillpot.

3) Removal of the Impurity: The heating coils in the stillpot were removed and the coils and the bottom of the pot were scraped and brushed thoroughly to remove all particles of deposit. The coils were replaced after the pot had been flushed with weak acid and with water. Lead gaskets were used to seal the coils to the pot.

4. Test Runs on the Experimental Column: Test runs were made on the experimental assembly as it was originally constructed and operated, as it was originally constructed and operated with the substitution of a simple condenser for the partial condensers, after redesign and recalibration, and after work to improve the clarity of the liquid on the intermediate plates. In all tests a chosen reflux ratio and steam pressure

were held constant, and samples were taken when the liquid in the weirs had remained at constant levels for at least fifteen minutes. Samples were taken from the bottom of the column upwards.

F. Experimental Data and Results:

The data and results of the investigation are presented in the following tables and charts:

TABLE 1

REFLUX WEIR CALIBRATION DATA

Weir Reading Inches	Collection Interval Seconds	Grams Collected	Reflux Temp. Of	Reflux Comp. Mol % Alcohol
-1.10	60	79	156	57
0.16	60	131	156	57
1.00	60	160	156	57
2.30	60	185	156	57
3.40	60	211	156	57
3.90	60	229	156	57
5.10	60	254	156	57
6.30	60	269	156	57
6.90	60	260	156	57
7.10	60	260	156	57
7.25	60	274	156	52
8.00	60	263	156	57
8.30	60	277	156	52
9.70	70	303	156	52

Weir calibrated with column assembly in operation.

Samples taken from petcock in reflux line.

Condensing water flow at 5.3 gallons per minute.

TABLE 2

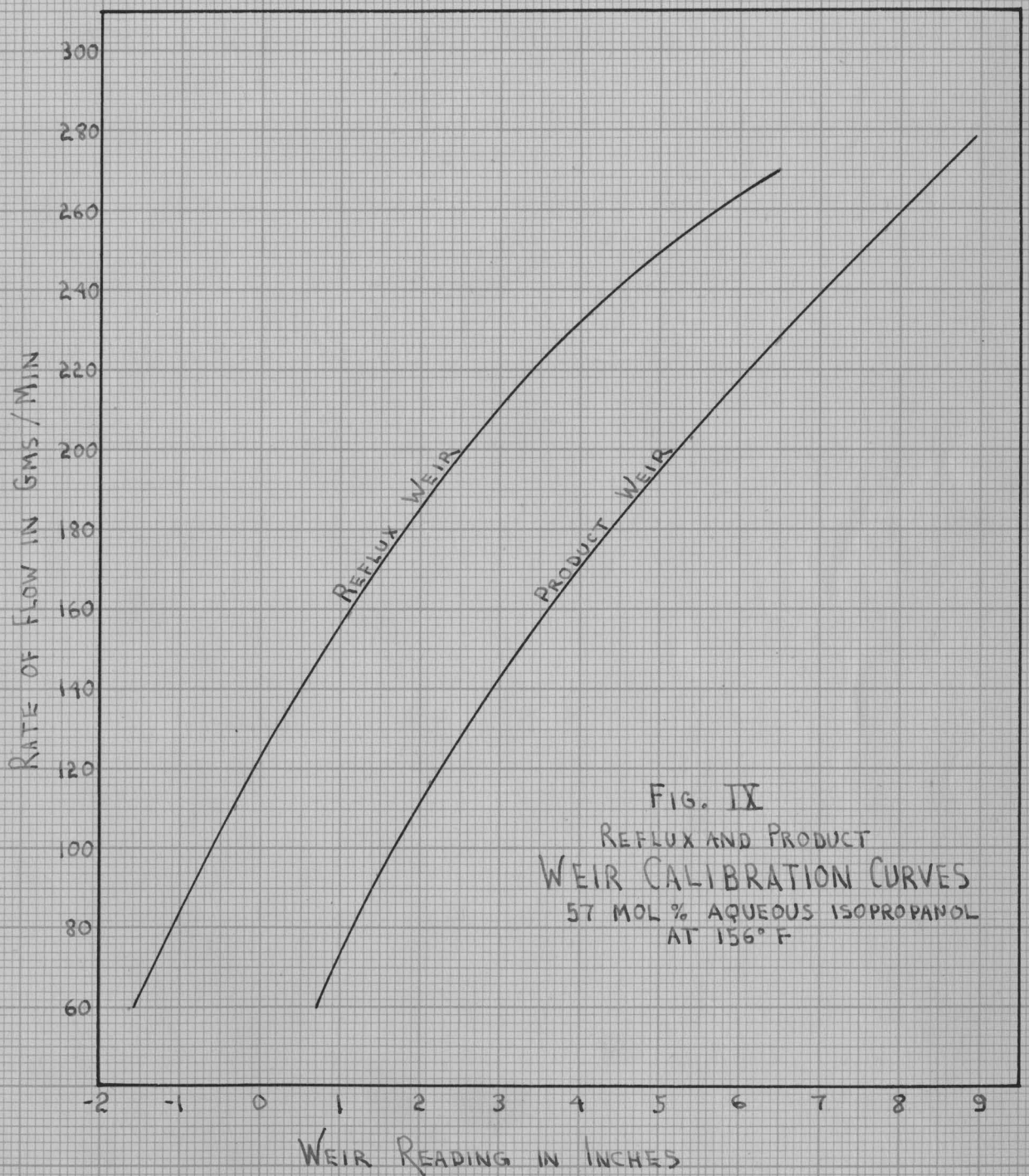
PRODUCT WEIR CALIBRATION DATA

Weir Reading Inches	Collection Interval Seconds	Grams Collected	Flow in Gms/Min	Prod. Temp. of	Prod. Comp. Mol % Alcohol
1.00	300	360	72	156	59
2.00	180	335	112	156	59
3.00	180	426	142	156	59
4.00	180	504	168	156	59
5.00	180	592	194	156	59
6.00	180	650	217	156	59
7.00	180	711	237	156	59
7.90	120	512	256	156	54
9.00	120	555	278	156	54
9.90	120	586	293	156	54

Weir calibrated with column assembly in operation.

Samples taken from outlet above product collector.

Condensing water flow at 5.3 gallons per minute.



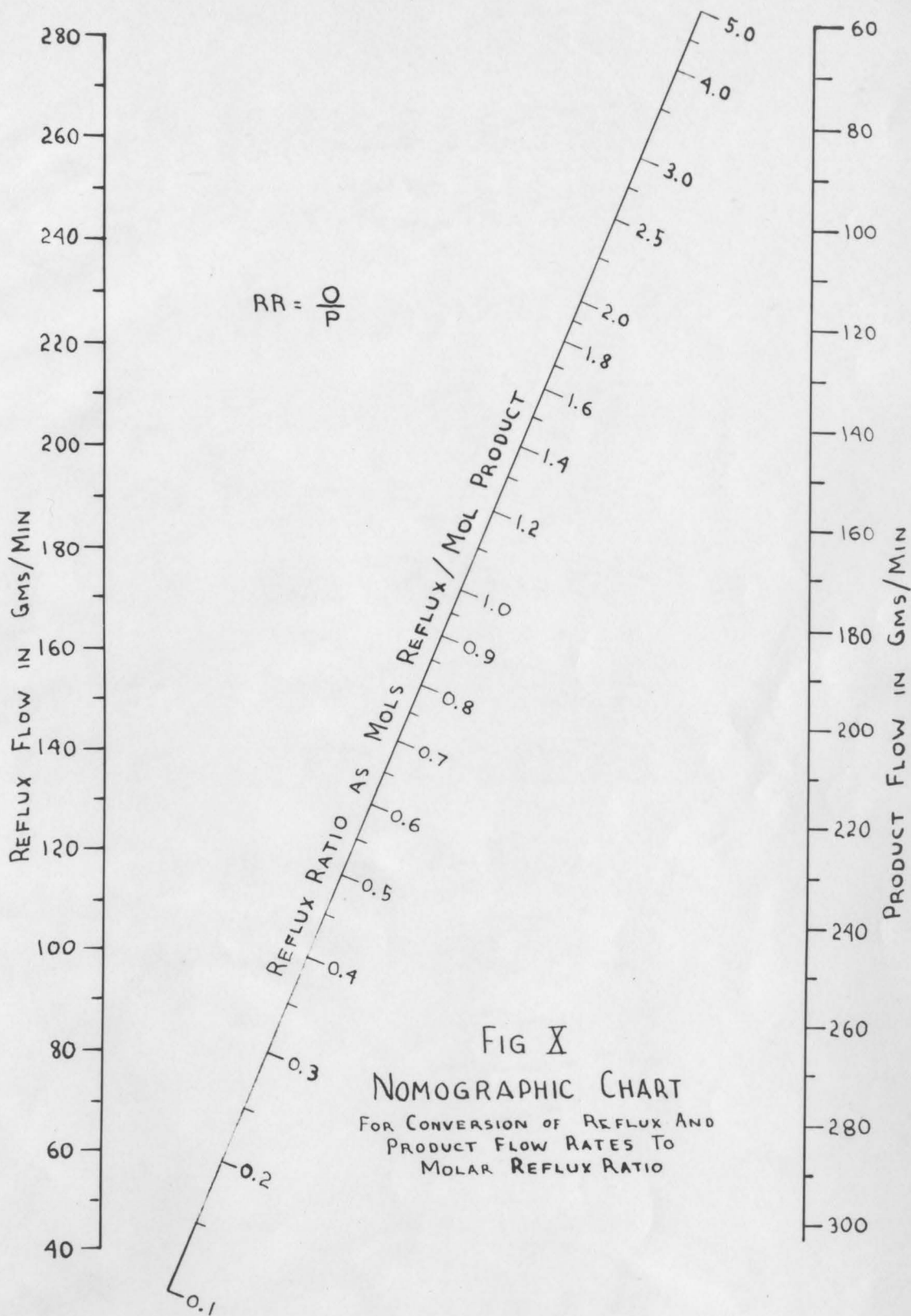


FIG X
 NOMOGRAPHIC CHART
 FOR CONVERSION OF REFLUX AND
 PRODUCT FLOW RATES TO
 MOLAR REFLUX RATIO

APPLICABLE ONLY TO COLUMN UTILIZING TOTAL CONDENSER

TABLE 3

THERMOMETER CALIBRATION DATA

Therm. Number	Location	Std. Temp. of	Obs. Temp. of	Std. Temp. of	Obs. Temp. of	Std. Temp. of	Obs. Temp. of	Std. Temp. of	Obs. Temp. of	Std. Temp. of	Obs. Temp. of
1	Plate 2	170	172	163	157	180	178	192	192	203	202
2	Plate 3	172	171	162	161	179	180	190	189	205	206
3	Plate 4	175	175	160	160	176	177	192	197	200	200
4	Plate 5	180	177	164	161	172	169	186	183	203	198
5	Plate 6	180	178	164	162	172	171	186	184	201	193
6	Plate 7	180	179	164	163	172	171	186	183	204	199
7	Plate 8	180	178	165	162	172	169	186	182	205	194
8	Plate 9	171	168	161	162	172	169	186	182	205	194
9	Plate 10	170	165	161	169	164	163	194	192	203	198
10	Plate 11	170	166	169	164	184	180	193	186	199	192
11	Plate 12	170	168	166	163	164	177	189	182	192	181
12	Plate 13	172	168	160	157	164	180	192	188	205	203
13	Plate 14	170	166	159	156	180	175	190	184	205	202
14	Plate 15	167	163	162	154	160	174	191	184	205	198
15	Feed	-	-	167	157	181	176	188	180	201	194
4m	Reflux at Weir	-	-	157	154	168	165	178	178	197	195
7m	Reflux at Plate	-	-	157	159	168	170	178	183	197	195
				157	155	168	166	178	180	195	194
				157	155	168	166	178	180	195	194

All calibrations by water bath

FIG. XI
THERMOMETER CALIBRATION CURVES
THERMOMETERS No. 1, 2, 3, 4

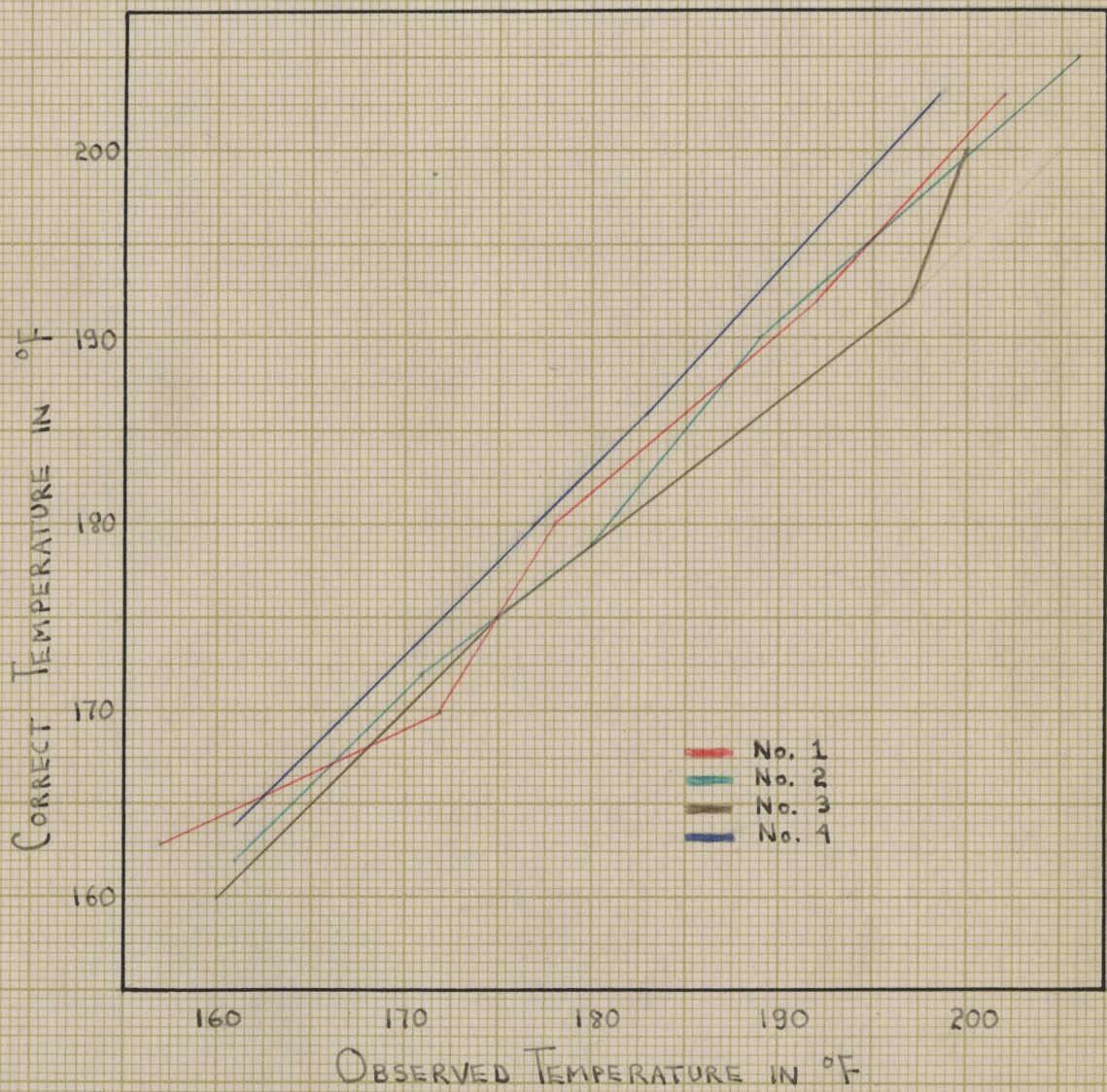


FIG. XII
THERMOMETER CALIBRATION CURVES
THERMOMETERS No. 5, 6, 7, 8

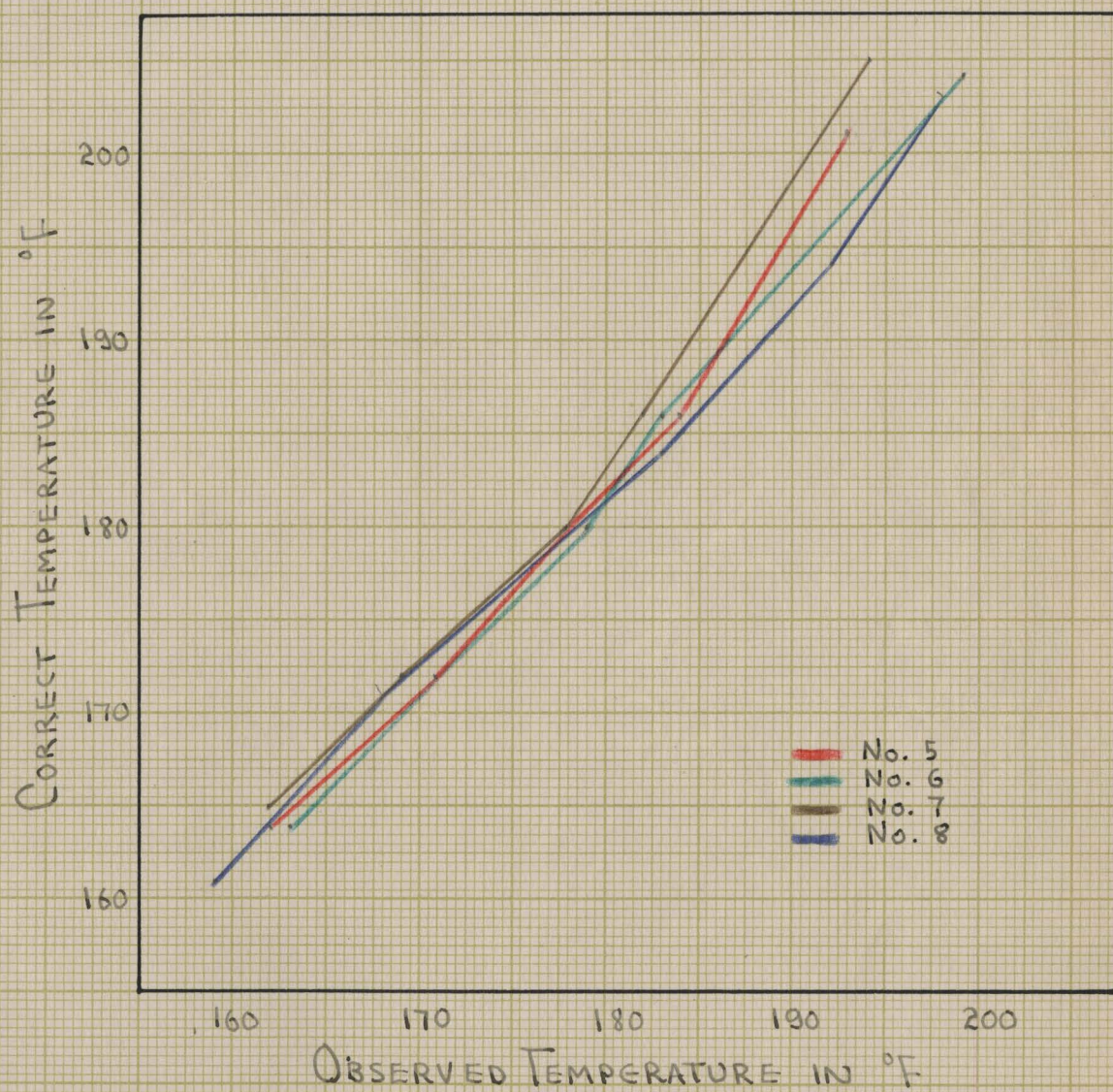


FIG. XIII
THERMOMETER CALIBRATION CURVES
THERMOMETERS No. 9, 10, 11, 12

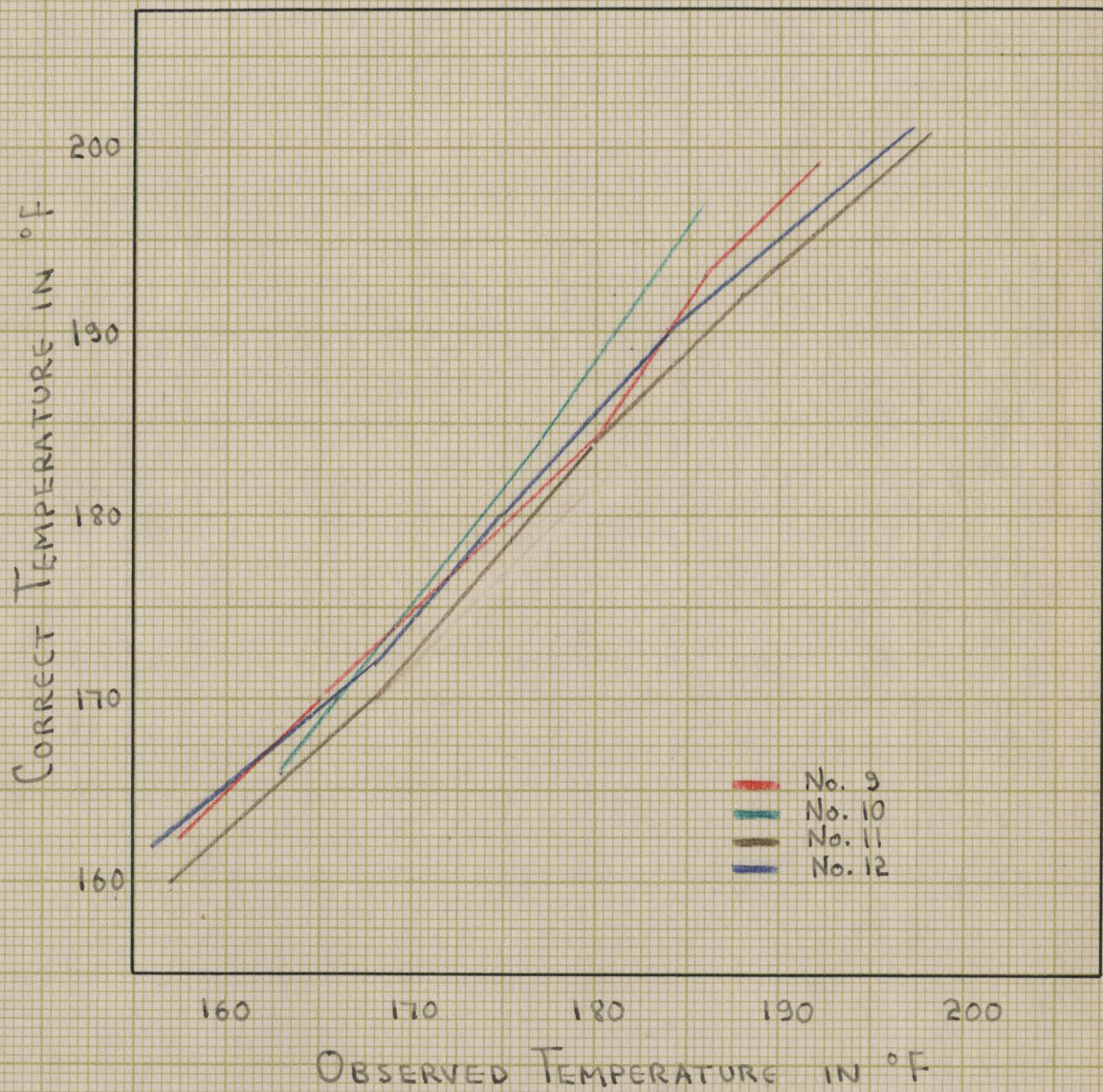


FIG. XIV
THERMOMETER CALIBRATION CURVES
THERMOMETERS No. 13, 14, 15

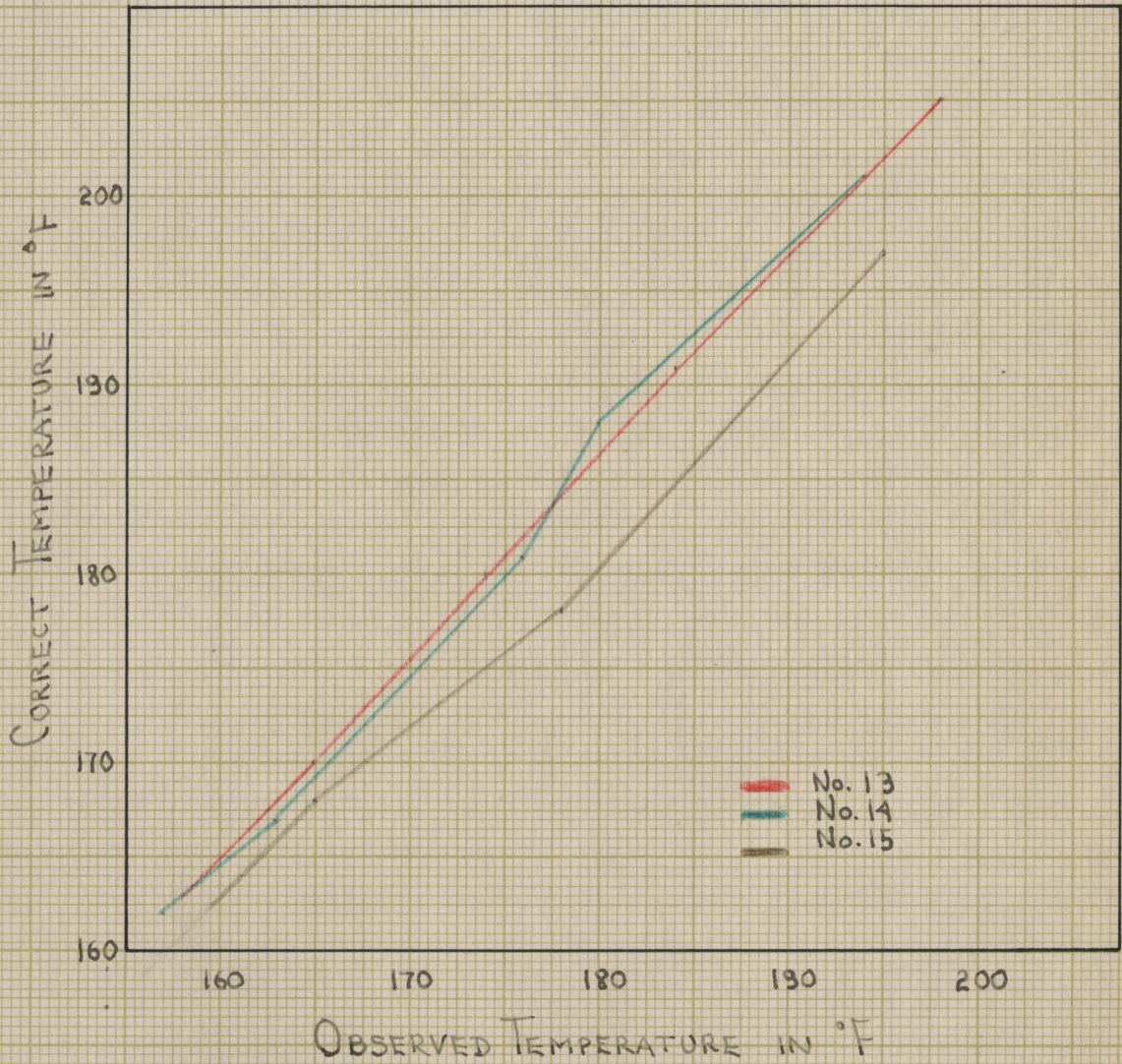


FIG. XV
THERMOMETER CALIBRATION CURVES
THERMOMETERS 4m, 7m

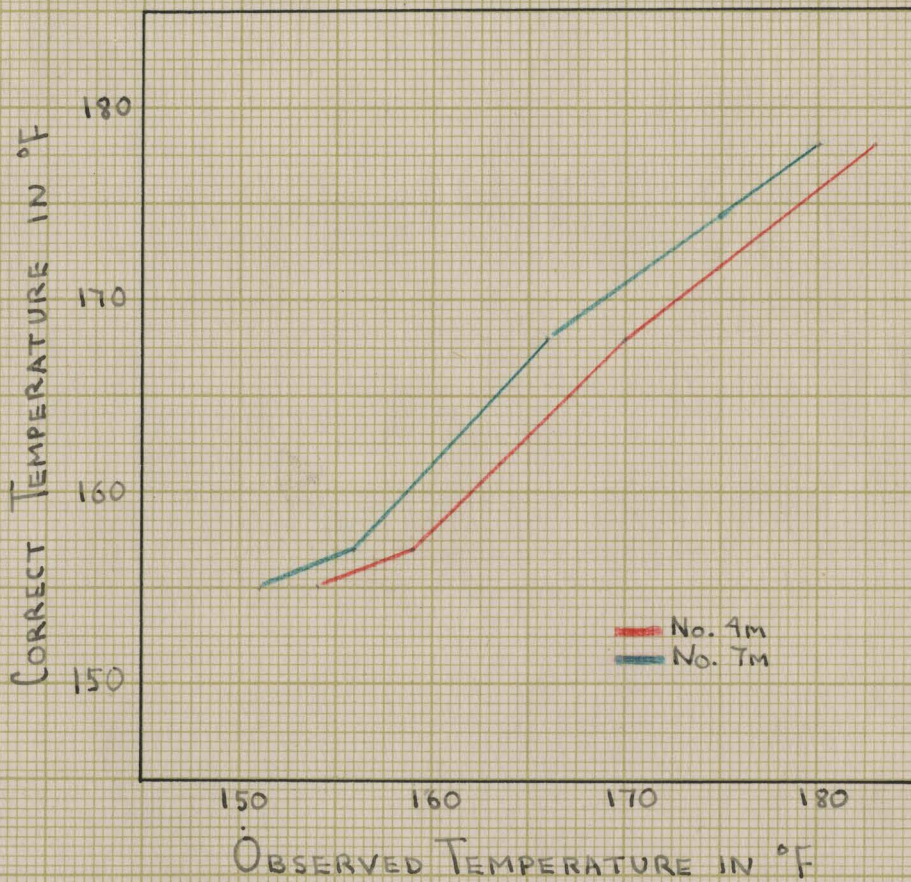


TABLE 4

STILLPOT CALIBRATION DATA AND RESULTS

Initial Reading* In.	Final Reading* In.	Wgt. of Water Collected Lbs.	Temp. of Water	Vol'm. Decrease Cu. Ft.**	Pot Volume at Initial Reading Cu. Ft.
12.0	11.0	19.0	53	0.305	5.054
11.0	9.9	20.8	53	0.334	4.749
9.9	9.0	16.3	53	0.262	4.415
9.0	7.0	37.4	54	0.600	4.153
7.0	6.0	18.3	54	0.293	3.553
6.0	5.0	18.0	54	0.289	3.260
5.0	4.0	19.3	55	0.310	2.971
4.0	3.0	18.4	55	0.294	2.661
3.0	2.0	18.6	55	0.298	2.367
2.0	1.0	18.1	56	0.290	2.069
1.0	0.0	18.4	57	0.294	1.779
0.0	empty	92.7	58	1.485	1.485

* Readings to bottom of water meniscus

** Specific Volume of water at 53-58°F = 0.01603

Calibration with tap water

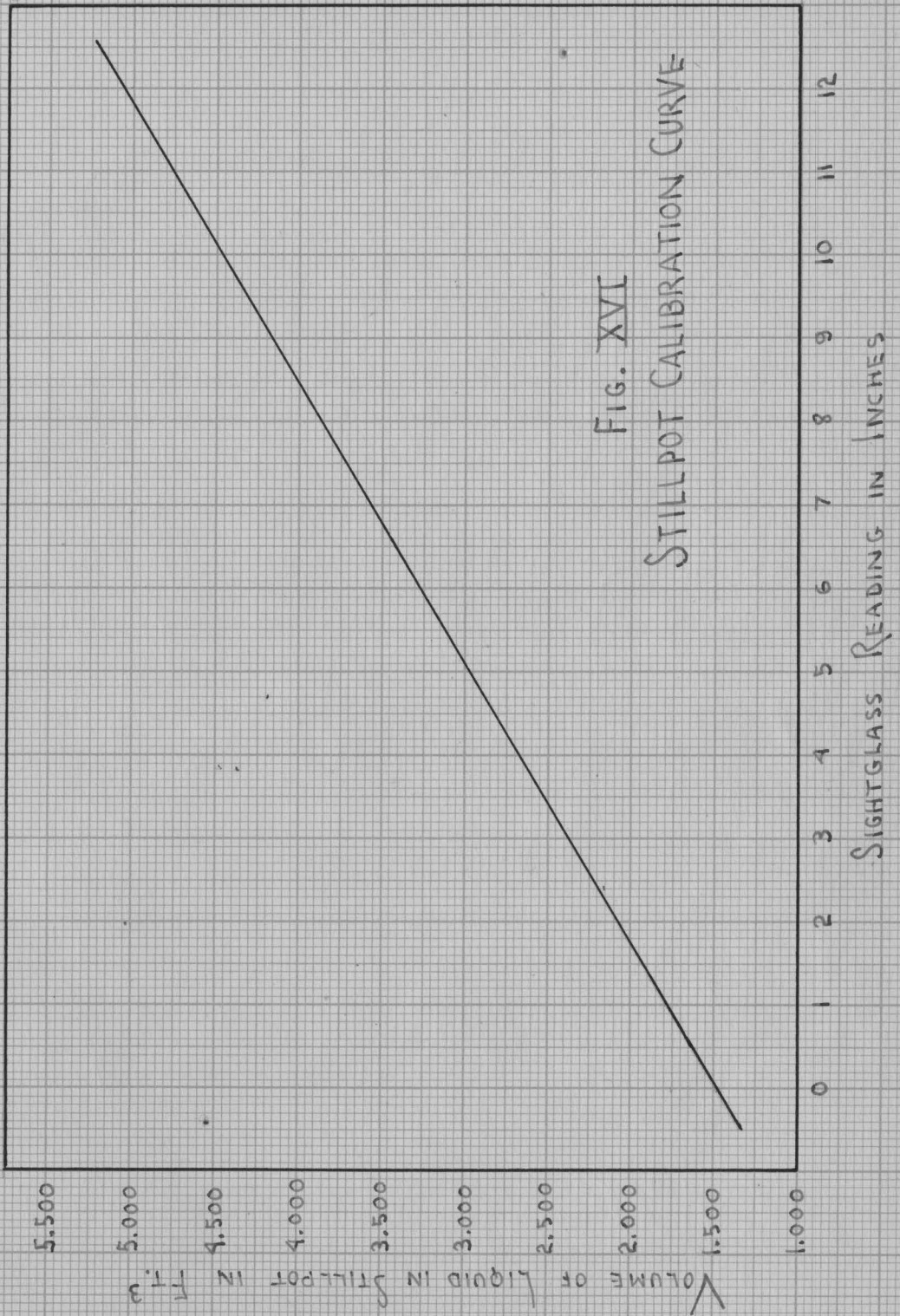


FIG. XVI
STILLPOT CALIBRATION CURVE

TABLE 5

DATA AND RESULTS
CORRELATION OF INDEX OF REFRACTION AND COMPOSITION OF
ISOPROPANOL-WATER SOLUTIONS

Sample Number	Wgt. ° of Pycnom. Gms.	Wgt. ° pyc. and Water Gms.	Wgt. ° of Water Gms.	Vol. of Pycnom. ml.	Wgt. ° pyc. and Sample Gms.	Wgt. ° of Sample Gms.	Density Sample Gms/ml	Concen. Alc. ° wgt. %	n_D^{20}
1	7.945	18.065	10.120	10.138	16.057	10.112	0.9974	0.4	1.3336
2	7.945	18.065	10.120	10.138	18.001	10.056	0.9919	3.4	1.3362
3	10.593	35.247	24.654	24.698	35.070	24.477	0.9910	4.0	1.3367
4	7.945	18.065	10.120	10.138	17.940	9.995	0.9859	7.2	1.3395
5	7.9450	18.065	10.120	10.138	17.815	9.868	0.9734	17.6	1.3482
6	10.593	35.247	24.654	24.698	34.624	24.031	0.9729	18.1	1.3483
7	10.593	35.247	24.654	24.698	32.958	22.365	0.9055	50.6	1.3686
8	7.945	18.065	10.120	10.138	17.076	9.731	0.9599	25.9	1.3557
9	10.593	35.247	24.654	24.698	34.291	23.698	0.9596	26.1	1.3549
10	10.593	35.247	24.654	24.698	33.922	23.329	0.9446	33.7	1.3598
11	7.945	18.065	10.120	10.138	17.406	9.461	0.9332	39.0	1.3625
12	10.593	35.247	24.654	24.698	33.239	22.646	0.9169	45.9	1.3653
13	7.945	18.065	10.120	10.138	17.192	9.247	0.9121	47.8	1.3668
14	10.593	35.247	24.654	24.698	32.985	22.392	0.9066	50.1	1.3677
15	7.945	18.065	10.120	10.138	17.016	9.071	0.8948	54.9	1.3697
16	10.593	35.247	24.654	24.698	32.201	21.608	0.8749	63.1	1.3718
17	7.945	18.065	10.120	10.138	16.833	8.693	0.8570	70.6	1.3735
18	7.945	18.065	10.120	10.138	16.242	8.297	0.8184	73.3	1.3777
19	7.945	18.065	10.120	10.138	16.505	8.560	0.8443	75.9	1.3749
20	10.593	35.247	24.654	24.698	31.152	20.569	0.8328	80.6	1.3762
21	7.945	18.065	10.120	10.138	16.359	8.414	0.8299	81.7	1.3766
22	10.593	35.247	24.654	24.698	30.737	20.144	0.8156	87.5	1.3771
23	7.945	18.065	10.120	10.138	16.160	8.215	0.8103	89.7	1.3771
24	10.593	35.247	24.654	24.698	30.352	19.769	0.8004	93.7	1.3776
25	10.593	35.247	24.654	24.698	30.071	19.478	0.7886	98.7	1.3774

*Measurements at 20°C

**perry(57), p.449

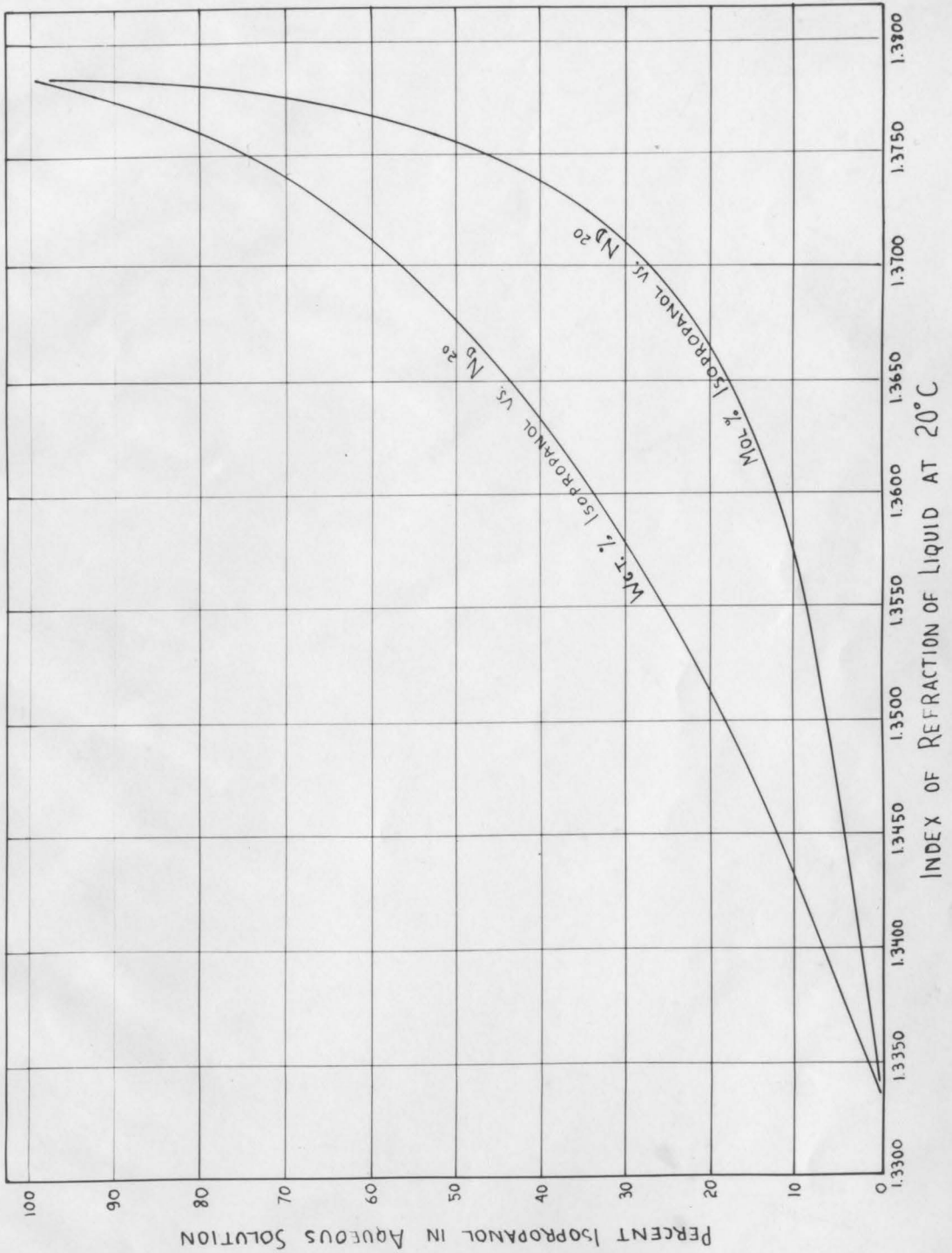
TABLE 6

RESULTS OF
CORRELATION OF INDEX OF REFRACTION AND COMPOSITION OF
ISOPROPANOL-WATER SOLUTIONS

Weight % Alcohol	n_d^{20}	Weight % Alcohol	n_d^{20}	Weight % Alcohol	n_d^{20}
0	1.3330	35	1.3604	70	1.3737
1	1.3338	36	1.3609	71	1.3740
2	1.3348	37	1.3615	72	1.3742
3	1.3358	38	1.3620	73	1.3745
4	1.3367	39	1.3625	74	1.3747
5	1.3376	40	1.3631	75	1.3749
6	1.3384	41	1.3636	76	1.3751
7	1.3393	42	1.3641	77	1.3753
8	1.3402	43	1.3645	78	1.3755
9	1.3410	44	1.3650	79	1.3757
10	1.3419	45	1.3654	80	1.3759
11	1.3427	46	1.3658	81	1.3761
12	1.3436	47	1.3663	82	1.3763
13	1.3444	48	1.3668	83	1.3764
14	1.3452	49	1.3671	84	1.3765
15	1.3460	50	1.3675	85	1.3767
16	1.3469	51	1.3678	86	1.3768
17	1.3477	52	1.3682	87	1.3769
18	1.3485	53	1.3686	88	1.3770
19	1.3493	54	1.3689	89	1.3771
20	1.3501	55	1.3693	90	1.3772
21	1.3508	56	1.3696	91	1.3773
22	1.3516	57	1.3699	92	1.3774
23	1.3524	58	1.3702	93	1.3774
24	1.3531	59	1.3705	94	1.3775
25	1.3539	60	1.3709	95	1.3775
26	1.3546	61	1.3712	96	1.3776
27	1.3554	62	1.3715	97	1.3776
28	1.3561	63	1.3718	98	1.3777
29	1.3567	64	1.3721	99	1.3777
30	1.3574	65	1.3724	100	1.3777
31	1.3580	66	1.3727		
32	1.3586	67	1.3729		
33	1.3592	68	1.3732		
34	1.3598	69	1.3735		

Taken from Curve Plotted from
Data in Table 5

FIG. XVII
INDEX OF REFRACTION VS. COMPOSITION OF AQUEOUS ISOPROPANOL SOLUTIONS



$$M = \frac{W}{333 - 2.33W}$$

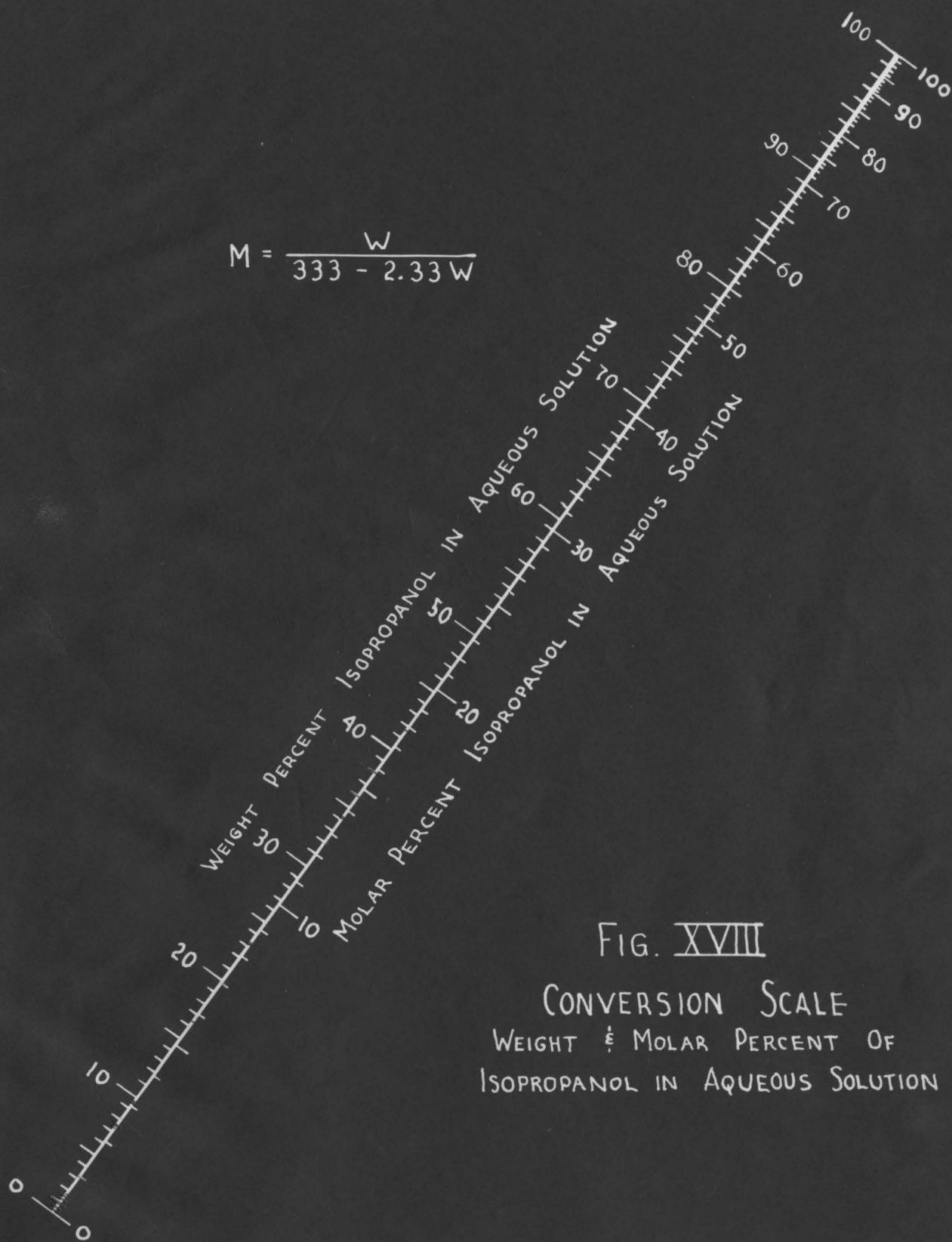


FIG. XVIII

CONVERSION SCALE
WEIGHT & MOLAR PERCENT OF
ISOPROPANOL IN AQUEOUS SOLUTION

TABLE 7MISCIBILITY DATA
ISOPROPANOL-WATER SYSTEM

Molar Percent Isopropanol	Observed miscibility		
	65°F	125°F	165°F
5.5	Complete	Complete	Complete
8.7	Complete	Complete	Complete
15.4	Complete	Complete	Complete
25.6	Complete	Complete	Complete
39.8	Complete	Complete	Complete
48.2	Complete	Complete	Complete
62.5	Complete	Complete	Complete
70.5	Complete	Complete	Complete

Determinations with tap water

TABLE 8EXPERIMENTAL DATA FROM
ANALYSIS OF ANTIFREEZE SOLUTION

Fraction Number	Distillation Range, °C	Volume Collected ml.	Color	Identifying Odor
1	75 - 84	6½	Clear	Strong Petroleum
2	85 - 94	32	Clear	Weaker Petroleum
3	95 - 96	50	Clear	Mineral Oil
4	residue	11½	Red	Undefined

100 ml antifreeze distilled after filtering

TABLE 9EXPERIMENTAL DATA ON SOLUBILITY
OF ANTIFREEZE FRACTIONS IN 15%
BY VOLUME AQUEOUS ISOPROPANOL

Temperature °C	Fraction No. 1	Fraction No. 2	Fraction No. 3
25	cloudy	clear	clear
60	cloudy	clear	clear

4 ml fraction added to 25 ml alcohol

TABLE 10
EXPERIMENTAL DATA
TEST RUN ON ORIGINAL ASSEMBLY

Position of Sample	Appearance of Sample	Vapor Temperature of	n_D^{20}	Wgt. Percent Isopropanol
Plate 1	cloudy	---	1.3360	3.0
Plate 2	cloudy	193	1.3364	3.3
Plate 3	cloudy	188	1.3374	4.5
Plate 4	cloudy	182	1.3561	27.7
Plate 5	cloudy	176	1.3726	64.7
Plate 6	clear	172	1.3755	77.0
Plate 7	clear	172	1.3760	79.0
Plate 8	clear	184	1.3764	81.2
Plate 9	clear	170	1.3768	83.7
Plate 10	clear	174	1.3768	83.7
Plate 11	clear	176	1.3769	84.5
Plate 12	clear	171	1.3768	83.4
Plate 13	clear	171	1.3768	83.4
Plate 14	clear	170	1.3771	86.0
Plate 15	clear	170	----	--
Reflux	clear	134	1.3770	85.2
Product	clear	87	1.3771	86.0
still Liq	cloudy	204	1.3353	2.5
still Vap	----	196	----	--

Reflux Rate..... 150 gms/min
 Product Rate..... 50 gms/min
 Reflux Ratio..... 3.00
 Steam Pressure..... 12.10 in.Hg. gage

Reflux not heated
 Column unlagged
 Dephlegmating condensers

Continuous Rectification in Closed System

TABLE 11

EXPERIMENTAL DATA

TEST RUN ON MODIFIED ASSEMBLY

Position of Sample	Appearance of Sample	Vapor Temperature of	N _d ²⁰	Wgt. Percent Isopropanol
Plate 1	cloudy	---	1.3353	2.2
Plate 2	cloudy	204	1.3355	2.4
Plate 3	cloudy	204	1.3356	2.5
Plate 4	cloudy	206	1.3357	2.6
Plate 5	cloudy	199	1.3358	2.7
Plate 6	cloudy	206	1.3358	2.7
Plate 7	cloudy	203	1.3360	2.9
Plate 8	cloudy	203	1.3371	5.1
Plate 9	cloudy	187	1.3433	11.3
Plate 10	cloudy	181	1.3702	57.0
Plate 11	clear	178	1.3753	75.5
Plate 12	clear	176	1.3766	82.2
Plate 13	clear	175	1.3770	85.0
Plate 14	clear	176	1.3772	86.8
Plate 15	clear	177	1.3773	87.7
Reflux	clear	156	1.3776	91.2
Still Liq	cloudy	205	1.3353	2.2
Still Vap	----	197	----	--

Reflux Rate..... 272 gms/min
 Product Rate..... 118 gms/min
 Reflux Ratio..... 2.31
 Steam Pressure..... 12 in. Hg. gage

Reflux not heated
 Column unlagged
 single condenser

Continuous Rectification in Closed System

TABLE 12

EXPERIMENTAL DATA
 TEST RUN ON REDESIGNED ASSEMBLY
 RUN NO. 1, SERIES A

Position of Sample	Appearance of Sample	Vapor Temperature of	n_d^{20}	Wgt. Percent Isopropanol
Plate 1	cloudy	---	1.3533	24.0
Plate 2	clear	178	1.3747	72.7
Plate 3	clear	177	1.3757	77.5
Plate 4	clear	180	1.3762	80.0
Plate 5	clear	184	1.3770	85.2
Plate 6	clear	173	1.3770	85.2
Plate 7	clear	174	1.3770	85.2
Plate 8	clear	174	1.3770	85.2
Plate 9	clear	176	1.3773	87.7
Plate 10	clear	176	1.3773	87.7
Plate 11	clear	175	1.3773	87.7
Plate 12	clear	175	1.3773	87.7
Plate 13	clear	174	1.3773	87.7
Plate 14	clear	175	1.3773	87.7
Plate 15	clear	175	1.3773	87.7
Reflux	clear	169	1.3773	87.7
still Lig	cloudy	204	1.3355	2.7
still Vap	clear	197	1.3645	42.2

Reflux Rate..... 112 gms/min
 Product Rate..... 99 gms/min
 Reflux Ratio..... 1.13
 Steam Pressure..... 8 in. Hg. gage
 Atm. Pressure..... 28.18 in. Hg.
 Reflux Temp. at Weir... 146°F
 Condensing Water Flow.. 4.36 gal/min

Column Lagged
 Reflux Heated

Continuous Rectification in Closed System

TABLE 13

EXPERIMENTAL DATA
 TEST RUN ON REDESIGNED ASSEMBLY
 RUN NO. 2, SERIES A

Position of Sample	Appearance of Sample	Vapor Temperature of	n_d^{20}	Wgt. Percent Isopropanol
Plate 1	clear	---	1.3395	7.0
Plate 2	clear	194	1.3397	7.2
Plate 3	s cloudy	195	1.3398	7.3
Plate 4	s cloudy	196	1.3400	7.5
Plate 5	s cloudy	190	1.3400	7.5
Plate 6	s cloudy	194	1.3400	7.5
Plate 7	cloudy	193	1.3401	7.6
Plate 8	cloudy	189	1.3428	10.7
Plate 9	cloudy	181	1.3530	23.5
Plate 10	clear	178	1.3710	59.5
Plate 11	clear	178	1.3744	71.5
Plate 12	clear	178	1.3758	77.7
Plate 13	clear	175	1.3764	81.1
Plate 14	clear	176	1.3770	85.2
Plate 15	clear	175	1.3772	86.8
Reflux	clear	169	1.3776	91.0
Still Liq	cloudy	197	1.3388	6.0
Still Vap	clear	186	1.3716	61.5

Reflux Rate..... 174 gms/min
 Product Rate..... 166 gms/min
 Reflux Ratio..... 0.934
 Steam Pressure..... 8 in. Hg. gage
 Atm. Pressure..... 28.18 in. Hg.
 Reflux Temp. at Weir.. 156°F
 Condensing Water Flow. 4.36 gal/min

Column Lagged
 Reflux Heated

Continuous Rectification in Closed System

TABLE 14

EXPERIMENTAL DATA
 TEST RUN ON REDESIGNED ASSEMBLY
 RUN NO. 3, SERIES A

Position of Sample	Appearance of Sample	Vapor Temperature OF	n_d^{20}	Wgt. Percent Isopropanol
Plate 1	clear	---	1.3409	8.5
Plate 2	clear	191	1.3410	8.7
Plate 3	clear	194	1.3410	8.7
Plate 4	clear	192	1.3411	8.8
Plate 5	s cloudy	188	1.3412	8.9
Plate 6	s cloudy	191	1.3410	8.7
Plate 7	s cloudy	191	1.3413	8.9
Plate 8	s cloudy	191	1.3417	9.4
Plate 9	cloudy	188	1.3418	9.6
Plate 10	cloudy	190	1.3418	9.6
Plate 11	cloudy	192	1.3419	9.7
Plate 12	cloudy	189	1.3423	10.1
Plate 13	cloudy	187	1.3442	12.3
Plate 14	cloudy	181	1.3601	34.0
Plate 15	clear	178	1.3726	64.7
Reflux	clear	169	1.3763	80.5
Still Liq	cloudy	196	1.3400	7.5
Still Vap	clear	186	1.3716	61.0

Reflux Rate..... 106 gms/min
 Product Rate..... 269 gms/min
 Reflux Ratio..... 0.394
 Steam Pressure..... 8 in. Hg. gage
 Atm Pressure..... 28.16 in. Hg.
 Reflux Temp. at Weir..... 156°F
 Condensing Water Flow..... 4.36 gal/min

Column Lagged
 Reflux Heated

Continuous Rectification in Closed System

TABLE 15

EXPERIMENTAL DATA
 TEST RUN ON REDESIGNED ASSEMBLY
 RUN NO. 4, SERIES A

Position of Sample	Appearance of Sample	Vapor Temperature of	n_d^{20}	Wgt. Percent Isopropanol
Plate 1	cloudy	---	1.3650	43.4
Plate 2	clear	178	1.3760	79.0
Plate 3	clear	177	1.3760	74.0
Plate 4	clear	180	1.3761	79.5
Plate 5	clear	174	1.3770	85.2
Plate 6	clear	175	1.3763	80.5
Plate 7	clear	174	1.3770	85.2
Plate 8	clear	176	1.3771	86.0
Plate 9	clear	176	1.3771	86.0
Plate 10	clear	175	1.3770	85.2
Plate 11	clear	176	1.3764	81.2
Plate 12	clear	174	1.3770	85.2
Plate 13	clear	175	1.3768	84.0
Plate 14	clear	175	1.3770	85.2
Plate 15	clear	176	1.3772	86.7
Reflux	clear	169	1.3772	86.7
still Liq	s cloudy	208	1.3342	1.1
still Vap	cloudy	199	1.3557	27.2

Reflux Rate..... 63 gas/min
 Product Rate..... 0
 Reflux Ratio..... infinite
 Steam Pressure..... 8 in. Hg. gage
 Atm. Pressure..... 28.18 in. Hg.
 Reflux Temp. at Weir... ----
 Condensing Water Flow.. 4.36 gal/min

Column Legged
 Reflux Heated

Continuous Rectification in Closed System

FIG. XIX
CONCENTRATION GRADIENTS
RUN SERIES "A"

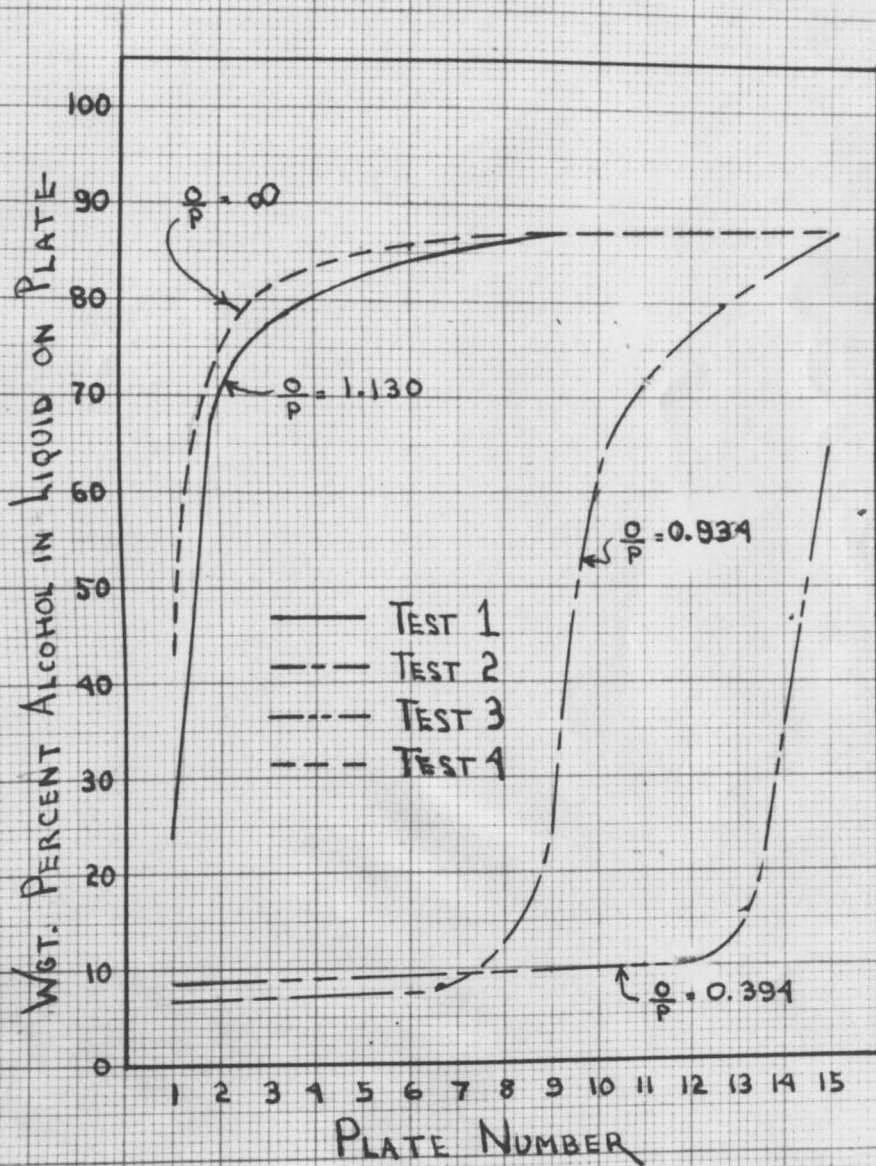


TABLE 16

EXPERIMENTAL DATA
 TEST RUN ON REDESIGNED ASSEMBLY
 RUN NO. 1, SERIES B

Position of Sample	Appearance of Sample	n_d^{20}	Wgt. Percent Isopropanol
Plate 1	clear	1.3400	7.5
Plate 2	clear	1.3401	7.6
Plate 3	clear	1.3404	7.9
Plate 4	clear	1.3405	8.0
Plate 5	clear	1.3405	8.0
Plate 6	clear	1.3402	7.7
Plate 7	clear	1.3403	7.8
Plate 8	clear	1.3409	8.5
Plate 9	clear	1.3413	9.0
Plate 10	cloudy	1.3473	16.1
Plate 11	clear	1.3608	35.2
Plate 12	clear	1.3719	62.3
Plate 13	clear	1.3742	70.7
Plate 14	clear	1.3760	79.1
Plate 15	clear	1.3764	81.0
Reflux	clear	1.3769	84.5
still Liq	clear	1.3390	6.4
still Vap	clear	1.3720	62.8

Reflux Rate..... 270 gas/min
 Product Rate..... 260 gas/min
 Reflux Ratio..... 1.035
 Steam Pressure..... 1.8 in. Hg. gage
 Atm Pressure..... 27.76 in. Hg.
 Cond. Water Flow..... 8.1 gal/min

Column Lagged
 Reflux Heated

Continuous Rectification in Closed System

TABLE 17

EXPERIMENTAL DATA
 TAKEN IN TEST RUN ON REDESIGNED COLUMN ASSEMBLY
 RUN NO. 2, SERIES B

Position of Sample	Appearance of Sample	n_d^{20}	Wgt. Percent Isopropanol
Plate 1	clear	1.3405	8.0
Plate 2	clear	1.3408	8.1
Plate 3	clear	----	---
Plate 4	clear	1.3409	8.5
Plate 5	clear	1.3410	8.6
Plate 6	clear	1.3409	8.5
Plate 7	clear	1.3413	9.0
Plate 8	clear	1.3415	9.2
Plate 9	clear	1.3419	9.8
Plate 10	cloudy	1.3485	17.7
Plate 11	clear	1.3632	39.8
Plate 12	clear	1.3725	64.3
Plate 13	clear	1.3750	74.0
Plate 14	clear	1.3760	79.0
Plate 15	clear	1.3768	84.0
Reflux	clear	1.3770	85.0
Still Liq	clear	1.3400	7.5
Still Vap	clear	1.3728	65.2

Reflux Rate..... 178 gms/min
 Product Rate..... 216 gms/min
 Reflux Ratio..... 0.822
 Steam Pressure..... 1.8 in. Hg. gage
 Atm. Pressure..... 27.76 in. Hg.
 Cond. Water Flow..... 3.1 gal/min

Column Lagged
 Reflux Heated

Continuous Rectification in Closed System

IV. DISCUSSION OF RESULTS

General: The results of this investigation show conclusively that the redesign of the fractionating assembly has resulted in greater operating ease and in more accurate control and determination of column variables, that the use of index of refraction as a method of analysis for aqueous isopropyl alcohol solutions is both accurate and practical, and that the heat economy of the assembly has been increased considerably. With the assembly in its present condition, and using the recommended analytical method, experimental runs involving continuous rectification of aqueous isopropyl alcohol solutions in the closed system can be made with greater ease and with a higher degree of accuracy than has heretofore been possible.

Calibration of Control Weirs: The calibration data presented in Tables 1 and 2 and graphed in Fig. IX is much more accurate than previous calibration data obtained using cold alcohol solutions as the calibrating liquid. Data in Table 2 (product weir) plotted to give a very smooth curve; however, data from Table 1 (reflux weir) did not plot well above weir readings of five inches, probably due to the fact that vapor velocity variations limited sampling times to only one minute. The

reflux weir calibration curve plotted in Fig. IX is a mean curve, especially above weir readings of five inches, and its accuracy is therefore limited. A more accurate calibration might be obtained by interchanging the two weirs and calibrating the reflux weir in the product weir position, since column vapor velocity is less dependant on product rate than it is on reflux rate. The nomograph of Fig. X is a simple correlation of flow rates, based on the fact that in using a simple condenser the reflux and product compositions are the same.

Calibration of Thermometers: As shown by inspection of the data tabulated in Table 3 and graphed in Figs. XI, XII, XIII, XIV, and XV, only three of the seventeen thermometers calibrated may be used with any degree of accuracy, their readings being the only ones that vary linearly with a standard temperature scale. Since it was impossible to obtain new thermometers (due to priority ratings) it will be necessary to use those available until a future date. Point-to-point curves were plotted instead of smooth curves in order that future investigators would note that most of the thermometers contained a large inherent error. Since it is probable that the standard thermometer would react more

quickly to small temperature changes than would those being calibrated, somewhat smoother curves might be obtained by holding the fluid bath at a constant temperature for a period long enough to insure the experimental thermometers measuring the full heat content of the bath; calibrations in this investigation were done over time intervals of only several seconds for each calibration.

Calibration of Stillpot: To aid in preparing batches of liquid to be fractionated, the stillpot was calibrated as shown in Table 4 and Fig. XVI. A given concentration of starting liquor can be obtained by proportional measurements of the amounts of water and isopropanol charged; however, it must be remembered that in the case of aqueous isopropanol solutions, molar and volume fractions are not the same since the liquids are associating. Bennett and Garratt⁽⁷⁾ have correlated volume percent and refractive index, and their data may be correlated with weight fraction if necessary. The amount of liquor in the stillpot while the column is in operation influences the operating characteristics and the heat economy of the assembly, and it is therefore necessary to keep this amount, and its concentration, as constant as possible during a series of experimental runs. An approach to this condition is made by using the same

volume of alcohol solution of a given concentration as the initial charge for each run. Since boiling within the stillpot influences the level of liquid in the sightglass, the calibration can not be used accurately to determine the amount of column holdup for a given set of operating conditions.

Analytical Method: Table 5 contains the experimental data and results of the investigation to determine the variation of index of refraction of aqueous isopropyl alcohol solutions with the concentration of the solutions. Density of the individual samples was calculated using pycnometric data, the corresponding weight percent isopropanol in solution being taken from tables in Perry's handbook⁽⁵⁷⁾. Since special Gay-Lussac bottles with outside ground-on caps were unobtainable, density measurements were difficult at high concentrations of alcohol where the volatility of the samples was high. Table 6 shows the variation of index of refraction with weight percent isopropanol by increments of one percent; the values were obtained from a smoothed curve plotted from the data in Table 5. Fig. XVII has been included to show that although the index of refraction is a direct measure of the molar concentration of the liquid sample, graphical interpolation is difficult above thirty^t mol percent alcohol because of the rapid break in the curve

at that point. The use of the weight percent curve is recommended for general use, since interpolation is more accurate at the higher concentrations of alcohol. Weight percent can be quickly converted to molar percent for efficiency calculations by use of the relationship:

$$M = \frac{W}{333 - 2.33 W}$$

where:

M = mol percent isopropanol in aqueous solution;

W = weight percent isopropanol in aqueous solution.

Fig. XVIII is a conversion scale based on the above relationship.

Removal of Impurities in Stillpot: The data in Tables 7, 8, and 9 was taken in the course of an investigation to discover the cause of the cloudy color imparted to alcohol solutions in the stillpot and on the lower plates of the column. The miscibility data of Table 7 was taken as a check on information in the literature; the fact that the commercial isopropanol was completely miscible with tap water indicated that some insoluble constituent within the assembly was responsible for the observed cloudiness. Tables 8 and 9 show the results of an investigation of a commercial antifreeze liquid which had been rectified in the column in attempts to recover its isopropanol base. As shown by Table 8, the

antifreeze could be separated into several distinct fractions on the basis of odor. The strong petroleum odor of the initial fraction was comparable to the odor noted in the stillpot when it was filled with water, and the solubility tests as listed in Table 9 showed that it was this initial fraction which caused a cloudiness upon addition to aqueous isopropanol solutions. Thorough cleansing of the stillpot, insuring removal of deposits which had adsorbed the initial fraction of the antifreeze, resulted in the almost complete disappearance of the cloudy color. Since the column itself was not disassembled and cleaned, it is not surprising that the liquid on one plate (No. 10) has continued to be somewhat cloudy.

Test Runs on the Assembly: Experimental test runs were made on the original column assembly (Table 10), on the original assembly after a simple condenser had been installed to replace the partial condensers (Table 11), on the final redesigned assembly before work to remove the immiscible impurity (Tables 12, 13, 14, and 15), and on the final, cleaned assembly (Tables 16 and 17). The experimental runs were made more to improve sampling methods, operational techniques, etc. than to obtain definite series of characteristic operating curves.

Tables 10 and 11: Inspection of Tables 10 and 11 shows the effect of the immiscible antifreeze fraction on the color of the liquid on the plates. The fact that the distribution of the cloudy liquid within the column is largely dependant on reflux ratio (see Tables 12-15 also) was indicative that the substance causing immiscibility was largely in the stillpot, being vaporized with the alcohol and passing through the column until condensed at approximately 180°F and passing back to the lower plates and stillpot. Since the runs of both Table 10 and Table 11 were made on the unlagged assembly with no facilities other than the stillpot coils for adding heat to the system, it would be expected that the heat economy of the assembly would be poor in these cases. Such was the case, for at a steam pressure of 12 inches of mercury gage it took as long as three hours to heat up the column, and steam had to be supplied at at least this pressure in order to result in a measurable vapor rate at equilibrium (i.e. internal reflux was high). Substitution of a simple condenser for the dephlegmating condensers resulted in much greater operating ease, and the equilibrium conditions were attained much more rapidly than formerly.

Run Series "A" : Run Series "A", data of which is shown in Tables 12, 13, 14, and 15, was made prior to

the removal of the immiscible constituent from the stillpot with the assembly in its final redesigned form but without the steam pressure regulator. The original charge to the pot consisted of four cubic feet (at 137°F) of 11 percent by weight aqueous isopropanol, and a 100 milliliter batch of 50 volume percent alcohol was added as makeup after each separate test. The individual runs were made by merely changing the reflux ratio over a range of from 0.394 to total reflux. The rate of cooling water flow was constant at 4.36 gal/min for all four runs. Equilibrium was assumed attained when the liquid levels in the control weirs remained substantially constant for thirty minutes. Sample petcocks on the plates were opened 10-15 minutes before sampling (average flow rate of one drop per three seconds) from the bottom of the column upwards, and were closed immediately upon taking the individual 3 milliliter samples. All samples were cooled in the laboratory transformer room (average temperature of 38°F) for approximately an hour before analysis. Care was taken, of course, that the 10 milliliter capacity glass sample bottles were clean and dry, and that the liquid samples did not come in contact with the aluminum bottle caps.

1. Test No. 1 (Table 12) was made under a reflux ratio of 1.130 with a manometer reading of 8 inches

of mercury. The reflux control valve was opened completely, and the product control valve was set to give the desired ratio. Fluctuations in vapor rate as conditions approached equilibrium resulted in a change in the head in the reflux weir, which in turn changed the reflux ratio to result in another change in vapor rate, etc. The concentration gradient curve for this test is shown in Fig. XIX.

2. Test No. 2 (Table 13) was made under a reflux ratio of 0.934 with a steam pressure of 8 inches of mercury gage. As in Test 1, control was by the product valve, with the reflux valve completely open. The vapor rate was very constant, and equilibrium was attained two hours after setting the control valves. The concentration gradient curve is shown in Fig. XIX.

3. Test No. 3 (Table 14) was made with a reflux ratio of 0.394 and a steam pressure of 8 inches of mercury gage. The vapor rate was very constant, and equilibrium conditions were attained within two hours after setting the control valves. Control was by the reflux valve, with the product valve completely open. The concentration gradient curve is shown in Fig. XIX.

4. Test No. 4 (Table 15) was made under conditions of total reflux and steam pressure of 8 inches

of mercury gage. Equilibrium conditions were not attained, since the vapor rate decreased rapidly; at time of sampling, the liquid level in the reflux weir was approaching the minimum level at which rate measurements could be made. The concentration gradient curve for this run is shown in Fig. XIX.

Gradient Curves and General Discussion: Plotted curves of the concentration gradient through the column for Run Series "A" are shown in Fig. XIX. The effect of changes in reflux ratio on the gradient is as would be expected, and is clearly demonstrated: higher ratios result in a purer product, and tend to cause rectification to take place to a larger degree on the lower plates. Since runs with a vapor-rate range comparable to that encountered in runs on the unlagged column were made with a steam pressure of 8 inches of mercury as compared to 12 inches of mercury pressure required on the unlagged column, it is obvious that the heat economy of the assembly has been increased appreciably by redesign and lagging. Notes made during the Series indicate that, in general:

1. The column holdup increases with decreases in the reflux ratio, approximating observations of liquor height in the stillpot indicating that the holdup was 0.45 cubic feet at a reflux ratio of 0.39, 0.36 cubic feet at a reflux ratio of 0.93, and 0.29

cubic feet at a reflux ratio of 1.13. If "y" is the column holdup in cubic feet, and "x" is the reflux ratio, the relationship may be expressed as:

$$y = 0.55 - 0.216 x$$

The equation is, of course, only approximate.

2. The vapor rate, expressed as weight of vapors condensed per unit time, is fairly constant below a reflux ratio of 1.00, averaging 370 gms/min. The vapor rate drops off sharply between reflux ratios of 1.0 and 1.2, approaching zero (complete internal reflux) at total reflux.

3. The highest overall column efficiency was attained under a reflux ratio of 0.93, when the assembly was 100 percent efficient. The column was 67 percent efficient under a reflux ratio of 1.13, and 13 percent efficient under a ratio of 0.39.

4. At least two hours should be allowed for conditions within the column to come to equilibrium after the column has been heated up. This time should be increased considerably if reflux ratios approaching infinity are used. The vapor rate should have remained constant for at least thirty minutes before sampling.

5. Four adjacent plates seem to do most of the work of enriching the weak alcohol solution in the column. Their location within the column depending on the reflux ratio (and on the steam pressure), these

four plates operate at close to 100% efficiency; the remaining eleven plates, with the exception of the plates immediately below and immediately above the section, operate at almost zero efficiency.

6. For more efficient rectification the feed to the column should be introduced at some plate intermediate between the first and final plates. As the column is now operated, the feed to the column is usually diluted on the lower plates, often not reaching its initial concentration until the eleventh and thelfth plates.

7. Condenser water flow of 5 gal/min is sufficient to condense all vapors from the column when the vapor rate does not exceed 370 gas/min.

Run Series "B" : Tables 16 and 17 show the experimental results of Run Series "B", made on the final redesigned assembly (Fig. VIII) after the stillpot had been cleaned for removal of a hydrocarbon which was immiscible with aqueous isopropanol to the extent that it resulted in a cloudiness of the liquid on the lower plates of the column. The initial charge to the stillpot consisted of 4.150 cubic feet (at 55°F) of a 7.5% by weight solution of isopropanol in water. A high flow of condenser water was used (8.1 gal/min) because of the unusually high vapor rates involved.

General observations made during the series indicated that:

1. The cleaning of the stillpot and the coils resulted in a high increase in the heat economy of the assembly, steam at 1.6 inches of mercury gage resulting in higher vapor rates than had steam of 8 inches of mercury gage before the cleaning (Tables 12-15).

2. Although the automatic pressure regulator held steam pressure constant to within 0.2 inch of mercury, it could not be adjusted to give pressures of less than 1.5 inches of mercury. In future tests, where low pressures are necessary, semi-automatic control may be attained by adjustments of the globe valve in the line between the regulator and the steam coils.

3. Steam pressures greater than 1.5 inches of mercury cause such violent boiling in the stillpot that liquid is forced from unsealed openings in the sample return system. Where this happened, the main sample return pipe was removed and the open pipe entering the product return line was plugged with a cork. Since it was impossible to use the continuously dripping sample method which had been previously devised, individual samples were taken by drawing off and discarding 2 ml from the petcocks (to purge the lines) and

collecting the regular sample immediately afterwards.

4. The fact that the liquid on plate No. 10 was cloudy in both tests indicates that the column itself contains an impurity similar to that removed from the stillpot. The amount of this impurity is probably not sufficient to influence the distillation characteristics of isopropanol-water mixtures.

Equilibrium conditions were not attained in either test No. 1 (Table 16) or test No. 2 (Table 17); the data is therefore limited in its usefulness for other purposes than forming generalities as to the operating characteristics of the assembly.

Recommendations: In view of the work done and the problems encountered in this investigation, the following recommendations are made to be applied to further studies along the lines of this thesis:

1. Steam at higher pressure than the 15 psig used should be admitted to the reflux heat exchanger in order to enable the temperature of the liquid returning to the column to be brought to at least 175°F.

2. The glass enclosing the first plate should be more securely sealed to the column to prevent a noticeable leak from the plate.

3. Facilities should be provided for introducing feed to a central plate, and for preheating this feed.

4. The sample return system should be redesigned to prevent overflowing of liquid at steam pressures above 1.5 inches of mercury gage.

5. More accurate facilities should be provided for the automatic control of steam pressure within the heating coils.

6. Thermometers on all plates should be replaced by industrial thermometers of greater accuracy.

7. The reflux weir should be recalibrated, using sample collection intervals of at least three minutes.

8. Gay-Lussac specific gravity bottles, provided with ground-on caps to prevent evaporation, should be used to obtain more accurate information regarding the relationships of index of refraction and composition of aqueous isopropanol at alcohol concentrations above 70% by weight.

9. After application of the above recommendations, an investigation to determine specific operating characteristics of the assembly as used to separate aqueous isopropanol solutions should give very interesting results.

10. An investigation should be made of the operating characteristics of the assembly as used to separate a normal binary solution such as benzene and

toluene. Emphasis should be placed on the determination of the maximum overall and individual plate efficiencies which can be attained in the continuous rectification of a normal solution in the closed system.

Limitations: The results obtained and the conclusions formed in this investigation, with the exception of the correlation of index of refraction and composition of isopropanol-water solutions and the nomograph of Fig. X, apply only to the 18-plate bubble-cap rectifying assembly in the unit operations laboratory of the Virginia Polytechnic Institute Department of Chemical Engineering. Results and conclusions obtained in test runs on the assembly apply only to the separation of binary solutions of isopropyl alcohol and water in the assembly under the conditions given on the individual data sheets.

V. CONCLUSIONS

The results of this investigation indicate that the following conclusions may be formed relative to the rectification of simple binary mixtures of isopropanol and water in the 15-plate, pilot-size, bubble-cap, fractionating column located in the unit operations laboratory of the Virginia Polytechnic Institute department of chemical engineering:

1. Substitution of a single, multi-tubular (twenty-one 1/4-inch tubes, vapor inside tubes) condenser of 430 square inches condensing area, operating with countercurrent flow of vapor and cooling water, for a set of two multi-tubular (twenty-two 1/8-inch tubes, vapor outside tubes) dephlegmating condensers with condensing areas of 302 square inches each; and the repiping of the stillhead assembly to allow for the proportioning of reflux to product over a range from zero reflux to total reflux by means of needle-valves and weirs; resulted in easier and more accurate (to ± 2 gms/min flow rates of 57 molar percent aqueous isopropanol at 156°F) control of reflux ratio than had been possible prior to this investigation.

2. The construction of an operator's platform to facilitate access to the stillhead and the sampling petcocks, and the placement of a steam pressure regulator

in the steam line to the heating coils within the stillpot, resulted in a reduction of the number of operators required from four to one.

3. The addition of a heat exchanger of 7.8 square inches heating surface, operating with counter-current flow of aqueous isopropanol reflux and steam at 15 psig, by means of which the reflux could be heated from 154°F to 169°F before being returned to the column; and the lagging of the column and stillpot with a 1-1/2 inch layer of flattened 85% magnesia pipe covering and a 1-inch layer of 85% magnesia cement; increased the heat economy of the assembly to such a degree that it was possible to duplicate with a steam pressure of 8 inches of mercury (gage) conditions which had previously required a steam pressure of 12 inches of mercury (gage).

4. The removal, by physical and chemical means, of all solid deposits (iron, copper, calcium, and magnesium compounds) from the stillpot and the heating coils increased the heat economy of the assembly to such a degree that it was possible to duplicate with a steam pressure of 1.8 inches of mercury (gage) conditions which had previously required a steam pressure of 8 inches of mercury (gage).

5. The indices of refraction by Spencer Abbe' refractometer, Model 547, at 20°C ± 0.5°C of binary solutions of isopropanol and water between the compositions

of 0% and 93% isopropanol by weight is a direct measure of the compositions of the solutions. The index of refraction of isopropanol-water solution varies from 1.3330 (n_d^{20}) at 0% isopropanol to 1.3776 (n_d^{20}) at 93% isopropanol.

6. No variation of index of refraction of aqueous isopropanol with composition of the solution can be detected in the composition range of 93% to 100% by weight isopropanol using the Spencer Abbe' refractometer Model 547, the index of refraction in this range remaining substantially constant at 1.3776.

7. A cloudiness of the isopropanol-water solutions on the lower plates of the column and in the stillpot which had been noted in early runs was due to an immiscible hydrocarbon of boiling range between the limits of 167°F and 185°F. This hydrocarbon had been adsorbed by solid deposits of iron, copper, calcium, and magnesium compounds within the stillpot from commercial "Ajax" antifreeze solution which had been fractionated in the assembly in 1944. Removal of the deposits within the stillpot, by physical and chemical means, resulted in the disappearance of all cloudiness, with the exception of a cloudiness of the liquid on the tenth plate from the bottom due to deposits within the column.

6. In all test runs made using reflux ratios from 0.39 to 1.13 the vapor feed to the column was from 12% to 54% by weight richer in isopropanol than was the liquid on the bottom plate of the column, and from two plates (at a reflux ratio of 1.13) to fifteen plates (at a reflux ratio of 0.39) were required to enrich the liquid in the column to the strength of the feed.

VI. SUMMARY

Redesign and Recalibration of a Bubble-Cap Column
Used in the Fractionation of
Isopropanol-Water Solutions

An investigation was made to improve upon the overall design of a pilot-size (column: 6- $\frac{1}{2}$ feet high, 10 inches overall diameter), 15-plate, bubble-cap, fractionating assembly used in the separation of simple binary mixtures of isopropanol and water by continuous rectification in the closed system, to develop an analytical method by which the composition of isopropanol-water solutions at various points within the assembly could be determined accurately and rapidly without disturbing equilibrium conditions within the column, and, in general, to place the assembly in such condition that experimental runs could be made more easily and with a higher degree of accuracy than had previously been possible.

The stillhead of the column was redesigned to employ a single, multi-tubular condenser (of 430 square inches condensing area, with vapor on inside of tubes) in place of a set of two multi-tubular dephlegmating condensers (of 302 square inches condensing area each, with vapor on outside of tubes), and to allow for the proportioning

of reflux and product flows over a range from zero reflux flow to total reflux flow (accurate to ± 2 gms/min) by means of needle-valves and weirs; an operator's platform was constructed to facilitate access to the stillhead; a heat exchanger was inserted in the reflux return line to heat (by 15 psig saturated steam) the reflux from 154^oF to 169^oF before returning it to the top plate; a steam pressure regulator was placed in the steam line to the heating coils within the stillpot; the stillpot and heating coils were thoroughly cleaned to remove solid deposits of iron, copper, calcium, and magnesium compounds; and the column and stillpot were lagged with a 1- $\frac{1}{2}$ inch layer of flattened 85% magnesia pipe covering and a 1-inch layer of 85% magnesia cement. A small concentric-pipe condenser (5 square inches condensing area) was attached to the feed line to aid in collecting samples of the vapor feed to the column, and a continuous drip-sampling system was constructed to facilitate the taking of liquid samples from the individual plates of the column.

An analytical method for determining the concentration of liquid samples of aqueous isopropanol was developed by which the Abbe' index of refraction of a single drop of liquid could be used as a direct measure of the weight percent of isopropanol in the sample over the concentration range of 0% to 93% by weight isopropanol.

Control weirs, thermometers, and the stillpot were calibrated, and a nomograph was developed by which reflux and product flow-rates could be converted directly to molar reflux ratios.

Eight test runs were made on the experimental assembly during the course of the investigation to check operating conditions and characteristics and to serve as a basis for recommendations to be observed in making future experimental tests on the assembly.

Results of the investigation indicated that the redesign of the stillhead assembly had resulted in more accurate control of reflux ratio than had previously been possible (to 2 gas/min flow); that the construction of an operator's platform and the installation of a steam pressure regulator had resulted in a reduction of the number of operators required from four to one; that heating of the reflux, removal of solid deposits from the stillpot and heating coils, and lagging of the column and stillpot had increased the heat economy of the assembly to the point where it was possible to duplicate with a steam pressure of 1.8 inches of mercury (gage) conditions which had previously required a steam pressure of 12 inches of mercury (gage); that Abbe's indices of refraction at $20^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ of binary solutions of isopropanol and water between compositions of 0% and 93% by weight isopropanol are direct measures of the compositions of the solutions; that no variation of index

of refraction with composition of aqueous isopropanol solutions can be detected in the range from 93% to 100% by weight isopropanol using the Spencer Abbe' refractometer, Model 547; that a cloudiness of aqueous isopropanol solutions in the stillpot and on the lower plates of the column had been due to an immiscible hydrocarbon impurity (from previous distillations of commercial "Ajax" antifreeze solution) in the assembly, and could be removed by removal of solid deposits (of iron, copper, calcium, and magnesium compounds) within the assembly to which the impurity was adsorbed; and that under reflux ratios from 0.59 to 1.13 the feed to the column was diluted on the first plate to such an extent that from two to fifteen plates were required to enrich the liquid in the column to the strength of the feed.

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