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Elements of Fractional Distillation

BY

CLARK SHOVE ROBINSON

AND

EDWIN RICHARD GILLILAND

Revised and Rewritten

by

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FOURTH EDITION

SECOND IMPRESSION

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ELEMENTS OF FRACTIONAL DISTILLATION

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PREFACE TO THE FOURTH EDITION

The first edition of this book and the early revisions were the result of the efforts of Professor Robinson, and he took an active part in guiding the revision of the previous edition. His death made it necessary to prepare this edition without his helpful guidance and counsel.

The present revision differs extensively from the previous edition. The material has been modified to bring it more closely into line with the graduate instruction in distillation at Massachusetts Institute of Technology. Much greater emphasis has been placed on the measurement, prediction, and use of vapor-liquid equilibria because it is believed that this is one of the most serious limitations in design calculations. Greater emphasis has also been placed upon the use of enthalpy balances, and the treatment of batch distillation has been considerably expanded. Unfortunately, the design calculations for this type of operation are still in an unsatisfactory status. Azeotropic and extractive distillation are considered as an extension of conventional multicomponent problems. The sections on column design and column performance have been completely rewritten and increased in scope. In all cases quantitative examples have been given because it has been found that this greatly aids the student in understanding descriptive material.

During the last 15 years a large number of design methods have been proposed for multicomponent mixtures, some of which are reviewed in Chapter 12. Most of these do not appear to offer any great advantage over the conventional Sorel method, and it is believed that the law of diminishing returns has been applying in this field for some time. It is hoped that the present edition will stimulate some of these investigators to transfer their efforts to more critical problems, such as vapor-liquid equilibria, batch distillation, transient conditions within the distillation system, and column performance.

EDWIN RICHARD GILLILAND

CAMBRIDGE, MASS.
July, 1950

PREFACE TO THE FIRST EDITION

The subject of fractional distillation has received but scant attention from writers in the English language since Sidney Young published his book "Fractional Distillation" in 1903 (London). French and German authors have, on the other hand, produced a number of books on the subject, among the more important of which are the following:

"La Rectification et les colonnes rectificatrices en distillerie," E. Barbet, Paris, 1890; 2d ed., 1895.

"Der Wirkungsweise der Rectificir—und Destillir—Apparate," E. Hausbrand, Berlin, 1893; 3d ed., 1916.

"Theorie der Verdampfung und Verflüssung von gemischen und der fraktionierten Destillation," J. P. Kuenen, Leipzig, 1906.

"Theorie der Gewinnung und Trennung der ätherischen Öle durch Destillation," C. von Rechenberg, Leipzig, 1910.

"La Distillation fractionée et la rectification," Charles Mariller, Paris, 1917.

Young's "Fractional Distillation," although a model for its kind, has to do almost entirely with the aspects of the subject as viewed from the chemical laboratory, and there has been literally no work in English available for the engineer and plant operator dealing with the applications of the laboratory processes to the plant.

The use of the modern types of distilling equipment is growing at a very rapid rate. Manufacturers of chemicals are learning that they must refine their products in order to market them successfully, and it is often true that fractional distillation offers the most available if not the only way of accomplishing this. There has consequently arisen a wide demand among engineers and operators for a book which will explain the principles involved in such a way that these principles can be applied to the particular problem at hand.

It has therefore been the purpose of the writer of this book to attempt to explain simply yet accurately, according to the best ideas of physical chemistry and chemical engineering, the principles of fractional distillation, illustrating these principles with a few carefully selected illustrations. This book is to be regarded neither as a complete treatise nor as an encyclopedia on the subject but, as the title indicates, as an introduction to its study.

In general, it has been divided into five parts. The first part deals with fractional distillation from the qualitative standpoint of the phase rule. The second part discusses some of the quantitative aspects from the standpoint of the chemical engineer. Part three discusses the factors involved in the design of distilling equipment. Part four gives a few examples of modern apparatus, while the last portion includes a number of useful reference tables which have been compiled from sources mostly out of print and unavailable except in large libraries.

The writer has drawn at will on the several books mentioned above, some of the tables being taken nearly bodily from them, and has also derived much help from Findlay's "Phase Rule" (London, 1920) and from "The General Principles of Chemistry" by Noyes and Sherrill (Boston, 1917). He wishes especially to express his gratitude for the inspiration and helpful suggestions from Dr. W. K. Lewis of the Massachusetts Institute of Technology and from his other friends and associates at the Institute and of the E. B. Badger & Sons Company. Finally, he wishes to express his appreciation of the assistance of Miss Mildred B. McDonald, without which this book would never have been written.

CLARK SHOVE ROBINSON

CAMBRIDGE, MASS.
June, 1920.

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INTRODUCTION

Definition of Fractional Distillation. By the expression fractional distillation was originally meant the process of separating so far as it may be feasible a mixture of two or more volatile substances into its components, by causing the mixture to vaporize by suitable application of heat, condensing the vapors in such a way that fractions of varying boiling points are obtained, revaporizing these fractions and separating their vapors into similar fractions, combining fractions of similar boiling points, and repeating until the desired degree of separation is finally obtained.

Purpose of Book. Such a process is still occasionally met with in the chemical laboratory, but it is a laborious and time-consuming operation which has its chief value as a problem for the student, for the purpose of familiarizing him with some of the characteristic properties of volatile substances. It is possible to carry on a fractional distillation by means of certain mechanical devices which eliminate almost all of this labor and time and which permit separations not only equal to those obtained by this more tedious process but far surpassing it in quality and purity of product. The purpose of this book is to indicate how such devices may be profitably used in the solution of distillation problems.

Origin of Fractional Distillation. Like all the older industries, fractional distillation is an art that originated in past ages and that developed, as did all the arts, by the gradual accumulation of empirical knowledge. It is probable that its growth took place along with that of the distilled alcoholic beverages, and to the average person today the word "still" is synonymous with apparatus for making rum, brandy, and other distilled liquors. To France, which has been the great producer of brandy, belongs the credit for the initial development of the modern fractionating still.

Physical Chemistry and Fractional Distillation. Fractional distillation has labored under the same sort of burden that the other industrial arts have borne. Empirical knowledge will carry an industry to a certain point, and then further advances are few and far between. It has been the function of the sciences to come to the rescue

of the arts at such times and thus permit advancement to greater usefulness. The science that has raised fractional distillation from an empirical to a theoretical basis is physical chemistry. By its aid the study of fractionation problems becomes relatively simple, and it is on this account that the subject matter in this book is based upon physical chemistry.

CHAPTER 1

DETERMINATION OF VAPOR-LIQUID EQUILIBRIA

The separation of a mixture of volatile liquids by means of fractional distillation is possible when the composition of the vapor coming from the liquid mixture is different from that of the liquid. The separation is the easier the greater the difference between the composition of the vapor and that of the liquid, but separation may be practicable even when the difference is small. The relation between the vapor and liquid compositions must be known in order to compute fractional distillation relationships. Usually this is obtained from information concerning the composition of the vapor which is in equilibrium with the liquid. On this account a knowledge of vapor-liquid equilibrium compositions is usually essential for the quantitative design of fractional distillation apparatus. In most cases the study is made on the basis of the composition of the vapor in equilibrium with the liquid. However, this is not a fundamental requirement and any method that would allow the production of a vapor of a different composition than that of the condensed phase, whether equilibrium or not, could be used for separation. However, most of the equipment employed depends on the use of a vaporization type of operation, and the equilibrium vapor is a good criterion of the possibilities of obtaining a separation.

The methods for obtaining vapor-liquid equilibrium compositions can be considered in two main classifications: (1) the experimental determination of equilibrium compositions and (2) the theoretical relationships.

EXPERIMENTAL DETERMINATIONS OF VAPOR-LIQUID EQUILIBRIA

The measurement of vapor-liquid equilibrium compositions is not simple. A highly developed laboratory technique is therefore needed to obtain reliable data in any of the several methods described here.

Circulation Method. A common method for obtaining vapor-liquid equilibrium (Refs. 11, 13, 16, 23, 27, 35) is by circulating the vapor through a system and bringing it into repeated contact with the liquid until no further change in the composition of either takes place. A schematic diagram of such a system is shown in Fig. 1-1. The vapor above the liquid in vessel A is removed, passed through

chamber B, and recirculated by pump C through the liquid in A. While the system appears simple, in actual practice it involves a number of complications:

1. The system must be completely tight; otherwise the total quantity of material will continually vary and the equilibrium compositions of the vapor and liquid will also change.

2. The quantities of liquid and of vapor when equilibrium is obtained must remain constant and not vary during the recirculation. To keep

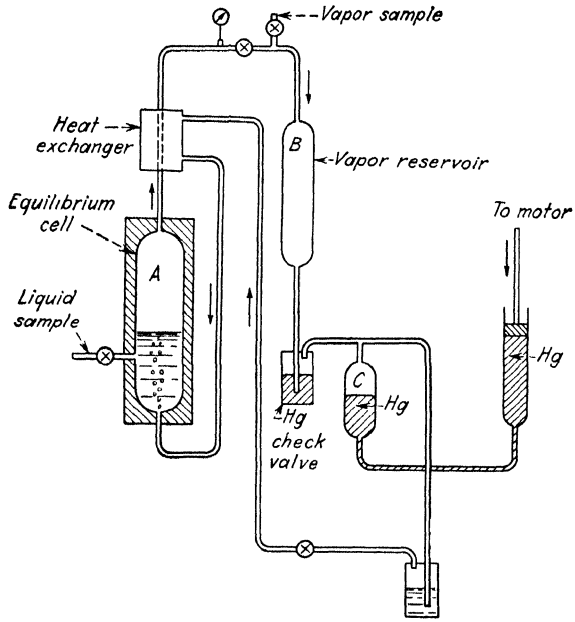


FIG. 1-1. Circulation apparatus for vapor-liquid equilibrium measurements.

them constant it is necessary for the system to remain isothermal and for the total volume to remain constant. The chief variation in the volume of the system is due to the fact that it is usually found expedient to use a reciprocating pump. The error due to this variation is usually minimized by making the displacement volume of the pump small. The pumps are generally of a mercury-piston type; *i.e.*, a mercury column is forced up and down in a steel or glass cylinder serving as the piston of the pump. This makes it possible to have an essentially leakproof pump and allows the pumping operation to be carried out with very little contamination of the circulating vapors.

3. This type of system has been used most successfully under con-

ditions where the vapor does not condense at room temperature. If it were necessary to operate the pumping system at a high temperature to avoid condensation of the vapor, difficulties might be encountered due to the vapor pressure of the mercury, in which case other lower vapor pressure metallic liquids should be suitable.

4. Another condition that could cause the relative volumes of vapor and of liquid to vary is the rate of flow. The rate of recirculation varies the pressure drop through the apparatus and thereby changes the quantity of vapor present. In most cases the rate of recirculation is such that the pressure differential for recirculation is not great. Both the volume variation due to pumping and the pressure changes due to recirculation can be made less detrimental by making the volume of the liquid in vessel A large.

5. It is necessary to ensure that there is no entrainment of liquid with the vapor leaving A. If liquid is carried over to vessel B, the vapor sample will be contaminated. This entrainment is eliminated by the use of low velocity and by efficient entrainment separators in the upper part of A.

6. Another precaution is the necessity to prevent any condensation of the vapor during recirculation. If any vapor condenses, the condensate will be of different composition and the results will be in error.

This type of apparatus has been used for a variety of systems. It is particularly suitable for very low temperature studies such as those involved in the equilibria associated with liquid air. In this case vessel A is maintained in a low-temperature cryostat, and the recycle vapor stream is heat-exchanged with the exit vapor; the rest of the system is maintained at essentially room temperature. One of the difficulties with the operation is the fact that the vapor sample is obtained as a vapor and, unless the pressure is high, the quantity of vapor obtained in vessel B may be so small as to offer difficulties in analysis.

The system has the great advantage that a vapor can be *repeatedly bubbled through* the *liquid* until equilibrium is obtained. Theoretically exact equilibrium is not obtained because of the fact that there are pressure differentials in the system. Thus the vapor entering at the bottom of A must be under a pressure higher than the vapor leaving A, at least by an amount equal to the hydrostatic head of the liquid in A. Since the vapor-liquid equilibria depend on pressure, it is obvious that there cannot be exact equilibrium. However, the change in the composition of the equilibrium vapor due to this small change of pressure is small in most cases. It could be serious in the critical region

where the vapor is very compressible. Basically this system is one of the best for obtaining true equilibrium.

Bomb Method. In the bomb method (Refs. 3, 4, 12, 14, 36) the liquid sample is placed in a closed evacuated vessel. It is then agitated by rocking, or by other means, at constant temperature until equilibrium is obtained between the vapor and the liquid. Samples of the vapor and the liquid are then withdrawn and analyzed.

The method appears simple, but it involves certain difficulties. During sampling there are pressure changes due to the removal of material, and these pressure changes can be large in magnitude. In order to avoid them, it is customary to add some fluid, such as mercury, to the system while the samples are being removed in order to prevent

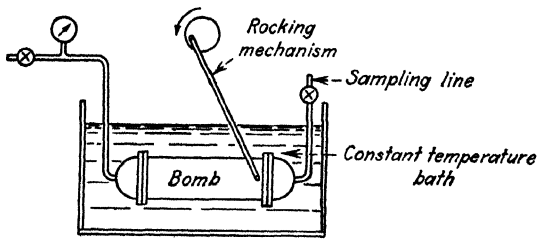


FIG. 1-2. Bomb apparatus.

any vaporization or condensation. Another difficulty with the method is the fact that in most cases it is necessary to use sampling lines of small cross sections. These may fill up with liquid during the initial part of the operation, and this liquid may never come to the true equilibrium. It is necessary to purge the sampling lines to remove such liquid. This liquid holdup is particularly serious in the case of the vapor sample since in quantity it may be large in comparison to the sample. A schematic diagram of the bomb-type apparatus is shown in Fig. 1-2.

Dynamic Flow Method. Another method that has been widely used (Refs. 10, 21, 25, 37) for the determination of vapor-liquid equilibria is one in which a vapor is passed through a series of vessels containing liquids of a suitable composition. The vapor entering the first vessel may be of a composition somewhat different from the equilibrium vapor, but as it passes through the system it tends to approach equilibrium. If all the vessels have approximately the same liquid composition, the vapor will more nearly approach equilibrium as it passes through the unit. The number of vessels employed should be such that the vapor entering the last unit is of essentially equilibrium composition.

This system has the advantage that it is simple and, in certain cases, it is possible to dispense with the analysis of the liquid sample, *i.e.*, the liquids can be made of a known composition, and since the change in the last vessel is small, it is possible to assume that the composition of the liquid in this case is equal to that originally charged. A schematic diagram of such a system is shown in Fig. 1-3.

It is obvious that it cannot be an exact equilibrium system because of the fact that a pressure drop is involved in passing the vapor through the system; *i.e.*, there are pressure variations which will affect equilibrium. There is also the danger of entrainment, although this can be minimized by low velocities.

In a great many cases, the gas introduced into the first vessel has been carrier gas of low solubility and not a component of the system.

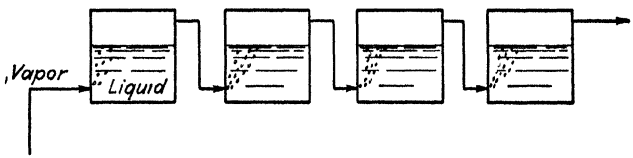


FIG. 1-3. Dynamic flow method.

Thus, in the determination of the vapor-liquid equilibria for systems such as ammonia and water, ammoniacal solutions are placed in the vessels, and a gas such as nitrogen is bubbled into the first of these and the resulting nitrogen-ammonia-water vapor mixture is passed through the succeeding vessels obtaining a closer approach to equilibrium. Equilibrium obtained in such a manner is not the true vapor-liquid equilibria for the water vapor–ammonia system. It closely approaches true equilibrium for the binary system under a total pressure equal to the partial pressure of the ammonia and the water vapor in the gaseous mixture. Even this is not exact. The carrier gas has some solubility in the liquid phase, and the partial pressure of these added constituents modifies the energy relations of the liquid and vapor phases. Usually for low-pressure operation these errors are not large in magnitude, but as the pressure becomes higher the errors are serious and the method can give erroneous results if the true vapor-liquid equilibria for mixtures without the carrier gas are desired.

Dew and Boiling-point Method. In essence this technique consists in introducing a mixture of known composition into an evacuated equilibrium container of variable volume (Refs. 6, 7, 9, 15, 17, 18, 20, 28). The system is maintained at a constant temperature, and by varying the volume the pressure is observed at which condensation

commences and is completed. The dew- and bubble-point curves of pressure vs. temperature for a number of these prepared samples are obtained and, by cross-plotting, conditions of phase equilibrium may be found by locating points at which saturated liquid and saturated vapor of different compositions exist at the same temperature and pressure.

The pressures are determined in two ways. One involves the measuring and plotting of the PV isotherm, the dew point and bubble point being indicated by the discontinuities in the curve at the beginning and the end of condensation. The other employs a glass or quartz equilibrium cell, and the conditions are determined visually.

The advantages of this method are that it allows the critical conditions to be determined, gives data on specific volumes of mixtures at high pressures, and requires no analysis of the phases since the total composition of the mixture is accurately determined gravimetrically upon charging.

There are disadvantages, however. For certain conditions the dew and bubble points are not sharply defined; hence they require measurements to be made with highly refined precision instruments. The simpler units using mercury as a variable volume confining fluid cannot be used below the freezing point of mercury. In addition, the materials used must be very pure and free in particular from traces of fixed gases, for in the critical region the saturation pressure is quite sensitive to small amounts of fixed gases. Further, a large amount of experimental work must be done in order to define completely and accurately the phase equilibria over all ranges of liquid and vapor composition. The major limitation, however, is the fact that the method can be used only on binary systems. As the phase rule dictates that more complex systems are not a unique function of pressure and temperature, dew and bubble points alone cannot define the composition of two phases in equilibrium.

Dynamic Distillation Method. The four previous methods involved repeated contact of the vapor with the liquid and thus afforded the time necessary for the attainment of equilibrium. The dynamic distillation method (Refs. 2, 5, 11, 19, 24, 26, 34, 39) involves a different procedure (see Fig. 1-4). In this system a distilling vessel is connected to a condenser and a receiver.

In the simplest case, a small sample of distillate is taken, and the compositions of this sample and the liquid in the still are determined. During such a distillation the composition of the distillate and the liquid in the still changes, and the samples represent average values.

To reduce this composition variation the quantity of liquid in the still is made large in comparison to the quantity of distillate. Frequently successive samples of condensate are obtained, and these are analyzed and the composition plotted vs. the quantity of liquid that has been distilled. An extrapolation of this curve back to zero quantity of liquid removed is taken as the composition of the vapor in equilibrium with the original liquid.

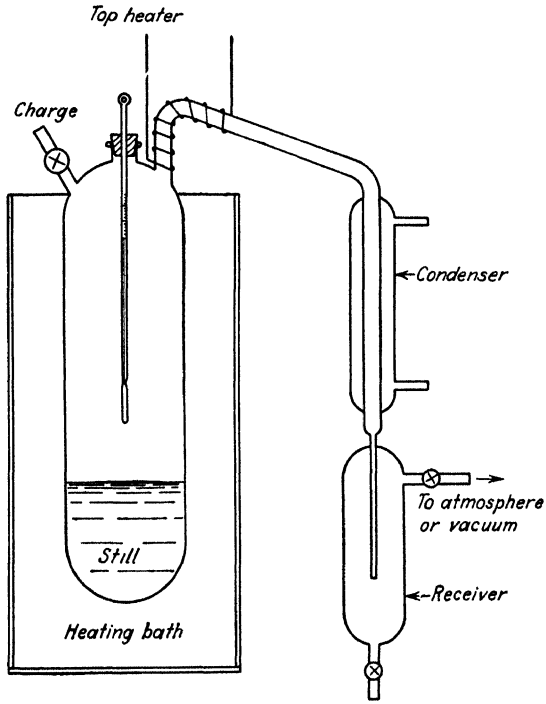


FIG. 1-4. Dynamic distillation apparatus.

The method involves a new assumption, namely, that the vapor obtained by boiling a liquid is in equilibrium with the liquid. There has been no adequate proof of this assumption, and theoretical considerations would tend to indicate that equilibrium should not be obtained. The few experimental data that are available would indicate that the difference in the composition between the vapor obtained in this manner and the true equilibrium is not great in most cases, but in a few systems significant differences have been found.

After the vapor leaves the liquid, any condensation in the upper part of the distilling vessel will change the composition of the vapor and

therefore introduce errors. Such condensation is usually reduced or eliminated by having the upper part of the system jacketed and at a higher temperature than the condensation temperature of the vapor. However, this higher temperature can introduce errors; for example, in such a boiling system there is a certain amount of spray and splashing. The spray that lands on the heated walls will tend to vaporize totally and give a vapor of the composition of the liquid rather than of the equilibrium composition.

The pressure involved in such a system is of course essentially that prevailing in the receiver, and this method can be used either for normal pressures, high pressures, or vacuum. The exact temperature of the operation is usually not known because the liquid is generally superheated. The vapor and the liquid therefore are not in thermal equilibrium, and it is doubtful whether they are in true composition equilibrium. The apparatus has been extensively used because of its simplicity, and the results are of sufficient accuracy to be of real value in distillation calculations.

In order to obtain a closer approach to equilibrium, various complicating arrangements have been used; for example, Rosanoff modified the system to obtain a second contact of the vapor with the liquid.

Continuous Distillation Methods. Continuous distillation methods involve distilling a liquid, condensing the vapor sample, and recycling the condensate back to the still. A schematic drawing of such an equilibrium still is given in Fig. 1-5. This system was developed by Yamaguchi (Ref. 38) and Sameshima (Ref. 29) and has been modified and improved by a number of other investigators (Refs. 1, 8, 22, 30, 31, 32, 33). This method has been widely used and has the great advantage that it is simple, and the unit can be placed in operation and allowed to come to a steady state without any great amount of attention. The same precautions relative to entrainment, condensation and total vaporization of splashed liquid must be observed in the still as was indicated for the dynamic distillation method. The condensate collects until the level is high enough to flow over the trap and back to the still. At the end of the distillation, this condensate is removed and analyzed to determine the composition of the vapor, and a sample is removed from the still to determine the still composition.

This method suffers from the same difficulties as the dynamic distillation method in that it is open to the question of whether the vapor formed by boiling a liquid is in equilibrium with the liquid. It is also difficult to obtain the true liquid temperature because of the superheating effects. The pressure is maintained by the pressure in the exit

tube, and in normal pressure determinations this is usually open to the atmosphere. This theoretically offers the possibility of errors in that it allows oxygen and nitrogen to dissolve in the condensate sample, which is then recycled back to the still. At low pressures the solubility of such gases is usually small and the error is slight, but in high-pressure operations the use of this gas system can lead to serious errors.

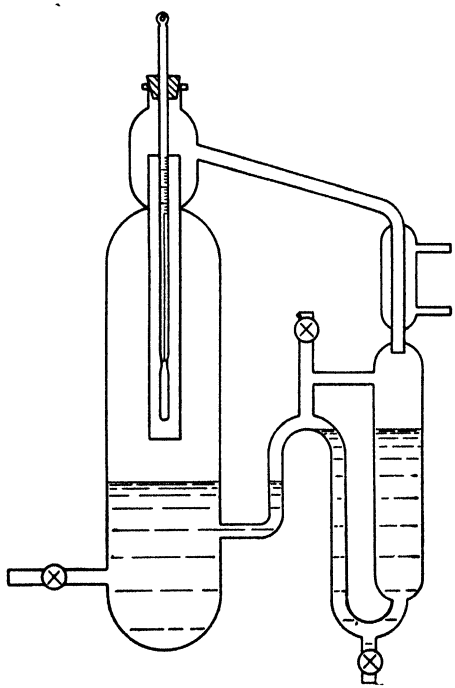


FIG. 1-5. Continuous distillation equilibrium still.

The gas pressuring system, however, is extremely desirable in that it regulates the condenser cooling capacity so that it exactly balances heat input to the still. At high pressures the errors become so serious that this benefit must be foregone. Figure 1-6 indicates a type of apparatus in which the heat input and removal are adjusted so that the pressure remains constant without the necessity of a sealing gas.

Another source of error in the system is possible because the condensate returned to the still is of a different composition from the liquid in the still and in general is of lower boiling point. If this vaporizes before it is completely mixed with all of the liquid in the still, this vapor composition will not be an equilibrium vapor.

Although the apparatus appears to be of the recirculation type and it might be supposed that the successive contacts would tend to give a closer approach to equilibrium, *this is not the case.* If the vapor evolved from the liquid is not an equilibrium vapor, this type of recycle

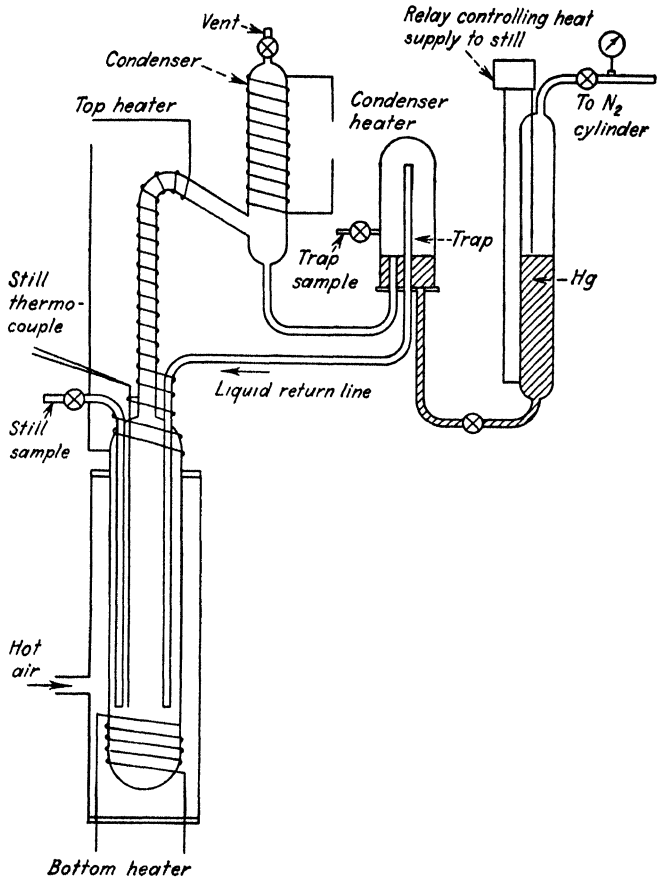


FIG. 1-6. Continuous distillation still for high-pressure operation.

system does not give a closer approach with repeated recycling since new vapor is formed and the recycled material is not brought to equilibrium by successive contacts. The recycling does give a steady-state condition, but the approach to equilibrium is only that obtained by boiling the liquid.

In order to eliminate some of the sources of error in continuous distillation systems, various modifications have been made. The most

important of these (Refs. 1, 8) would appear to be one in which the condensate stream is revaporized before it is returned to the still; *i.e.*, the heat is added to revaporize the condensate stream instead of forming a new vapor in the still. Such an apparatus is shown in Fig. 1-7. In this case, the result is equivalent to recycling the vapor, and the operation tends to be equivalent to the usual recycle system. It is more difficult to operate than the conventional continuous distillation system. The condensate must be completely vaporized. If any

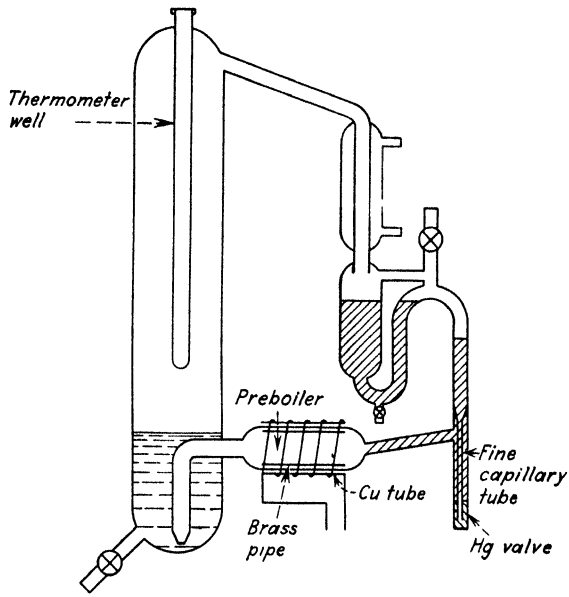


FIG. 1-7. Continuous distillation still with revaporized condensate.

liquid is allowed to return to the still, the purpose of the system is defeated and the rate of distillation decreases; *i.e.*, less vapor leaves the still. If the vapor returned to the still is greatly superheated, it will cause additional evaporation in the still and the operation will speed up. By proper adjustment a satisfactory balance can be obtained. It is believed that this apparatus is a definite improvement over the regular continuous distillation system, and comparative data on the same system taken with this and the usual continuous distillation system show definite differences of the type that would be anticipated.

Both the continuous distillation system and the modifications of it suffer from the difficulty that the vapor must be totally condensable under the operating conditions. This is usually not a serious difficulty.

It is also necessary that the condensate be a homogeneous mixture. Thus, if the condensate separates into two layers, the operation is not satisfactory. The other vapor-liquid equilibrium methods are suitable for multilayer systems either in the still or in the vapor sample.

ACCURACY OF VAPOR-LIQUID EQUILIBRIUM DATA

A satisfactory investigation of the accuracy of the various experimental methods has not been made, and there is real question concerning a large amount of the published experimental vapor-liquid equilibrium data. The circulation and the bomb methods have the potentiality of giving high accuracy, and the value of the results depends on the care employed by the experimentalist in eliminating sources of error. The dynamic distillation and the continuous distillation methods involve the assumption that the vapor produced by boiling a liquid is of a composition that is in equilibrium with the remaining liquid. The adequacy of this assumption has not been proved experimentally, but there are experimental results which cast doubt on its validity for all cases. Analysis of the published data obtained by employing the continuous distillation method would indicate that it may give values for the differences of the vapor and liquid compositions at a given liquid composition that are within 10 to 15 per cent of the true values. When results for the same system are compared on this basis, it is not uncommon to find deviations of ± 10 per cent between different investigators employing essentially the same techniques. A critical study of the methods of determining vapor-liquid equilibria is needed.

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CHAPTER 2

PRESENTATION OF VAPOR-LIQUID EQUILIBRIUM DATA

It is usually desirable to present the experimental vapor-liquid equilibrium data graphically. A number of methods of presentation have been developed, but the most important are the temperature-composition and the vapor-liquid composition diagrams.

Phase Rule. The method of presentation must be consistent with the number of variables involved. For equilibrium conditions the number of independent variables can be obtained from the phase rule which states that the number of phases ϕ plus the degrees of variance F is equal to the number of components C plus 2.

$$\phi + F = C + 2 \tag{2-1}$$

In the usual vapor-liquid equilibria two phases are involved: liquid and vapor. However, in some systems more than one liquid phase may be encountered. For the two-phase system the phase rule states that the degrees of freedom or variance are equal to the number of components. Thus a binary system has two degrees of freedom and can be represented by two variables on rectangular coordinates. Three-component systems involve three degrees of freedom and are usually presented on triangular coordinates. Multicomponent systems with more than three components are difficult to present, and special methods are employed for such systems.

Temperature-Composition Diagrams. By fixing the total pressure of a two-component system, a temperature-composition diagram can be made. Figure 2-1 shows a temperature-composition curve for carbon tetrachloride–carbon bisulfide at a total pressure of 760 mm. Any point on the curve ABC gives the composition x, of a mixture of CCl_4 and CS_2, which boils at a pressure of 760 mm. at a temperature t, where t is in degrees centigrade and x is the mol fraction of CS_2. The use of the "mol fraction" greatly facilitates calculations of vapor-pressure phenomena. It is the ratio of the number of molecular weights of one component in a mixture divided by the sum of the number of the molecular weights of all components. Mol per cent is equal to 100 times the mol fraction. The line ADC represents the composition of the vapor that is in equilibrium with the liquid at any

given temperature. Thus a liquid with the composition x_1 will have a vapor pressure of 760 mm. at the temperature t_2, and the vapor in equilibrium with it will have the composition $y_1 = x_2$.

Starting with a mixture of the composition x_1, at a constant total pressure equal to 760 mm., and at a temperature below t_2, there will be but one phase present, the liquid mixture of CCl_4 and CS_2. As the temperature is raised, only a liquid phase will be present until the vertical line at x_1 intersects the curve ABC, when a vapor phase of

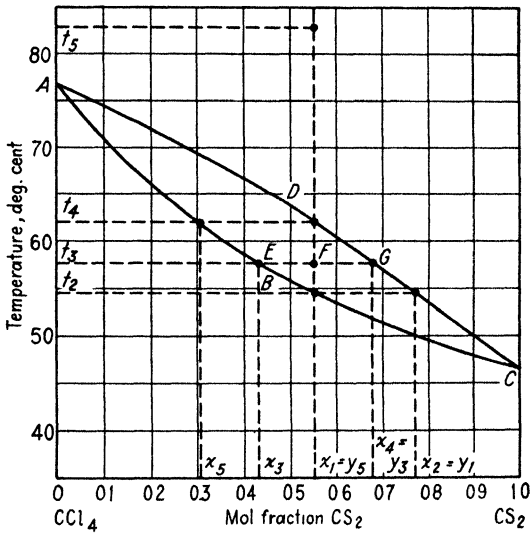


FIG. 2-1. Boiling-point curve for CCl_4-CS_2 mixtures.

the composition x_2 will appear. Since there are now two phases and the pressure is fixed, there can be but one variable, temperature, and the composition of the phases will depend upon it. Let the temperature then be raised to some point t_3 and the liquid and vapor compositions, being no longer independent variables, must change accordingly, which they do along the curves ABC and ADC, respectively, the liquid now having a composition x_3, and the vapor in equilibrium with it a composition $y_3 = x_4$. It should be remembered that the quantity of CCl_4 and CS_2 in the system has not changed during this process; therefore, the change in the compositions of the liquid and the vapor includes such a corresponding change in the relative proportions of each phase that the total composition of the system remains the same, x_1. Furthermore, the relative proportions of the liquid phase and the vapor phase, at the temperature t_3, are as the distances FG and EF. It will

be seen that, as the temperature is raised farther, the proportion of liquid phase decreases until, when the temperature reaches a point corresponding to the intersection of the vertical line x_1 and the curve ADC, which occurs at a temperature t_4, the vapor has the same composition as the original liquid, and the liquid phase disappears. At higher temperatures, there is but one phase, and the system again becomes trivariant, so that at constant pressure it is possible to vary

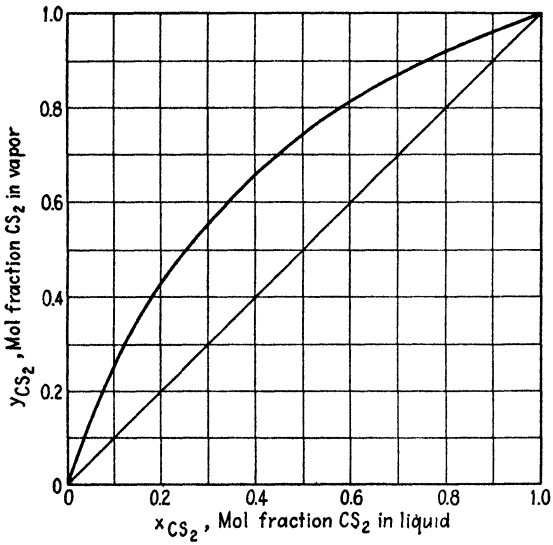


FIG. 2-2. Equilibrium y,x data for CCl_4-CS_2 mixtures.

both the temperature and the composition of the vapor. This is the region of superheated vapor.

If the foregoing process is reversed, the steps can be followed in the same way. Starting with superheated vapor of a composition $y_5 = x_1$ and at a temperature t_5, condensation will first occur when the vertical line y_5 cuts the vapor line ADC, when liquid of a composition x_5 will separate out. Further cooling will change both the composition of the liquid and the vapor along the lines ABC and ADC, respectively, until the liquid has reached the composition x_1 when all the vapor will have disappeared.

Vapor-Liquid Equilibrium. It is possible to plot the same data as were used in Fig. 2-1 as vapor composition vs. liquid composition at either constant pressure or constant temperature. The data presented in Fig. 2-1 were for constant pressure so they have been replotted in

Fig. 2-2 for the same conditions. In this curve the composition $y_1 = x_2$ is plotted as ordinate with composition x_1 as abscissa, $y_3 = x_4$ as ordinate with x_3 as abscissa, and so forth. This particular relation is very useful in distillation calculations. It does not give so much information as Fig. 2-1, owing to the elimination of temperature. However, in most distillation calculations it is desired to make a given separation between the components and the temperatures are allowed

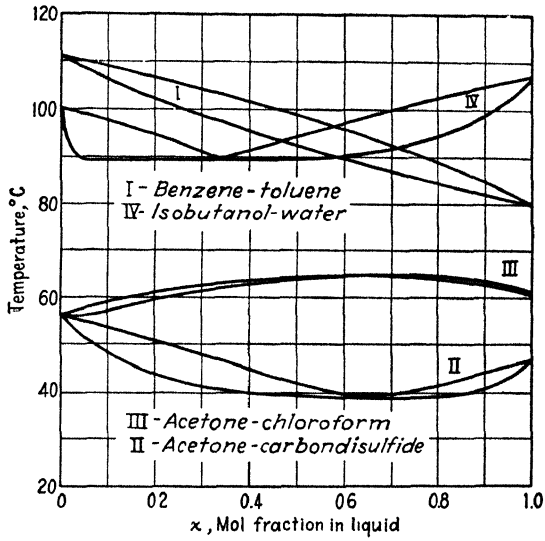


FIG. 2-3. Temperature-composition diagram.

to adjust themselves accordingly. On Fig. 2-2 the 45° line represents a vapor of the same composition as the liquid. If the temperature is important, this variable can be plotted vs. the liquid composition on the same figure.

The curves given in Figs. 2-1 and 2-2 are termed the normal type. However, there are several other common types of curves. In Fig. 2-3 temperature-composition diagrams for constant total pressure are given for four different types of binary mixtures, and in Fig. 2-4 the corresponding vapor-liquid diagrams are given for the four same mixtures.

Type I is normal, *i.e.*, the composition of the equilibrium vapor is always richer in the same component than the composition of the liquid, thus by repeated operations it is possible to obtain complete separation.

In type II the temperature-composition diagram passes through a minimum, and the vapor-liquid composition diagram crosses the diagonal. Thus there are mixtures that have lower boiling points than either of the pure components at the same pressure. In other words, the mixture is the minimum boiling-point type. When such temperature-composition diagrams are encountered, the vapor-liquid composition curve will always cross the 45° line. In the region below this intersection with the diagonal, the equilibrium vapor is richer in one

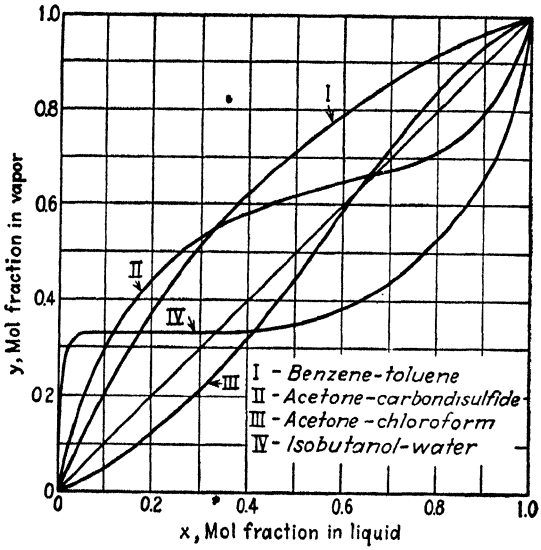


FIG. 2-4. Vapor-liquid equilibrium curves.

component than the liquid; above this intersection, the vapor is poorer in this component than the corresponding liquid from which it came. Thus the volatilities have reversed. Where the vapor-liquid curve crosses the 45° line, the vapor has the same composition as the liquid and operations based on producing an equilibrium vapor from this liquid would not be able to separate mixtures of this composition. This particular composition is called a constant boiling mixture, or azeotropic mixture, since it will vaporize without any change in composition and, therefore, without any change in temperature during the evaporation.

Type III is the reverse of type II. In this case there are mixtures that have boiling points higher than either of the pure components at the same pressure. It will be noted in Fig. 2-4 that the curve of type

III also crosses the 45° line but curve II cuts the 45° line with the slope less than 1 while curve III crosses the 45° line with the slope greater than 1. Curve III is of the maximum boiling-point type, and the particular composition at which the curve crosses the 45° line is called a maximum constant boiling mixture or a maximum boiling azeotrope.

The curve of type IV is similar to that of type II except that, for a considerable range of composition, the temperature of the liquid phase is constant. This curve type is characteristic of a partly miscible liquid system. In the immiscible region, two liquid phases are present and the phase rule indicates that the boiling temperature of the mixture must be constant. In the diagram, the over-all composition of the liquid is plotted as x regardless of whether one or two phases are present. There is no single liquid phase that has a composition equal to the value given in the two-phase region. The y,x data for this system are given in Fig. 2-4. In this case the y,x curve crosses the diagonal in the two-phase region; thus at this intersection the composition of the vapor is the same as that of the combined liquid phases. Such a mixture can be evaporated to dryness at constant pressure without change in composition or temperature. The mixture of this particular composition is termed a pseudo-azeotrope. This terminology is sometimes applied to any two-phase mixture, but the original usage of the term azeotrope by Wade and Merriman (Ref. 50) implied that the liquid could be evaporated to dryness without change in composition. Only the two-phase mixture corresponding to the intersection of the y,x curve with the $y = x$ line can be evaporated without changing composition.

In other cases the y,x curve may not cross the diagonal in the two-phase region, and such mixtures do not form pseudo-azeotropes, but they may form, and usually do, true azeotropes in one of their single-phase regions.

Literature Data. The vapor-liquid equilibria for a large number of mixtures have been experimentally determined, and Table 2-1 lists some of the more reliable and useful determinations.

The data given in the table represent a large amount of experimental effort, and owing to the difficulties of making such determinations a number of investigators have tried to develop theoretical and empirical methods of predicting such vapor-liquid equilibria from the physical properties of the pure components. While certain correlations have been developed by this method, reliable experimental determinations are still to be preferred to any such calculated values.

TABLE 2-1. VAPOR-LIQUID EQUILIBRIUM DATA

System	Constant T or P	Technique*	Ref.
Acetaldehyde–water	760 mm.	—	19
Acetic acid–acetic anhydride	750 mm.	C.D.	27
–acetone	760 mm.	C.D.	55
–acetone–water	760 mm.	C.D.	55
–benzene	758 mm.	C.D.	27
–ethyl acetate	760 mm.	C.D.	13
–methyl amyl ketone	760 mm.	C.D.	29
–water	125, 250, 300, 760 mm.	C.D.	14
	760 mm.	C.D.	55
Acetone–carbon disulfide	35.2°C.	B.M.	17
	760 mm.	—	19
–chloroform	760 mm.	D.D.	38
–ethyl ether	30°C.	C.D.	39
–isopropanol	25°C.	D.F.	32
–methanol	755 mm.	C.D.	28
–*n*-butanol	760 mm.	C.D.	7
–nitrobenzene	20°C.	D.F.	52
–trichloroethylene	755 mm.	C.D.	47
–water	25°C.	B.M.	1
	760 mm.	C.D.	5
	200, 350, 500, 760 mm.	C.D.	29
	50, 100, 200 p.s.i.a.	C.D.	31
Acetonitrile–water	150, 300, 760 mm.	C.D.	30
Ammonia–water	1 to 20 atm.	—	3
Aniline–benzene	70°C.	C.D.	24
Benzene–carbon disulfide	19.9°C.	B.M.	17
–carbon tetrachloride	40°C.	C.D.	40
	760 mm.	D.D.	38
–chloroform	760 mm.	—	48
–cyclohexane	740 mm.	C.D.	16
–ethyl bromide	760 mm.	—	48
–ethylene chlorohydrin	760 mm.	C.D.	44
–ethylene dichloride	100, 200, 400, 760 mm.	C.D.	4
–methanol	40°C.	C.D.	22
	760 mm.	C.D.	53
–*n*-hexane	735 mm.	C.D.	46
–nitrobenzene	20°C.	D.F.	52
–phenol	70°C.	C.D.	25
–*n*-propanol	40°C.	C.D.	22
–2,2,3 trimethylbutane	740 mm.	C.D.	16

*B.M. = bomb method
C.D. = continuous distillation
C.M. = circulation method
D.B. = dew-point, bubble-point method
D.D. = dynamic distillation
D.F. = dynamic flow

TABLE 2-1. VAPOR-LIQUID EQUILIBRIUM DATA (*Continued*)

System	Constant T or P	Technique*	Ref.
Bromine–water	750 mm.	D.D.	35
n-Butanol–*n*-butyl acetate	760 mm.	C.D.	7
–ethylene chlorohydrin	760 mm.	C.D.	44
–water	760 mm.	D.D.	45
i-Butanol–ethylene chlorohydrin	760 mm.	C.D.	44
–water	760 mm.	D.D.	45
Carbon disulfide–carbon tetrachloride	760 mm.	D.D.	38
–chloroform	20°C.	B.M.	17
–cyclohexane	19 8°C.	B.M.	17
–ethyl ether	29.2°C.	B.M.	17
–isobutyl chloride	20.0°C.	B.M.	17
–isopentane	17 0°C.	B.M.	17
–nitrobenzene	20 0°C.	D.F.	52
Carbon tetrachloride–ethanol	745 mm.	—	48
–ethyl acetate	49.9°C.	D.D.	56
	745 mm.	—	48
–ethyl ether	760 mm.	—	48
–tetrachloroethylene	760 mm.	C.D.	34
–toluene	762 mm.	C.D.	8
Chlorobenzene–ethylene bromide	100°C.	C.D.	20
Chloroform–methanol	757 mm.	—	48
–nitrobenzene	20°C.	D.F.	52
–toluene	760 mm.	D.D.	37
Cyclohexane–cyclohexane	740 mm.	C.D.	16
–ethanol	25°C.	D.F.	51
–2,2,3 trimethylbutane	740 mm.	C.D.	16
Diethyl benzene–*o*-dichlorobenzene	10, 50 mm.	C.D.	4
Diethyl hexyl phthalate–diethyl hexyl sebacate	0 1 mm.	C.D.	33
Dioctyl phthalate–diethyl hexyl sebacate	0 1 mm.	C.D.	33
Ethane–ethylene	−25.5, −12, 0, 12, 23°C.	C.M.	26
Ethanol–ethyl acetate	760 mm.	C.D.	13
–ethyl ether	20°C.	D.F.	10
–methanol–water	760 mm.	C.D.	15
–*n*-heptane	30°C.	B.M.	12
–water	760 mm.	C.D.	23
	95, 190, 380 mm.	C.D.	2
	760 mm.	C.D.	21
Ethyl acetate–methanol	39.8°C.	D.D.	5
–nitrobenzene	20°C.	D.F.	52
Ethyl ether–nitrobenzene	20°C.	D.F.	52
Ethylene bromide–1-nitropropane	120°C.	C.D.	20

TABLE 2-1. VAPOR-LIQUID EQUILIBRIUM DATA (*Continued*)

System	Constant T or P	Technique*	Ref.
Ethylene chlorohydrin–toluene	760 mm.	C.D.	44
Formic acid–water	750 mm.	C.D.	27
Furfural–2-methylfuran	738 mm.	C.D.	18
–water	760 mm.	—	19
n-Heptane–*n*-pentane	10.3, 20.6, 31.1 atm.	D.B.	9
–toluene	760 mm.	C.D.	6
n-Hexane–methanol	45°C.	B.M.	12
Hydrochloric acid–water	751 mm.	C.D.	28
Isobutylene–propane	14.1, 21.1, 28.2, 35 2, 42.2 atm.	C.D.	41
Isopentane–propane	0 to 180°C.	D.B.	49
Isopropanol–nitromethane–water	760 mm.	C.D.	42
–water	760 mm.	C.D.	42
	760 mm.	C.D.	21
	760 mm.	—	19
Methanol–methyl acetate	39 8°C.	D.D.	5
–nitrobenzene	20°C.	D.F.	52
–water	59.4°C.	D.D.	54
	60, 115, 165 p.s.i.a.	C.D.	31
	200, 350, 500, 760 mm.	C.D.	29
Methyl ethyl ketone–water	200, 350, 500, 760 mm.	C.D.	29
Nitric acid–water	760 mm.	—	19
Nitrogen–oxygen	0.4 to 45 atm.	C.M.	11
Nitromethane–water	760 mm.	C.D.	42
n-Octane–toluene	760 mm.	C.D.	6
Phenol–*m*-cresol	760 mm.	D.D.	36
–*o*-cresol	760 mm.	D.D.	36
–water	40, 260, 760 mm.	D.D.	36
	43.4, 58.4, 73.4, 98.4°C.	C.D.	43
n-Propanol–water	30.5°C.	D.D.	54
Pyridine–water	80.1°C.	C.D.	56
Sulfuric acid–water	760 mm.	—	57

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CHAPTER 3

CALCULATION OF VAPOR-LIQUID EQUILIBRIA

The calculation of vapor-liquid equilibria is important because of the difficulty of obtaining experimental values and because it gives a picture of the general behavior of liquid-vapor mixtures. The basic thermodynamic relationships for such equilibria are complex, and in most cases they involve unknown factors or quantities which limit their usefulness until simplifying assumptions are made. It is the limitations of the simplifying assumptions that restrict the applicability of the thermodynamic relations. However, even for the cases in which such approximations do not give satisfactory quantitative relationships, they do serve as valuable criteria for estimating the behavior of a distillation process and they help to clarify and explain the divergencies that are frequently noted.

VAPOR PRESSURES OF COMPLETELY MISCIBLE LIQUID MIXTURES AT CONSTANT TEMPERATURE

Raoult's Law. When one liquid is dissolved in another, the partial pressure of each is decreased. Assume two liquids, the molecules of which are the same size and which mix without the complicating effects of molecular association, chemical combination, and the like. In an equimolecular mixture of two such liquids, each unit of surface area of the liquid mixture will have in its surface half as many molecules of each component as exist in the liquid surface of that component in the pure state. Hence the escaping tendency or partial pressure of each component in the mixture will be half that of the same component in the pure state. Similarly, in a mixture containing 25 mol per cent of the first component and 75 mol per cent of the second, the first will exert a partial pressure 25 per cent of that of this component in the pure state. In more general terms, for any such mixture the partial pressure of any component will equal the vapor pressure of that component in the pure state times its mol fraction in the liquid mixture. This generalization is known as *Raoult's law* (Ref. 19). It is expressed in the relationship, $p_a = P_a x_a$, where p_a is the partial pressure of the component A in the solution, x_a is its mol fraction in the solution and

P_a is the vapor pressure of the component A in its pure state. If P_b is the vapor pressure of pure B, and p_b the partial pressure in the mixture, then $p_b = P_b x_b$. This relationship is shown graphically in Fig. 3-1, where the abscissas are the mol per cent of the two components, A and B, in the liquid portion. The ordinates are pressures, C being the vapor pressure of pure A, and D that of pure B. The lines AD and BC represent the partial pressures of the components over any mixture, while the line CD is the total pressure of the mixture.

Deviations from Raoult's Law. In view of the above assumptions as to equal molecular size, absence of association, etc., it is not surprising to find Raoult's law honored more in the breach than in the observance. Nonetheless mixtures of some organic liquids, such as benzene-toluene, deviate from it but little. The deviations of mixtures of hydrocarbons of the same series can usually be neglected for a great deal of engineering work, and even for mixtures of a number of series this is often true. For mixtures of aromatic and aliphatic compounds, however, the deviations are often large, though never of the order of magnitude of such mixtures as hydrochloric acid and water, and the like. Organic stereoisomers obey it very closely as would be expected from the considerations upon which it is based. However, the data for the great majority of other liquids, when plotted as shown in Fig. 3-1, deviate largely from the lines BC and AD. When very near points C and D, the deviation for any component is slight if that component is present in very large amount. This ordinarily is expressed by saying that in dilute solution Raoult's law applies to the solvent. Since the deviation from Raoult's law may be either positive or negative, great or small, this graphical generalization serves as a convenient standard of comparison.

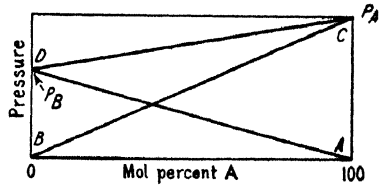


FIG. 3-1. Schematic diagram for Raoult's law.

Henry's Law. This relation is a modification of Raoult's law which applies to the vapor pressure of the *solute* in dilute solutions, just as Raoult's law applies to that of the *solvent*. Henry's law states that the partial pressure of the solute is proportional to its concentration in the solution. In analogy with Raoult's law it may be expressed by the equation

$$p_a = kx_a \tag{3-1}$$

where p_a = partial pressure of the solute
x_a = its mol fraction
k = an experimentally determined constant

Comparison with Raoult's law, $p_a = P_a x_a$, shows that they differ only in the constant that determines the slope of the line. This constant is the vapor pressure of the pure component in the one case, while it must be experimentally determined in the other. A typical partial pressure curve for one component of a liquid mixture is shown in Fig. 3-2 where BD is the range over which Henry's law applies, while Raoult's law holds over the section EC, where C is the vapor pressure of pure A.

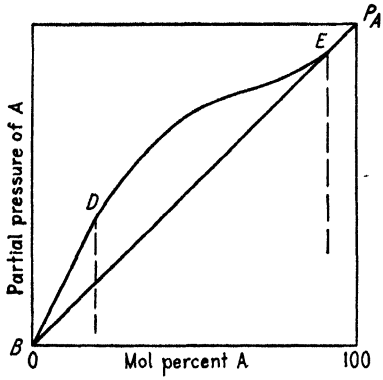


FIG. 3-2. Schematic diagram for Henry's law.

Dalton's Law. The most commonly used rule for relating the composition of the vapor phase to the pressure and temperature is Dalton's law (Ref. 8). It states that the total pressure is equal to the sum of the partial pressures of the components present, *i.e.*,

$$p_1 + p_2 + p_3 + \cdots = \pi \tag{3-2}$$

where p_1, p_2, p_3 = partial pressures of components 1, 2, and 3
π = total pressure

For Dalton's law partial pressure is defined as the pressure that would be exerted by a component alone at the same molal concentration that it has in the mixture. If the perfect-gas laws apply to each of the components individually and to the mixture, it can be shown that the partial pressure of any component is equal to the mol fraction times the total pressure, *i.e.*,

$$p_1 = y_1 \pi \tag{3-3}$$

where y_1 is the mol fraction of component 1 in the vapor.

This is the most commonly used form of Dalton's law. For the prediction of vapor-liquid equilibria, it is usually combined with Raoult's law to give

$$y_1 \pi = x_1 P_1 \tag{3-4}$$

This combination gives the composition of vapor as a function of the composition in the liquid with the total pressure and vapor pressure as proportionality constants. Thus, fixing the temperature and the total pressure defines π, P_1, and the relationship between the vapor and the liquid composition. It is to be noted that the assumption of Raoult's and Dalton's laws leads to the conclusion that the relationship between the vapor and liquid composition of a given component is a function of the temperature and pressure only and is independent of the other components present. The only influence of the other components is the fact that they may be instrumental in determining the relationship between the temperature and the total pressure.

Deviations from Dalton's Law. Both forms of Dalton's law are satisfactory for engineering uses for most gas mixtures at pressures of 1 atm. or lower because deviations from the perfect-gas law are usually small in this region. However, when higher pressures are encountered and appreciable deviations from the perfect-gas law are found, Dalton's law becomes unsatisfactory. A later section of this chapter will consider methods of handling these deviations, but as a general rule Dalton's law should not be employed for cases in which the deviations from the perfect-gas law are large.

Volatility. The term "volatility" is loosely used in the literature, generally as equivalent to vapor pressure when applied to a pure substance; as applied to mixtures, its significance is very indefinite. Because of the convenience of the term, the volatility of any substance in a homogeneous liquid will be defined as its partial pressure in the vapor in equilibrium with that liquid, divided by its mol fraction in the liquid. If the substance is in the pure state, its mol fraction is unity and its volatility is identical with its vapor pressure. If the substance exists in a liquid mixture that follows Raoult's law, its volatility as thus defined is still obviously equal to its vapor pressure in the pure state; *i.e.*, its volatility is *normal*. If the partial pressure of the substance is lower than that corresponding to Raoult's law, *e.g.*, that of hydrochloric acid in dilute aqueous solutions, the volatility according to this definition is less than that of the pure substance, *i.e.*, is abnormally low. Similarly, if the partial pressure is greater than that indicated by Raoult's law, *e.g.*, that of aniline dissolved in water, the volatility is abnormally high. The volatility of a substance in mixtures is therefore not necessarily constant even at constant temperature but depends on the character and amount of the components.

Relative volatility is the volatility of one component divided by that of another. Since the volatility of the first component of a mixture, β_a, is its partial pressure, p_a divided by its mol fraction x_a, and that of the second $\beta_b = p_b/x_b$, the volatility of the first relative to the second is $\beta_a/\beta_b = p_a x_b/p_b x_a$. When Dalton's law applies, the relative amount of any two components in the vapor (expressed in mols) is $y_a/y_b = p_a/p_b$.

$$\frac{\beta_a}{\beta_b} = \frac{y_a}{y_b}\frac{x_b}{x_a} = \alpha \tag{3-5}$$

Owing to the utility of the mol fraction ratio given in Eq. (3-5) for distillation calculations, the group will be used as the definition of the relative volatility for all cases whether or not Dalton's law applies. Thus, in this text the relative volatilities of any two components in a mixture will be defined as the ratio of y/x values for the two components.

In any constant-boiling homogeneous liquid mixture the composition of the liquid is identical with that of the vapor in equilibrium with it, *i.e.*, $x = y$; hence, the relative volatility α is unity.

Volatility, like vapor pressure, increases rapidly with rise in temperature. The *ratio* of the pressures of pure substances does not change rapidly with change in temperature, and the same is true of relative volatilities; whereas vapor pressures always increase with temperature, *relative volatility* may, in a given case, either rise or fall, depending on the nature of the components. At constant temperature the relative volatility is independent of the liquid composition for systems that obey Raoult's law; however, for most systems α is a function of the liquid composition and frequently is greater than unity for one range of concentrations and less than unity for another range. Relative volatility is the most important factor in determining ease of separation of components by distillation.

Raoult-Dalton Laws; Example. The data of Rhodes, Wells, and Murray (Ref. 20) indicate that the system phenol–*o*-cresol obeys Raoult's law. Using the vapor pressure data tabulated at the top of page 31 together with Raoult's and Dalton's laws, construct the following curves for 75 mm. Hg abs. pressure:

1. Temperature–mol fraction diagram giving both the vapor and the liquid curves.
2. Mol fraction of phenol in vapor phase, y, vs. the mol fraction of phenol in liquid, x.
3. Relative volatility vs. the mol fraction of phenol in the liquid.
4. Mol fraction of phenol in the vapor vs. the mol fraction of phenol in the liquid, using as an average value of the relative volatility, α, the arithmetic mean value of α at $x = 0$, and $x = 1.0$.

DATA ON VAPOR PRESSURES

T, °C.	Phenol, pressure, mm.	o-Cresol, pressure, mm.
113.7	75.0	57 8
114.6	78.0	59.6
115.4	81.0	61 6
116 3	84.0	63 8
117.0	87.0	65.7
117.8	90.0	68 0
118 6	93.0	70.5
1919.4	96.0	73.0
120 0	98 6	75.0

Solution

1. Let mol fraction of phenol in liquid = x_p.
2. Choose a temperature, T.
3. Read vapor pressures at T: P_p, P_{oc}.
4. Employ the combined form of Raoult's and Dalton's laws.

$$x_p P_p + x_{oc} P_{oc} = 75$$

$$x_p = \frac{75 - P_{oc}}{P_p - P_{oc}}$$

$$y_p = \frac{x_p P_p}{75}$$

TABLE 3-1

T, °C.	P_{oc}	P_p	x_p	y_p	α	y_p (calc. on $\alpha = 1.313$)
113.7	57.8	75	1.0	1.0	1.295	1.0
114.6	59.6	78	0.837	0.87	1 31	0.87
115.4	61.6	81	0.691	0.746	1.315	0.748
116.3	63.8	84	0.555	0.622	1.315	0.622
117.0	65.7	87	0.437	0.507	1.32	0.506
117.8	68	90	0.318	0.383	1.323	0.382
118.6	70.5	93	0.2	0 248	1.32	0.247
119.4	73.0	96.7	0.084	0.109	1.325	0.108
120.0	75	99.8	0	0	1.33	0

$$\alpha = \frac{y_p x_{oc}}{y_{oc} x_p} = \frac{y_p(1 - x_p)}{(1 - y_p)x_p}$$

$$y_p = \frac{x_p \alpha}{1 + (\alpha - 1)x_p}$$

These values are plotted in Fig. 3-3. An α of 1.313 was chosen to calculate equilibrium curve. Within the accuracy of the calculations, this curve was coincident with the curve obtained in Part 2.

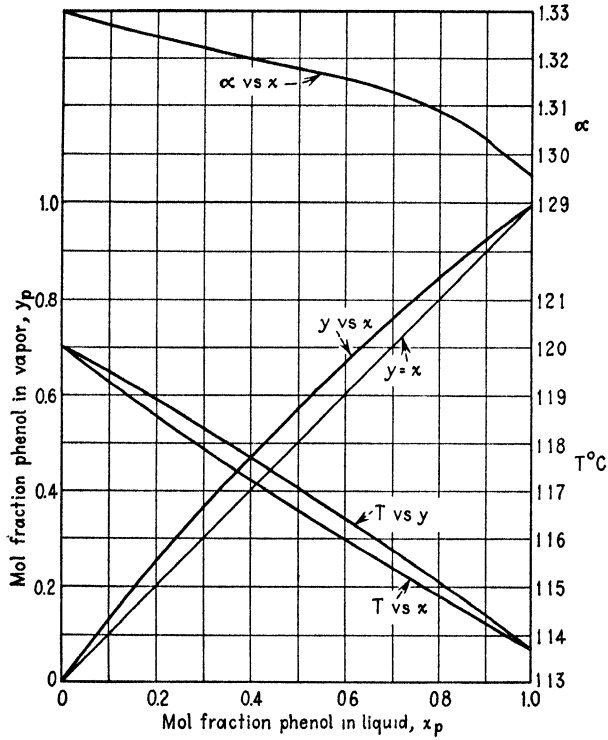


FIG. 3-3. Calculated vapor-liquid equilibria for system phenol—*o*-cresol.

Basic Thermodynamic Relations. Most mixtures are not ideal, and the deviations from Raoult's law are large in all but a limited number of cases. For such mixtures, the basic thermodynamic relations can be employed to formulate expressions for the equilibria involved. It is not the purpose of this text to consider in detail the thermodynamics of solutions, but an appreciation of this subject is necessary for an understanding of the following sections on vapor-liquid equilibria. For background in this field the reader is referred to any modern text on chemical thermodynamics.

In the study of vapor-liquid equilibria, one of the most important of the basic relations states that at equilibrium the fugacity of a given

component is the same in all phases. Thus,

$$f_V = f_L \tag{3-6}$$

where f is the fugacity, V refers to the vapor phase, and L refers to the liquid phase. This same equation applies to each component in the mixture at equilibrium. To be useful for distillation calculations, the fugacity terms in Eq. (3-6) must be related to the compositions of the phases. For isothermal changes in conditions at constant composition, the change in fugacity is evaluated by the following equation:

$$RT\, d \ln f = v\, dp \tag{3-7}$$

where R = gas law constant
T = absolute temperature
f = fugacity
v = molal volume, *i.e.*, volume of 1 mol of substance under consideration = partial molal volume for a component in a mixture
p = pressure

For mixtures that obey the perfect-gas law this relationship makes the fugacity of a component in the vapor proportional to the partial pressure of the component, *i.e.*, the mol fraction of the component times the total pressure. It is customary to define the standard state for fugacity such that it is numerically equal to the pressure for a perfect gas; *i.e.*, the proportionality factor is made equal to unity.

The fugacity of a component in an ideal liquid is defined as proportional to the mol fraction of that component in the liquid times the fugacity of the pure component under the same temperature and pressure as the mixture. Thus for a perfect gas and an ideal solution,

$$f_V = y_1\pi = f_L = f_{p1}^* x_1 \tag{3-8}$$

where y_1 = mol fraction of component 1 in vapor
x_1 = mol fraction of component 1 in liquid
π = total pressure of mixture
f_{p1}^* = fugacity exerted by the pure liquid at temperature T under total pressure, π

This equation is not identical with Raoult's law, and f_{p1}^* is not in general equal to P_1, the vapor pressure of pure liquid 1 at temperature T, because the liquid is under a pressure different from P_1. This difference can be evaluated by Eq. (3-7).

$$f_{p1}^* = f_{p1} e^{\int_{P_1}^{\pi} v\, dp/RT} \tag{3-9}$$

where v = partial molal volume of liquid 1
P_1 = vapor pressure of pure component 1 at temperature T
R = gas-law constant
f_{p1} = fugacity of component 1 at temperature T and pressure P_1
Over the pressure range usually involved, v is essentially constant and

$$f^*_{p1} = f_{p1} e^{v(\pi - P_1)/RT} \tag{3-10}$$

Equations (3-8) and (3-10) differ from Raoult's law by the exponential term, and f_{p1} instead of P_1. These corrections are frequently small and can be neglected. However, in high-pressure equilibria the corrections become large, and even an ideal solution would not be expected to obey Raoult's law because (1) the components in the liquid mixture at a given temperature are under a different total pressure than they would be as pure components and (2) the fugacity of the pure liquid is not equal to its vapor pressure. An equation similar to (3-8) applies to each of the components in an ideal mixture.

Most mixtures do not obey Raoult's law or the corrected Raoult's law given by Eqs. (3-8) and (3-10). The deviations from the ideal solution laws can be due to the vapor phase, the liquid phase, or both. These deviations are both chemical and physical in nature. The most important factors involved in these deviations are believed to be (1) the fact that the molecules have volume and (2) the fact that the molecules exert forces on each other that may be attractions, or repulsions, or actual chemical effects.

The problem for such mixtures becomes one of relating the fugacities of the components in the vapor and the liquid to the composition and the physical properties of the components, and it has been found desirable to consider separately the deviations in the liquid and the vapor phase.

VAPOR PHASE

Pure gases or gaseous mixtures approach agreement with the perfect-gas law if the pressures are low enough.[1] Under these conditions, the volume of the gaseous mixture is so large that the volume of the molecules is a negligible percentage of the total, and the molecules on the

[1] The reduction to zero pressure may cause a change in species. Thus, if the pressure on pure Cl_2 gas is reduced, the gas may never obey the perfect-gas law since, before exact agreement is reached, the Cl_2 will dissociate to atomic chlorine. The atomic chlorine should agree with the perfect-gas law at zero pressure, and for all practical engineering purposes diatomic chlorine gas agrees with the gas laws at a pressure less than one-tenth of an atmosphere, and under these conditions, the dissociation to atomic chlorine is negligible at moderate temperatures.

average are so far apart that the forces between them are small. As the pressure increases, the effect of the volume of, and the attraction between, the molecules become so great that deviations from the ideal solution laws become large and it is necessary to employ the fugacity instead of the pressure in vapor-liquid relationships. The isothermal change in fugacity of a mixture of given composition can be calculated by integrating Eq. (3-7). In this integration the absolute value of the fugacity at any given state can be arbitrarily chosen. Defining the fugacity equal to the pressure for a perfect gas, Eq. (3-7) can be rearranged as follows:

$$RT\,d\ln f = v\,dp \tag{3-11}$$

$$RT\,d\ln\frac{f}{p} = (v_a - v_i)\,dp \tag{3-12}$$

where v_a = actual molal volume
v_i = perfect-gas law molal volume

Fugacity of Pure Gases. In order to utilize Eq. (3-12) it is necessary to have information on the actual molal volume as a function of the pressure at the temperature in question. The lack of these data limits the utility of this equation. However, it has been found possible to develop correction factors to the perfect-gas law that will apply to almost all gases and gaseous mixtures. One method of representing these deviation factors is to plot the compressibility factor μ, which is equal to PV/RT, as a function of the reduced pressure at constant reduced temperature, where reduced pressure P_R is the pressure divided by the critical pressure, and reduced temperature T_R is the absolute temperature divided by the absolute critical temperature. Such a plot is given in Fig. 3-4; similar plots for higher temperatures and pressures are available.

These plots give good agreement with the experimental data for most vapors with the exception of hydrogen and helium, both of which have low critical temperatures and pressures. It has been found possible to use the plot for these two gases by using modified critical constants. However, neither gas is particularly important in vapor-liquid equilibria.

Using the μ factor correction, the actual molal volume v_a becomes $\mu RT/p$. When this is substituted in Eq. (3-12), it gives

$$RT\,d\ln\frac{f}{p} = (\mu - 1)RT\frac{dp}{p} \tag{3-13}$$

or

$$d\ln\frac{f}{p} = (\mu - 1)\frac{dp}{p} \tag{3-14}$$

If this equation is integrated from zero pressure up to the pressure in question, the limits on the left-hand side are from 1.0 to the ratio of fugacity to pressure at the pressure in question. Thus ln (f/p) equals the integral from zero to p of $(\mu - 1)\, dp/p$.

Equation (3-14) can be modified and dP_R/P_R used instead of dp/p. The limits of integration then become from zero to P_R. At constant temperature, it is therefore obvious that the integral is a function only of P_R, T_R, and the variables determining μ. If the μ values are a func-

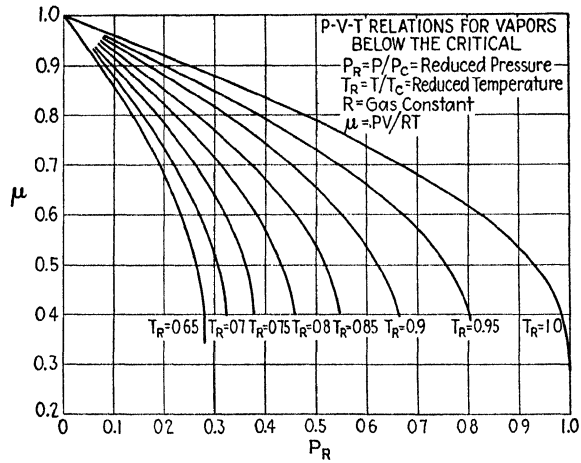


FIG. 3-4.

tion of P_R and T_R only, the ratio of fugacity to the pressure is also a unique function of the reduced pressure and the reduced temperature. Integration using the μ plots have been made, and one method of presentation is given in Fig. (3-5).

With an accuracy suitable for engineering purposes these plots make it possible to calculate the fugacity of a pure gas at any temperature and pressure, assuming that the critical constants of the gas are known. Even in cases where the critical constants are not known, highly satisfactory methods have been developed for estimating these constants.

Fugacity of Mixtures. When applying the μ plot and the fugacity plot to mixtures, the question arises as to the proper values to be employed for the critical temperature and the critical pressure. Mixtures have critical temperatures and critical pressures, but it has been found that these values do not give satisfactory results when used for calculating reduced temperatures and pressures to be used with the charts, but pseudocritical constants can be calculated which give better agreement. For these pseudo constants one of the best methods of

calculation is the mol fraction average; *i.e.*, the calculated pseudocritical temperature is equal to the sum of the products of the mol fraction times the critical temperature for each of the pure components. The pseudocritical pressure is calculated in an analogous manner. When these values are employed for calculating the reduced tempera-

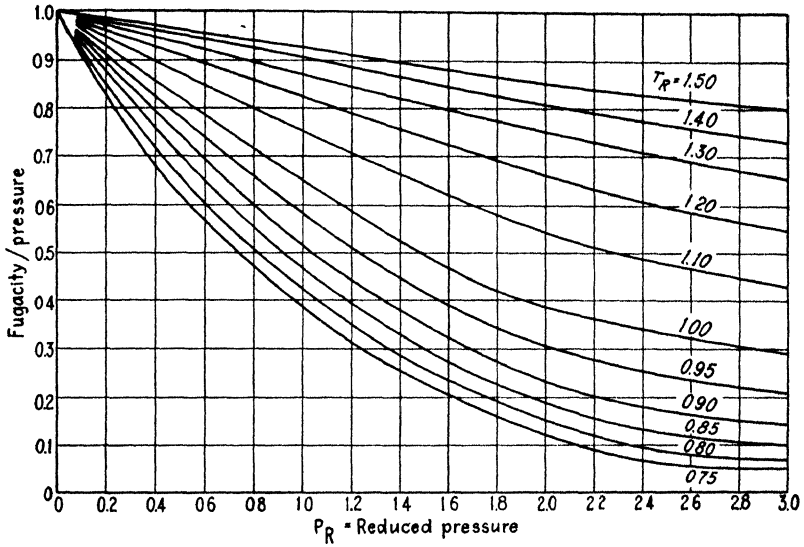


FIG. 3-5 Fugacities of hydrocarbon vapors.

ture and pressure, satisfactory agreement is attained with μ charts. It should be emphasized that these calculated values are not true critical constants for the mixture.

Fugacity of a Component in a Mixture. In vapor-liquid equilibria, vapor mixtures are generally involved, and Eq. (3-6) requires, not the fugacity of the mixture, but the fugacity of the components in the mixture. In order to estimate the fugacity of the components in the mixture, Lewis and Randall (Ref. 16) suggested that this fugacity was equal to the mol fraction of the component in the mixture times the fugacity of the pure component at the same temperature and total pressure as the mixture. Thus,

$$f_{v1} = y_1 f_{\pi 1} \tag{3-15}$$

where f_{v1} = fugacity of component in vapor
y = mol fraction in vapor
$f_{\pi 1}$ = fugacity of pure component at same temperature and pressure as mixture

The value of f_x can be estimated from the fugacity plots, and this fugacity rule has been widely used in vapor-liquid and other equilibrium calculations. It can be shown that this is true if the vapor mixture obeys Amagat's law, which states that the volume of a mixture is equal to the sum of the volumes of the pure components when these are measured at the same temperature and total pressure as the mixture. Experimental data have shown this rule to be a reasonable approximation if the pressures are not too high; at high pressures, large deviations are found to occur. However, in essentially all cases it is better than Dalton's law.

A large number of additional methods of predicting the fugacity of a component in a gaseous mixture have been proposed. In general these have been based on different rules for the PVT relations of mixtures used to evaluate the fugacity. None of them has been satisfactory in all cases although some of them are better than the Lewis and Randall rule, but they are more difficult to employ, and a number of them require more experimental information than is usually available. This complexity has greatly limited their use.

The Lewis and Randall fugacity rule can generally be used with reasonable accuracy for vapor mixtures up to pressures approximately one-half of the critical pressure; *i.e.*, 300 to 500 p.s.i.g. in the case of hydrocarbons. This is only an approximate limit, but large errors will not generally be encountered at values of P_R, based on the pseudocritical pressure of the mixture, less than one-half. If the components in the mixture are of similar types, *i.e.*, O_2 and N_2, ethylene and ethane, benzene and toluene, etc., satisfactory results can often be obtained for values of P_R as high as 0.9. The rule is not satisfactory at the critical condition. Figure 3-5 gives values of the fugacity for conditions where a pure component cannot exist as a vapor. These values were obtained by using the Lewis and Randall rule with actual vapor-liquid equilibria to calculate the fugacity values.

Instead of using the reduced correlations, it is thermodynamically possible to calculate the true fugacity of a component in a gaseous mixture, if sufficient PVT data are available. The methods of calculation are very laborious and require PVT data of high precision. This method has not had any significant engineering use owing to the great difficulty in obtaining the extensive PVT data necessary and the work involved in making the calculations from such data. Its chief value is furnishing an exact basis to evaluate the empirical rules.

LIQUID PHASE

Deviations from ideal solution laws are more important for the liquid phase than those for the vapor phase because they are encountered even at low pressures, and in general their magnitudes are greater. The densities of the liquids are such that the volume of the molecules and the forces between them are always significant. Deviations for the liquid phase are of at least two main types: (1) Those due to the fact that the vapor does not obey the perfect-gas law. Thus, if one tries to define the fugacity of a component in the liquid phase as mol fraction times the vapor pressure of the pure component, this can be satisfactory only when the vapor at a pressure equal to the vapor pressure is essentially a perfect gas. (2) The deviations that are due to special phenomena associated with the liquid phase such as associations or chemical combinations.

Gas Law Deviation. In the ideal solution the partial pressure, or activity, of a component was equal to the mol fraction times the vapor pressure of the pure component at the temperature in question. If the pressures are such that the vapor under these conditions does not obey the perfect-gas law, then a fugacity correction should be applied. For such a case, the Lewis and Randall rule would be

$$f_{L1} = x_1 f_{p1}^* \tag{3-16}$$

where f_{L1} = fugacity of component 1 in liquid phase
x_1 = mol fraction of component 1 in liquid phase
f_{p1}^* = fugacity of pure liquid component 1 at temperature and pressure of mixture

In general the total pressure is different from the vapor pressure of the pure components at the same temperature, and f_{p1}^* is not equal to the fugacity of the pure liquid under its own vapor pressure, f_{p1}. They are related:

$$f_{p1}^* = f_{p1} e^{\int_{P_1}^{\pi} v\, dp/RT}$$

or, assuming v = constant,

$$f_{p1}^* = f_{p1} e^{v(\pi - P_1)/RT} \tag{3-17}$$

where π = total pressure
v = partial molal volume of component
P_1 = vapor pressure of component at temperature of mixture
T = absolute temperature
R = gas law constant

From equilibrium consideration, the fugacity of the pure liquid under its own vapor pressure, f_{p1}, is equal to the fugacity of the saturated vapor at the same temperature and pressure. Thus, Fig. 3-5 can be used to evaluate f_p, but it should be emphasized that the reduced pressure is calculated at the *vapor* pressure of the pure component instead of at the *total* pressure. This application of the fugacity to the liquid phase corrects for the fact that the vapor is not a perfect gas, but it does not correct for the special phenomena associated with the liquid phase.

Combining Eqs. (3-15), (3-16), and (3-17) gives

$$y_1 f_{\pi 1} = x_1 f_{p1} e^{v(\pi - P_1)/RT} \tag{3-18}$$

In using Eq. (3-18) certain difficulties are encountered. Considering the vapor phase, the temperature and pressure of the mixture usually are intermediate between those of the pure components, and it is often found that the temperature and pressure are such that one of the pure components at these conditions would be superheated vapor and the other a supersaturated vapor. The superheated vapor offers no difficulty since it is easily possible to obtain PVT data for superheated vapors, and this type of information was used to develop the μ plots. However, it is essentially impossible to obtain PVT data on supersaturated vapors since they tend to condense easily. In the liquid phase such difficulties are not encountered at moderate temperatures. If the temperature is not too high, the vapor pressure of the components can be obtained and the fugacity can be determined. However, at higher temperatures, it is possible for the temperature of the mixture to be greater than the critical temperature of one of the components and still have this component present in the liquid phase in large amounts. The calculation of f_p for such conditions is complicated because data are not available on the vapor pressure of a liquid above the critical temperature.

Empirical rules have been developed to handle these fugacity difficulties for the vapor and liquid. In the case of the liquid phase, it has been customary to plot the logarithm of the vapor pressure vs. the reciprocal of the absolute temperature. It is well known that such plots are remarkably straight, and for fugacity calculations the straight line has been extrapolated past the critical to higher temperatures. Such extrapolations have given satisfactory results. In the case of the vapor, the problem is more complex, and the main solution has been to calculate f_π by Eq. (3-18), using the experimental data and the estimated value of f_p. This has been done for a number of mixtures,

TABLE 3-2. *K* VALUES

Temp., °F.	Absolute pressures, atm.											
	1	2	3	4	5	6	8	10	20	30	40	50
						CH_4						
−90	41	21	14	10 5	8 5	7 1	5 4	4 3	2 3	1 7	1 3	1 2
−20	83	42	28	21	17	14	10 6	8 6	4 4	3 0	2 3	2 0
20	115	57	38	29	23	19	14 5	11 5	6 0	4 1	3 1	2 6
100	190	96	64	48	38	32	24	19	9 7	6 6	5 0	4.1
200	300	150	100	76	61	51	39	31	15 5	10 3	7.8	6.2
400	580	290	195	145	116	98	73	58	29	19.5	14.5	12.0
						C_2H_4						
−60	7.7	3 9	2 6	2 0	1 6	1 4	1.1	0 9	0 51	0 42	0 38	0 36
20	24 5	12 3	8 3	6 3	5 1	4 2	3 2	2 6	1 44	1 08	0 92	0 84
100	51	25 5	17 2	13 0	10 2	8 8	6 5	5 3	2 8	2.0	1 6	1 35
200	103	51	34 5	26	20 5	17 2	13 0	10 4	5 3	3 7	2 8	2 35
300	172	87	58	44	35	29	22	17 5	8 9	6 0	4 7	3 9
400	265	132	88	66	54	45	34	27	14	9 2	7 0	5 6
						C_2H_6						
−60	4 8	2 4	1.6	1 3	1 0	0 88	0 69	0 58	0 36	0 29	0 26	0.26
20	16 0	8 0	5 4	4 1	3 3	2 8	2 1	1 75	1 0	0 79	0 69	0 66
100	34	17	11 7	8 8	7 1	5 9	4 5	3 7	2 0	1 45	1 18	1.0
200	71	36	24	18	14 5	12 1	9 2	7 4	3 8	2 7	2.1	1 75
300	123	62	42	32	25 5	21	16	13	6 6	4 5	3 4	2 8
400	195	98	66	50	40	33	25	20	10	6 9	5 2	4 3
						C_3H_6						
−60	0 79	0.35	0 27	0 21	0 17	0 15	0 12	0 10	0 07	0 06	0 05	0 05
20	4 5	2 3	1 55	1 2	0.95	0 82	0 64	0 54	0 34	0 28	0 26	0 26
100	12 2	6 3	4 3	3 3	2 6	2 2	1 7	1 4	0 82	0 66	0 59	0.58
200	30	15	10	7 7	6 2	5 2	4 0	3 2	1 75	1 3	1 1	0 98
300	59	30	20	15	12	10	7 7	6 2	3 2	2 3	1 8	1 5
400	100	50	33	25	20	16	12 5	10 0	5 2	3.6	2 8	2.3
						C_3H_8						
−60	0 67	0 34	0 23	0 18	0 15	0 13	0 10	0 09	0 06	0.05	0 05	0 05
20	3 7	1 9	1 3	0 98	0 8	0 69	0.54	0 45	0 29	0 24	0 23	0 24
100	11	5 5	3 7	2 8	2 3	1.9	1 5	1.2	0 75	0.6	0 54	0 54
200	25	13	8 6	6 5	5 2	4 4	3.4	2 8	1 5	1 1	0 95	0.85
300	51	25	17	13	10	8.7	6.5	5 3	2 8	2.0	1 6	1 3
400	85	43	29	22	17	14	11	8 8	4 5	3.1	2 4	2.0
						i-C_4H_{10}						
−60	0 18	0 09	0 07	0.05	0 04	0 04	0 03	0 03	0 02	0.02	0 02	0 02
20	1 2	0 63	0 43	0 34	0 28	0 24	0 19	0 16	0 11	0.10	0 09	0 11
100	4 5	2 3	1 6	1 2	1.0	0.86	0 67	0 57	0 36	0.31	0 30	0 32
200	13	6 7	4 5	3 5	2 8	2.4	1 8	1 5	0 91	0 74	0 68	0 67
400	51	25	17	13	10 5	8 8	6.6	5 3	2 9	2 0	1 6	1 4
600	125	63	42	32	25.5	21 5	16	13	6.6	4.5	3.4	2 9

TABLE 3-2. *K* VALUES (*Continued*)

Temp., °F.	Absolute pressures, atm.											
	1	2	3	4	5	6	8	10	20	30	40	50
						n-C_4H_{10}						
−60	0 10	0 05	0 03	0 03	0 02	0 02	0 02	0 01	0 01	0 01	0 01	0 01
20	0 81	0 43	0 29	0 23	0 19	0 16	0 13	0 11	0 07	0 07	0 07	0 08
100	3 4	1 7	1 2	0 9	0 73	0.63	0 5	0 43	0 28	0 24	0 24	0 26
200	10 5	5.4	3 7	2 8	2 3	1.9	1.5	1 3	0 77	0 64	0 61	0 61
400	43	21	14	11	8 8	7.3	5 5	4.5	2 4	1 7	1 4	1 3
600	110	54	36	27	22	18	14	11	5.6	3 9	3 0	2 5
						i-C_5H_{12}						
−20	0 09	0.05	0 03	0 02	0 02	0 02	0 01	0 01	0 01	0 01	0 01	0 01
60	0 63	0.32	0 22	0.17	0 14	0 13	0.10	0 08	0 06	0 06	0.06	0 07
100	1 3	0 67	0 47	0 36	0 30	0 26	0 21	0 18	0 12	0 11	0 12	0 14
200	5.2	2 7	1 8	1 4	1 2	1 0	0 77	0 65	0 43	0 37	0.37	0 40
400	25.5	13	8.8	6 7	5 4	4 5	3 4	2 8	1 6	1 2	1 0	0 94
600	69	34	23	17	14	12	8 7	7.0	3.7	2 6	2 1	1 72
						n-C_5H_{12}						
−20	0 05	0 03	0 02	0 02	0.01	0 01	0.01	0 01	—	—	—	—
60	0.47	0 24	0 17	0 13	0.11	0 09	0 07	0 06	0 05	0 04	0 04	0 05
100	1.0	0.53	0 36	0 28	0 23	0 20	0 16	0 14	0 10	0 09	0 09	0 10
200	4.3	2.2	1 5	1 2	0 96	0 83	0 65	0 55	0 36	0 32	0 32	0 35
400	22 5	12	7.8	5 9	4 8	4 0	3 1	2 5	1 4	1.1	0 93	0 89
600	65	33	22	17	13 4	11 2	8 5	6.9	3 6	2 6	2 0	1 7
						n-C_6H_{14}						
60	0 13	0 07	0 05	0 04	0 03	0 02	0 02	0 02	0 01	0 01	0 02	0 02
100	0.35	0.18	0 13	0 10	0 08	0 07	0 06	0 05	0 04	0 04	0 04	0 05
200	1.9	0.97	0 67	0 51	0 43	0 37	0 30	0 26	0 18	0 17	0 18	0 22
400	13 6	7 0	4 7	3.6	2 9	2 5	1 9	1 6	0 98	0 80	0 77	0 77
600	42	21	14	11	8.6	7 2	5.5	4.4	2.4	1.8	1 5	1 3
						n-C_7H_{16}						
100	0 11	0 05	0 04	0.03	0 03	0.02	0 02	0.02	0.01	0 01	0 02	0.02
200	0.83	0.43	0.29	0 23	0 20	0 17	0.14	0.12	0 09	0.09	0.10	0 14
400	8.4	4 3	2 9	2 2	1 8	1.6	1 2	1 0	0 67	0.60	0.60	0 67
600	29	15	10	7.6	6.1	5.1	3.9	3.2	1.75	1.3	1.1	1.05
						n-C_8H_{18}						
100	0.04	0 02	0 01	0 01	0 01	—	—	—	—	—	—	—
200	0 39	0 20	0.14	0 11	0.09	0 08	0.07	0.06	0.04	0.05	0.06	0.09
400	5.3	2.6	1.8	1.4	1.15	1.0	0.78	0 67	0 47	0 45	0 49	0.57
600	19.5	10	6.7	5.1	4.2	3.5	2.7	2.25	1 3	1.1	0.95	0.91

and these calculated values for the supersaturated region have been plotted on the fugacity plot and used as a basis for extrapolating the curves based on PVT relations. In most cases, the extrapolation is not large, and the deviations should not be too great.

When equilibrium calculations are to be made a number of times for the same components, it is convenient to simplify the equation and express it the form of $y_1 = Kx_1$ where

$$K = \frac{f^*_{p1}}{f_\pi} \tag{3-19}$$

K values based on fugacity calculations have been prepared for the common lower molecular weight petroleum hydrocarbons and are presented in Table 3-2. On the whole, they are equivalent to results obtained with Eq. (3-18) and the fugacity plots, but they are simpler to use in vapor-liquid calculations. If such values have not been calculated for the components in question, it is necessary to employ the fugacity plot.

Equation (3-18) includes the exponential correction term, and this term is appreciable at high pressure. However, it has been found that in hydrocarbon systems up to about 600 p.s.i. the agreement is about the same whether or not this factor is included. This is probably because the values of f_π in Fig. 3-5 for the supersaturated region were evaluated from experimental data without the use of the exponential term. If an exact method of computing the fugacity of the components were available, the exponential correction should be applied. However, in using values from this figure it is suggested that it be neglected for distillation calculations.

Equation (3-18) has been found to give good agreement with the experimental data on mixtures of similar compounds up to pressures equivalent to a reduced pressure of about 0.5. It has been extremely useful in high-pressure calculations associated with petroleum mixtures. The vapor-liquid equilibrium data for mixtures of oxygen and nitrogen are well correlated by the equation. Basically, the equation should be useful for any mixtures that agree reasonably well with Raoult's law at low pressure. At pressures greater than $P_R = 0.5$, the agreement is not so good, but it is still a useful approximation. However, this method of calculation breaks down completely in the neighborhood of the critical region of the mixtures. This condition will be considered in a later section.

The fugacity equation can be applied to each component in the mix-

ture. It is suitable for multicomponent mixtures as well as for binary mixtures.

Example Illustrating the Use of Fugacity Corrections. Scheeline (Ref. 23) has studied the vapor-liquid equilibrium of propane-isobutylene mixtures at high pressures. Using the data and notes given below, make a y,x plot for a total pressure of 400 p.s.i.a. showing

1. Experimental data.
2. Curve calculated by Raoult's law.
3. Curve calculated by using fugacity corrections.

CRITICAL CONSTANTS

	P_c, p.s.i.a.	T_c, °F.
C_3	632	209
C_4	580	291

1. Experimental data:

Absolute pressure, p.s.i.a.	Temp., °F.	x_{C_3}	y_{C_3}
400	242	0 086	0 140
400	222	0 286	0 413
400	206	0.438	0.572
400	190	0.648	0.754
400	184	0 734	0.827
400	175	0.847	0.895

Solution. Calculate the y,x values at 400 p.s.i.a. and 200°F.

2. Raoult's and Dalton's laws:

$$x_3P_3 + x_4P_4 = 400$$
$$x_4 = 1 - x_3$$
$$x_3 = \frac{400 - P_4}{P_3 - P_4}$$

At 200°F. from Table 3-3 $P_3 = 569$ p.s.i.a., $P_4 = 232$ p.s.i.a., $x_3 = 0.498$, and $y_3 = 0.498\ (569/400) = 0.709$.

3. Fugacity corrections:

$$y_3f_{\pi 3} = x_3f_{p3} \qquad x_4 = 1 - x_3$$
$$y_4f_{\pi 4} = x_4f_{p4} \qquad y_4 = 1 - y_3$$

Combining and solving,

$$x_3 = \frac{f_{\pi 4} - f_{p4}}{(f_{p3}f_{\pi 4}/f_{\pi 3}) - f_{p4}}$$

$T_{R4} = {}^{66}\!/_{151} = 0.88$; $P_{R4} = {}^{232}\!/_{580} = 0.403$; $\pi_{R4} = {}^{400}\!/_{580} = 0.69$

$T_{R3} = {}^{66}\!/_{669} = 0.986$; $P_{R3} = {}^{569}\!/_{632} = 0.90$; $\pi_{R3} = {}^{400}\!/_{632} = 0.633$

From Fig. 3-5,

$$\left(\frac{f_p}{p}\right)_3 = 0.665 \qquad \left(\frac{f_\pi}{\pi}\right)_3 = 0.755$$

$$\left(\frac{f_p}{p}\right)_4 = 0.78 \qquad \left(\frac{f_\pi}{\pi}\right)_4 = 0.64$$

$$f_{p3} = 0.665 \times 569 = 379 \qquad f_{\pi 3} = 0.755 \times 400 = 302$$

$$f_{p4} = 0.78 \times 232 = 181 \qquad f_{\pi 4} = 0.64 \times 400 = 256$$

$$x_3 = \frac{256 - 181}{\frac{379(256)}{302} - 181} = 0.53$$

$$y_3 = \frac{0.53(379)}{302} = 0.665$$

In a similar manner, the data in Tables 3-3 and 3-4 were calculated.

TABLE 3-3. RAOULT'S LAW
(400 p.s.i.a.)

T, °F.	P_4, p.s.i.a.	P_3, p.s.i.a.	x_3	y_3
255	399	—	0	0
237	305	730	0.224	0.409
220	287	688	0.282	0.485
200	232	569	0.498	0 709
180	187.5	470	0.753	0.885
163	150	400	1.0	1.0

TABLE 3-4 FUGACITY CALCULATION

T, °R.	697	680	660	640	623
T_{R3}	1.041	1.017	0.986	0.957	0.931
P_3	730	688	569	470	400
P_{R3}	1.16	1.09	0.90	0.744	0.633
$(f_p/P)_3$	0 64	0.65	0.665	0.68	0.71
f_{p3}	466	447	379	319	284
$(f_\pi/\pi)_3$	0.8	0.78	0 755	0.74	0.71
$f_{\pi 3}$	320	312	302	296	284
T_{R4}	0.929	0.906	0.88	0.853	0 830
P_4	305	287	232	187.5	150
P_{R4}	0.526	0.495	0.40	0.324	0.258
$(f_p/P)_4$	0.76	0.77	0.78	0.79	0.82
f_{p4}	232	221	181	148	123
$(f_\pi/\pi)_4$	0.68	0.655	0.64	0.605	0.59
$f_{\pi 4}$	272	262	256	242	236
x_3	0.244	0.266	0 53	0.832	1.0
y_3	0.356	0.381	0.665	0.896	1.0

The experimental data and the calculated results are shown in Fig. 3-6. It will be noted that the fugacity calculations for the y,x values are in excellent agreement with the experimental results, but that Raoult's and Dalton's laws give values of the vapor composition that are much too high. For average relative volatility these laws give 2.45; fugacity, 1.77; and experimental, 1.71.

Solution Deviations. The corrections so far considered have been limited to those associated with the fact that the vapor does not obey the perfect-gas law. A large number of mixtures, in fact most of them, do not obey the ideal solution laws even at very low pressure, and the deviations cannot be predicted by the use of gas-phase fugacity corrections. The deviations are the result of the forces between the molecules in the liquid phase, and these forces can be very largely due

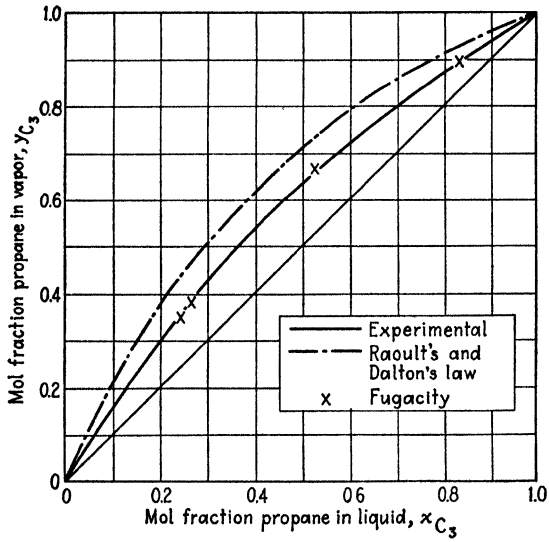


FIG. 3-6. Vapor-liquid curves for system propane-isobutylene.

to the close packing in the dense phase. The theoretical method of attack for the liquid phase is not so simple as for the vapor phase. For the vapor-phase calculations a convenient basis was possible because at low pressure all vapor mixtures obey the perfect-gas laws. Thus the deviations could be calculated on the basis of the differences between the mixture at low pressure and at high pressure. In the case of the liquid phase no such convenient basis is possible. Thus a mixture of ethyl alcohol and water does not agree with the ideal solution rules under any practical conditions of temperature and pressure.

Basic thermodynamic relations are available for the liquid phase, but their practical application has not been so well developed as those for the vapor phase. They are helpful in formulating general concepts and are directly applicable in certain special cases. One of the most useful relations follows:

$$x_1\left(\frac{\partial \ln f_1}{\partial x_1}\right)_{\pi,T} + x_2\left(\frac{\partial \ln f_2}{\partial x_1}\right)_{\pi,T} + x_3\left(\frac{\partial \ln f_3}{\partial x_1}\right)_{\pi,T} + \cdots = 0 \quad (3\text{-}20)$$

For a binary mixture $dx_1 = -dx_2$, Eq. (3-20) reduces to

$$x_1\left(\frac{\partial \ln f_1}{\partial x_1}\right)_{\pi,T} = x_2\left(\frac{\partial \ln f_2}{\partial x_2}\right)_{\pi,T} \quad (3\text{-}21)$$

If the pressure is such that the vapor satisfies the perfect-gas law, then the equation can be modified as follows:

$$x_1\left(\frac{\partial \ln p_1}{\partial x_1}\right)_{\pi,T} = x_2\left(\frac{\partial \ln p_2}{\partial x_2}\right)_{\pi,T} \quad (3\text{-}22)$$

This equation is called the Duhem equation (Ref. 9). Equation (3-20) is applicable to any system of any number of components, but the Duhem equation is limited to a binary mixture under conditions such that the perfect-gas law applies to the vapor.

Theoretically these equations apply only to a process carried out at *constant temperature* and *constant total pressure* on the liquid phase. In most mixtures encountered in distillation, if one varies the composition at constant temperature, the total pressure also varies and Eqs. (3-20) to (3-22) are not strictly applicable. The equations would apply for this constant-temperature case if some method other than the vapor pressure were employed to exert pressure on the liquid which was adjusted to keep the total pressure constant; *e.g.*, a gas insoluble in the liquid could be added to the vapor to maintain constant total pressure. Actually, these equations apply satisfactorily for most engineering purposes if they are employed at constant temperature and a variable total pressure equal to the vapor pressure. The error introduced is that due to the change in the fugacity of the liquid with the total pressure which can be calculated by Eq. (3-7). A more exact relationship for binary mixtures at constant temperature is

$$x_1\left[\frac{\partial \ln (p_1/p_1^*)}{\partial x_1}\right]_T = x_2\left[\frac{\partial \ln (p_2/p_2^*)}{\partial x_2}\right]_T \quad (3\text{-}23)$$

where $\partial \ln p_1^*$ is the fractional change in effective pressure of component

1 due to the change in total pressure on the liquid. It is calculated by Eq. (3-7).

$$\frac{d \ln p_1^*}{d\pi} = \frac{v_1}{RT} \tag{3-24}$$

where π = total pressure on liquid phase
v_1 = partial molal volume of component 1
R = gas law constant
T = absolute temperature

The value of $\partial \ln p_2^*$ is calculated in the same manner with v_2 instead of v_1. In most cases these corrections at constant temperature are small in comparison to the change in fugacity due to the change in composition; for this reason Eq. (3-22) is frequently accepted as applying to mixtures under their own vapor pressure. It can be in serious error at high pressure, and Eq. (3-23) would be more exact.

For constant pressure, variable temperature conditions, Eq. (3-22) generally is unsatisfactory owing to the rapid change in fugacity or vapor pressure of a liquid with changes in temperature. Equation (3-22) can be modified to compensate for this effect as follows:

$$x_1 \left[\frac{\partial \ln (p_1/P_1')}{\partial x_1} \right]_\pi = x_2 \left[\frac{\partial \ln (p_2/P_2')}{\partial x_2} \right]_\pi \tag{3-25}$$

where $\partial \ln P_1'$ is the fractional change in the partial pressure of component 1 at a composition x_1, with the change in temperature. It is evaluated by

$$\frac{\partial \ln P'}{\partial T} = \frac{\Delta H'}{RT^2} \tag{3-26}$$

where $\Delta H'$ is the heat of vaporizing 1 mol of the component from the solution into a vacuum.

Equations (3-23) and (3-25) can be combined and expressed in the more exact fugacity form,

$$x_1 \left[\frac{\partial \ln (f_1/f_1^0)}{\partial x_1} \right] = x_2 \left[\frac{\partial \ln (f_2/f_2^0)}{\partial x_2} \right] \tag{3-27}$$

where $\partial \ln f^0$ is the fractional change of the fugacity of the component in the liquid phase at the given composition and is calculated by Eq. (3-26) for constant pressure changes and by Eq. (3-24) for constant temperature changes.

The Duhem equation as such cannot be integrated, but if a relationship between the pressure of one of the components and the mol frac-

tion is available, it is possible to calculate the relationship between the partial pressure of the other component and the mol fraction. This is not of any real engineering utility for predicting vapor-liquid equilibria since in general when the partial pressure of one component is known that of the other component is also known. However, the Duhem equation is useful in checking experimental data and also in guiding the development of correlations. For example, Eqs. (3-22) to (3-27) can be used to evaluate the accuracy of vapor-liquid equilibrium data. Consider the case of a binary mixture at constant temperature for which the liquid-vapor data are available. By Eq. (3-23),

$$\left.\begin{aligned} d \ln \frac{p_1}{p_1^*} &= -\frac{x_2}{1 - x_2} d \ln \frac{p_2}{p_2^*} \\ \ln \left(\frac{p_1}{p_1^*}\right)_b - \ln \left(\frac{p_1}{p_1^*}\right)_a &= -\int_a^b \frac{x_2}{1 - x_2} d \ln \frac{p_2}{p_2^*} \end{aligned}\right\} \tag{3-28}$$

If one experimental value of p_1/p_1^* is taken as a base, then the value of this ratio can be determined at other compositions by the integration of the right-hand side of the equation. This integration must usually be performed graphically, and a convenient method is plotting $x_2/(1 - x_2)$ vs. $\ln (p_2/p_2^*)$ and determining the area under the curve. The experimental data for p_2 as a function of x_2 and one value of p_1 allow the value of p_1 to be predicted at other compositions. If corrections for total pressure on p_1^* and p_2^* are to be included, they can be evaluated from the experimental total pressure data or by summing the calculated value of p_1 and p_2; in the latter case, the integration becomes trial and error.

Constant pressure conditions are more important in distillation calculations than constant temperature, and for this condition Eq. (3-25) can be modified to

$$\left.\begin{aligned} d \ln \frac{y_1}{P_1'} &= -\frac{x_2}{1 - x_2} d \ln \frac{y_2}{P_2'} \\ \ln \left(\frac{y_1}{P_2'}\right)_b - \ln \left(\frac{y_1}{P_1'}\right)_a &= -\int_a^b \frac{x_2}{1 - x_2} d \ln \frac{y_2}{P_2'} \end{aligned}\right\} \tag{3-29}$$

The evaluation of the P' terms involves the heat of vaporizing 1 mol of the component from the mixture. At moderate pressure this is equal to the latent heat of vaporization at the same temperature plus the heat effects of mixing the liquids at this temperature and bringing them to the total pressure. As an approximation the latent heat of vaporization of the pure liquids can be employed in Eq. (3-26), but it will not give satisfactory results if (1) the heat of mixing is large or (2)

the total pressure is so high that the pressure-enthalpy corrections for the vapor are large.

One of the cases in which the Duhem equation is of real utility in determining vapor-liquid equilibria is where the analysis of the composition of the two phases offers serious difficulties. In such a case, if it is possible to prepare known mixtures of the two components and to determine their equilibrium total pressure at a given temperature, these data can be used with the Duhem equation to calculate the composition of the equilibrium vapor.

Activity Coefficient. Because there are no convenient conditions for the liquid mixture upon which to base calculations, it is customary to use the pure liquids before they are mixed as the basis, and then calculate the deviations that result from the mixing operation. The deviations in the liquid phase are summed up in what is termed an activity coefficient. Thus Raoult's law and the idealized fugacity law are modified by the insertion of a factor on the right-hand side.

$$p_1 = y_1\pi = \gamma_1 P_1 x_1 \tag{3-30}$$

$$f_1 = y_1 f_{\pi 1} = \gamma_1 f_{p1} x_1 \tag{3-31}$$

The value of the activity coefficient, γ, is the factor that will make these equations correct for the case in question. All deviations other than those associated with the gas law are lumped into the one value, and the problem is thus made into one of predicting the activity coefficient. These factors will be different for each component, but they are interrelated by Eq. (3-20) and, for a binary mixture, Eqs. (3-21), (3-22), (3-30), and (3-31) become

$$x_1 \left(\frac{d \ln \gamma_1}{dx_1}\right)_{\pi,T} = x_2 \left(\frac{d \ln \gamma_2}{dx_2}\right)_{\pi,T} \tag{3-32}$$

The methods that have been used for predicting the activity coefficient are either empirical or semitheoretical, the theoretical part being the use of thermodynamic equations to direct the development of empirical rules. A number of rules have been proposed (Refs. 3, 5, 13, 15, 28), but the two most commonly used methods of estimating the activity coefficients for solutions of the type employed in distillation are the Margules and Van Laar equations.

Example Illustrating the Use of Duhem Equation. Data on the vapor-liquid equilibria of benzene–*n*-propanol and ethanol-water are given in the accompanying tables. Using the Duhem equation, check the consistency of the data.

EQUILIBRIUM DATA FOR THE SYSTEM BENZENE–*n*-PROPANOL
[From Lee (Ref. 14). Temp. = 40°C.]

Mol fraction in liquid		Partial pressure, mm. Hg	
Benzene	*n*-Propanol	Benzene	*n*-Propanol
0	1.0	0	50.2
0.099	0.901	59.6	42.4
0.209	0.791	95.0	39.6
0.291	0 709	118.6	37.4
0.360	0.640	132.2	36.2
0.416	0.584	139.1	35.9
0.508	0.492	149.2	34.3
0.700	0.300	161.6	31.4
0.820	0.180	167 4	28.6
0 961	0.039	175 6	15.7
1 0	0	183 5	0

VAPOR PRESSURE DATA FOR SYSTEM ETHANOL-WATER
(Ref. 12)

T, °C.	Vapor pressure, mm.	
	Ethanol	Water
76	693	301.4
78	750	327.3
80	812	355.1
82	877	384 9
84	950	416.8
86	1,026	450.9
88	1,102	487.1
90	1,187	525.76
92	1,280	566.99
94	1,373	610.9
96	1,473	657.6
98	1,581	707.3
100	1,693	760.0

ETHANOL-WATER EQUILIBRIUM DATA AT NORMAL BAROMETRIC PRESSURE (Ref. 4)

T, °C.	Mol fraction of ethanol	
	Liquid x	Vapor y
95.7	0.0190	0.1700
90.0	0.0600	0.3560
86.4	0.1000	0 4400
84.3	0.1600	0.5040
83.3	0.2000	0 5285
82.3	0.2600	0.5570
81.8	0.3000	0 5725
81.2	0.3600	0.5965
80.7	0.4000	0 6125
80.2	0.4600	0.6365
79.8	0.5000	0.6520
79.4	0.5600	0.6775
79.13	0.6000	0.6965
—	0.6600	0.7290
78.6	0.7000	0.7525
—	0.7600	0.7905
78.3	0.8000	0 8175
—	0.8600	0.8640
78.17	0 8943	0.8943

Solution for Benzene–n-Propanol System at Constant Temperature. Using Eq. (3-28) given on page 49,

$$d \ln \frac{p_1}{p_1^*} = -\frac{x_2}{1 - x_2} d \ln \frac{p_2}{p_2^*}$$

$$\ln \left(\frac{p_1}{p_1^*}\right)_b - \ln \left(\frac{p_1}{p_1^*}\right)_a = -\int_a^b \frac{x_2}{1 - x_2} d \ln \frac{p_2}{p_2^*}$$

The right-hand side of this equation requires graphical integration. At the low pressures involved the variation in the values of p_1^* and p_2^* will be neglected. In order to reduce the variation in the groups involved, the equation was rearranged to

$$\ln \frac{p_{1a}}{p_{1b}} = -\frac{1}{2} \int_{p_{2b}}^{p_{2a}} \frac{x_2}{(1 - x_2)p_2^2} d(p_2)^2$$

The values utilized for preparing the graphical integration plot are given in the first five columns of Table 3-5. As a basis for calculations, propanol was taken as component 1 and benzene as component 2. As the check point, the value for the partial pressure of propanol of 28.6 mm. Hg at a mol fraction of propanol of 0.180 was chosen.

TABLE 3-5. BENZENE–*n*-PROPANOL

x_2	$1 - x_2$	p_2	$10^{-4}p_2^2$	$\frac{10^4 x_2}{(1-x_2)p_2^2}$	$\ln \frac{p_1}{28.6}$	$p_{1\,\text{calc}}$	$p_{1\,\text{exp}}$	$y_{2\,\text{calc}}$	$y_{2\,\text{exp}}$	$\frac{100\,\Delta y}{y-x}$
0	1.0	0	0	—	—	—	50.2	—	0	—
0.099	0.901	59.6	0 356	0.309	0.554	49.8	42.4	0.545	0 585	9.2
0.209	0.791	95.0	0 903	0 293	0.472	45.8	39.6	0.675	0.706	6.2
0.291	0.709	118.6	1.406	0.292	0.398	42.6	37.4	0.736	0.760	5.1
0.360	0.640	132.2	1.747	0.322	0.346	40.4	36.2	0.767	0.783	3.8
0.461	0 584	139.1	1.933	0.408	0.312	39.1	35.9	0.781	0.795	4 2
0.508	0.492	149.2	2.225	0 464	0.249	36.7	34.3	0.803	0.814	3.6
0 700	0.300	161.6	2.612	0.894	0.118	32.2	31.4	0.833	0.838	3.6
0 820	0.180	167 4	2 800	1.625	0.0	28 6	28.6	0.855	0 855	0.0
0 961	0.039	175.6	3 080	8.0	−0.673	14.6	15.7	0 923	0.917	11.4
1.0	0	183.5	3 367	0	—	—	0	—	1 0	—

The sixth column of the table gives the area on each side of the check point, and these are of course equal to the left-hand side of the equation with the base value, p_{1b}, equal to 28.6. The seventh column lists the calculated values for the partial pressure of propanol, and the eighth column gives the experimental values. The agreement is not so good as would be desired but is a fair correlation. When the partial pressure values are converted to mol fractions in the vapor, the agreement appears somewhat better. The ninth and tenth columns of the table give calculated and experimental values for mol fractions of benzene in the vapor phase. The last column of the table gives the difference in these vapor compositions as a percentage of the difference between the experimental vapor and liquid compositions. Most of the calculated points are within 5 per cent of the experimental points on this basis, and this is probably reasonably good accuracy for vapor-liquid equilibrium measurement.

Solution for Ethanol-Water at Constant Pressure. For this case, it is convenient to use the mol fraction form of Eq. (3-29) instead of partial pressures.

$$d \ln \frac{y_1}{P_1'} = -\frac{x_2}{1-x_2} d \ln \frac{y_2}{P_2'}$$

$$\ln \left(\frac{y_1}{P_2'}\right)_b - \ln \left(\frac{y_1}{P_1'}\right)_a = -\int_a^b \frac{x_2}{1-x_2} d \ln \frac{y_2}{P_2'}$$

For convenience in plotting, this equation was rearranged to

$$\ln \frac{(y_1/P_1')_b}{(y_1/P_1')_a} = -\frac{1}{2} \int_{(y_2/P_2')_a}^{(y_2/P_2')_b} \frac{x_2}{(1-x_2)(y_2/P_2')^2} d\left(\frac{y_2}{P_2'}\right)^2$$

The integration of this equation requires a knowledge of the variations of P' with temperature. Equation (3-26) indicates that the variation of the pressure with the temperature could be calculated if the heat of vaporization of 1 mol of the component from the solution into a vacuum were known. This heat of vaporiza-

tion differs from the true heat of vaporization of the liquid by two main effects: (1) enthalpy effect due to mixing of the liquid phase and (2) enthalpy effects resulting from nonideal behavior of the vapor phase. In the present case the pressure is low enough that the vapor-phase effects should be very small, and for illustration purposes the enthalpy of the mixing in the liquid phase will be neglected. On the basis of such an assumption $d \ln P'$ becomes equal to $d \ln P$, where P is the vapor pressure of the pure component at the temperature in question. With this modification and the data given in the table, it is possible to carry out the integration. The results of such calculations are given in Table 3-6. The first five columns of

TABLE 3-6. ETHANOL-WATER

x_2	y_2	P_2	$10^5 \left(\frac{y_2}{P_2}\right)^2$	$\frac{10^{-3}x_2}{[(1-x_2)(y_2/P_2)]^2}$	$\ln \frac{y_1/P_1}{0.000318}$	$10^3 \frac{y_1}{P_1}$	P_1	y_1	y_2 calc	$\frac{100\,\Delta y}{y-x}$
0 019	0 170	1450	0 138	14 0	1.428	1.325	647	0 856	0 144	17.2
0 060	0 356	1180	0 926	6 9	1 387	1 272	527	0 670	0 330	8.8
0 100	0 440	1035	1 808	6.1	1.359	1 237	459	0 568	0 432	2 4
0 2	0.528	916	3 325	7 5	1 308	1.177	404	0 475	0 525	0 9
0.3	0.572	865	4 40	9.7	1 262	1 122	380	0.426	0.574	0.7
0.4	0.612	827	5 48	12.2	1 203	1 058	363	0.384	0 616	1.9
0.5	0 652	802	6 60	15 2	1.129	0.984	351	0 345	0 655	2.0
0.6	0 696	782	7.90	19 0	1 019	0.880	343	0.304	0 694	2 1
0.7	0 752	769	9 57	24 4	0 839	0 736	337	0.248	0 752	0 0
0.8	0.817	760	11.54	34.7	0.555	0 554	333	0 184	0 816	5 9
0.8943	0 8943	757	13.96	60 6	0	0.318	332	0.1057	0 8943	0

this table give the values of the groups used for preparing the graphical integration plot. Ethanol was taken as component 2, and the check point for the system was taken at the azeotrope. The sixth column gives the measured areas from the azeotrope and is therefore equal to the left-hand side of the equation. The seventh column gives calculated mol fraction in the vapor divided by vapor pressure for the water component. The ninth column lists the calculated mol fractions of water vapor. The tenth column gives the calculated values of alcohol in the vapor and is obtained by subtracting the ninth column from 1. This column is directly comparable to the second column and indicates that, except for the first two points, the agreement is excellent. These first two points are at low composition and may be somewhat in error. The last column in the table gives the percentage deviations.

Margules Equation. Margules (Ref. 17) developed an expression for the activity coefficient of the components in a binary mixture by taking empirical expressions for these coefficients as follows:

$$\ln \gamma_1 = ax_2 + bx_2^2 + cx_2^3$$
$$\ln \gamma_2 = a'x_1 + b'x_1^2 + c'x_1^3$$

When the Margules equations for the activity coefficients are substituted in Eq. (3-32), the following relations are obtained:

$$x_1 \frac{d \ln \gamma_1}{dx_1} = -x_1 \frac{d \ln \gamma_1}{dx_2} = -(ax_1 + 2bx_1x_2 + 3cx_1x_2^2)$$
$$x_2 \frac{d \ln \gamma_2}{dx_2} = -x_2 \frac{d \ln \gamma_2}{dx_1} = -(a'x_2 + 2b'x_1x_2 + 3c'x_2x_1^2)$$

By Eq. (3-32) the right-hand side of the two preceding equations must be equal for all compositions, and this relation will be satisfied when the coefficients of corresponding terms are equal; thus, using $x_1 = 1 - x_2$ and equating the components of the corresponding terms gives the following solution:

$$\left.\begin{aligned} a &= 0 \\ c' &= -c \\ a' &= 0 \\ b' &= \frac{2b + 3c}{2} \\ \ln \gamma_1 &= bx_2^2 + cx_2^3 \\ \ln \gamma_2 &= bx_1^2 + \tfrac{3}{2}cx_1^2 - cx_1^3 \end{aligned}\right\} \qquad (3\text{-}33)$$

It will be noted that the equations have two independent constants. However, only one experimental point is needed to evaluate both of these, since one determination of the vapor-liquid equilibrium for a binary mixture gives both γ_1 and γ_2, and these values can be used to evaluate the constant. If more data are available, it is convenient to plot the logarithm of the activity coefficient divided by the mol fraction squared for the other component vs. the mol fraction of one of the components. If the Margules equation agrees with the data, both of the activity coefficients should give straight lines which are parallel when plotted in this manner, and the slope should be equal to the value of the constant c. The intercepts will be different but can be used for evaluating the constant b. The two activity coefficient equations can be arranged to plot as a single line.

$$\left.\begin{aligned} \frac{\ln \gamma_1}{x_2^2} &= b + cx_2 \\ \frac{\ln \gamma_2}{x_1^2} &= b + c(0.5 + x_2) \end{aligned}\right\} \qquad (3\text{-}34)$$

Thus if $(\ln \gamma_1)/x_2^2$ is plotted vs. x_2, and $(\ln \gamma_2)/x_1^2$ is plotted against $0.5 + x_2$, they will both give a line of slope c and intercept b. Such a plot facilitates the evaluation of the constants.

The constants in the Margules equation are a function of temperature; thus, if one experimental point is used to evaluate them, then

assuming the equation to apply, they should be suitable for other compositions at the same temperature. A generalized relationship for the effect of temperature on the activity coefficient is not available, but as an approximation it is suggested that the constants be taken as inversely proportional to the one-fourth power of the absolute temperature. Thus,

$$\frac{T^{0.25} \ln \gamma_1}{x_2^2} = b'' + c''x_2$$

$$\frac{T^{0.25} \ln \gamma_2}{x_1^2} = b'' + c''(0.5 + x_2) \qquad (3\text{-}34a)$$

Van Laar Equation. Van Laar (Ref. 25) attempted to follow a more theoretical approach than did Margules. He based his derivation on the thermodynamic changes occurring on the mixing of pure liquids. Two of the basic thermodynamic equations relating to isothermal processes are

$$\Delta\bar{F} = \Delta\bar{H} - T\,\Delta\bar{S} \qquad (3\text{-}35)$$

$$d\Delta\bar{F} = RT\,d \ln f \qquad (3\text{-}36)$$

where $\Delta\bar{F}$ = partial molal change in free energy
$\Delta\bar{H}$ = partial molal change in enthalpy
T = absolute temperature
$\Delta\bar{S}$ = partial molal change in entropy
f = fugacity

For an ideal mixture, there is no change in volume when the mixing is carried out at constant temperature and under a constant total pressure, and there are no heat effects. Thus $\Delta\bar{H}$ is equal to zero, and the partial molal change in free energy is equal to $-T\,\Delta\bar{S}$ for each component. For such an ideal solution, the partial molal entropy of mixing is $-R \ln x$, and the fugacity is proportional to the mol fraction (Lewis and Randall rule). However, in most actual solutions there are changes of volume on mixing, heat effects, and the entropy of mixing differs from that for an ideal solution.

The combination of Eqs. (3-30) and (3-31) with Eq. (3-36) gives

$$RT\,d \ln \gamma = d\,\Delta\bar{F}_a - d\,\Delta\bar{F}_i = d\,\Delta\bar{F}_e \qquad (3\text{-}37)$$

and

$$\Delta\bar{F}_e = \Delta\bar{H}_e - T\,\Delta\bar{S}_e \qquad (3\text{-}38)$$

where $\Delta\bar{F}_a$ = actual partial molal free energy
ΔF_i = partial molal free energy of ideal solution of same composition $= RT \ln x$
$\Delta\bar{F}_e$ = excess partial molal free energy $= \Delta F_a - \Delta\bar{F}_i$
$\Delta\bar{H}_e$ = excess partial molal enthalpy $= \Delta\bar{H}_a$
$\Delta\bar{S}_e$ = excess partial molal entropy $= \Delta S_a - R \ln x$

Thus in calculating the activity coefficient, γ, the value of the excess partial molal free energy is desired. If methods were available for calculating the partial molal entropy and enthalpy effects upon mixing, the deviations from the ideal solution law could be determined. As a first approximation for systems containing molecules not too dissimilar, several writers (Refs. 11, 22, 25) have recommended the assumption of a solution in which only the internal energy change on mixing is different from an ideal solution. In such solutions, which Hildebrand terms "regular," the partial molal volume of each component remains constant, and the change in entropy is equal to that of an ideal solution; *i.e.*, complete "randomness" exists. Thus the only deviation of a "regular" solution from an ideal solution is due to the fact that there is an excess partial molal internal energy of mixing. In addition to these assumptions, Van Laar attempted to calculate the internal energy of mixing by the use of the van der Waals equation of state. The assumptions used by Van Laar in deriving his equations are

1. $\Delta\bar{S}_e = 0$; *i.e.*, $\Delta\bar{S}_a = \Delta\bar{S}_i$.
2. No volume change on mixing.
3. The van der Waals equation applies to each of the components and to the mixture, both as liquids and as vapors.
4. The van der Waals constants of the mixture can be calculated from the constants of the pure constituents.

For a van der Waals fluid, *i.e.*, one that satisfies the relationship $P = \frac{RT}{V - b} - \frac{a}{V^2}$, it can be shown that

$$\left(\frac{\partial E}{\partial \bar{V}}\right)_T = \frac{a}{V^2}$$

where E = internal energy
V = volume
a = van der Waals constant
T = absolute temperature

When this relationship is integrated from a vapor at zero pressure to the liquid state,

$$E_L - E_\infty = \int_\infty^{V_L} \frac{a}{V^2}\, dV = -\frac{a}{V_L} \tag{3-39}$$

Van Laar substituted the volume constant, b, of the van der Waals equation, for the molal volume of the liquid and used the values developed by other investigators (Refs. 2, 10) for evaluating the constants of a mixture.

$$\left.\begin{aligned} a_{\text{mix}} &= (x_1\sqrt{a_1} + x_2\sqrt{a_2} + x_3\sqrt{a_3} + \cdots)^2 \\ b_{\text{mix}} &= x_1 b_1 + x_2 b_2 + x_3 b_3 + \cdots \end{aligned}\right\} \tag{3-40}$$

where a_{mix}, b_{mix} = van der Waals constants of mixture
a_1,a_2,a_3, b_1,b_2,b_3 = van der Waals constants of pure components
For a binary mixture the internal energy of mixing the pure liquid components at constant temperature per mol of mixture is

$$\Delta E_L = E_{LM} - x_1 E_{L_1} - x_2 E_{L_2}$$

where ΔE_L = internal energy change in mixing per mol of mixture
E_{LM} = molal internal energy of liquid mixture
E_{L_1} = molal internal energy of pure component 1 as a liquid before mixing
E_{L_2} = molal internal energy of pure component 2 as a liquid before mixing

By Eq. (3-39) and using $b = V$,

$$\Delta E_L = \left(-\frac{a_{mix}}{b_{mix}} + E_{mix\,\infty}\right) - x_1\left(-\frac{a_1}{b_1} + E_{1\infty}\right) - x_2\left(-\frac{a_2}{b_2} + E_{2\infty}\right)$$

$$= -\frac{a_{mix}}{b_{mix}} + x_1\frac{a_1}{b_1} + x_2\frac{a_2}{b_2} + \left(E_{mix\,\infty} - x_1E_{1\infty} - x_2E_{2\infty}\right)$$

The last term is the internal energy of mixing of the vapors at zero pressure and is, therefore, equal to zero. The values of Eq. (3-40) give

$$\Delta E_L = \frac{x_1x_2b_1b_2}{x_1b_1 + x_2b_2}\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)^2 \tag{3-41}$$

From Eq. (3-41) the partial molal change in internal energy is

$$\frac{\partial(\Delta E)_L}{\partial n_1} = (\Delta\bar{E}_1)_L = b_1\left(\frac{x_2b_2}{x_1b_1 + x_2b_2}\right)^2\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)^2 \tag{3-42}$$

and on the basis of Van Laar's assumptions:

$$\ln\gamma_1 = \frac{(\Delta\bar{E}_1)_L}{RT} = \frac{\dfrac{b_1}{RT}\left(\dfrac{\sqrt{a_1}}{b_1} - \dfrac{\sqrt{a_2}}{b_2}\right)^2}{\left(1 + \dfrac{(b_1)}{(b_2)}\dfrac{x_1}{x_2}\right)^2} \tag{3-43}$$

combining constants,

$$\ln\gamma_1 = \frac{B/T}{\left(1 + A\dfrac{x_1}{x_2}\right)^2} \tag{3-44}$$

where $A = b_1/b_2$

$$B = \frac{b_1}{R}\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)^2$$

By combining Eq. (3-44) with Eq. (3-32),

$$\ln \gamma_2 = \frac{AB/T}{\left(A + \frac{x_2}{x_1}\right)^2} \tag{3-45}$$

Scatchard and Hildebrand obtained similar expressions without the use of a van der Waals fluid. They recommend evaluating the expression for $(\Delta E_1)_L$ as

$$V_1\left(\frac{x_2 V_2}{x_1 V_1 + x_2 V_2}\right)^2 \left(\sqrt{\frac{u_1}{V_1}} - \sqrt{\frac{u_2}{V_2}}\right)^2 \tag{3-46}$$

where u = internal energy of vaporization
V = molal volume

This leads to equations of the same form as Eqs. (3-44) and (3-45), except that

$$A = \frac{V_1}{V_2}$$

$$B = \frac{V_1}{R}\left(\sqrt{\frac{u_1}{V_1}} - \sqrt{\frac{u_2}{V_2}}\right)^2$$

It has been pointed out by Cooper (Ref. 7) that the same relationship can be obtained more simply than the method employed by Van Laar. What is desired in calculating the activity coefficient is the difference between the partial molal free energy of mixing of an actual solution and that of an ideal solution. If the excess free energy of mixing per unit volume of mixture is assumed proportional to the product of the volume fractions of the two components, an expression identical in form to the Van Laar equation is obtained. Thus,

$$\frac{\Delta F_e}{n_1 v_1 + n_2 v_2} = K' \frac{n_1 V_1}{n_1 V_1 + n_2 V_2} \frac{n_2 V_2}{n_1 V_1 + n_2 V_2} \tag{3-47}$$

where ΔF_e = excess free-energy change of mixing = actual free-energy change minus ideal free-energy change
n_1 = mols of component 1
n_2 = mols of component 2
V_1 = molal volume of component 1
V_2 = molal volume of component 2

But

$$\Delta \bar{F}_{e1} = RT \ln \gamma_1 = \left[\frac{\partial(\Delta F_e)}{\partial n_1}\right]_{n_2} \tag{3-48}$$

and

$$\ln \gamma_1 = \frac{K'V_1}{RT} \frac{1}{\left(\frac{x_1V_1}{x_2V_2} + 1\right)^2} \quad (3\text{-}49)$$

$$\ln \gamma_1 = \frac{B/T}{\left(\frac{x_1}{x_2}A + 1\right)^2} \quad (3\text{-}50)$$

where $B = K'V_1/R$

$A = V_1/V_2$

These equations are identical with those given by Van Laar, but the assumptions are somewhat different. In the case of the Van Laar, Scatchard, and Hildebrand derivations, both A and B should be positive, while in Cooper's equation B could be either positive or negative.

On the basis of the derivations, the two constants of the Van Laar equations and the modifications of it are related to the physical properties of the pure components. When the best values of the constants are chosen to fit the data, they usually do not agree with the predicted values, although the trends are approximately the same. Generally the constants are chosen to agree with the data, and the equations are used empirically.

As was the case with the Margules equation, two constants are involved. For a binary mixture one vapor-liquid equilibrium point will give the activity coefficients of both components and thus define the whole equation. The form of the equations are significantly different from that of the Margules. It includes a temperature correction, and the value of the constants should be independent of temperature. Thus an experimental determination at one temperature should allow equilibrium data to be calculated at other temperatures. There are several ways in which Van Laar equations can be rearranged to plot as a straight line in order that the data for more than one determination can be easily correlated. One of the most convenient methods of making such a plot is to use the reciprocal of the square root of the temperature times the logarithm of the activity of component 1, $1/(T \ln \gamma_1)^{1/2}$, vs. the ratio, x_1/x_2. A similar plot can be made for the other component. The plots should both be straight lines; the slopes and intercepts will be different but related because they are based on the same constants.

Clark Equation. For the vapor-liquid equilibria of a binary mixture at either constant pressure or constant temperature, Clark (Ref. 6) has suggested that the ratio of the mol fractions in one phase is a linear

function of the ratio of the mol fractions in the other phase, when the ratios are utilized such that the component in largest amount appears in the numerator.

Thus, when component 1 is present in largest amount,

$$\frac{y_1}{y_2} = a\frac{x_1}{x_2} + b \tag{3-51}$$

and, when component 2 is present in largest amount,

$$\frac{y_2}{y_1} = a'\frac{x_2}{x_1} + b' \tag{3-52}$$

Clark uses the value $x_1/x_2 = \sqrt{a'b/ab'}$ as the change-over point between the two equations. The use of these equations requires three experimental points. This greatly limits its utility.

Evaluation of Empirical Equations. Tucker (Ref. 24) and Mason (Ref. 18) have studied the agreement of the various equations with published experimental data. The data available were screened, and only those that gave good agreement with the Duhem-type equations were selected for the evaluation. The experimental data were plotted to evaluate the equation constants, and the average constants so obtained were used to recalculate the y,x curve. In distillation calculations the difference between the vapor and the liquid compositions gives a better indication of the ease of separation than the absolute value of the vapor composition. Mason therefore made the comparison on the basis of

$$\text{Per cent deviation} = \left[\frac{y_{\text{calc}} - y_{\text{exp}}}{(y - x)_{\text{exp}}}\right] 100$$

As a qualitative standard, he classified average deviation of 0 to 5 per cent as good, 5 to 11 per cent as fair, and greater than 11 per cent as poor. Some of the results are given in Table 3-7. The table gives the average deviation and the maximum deviation. In certain cases, the agreement between the experimental and the calculated values is very good but very poor in other cases. It is difficult to determine any definite types of mixtures that give good or poor agreement. However, in all cases, mixtures approaching immiscibility, *i.e.*, y,x curves that are nearly horizontal over an appreciable concentration region, gave poor agreement with the Margules and Van Laar equations. Good agreement was obtained with all the maximum boiling mixtures studied. These latter mixtures give negative values of the Van Laar

TABLE 3-7

System	Margules			Scatchard			Van Laar			Clark		
	Max. % dev.	Av. % dev.	Correlation	Max. % dev.	Av. % dev.	Correlation	Max. % dev.	Av. % dev.	Correlation	Max. % dev.	Av. % dev.	Correlation
Ethanol–water	14 6	4.5	Good	5 8	3 1	Good	5 7	4 4	Good	10 6	2.4	Good
Methanol–water	6 9	4 9	Good	6 2	5 1	Good	14 7	5 8	Good	2 3	1.0	Good
Ethylenebromide–1-nitropropane	23 8	5 8	Good	$V_1 = V_2$, see Margules		Good	8 2	2 9	Good			
Carbondisulfide–benzene	13.9	5 3	Good	6 7	3 0	Good	11 1	4 3	Good			
Benzene–aniline	1.5	0.5	Good	$V_1 = V_2$, see Margules		Good	2.0	0.5	Good			
Carbondisulfide–nitrobenzene*	2 5	1.8	Good	1 3	0 7	Good	7 5	2 7	Good			
Chloroform–nitrobenzene*	1 4	0 5	Good	0 8	0 2	Good	6 8	2 2	Good			
Ethyl ether–nitrobenzene*	0.7	0.3	Good	$V_1 = V_2$ see Margules		Good	11 8	4 2	Good			
Methanol–nitrobenzene*	4.1	1.7	Good	19 9	5 9	Good	16 2	5 5	Good			
Carbontetrachloride–benzene	6.6	3.6	Good	6 6	3 6	Good	15 0	6 2	Fair	18 2	8 5	Fair
Acetone–chloroform	12 5	4 3	Good	17.6	4 8	Good	52 9	13 5	Fair	55.2	13 5	Fair
Ethyl ether–acetone	21.7	6.0	Good	12 1	4 7	Good	21 0	8.5	Fair			
Benzene–phenol	0.8	0 5	Good	$V_1 = V_2$ see Margules		Good	50 0	16 5	Poor			
Benzene–nitrobenzene*	1.8	0.7	Good	1.8	0.8	Good	No correlation		Poor			
CS_2–isobutylene-chloride	14 7	7 0	Fair	16 4	6 8	Fair	14 2	6 7	Fair			
Isopentane–CS_2	23.3	9 0	Fair	26 8	9.1	Fair	10 9	6 5	Fair			
CCl_4–ethyl acetate	40.0	11.5	Fair	40 0	11.1	Fair	54 5	32 8	Poor	40 0	10.1	Fair
n-Heptane–toluene	53 5	9.6	Fair	53 4	9 8	Fair	15 9	8 9	Fair	8 7	4 2	Good
Benzene–*n*-propanol	53.3	8.6	Fair	68 4	11 4	Poor	18.8	17 8	Poor	16 3	4 7	Good
Methanol–benzene	23 0	8 5	Fair	65 2	18 4	Poor	76 8	28 8	Poor			
Water–pyridine	54.4	21.1	Poor	32 0	12 1	Poor	47 7	18.4	Poor	3 9	1.5	Good
CS_2–chloroform	23 2	11.2	Poor	14 7	13.9	Poor	23 5	16 3	Poor	12 3	4.5	Good
Ethyl ether–CS_2	65.0	32.1	Poor	50.0	21.3	Poor	40 0	15.5	Poor			
CS_2–acetone	29.1	16.0	Poor	33 7	18 8	Poor	94.4	59.2	Poor			
CS_2–cyclohexane	51 0	24.4	Poor	26.6	14.6	Poor	73 3	74.9	Poor			
Cyclohexane–ethanol	48.2	11.8	Poor	50.0	12.8	Poor	29 1	11 0	Fair	18.8	3.8	Good

The per cent deviations are based on $[(y_{calc} - y_{exp})/(y - x)_{exp}]100$.
These systems marked * are based on $[(p_{calc} - p_{exp})/p_{exp}]$ 100.

constant, B, which is not consistent with the derivation, but the use of the negative value gave satisfactory predictions. It was also found that the use of one point for the estimation of the constants of the Van Laar equation was not very satisfactory. In some cases the single-point method worked well and in other cases very poorly, and it depends upon the accuracy of the particular point in question. However, if only one point is available, such as is frequently the case when the azeotrope only is known, the Van Laar and Margules equations probably offer the best method of estimating the vapor-liquid equilibria for other conditions. When data on the azeotropic condition are not available, they can be estimated from Figs. 3 to 5 of the Appendix.

The Van Laar equation is also very useful for transferring data obtained at constant temperature to constant pressure and the reverse. It is also useful for transferring data from one temperature to another. The unsatisfactory agreement in the cases of solutions approaching immiscibility is not surprising. In these cases, the entropy of mixing cannot be equal to that for an ideal solution, and for complete immiscibility the entropy of mixing would be zero. It is therefore not surprising that solutions approaching immiscibility deviate from the Van Laar equation.

Other Applications of the Van Laar Equation. The Van Laar equation can be used to indicate qualitatively the type of phenomena encountered in liquid mixtures. Thus, it can be arranged as follows:

$$\ln\left[\left(\frac{P_1}{P_2}\right)\left(\frac{1}{\alpha}\right)\right] = \frac{\left[A\left(\frac{x_1}{x_2}\right)^2 - 1\right]\frac{B}{T}}{\left(1 + \frac{x_1}{x^2}A\right)^2} \tag{3-53}$$

This equation gives the logarithm of the ratio of the vapor pressures divided by the relative volatility as a function of the Van Laar constants and the concentrations. If the solution were ideal, the logarithm term would be zero. Thus the real fact determining deviation from ideal solution is the constant B. If B is equal to zero, the relative volatility will be equal to the ratio of vapor pressures, and the y,x values will be the same as those calculated by Raoult's and Dalton's laws. If B is not equal to zero, the system is not ideal. The terms involving A and the concentrations would have about the same variation independent of the value of B.

It is interesting to consider this equation for various limits. For example, for x_1 equal to zero, the logarithm term equals $-B/T$. For

most mixtures encountered, B is positive. (B is negative for solutions having maximum boiling azeotropes and for certain other solutions.) Thus the logarithm is negative, and the relative volatility is greater than the ratio of the vapor pressures. In these cases, it is easier to remove the component in low concentration than would be expected from the ideal solution law. At the other extreme, *i.e.*, x_2 equals zero, then x_1 over x_2 is infinity, and the logarithm becomes B/AT, and with B positive (in all cases so far encountered A is positive) the relative volatility is less than the ideal relative volatility. These conditions are found in most common mixtures; *i.e.*, the relative volatility at low concentration is greater than that of an ideal solution and the relative volatility at high concentration is lower. It is often expressed by saying that the components in small amount are squeezed out. Thus, at the low concentration of the volatile component, it is squeezed out and the relative volatility is high. At high concentration of the volatile component, the nonvolatile component is squeezed out, and the relative volatility is low. For the mixture in which B is negative, the reverse phenomena are true.

The Van Laar equation also would state that a mixture would agree with Raoult's law, independent of the value of B, when the ratio of the mol fractions equals $1/\sqrt{A}$. For most mixtures, the value of A is somewhere between 0.5 and 2, which would indicate that the vapor-liquid equilibria at some concentration in the middle range would agree with Raoult's law. Thus, the Van Laar equation would imply that the assumption of Raoult's law for the region around a mol fraction of 0.5 would be more satisfactory than at the two ends of the curve. It should be emphasized that this relation does not state that Raoult's law is valid at this condition. It indicates that the relative volatility is equal to the ideal relative volatility at this concentration, but the temperature–total pressure relationships may be far from those indicated by Raoult's law. Thus, in the system ethyl alcohol and water, the total pressure is always higher than would be indicated by Raoult's law, but the vapor-liquid equilibrium curve crosses the Raoult's law curve. Below this intersection, ethyl alcohol is more volatile than would be indicated by Raoult's law; above this concentration, it is less volatile than would be indicated by Raoult's law.

The Van Laar equation would indicate that the mixtures would become more ideal as the temperature increased. In other words, the ratio of B/T becomes smaller and nearer to the value for an ideal solution.

The Van Laar equation gives interesting relationships for the condi-

tion under which the relative volatility becomes unity, *i.e.*, the formation of an azeotrope. For this condition, the equations can be arranged as follows:

$$\gamma = \frac{\pi}{P}$$

and for azeotropic conditions:

$$A = \frac{\ln (\pi/P_2)}{\ln (\pi/P_1)} \left(\frac{x_2}{x_1}\right)^2 \tag{3-54}$$

$$\frac{B}{T} = \ln \left(\frac{\pi}{P_1}\right) \left[1 + \frac{x_2}{x_1} \frac{\ln (\pi/P_2)}{\ln (\pi/P_1)}\right]^2 \tag{3-55}$$

COMBINED GAS LAW AND SOLUTION DEVIATION

In the preceding discussion the deviations of the vapor-liquid equilibria due to gas law and solution abnormalities have been treated separately; however, such deviations frequently occur simultaneously. In such cases, the factors are combined into a single equation as follows:

$$yf_\pi = \gamma f_p x \tag{3-56}$$

In many cases, by combining the Van Laar and Margules equations with the fugacity corrections, it is possible to correlate vapor-liquid equilibrium data up to high pressure.

At very high pressures, it is probable that the density of the vapor phase may be such that deviations of the type handled by the activity coefficient equations also occur in this phase. Thus,

$$y\gamma_v f_\pi = \gamma_L f_p x \tag{3-57}$$

The deviations encountered in γ_v would probably be of a lower degree than those for the liquid phase, but equations of the type of the Van Laar should be applicable. Two experimental points should be sufficient to calculate the constants involved for the activity coefficients of the liquid and vapor phase.

Van Laar-Margules Equations; Example. The table of data below gives the vapor-liquid equilibria for the system acetone-chloroform obtained by Rosanoff and Easley (21), for a total pressure of 760 mm. Hg.

1. Using the Van Laar equation, calculate the y,x curve,

   a. Employing the azeotrope data only to evaluate the constants.
   b. Using all of Rosanoff's points to obtain best average constants.

2. Repeat 1*a* and 1*b* using the Margules equation.

VAPOR-LIQUID EQUILIBRIUM VAPOR PRESSURE DATA

Temp., °C.	x_1	y_1	P_1, mm. Hg	P_2, mm. Hg
57 45	0.9145	0.9522	780	675
58.34	0 8590	0.9165	805	695
59.44	0.7955	0.8688	835	745
60.42	0 7388	0.8235	865	725
61.60	0.6633	0.7505	900	775
62.84	0.5750	0.6480	935	805
63.91	0.4771	0.5170	970	835
64.6	0 3350	0.3350	995	855
64.36	0.2660	0.2370	990	850
63.84	0.2108	0.1760	965	830
63.08	0.1375	0.100	950	810
62 77	0 1108	0.0650	930	795

x_1 = mol fraction of acetone in liquid
y_1 = mol fraction of acetone in vapor
P_1 = vapor pressure of acetone
P_2 = vapor pressure of chloroform

Solution of Part 1a. Employing azeotrope data only,
Constant boiling temperature = 64.6°C. or 337.6°K

$$y\pi = \gamma P x \qquad \text{or} \qquad \gamma = \frac{\pi y}{Px}$$

At azeotropic point, $x = y$, therefore, $\gamma = \pi/P$.

$$\gamma_1 = {}^{760}\!/_{995} = 0.764; \qquad \ln \gamma_1 = -0.269$$
$$\gamma_2 = {}^{760}\!/_{855} = 0.889; \qquad \ln \gamma_2 = -0.118$$

$$\ln \gamma_1 = \frac{B/T}{\left(A\frac{x_1}{x_2} + 1\right)^2}$$

$$\ln \gamma_2 = \frac{\frac{AB}{T}\left(\frac{x_1}{x_2}\right)^2}{\left(A\frac{x_1}{x_2} + 1\right)^2}$$

$$x_1 = 0.335 \qquad x_2 = 0.665$$

Solving the Van Laar equations, one obtains

$$A = 1.74 \qquad \text{and} \qquad B = -320$$

The following is the procedure used to calculate y at various values of x:
Let $x_1 = 0.796$ and $x_2 = 0.204$,

$$\frac{x_1}{x_2} = 3.90$$

Assume $T = 332$°K.

$$\ln \gamma_1 = \frac{-320/332}{[1.74(3.90) + 1]^2} = -0.0159$$

$$\gamma_1 = 0.998$$

$$\frac{\ln \gamma_1}{\ln \gamma_2} = \frac{1}{A(x_1/x_2)^2} \quad \text{or} \quad \ln \gamma_2 = A\left(\frac{x_1}{x_2}\right)^2 \ln \gamma_1$$

$$\ln \gamma_2 = 1.74(3.90)^2(-0.0159) = -0.421$$

$$\gamma_2 = 0.685$$

$$y = \frac{\gamma P x}{\pi}$$

$$y_1 = \frac{0.998(835)(0.796)}{760} = 0.871$$

$$y_2 = \frac{0.685(725)(0.204)}{760} = 0.133$$

$$y_1 + y_2 = 1.004$$

The fact that the sum of the mol fractions is greater than 1.0 indicates the assumed temperature is too high, but the relative volatility is nearly constant with small temperature changes, and

$$y_1 = \frac{0.871}{1.004} = 0.868$$

$$y_2 = \frac{0.133}{1.004} = 0.132$$

Other results are tabulated as follows:

x	y_{calc}	y_{exp}	$\frac{100\,\Delta y}{(y - x)_{exp}}$
0.9145	0.955	0 9522	7 9
0 7955	0 868	0.8688	1 1
0 6633	0.758	0.7505	8 6
0.4771	0.521	0.5170	10 0
0.3350	0 3350	0 3350	0 0
0.2108	0 175	0.1760	2 9
0.1108	0 070	0.0650	10 9

Solution of Part 1b

$$\ln \gamma_1 = \frac{B/T}{\left(1 + A\frac{x_1}{x_2}\right)^2}$$

or

$$\frac{1}{(T \ln \gamma_1)^{1/2}} = \frac{1}{B^{1/2}} + \frac{A}{B^{1/2}}\left(\frac{x_1}{x_2}\right) \qquad (a)$$

Also,

$$\ln \gamma_2 = \frac{AB/T}{(A + x_2/x_1)^2}$$

or

$$\frac{1}{(T \ln \gamma_2)^{1/2}} = \left(\frac{A}{B}\right)^{1/2} + \frac{1}{(AB)^{1/2}}\frac{x_2}{x_1} \qquad (b)$$

By plotting $\frac{1}{(T \ln \gamma_1)^{1/2}}$ vs. $\frac{x_1}{x_2}$, or $\frac{1}{(T \ln \gamma_2)^{1/2}}$ vs. $\frac{x_2}{x_1}$, the constants A and B can be evaluated.

TABLE 3-8

x_1	x_2	T, °K.	γ_1	$\frac{1}{(-T \ln \gamma_1)^{1/2}}$	$\frac{x_1}{x_2}$
0.9145	0.0855	330	1.015	—	—
0.8590	0.1410	331	1 007	—	—
0.7955	0.2045	332	0 991	0.709	3.89
0.7388	0 2612	333	0.980	0.376	2.83
0.6633	0.3367	335	0.956	0.258	1 965
0.5750	0.4250	336	0.916	0.185	1 35
0.4771	0.5229	337	0.849	0.135	0.913
0 3350	0.6650	338	0.762	0.105	0 504
0.2660	0.7340	337	0 684	0.088	0 363
0.2108	0.7892	337	0.657	0.084	0 268
0.1375	0.8625	336	0.582	0.074	0.1596
0.1108	0.8892	336	0.479	0 063	0.1246

In this case the mixture is of the maximum boiling point type, and the activity coefficients are less than unity, resulting in negative values for $\ln \gamma$. This negative value is handled in the square roots by multiplying Eq. (*a*) by $1/\sqrt{-1}$. The intercept is then $1/\sqrt{-B}$, and the slope is $A/\sqrt{-B}$. A similar procedure is employed for $\ln \gamma_2$. The first two values of γ_1, given in Table 3-8 are greater than

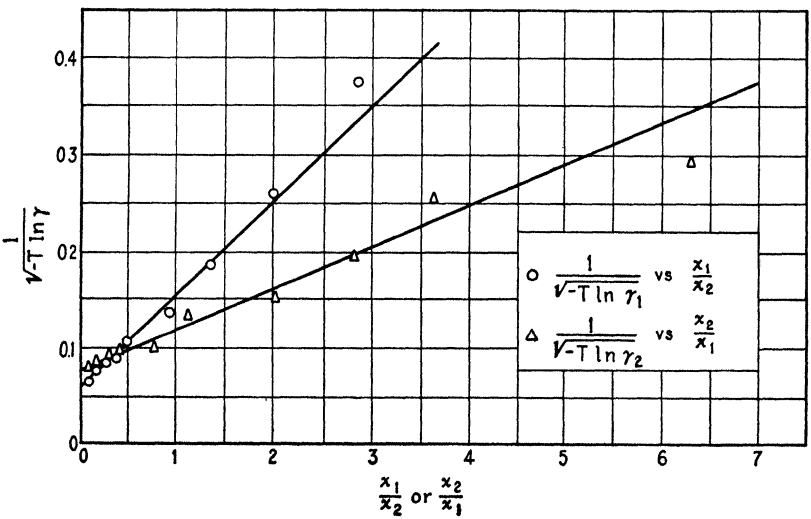


FIG. 3-7. Van Laar plot for system acetone-chloroform.

unity, while the values of γ_2 at the same point are less than unity, and it can be shown that this is not consistent with the Duhem equation. These two values of γ_1 are so near to unity that a very small error would account for the discrepancy, and the values were not used in the calculations. In all cases the values of the activity coefficients near unity tend to be of little value for calculating the constants of either the Van Laar or Margules equations because ln γ is small and subject to large errors. Unfortunately, the method of plotting used in Fig. 3-7 emphasizes these inaccurate points and gives less weight to the better values. The plotting for the Margules equation is better in this respect and tends to weigh all the values about equally.

$$\text{Intercept of plot} = 0.056 = \frac{1}{-B^{1/2}}$$

$$\text{Slope of plot} = 0.097 = \frac{A}{-B^{1/2}}$$

Thus, $B = -319$ and $A = 1.73$. Similar values for the other component are given in Table 3-9.

TABLE 3-9

x_1	y_2	γ_2	$\frac{1}{(-T \ln \gamma_2)^{1/2}}$	$\frac{x_2}{x_1}$
0.9145	0 0478	0.610	0.078	0 093
0 8590	0 0835	0 643	0.083	0 164
0 7955	0 1312	0 675	0.087	0 294
0.7388	0 1765	0.690	0 090	0 354
0.6633	0 2495	0 724	0.096	0 410
0 5750	0 3520	0.782	0.098	0.740
0.4771	0.4830	0.841	0.131	0.095
0.3350	0.6650	0.884	0.155	1.987
0.2660	0.7630	0.925	0.195	2 76
0 2108	0.8240	0 957	0.257	3 62
0.1375	0 900	0 964	0.294	6 27
0 1108	0.9350	0.985	0 445	8 02

From Fig. 3-7,

$$\text{Intercept is } 0.074 = \left(-\frac{A}{B}\right)^{1/2}$$

$$\text{Slope is } 0.0434 = \frac{1}{-AB^{1/2}}$$

Thus $B = -310$ and $A = 1.72$. Average $A = 1.725$ and average $B = -315$. The values of A and B obtained here are, within the accuracy of the method, the same as those obtained from the azeotrope data alone, and the y,x calculations will not be repeated.

Solution of Part 2a

NOTE. Some values used below are taken from **Part 1.**

$$\ln \gamma_1 = bx_2^2 + cx_2^3$$
$$\ln \gamma_2 = bx_1^2 + \tfrac{3}{2}cx_1^2 - cx_1^3$$
$$\gamma_1 = 0.764, \qquad \gamma_2 = 0.889 \text{ (from Part 1)}$$
$$x_1 = 0.335, \qquad x_2 = 0.665$$
$$-0.269 = b(0.665)^2 + c(0.665)^3$$
$$-0.118 = b(0.335)^2 + \tfrac{3}{2}c(0.335)^2 - c(0.335)^3$$

Thus $b = -0.0106$ and $c = -0.894$.

$$\ln \gamma_1 = -(0.0106 + 0.894x_2)x_2^2$$
$$\ln \gamma_2 = -(1.351 - 0.894x_1)x_1^2$$

Let $x_1 = 0.4771$, $x_2 = 0.5229$,

$$\ln \gamma_1 = -(0.0106 + 0.894x_2)x_2^2 = -0.131$$
$$\gamma_1 = 0.878$$
$$\ln \gamma_2 = -(1.351 - 0.894x_1)x_1^2 = -0.210$$
$$\gamma_2 = 0.810$$

Assuming $T = 63.91°C.$,

$$y_1 = \frac{0.878(970)(0.4771)}{760} = 0.535$$
$$y_2 = \frac{0.810(835)(0.5229)}{760} = 0.465$$

$\Sigma y = 1.000$. If the sum of y is not equal to 1.000, then other values of P should be used until $y = 1.0$.

Values of y corresponding to various other values of x may be similarly calculated. The results are given in Table 3-10.

TABLE 3-10

x_1	$y_{1\text{calc}}$	$y_{1\text{exp}}$	$\frac{100\,\Delta y}{(y-x)_{\text{exp}}}$
0.9145	0.951	0.9552	3.2
0.7955	0.869	0.8688	0.3
0.6633	0.753	0.7505	2.9
0.4771	0.519	0.5170	5.0
0 3350	0.3350	0.3350	0.0
0.2108	0.173	0.1760	8.6
0.1108	0.072	0.0650	15.0

Solution of Part 2b. Since $\ln \gamma_1 = bx_2^2 + cx^3$,

$$\frac{\ln \gamma_1}{x_2^2} = b + cx_2 \cdots \qquad (c)$$

Also $\ln \gamma_2 = bx_1^2 + \frac{3}{2}cx_1^2 - cx_1^3$

$$\frac{\ln \gamma_2}{x_1^2} = b + \frac{3}{2}c - cx_1$$

or, substituting,

$$x_1 = 1 - x_2$$

$$\frac{\ln \gamma_2}{x_1^2} = b + \frac{1}{2}c + cx_2 \qquad (d)$$

$$= b + c(0.5 + x_2) \qquad (e)$$

By plotting Eqs. (*c*) and (*e*), a single line should be obtained with a slope = c, and intercept at $x_2 = 0$ equal to b. The values for these equations are given in Table 3-11.

TABLE 3-11

x_1	x_2	$\ln \gamma_1$	$\ln \gamma_2$	$\frac{\ln \gamma_1}{x_2^2}$	$\frac{\ln \gamma_2}{x_1^2}$
0.9145	0.0855	—	−0.495	—	−0 591
0 8590	0.1410	—	−0.441	—	−0.599
0 7955	0.2045	−0.0091	−0.394	−0.217	−0 621
0.7388	0 2612	−0.0202	−0 371	−0.296	−0.680
0 6633	0.3367	−0 045	−0 324	−0.396	−0.737
0.5750	0.4250	−0.0878	−0.246	−0.486	−0.744
0.4771	0.5229	−0.164	−0.173	−0.600	−0.760
0 3350	0.6650	−0.271	−0.123	−0.613	−1.094
0.2660	0.7340	−0.380	−0.0780	−0.706	−1.101
0.2108	0 7892	−0 420	−0.0440	−0.675	−0.986
0.1375	0.8625	−0.540	−0.0366	−0.726	−1.937
0.1108	0 8892	−0.739	−0.0152	−0.936	−1.239

The values of Table 3-11 are plotted in Fig. 3-8.

Slope of plot = $-0.74 = c$
Intercept of plot = $-0.11 = b$

Thus, $\ln \gamma_1 = -(0.11 + 0.74x_2)x_2^2$ and $\ln \gamma_2 = -(0.48 + 0.74x_2)x_1^2$

Values of y at various values of x are calculated as in Part 2*a*. The results are given in Table 3-12.

TABLE 3-12

x_1	y_{calc}	x_{exp}	$\frac{100\,\Delta y}{(y - x)_{exp}}$
0.9145	0.959	0 9522	18 0
0.7955	0.871	0.8688	3.0
0.6633	0.753	0.7505	2.9
0.4771	0.520	0 5170	7.5
0 3350	0.336	0.3350	0.0
0.2108	0.175	0.1760	2.9
0.1108	0.076	0.0650	15.0

An appreciable portion of the variations in $100\,\Delta y/(y - x)$ is probably due to the errors in the experimental calculation and the data. The agreement with both the Van Laar and the Margules equations is fairly good for this system. The azeotrope point for the Margules equation gave better agreement than the line

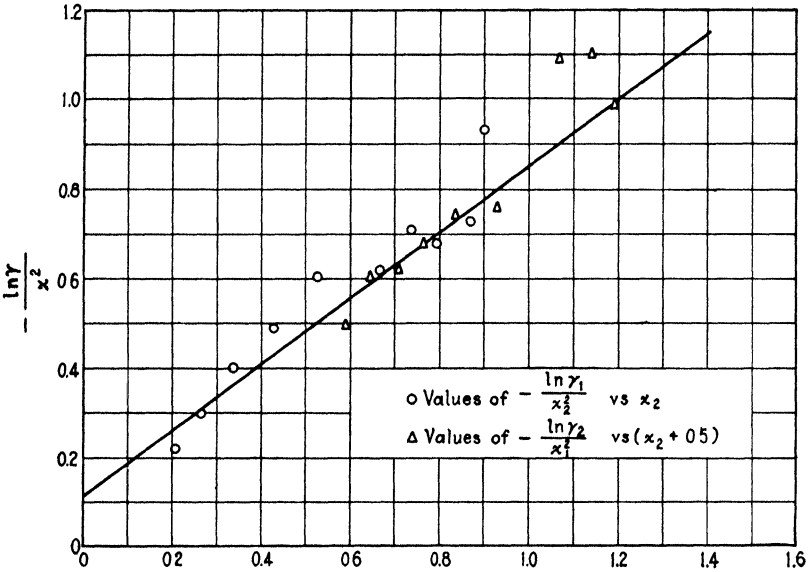


FIG. 3-8. Margules plot for system acetone-chloroform.

drawn through the points, but a line drawn on the basis of the azeotrope constants would agree with the plotted points as well as the line employed. In drawing the plot for the Margules evaluation no attempt was made to place the line to give the minimum average deviation in $100\,\Delta y/(y - x)$. Mason studied the "optimum line" and obtained constants that gave a maximum deviation of 12.5 per cent and an average deviation of 4.3 for $100\,\Delta y/(y - x)$.

MULTICOMPONENT SYSTEMS

The ideal solution laws such as Raoult's law and Raoult's law corrected for gas law deviation are applicable to binary or multicomponent systems. They treat each component independently of any other component present; *i.e.*, the relationship between the mol fraction in the vapor and in the liquid for a given component depends only on the temperature and total pressure. In many cases, these simplified rules are not applicable, and there is interreaction between the various components. It would be particularly desirable to have a satisfactory theoretical approach to the problem of multicomponent vapor-liquid equilibria since the experimental determination for this

case is an order of magnitude more difficult than for binary mixtures. The equations as originally given by Margules and Van Laar were limited to binary mixtures, although Van Laar did indicate the method for multicomponent problems. In recent years, there have been a number of derivations of multicomponent, Van Laar-type equations (Refs. 1, 7, 22, 26, 27). For example, Bonham (Ref. 1) obtained a multicomponent Van Laar equation by using multicomponent mixture constants for the van der Waals equation, a_{mix} and b_{mix}, given by Eq. (3-40).

A similar derivation to that employed for the binary Van Laar equation leads to

$$\left.\begin{aligned} T \ln \gamma_1 &= \frac{(x_2\sqrt{B_{12}} + x_3 A_{32}\sqrt{B_{13}})^2}{(x_1 A_{12} + x_2 + x_3 A_{32})^2} \\ T \ln \gamma_2 &= \frac{(x_1 A_{12}\sqrt{B_{21}} + x_3 A_{32}\sqrt{B_{23}})^2}{(x_1 A_{12} + x_2 + x_3 A_{32})^2} \\ T \ln \gamma_3 &= \frac{(x_1 A_{12}\sqrt{B_{31}} + x_2\sqrt{B_{32}})^2}{(x_1 A_{12} + x_2 + x_3 A_{32})^2} \end{aligned}\right\} \qquad (3\text{-}58)$$

In the above equations, the values of A and B are similar to those given for a binary, but in this case, considerable care must be exercised with respect to the subscripts. Thus A_{12} is equal to b_1/b_2, A_{32} is equal to b_3/b_2, and similarly for other subscripts. It should be pointed out that for a ternary mixture, there are only two independent A terms. Any other A terms can be calculated from these two by multiplication or division. The three activity coefficient equations contain only the values of A and B associated with the three binary mixtures possible from the three components. If the Van Laar equation for multicomponent mixtures is applicable, the only information needed is the vapor-liquid equilibrium data for the binary mixtures.

In the case of the value of B, it should be noted that it occurs in the multicomponent equation as a square root, and this immediately raises the question of whether the value is positive or negative. This question can be answered by considering the relationships given on page 58. On the basis of the relations employed for a_{mix} and b_{mix}, the square root of B_{12} is equal to

$$\sqrt{\frac{b_1}{R}}\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)$$

and the value is negative or positive depending on whether $\sqrt{a_1}/b_1$ is greater or less than $\sqrt{a_2}/b_2$. There are at least two ways of deter-

mining the sign of the $\sqrt{B}$. The first involves having sufficient data on the multicomponent mixture in order that the three equations can be forced to fit. This method is of little value since it requires a large amount of data on the mixture, and the mathematical procedure is complicated. It is useful, however, in cases where data are available, and it is desirable to interpolate or extrapolate. The other method is based on evaluating the sign of these terms independent of vapor-liquid equilibria data and determining their magnitude from binary data.

Applying the Van Laar to a binary mixture does not indicate the sign of the $\sqrt{B}$. The basis for deciding the sign is the relative values of the $\sqrt{a}/b$, which corresponds to the square root internal pressure of the liquid. Thus polar compounds which have high internal pressures would be expected to have high values of this group, while compounds of low polarity would be expected to have low values. If the compounds in the binary mixture are of widely different polarity, it is fairly easy to determine whether the square root should be positive or negative. For example, for a mixture of ethyl alcohol and water, components 1 and 2, respectively, it is well established that water is the more polar; therefore, if $\sqrt{B_{21}}$ is taken to be positive, $\sqrt{B_{12}}$ would be negative.

If the square roots of the B_{12}/b_1, B_{23}/b_2, and B_{31}/b_3 are added, it will be found that, on the basis of the definition given on page 58, the sum is zero. In fact, all that is necessary to obtain this conclusion is to have each one of the subscripts appear first on one of the B's and last on another, and to have the subscript on the b correspond to the first subscript. These relationships are extremely useful since any two independent values of B together with the corresponding A's are sufficient to evaluate the other. Thus, for a ternary mixture, it is necessary to have data on only *two* of the binaries. This is useful in several ways, *e.g.*, predicting the three-component data from data on two of the binaries or predicting the vapor-liquid equilibria for a binary for which there are no data. In this latter case, it is necessary to find data on two binaries which have a common component, the other components being the ones for the desired mixture. For example, if data are available on ethanol and water and methanol and water, it is possible to calculate the vapor-liquid equilibria for methanol and ethanol on the basis of these data, assuming that the systems agree with the Van Laar-type equation.

The various relations of the A's and B's of the Van Laar equations for a ternary mixture are summarized below:

$$A_{12} = \frac{1}{A_{21}} = \frac{b_1}{b_2} \text{ or } \frac{V_1}{V_2}; \qquad A_{32} = \frac{1}{A_{23}} = \frac{b_3}{b_2} \text{ or } \frac{V_3}{V_2}; \qquad A_{22} = 1$$

$$\sqrt{B_{12}} = -\sqrt{B_{21}A_{12}}, \qquad \sqrt{B_{13}} = -\sqrt{B_{31}A_{13}} = -\sqrt{\frac{B_{31}A_{12}}{A_{32}}}$$

$$\sqrt{\frac{B_{12}R}{b_1}} = \frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}; \qquad \sqrt{\frac{B_{23}R}{b_2}} = \frac{\sqrt{a_2}}{b_2} - \frac{\sqrt{a_3}}{b_3}$$

$$\sqrt{\frac{B_{12}}{A_{12}}} + \sqrt{\frac{B_{23}}{A_{22}}} + \sqrt{\frac{B_{31}}{A_{32}}} = 0 \tag{3-59}$$

or, alternatively,

$$\sqrt{\frac{B_{21}}{A_{22}}} + \sqrt{\frac{B_{13}}{A_{12}}} + \sqrt{\frac{B_{32}}{A_{32}}} = 0 \tag{3-60}$$

In the case of more than three components, the relationship is obtained by the same procedure, but it is relatively easy to write the activity coefficient equations simply by inspection. Returning to the three component equations, Eq. (3-58), it is noted that the denominator is always the same and simply involves the square of the sum of the mol fraction times the A for the term in question relative to some given base component. In the equations given, component 2 is used as the base, and A_{22} was omitted since it is obviously 1. The numerator involves terms for the components other than the one under consideration. These terms are all of a general type and can best be explained by considering the specific equations. Thus, for the $T \ln \gamma_1$, there are terms involving x_2 and x_3, each term has the A value corresponding to its component and the $\sqrt{B}$ for component 1 relative to it. The same rules apply to $T \ln \gamma_2$ and $T \ln \gamma_3$ with appropriate shifts of subscripts. For n components, the equations become

$$T \ln \gamma_1 = \frac{(x_2\sqrt{B_{12}} + x_3A_{32}\sqrt{B_{13}} + x_4A_{42}\sqrt{B_{14}} + \cdots + x_nA_{n2}\sqrt{B_{1n}})^2, \text{ etc.}}{(x_1A_{12} + x_2 + x_3A_{32} + x_4A_{42} + \cdots + x_nA_{n2})^2}$$

$$T \ln \gamma_n = \frac{(x_1A_{12}\sqrt{B_{n1}} + x_2\sqrt{B_{n2}} + x_3A_{32}\sqrt{B_{n3}} + \cdots + x_{n-1}A_{(n-1)2}\sqrt{B_{n(n-1)}})^2}{(x_1A_{12} + x_2 + x_3A_{32} + x_4A_{42} + \cdots + x_nA_{n2})^2} \tag{3-61}$$

and the following relationships apply:

$$\sqrt{\frac{B_{12}}{A_{12}}} + \sqrt{\frac{B_{23}}{A_{22}}} + \sqrt{\frac{B_{34}}{A_{32}}} + \sqrt{\frac{B_{45}}{A_{42}}} + \cdots + \sqrt{\frac{B_{n1}}{A_{n2}}} = 0 \tag{3-62}$$

A large number of equations of this latter type can be written as long as the number for each component appears first in the subscript of one B and last in another subscript, and the A terms are made to correspond to the first subscript of the associated B term. Depending

on what particular values of B are available, there may be a preference for some particular series. The other relationships for the A's and B's are the same as listed for the ternary system.

To use these equations with the evaluation of the constants from binary data, it is necessary to have information on $n - 1$ binary mixtures.

As was shown in a previous section, the application of Van Laar's equation to a binary mixture showing negative deviations from Raoult's law, *i.e.*, tendency to form a maximum boiling mixture, gives negative values for the B term. If some of the binary mixtures give negative values and some give positive values, they cannot be used in Eq. (3-58). If all the B terms are either negative or positive, the equation can be applied. If any of the binary systems involved does not agree with Van Laar's equation, then the multicomponent relationship should not be applied in the region near this binary. Multicomponent equations of the Margules type have been presented, but they involve so many independent constants that their engineering utility is small.

Cooper's relationship (see page 59) can be applied to multicomponent mixtures. Thus for a three-component mixture Eq. (3-47) becomes

$$\frac{\Delta F_e}{n_1v_1 + n_2v_2 + n_3v_3} = \frac{K'_{12}n_1v_1n_2v_2 + K'_{13}n_1v_1n_3v_3 + K'_{23}n_2v_2n_3v_3}{(n_1v_1 + n_2v_2 + n_3v_3)^2} \tag{3-63}$$

and, by partial differentiation and substituting for K,

$$T \ln \gamma_1 = \frac{x_2^2B_{12} + x_3A_{32}^2B_{13} + x_2x_3(A_{32}B_{12} + A_{12}B_{31} - A_{12}A_{32}B_{23})}{(x_1A_{12} + x_2 + x_3A_{32})^2}$$

$$T \ln \gamma_2 = \frac{x_1^2A_{12}^2B_{21} + x_3^2A_{32}^2B_{23} + x_1x_3(A_{32}B_{12} + A_{12}A_{32}B_{23} - A_{12}B_{31})}{(x_1A_{12} + x_2 + x_3A_{32})^2}$$

$$T \ln \gamma_3 = \frac{x_1^2A_{12}^2B_{31} + x_2^2A_{32}^2B_{32} + x_2x_3(A_{12}B_{13} + A_{12}A_{32}B_{23} - A_{32}B_{12})}{(x_1A_{12} + x_2 + x_3A_{32})^2} \tag{3-64}$$

In these equations the A values are related in the same manner as for Eq. (3-58), but no assumption has been made relative to the values of the B terms. To be consistent with the binary equations, $B_{12} = A_{12}B_{21}$, etc., and this leaves three independent B terms. If the values of these terms are made to fit Eqs. (3-59) and (3-60), then Eq. (3-64) reduces to Eq. (3-58). However, the values can be used independently, and the equation then is more general than Eq. (3-58). If binary data are used to evaluate the constants, information on all three binaries must be available, and frequently this limits the useful-

ness of Eq. (3-64) as compared to (3-58). Negative values of B may lead to mathematical difficulties in the use of Eq. (3-58), but they can be handled by Eq. (3-64). Because Eq. (3-58) requires less experimental data to evaluate the constants and is easier to use, it has been more widely applied than Eq. (3-64).

Nomenclature

A,B = constants in Van Laar equation
E = internal energy
$\Delta\bar{F}$ = partial molal change in free energy
$\Delta\bar{F}_a$ = actual value of $\Delta\bar{F}$
$\Delta\bar{F}_i$ = ideal value of $\Delta\bar{F}$
$\Delta\bar{F}_e$ = excess partial molal free energy change = $\Delta\bar{F}_a - \Delta\bar{F}_i$
ΔF_e = excess free-energy change on mixing
f = fugacity
f_L = fugacity of component in liquid phase
f_p = fugacity of pure liquid under its own vapor pressure
f_p^* = fugacity of pure liquid under total pressure of mixture
f_v = fugacity of component in vapor phase
f_π = fugacity of pure vapor at pressure, π
$\Delta\bar{H}$ = partial molal change in enthalpy
$\Delta\bar{H}_e$ = excess partial molal change in enthalpy
$\Delta H'$ = enthalpy of vaporizating 1 mol of a component from a liquid into a vacuum
K = equilibrium constant = y/x
K' = proportionality constant
n = mols
P = vapor pressure
p = partial pressure
R = gas law constant
$\Delta\bar{S}$ = partial molal change in entropy
ΔS_e = excess partial molal entropy change
T = absolute temperature
V = volume
v = molal volume or partial molal volume
x = mol fraction in liquid
y = mol fraction in vapor
α = relative volatility
β = volatility = p/x
γ = activity coefficient
π = total pressure
μ = gas law correction factor = PV/RT

Subscripts:

$a,b,1,2,3$ refer to components
L refers to liquid phase
R refers to reduced conditions
V refers to vapor phase

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CHAPTER 4

CALCULATION OF VAPOR-LIQUID EQUILIBRIA

(Continued)

Critical Regions. At very high pressures special phenomena associated with the critical region are encountered in vapor-liquid equilibria. If the vapor pressure of a pure component is plotted vs. the temperature, a line concave upward is obtained. This line terminates at the critical point. Conditions below the line in region *A*, Fig. 4-1,

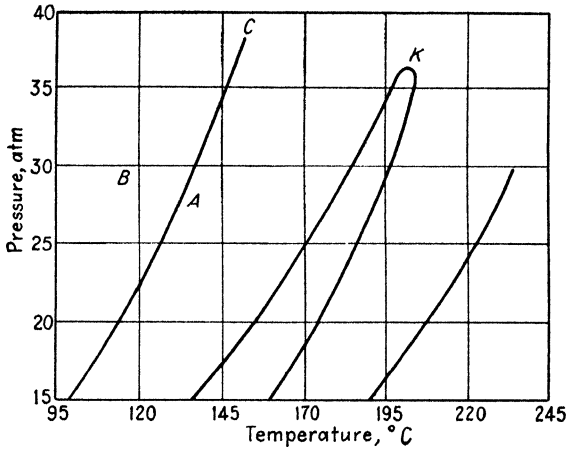


FIG. 4-1. Typical pressure-temperature curves.

correspond to all vapor and no liquid. The line represents conditions under which the vapor and liquid are in equilibrium. Conditions above the line in region *B* represent all liquid. In region *C* the state of the substance is in question since it is possible to obtain either vapor or liquid without a change in phase. If a given binary mixture is plotted in the same way, similar conditions are attained except that a loop region is obtained for a mixture of given composition instead of a single line, Fig. 4-1. The upper line of the loop represents the bubble-point curve, *i.e.*, the condition under which the mixture first forms vapor. The lower side of the loop is the dew point curve, *i.e.*, the condition under which the mixture begins to condense. In the case

of the pure substance these two lines coincide, and the critical temperature and pressure are the maximum for both variables that can exist and have coexistence of liquid and vapor phase. In the case of the mixture the maximum temperature does not coincide with the maximum pressure.

For a pure component at the critical condition, the properties of the vapor and the liquid phases become identical in all respects. In the case of the loop curve for a binary mixture, the property of the vapor

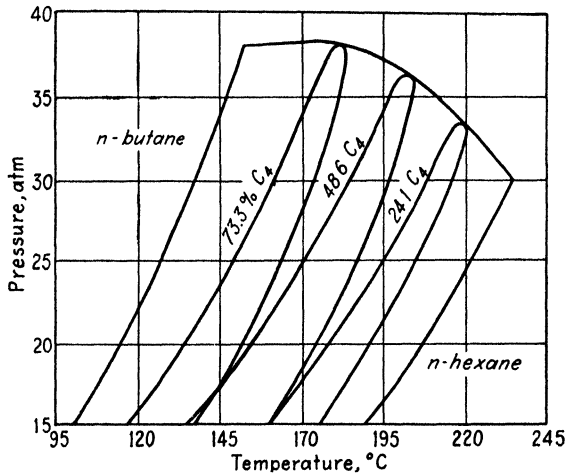


FIG. 4-2. Pressure-temperature curves for butane-hexane system.

and the liquid are in general different, both at the point of maximum temperature and at the point of maximum pressure. There is a point on the loop, usually between the maximum temperature and the maximum pressure points, at which the properties of the liquid and the vapor are identical. This is taken as the critical of the mixture. This critical point K is shown on Fig. 4-1. Figure 4-2 shows loop curves for three different mixtures of butane and hexane, and a curve indicating the loci of critical points is shown. If the conditions inside a single loop curve are analyzed, it is found possible to plot lines of constant fraction vaporized; such curves for 0, 20, 40, 60, 80, and 100 per cent vapor have been drawn in Fig 4-3. All these curves converge to a common point at the critical.

The curves of Fig. 4-3 indicate the phenomena of retrograde condensation, *i.e.*, conditions under which an increase in pressure causes vaporization instead of condensation, or in which a decrease in temperature causes vaporization instead of condensation. Thus, start-

ing at point A, Fig. 4-3, and increasing the temperature at constant pressure, the bubble-point curve is first contacted and vapor begins to form. An increase in temperature causes more vaporization up to about 20 per cent. Higher temperatures then cause a decrease in vapor until the mixture is again all liquid at point C. A similar type of phenomenon is exhibited by curve EL. If at constant temperature the pressure is lowered from point E, the conditions first reach the dew-point curve; *i.e.*, the mixture is all vapor. On lowering the pres-

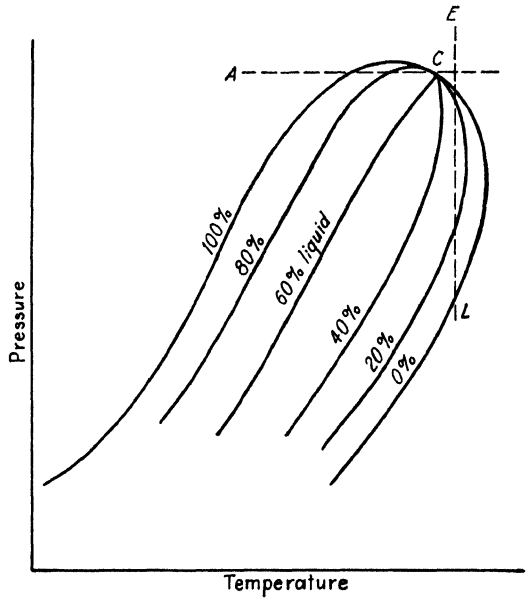
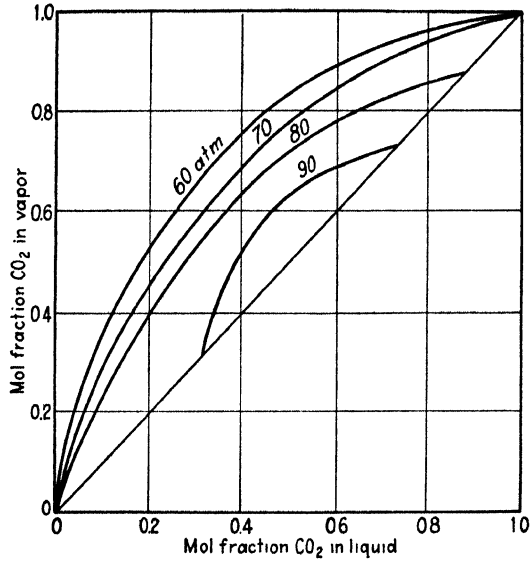


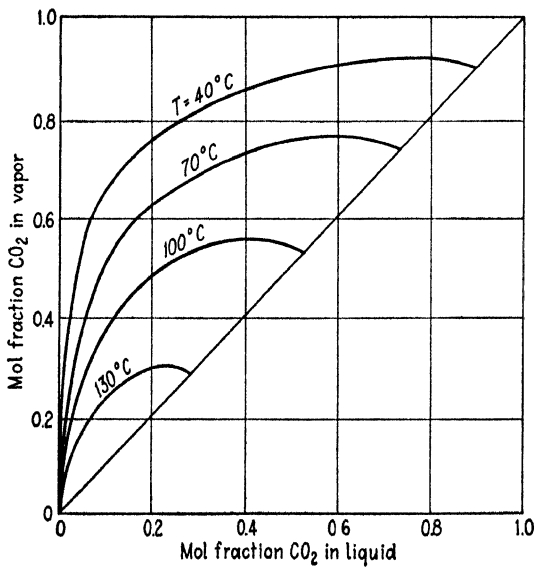
FIG. 4-3. Typical pressure-temperature loop curve.

sure, the mixture becomes more and more liquid until about 25 per cent is condensed. In this region it has exhibited the retrograde phenomena. At still lower pressures, the mixture behaves normally and vaporizes with decrease in pressure.

In a binary mixture, if two of the loop curves intersect, *i.e.*, if the vapor curve of one crosses the liquid curve of the other, then the two compositions determine a vapor-liquid equilibrium point. This is due to the fact that, for a binary system of two phases, the phase rule allows two degrees of freedom. However, the value may not be unique, *i.e.*, in the higher pressure region, particularly very near the critical, it is possible for a given vapor to have two possible equilibrium liquids of different compositions. These two conditions can be at the



(*a*)



(*b*)

FIG. 4-4. *a*. Vapor-liquid equilibria for CO_2-SO_2 at constant pressure. *b*. Vapor-liquid equilibria for CO_2-SO_2 at constant temperature.

same temperature, but at different total pressures. This is shown in Fig. 4-4 which gives the vapor-liquid equilibrium data for the system carbon dioxide–sulfur dioxide.

In general, it is found that the relative volatility decreases as the total pressure increases, and there are several factors that combine to give this effect. It is generally found that (1) the ratio of the vapor pressures of two components becomes nearer to unity as the pressure increases and (2) the deviations from the perfect-gas laws also tend to reduce the relative volatility. Actually the decrease in relative

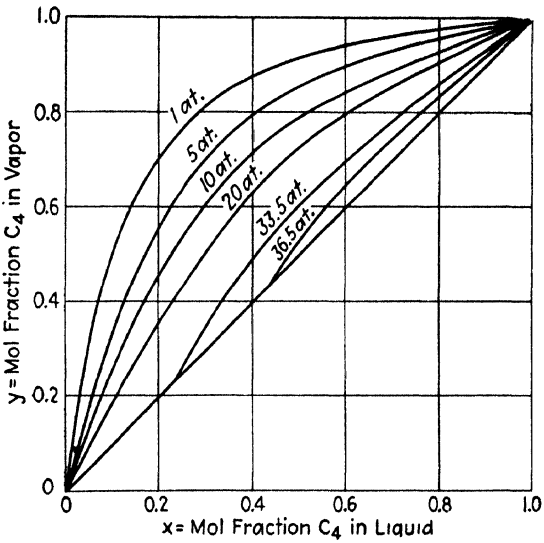


FIG. 4-5. Effect of pressure on vapor-liquid equilibria.

volatility is even larger than the result of these two factors. At the critical pressure of a binary mixture, the vapor and liquid phases become identical in all respects, and the relative volatility becomes unity. No separation is possible, not only because of the relative volatility effects but because differentiation between the vapor and liquid is no longer possible. This decrease in relative volatility to the value of 1 at the critical is a progressive effect, although a large part of it occurs close to the critical condition. The Lewis and Randall fugacity rule does not show the convergence of the relative volatility to unity at the critical. For example, in the case of a mixture like ethane and propane, the rule would show a finite relative volatility not only at the critical condition but at pressures much higher.

This effect of total pressure on the vapor-liquid equilibria of the

system *n*-butane–*n*-hexane (Ref. 1) is shown in Fig. 4-5. The decrease in the relative volatility with increasing pressure is apparent, and the y,x curves become discontinuous at pressures above 30 atm. Thus, at 33.5 atm. the y,x curves exist only for liquids containing more than 24 mol per cent butane. Mixtures containing less than this amount of butane are at pressures above the envelope curve of Fig. 4-2, and only a single phase is present. At higher pressures the range of the discontinuity increases, and above 37.5 atm. the y,x curve becomes discontinuous at both ends because there are mixtures of butane and hexane which have higher critical pressures than either of the pure components. Above 38 atm. only one phase is present for all compositions.

From the viewpoint of the ease of separation, it is almost always disadvantageous to operate at high pressure, but it is frequently necessary to accept this more difficult separation in order to obtain other desirable features of high pressure, such as higher condensation temperatures and lower volume of apparatus.

The relative volatilities of all vapor-liquid systems do not decrease with increasing pressure in all regions. Thus, it is possible for abnormal mixtures to have an increase in relative volatility in some regions for an increase in pressure. It is in general true that they will not increase the relative volatility at all compositions. For example, in the case of ethyl alcohol and water at atmospheric pressure, the constant-boiling mixture is about 89 mol per cent alcohol. As the pressure is increased, the composition of the constant-boiling mixture becomes lower in alcohol, and the relative volatility of water to alcohol at a composition of 89 mol per cent becomes greater than 1 as the pressure is increased above 1 atm. and then decreases at still higher pressures.

The approach of the relative volatility to unity at the critical means that the compositions of the vapor and liquid are identical. Thus the K values for all components equal 1. The temperature and pressure at which these values become unity are functions of the other components present. Thus, a mixture of butane and ethane would have a certain critical temperature and pressure, while a mixture of butane with hexane would have different critical temperature and pressure, but under both conditions the K value for butane would have to be equal to unity. Thus, the values given in Table 3-2, which were taken to be independent of the character of the other components and a function of the temperature and pressure only, cannot apply in the critical region. In most cases, these effects of the critical region are not serious at total pressures less than 0.5 to 0.7 of the critical pressure. Modifications of the method of utilizing the K values in the critical

region have been suggested which allow for the effect of the other components present (Ref. 2).

Immiscible Liquids. Immiscible liquids are not an important case encountered in fractional distillation. It is much simpler to separate two liquids which are insoluble in each other by simple decantation than it is by fractionation. However, the physical-chemical laws that apply to such cases are helpful in explaining certain of the phenomena involved in the intermediate case of partially miscible liquids.

The various rules developed for the vapor phase for miscible liquids apply equally well to this case. In the case of the liquid phase, if the liquids are completely immiscible, at equilibrium each component would exert its own vapor pressure independent of the others present. For this case, the vapor-liquid equilibrium expression will be

$$\left.\begin{aligned} p_1 &= y_1\pi = P_1 \\ p_2 &= y_2\pi = P_2 \end{aligned}\right\} \tag{4-1}$$

at high pressures,

$$\left.\begin{aligned} f_1 &= y_1 f_{\pi 1} = f_{p1} e^{v_1(\pi - P)/RT} \\ f_2 &= y_2 f_{\pi 2} = f_{p2} e^{v_2(\pi - P)/RT} \end{aligned}\right\} \tag{4-2}$$

where p = partial pressure
P = vapor pressure
π = total pressure
y = mol fraction of vapor
f = fugacity
f_π = fugacity of pure component at total pressure
f_p = fugacity of pure liquid under its own vapor pressure
v = partial molal volume
R = gas-law constant
T = absolute temperature

These equations are similar to those for miscible liquids except that the mol fraction in the liquid is omitted. It is to be expected that the fugacity relationship would give satisfactory results up to a pressure of approximately one-half of the critical pressure. At higher pressures the Lewis and Randall fugacity rule for the vapor mixture would tend to be less satisfactory. Actually it is doubtful whether absolute immiscibility ever occurs. However, there are cases in which the miscibility is so limited that each phase would act as essentially a pure material, *e.g.*, mercury and water.

Example for Immiscible Liquids. 1. A two-phase liquid mixture comprised of 30 mols of toluene and 70 mols of water existing as liquids at 1 atm. pressure and

60°C. is heated at constant pressure. Assuming that water and toluene are completely nonmiscible and that all the vapors formed were at all times in equilibrium with the remaining liquids, and using the vapor pressure data given below construct the following curves:

a. Mol per cent vaporized vs. temperature.
b. Mol fraction of toluene in vapor vs. temperature.

2. A two-phase liquid mixture consisting of 30 mols of toluene and 70 mols of water is vaporized at a constant temperature of 85°C. by reducing the total pressure.

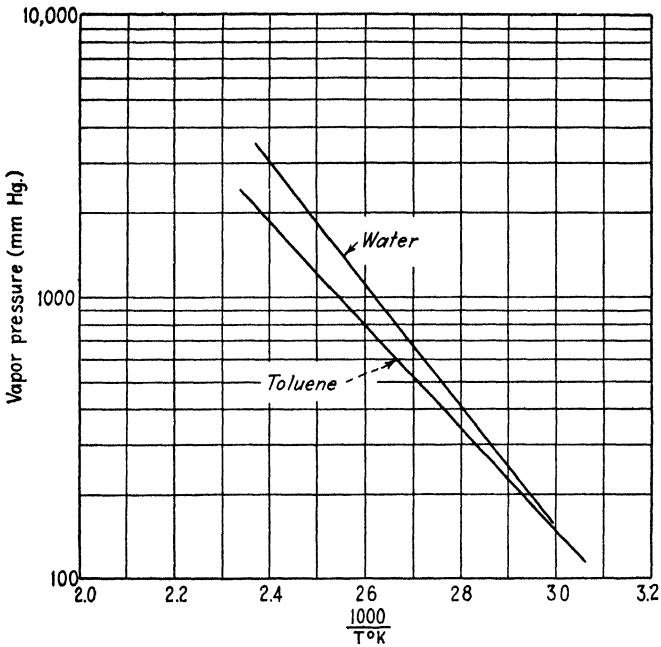


FIG. 4-6. Vapor pressures of toluene and water

sure. The initial pressure is 2 atm. absolute. Assuming that the vaporization is carried out such that equilibrium between vapor and liquid exists at all times, plot

a. Mol per cent vaporized vs. pressure.
b. Composition of vapor vs. pressure.

Solution of Part 1. System: 30 mols toluene, 70 mols H_2O. (Let subscripts T and W refer to toluene and water, respectively.)

Assuming complete immiscibility, from the phase rule it follows that for the three-phase–two-component system there exists only one degree of freedom. Hence, vaporization will occur at constant temperature as long as two liquid phases are present.

Vaporization occurs when $\pi = P_W + P_T = 760$ mm. From Fig. 4-6 this temperature = 84.4°C.

$$P_T = 336 \text{ mm.} \qquad y_T = {}^{336}\!/_{760} = 0.442$$
$$P_W = 424 \text{ mm.} \qquad \pi = 760 \text{ mm.}$$

Both water and toluene will vaporize, but the composition of the vapor will remain constant at $y_T = 0.442$ as long as two phases are present. Since the ratio of the vapor pressures of toluene to water is greater than the ratio in the charge, the toluene liquid phase will disappear first. When all of the toluene has just vaporized, the water vaporized will be

$$30 \times {}^{424}\!/_{336} = 37.9 \text{ mols}$$
$$\text{Per cent vaporized} = 37.9 + 30 = 67.9$$

At 70 per cent vaporized, the vapor will contain 30 mols of toluene and 40 mols of water.

$$P_W = 760({}^{40}\!/_{70}) = 434 \text{ mm.} \qquad t = 85°\text{C.}$$
$$y_T = {}^{30}\!/_{70} = 0.425$$

The following table was prepared in this manner:

T, °C.	Per cent vaporized	y_T
60	0	—
70	0	—
80	0	—
84.4	0	—
84.4	67.9	0.442
85	70	0.429
87.4	80	0.375
89	90	0 333
90 3	100	0 300

These results are plotted in Fig. 4-7.

Solution of Part 2. Basis: 30 mols toluene, 70 mols H_2O. Vaporization will not occur until the total pressure is equal to the sum of the partial pressures. At 85°C.,

$$P_T = 341 \text{ mm.}$$
$$P_W = 434 \text{ mm.}$$
$$\pi = 775 \text{ mm.}$$

Reasoning as in Part 1, all of the toluene will be vaporized at this pressure together with ${}^{434}\!/_{341} \times 30 = 38.2$ mols of H_2O.

$$\text{Per cent vaporized} = 30 + 38.2 = 68.2$$
$$y_T = \frac{30}{68.2} = 0.440$$

In order to vaporize the remaining H_2O, the pressure must be lowered. Let

$$N = \text{per cent vaporized}$$

$$y_W = \frac{N - 30}{N}; \qquad y_T = \frac{30}{N}$$

$$P_W = \pi y_W$$

$$\pi = \frac{P_W N}{N - 30} = \frac{434N}{N - 30}$$

Using this relationship,

N (% vaporized)	π, mm.	y_T
70	759	0 429
80	694	0.375
90	651	0.333
100	620	0.300

The results of these calculations are plotted in Fig. 4-8.

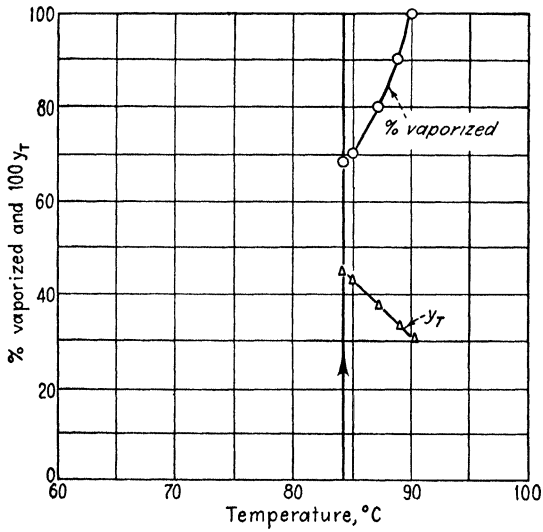


FIG. 4-7.

Partially Miscible Liquids. There are a large number of systems in which the components are miscible only over limited ranges of concentration. These mixtures form a very important group for fractional distillation. The fact that the liquids are partially miscible greatly alters the normal type of vapor-liquid relationships, and the fact that two liquid phases are present requires that one less degree of freedom be available than is normal for a system of a given number of components. In general, the vapor-liquid equilibria of these systems

are very abnormal and, by properly exploiting these abnormalities and combining distillation and decanting operations, separations can easily be made.

The types of systems in this category range from those which are almost immiscible, such as water and benzene, to those that are miscible except for very limited regions, such as phenol and water. Even though benzene and water are essentially immiscible, distillation is often employed for the purpose of drying benzene. Benzene saturated with water contains a very small percentage of the latter. By the

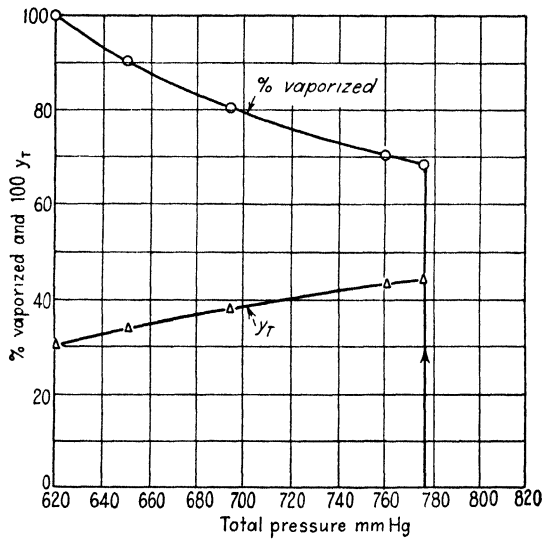
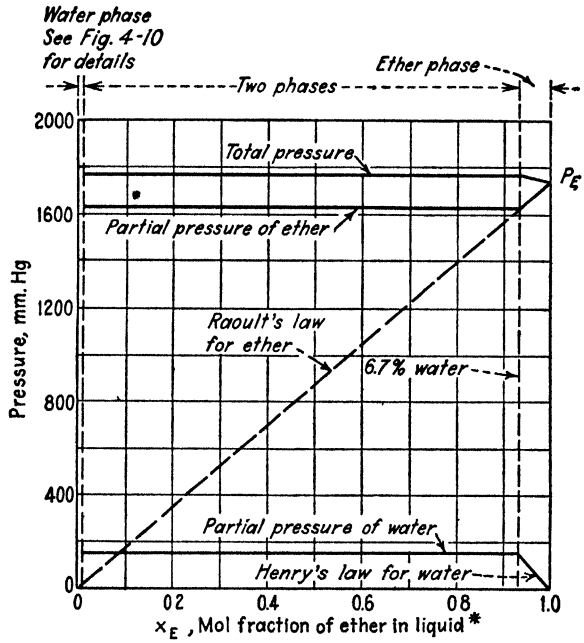


FIG. 4-8.

proper distillation technique this water can be completely and easily removed. This type of operation is employed chiefly for drying materials that are partially miscible with water. If the solubility of water in the material is low, distillation is an economical method of drying the liquid and is effective down to the extremely low concentrations of water. As an example of the method of estimating the vapor-liquid equilibria for systems in which the mutual solubility is low, the mixture ethyl-ether and water will be considered.

In Fig. 4-9 a constant-temperature diagram for this system has been constructed in which the ordinate is the partial pressure of the components, and the abcissa is the mol fraction of ether in the mixture. This mol fraction is the mols of the ether in the combined liquid phases divided by the total mols of ether and water in all of the liquid present.

It is a "pseudo" mol fraction. At the left-hand side of the diagram the water partial-pressure curve starts at the vapor pressure of water, and the ether curve starts at zero, since none is present. As ether is added to the system, it first dissolves in the water, giving only one liquid phase, until a concentration of 0.9 mol per cent ether is reached, which is the solubility of ether in water at 60°C. In the



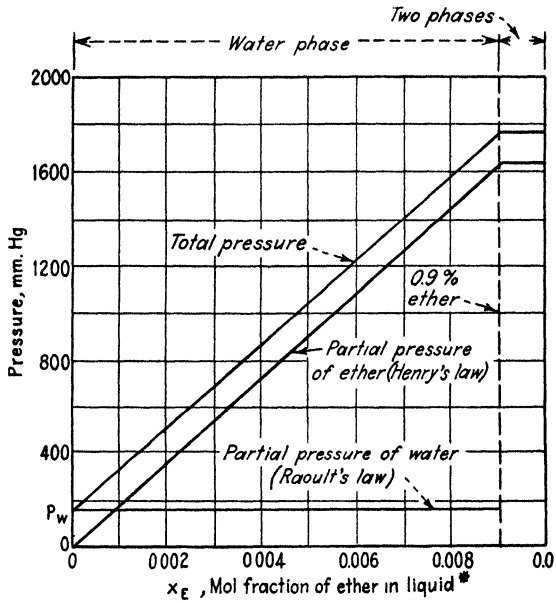
* In the two-phase region mol fraction values are based on total of both phases.

FIG. 4-9. Estimation of vapor-liquid equilibria for system ethyl ether–water at 60°C.

region below 0.9 mol per cent ether, the water partial pressure will agree closely with that predicted by Raoult's law since there is not enough ether present in the liquid phase to alter significantly the water properties. If one component of a binary mixture obeys Raoult's law, the Duhem equation states that the other equation must obey Henry's law, $p = Hx$. Thus in this region it is reasonable to assume Henry's law for ether.

When the amount of ether present in the liquid exceeds 0.9 mol per cent, two phases form. The water phase will consist of 99.1 mol per cent water and 0.9 mol per cent ether. The ether phase will consist of 93.3 mol per cent ether and 6.7 mol per cent water. These are the solubility relationship of these two components at a temperature of

60°C. Thus, at a mol per cent of ether equal to 0.9, two liquid phases will be formed. As more and more ether is added to the system, the amount of the liquid ether phase increases, but the compositions of the ether and the water phases remain constant. This is in agreement with the phase rule which states that, for two-component systems involving three phases, only one degree of freedom is available, and in



* In the two-phase region mol fraction values are based on total of both phases.

FIG. 4-10. Estimation of vapor-liquid equilibria for system ethyl ether–water at 60°C.

this case the temperature has been fixed. Therefore, the compositions of all phases are fixed, as well as the pressure, as long as the three phases are present.

On adding more ether, a condition is finally reached at which sufficient ether is present to dissolve all of the water, and the water phase disappears. The concentration of the phases just at this condition is the same as it has been throughout the two-phase region. Thus, at mol per cents of ether from 0.9 to 93.3, two phases are present, and the partial pressures of water and ether in the vapor are constant. Above a mol percentage of ether of 93.3 only one liquid phase is present, and the system then has two degrees of freedom; *i.e.*, the vapor composition then becomes a function of the liquid composition. For the ether phase it is logical to assume Raoult's law for the ether and Henry's law

for the water, but the assumptions are probably not so good as those made for the water phase because of the high solubility of water in ether. With these assumptions, the pressure-composition diagram can be completed.

At 60°C. the vapor pressures of ether and water are 1,730 and 149.4 mm. Hg, respectively. Thus for mol fractions of ether of 0.9 or less, the partial pressure of water by Raoult's law is $p_W = 149.4x_W$, and the partial pressure of ether is $p_E = H_E x_E$. For mol fractions of ether of 93.3 or greater, $p_E = 1{,}730x_E$, and $p_W = H_W x_W$, where H_E and H_W are the Henry's law constants for ether in water and water in ether, respectively. The partial pressures of a component must be the same in both liquid phases in the two-liquid-phase region and the above equations can be equated.

For water,

$$149.4(0.991) = H_W(0.067)$$
$$H_W = 2{,}210$$

For ether,

$$(0.009)H_E = 1{,}730(0.933)$$
$$H_E = 179{,}500$$

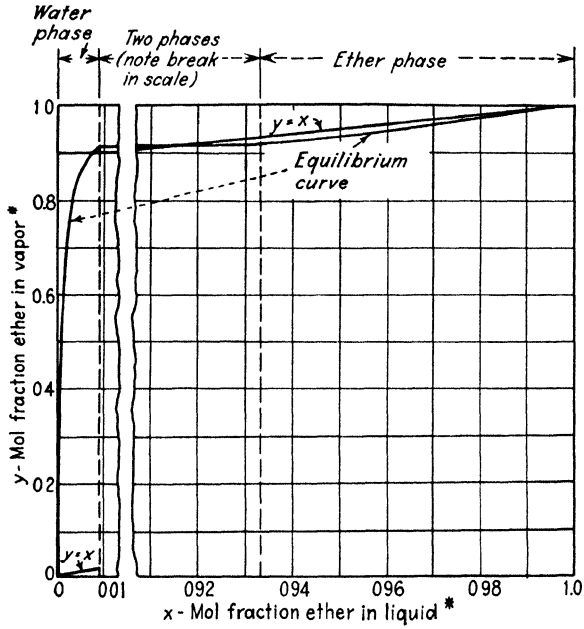
It is interesting to note that ether at a mol fraction of 0.009 in water exerts a partial pressure equal to 93.3 per cent of that of pure ether. Thus its volatility, p/x, is extremely high.

The results of such calculations are shown in Figs. 4-9 and 4-10. The latter figure is an expansion of the left-hand side of Fig. 4-9. Raoult's law for ether is shown as a straight line from the vapor pressure of ether at the right-hand side of the diagram to zero at the left-hand side. On the basis of the above assumptions, this line is used only for values x_E from 0.933 to 1.0. From $x_E = 0.009$ to 0.933 the partial pressure of ether is constant, and from $x_E = 0.009$ the partial pressure drops on a straight line to 0 at $x_E = 0$. A similar construction is used for water. The sum of the two partial-pressure curves is the total pressure. This is also shown.

If these data are replotted as mol fraction of ether in the vapor vs. mol fraction of ether in the liquid, assuming that the vapors obey the perfect-gas law, one obtains the results given in Fig. 4-11. The value of the mol fraction of ether in the vapor increases very rapidly with the mol fraction in the liquid and becomes constant at 0.915 in the two-phase-liquid region. The vapor-liquid curve crosses the 45° line at a composition of 0.915 mol per cent ether. The mixture of this composition is a pseudo-azeotrope. For mol fractions of ether greater than

0.915, water is more volatile than ether in spite of the fact that the vapor pressure of ether is over eleven times that of water. If a liquid corresponding to a composition in the ether phase region were distilled at 60°C., water would tend to pass off in the vapor leaving ether in the still. Thus, ether could be dried by fractionally distilling water overhead.

This simplified analysis is probably of sufficient accuracy for most distillation calculations, but it is not suitable for cases of partially



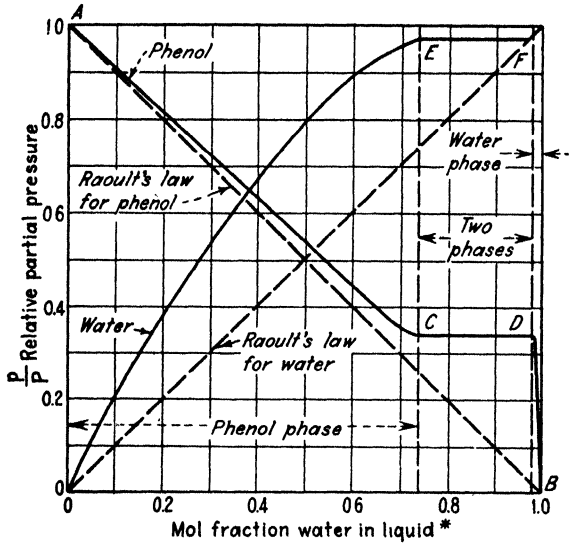
* In the two-phase region mol fraction values are based on total of both phases.

FIG. 4-11. Estimated vapor-liquid equilibria for ethyl ether–water at 60°C.

miscible liquids in which the mutual solubility is much greater. The experimental data on such systems indicate that the partial pressure vs. mol fraction curves pass from the one-phase region to the two-phase region in a smooth type of curve; *i.e.*, the corner at the end of the horizontal line rounds into the Henry law region. The construction used for Fig. 4-9 indicated a sharp corner. This rounding effect tends to make the Henry law constant larger. If one component obeys Raoult's law, the Duhem equation indicates that the other component must obey Henry's law, which in the special case may also be Raoult's law. It follows that, in the region where the curvature

occurs and Henry's law does not apply, the other components cannot agree with Raoult's law.

These effects are more clearly illustrated by mixtures in which the immiscibility is limited to a narrow region. In such cases the straight-line construction applied in Fig. 4-9 is entirely unsatisfactory. The data of Sims (Ref. 3) for the system phenol-water for the constant-temperature conditions of 43.4°C. are presented in Fig. 4-12. In this case the partial pressure of each component divided by the vapor pres-



* In the two-phase region mol fraction values are based on total of both phases.

FIG. 4-12. System, phenol-water at 43.4°C.

sure of the pure component at 43.4°C. is plotted vs. the mol fraction in the liquid. This method of plotting is applied since the vapor pressures of water and phenol are so greatly different that it is difficult to represent both of them on the same graph.

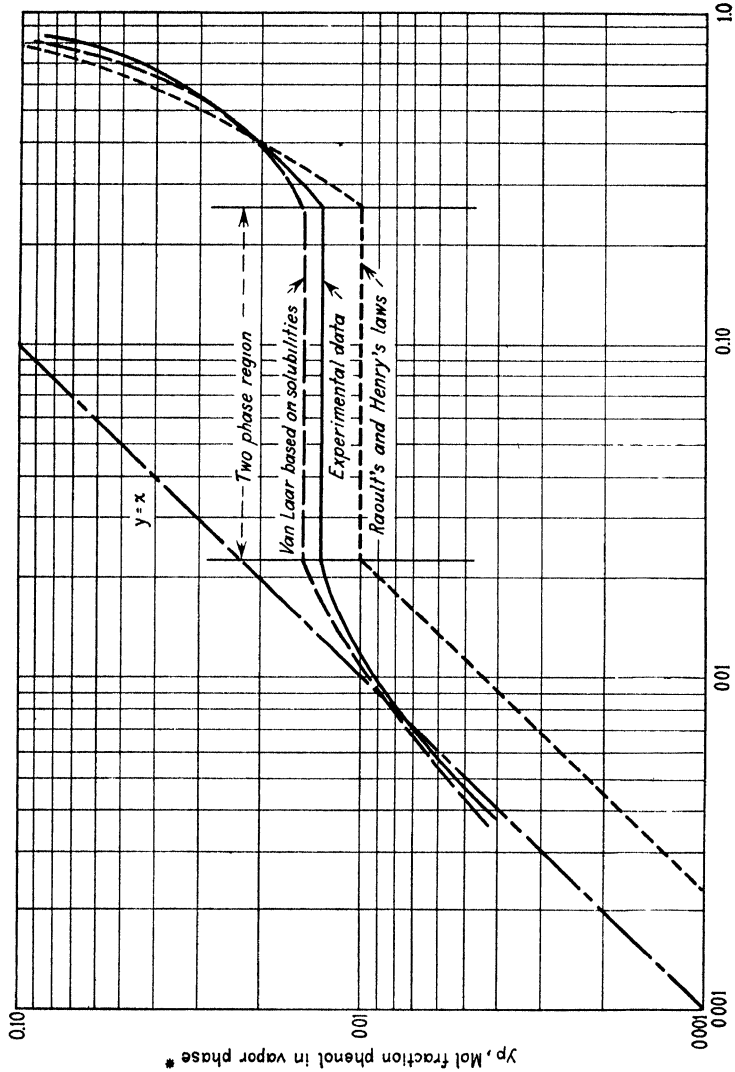
The limit of solubility of water in phenol corresponds to a mol fraction of water of 0.74, while the solubility of phenol in water is 0.0225 mol fraction phenol. For mol fractions of water between 0.74 and 0.9775, the components exist as two liquid layers. Throughout this range in which two liquid phases are present and where the compositions of these phases are therefore constant, the partial pressures remain constant and are represented by the horizontal line *EF* and *CD*. The 45° lines corresponding to Raoult's law are drawn for both components. The data for the water phase cover such a short region that

deviations from Raoult's law for the water component are not obvious. In the phenol phase a moderate deviation from Raoult's law is apparent. It will be noted in the figure that the curves tend to approach the immiscible region with rounded corners instead of with sharp angles.

The two points of importance regarding the diagram are (1) constancy of partial pressure so long as two liquid phases are present and (2) the character and extent of the deviation from Raoult's law. The diagram shows that the partial pressure in phenol, when dissolved in water is abnormally high; *i.e.*, it is much greater than is called for by Raoult's law, the line AB. Limited miscibility of two liquids implies that the molecules of one find it difficult to force their way into the other. Thus, it requires a relatively high pressure for phenol to force a small amount of itself into water. This is equivalent to saying that, when phenol has been dissolved in water, the volatility of phenol is abnormally high. The less the mutual solubility, the more abnormal the partial pressure; hence the greater the volatility of the dissolved component. The practical results of these relationships are shown in the following example.

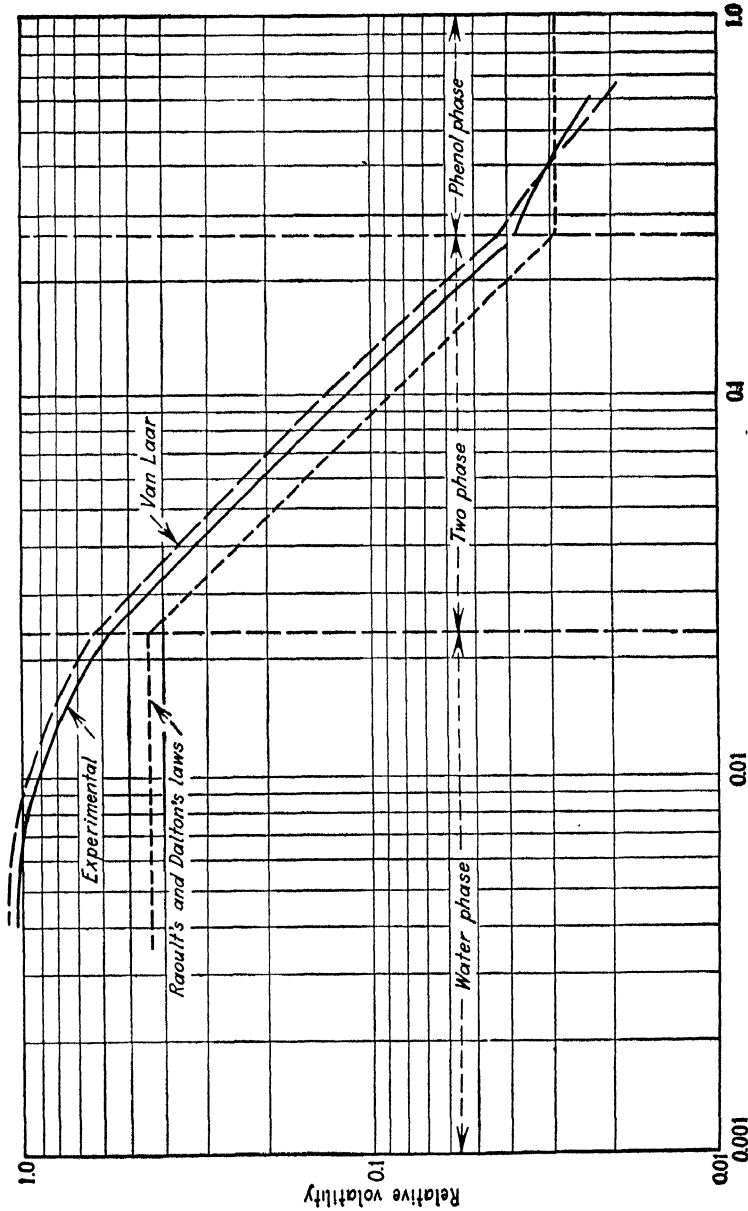
Despite the fact that phenol boils almost 80° higher than water, in certain regions, *i.e.*, low concentrations of phenol, the volatility of phenol is greater than that of water; *i.e.*, the vapor given off by such a solution is richer in phenol than the solution itself. If a solution in this low concentration region is distilled, the water is discharged from the bottom of the column essentially free of phenol, which is found in the distillate.

These data for phenol and water are replotted in Fig. 4-13 as the vapor-liquid equilibrium, *i.e.*, the mol fraction of the phenol in the vapor as a function of the mol fraction of phenol in the liquid. The data curve is labeled "experimental." These data indicate that this system forms a minimum boiling azeotrope at a concentration of about 0.0073 mol fraction phenol. At concentrations lower than this, phenol is more volatile than water. At all concentrations greater than this, water is more volatile than phenol. This y,x curve indicates the constancy of vapor composition in the two-phase region. The procedure involving the use of Raoult's and Henry's laws employed for the ethyl ether-water system is probably not suitable for the phenol-water system because of the high mutual solubilities. However, such calculations were made for illustrative purposes and the results are shown on Figs. 4-13 and 4-14. The latter figure gives the relative volatilities corresponding to the vapor-liquid curve of Fig. 4-13. It is apparent



* In the two-phase region mol fraction values are based on total of both phases.

FIG. 4-13. Vapor-liquid relations for system, phenol-water at 43.4°C.



* In the two-phase region mol fraction values are based on total of both phases.

FIG. 4-14. Relative volatility of phenol to water.

that this simplified method is not very satisfactory. In fact it would indicate that water was more volatile than phenol at all compositions and that no azeotrope was formed. The results obtained would not be of much utility and would actually be very misleading. Thus, if water containing a low concentration of phenol were to be distilled, the calculations based on Raoult's and Henry's laws would indicate that water was the more volatile component, while the actual data indicate that phenol is the more volatile. This simplified procedure gives only very approximate results if the mutual solubilities are over a few mol per cent.

A better prediction of the actual vapor-liquid equilibria can be obtained by the use of the Van Laar equation. It has been found that in general this equation can be employed empirically to give satisfactory correlation for each of the single-phase regions of a partially miscible system. Because of the constancy of partial pressure over the two-phase region, the Van Laar constants for two single phases should be related to each other by the values of the mutual solubilities. However, in most cases it is found that the constants obtained for the two single-phase regions do not correlate with each other and the solubility limits in a manner theoretically required. This is undoubtedly because the assumptions made by Van Laar are not satisfied in partially miscible systems. For example, it is obvious that the entropy of mixing for such a system would not be equal to that for the ideal case.

To apply the Van Laar equation independently to each of the two single-phase regions requires experimental vapor-liquid data; where such data are available, the equation is useful for interpolating, extrapolating, and smoothing the results. However, if such experimental data are not available, the Van Laar equation can be used with the solubility limits to predict vapor-liquid equilibria. This method forces the constants for the two single-phase regions to be identical and, as has already been pointed out, the experimental data for a number of systems give different constants for the two regions. However, in general, this method is a better approximation of the vapor-liquid equilibria than calculations based on Raoult's and Henry's laws. The only information required is the solubility limits at the temperature in question and the vapor pressure of the two pure components at this temperature. Thus at constant temperature,

$$\gamma_{ww}x_{ww} = \gamma_{wp}x_{wp}$$
$$\gamma_{pw}x_{pw} = \gamma_{pp}x_{pp}$$

where ww = water in water phase
wp = water in phenol phase
pw = phenol in water phase
pp = phenol in phenol phase
and by Van Laar relationships,

$$T \ln \gamma_{ww} = \frac{B}{\left(1 + A \frac{x_{ww}}{x_{pw}}\right)^2}$$

$$T \ln \gamma_{wp} = \frac{B}{\left(1 + A \frac{x_{wp}}{x_{pp}}\right)^2}$$

$$T \ln \gamma_{pw} = \frac{BA(x_{ww}/x_{wp})^2}{\left(1 + A \frac{x_{ww}}{x_{wp}}\right)^2}$$

$$T \ln \gamma_{pp} = \frac{BA(x_{wp}/x_{pp})^2}{\left(1 + A \frac{x_{wp}}{x_{pp}}\right)^2}$$

Using $T = 316.4°\text{K.}$, $x_{wp} = 0.74$, and $x_{ww} = 0.9775$ gives six equations with six unknown quantities which can be solved to give $A = 0.206$ and $B = 238$. With these constants, the vapor-liquid equilibria were calculated for the system phenol and water at a temperature of 43.4°, and the calculated results are given in Figs. 4-13 and 4-14, labeled "Van Laar." It will be noted in this case that the agreement with the experimental results is satisfactory and would be of great utility for actual distillation calculations. The water phase, *i.e.*, the low phenol concentration, shows a constant-boiling mixture very close to that determined experimentally.

Where it is necessary to estimate vapor-liquid equilibria for partially miscible systems for which such data are not available, it is believed that the Van Laar equation combined with the solubility limits is of real utility. This method of calculation becomes equivalent to the assumption of Henry's and Raoult's laws if the mutual solubility of the two components becomes extremely low.

In all cases, miscible, partially miscible, or immiscible, fugacity should be used instead of partial pressure and vapor pressure if the pressures are such that deviations from perfect-gas law are significant.

If more than two components are involved and are partially miscible, the relationships become so complicated that the theoretical method of attack in its present form is not particularly helpful. In such cases, it

is necessary to determine experimental values. However, even in these cases the general principles that have been developed for the binary mixture are useful in attaining a picture of phenomena to be expected.

Nomenclature

A,B = constants of Van Laar equation
f = fugacity
f_p = fugacity of pure liquid under its own vapor pressure
f_π = fugacity of pure vapor under total pressure, π
H = Henry's law constant
P = vapor pressure
p = partial pressure
T = temperature
x = mol fraction in liquid
y = mol fraction in vapor
γ = activity coefficient
π = total pressure

References

1. CUMMINGS, Sc.D. thesis in chemical engineering, M.I.T., 1933.
2. GILLILAND and SCHEELINE, *Ind. Eng. Chem.*, **32**, 48 (1940).
3. SIMS, Sc.D. thesis in chemical engineering, M.I.T., 1933.

CHAPTER 5

GENERAL METHODS OF FRACTIONATION

There are several methods by which fractionation can be obtained. The more important among them are (1) successive distillation of condensed distillate, (2) fractional condensation, and (3) rectification.

Successive Distillation. The first method, successive distillation of the condensed distillate, can be shown best by referring to Fig. 2-1. Starting with a large amount of liquid of the composition x_5 which boils at 760 mm. pressure, temperature t_4, a small amount of vapor of the composition x_1 is removed from the apparatus and condensed, giving a liquid of the composition x_1. If this new liquid is again distilled, the first portion of the distillate will have a composition x_2. Continuing this process, successive compositions of the distillates can be estimated by following a series of steps which eventually approach the point C, pure carbon disulfide, as a limit.

Removal of any vapor of the composition x_1 from the liquid of the composition x_5 will change the composition of the liquid in the direction of pure carbon tetrachloride. Therefore, if the distillation of the liquid is continued, the composition will approach pure carbon tetrachloride as a limit, and the last of the liquid to be distilled would have this composition.

It is therefore possible by a systematic series of distillations to separate any mixture of carbon disulfide and carbon tetrachloride into practically pure carbon disulfide and pure carbon tetrachloride. This systematic fractionation may be shown diagramatically as in Fig. 5-1, in which the original mixture (1) is divided into a distillate (3) and a residue (2). (3) and (2) are then distilled separately and produce distillates and residue. The distillate from (2) and the residue (3) being combined into a new liquid (5) which is again distilled with (4) and (6) to continue the separation. This process is continued until practically complete separation is obtained. Such a process is sometimes carried out in the laboratory, but it is extremely tedious and the same results usually can be obtained in other more convenient ways.

The procedure outlined in Fig. 5-1 would appear to result in a number of intermediate products and only a small amount of the desired

fractions. Actually by a sufficient number of distillations the original mixture can be obtained essentially as the desired products. For example, assume that fractions 11 and 15 represent the desired separation, then fractions 12, 13, and 14 can be redistilled as shown in Fig. 5-2 to give fractions 11′ and 15′ which can be obtained as the same

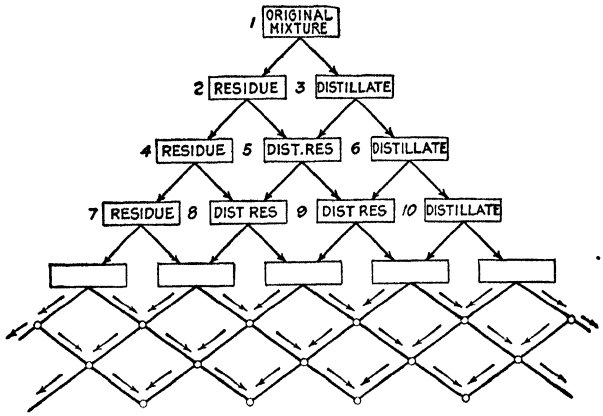


FIG. 5-1. Fractionation diagram.

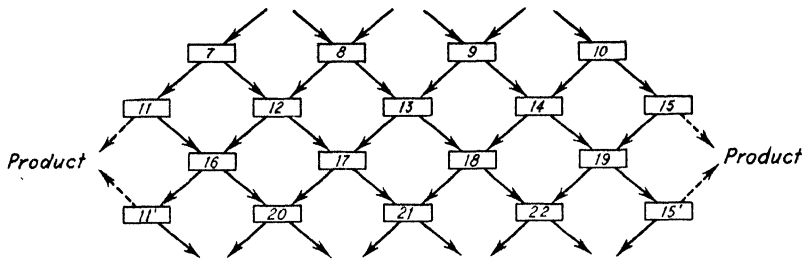


FIG. 5-2. Fractionation diagram.

composition as fractions 11 and 15. Samples 20, 21, and 22 can be redistilled in the same manner, and by a repetition of the procedure essentially all of the material will be given the desired separation.

The method outlined in the preceding paragraph can be made continuous. Thus by regulating the fractions vaporized in the various distillations it is possible to have fractions 5 and 13 of the same composition as the original mixture, and fresh feed can be added to these fractions before they are distilled.

Fractional Condensation. Instead of partially distilling a liquid into a distillate and a residue, a vapor can be partly condensed into a condensate and a residual vapor. The results obtained are exactly

analogous to those for the successive distillation and, by a similar series of successive vaporization and partial condensation, similar separation can be effected. In fact, successive distillation and successive fractional condensation can be combined to increase the efficiency of the operation.

Multiple Distillation. Suppose an apparatus as in Fig. 5-3 consisting of a series of distilling kettles A, B, C, etc., each kettle containing a heating coil and necessary connection for vapors and liquid. Suppose that kettle A contains a liquid mixture of carbon disulfide and carbon tetrachloride of the composition x_5 as in Fig. 2-1; the kettle B,

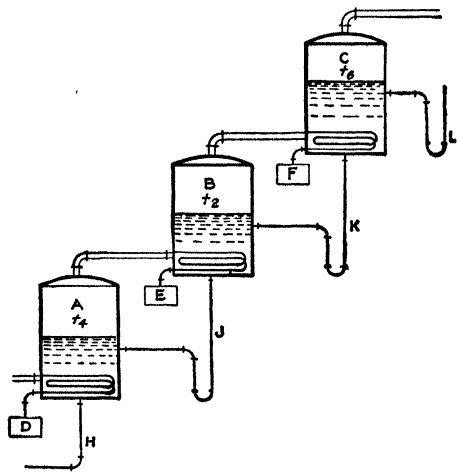


FIG. 5-3. Diagram of multiple distillation.

a liquid of composition x_1; the kettle C, a composition of x_2; and so on. The liquid in A boils at t_4, that in B at t_2, and that in C at t_6. Since the vapor leaving A is at a temperature t_4 which is higher than the boiling temperature t_2 in B, then, if the vapor from A is led into the heating coil of B, it will give up its heat to the contents of B, boiling the liquid and itself being partly condensed. The vapor from B, if led into the heating coil of C will in the same way boil the liquid in C, the vapor being itself condensed as before. The condensed vapors in the coil may be drawn off into receiver D, E, and F, etc. However, since the composition of the liquid in B was selected to be the same as that of the vapor coming from the kettle A, from Fig. 2-1, the condensed vapor in the coil can be allowed to mix with the contents of B instead of being withdrawn into the receiver E. Now since the vapor from A is being mixed with the liquid in B and since there is a heat inter-

change between the two, it is much simpler to blow the vapor directly into the liquid thus dispensing with the coil.

The vapor leaving still B will be richer in carbon disulfide than the vapor from still A, and the liquid in B will therefore tend to become poor in carbon disulfide. The concentration of the liquid in B can be maintained constant by adding liquid from C which is rich in carbon

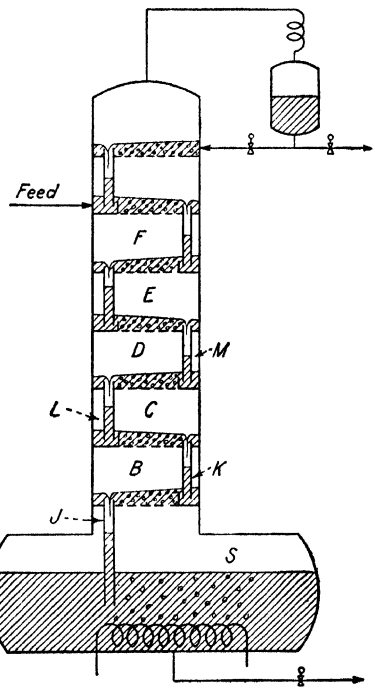


FIG. 5-4. Schematic diagram of rectifying column.

disulfide, and removing liquid from B and adding it to A. By a similar procedure the operation of the other stills can be maintained at a steady state. A little consideration of Fig. 2-1 will show that to make the system operate at the compositions indicated would require that all the vapor from C be condensed and returned through line L to C and that no liquid be withdrawn.

Rectification. An apparatus in which this direct interchange of heat, condensation, and evaporation can take place is called a rectifying tower, and the process carried on within it is called rectification.

Such a system is shown in Fig. 5-4, where S is the still body, or kettle. Resting on the outlet of the still is a column divided into com-

partments by plates perforated with small holes. Each plate has an overflow pipe discharging into a pool of liquid on the plate below. The layer of liquid on each plate is prevented from passing down through the holes by vapor which is rising up through these holes from the compartment next below. Any excess liquid accumulated on the plate flows down through the overflow pipe. The letters on the apparatus correspond to those of Fig 5-3. The vapor from the still at temperature t_4 and composition x_1 passes up and exchanges heat and molecules with the liquid in compartment B. A binary vapor of the composition x_2 is produced which bubbles up through the liquid on the next higher plate which is richer in carbon disulfide with the composition x_2. Here again exchange between the vapor and liquid takes place, and a vapor of composition x_6 even richer in the carbon disulfide is produced. This can be repeated any number of times, and the vapor finally issuing from the apparatus at the top and into the condenser is practically pure carbon disulfide. As in the previous case, each one of the compartments in the column may be considered a small still, in which the source of heat is the hot vapor coming from below and the cooling element is the cooler liquid from the plate above.

The quantitative relationships given are valid only in case the molal ratio of liquid overflowing from plate to plate to the vapor flowing through the plate is practically unity; *i.e.*, the ratio of distillates to liquid vaporized is exceedingly small. In practice, less overflow must be employed to reduce the heat consumption, and the rate of enrichment is less rapid than that indicated in the explanation.

The analogy between this fractionating column and the series of kettles would be better if the vapor leaving the liquid on the plate had the equilibrium composition assumed. But, unfortunately, no design has been able to prevent some of the vapor from the plate below from passing through the liquid on the plate without coming into equilibrium with it. The vapor above any plate, therefore, will contain less of the volatile component than would be the case if complete equilibrium were reached. This ideal case is discussed here because it brings out clearly the nature of the underlying phenomena. The more practical cases will be considered in Chap. 7 on the Rectification of Binary Mixtures.

The interchange between the vapor bubbles and the liquid on the plate is a result of the fact that the two are not at equilibrium. Thus in the ideal case considered a vapor of composition x_1 was bubbling through a liquid of the same composition. The vapor in equilibrium with a liquid of composition x_1 would have been x_2. Thus, as the sys-

tem tends to approach equilibrium, carbon tetrachloride molecules pass from the vapor to the liquid and carbon disulfide molecules will pass from the liquid to the vapor. The number of molecules passing in the two directions will be essentially equal since in most cases the energy released when one molecule of carbon tetrachloride goes into the liquid phase will be about equal to that required for vaporizing one molecule of the carbon disulfide. Thus the total number of molecules in the vapor tends to remain about constant. This interchange between the vapor and the liquid is governed by the usual mass-transfer mechanism, and the rate of exchange increases with the amount of interfacial area and the turbulence involved. A close approach to equilibrium is desired, and the equipment is designed to give intimate contact between the two phases. Besides the bubbling action already described, the process produces a considerable amount of spray, and there is also an interchange between the vapor and the liquid droplets above the main body of liquid that is helpful in obtaining a closer approach to equilibrium.

This process of countercurrent contact of a vapor with a liquid which has been produced by partial condensation of the vapor is termed rectification. Its result is equivalent to a series of redistillations with the consumption of no additional heat and is analogous in this respect to multieffect evaporation. However, it is only the result that is similar and not the mechanism of obtaining it.

CHAPTER 6

SIMPLE DISTILLATION AND CONDENSATION

Simple Distillation. Distillation without rectification can be carried out by several methods. The two most generally considered cases are (1) *continuous simple distillation* and (2) *differential distillation.* In continuous distillation, a portion of the liquid is vaporized under conditions such that all the vapor produced is in equilibrium with the unvaporized liquid. In differential vaporization, the liquid is vaporized progressively, and each increment of vapor is removed from contact with the liquid as it is formed and, although each increment of vapor can be in equilibrium with the liquid as it is formed, the average composition of all of the vapor produced will not be in equilibrium with the remaining liquid.

Continuous Simple Distillation. Distillations that approximate this type are usually carried out on a continuous basis such that the liquid feed is added continuously to a well-mixed still in which a definite fraction is vaporized and removed and the excess unvaporized liquid is withdrawn from the still. An alternate arrangement is to preheat the feed and add it to a flash or disengaging section where vapor and liquid are separated and removed without additional heat requirements. In either case, assuming that the vapor and liquid leaving are in equilibrium with each other, the two fractions are related to each other by equilibrium constants and material balances. Thus for each component in a mixture the following material balance can be written:

$$Vy + Lx = Fz \tag{6-1}$$

where V, L, F = mols of vapor, unvaporized liquid, and feed, respectively

y, x, z = mol fractions of components in corresponding streams

By over-all material balance $V + L = F$ and the fraction vaporized,

$$\frac{V}{F} = \frac{z - x}{y - x} \tag{6-2}$$

Thus if the fraction vaporized, the feed composition, and the relation

between y and x are known, both the vapor and the liquid compositions can be calculated. In order to determine the equilibrium relationships either the temperature or the total pressure must be known. Given either of these, the other can be determined from the equilibrium relationship for all the components involved.

Differential Distillation. This type of distillation is usually carried out as a batch operation although continuous units may also operate in this manner. Considering first a batch distillation, if a mixture of liquid is distilled, the distillate contains a greater portion of the more volatile material than the residue, and as distillation proceeds both the distillate and the residue become poorer in the more volatile components. This change in composition may be estimated quantitatively if the relation of the composition of vapor to that of the liquid is known. Consider W parts of original mixture containing x_o fraction of component A. Allow a differential amount $-dW$ to be vaporized of a composition, y, under such conditions that the vapor is continually removed from the system.

By material balance,

$$\begin{aligned} -y\,dW &= -d(Wx) \\ &= -W\,dx - x\,dW \\ \frac{W\,dx}{dW} &= y - x \\ \int_{W_0}^{W} \frac{dW}{W} &= \int_{x_0}^{x} \frac{dx}{y - x} \\ \ln \frac{W}{W_o} &= \int_{x_0}^{x} \frac{dx}{y - x} \end{aligned} \tag{6-3}$$

This equation was developed by Rayleigh (Ref. 2) and is often termed the Rayleigh equation. It can be used with W as weight and x as weight fraction, or with W as mols and x as mol fraction. It is usually applied on the basis that, at any given instant, y is in equilibrium with x, but the derivation does not require this condition. A similar equation applies to each component in a mixture.

The use of Eq. (6-3) requires the relationship between y and x and, even if they are assumed to be in equilibrium with each other as the vapor is formed, it is usually difficult to express the equilibria mathematically for a general integration. The integration can be performed graphically if the relationship between y and x is available.

Batch Distillation Example. As an illustration of the use of this equation, consider the experiment performed by Rayleigh. 1,010 g. of a 7.57 mol per cent solution of acetic acid in water was distilled until the still contained 254 g. whose com-

position was 11 mol per cent acetic acid. Assuming that the vapor leaves in equilibrium with the liquid, calculate the final composition to be expected on the basis of Eq. (6-3). Equilibrium data for the system acetic acid-water are given in Table 6-1.

There are several approximate methods that may be followed in integrating Eq. (6-3). First, for small temperature and composition ranges, the relation between the vapor and liquid may be approximately represented by a straight line, or $y = cx$, where c is a constant.

$$\ln \frac{W}{W_o} = \int_{x_o}^{x} \frac{dx}{cx - x} = \int_{x_o}^{x} \frac{dx}{x(c-1)} = \frac{1}{c-1} \ln \frac{x}{x_o}$$

TABLE 6-1

Mol fraction of acetic acid in liquid, x	Mol fraction of acetic acid in vapor, y	$c = \frac{y}{x}$	Relative volatility of acetic acid to water, α
0 0677	0 0510	0.75	0 74
0 1458	0.1136		
0 2682	0.2035	0.76	0.70
0 3746	0.2810		
0.4998	0.3849	0.77	0.625
0.6156	0.4907		
0 7227	0 6045	0.84	0.59
0.8166	0.7306		
0 9070	0.8622	0.95	0.64

Clearing of logarithms,

$$\frac{W}{W_o} = \left(\frac{x}{x_o}\right)^{1/c-1} \quad \text{or} \quad \frac{x}{x_o} = \left(\frac{W}{W_o}\right)^{c-1} \tag{6-4}$$

From the table a value of $c = 0.75$ is appropriate and

$$\left(\frac{254}{1{,}010}\right)^{0.75-1} = \frac{x}{0.0757}$$

$$x = 0.107 \text{ (10.7 mol per cent)}$$

The calculated value is in good agreement with the experimental result and indicates that the various assumptions made are reasonably satisfied.

Another method is by the use of the relative volatility which is defined by Eq. (3-5).

$$\frac{y_A/x_A}{y_B/x_B} = \alpha_{AB}$$

where α_{AB} is the relative volatility of component A to component B. For a large number of mixtures, the variation of α with composition is small, and an average value may be employed. For a binary mixture, the expression can be rewritten

$$y_A = \frac{\alpha x_A}{1 + (\alpha - 1)x_A}$$

The use of this relation with Eq. (6-3) gives

$$\ln \frac{W}{W_o} = \int_{x_o}^{x} \frac{dx}{\dfrac{\alpha x}{1 + (\alpha - 1)x} - x}$$

$$= \frac{1}{\alpha - 1} \ln \frac{x(1 - x_o)}{x_o(1 - x)} + \ln \frac{1 - x_o}{1 - x} \tag{6-5}$$

Using $\alpha = 0.74$ (see Table 6-1) gives $x = 0.106$.

In other cases, it will be found that the variations in c and α are so great that these methods are not satisfactory. In such cases they can be applied successively over small concentration ranges but graphical integration is usually preferable.

There is an alternate form of the differential distillation equation that is frequently more convenient to use than Eq. (6-3). Consider a mixture containing A mols of one component and B mols of some other. Let a differential quantity of vapor be produced containing $-dA$ and $-dB$ mols of the two components, respectively, then assuming vapor-liquid equilibria,

$$\frac{-dA}{-dB} = \alpha \frac{A}{B} \tag{6-6}$$

A similar equation can be written between any two components of the mixture. If the relative volatility is constant, the equation can be integrated directly,

$$\int_{A_o}^{A} \frac{-dA}{A} = \alpha \int_{B_o}^{B} \frac{-dB}{B}$$

where A_o, B_o = mols of the two components in still at some base time
A, B = mols in still at some later time

$$\ln \frac{A}{A_o} = \alpha \ln \frac{B}{B_o}$$

$$\frac{A}{A_o} = \left(\frac{B}{B_o}\right)^{\alpha} \tag{6-7}$$

If the vapor formed is not in equilibrium with the liquid, the value of α in Eq. (6-6) will have to be modified to express the true relationship.

Batch Dehydration of Benzene. As another example of the use of Rayleigh's equation, consider the dehydration of benzene. Benzene saturated with water at 20°C. contains 0.25 mol per cent water, and it is to be given a simple differential distillation at a constant pressure of 1 atm. The operation is to proceed until the mol per cent water in the liquid remaining in the still is 0.00025. The following data and simplifying assumptions will be used in the calculations:

1. Over the temperature range involved it is assumed that the vapor pressure of pure benzene is 2.1 times the vapor pressure of water.

2. At the distillation temperature, benzene saturated with water contains 1.5 mol per cent water, and water saturated with benzene contains 0.039 mol per cent benzene.

3. It is assumed that the vapor leaves in equilibrium with the liquid.

4. No condensate will be returned to the still.

5. For the two single-phase regions of benzene containing water and water containing benzene, it is assumed that Raoult's law applies to the component in large amount, and Henry's law to the component in small amount.

Solution. By a procedure similar to that employed for ether and water in Chap. 4, it is possible to calculate the relative volatility. The solubility of water in benzene is higher at the distillation temperature than at 20°C., and only a benzene phase will be present in the still. The partial pressure of benzene will follow Raoult's law.

$$p_B = x_B P_B$$

For water the partial pressure will follow Henry's law with a constant such that a mol fraction of 0.015 will give a partial pressure equal to that over water saturated with benzene. Thus,

$$p_W = \frac{0.99961 x_W P_W}{0.015}$$

and the relative volatility of water to benzene is

$$\begin{aligned} \alpha &= \frac{p_W/x_W}{p_B/x_B} \\ &= \frac{99{,}961 P_W}{0.015 P_B} \\ &= 31.7 \end{aligned}$$

Even though the vapor pressure of benzene is over twice that of water at the distillation temperature, the volatility of water in benzene is over 30 times that of the benzene because of the abnormalities indicated by the low mutual solubilities.

The value of the relative volatility can be used with Eq. (6-5) and gives

$$\ln \frac{W}{W_o} = \frac{1}{31.7 - 1} \ln \frac{0.0000025(0.9975)}{0.0025(0.9999975)} + \ln \frac{0.9975}{0.9999975}$$

$$\frac{W}{W_o} = 0.796$$

Therefore, 20.4 per cent of the charge should be vaporized.

The example given assumed that no condensate would be returned to the still. Actually the condensate will break in two layers, a water layer and a benzene layer, and the benzene layer saturated with water could be returned continually to the still for redistillation or it could be stored and added to a subsequent cycle. The amount of heat required for the drying operation could be reduced by rectification or partial condensation. These operations will be considered in a later chapter.

Steam Distillation. A common example of simple distillation is the so-called *steam distillation.* The term is generally applied to distillations carried out by the introduction of steam directly into the liquid

in the still and is usually limited to those cases in which the solubility of the steam in the liquid is low at the temperature and pressure in question. It is usually applied to relatively high-boiling organic materials which would decompose if they were distilled directly at atmospheric pressure or to liquids that have such poor heat-transfer characteristics that excessive local superheating would result with indirect heating. By steam distillation a volatile organic material may be separated from nonvolatile impurities, or mixtures may be separated with results about equivalent to those predicted by the Rayleigh equation.

The molal ratio of the organic material to the steam is the ratio of the mol fractions in the vapor, and, assuming that the gas laws apply,

$$\frac{n_O}{n_W} = \frac{y_O}{y_W} = \frac{p_O}{p_W} = \frac{p_O}{\pi - p_O} \tag{6-8}$$

where n = mols
y = mol fraction in vapor
p = partial pressure
π = total pressure
Subscripts O and W refer to organic and water, respectively.

If the organic material is immiscible with water, and equilibrium is attained, p_O would be the vapor pressure of the organic material, and the partial pressure of water would be the total pressure minus p_O. If a liquid water phase were present, the partial pressure of water would have to be the vapor pressure of water, thus fixing the distillation temperature at a given total pressure. For this case, the distillation temperature will always be less than that corresponding to the boiling point of water at the total pressure in question. This illustrates one of the real advantages of steam distillation. Thus high-boiling organic material can be steam-distilled in an atmospheric pressure operation at a temperature below 100°C. If a liquid water phase is not present, then both the total pressure and the temperature can be arbitrarily chosen, and the partial pressure of water is the difference between the total pressure and the vapor pressure of the organic material. Of course, this partial pressure of water must not be greater than the vapor pressure of pure water, or a liquid phase will form.

If water and the material being distilled are not immiscible, the vapor-liquid equilibria for the system in question will have to be known in order to determine the relation between the vapor and the liquid composition.

Steam distillation can be carried out in several manners. It is possi-

ble to pass steam directly through the liquid without any other source of heat. Because heat must be supplied for the vaporization of the organic material, steam will condense and form a liquid phase unless it is very highly superheated. If water does condense, the distillation temperature will be less than the boiling point of pure water, and at such a temperature the value of p_o will frequently be very small and Eq. (6-8) would require a large number of mols of steam per mol of organic material distilled. Actually the molal ratio given by this equation is simply the overhead vapor ratio, and any condensation of steam in the still would be in addition to the values so obtained. Owing to the low molecular weight of steam relative to that of the high-boiling organic material the consumption of steam may not be excessive. However, in some cases it may be desirable to reduce the steam consumption. This can be accomplished by indirectly heating the still and maintaining the distillation temperature higher than that obtained when a liquid water phase is present. For maximum steam economy, the temperature should be as high as is possible without undesirable thermal effects. This higher temperature increases the value of p_o and reduces that of $\pi - p_o$ thus decreasing the ratio of the steam required per unit of organic material distilled. Another method of reducing the steam consumption is to reduce the total pressure. Thus, if the total pressure was reduced to the value of p_o, no steam would be required and the organic material would boil directly. Frequently this is not feasible because of the very high vacuum required or the undesirable heat-transfer characteristics of the liquid. However, by the use of reduced pressure the amount of steam required can be made relatively small, and if the vacuum is adjusted such that the vapor mixture will condense with the cooling water available, the load on the vacuum pump will be low.

Steam Distillation Example. As an example of steam distillation, consider the separation of a mixture of two high-boiling organic acids from a small amount of nonvolatile carbonaceous material. The steam distillation is carried out at 100°C. under a total pressure of 150 mm. Hg. The organic acid mixture contains 70 and 30 mol per cent of the low- and high-boiling acids, respectively, and at 100°C. the vapor pressures of the two acids are 20 and 8 mm. Hg. It is assumed that the mixture of the two acids obeys Raoult's law and that they are immiscible with water. The nonvolatile carbonaceous material is assumed to have no effect on the vapor-liquid equilibria. It will be assumed that the vapor leaves in equilibrium with the liquid in the still, and two cases will be considered. In the first, the mixture of acids will be fed continuously to a still of small capacity, and it will be assumed that steady-state conditions have been reached in which the composition of the organic acids in the condensate is the same as in the feed. In the second

case, a batch distillation of the differential type will be carried out. It is assumed that all the sensible and latent heat is supplied either externally or by superheat in the steam. The calculations are to determine how many pounds of steam must be used per mol of acid recovered in each case.

Solution of Part 1. *Continuous Operation.* In this case the ratio of the two organic acids in the vapor is the same as in the feed and, since Raoult's law has been assumed for the organic acids mixture, it is possible to calculate the ratio of the two acids in the still. Thus,

$$\frac{y_1}{y_2} = \frac{P_1 x_1}{P_2 x_2} = \alpha \frac{x_1}{x_2} = \frac{A_1^o}{A_2^o}$$

where x = mol fraction based on the two acids only
A_1^o, A_2^o = original mols of the more and less volatile acids, respectively
With $x_2 = 1 - x_1$,

$$x_1 = \frac{A_1^o/A_2^o}{\alpha + (A_1^o/A_2^o)}$$

$$p_1 + p_2 = P_1 x_1 + P_2 x_2 = P_2[(\alpha - 1)x_1 + 1] = \frac{P_1(A_1^o + A_2^o)}{\alpha A_2^o + A_1^o}$$

where p_1, p_2 = partial pressures of acids
P_1, P_2 = vapor pressures of acids
and

$$p_{H_2O} = \pi - (p_1 + p_2)$$

The pounds of water required per pound mol of acid is

$$\frac{18(\pi - p_1 - p_2)}{p_1 + p_2} = 18\left[\frac{\pi\left(\alpha + \dfrac{A_1^o}{A_2^o}\right)}{P_1\left(1 + \dfrac{A_1^o}{A_2^o}\right)} - 1\right]$$

$$= 18\left[\frac{150\left(2.5 + \dfrac{0.7}{0.3}\right)}{20\left(1 + \dfrac{0.7}{0.3}\right)} - 1\right]$$

$$= 178$$

Solution of Part 2. In this case, it is assumed that the still is charged with the mixture of acids and that the distillation is continued until all the acids have been vaporized.

Considering the acids only, the differential distillation Eq. (6-6) gives

$$\frac{-dA_1}{-dA_2} = \alpha \frac{A_1}{A_2}$$

where A_1 = mols of more volatile acid in still
A_2 = mols of less volatile acid in still

and for constant α

$$\int_{A_1^o}^{A_1} \frac{dA_1}{A_1} = \alpha \int_{A_2^o}^{A_2} \frac{dA_2}{A_2}$$

$$\frac{A_1}{A_1^o} = \left(\frac{A_2}{A_2^o}\right)^\alpha$$

$$\frac{A_1}{A_2} = \frac{A_1^o}{(A_2^o)^\alpha} A_2^{\alpha-1}$$

$$x_1 = \frac{A_1}{A_1 + A_2}$$

$$p_1 + p_2 = P_2 \left(\frac{\alpha A_1 + A_2}{A_1 + A_2}\right)$$

By steam distillation Eq. (6-8),

$$\frac{-dN}{dA_1 + dA_2} = \frac{-dN}{\left(\alpha \frac{A_1}{A_2} + 1\right) dA_2} = \frac{\pi - p_1 - p_2}{p_1 + p_2} = \frac{\left(\frac{\pi}{P_2} - \alpha\right)\frac{A_1}{A_2} + \left(\frac{\pi}{P_2} - 1\right)}{\alpha \frac{A_1}{A_2} + 1}$$

where N = mols of steam

$$-\int^N dN = \int_{A_2^o}^{o} \left[\left(\frac{\pi}{P_2} - \alpha\right) \frac{A_1^o}{(A_2^o)^\alpha} A_2^{\alpha-1} + \left(\frac{\pi}{P_2} - 1\right)\right] dA_2$$

$$N = \frac{\pi}{P_2}\left(\frac{A_1^o}{\alpha} + A_2^o\right) - (A_1^o + A_2^o)$$

The pounds of steam per pound mol of acid is

$$\frac{18N}{A_1^o + A_2^o} = 18\left[\frac{\pi}{P_1}\left(\frac{\alpha + \frac{A_1^o}{A_2^o}}{1 + \frac{A_1^o}{A_2^o}}\right) - 1\right]$$

This is identical to the relation found in Part 1, and the steam requirement is the same. Less steam per mol of acids distilled would be required in the first part of the batch distillation, but more would be required in the last portion. The above analysis indicates that the two differences would just balance out.

Partial Condensation. It is frequently desirable to partially condense a vapor. Such an operation can be used to produce a separation of the components but, in general, it is employed for obtaining a portion as condensate for some specific purpose.

The partial condensation of a vapor mixture can produce a wide variation in degree of separation obtained. If the condensation is carried out rapidly, the time for interchange between the condensate and the vapor may be so short that essentially no selective mass transfer of the components occurs. In this case, the composition of the condensate will be the same as that of the vapor. If the condensation

is carried out at a slow rate, mass-transfer interchange will occur and several different degrees of separation can be obtained. The operation can be carried out such that the condensate is essentially in equilibrium with the uncondensed vapor, and this type of operation will be termed *equilibrium partial condensation.* Alternatively, the condensation can be carried out such that the condensate as it is formed is in equilibrium with the vapor, but the condensate is removed continuously and thus the total condensate would not be in equilibrium with the uncondensed vapor. This type of operation will be termed *differential partial condensation.* In a third distinct type of partial condensation, the vapor passes through the condenser unit countercurrent to the condensate. Assuming that efficient countercurrent contact is obtained, it should be possible to produce a higher degree of separation than is possible with equilibrium partial condensation.

Equilibrium partial condensation is handled mathematically in a manner completely analogous to that for equilibrium distillation. It is a type of condition that is frequently encountered in the partial condenser of a rectification unit in which the uncondensed vapor and the condensate flow along together and reach a close approach to equilibrium.

Differential partial condensation is not a common type of operation, but the countercurrent version of partial condensation is probably approached in condensers in which the vapor flows upward condensing on the tube walls and the condensate flows down along the walls in contact with the upward flowing vapor. Such a wetted-wall unit will give mass transfer between the vapor and the liquid, but in general the sizes of the tubes desirable for heat transfer and fluid flow are such that the interchange between vapor and liquid is relatively poor, and the separation obtained in practice is probably not much greater than that equivalent to equilibrium partial condensation. While a condenser could be designed such that it would give more efficient countercurrent action, it has been found to be more economical to design a condenser for the liquefaction function and to obtain the desired separation of the components by more effective means.

Analysis of Partial Condenser Data. Gunness (Ref. 1) reports experimental data obtained on the partial condenser of a rectifying column stabilizing absorption naphtha. The vapor from the column was passed downward through the partial condenser, and the uncondensed vapor and condensate from the bottom of the condenser passed together to the reflux drum where they were separated. Owing to the concurrent flow of the vapor and the liquid, it would be expected that this system might approximate equilibrium partial condensation. The data for a test

taken when the pressure was 254 p.s.i.a. and the temperature in the reflux drum was 117°F. are given in the first three columns of Table 6-2. The fourth column gives values of the equilibrium constant obtained from Table 3-2, page 41, at the temperature and pressure corresponding to the reflux drum. If the uncondensed vapor and the liquid were in equilibrium with each other, their composition should be related by the equilibrium constants. As a method of making this comparison, the last column in the table gives the values of the vapor composition divided by the equilibrium constant for each of the components. If the vapor and liquid were at equilibrium, the compositions so calculated should be the same as those given for the liquid reflux. It will be noted that the experimental composition and the calculated values are in good agreement. In fact it is probable that the agreement is within the accuracy of the experimental data and the equilibrium constants. The close agreement indicates the reliability of the experimental data and the applicability of the vapor-liquid equilibrium constant to this system.

TABLE 6-2

Component	Residue gas, y	Liquid reflux, x	K	$x_{cal} = \frac{y}{K}$
CH_4	0.053	0.007	12	0.0044
C_2H_4	0.011	0.002	3.6	0.003
C_2H_6	0.146	0.0618	2.55	0.057
C_3H_6	0.140	0.12	1.05	0.133
C_3H_8	0.537	0.580	0.94	0.572
i-C_4	0.081	0.160	0.50	0.162
n-C_4	0.032	0.069	0.40	0.080

Nomenclature

A = mols of A in still
B = mols of B in still
c = constant
F = mols of feed
L = mols of unvaporized liquid
N = mols of steam
n = mols
p = partial pressure
P = vapor pressure
V = mols of vapor
W = mols of liquid in still
x = mol fraction in liquid
y = mol fraction in vapor
z = mol fraction in feed
α = relative volatility
π = total pressure

References

1. GUNNESS, Sc.D. thesis in chemical engineering, M.I.T., 1936.
2. RAYLEIGH, *Phil. Mag.*, 6th series, **4**, 521 (1902).

CHAPTER 7

RECTIFICATION OF BINARY MIXTURES

The separation of two liquids from each other by fractional distillation may be accomplished in two general ways: (1) the batch, or intermittent, method and (2) the continuous method. In the former, the composition and temperature at any point in the system are changing continually; in the latter, conditions at any point are constant.

It will be recalled that a fractionating column consists of a system up through which vapors are passing and down through which a liquid is running, countercurrent to the vapor, the liquid and vapor being in more or less intimate contact with each other. Furthermore, the vapor and liquid tend to be in equilibrium with each other at any point in the column, the liquid and vapor at the bottom of the column being richer in the less volatile component than at the top. It is evident, therefore, that the action of such a column is similar to that of a scrubbing or washing column, where a vapor is removed from a gas that is passing up through the column, by bringing into contact with it, countercurrent, a liquid in which the vapor is soluble, and that will remove it from the gas.

Sorel's Method. Sorel (Ref. 17) developed and applied the mathematical theory of the rectifying column for binary mixtures. He calculated the enrichment, the change in composition from plate to plate, by making energy and material balances around each plate and assumed that equilibrium was attained between the vapor and liquid leaving the plate. He proceeded stepwise through the column by applying this method successively from one plate to the next.

Owing to the steady-state condition involved in continuous distillation, its analysis is simpler than batch operation and so will be considered first.

The equations for Sorel's method will be derived for the case illustrated in Fig. 7-1. The column is assumed to be operating continuously on a binary mixture with the feed entering on a plate between the top and bottom. The column is provided with heat for reboiling by conduction such as steam coils in the kettle; the case of the use of live or open steam will be considered later. A simple total condenser

is assumed where all of the overhead vapor is liquefied, this condensate being divided into two portions, one of which is returned to the column for reflux and the other withdrawn as overhead product. The bottoms are continuously withdrawn from the still or reboiler. (See end of chapter for nomenclature.)

Consider the region bounded by the dotted line in Fig. 7-1. The only material entering this section is the vapor from the nth plate V_n, while leaving the section is the distillate D and the overflow from the $(n + 1)$th plate O_{n+1}. By material balance,

$$V_n = O_{n+1} + D \qquad (7\text{-}1)$$

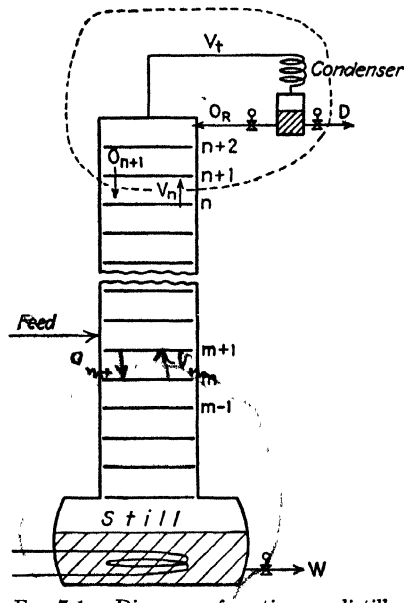


FIG. 7-1. Diagram of continuous distillation column.

Considering only the more volatile component, the mols entering this section are the total mols of vapor from the nth plate multiplied by the mol fraction of the more volatile component in this vapor $V_n y_n$. Likewise, the mols of the more volatile component in the distillate are Dx_D; and in the overflow from the $(n + 1)$th plate are $O_{n+1}x_{n+1}$. A material balance on the more volatile component for this section therefore gives

$$V_n y_n = O_{n+1}x_{n+1} + Dx_D \qquad (7\text{-}2)$$

or

$$y_n = \frac{O_{n+1}}{V_n} x_{n+1} + \frac{D}{V_n} x_D \qquad (7\text{-}2a)$$

$$y_n = \frac{O_{n+1}}{O_{n+1} + D} x_{n+1} + \frac{D}{O_{n+1} + D} x_D \qquad (7\text{-}2b)$$

Thus, starting at the condenser, the composition of the reflux to the tower, with the type of condenser employed, is the same as the composition of the distillate, which makes the composition of the vapor to the condenser the same as that of the distillate. The mols of vapor from the top plate are equal to $O_R + D$, and the reflux to this plate is O_R. Sorel's assumption of the vapor and liquid leaving the plate being in equilibrium, called a theoretical plate, makes it possible to calculate

the composition of the liquid leaving the top plate of the tower from the composition of the overhead vapor and vapor-liquid equilibrium data.

In the design of such a tower, it is generally customary to set or fix certain operating variables such as the composition of the distillate and of the bottoms, the reflux ratio O_R/D, and the composition and thermal condition of the feed. With these values and a known quantity of feed per unit time, by over-all material balances it is possible to calculate D, O_R, and W. To calculate the composition of the vapor

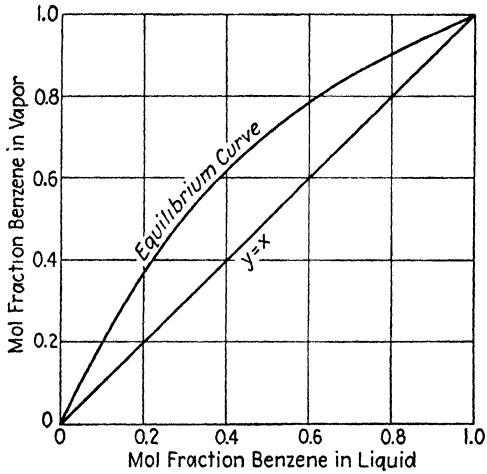


FIG. 7-2. Equilibrium curve for benzene-toluene mixture.

from the plate below the top plate by Eq. (7-2a), it is necessary to know the mols of overflow from the top plate and the mols of vapor from the plate below as well as the known quantities D, x_D, and the mol fraction of the more volatile component in the liquid overflow from the top plate. Sorel obtained the mols of overflow from, and the mols of vapor to, the plate by heat (enthalpy) balances. Thus the heat brought into the plate must equal that leaving.

$$O_R h_R + V_{t-1} H_{t-1} = V_t H_t + O_t h_t + \text{losses} \qquad (7\text{-}3)$$

Equation (7-3) gives a relation between V_{t-1} and O_t; if the enthalpies are known, this equation can be solved simultaneously with Eq. (7-1) to give V_{t-1} and O_t. This, in general, involves trial-and-error solutions, since H_{t-1} is not known and must be assumed until the conditions of the next plate are known. The values of V_{t-1} and O_t obtained in this manner are used in Eq. (7-2a) to give y_{t-1}. From this compo-

sition the value of x_{t-1} is obtained from vapor-liquid equilibrium data as well as the temperature on this plate. The value of H_{t-1} can then be accurately checked, and the calculations corrected if necessary. This operation is continued plate by plate down the tower to the feed plate.

A similar derivation for the plates below the feed gives

$$y_m = \frac{O_{m+1}x_{m+1}}{V_m} - \frac{Wx_W}{V_m} \tag{7-4}$$

$$= \frac{O_{m+1}x_{m+1}}{O_{m+1} - W} - \frac{Wx_W}{O_{m+1} - W} \tag{7-4a}$$

These equations are used in the same way as Eq. (7-2).

Because of the complexity of Sorel's method, it is usually modified by certain simplifying assumptions. The heat supply to any section of the column above the feed is solely that of the vapor entering that section. This supply of heat to the next plate goes to supply vapor from this plate, to heat loss from the section of the tower that corresponds to this plate, and to heating up the liquid overflow across this plate. In a properly designed column, the heat loss from the column should be reduced as far as is practicable and is generally small enough to be a negligible quantity relative to the total quantity of heat flowing up the column. Thus the enthalpy of the vapor per unit time tends to be constant from plate to plate, and in order to simplify the calculations for such systems, Lewis (Ref. 9) assumed that the molal vapor rate from plate to plate was constant except as changed by additions or withdrawals of material from the column. This assumption also leads to a constant overflow rate for such a section. In the case illustrated in Fig. 7-1, this simplifying assumption would give constant vapor and overflow rates above and below the feed plate, but the rates in the two sections of the tower would be different due to the introduction of the feed. This assumption, together with the theoretical plate concept, has been of great assistance in the analysis and design of fractionating column. The validity of these two assumptions will be considered in later sections.

On the basis of Lewis' assumption O_{n+1} and V_n are constant in the section above the feed plate, and the relation between y_n and x_{n+1} becomes a straight line with the slope equal to O/V. Similarly, below the feed, y_m is linear in x_{m+1}. On the basis of the operating variables previously fixed, O_{n+1}, V_n, D, and x_D are known, and the equation between y_n and x_{n+1} is completely defined; likewise for y_m and x_{m+1}.

A plate on which Sorel's conditions of equilibrium are attained is

defined as a "theoretical plate," *i.e.*, a plate on which the contact between vapor and liquid is sufficiently good so that the vapor leaving the plate has the same composition as the vapor in equilibrium with the overflow from the plate. For such a plate the vapor and liquid leaving are related by the equilibrium y,x curve (see page 18). Rectifying columns designed on this basis serve as a standard for comparing actual columns. By such comparisons it is possible to determine the number of actual plates equivalent to a theoretical plate and then to reapply this factor when designing other columns for similar service.

Sorel-Lewis Method. As an illustration of the Sorel-Lewis method, consider the rectification of a 50 mol per cent benzene and 50 mol per cent toluene mixture into a product containing 5 mol per cent toluene and a bottoms containing 5 mol per cent benzene. The feed will enter as a liquid sufficiently preheated so that its introduction into the column does not affect the total mols of vapor passing the feed plate; *i.e.*, such that $V_n = V_m$. A reflux ratio O_n/D, equal to 3, will be employed, and the column will operate with a total condenser and indirect heat in the still. The y,x equilibrium curve is given in Fig. 7-2.

Taking as a basis 100 lb. mols of feed mixture, an over-all benzene material balance on the column gives

$$\begin{aligned} 0.5(100) &= 0.95D + 0.05W \\ &= 0.95D + 0.05(100 - D) \end{aligned}$$

gives

$$\begin{aligned} D &= 50 \text{ lb. mols} \\ W &= 50 \text{ lb. mols} \end{aligned}$$

Since

$$\begin{aligned} \frac{O_n}{D} &= 3 \\ O_n &= 150 \\ V_n &= O_n + D = 200 \end{aligned}$$

by Eq. (7-2*a*),

$$y_n = (^{150}/_{200})x_{n+1} + (^{50}/_{200})(0.95) = 0.75x_{n+1} + 0.2375 \qquad (7\text{-}5)$$

Since a total condenser is used,

$$y_t = x_D = x_R = 0.95$$

from the equilibrium curve at $y = 0.95$, $x = 0.88$; *i.e.*, x_t in equilibrium with y_t is 0.88.

Equation (7-5) then gives

$$y_{t-1} = 0.75x_t + 0.2375 = 0.75(0.88) + 0.2375 = 0.8975$$

by equilibrium curve, x_{t-1} at $y_{t-1} = 0.8975$ is 0.77 and

$$\begin{aligned} y_{t-2} &= 0.75(0.77) + 0.2375 = 0.8145 \\ x_{t-2} &= 0.64 \\ y_{t-3} &= 0.75x_{t-2} + 0.2375 = 0.75(0.64) + 0.2375 = 0.7165 \\ x_{t-3} &= 0.505 \end{aligned}$$

Since the value of x_{t-3} is close to the composition of the feed, this plate will be taken as the feed plate. Below this plate, the equation for the lower portion of the tower must be used. Since the feed was preheated such that

$$V_n = V_m$$
$$V_m = 200$$
$$W = 50$$
$$O_m = 250$$

and

$$y_m = (^{25}\!/_{200})x_{m+1} - (^{5}\!/_{200})(0.05) = 1.25x_{n+1} - 0.0125$$

since $x_{t-3} = x_f = 0.505$

$$y_{f-1} = 1.25(0.505) - 0.0125 = 0.615$$
$$x_{f-1} = 0.392 \text{ from equilibrium curve}$$
$$y_{f-2} = 1.25(0.392) - 0.0125 = 0.478$$
$$x_{f-2} = 0.275$$
$$y_{f-3} = 1.25(0.275) - 0.0125 = 0.323$$
$$x_{f-3} = 0.172$$
$$y_{f-4} = 1.25(0.172) - 0.0125 = 0.21$$
$$x_{f-4} = 0.100$$
$$y_{f-5} = 1.25(0.100) - 0.0125 = 0.122$$
$$x_{f-5} = 0.058$$
$$y_{f-6} = 1.25(0.058) - 0.0125 = 0.06$$
$$x_{f-6} = 0.03$$

The desired strength of the bottoms was $x_W = 0.05$; x_{f-5} is too high, and x_{f-6} is too low. Thus it is impossible to satisfy the conditions chosen and introduce the feed on the fourth plate from the top with an even number of theoretical plates. However, by slightly reducing the reflux ratio it would be possible to make x_{f-6} equal to x_W, or by increasing the reflux ratio to make x_{f-5} equal to x_W. In general, such refinements are not necessary, and it is sufficient to say that between eight and nine theoretical plates are required in addition to the still, three plates above the feed plate, the feed plate, and four or five plates below the feed, and the still, approximately 8½. The percentage difference between eight and nine is much less than the accuracy with which the ratio of actual to theoretical plates is known; whichever is used, a sufficient factor of safety must be utilized to cover the variation of this latter factor.

McCabe and Thiele Method (Ref. 11). By the Sorel-Lewis method, the relation between y_n and x_{n+1} is a straight line, and the equation of this line may be plotted on the y,x diagram. Thus, for the example worked in the preceding section,

$$y_n = 0.75x_{n+1} + 0.2375$$

This is a straight line of slope $0.75 = O_n/V_n$ which crosses the $y = x$ diagonal at $y_n = x_{n+1} = 0.95 = x_D$. On the y,x diagram for benzene-toluene, a line of slope 0.75 is drawn through $y = x = x_D$ (see line

AB, Fig. 7-3). Likewise, below the feed,

$$y_m = \frac{O_m}{V_m} x_{m+1} - \frac{W}{V_m} x_W = 1.25x_{m+1} - 0.0125$$

This represents a straight line of slope $O_m/V_m = 1.25$ and passes through the $y = x$ diagonal at $x = x_W = 0.05$ (see line CD, Fig. 7-3) These two lines are termed the operating lines, since they are deter-

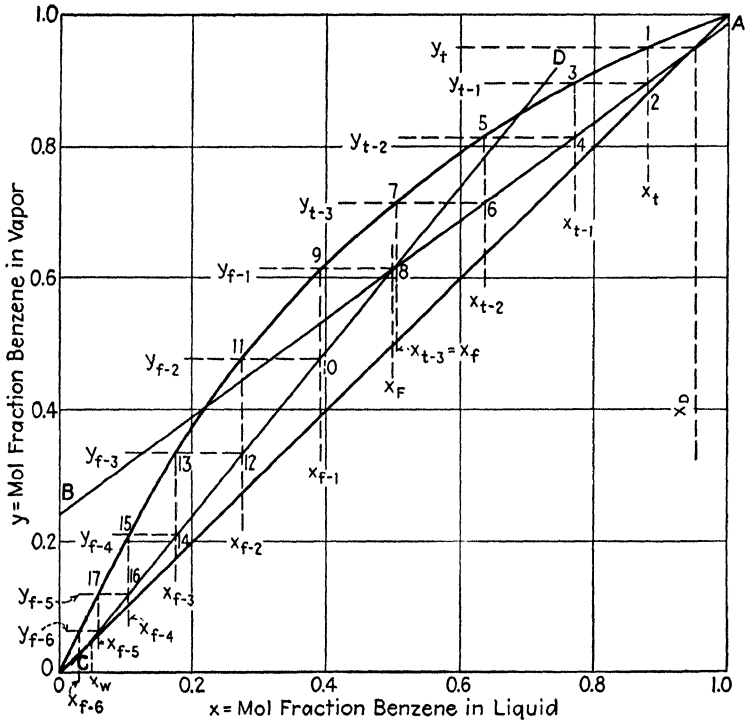


FIG. 7-3. McCabe and Thiele diagram.

mined by the tower operating conditions, AB being the operating line for the enriching section and CD the operating line for the stripping, or exhausting, section. To determine the number of theoretical plates by Fig. 7-3, start at x_D; as before, $y_t = x_D = 0.95$, and the value of x_t is determined by the intersection of a horizontal line through $y_t = 0.95$ with the equilibrium curve at 1, giving $x_t = 0.88$. Now, instead of using Eq. (7-2a) algebraically as in the Sorel-Lewis method, it is used graphically as the line AB. A vertical line at $x_t = 0.88$ intersects this operating line at 2, giving $y_{t-1} = 0.89$. By proceeding

horizontally from intersection 2, an intersection is obtained with the equilibrium curve at 3. Since the ordinate of intersection 3 is y_{t-1}, the abscissa must be the composition of the liquid in equilibrium with this vapor; *i.e.*, $x_{t-1} = 0.77$. As before, the intersection of the vertical line through the point 3 with the operating line at 4 gives the y on the plate below, or $y_{t-2} = 0.815$. This stepwise procedure is carried down the tower. At intersection 8, x_{t-3} is approximately equal to x_F; and at this plate, the feed will be introduced. The stepwise method is now continued, using the equilibrium curve and the operating line CD.

Such a stepwise procedure must yield the same answer as the previous calculations, since it is the exact graphical solution of the algebraic equation previously used. It has a number of advantages over the latter method: (1) It allows the effect of changes in equilibrium and operating conditions to be visualized. (2) Limiting operating conditions are easily determined, and if a column contains more than two or three plates, it is generally more rapid than the corresponding algebraic procedure. Because of the importance of this diagram it will now be considered in further detail.

Intersection of Operating Lines. In Fig. 7-3, the operating lines intersected at $x = x_F$. This intersection is not fortuitous, since the positions of the two operating lines are not independent but are related to each other by the composition and thermal condition of the feed. This relation is most easily shown by writing a heat balance around the feed plate. Let p be the difference between the mols of overflow to and from the feed plate divided by the mols of feed.

$$p = \frac{O_{f+1} - O_f}{F} \tag{7-6}$$

A material balance gives

$$p + 1 = \frac{V_f - V_{f-1}}{F} \tag{7-6a}$$

Let x_i and y_i be the coordinates of the intersection of the operating lines. At this intersection, y_n must equal y_m, and x_n must equal x_m. An over-all material balance on the more volatile component gives $Dx_D + Wx_W = Fz_F$, where z_F is the average mol fraction of this component in the feed. Writing Eqs. (7-2a) and (7-4) for the intersection and using the values y_i and x_i,

$$V_f y_i = O_{f+1} x_i + Dx_D \tag{7-2a'}$$
$$V_{f-1} y_i = O_f x_i - Wx_W \tag{7-4'}$$

and subtracting,

$$\begin{aligned}(V_f - V_{f-1})y_i &= (O_{f+1} - O_f)x_i + Dx_D + Wx_W \\ &= (O_{f+1} - O_f)x_i + Fz_F \\ \frac{(V_f - V_{f-1})y_i}{F} &= \left(\frac{O_{f+1} - O_f}{F}\right)x_i + z_F\end{aligned}$$

Substituting values of p and $p + 1$ gives the point on the diagram at which the intersection must occur.

$$\begin{aligned}(p + 1)y_i &= px_i + z_F \\ y_i &= \frac{p}{p + 1}x_i + \frac{z_F}{p + 1} \qquad (7\text{-}7)\end{aligned}$$

Equation (7-7) together with Eq. (7-2*b*) gives

$$x_i = \frac{\left(\frac{O}{D} + 1\right)z_F - (p + 1)x_D}{(O/D) - p} \qquad (7\text{-}8)$$

and

$$y_i = \frac{(O/D)z_F - px_D}{(O/D) - p} \qquad (7\text{-}9)$$

This line of intersections crosses the $y = x$ diagonal at

$$y_i = x_i = z_F$$

and has a slope of $p/(p + 1)$. The effects of various values of p are shown in Fig. 7-4 for a given slope of the operating line above the feed. Thus, if $p = 0$, the mols of overflow above and below the feed are equal, and the operating lines must intersect in a horizontal line through the diagonal at z_F. A value of $p = -1$, *i.e.*, $V_f = V_{f-1}$, would put the intersection on a vertical line at z_F.

The value of p is best obtained by an enthalpy balance around the feed plate. However, when the molal enthalpy of the overflow from the feed plate and the plate above is essentially the same and the enthalpy of the vapor from the feed plate and the plate below is also the same, then, by Eqs. (7-6) and (7-6*a*), $-p$ becomes approximately the heat necessary to vaporize 1 lb. mol of the feed divided by the latent heat of vaporization of the feed. Thus, an all-vapor feed at its boiling point would have a value of $p = 0$, for an all-liquid feed at its boiling point, p would equal -1; p would be less than -1 for a cold feed, between -1 and zero for a partially vaporized feed, and greater than zero for a superheated vapor feed.

A little study of Fig. 7-4 indicates that for a given O/D fewer plates are required for a given separation the colder the feed. This results from the fact that the cold feed condenses vapor at the feed plate and increases the reflux ratio in the lower portion of the column. This higher reflux ratio is obtained at the expense of a higher heat consumption in the still.

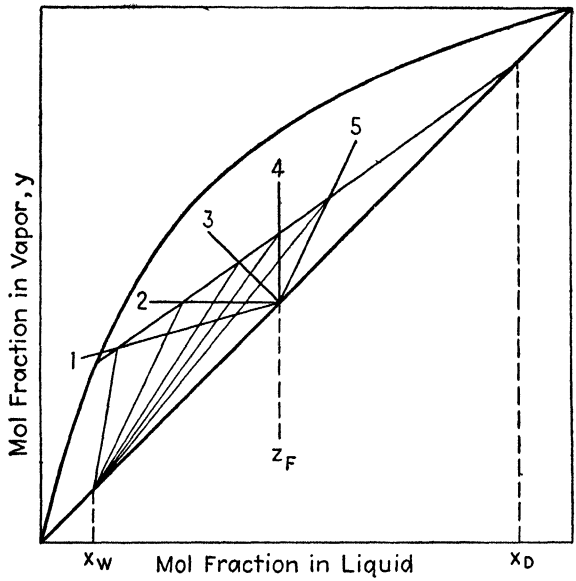


FIG. 7-4. The effect of the thermal condition of the feed on the intersection of the operating lines.

1, p is greater than 0 (superheated vapor feed)
2, $p = 0$ ($O_{f+1} = O_f$)
3, $0 > p > -1$ (partly vapor feed)
4, $p = -1$ ($V_{f-1} = V_f$)
5, $p < -1$ (cold feed)

Logarithmic Plotting. When the design involves low concentrations at the terminals of the tower, it is necessary to expand this part of the diagram in order to plot the steps satisfactorily. This may be done by redrawing these regions of the y,x diagram to a larger scale. In some cases, it may be necessary to make more than one expansion of successive portions of the diagram. Alternately, the y,x diagram may be plotted on logarithmic paper, and the steps constructed in the usual manner. On this type of plot in the low-concentration region, the equilibrium curve is generally a straight line, since, for small values of x: $y = \dfrac{\alpha x}{1 + (\alpha - 1)x}$ becomes $y = \alpha x$; however, the operating line

which is of the form $y_m = ax_{m+1} + b$ is a curved line unless $b = 0$. The operating line is constructed from points calculated from the operating-line equation.

Minimum Number of Plates. The slope of the operating line above the feed is O_n/V_n, and as this slope approaches unity the number of theoretical plates becomes smaller. When O_n/V_n is equal to 1, O_R/D is equal to infinity, and only an infinitesimal amount of product can be withdrawn from a finite column. Frequently it is assumed that total reflux corresponds to the addition of no feed or to the removal of no products. If such is the case, the tower is not meeting the design conditions. It is better to visualize a tower with an infinite cross section, which is separating the feed at a finite rate into the desired products. Under such conditions the column is said to operate at total reflux or with an infinite reflux ratio, and both operating lines have a slope of unity causing them to coincide with the $y = x$ diagonal. Since a higher reflux ratio than this is not possible, the size of the steps on the y,x diagram is a maximum, and a minimum number of theoretical plates to give a given separation is obtained. This number is determined by simply using the $y = x$ diagonal as the operating line and constructing the steps from x_D to x_W. A column with the minimum number of plates serves as a reference below which no column with fewer plates can give the desired separation, but such a column would have a zero capacity per unit volume and would require infinite heat consumption per unit of product.

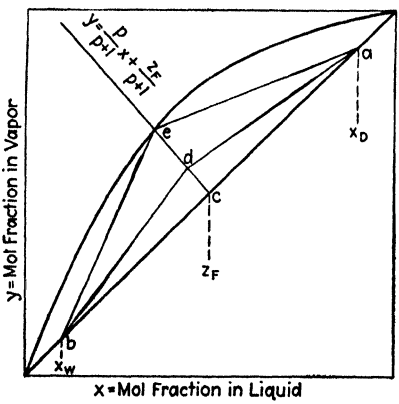


FIG. 7-5. Plot for minimum reflux ratio.

Minimum Reflux Ratio. In general, it is desired to keep the reflux ratio small in order to conserve heat and cooling requirements. As the reflux ratio O_R/D is reduced from infinity, the slope of the operating line $\frac{O_n}{V_n} = \frac{O/D}{(O/D) + 1}$ decreases from unity. Thus, in Fig. 7-5 a reflux ratio of infinity would correspond to operating lines coinciding with the diagonal as *acb*, and a lower reflux ratio would correspond to *adb*. It is obvious that the average size of the steps between the equilibrium curve and the line *adb* will be much smaller than the size of the steps

between the equilibrium curve and the line *acb*. Thus, a reduction of the reflux ratio requires an increase in the number of theoretical plates to effect a given separation. As the reflux ratio is further decreased, the size of the steps between the operating lines and the equilibrium curve becomes still smaller, and still more theoretical plates are required, until the conditions represented by *aeb* are encountered, when the operating line just touches the equilibrium curve. In this final case, the size of the step at the point of contact would be zero, and an infinite number of plates would be required to travel a finite distance down the operating line. The reflux ratio corresponding to this case is called the minimum reflux ratio and represents the theoretical limit below which this ratio cannot be reduced and produce the desired separation even if an infinite column is employed. This reflux ratio is easily determined by laying out the operating line of the flattest slope through x_D that just touches but does not cut the equilibrium curve at any point; the slope of this line $\frac{O}{V} = \frac{O/D}{(O/D) + 1}$ gives the value of O/D. Alternately, it may be calculated from the equation

$$\frac{O_R}{D} = \frac{x_D - y_c}{y_c - x_c} \tag{7-10}$$

where x_c and y_c are the coordinates of the point of contact. For mixtures having normal-shaped equilibrium curves, such as benzene-toluene, the point of contact of the operating line with the equilibrium curve will occur at the intersection of the operating lines. For cases that deviate widely from Raoult's law, the operating line may become tangent to the equilibrium curve before the intersection of the operating lines touches the equilibrium curve, and in such cases it is usually best to plot the diagram and determine the slope O_n/V_n.

Optimum Reflux Ratio. The choice of the proper reflux ratio is a matter of economic balance. At the minimum reflux ratio, fixed charges are infinite, because an infinite number of plates is required. At total reflux, both the operating and the fixed charges are infinite. This is due to the fact that an infinite amount of reflux and a column of infinite cross section would be required for the production of a finite amount of product. The tower cost therefore passes through a minimum as the reflux ratio is decreased above the minimum. The costs of the still and condenser both increase as the reflux ratio is increased. The heat and cooling requirements constitute the main operating costs, and the sum of these increases almost proportionally as the

reflux ratio is increased. The total cost, the sum of operating and fixed costs, therefore passes through a minimum.

Optimum Reflux Ratio Example. The following estimates illustrate these factors for the fractional distillation of a methanol-water mixture to produce 250 gal. of methanol per hour. In making the calculations, it was assumed that the heat-transfer surface required was proportional to the vapor rate which is equal to $D\left(\frac{O}{D}+1\right)$ and that the tower costs were proportional to the total square feet of plate area. The charges on the equipment, including maintenance, repairs, depreciation, interest, etc., were taken at 25 per cent per year, and the heating costs were based on the heat load. The costs per hour as a function of the reflux ratio are summarized in Table 7-1. Labor charges have been excluded since these should be

TABLE 7-1. ESTIMATED COST FOR THE FRACTIONATION OF A METHANOL-WATER MIXTURE

$\frac{O}{D}$	$\frac{O}{V}$	Costs, dollars per hour			
		Charges on tower	Charges on condenser and reboiler	Steam and cooling water	Total
0 65	0.39	∞	0.023	0.33	∞
0.68	0.40	0.11	0.024	0.335	0.47
0 71	0.41	0 09	0.025	0.34	0 455
0.84	0 46	0.064	0.026	0.37	0.46
1.1	0 52	0 057	0.030	0.42	0 51
1.6	0.61	0.06	0.037	0.52	0.62
2.6	0.72	0.07	0.051	0.71	0.82
6.5	0.87	0.12	0.017	1.48	1.71
∞	1.0	∞	∞	∞	∞

relatively independent of the reflux ratio. These results are plotted in Fig. 7-6. It will be noted that the total of these costs passes through a minimum at a reflux ratio, O/V, equal to about 0.43, (O/D = 0.75). This is very close to the minimum reflux ratio, 0.65 and is a result of the fact that the heating and cooling costs are large and increase rapidly with the reflux ratio.

The calculated economic reflux ratio for most cases is so close to the minimum reflux ratio that the accuracy of the latter becomes a critical matter. In the present case, the most economical reflux ratio, O/D, is only 15 per cent above the minimum, and it is doubtful whether the equilibrium data available are sufficiently accurate to make the calculation of the minimum reflux ratio better than ±10 per cent. For this reason, it is industrial practice to employ a reflux ratio somewhat higher than the most economical, and values of 1.3 to 2 times the minimum reflux ratio are common. For the case here considered, reflux ratios in this range would give operating costs only slightly greater than the minimum. This small increase in cost gives a design that will be less sensitive to slight inaccuracies in the data employed.

One of the important pieces of data needed for such an economic study is the number of theoretical plates as a function of the reflux ratio. Approximate methods for the rapid estimation of such data are given in Chap. 12, page 348.

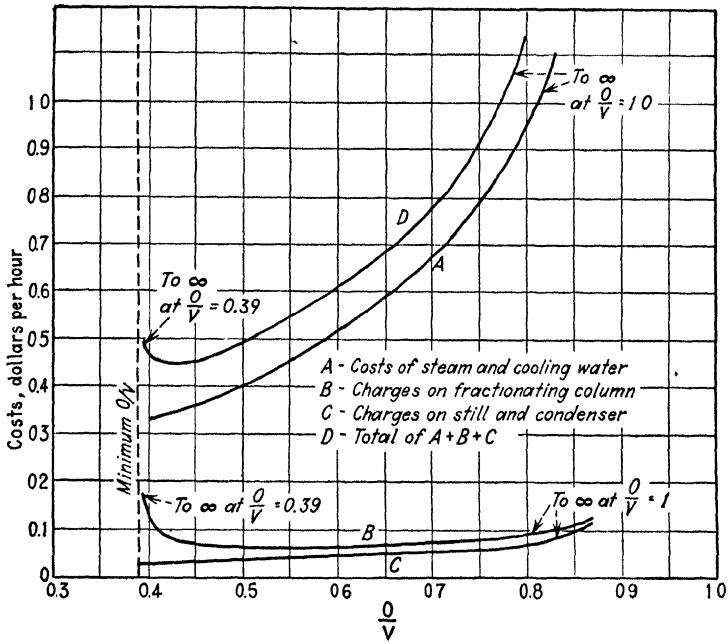


FIG. 7-6. Optimum reflux ratio.

Feed-plate Location. One step between the equilibrium curve and the operating line for the enriching section corresponds to one theoretical plate in the enriching section above the feed, and one step between the equilibrium curve and the other operating line corresponds to one theoretical plate below the feed. Therefore the step that passes from one operating line to the other corresponds to the feed plate. Thus, in Fig. 7-7, when plates are stepped off down the operating line *abc*, it is not possible to step on the operating line *dbe* until the value of x is less than the value corresponding to point *e*. However, as soon as the value of x is less than *e*, it is possible to shift to the other operating line, but it is not necessary to do so at this value, since steps can be continued down *abc* until they are pinched in at *c*, but a value less than *c* cannot be obtained unless the shift is made. The step from one

operating line to the other must therefore occur at some value of x between the values corresponding to c and e, and a change at any value within this range will give an operable design. In general, for a given reflux ratio, it is desired to carry out the rectification with as few plates as possible in order to reduce the plant costs; *i.e.*, the minimum number of steps from a to d between the equilibrium curve and the operating line is desired. This minimum number of steps for the design conditions selected is obtained by taking the largest possible steps at all points between a and d. It is obvious that for values between e and b larger steps will be obtained between the equilibrium curve and operating line abc than would be obtained with operating line dbe. Likewise, for values between c and b larger steps will be obtained by using line dbe than by using abc. Therefore it is desirable to use operating line abc for values from a to b, and line dbe for values between d and b; and by making the feed plate, *i.e.*, the shift from one line to the other, straddle the value b, the minimum number of theoretical plates will be obtained for the operating conditions chosen. If a step happens to fall directly on b, then the feed may be introduced either at b or on the plate below without changing conditions.

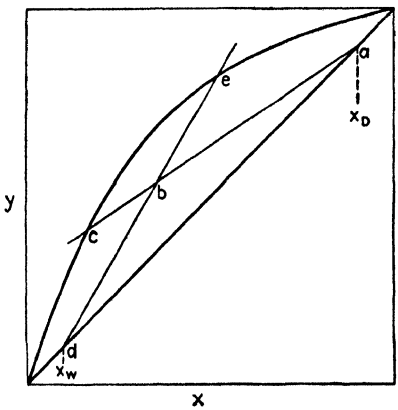


FIG. 7-7. Diagram for limits of feed-plate composition.

Partial vs. Total Condenser. In the foregoing discussion the column was assumed to be operating with a total condenser, *i.e.*, a condenser that completely liquefies the overhead vapor and returns a portion of the condensate as reflux, removing the remainder as product. However, partial condensers are quite frequently used in commercial operations, especially where complete liquefaction of the overhead would be difficult. In this case, only enough condensate for the reflux to the column may be produced, and the product is withdrawn as a vapor. In other cases, mixtures of vapor and liquid are withdrawn. For example, in gasoline stabilizers employed by the petroleum industry, where the overhead contains appreciable percentages of methane, ethane, and ethylene, together with C_3 and C_4 hydrocarbons, in order to condense the methane and C_2 hydrocarbons, very low temperatures

would be required with resulting high refrigeration costs. However, sufficient of the C_3 and C_4 hydrocarbons can be liquefied at moderate temperatures and pressures to serve as reflux, and the remainder of the overhead containing a large portion of the C_1 and C_2 hydrocarbons can be removed as vapor and sent to the gas lines.

A partial condenser may operate in any of several ways:

1. The cooling may be so rapid and the contact between condensate and uncondensed vapor so poor that essentially no transfer of components back and forth is obtained, with the result that the condensate and uncondensed vapor are of the same composition. (This is possible if part of the vapor condenses completely and the balance does not condense at all.) In this case, the partial condenser is equivalent to the total condenser with the exception that the product is removed as vapor instead of as liquid.

2. The vapor product may be in sufficiently good contact with the returning reflux for the two to be in equilibrium with each other, in which case the partial condenser acts as a theoretical plate, and one less theoretical plate may be used above the feed plate in the column when this condition exists than when a total condenser is employed. Such a condition can be approximated by requiring an overhead vapor to bubble through a pool of reflux to the column.

3. The vapor is differentially condensed, and the equilibrium condensate continually removed, giving a differential partial condensation. Alternately, the vapor may be condensed on vertical tubes such that the condensate flows countercurrent to the rising vapor, and fractionation occurs between the vapor and condensate. Theoretically, such a condenser can give a separation equal to a number of theoretical plates; actually, such conditions are seldom employed, since to obtain efficient transfer of components from vapor to liquid, low rates of condensation per unit area are required, thus necessitating large and costly condensers, and, in general, it is found more satisfactory and cheaper to obtain additional rectification by adding more plates to the column and using a condenser to produce condensate rather than make it perform composite duties.

Actual partial condensers usually operate somewhere between Cases 1 and 2. For an absorption naphtha stabilizer, Gunness (Ref. 6) (see page 116) found good agreement with Case 2. In actual design calculation, the conservative assumption is to assume operation as in Case 1, and any fractionation that does occur will act as a factor of safety; with ordinary condenser design, with the most optimistic assumption,

not more than one theoretical plate should be taken for the partial condenser.

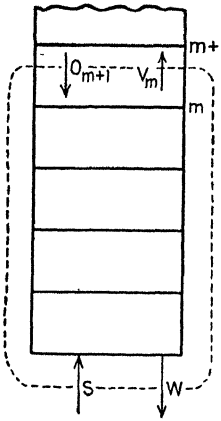


FIG. 7-8. Diagram of column using live steam.

Open vs. Closed Steam. When rectifying mixtures in which the residue is water and in some cases where the mixture undergoing fractionation is immiscible with water, the steam for heating may be introduced directly into the still. Such a procedure may materially reduce the temperature and pressure of the steam necessary for the distillation by giving in effect a steam distillation.

Considering the distillation of an ethyl alcohol–water mixture, the lower operating line when a closed-steam heating is used was shown to have a slope of $(O/V)_m$ and to pass through the $y = x$ line at $x = x_W$. In Fig. 7-8, a column operating with S mols of live steam is shown. A material balance between the m and $m + 1$ plate gives

$$O_{m+1} + S = V_m + W \tag{7-11}$$

and with the usual simplifying assumptions, S would equal V_m, making $O = W$. An alcohol balance gives

$$O_{m+1}x_{m+1} = V_m y_m + W x_W$$
$$y_m = \frac{O_{m+1}x_{m+1}}{V_m} - \frac{W}{V_m} x_W$$

This is an operating line of slope O_m/V_m; but at $x = y$, x is equal to $\left(\frac{W}{W - S}\right) x_W$ instead of x_W; and at x equal to x_W, y becomes zero corresponding to the composition of the vapor (steam) to the bottom plate. For a given O/D and feed condition, O_m/V_m must be the same whether closed or open steam is used, so that the lower operating line must cross the $y = x$ diagonal at the same x value in both cases, x_W for the live steam being lower than x_W for closed steam because of the dilution effect of the steam. In stepping off theoretical plates, the step must start at $y = 0$ and x_W; *i.e.*, in Fig. 7-9, the bottom plate corresponds to the step *abc*. In such a case, the introduction of live steam can eliminate the still, but it dilutes the bottoms and requires more plates in the lower section of the column. Since the steps in the

case of live steam start lower, it always requires at least a portion of a step to come up to the intersection of the operating line and the $y = x$

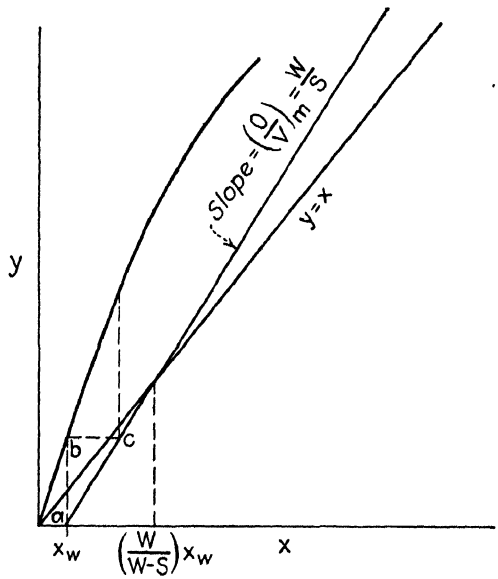


FIG. 7-9. y,x diagram for case of live steam.

diagonal, and more plates are required with live steam than with closed steam. In Fig. 7-9, about 1⅓ more plates would be necessary. One plate is needed to replace the still, and the additional "fraction of a plate" is required to offset the dilution.

As an example of using open steam to obtain a steam distillation, consider the steam stripping of an oil containing 2.54 mol per cent propane at 20 p.s.i. The temperature will be maintained constant at 280°F. by internal heating. The molecular weight of oil may be taken as 300, and 4 mols of steam will be used per 100 mols of oil stripped. It is desired to estimate the number of theoretical plates necessary to reduce the propane content of the oil to 0.05 mol per cent. The oil may be assumed nonvolatile, and the vapor-

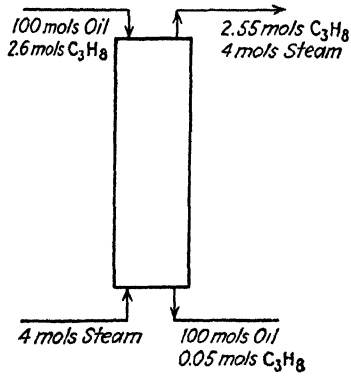


FIG. 7-10. Figure for illustration.

liquid relation of the propane in the oil may be expressed as $y = 33.4x$.

It is obvious that the mols of vapor will increase up the tower, since the steam does not condense under the conditions given, and the propane vaporizes into it as it passes up the tower. This will cause O/V to vary through the tower, and points on the operating line must

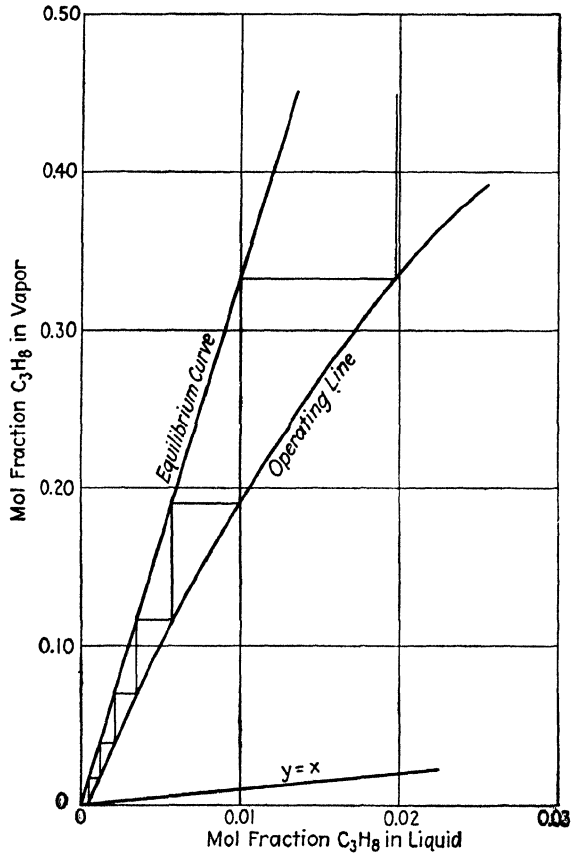


FIG. 7-11. Steam stripping diagram.

be calculated, since it will not be a straight line on a y,x diagram. This is easily done by taking a basis of 100 mols of entering oil, for which the terminal conditions are given in Fig. 7-10. Now, assume that the liquid flowing down the tower at some position contains 1.3 mols of C_3H_8. The vapor at this point must then contain 1.25 mols of C_3H_8, giving $x_{n+1} = 1.3/101.3 = 0.0128$ and $y_n = 1.25/5.25 = 0.238$.

In a similar manner, other values on the operating line are calculated and plotted in Fig. 7-11 together with the equilibrium curve, and a little more than six steps are required to give the desired stripping.

Side Streams. Side streams are removed from a column most often in multicomponent mixtures; however, they are occasionally used in the distillation of binary mixtures. Thus, a plant separating alcohol and water might have uses for both 80 and 95 per cent alcohol mixtures, which of course could be produced by making only 95 per cent alcohol and diluting with water to produce the required 80 per cent; or alternately liquid could be tapped off of a plate in the column on which the concentration was approximately 80 per cent. The proper plate in the tower can be determined by constructing the usual operating lines. Figure 7-12 illustrates the removal of a liquid side stream L. Considering this figure and making the usual simplifying assumptions, the operating line above the side stream is, as before,

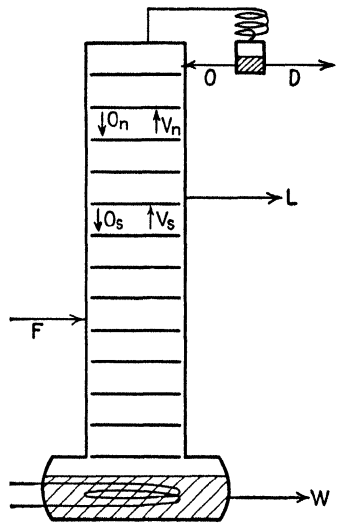


FIG. 7-12. Diagram of continuous column with side stream.

$$y_n = \left(\frac{O}{V}\right)_n x_{n+1} + \frac{Dx_D}{V_n}$$

A material balance around the top of the column and some plate between the feed plate and the side-stream plate gives

$$y_s = \left(\frac{O}{V}\right)_s x_{s+1} + \frac{Lx_L + Dx_D}{V_s} \tag{7-12}$$

The operating line above the side stream passes through $y = x = x_D$ and has a slope of $(O/V)_n$, while the operating line below the side stream passes through $y = x = \dfrac{Lx_L + Dx_D}{L + D}$ (*i.e.*, the molal average composition of the product and side stream) and has a slope $(O/V)_s$. Since x_L is less than x_D and O_s is less than O_n, $(O_s = O_n - L)$; this latter operating line will cross the $y = x$ diagonal at a lower value than

the upper operating line and will have a flatter slope. The two operating lines will intersect at $x = x_L$. Figure 7-13 illustrates these lines.

Theoretical plates are stepped off in the usual manner, using the operating line *ac* from *a* to *c*, the operating line *bcf* from *c* to some value between *e* and *f*, and then the line *edg* from there to *g*. Although the feed plate may have any composition between *e* and *f* and the feed-plate step may be made at any value between these two, the side-stream step must fall exactly on *c*. This is because the feed

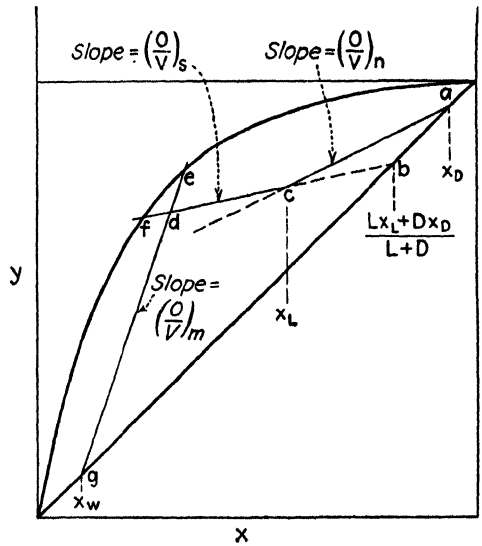


FIG. 7-13. y,x diagram for column with side stream.

can be actually introduced into plates of different composition, but a side stream has to be of the same composition as the plate from which it was withdrawn unless a partial separation of the side stream is made and a portion returned to the column. By altering the reflux ratio slightly, the step can be made to fall very close to *c*.

Unequal Molal Overflow. 1. *Above Feed Plate.* The analysis given in the preceding sections was based on constant molal overflow rate, and it is necessary to consider the validity of this assumption.

Equations (7-1) and (7-2) can be combined with the following enthalpy balance:

$$V_n H_n = Q_c + O_{n+1} h_{n+1} + D h_D + \text{losses}$$

where H_n = molal enthalpy of vapor entering plate $n + 1$
Q_c = heat removed in condenser
h_{n+1} = molal enthalpy of liquid leaving plate $n + 1$
h_D = molal enthalpy of product

to give

$$\frac{x_D - x_{n+1}}{M_D - h_{n+1}} = \frac{x_D - y_n}{M_D - H_n} \tag{7-13}$$

where M_D equals $\frac{Q_c}{D} + h_D + \frac{\text{losses}}{D}$ or, in general, DM_D equals the total enthalpy removed from the section in question other than by V_n and O_{n+1}. Equation (7-13) can be rearranged as

$$y_n = \frac{M_D - H_n}{M_D - h_{n+1}} x_{n+1} + \frac{H_n - h_{n+1}}{M_D - h_{n+1}} x_D \tag{7-14}$$

$$= \left(1 - \frac{H_n - h_{n+1}}{M_D - h_{n+1}}\right) x_{n+1} + \frac{H_n - h_{n+1}}{M_D - h_{n+1}} x_D \tag{7-15}$$

By comparison with Eq. (7-2) it is obvious that

$$\frac{D}{V_n} = \frac{H_n - h_{n+1}}{M_D - h_{n+1}} \tag{7-16}$$

and

$$\frac{O_{n+1}}{V_n} = \frac{M_D - H_n}{M_D - h_{n+1}} = 1 - \frac{H_n - h_{n+1}}{M_D - h_{n+1}} \tag{7-17}$$

The condition for constant molal overflow rate is that the group, $\frac{H_n - h_{n+1}}{M_D - h_{n+1}}$, should be a constant. In general the losses are or should be small making M_D a constant for a section having no additions or withdrawals except at its ends, and the value of M_D is usually large in comparison to h_{n+1}. Thus, a constant value of $H_n - h_{n+1}$ will lead to essentially constant molal rates of vapor and overflow. The difference $H_n - h_{n+1}$ is not a conventional latent heat but is the difference in molal enthalpy between the vapor entering and the liquid leaving a plate. In order to analyze this difference, it is desirable to evaluate H_n and h_{n+1}.

In the case of the liquid phase, the enthalpy will be calculated on the basis of heating the pure components to the mixture temperature and then mixing at this condition.

$$h_{n+1} = (x_1)_{n+1} \int_{t_{lb}}^{t_{n+1}} c_1 \, dt + (x_2)_{n+1} \int_{t_{lb}}^{t_{n+1}} c_2 \, dt + \Delta h_m \tag{7-18}$$

where $(x_1)_{n+1}$, $(x_2)_{n+1}$ = mol fractions of components 1 and 2 in liquid leaving $(n + 1)$th plate
h_{n+1} = molal enthalpy of liquid
c_1, c_2 = molal specific heat
t_{n+1} = temperature of liquid leaving $(n + 1)$th plate
t_{1b}, t_{2b} = base temperatures for calculating enthalpy, enthalpy of pure component 1 taken as zero at t_{1b}, enthalpy of pure component 2 taken as zero at t_{2b}
Δh_m = enthalpy change on mixing pure liquids to give 1 mol of desired composition

In most cases it is desirable to choose the base temperatures reasonably close to the distillation temperatures. For such cases c_1 and c_2 can be taken at constant average values and

$$h_{n+1} = (x_1)_{n+1}(c_1)(t_{n+1} - t_{1b}) + (x_2)_{n+1}(c_2)(t_{n+1} - t_{1b}) + \Delta h_m \quad (7\text{-}19)$$

In the case of the vapor enthalpy, several paths for calculating the mixture value relative to the pure components are possible: (1) The pure components can be heated as liquids from the base temperature to their boiling point at the pressure under consideration, (2) the liquids can be vaporized, and (3) the vapors can be mixed and then heated or cooled to the desired mixing temperature. Alternately, the pure components can be (1) heated from the base temperature to the desired mixture temperature, (2) vaporized at this temperature, and (3) mixed. Thus, for the two cases,

$$H_n = (y_1)_n \int_{t_{1b}}^{t_{1B}} c_1\,dt + (y_2)_n \int_{t_{2b}}^{t_{2B}} c_2\,dt + (y_1)_n\,\Delta H_1 + (y_2)_n\,\Delta H_L + \Delta H_m + (y_1)_n \int_{t_{1B}}^{t_n} C_1\,dt + (y_2)_n \int_{t_{2B}}^{t_n} C_2\,dt \quad (7\text{-}20)$$

or

$$H_n = (y_1)_n \int_{t_{1b}}^{t_n} c_1\,dt + (y_2)_n \int_{t_{2b}}^{t_n} c_2\,dt + (y_1)_n\,\Delta H_1' + (y_2)_n\,\Delta H_2' + \Delta H_m' \quad (7\text{-}21)$$

where H_n = molal enthalpy of vapor
y_1, y_2 = mol fractions
c_1, c_2, t_{1b}, t_{2b} = same as for Eq. (7-18)
t_{1B}, t_{2B} = boiling temperatures for pure components at pressure in question
t_n = temperature of vapor entering plate $n + 1$
ΔH_1, ΔH_2 = latent heats of vaporization of the pure components at t_{1B} and t_{2B}
$\Delta H_1'$, $\Delta H_2'$ = latent heats of vaporization of the pure components at t_n
ΔH_m, $\Delta H_m'$ = enthalpy changes on mixing pure vapors
C_1, C_2 = molal heat capacities of the pure vapors

For most of the following discussion the second equation will b employed, and the heat capacities will be taken constant at averag values, giving

$$H_n = (y_1)_n c_1(t_n - t_{1b}) + (y_2)_n c_2(t_n - t_{2b}) + (y_1)_n \Delta H'_1 + (y_2)_n \Delta H'_2 + \Delta H'_m \quad (7\text{-}22$$

At low and moderate pressures, the enthalpy effects on mixin vapors are small and $\Delta H'_m$ and ΔH_m will be neglected, although at hig pressures this procedure could lead to large errors.

Combining Eqs. (7-19) and (7-21),

$$H_n - h_{n+1} = (y_1)_n \Delta H'_1 + (y_2)_n \Delta H'_2 - \Delta h_m + c_1\{[(y_1)_n - (x_1)_{n+1}](t_{n+1} - t_{1b}) + (y_1)_n(t_n - t_{n+1})\} + c_2\{[(y_2)_n - (x_2)_{n+1}](t_{n+1} - t_{2b}) + (y_2)_n(t_n - t_{n+1})\} \quad (7\text{-}23$$

The values of t_{1b} and t_{2b} can be arbitrarily chosen. For convenienc they will be taken as the boiling points of the pure components at th pressure in question. On this basis, $(t_{n+1} - t_{1b})$ and $(t_{n+1} - t_{2b}$ seldom exceed 50 to 100°F. and $(y_n - x_{n+1})$ and $(t_n - t_{n+1})$ are small As a result, the last two brackets of Eq. (7-23) are usually only a fev per cent of the value of $(H_n - h_{n+1})$ and are not of real significance i determining the constancy of this difference. The most importan factors are $(y_1)_n \Delta H'_1$ and $(y_2)_n \Delta H'_2$, although Δh_m may be large i some cases. As the calculations are made from plate to plate, (y_1) will vary, and $(H_n - h_{n+1})$ will vary or remain constant depending o whether or not $\Delta H'_1$ equals $\Delta H'_2$. Thus for most cases, the criterion o the constancy of $(H_n - h_{n+1})$ will be the difference in the latent hea of vaporization of the pure components at the operating pressure.

Figure 7-14 gives the values of the molal latent heat divided by th absolute temperature plotted as a function of the ratio of the vapo pressure divided by the absolute temperature. (See also page 479. As a rule, the maximum variation in $(y_1 \Delta H'_1 + y_2 \Delta H'_2)$ is obtained b going from $y_1 = 1.0$ to $y_1 = 0$, although abnormal mixtures may sho greater values at some intermediate point. As an example, con sider a mixture of ethanol and water at atmospheric pressure. Fo ethanol $P/T = 760/351.5 = 2.16$, $\Delta H/T = 27$, $\Delta H' = 9{,}470$; fo water $P/T = 760/373 = 2.04$, $\Delta H/T = 26.2$,$\Delta H' = 9{,}750$. Unles this mixture has a very large heat of mixing for the liquid phase, i would be expected that the value of $(H_n - h_{n+1})$ would be essentiall constant and the assumption of constant rates of vapor and ove flow would be well justified. At higher pressures the variation i

of vaporization of ethanol. As another case, consider the distillation of an ammonia-water mixture at 20 atm. abs. For ammonia

$$\frac{P}{T} = \frac{(20 \times 760)}{321.5} = 47.3$$

$\Delta H/T = 13.5$, and $\Delta H' = 4{,}340$; for water

$$\frac{P}{T} = \frac{(20 \times 760)}{484.5} = 31.4$$

$\Delta H/T = 17.0$, and $\Delta H' = 8{,}230$, and the variation in vapor and overflow rates from plate to plate would be large and calculations based on the constancy of these rates would be appreciably in error.

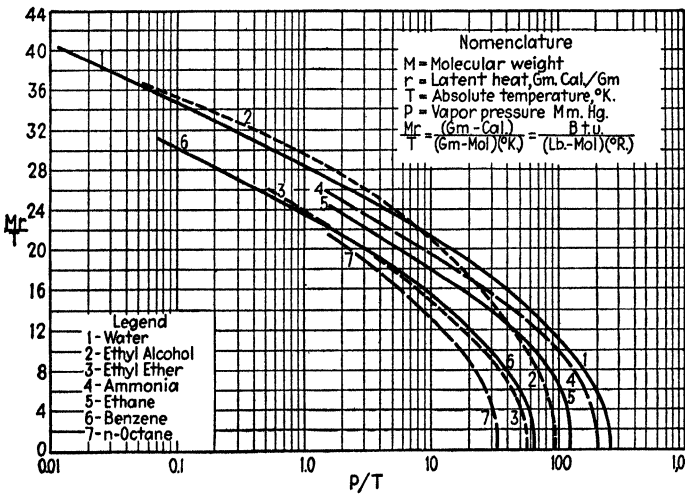


FIG. 7-14. Hildebrand chart for estimating latent heats of vaporization. (Ref. 19.)

It is possible to have mixtures of similar components that would not satisfy the constant O/V assumption even approximately and to have mixtures of unlike components that give good agreement. Thus, in a mixture of hydrocarbons the operating pressure could be such that one of the components is near its critical pressure as a pure component while the other could be at more normal conditions. Under such conditions, the difference in latent heats of vaporization of the two pure components could be very large. At high pressures, most mixtures give large variation in $(H_n - h_{n+1})$ because one of the components will be nearer its critical conditions than the other.

In order to carry out more exact calculations, it is necessary to

evaluate the other terms of Eq. (7-23). The specific heat terms require the heat capacity of the pure liquid components. Values for a number of materials can be obtained from Fig. 2 in the Appendix. (Ref. 10.)

The value of Δh_m is difficult to obtain, owing to the lack of published data. Such data are available in a few cases and can be calculated if vapor-liquid equilibrium data are available at several temperatures and pressures. Thus, by Eqs. (3-37) and (3-38),

$$RT\, d \ln \gamma_1 = d(\Delta \bar{F}_e)_1$$
$$RT\, d \ln \gamma_2 = d(\Delta \bar{F}_e)_2$$

and

$$(\Delta \bar{F}_e)_1 = (\Delta \bar{H}_e)_1 - T(\Delta \bar{S}_e)_1 = RT \ln \gamma_1$$
$$(\Delta \bar{F}_e)_2 = (\Delta \bar{H}_e)_2 - T(\Delta \bar{S}_e)_2 = RT \ln \gamma_2$$

It can be shown that, at constant composition and total pressure,

$$\frac{d(\Delta \bar{F}_e/T)}{d(1/T)} = \Delta \bar{H}_e = -RT^2 \frac{d \ln \gamma}{dT}$$

and

$$\Delta h_m = x_1(\Delta \bar{H}_e)_1 + x_2(\Delta \bar{H}_e)_2 = -RT^2\left(x_1 \frac{d \ln \gamma_1}{dT} + x_2 \frac{d \ln \gamma_2}{dT}\right) \quad (7\text{-}24)$$

Thus if vapor-liquid equilibrium data are available to evaluate the activity coefficients at constant composition as a function of the temperature, the heat of mixing can be calculated. This heat of mixing, so calculated, will be slightly in error due to neglecting the effect of pressure on the enthalpy of liquids.

It is to be noted that Δh_m is usually of such a sign as to make the enthalpy of the liquid more nearly constant. In using Eq. (7-19) with the base temperatures taken at the boiling point for each pure component, the enthalpy of the liquid is equal to zero at both $x_1 = 1$ and $x_1 = 0$, but at intermediate values the enthalpy may be greater or less than zero. For mixtures with positive deviations from Raoult's law, *i.e.*, activity coefficients greater than unity, the temperatures of the mixtures at constant pressure are lower than for ideal solutions, and the sum of the sensible heat terms of Eq. (7-23) is negative. This is partly offset by the fact that $(d \ln \gamma/dT)$ is usually negative for such mixtures, making Δh_m positive. Mixtures with negative deviations from Raoult's law give similar compensations. Thus, in most cases the variation in the enthalpy of the liquid (with the base temperature assumed) with composition is small.

If the Van Laar equation for the activity coefficient is used, Eq.

(7-24) becomes

$$\Delta h_m = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \tag{7-25}$$

and, using the Van Laar relations,

$$\Delta h_m = \frac{x_1 x_2 BR}{x_2 + Ax_1} \tag{7-26}$$

Comparison with experimental data for a number of mixtures of organic liquids indicates that the Van Laar relations give high values and that better results are obtained by

$$\Delta h_m = 0.5RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2)$$

The use of the modified Margules relations, Eq. (3-34*a*), would give a similar relation with the constant equal to 0.25.

2. *Below Feed Plate.* A similar analysis using

$$\begin{aligned} O_{m+1} &= V_m + W \\ O_{m+1}x_{m+1} &= V_m y_m + W x_W \\ O_{m+1}h_{m+1} + Q_s &= V_m H_m + W h_W \end{aligned}$$

where Q_s is the heat added in the still, gives

$$\frac{y_m - x_W}{H_m - \left(h_W - \dfrac{Q_s}{W}\right)} = \frac{x_{m+1} - x_W}{h_{m+1} - \left(h_W - \dfrac{Q_s}{W}\right)} \tag{7-27}$$

or

$$y_m = \frac{M_W - H_m}{M_W - h_{m+1}} x_{m+1} + \frac{H_m - h_{m+1}}{M_W - h_{m+1}} x_W \tag{7-28}$$

$$= \left(1 - \frac{H_m - h_{m+1}}{M_W - h_{m+1}}\right) x_{m+1} + \frac{H_m - h_{m+1}}{M_W - h_{m+1}} x_W \tag{7-29}$$

where $M_W = h_W - \dfrac{Q_s}{W}$,

$$\frac{-W}{V_m} = \frac{H_m - h_{m+1}}{M_W - h_{m+1}} \tag{7-30}$$

$$\frac{O_{m+1}}{V_m} = 1 - \frac{H_m - h_{m+1}}{M_W - h_{m+1}} \tag{7-31}$$

These equations are similar to Eqs. (7-16) and (7-17), and the same considerations relative to the constancy of molal rates of vapor and overflow apply in this case.

3. *General Case.* The derivations given in the two previous sections were for the case with no side streams, but the general case is similar.

In the system shown in Fig. 7-15, the over-all and component material balances above plate a are

$$V_a = O_{a+1} + N \tag{7-32}$$

$$V_a y_a = O_{a+1} x_{a+1} + N x_N \tag{7-33}$$

where V_a = vapor rate to plate $a + 1$
O_{a+1} = overflow rate from plate $a + 1$
N = net mols leaving section = $V_a - O_{a+1}$
y_a, x_{a+1} = mol fractions
Nx_N = total mols of component leaving section other than with V_a and O_{a+1}

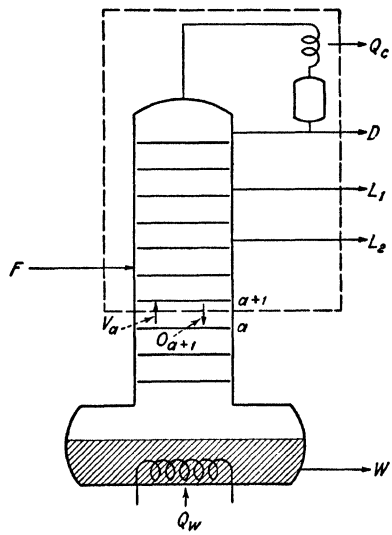


FIG. 7-15. Schematic diagram of fractionating system with side streams.

The enthalpy balances are

$$V_a H_a = O_{a+1} h_{a+1} + NM \tag{7-34}$$

where H_a = molal enthalpy of vapor entering plate $a + 1$
h_{a+1} = molal enthalpy of liquid leaving plate $a + 1$
NM = net enthalpy removed from the column above plate $a + 1$

For Fig. 7-15,

$$N = L_1 + L_2 + D - F$$

$$Nh_N = L_1(h_L)_1 + L_2(h_L)_2 + Dh_D - Fh_F + Q_c + \text{losses}$$

These equations can be combined to give

$$\frac{x_N - y_a}{M - H_a} = \frac{x_N - x_{a+1}}{M - h_{a+1}} \tag{7-35}$$

or

$$y_a = \frac{M - H_a}{M - h_{a+1}} x_{a+1} + \frac{H_a - H_{a+1}}{M - h_{a+1}} x_N \tag{7-36}$$

$$= \left(1 - \frac{H_a - h_{a+1}}{M - h_{a+1}}\right) x_{a+1} + \frac{H_a - h_{a+1}}{M - h_{a+1}} x_N \tag{7-37}$$

where

$$\frac{H_a - h_{a+1}}{M - h_{a+1}} = \frac{N}{V_a} \tag{7-38}$$

$$1 - \frac{H_a - h_{a+1}}{M - h_{a+1}} = \frac{O_{a+1}}{V} \tag{7-39}$$

These equations reduce to Eqs. (7-14), (7-17), (7-27), and (7-31) for the special cases considered.

Method of Ponchon and Savarit. Ponchon (Ref. 14) and Savarit (Ref. 15) showed that Eqs. (7-13) and (7-27), or in general any equation

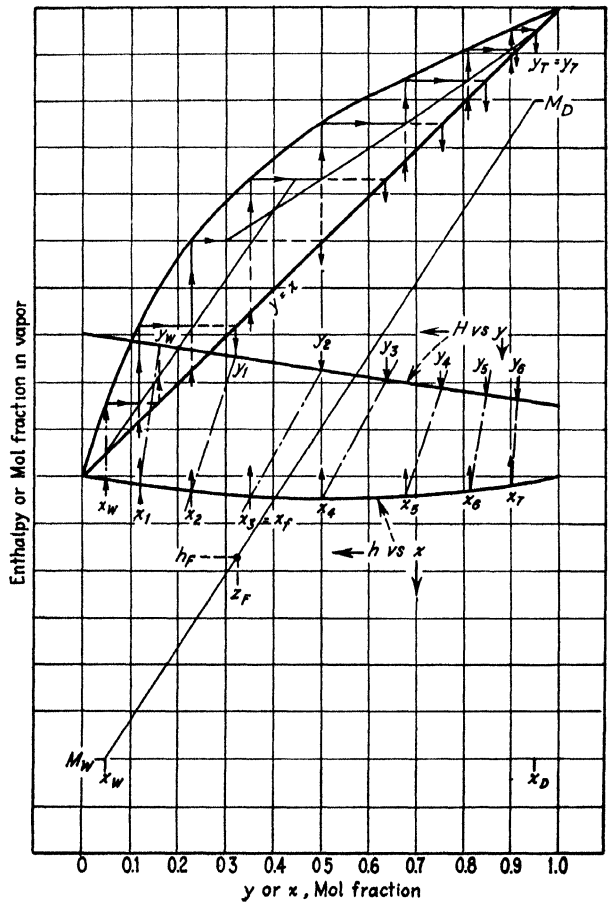


FIG. 7-16. Enthalpy-composition diagram.

of this type, could be easily solved by plotting the enthalpy (or other property) of the saturated vapor and liquid vs. the mol fraction. For example, in Fig. 7-16, if the value M_D for the upper section is plotted at x_D, it is easily shown that any straight line drawn through the point (M_D, x_D) will intersect the enthalpy lines to give values of x and

y that will satisfy Eq. (7-13). Thus if y_n is known, a line through the vapor enthalpy curve at this composition and the point (M_D, x_D) will cut the liquid enthalpy at h_{n+1} and x_{n+1}. When x_{n+1} is known, y_{n+1} is obtained from the equilibrium curve and x_{n+2} is determined by drawing a new line through (y_{n+1}, H_{n+1}), (M_D, x_D), etc.

Similarly if M_W for the lower section is plotted at x_W, then a straight line through this point intersects the two enthalpy curves at values that satisfy Eq. (7-27) and these straight lines give the relation between y_m and x_{m+1}.

A heat and material balance around the whole column (no side streams) gives

$$Fh_F = Wh_W + Dh_D + Q_c - Q_s + \text{losses} = WM_W + DM_D$$

and

$$Fz_F = Wx_W + Dx_D$$

By rearranging,

$$\frac{z_F - x_W}{h_F - M_W} = \frac{z_F - x_D}{h_F - M_D} \tag{7-40}$$

Equation (7-40) is of the same type as Eqs. (7-13) and (7-27), and similar reasoning leads to the conclusion that a straight line through (z_F, h_F) and (x_W, M_W) will also pass through (x_D, M_D). In other words, the point (z_F, h_F) lies on a straight line between (x_D, M_D) and (x_W, M_W). This line will be termed the terminal tie line.

In general the same type of information given by the constant O/V method can be obtained by the use of the Ponchon and Savarit method. For example, the cases of total reflux, minimum reflux ratio, and optimum feed-plate location can be easily solved.

Total Reflux. In the case of total reflux the values of M_D and M_W are infinite, and lines drawn through them and the enthalpy curves will therefore be vertical. Thus, for this case the diagram shows that the composition of the liquid leaving the plate is equal to the composition of the vapor entering the plate, and the same number of theoretical plates will be obtained by both the constant O/V method and Ponchon-Savarit methods, regardless of the value of the enthalpies.

Minimum Reflux Ratio. The case of the minimum reflux ratio corresponds to conditions that require an infinite number of plates to obtain the desired separation. As in the case of the y,x diagram, this necessitates a region in which succeeding plates differ only differentially in composition, *i.e.*, a pinched-in region.

The step equivalent to a theoretical plate on the enthalpy diagram

involves going from the vapor below a plate to the liquid on a plate by means of the enthalpy operating line through one of the terminal enthalpy points and then proceeding from the composition of the liquid on the plate to the vapor above the plate by the equilibrium relationship, *i.e.*, by an equilibrium tie line. If the composition of this vapor above the plate is to be equal to the composition of the vapor entering the plate, it is necessary for the enthalpy operating line to coincide with the equilibrium tie line. In the general case it is a trial-and-error procedure to determine the least value of M_D that can be employed. However, if the pinched-in region occurs at the feed plate, the minimum reflux ratio can be easily determined by finding the equilibrium tie line that passes through the point (h_F, z_F) and extrapolating this line until it intersects the vertical line at x_D. The enthalpy value at this intersection will correspond to the minimum M_D. In other cases, the equilibrium tie lines for a number of compositions above the feed plate can be extrapolated to the vertical line through x_D, and the maximum value of M_D so obtained corresponds to the minimum reflux ratio for this section. A similar procedure can be used below the feed plate and the minimum value of M_W determined. Since M_D and M_W must fall on the line through the feed point, it can be determined which of the two values is the limiting one, and thus whether the pinched-in region is above or below the feed plate.

Optimum Feed-plate Location. The optimum feed-plate location again corresponds to making the total number of theoretical plates required for the operating conditions chosen a minimum, which is equivalent to making the change in composition per plate a maximum at all points. In general, it will be found that, when the enthalpy operating line is on the x_D side of the terminal tie line through (M_D, x_D) and (M_W, x_W), larger steps will be obtained by using enthalpy operating lines drawn through (M_D, x_D) than those drawn through (M_W, x_W); on the x_W side of the terminal tie line the reverse will be true. The enthalpy operating lines should be drawn through M_W for values of x less than the composition given by the intersection of the terminal tie line with the liquid enthalpy curve, and the (M_D, x_D) point should be used for all operating lines corresponding to liquid mol fractions greater than this value. It should be noted that the value of the mol fraction at which the change-over is made is not equal to the composition of the feed. It will be equal to the composition of the feed when the feed enters with an enthalpy equal to that of a saturated liquid. If the enthalpy of the feed is greater than that of a saturated liquid, the change-over value will be at composition lower

than that of the feed. If the enthalpy of the feed is less than that of the saturated liquid, the reverse will be true. This is similar to the conditions found for the y,x diagram.

General. It is frequently advantageous to use enthalpy diagrams to determine a series of values of y_n, x_{n+1}, and y_m, x_{m+1}, which can be plotted on the y,x diagram to give the actual operating lines which are then employed in the usual stepwise manner. The y,x curves and the enthalpy composition values can be plotted on the same diagram, and the combined graphical procedure shown in Fig. 7-16 completes both the y,x and the enthalpy diagrams. To illustrate the procedure, (1) starting at (h_W, x_W), a vertical line is drawn to the equilibrium curve giving y_W, (2) this value is transposed to the H,y line by going horizontally to $y = x$ and then vertically to the H curve giving the point (H_W, y_W), (3) the line through this point and (M_W, x_W) gives the value of x_1 on the h curve, and (4) the process is repeated. The intersection of the vertical lines with the horizontal lines on the y,x diagram corresponds to points of the operating lines, and the triangles above the lines drawn through these points are the usual steps on the y,x diagram.

Heat losses from the column can be taken into account by shifting the value of M_D from plate to plate by an amount equal to the heat loss per plate divided by N. A side stream in the upper section of the column is handled by locating a point (M_S, x_{NS}) where

$$M_S = \frac{Lh_L + Dh_D + Q_c}{L + D} \qquad \text{and} \qquad x_{NS} = \frac{Lx_L + Dx_D}{L + D}$$

and drawing lines through this point.

In this case, (z_F, h_F) lies on a straight line through (x_W, M_W) and (x_{NS}, M_S), and (x_{NS}, M_S) lies on a straight line through (x_D, M_D) and (x_L, h_L). In a similar way any number of side streams or feeds can be handled.

In general the Ponchon-Savarit diagram is somewhat more difficult to use than the constant O/V diagram, but it is the exact solution for theoretical plates assuming that the enthalpy data employed are correct. This graphical procedure suffers because the absolute values of M_D and M_W are frequently large, and to plot them on the diagram requires the use of an ordinate scale such that the enthalpy curves for the liquid and vapor are crowded together, making it difficult to obtain accurate results. Likewise when low concentrations are encountered, it is impossible to obtain accurate results from the diagram unless the plot is greatly expanded. For such regions Eqs. (7-14) and (7-28) can be used algebraically, or in most cases the con-

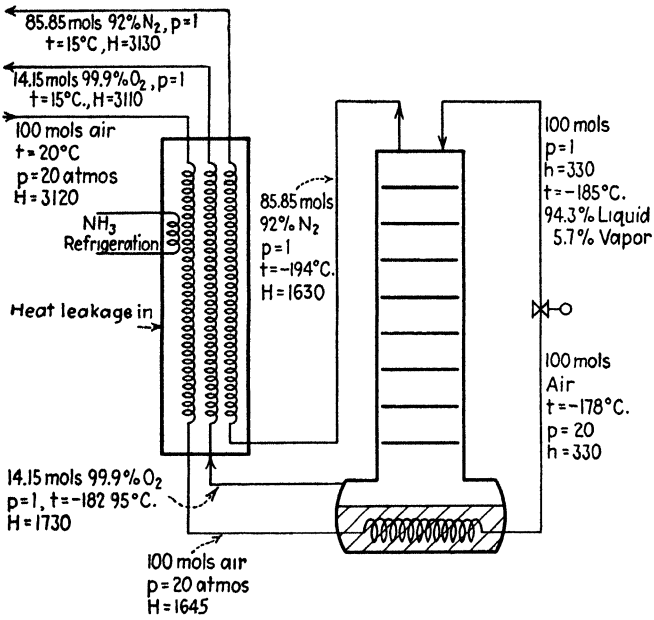


FIG. 7-17. Liquid-air distillation.

stant O/V diagram is useful since in such regions the value of $(H_a - h_{a+1})$ is essentially constant.

EXAMPLES OF ENTHALPY-COMPOSITION METHOD

Liquid-Air Fractionation Example. The enthalpy-composition method will be illustrated by several examples. Figure 7-17 gives a schematic diagram of a liquid-air fractionating system. In this particular case the system employed involves

TABLE 7-2

x_{n+1}	y_n calc	
	Constant O/V	Heat balance
0.001	0.001	
0.002	0.00218	
0.004	0.0045	
0.01	0.0116	
0.02	0.0233	0 024
0.04	0.0468	0 048
0.1	0.1175	0.12
0.2	0.235	0.24
0.4	0.470	0.475
0.6	0.705	0.71
0.8	0.94	0.94

only a stripping column, and the enthalpy diagram (Fig. 7-18) is only for the lower portion. The heat supply to the still is from the ingoing air and, on the basis given for Fig. 7-17, Q_s is equal to 100(1,645 − 330) = 131,500. The molal enthalpy of the bottoms from the still, H_W, is 1,730, and for Eq. (7-27) the terminal enthalpy point becomes

$$H_W - \frac{Q_s}{W} = -7{,}550$$

This construction is given in Fig. 7-18. The enthalpy values employed are those given by Keesom (Ref. 7) and, since they were already available, they were not recalculated to the basis suggested in the foregoing section. The diagram of Fig. 7-18 is not very suitable for a major portion of the concentration region under consideration. This diagram and Eq. (7-28) were used to calculate y and x values for the operating line. The results of these calculations are compared with those for constant O/V in Table 7-2. It will be noted that within the accuracy of the calculation the operating line coordinates calculated by the two methods are in agreement, indicating that the constant O/V method is satisfactory for this case.

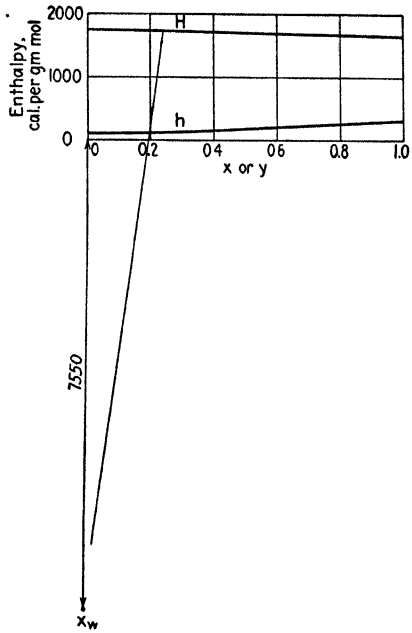


FIG. 7-18. Heat diagram for liquid-air separation.

The operating line values and the equilibrium data of Dodge (Ref. 4) are shown in Fig. 7-19. Logarithmic plotting is employed so that steps can be satisfactorily made in the low concentration region. Nine theoretical plates in addition to the still give the desired separation.

TABLE 7-3. O_2-N_2 AT 10 ATM.

x_{n+1}	$y_{n\ \text{calc}}$	
	Constant O/V	Heat balance, data of Bosnjakovic (Ref. 2)
1.0	1.0	1.0
0.9	0.955	0.953
0.8	0.91	0.91
0.7	0.865	0.867
0.6	0.82	0.823

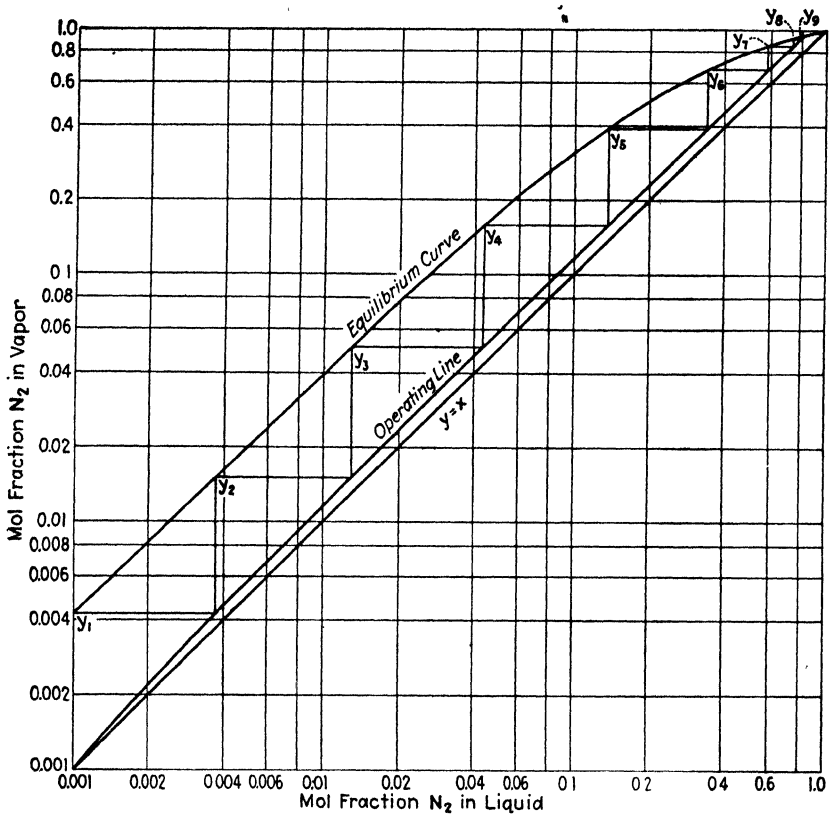


FIG. 7-19. x,y diagram for liquid-air separation.

TABLE 7-4. NH_3-H_2O AT 10 ATM.

x_{n+1}	$y_{n\ calc}$	
	Constant O/V	Heat balance, data of Bosnjakovic (Ref. 2)
0.1	0.701	0 705
0.09	0.624	0.625
0.08	0 547	0.547
0.07	0.47	0.46
0.06	0.393	0.385
0.05	0.316	0.305

Oxygen-Nitrogen and Ammonia-Water Example. Tables 7-3 and 7-4 give similar comparisons for other systems. In Table 7-3 the comparison is for the oxygen-nitrogen system at 10 atm., and again the agreement between the two methods is good. The other data are for ammonia-water at 10 atm., and even in this case the two methods are in fair agreement.

Ammonia-Water Example. In order to illustrate the fact that the assumption of constant molal overflow rate is not always justified, consider the following example in which the molal latent heat of vaporization varies approximately twofold over the tower. An aqueous solution containing 20 weight per cent ammonia is to be separated into a distillate containing 98 mol per cent ammonia and a bottoms containing 0.1 mol per cent ammonia. The tower and total condenser will operate at an absolute pressure of 20 atm. The feed will enter the system at 20°C. and be heated to 40°C in the condenser as shown in Fig. 7-20.

Using the data and notes given below, calculate:

1. The minimum reflux ratio O/D, using the enthalpy-composition method.
2. The number of theoretical plates required at O/D equal to 1.5 times the minimum value found in Part 1, using the enthalpy-composition method.
3. The number of theoretical plates required at total reflux.
4. The minimum reflux ratio O/D, assuming constant molal overflow rates.
5. The number of theoretical plates required for O/D equal to 1.5 times the value obtained in Part 4, using constant molal overflow rates.

Data and Notes. As a basis, the enthalpies of pure liquid water and pure liquid ammonia are taken as zero at their boiling points. On this basis a 20 weight per cent ammonia solution at 40°C. has an enthalpy equal to −3,180 cal per g. mol. Other enthalpy and equilibrium data (Ref. 2) for 20 atm. follow.

Mol fraction NH_3, in liquid or vapor	Enthalpy liquid cal. per g. mol vs. mol fraction in liquid	Enthalpy vapor cal. per g mol vs. mol fraction in vapor	T, °C. vs. mol fraction in liquid
0.0	0	8,430	211.5
0.1053	−500	7,955	182 5
0 2094	−970	7,660	165 5
0.312	−1,310	7,495	131 5
0 414	−1,540	7,210	113 0
0 514	−1,650	6,920	91 0
0.614	−1,580	6,620	76 0
0.712	−1,400	6,300	65 5
0.809	−960	5,980	58.0
0.905	−520	5,470	52.5
0.923	−430	5,350	51.6
0.942	−310	5,240	50.8
0.962	−210	5,050	50.0
0.981	−110	4,870	49.3
1.000	0	4,250	48.5

VAPOR-LIQUID EQUILIBRIA AT 20 ATM.

x Mol Fraction NH_3	y Mol Fraction NH_3
0.0529	0.262
0.1053	0.474
0.2094	0.742
0.312	0.891
0.414	0.943
0.514	0.977
0.614	0.987
0.712	0.990
0.809	0.995
1.00	1.000

Solution of Part 1. Basis: 100 mols of feed.
Feed composition

$$z_F = \frac{^{20}/_{17}}{^{20}/_{17} + ^{80}/_{18}} = 0.209$$

NH_3 balance,

$$0.209(100) = 0.98D + 0.001(100 - D)$$
$$D = 21.25 \quad \text{and} \quad W = 78.75$$

An enthalpy balance on the exchanger between the bottoms and the feed is

$$WC_p(t_B - 45) = F(h_F - h_{40})$$

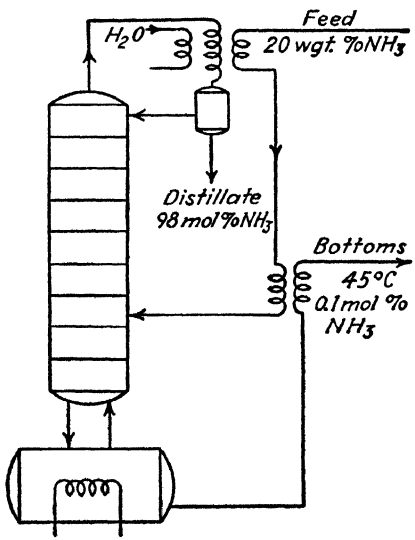


FIG. 7-20. Flowsheet for ammonia-water example.

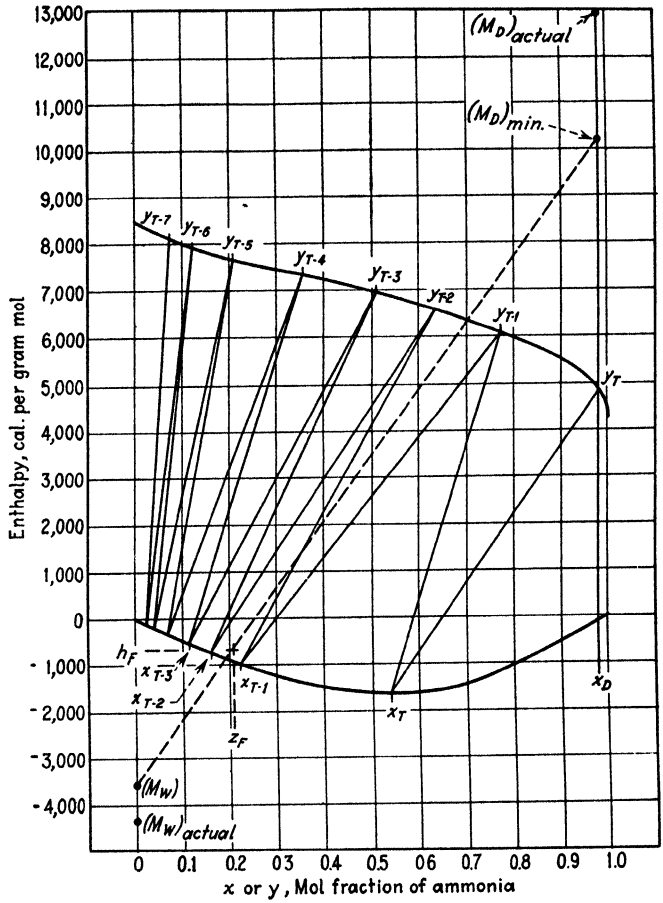


FIG. 7-20*a*. Enthalpy-composition diagram for ammonia-water example.

where t_B = temperature in reboiler = 211.2°C.

h_F = enthalpy of feed entering tower

C_p = heat capacity of bottoms = 19.0 cal. per g. mol/°C. (used same as C_p of H_2O at 20 atm.)

h_{40} = enthalpy of feed at 40°C. = −3,180

$78.75(19.0)(211.2 - 45) = 100(h_F + 3{,}180)$

h_F = −690 cal. per g. mol

This point is located on the enthalpy-composition diagram (Fig. 7-20*a*). Utilizing the y,x diagram it is found that the equilibrium tie line that passes through this point corresponds to $x = 0.193$ and $y = 0.70$. The extrapolation of this tie line to $x_D = 0.98$ gives $M_D = 10{,}230$ and at $x_W = 0.001$, $M_W = -3{,}630$.

Also

$$V_T H_T = O_R h_R + Q_c + D h_D = O_R h_R + D M_D$$

Assuming that $h_R = h_D$ = enthalpy of saturated liquid, and using $V_T = O_R + D$, by a derivation similar to that for Eq. (7-16),

$$\frac{O_R}{D} = \frac{M_D - H_T}{H_T - h_D}$$

$$\left(\frac{O_R}{D}\right)_{\min} = \frac{10{,}230 - 4{,}850}{4{,}850 + 100} = 1.09$$

The above calculations assume that the minimum reflux ratio corresponded to a pinched-in condition at the feed point. A check of the other tie line above and below the feed plate indicated that this corresponded to the maximum value for M_D. It is apparent from Fig. 7-21 that the operating line on the y,x diagram would have to be very curved in order to have the pinch occur at any place but the feed plate.

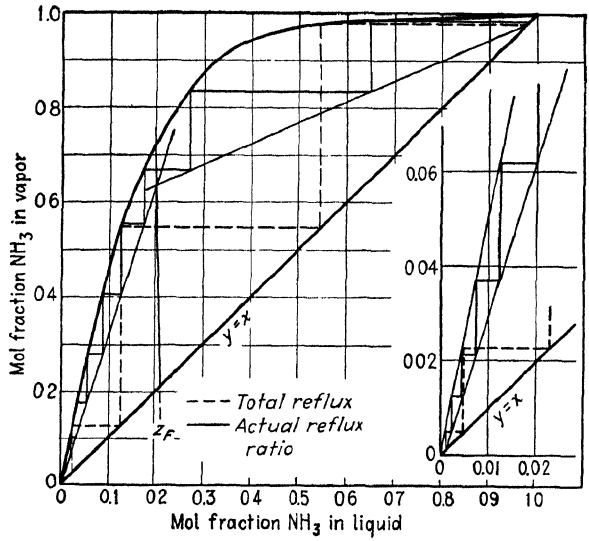


FIG. 7-21. y,x diagram for NH_3-water example.

Solution of Part 2

$$\left(\frac{O_R}{D}\right)_{act} = 1.5(1.09) = 1.635 = \frac{M_D - 4{,}850}{4{,}950}$$

$$M_D = 12{,}940 \qquad \text{and} \qquad M_W = -4{,}360$$

Using this value, the steps corresponding to theoretical plates are stepped off. In this manner the lines on Fig. 7-20*a* were constructed for the top seven plates giving the vapor entering the $T - 6$ plate equal to 0.073. Below this value the diagram becomes difficult to use, and the calculations were completed by the use of Eq. (7-31), using $H_m = 8{,}400$, and $h_{m+1} = -20$.

$$\left(\frac{O}{V}\right)_m = 1 - \frac{H_m - h_{m+1}}{M_W - h_{m+1}} = 1 - \frac{8{,}420}{-4{,}360 + 20} = 2.92$$

$$y_m = 2.92x_{m+1} - 1.92(0.001)$$

Over the low concentration region involved, Fig. 7-21 indicates that the vapor-liquid equilibrium curve can be expressed as

$$y_m = 5x_m$$

The liquid on plate $T - 7$ will be in equilibrium with a vapor composition of 0.073 and, from the equilibrium relationship just assumed, x_{T-7} would equal 0.0145. This lower section is to reduce this mol fraction to 0.001 and, by Eq. (7-77),

$$N_W = \frac{\ln\left[\dfrac{\left(\dfrac{5}{2.92} - 1\right)\left(\dfrac{0.0145}{0.001} - 1\right)}{4/2.92} + 1\right]}{\ln (5/2.92)} = 3.9 \text{ plates}$$

Thus a still and about eleven $(7 + 3.9)$ theoretical plates are required.

Solution of Part 3. At total reflux the plates are stepped off on Fig. 7-21, and a still plus four theoretical plates are required.

Solution of Part 4. The determination of the minimum reflux ratio on the basis of the usual simplifying assumptions requires determining the difference $V_m - V_n$. A given enthalpy for the feed does not determine this difference for the general case because the feed-plate location is still a variable; however, in this case, a definite value is obtained at the minimum reflux ratio, because the pinched-in condition occurs at the feed plate.

By an enthalpy balance around the feed plate,

$$Fh_F + V_{f-1}H_{f-1} + O_{f+1}h_{f+1} = V_fH_f + O_fh_f$$

where subscripts f, $f + 1$, $f - 1$, refer to feed plate, plate above, and plate below, respectively.

For the pinched-in condition,

$$H_{f-1} = H_f = H \qquad \text{and} \qquad h_f = h_{f+1} = h$$

Also,

$$F + V_{f-1} + O_{f+1} = V_f + O_f$$

Solution of these equations gives

$$V_f - V_{f-1} = \frac{F(h_F - h)}{H - h}$$

For a first approximation take the enthalpy values H and h, corresponding to a mol fraction of ammonia in the liquid of 0.19; $h = -900$ and $H = 6{,}300$. From Part 1, $h_F = -690$.

$$V_f - V_{f-1} = \frac{F(-690 + 900)}{6{,}300 + 900} = 0.029F$$

The intersection of the operating lines for this condition falls on a line of slope $-(0.971/0.029) = -33.5$, which passes through the $y = x$ line at $z_F = 0.209$. Such a line on Fig. 7-21 cuts the equilibrium curve at $x = 0.193$, $y = 0.71$ which is close enough to the assumed value, and

$$\left(\frac{O}{V}\right)_{\min} = \frac{0.98 - 0.71}{0.98 - 0.193} = 0.343$$

$$\left(\frac{O_R}{D}\right)_{\min} = \frac{0.343}{0.657} = 0.522$$

It will be noted that this value is much lower than that obtained in Part 2, and designing for an actual reflux ratio even twice this value would still give heat requirements less than the true minimum.

Solution of Part 5. For this case, the actual value of (O/D) is to be 1.5 times that obtained in Part 4, and the plates are to be calculated with the usual simplifying assumptions.

$$\left(\frac{O}{D}\right)_{act} = 1.5(0.522) = 0.783$$
$$O_n = 0.783(21.25) = 16.65$$
$$V_n = 37.9$$

In this case the value of $V_n - V_m$ will not be quite equal to that calculated in Part 4 because H_f will not equal H_{f+1}, and h_f will not equal h_{f+1}, but the change will not be large and the same difference will be used as an approximation.

$$V_m - V_n = -2.9$$
$$V_m = 35 \qquad O_m = 113.75$$
$$\left(\frac{O}{V}\right)_n = \frac{16.65}{37.9} = 0.44 \quad \text{and} \quad \left(\frac{O}{V}\right)_m = \frac{113.75}{35} = 3.25$$

These lines are drawn on Fig. 7-21, and the corresponding steps are shown. A still plus approximately 12 theoretical plates are required. This is in close agreement with the result of Part 2, and this is generally the case. Thus, if a tower is calculated on the basis of a certain factor times the minimum reflux ratio, the theoretical plates required are usually approximately the same on either the (y,x) or enthalpy-composition basis, provided the method chosen is used consistently throughout the calculation. However, the heat and cooling requirements may be seriously in error when calculated on the constant overflow basis.

Modified Latent Heat of Vaporization Method. The use of the Ponchon-Savarit method has two major disadvantages: (1) The enthalpy-composition relations for the vapor and liquid are required over the whole operating range and (2) it is limited to binary mixtures. On page 141 it was shown that the variation in O/V was due mainly to a variation in the difference between the enthalpy of the vapor entering and the liquid leaving a plate, and since the enthalpy of either the vapor or liquid does not vary greatly over the concentration range corresponding to one plate, this difference in enthalpy is essentially equal to the latent heat of vaporization for the concentration region involved. Neglecting heat of mixing effects, this heat of vaporization can be approximated as

$$(H - h)_n = [y_1(H - h)_1 + y_2(H - h)_2 + y_3(H - h)_3 + \cdots]_n$$

where $(H - h)_1$, $(H - h)_2$ are the latent heats of vaporization of the pure components.

The values of this molal enthalpy difference vary chiefly because the heats of vaporization of the individual components are different rather

than because their values vary over the temperature range of the column. Thus, if the latent heats of vaporization of all the components were the same, the enthalpy difference would be approximately constant, independent of the composition. It is pointed out on page 141 that this condition leads to essentially straight operating lines for most cases.

If pseudo mol fractions, y', x', z', and flow quantities, V', O', W', F', could be defined such that the following five relationships apply:

$$V'y'(H - h)_R = Vy(H - h) \text{ for each component}^1$$
$$y'_1 + y'_2 + y'_3 + \cdots = 1$$
$$x'_1 + x'_2 + x'_3 + \cdots = 1$$
$$V'_n = O'_{n+1} + D'$$
$$V'_n y'_n = O'_{n+1} x'_{n+1} + D' x'_D \text{ for each component}$$

then the design could be carried out with the pseudo quantities, and the molal enthalpy difference $(H - h)$ would be equal to $(H - h)_R$ for all compositions and would make the usual simplifying assumptions a good approximation. Such relations for the pseudo values in terms of the normal variables are

$$y'_1 = \frac{\beta_1 y_1}{\Sigma \beta y}, \qquad y'_2 = \frac{\beta_2 y_2}{\Sigma \beta y}, \text{ etc.}$$

where $\Sigma \beta y = \beta_1 y_1 + \beta_2 y_2 + \beta_3 y_3 + \cdots$

$$x'_1 = \frac{\beta_1 x_1}{\Sigma \beta x}, \text{ etc.}$$

where $\Sigma \beta x = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \cdots$

$$V'_n = V_n \Sigma \beta y_n$$
$$O'_{n+1} = O_{n+1} \Sigma \beta x_{n+1}$$
$$D' = D \Sigma \beta x_D$$
$$F' = F \Sigma \beta z_F$$
$$W' = W \Sigma \beta x_W$$

In these equations the values of β are equal to the $(H - h)$ values for the component in question divided by $(H - h)_R$. If the $(H - h)$ values for individual components are constant over the operating range involved, β will be constant and a design problem in the new

[1] Where $(H - h)_R$ = same constant for all components and $(H - h)$ = enthalpy difference value for the individual component and is assumed to be constant over the temperature range involved.

coordinates will give straight operating lines. This method necessitates calculating the equilibrium curves and all the flow quantities over to the new coordinates. At the same temperature, the relative volatility is the same for both coordinates. However, if the relative volatility varies with the temperature the y',x' curve will be different from the y,x curve because the temperature will be different for equal values of x and x'. The design problems can then be carried out with these new variables, making the usual simplifying assumptions. After the number of theoretical plates and design conditions is obtained on this pseudo basis, the results can be converted to the true flow quantities and mol fractions. The $(H - h)_R$ value can be arbitrarily chosen although it is usually convenient to make it equal to the $(H - h)$ value for one of the components because this makes β for that component equal to 1. The use of these pseudo variables is equivalent to assigning a fictitious molecular weight to a component such that its molal heat of vaporization on the new basis will be a specified value. The use of this method will be illustrated by the ammonia-water example already considered.

Ammonia-Water Example. From page 153 the latent heats of vaporization for ammonia and water are 4,250 and 8,430 cal. per g. mol, respectively. Using $(H - h)_R = 8{,}430$ gives $\beta_{H_2O} = 1.0$ and $\beta_{NH_3} = 4{,}250/8{,}430 = 0.504$. Recalculating the feed and terminal concentrations to the pseudo units,

$$x'_D = \frac{0.504(0.98)}{0.504(0.98) + 0.02} = 0.961$$

$$z'_F = \frac{0.504(0.209)}{0.504(0.209) + 0.791} = 0.1175$$

$$x'_W = \frac{0.504(0.001)}{0.504(0.001) + 0.999} = 0.000505$$

Per 100 mols of original feed,

$$D' = 21.25[0.504(0.98) + 0.02] = 10.9$$
$$F' = 100[0.504(0.209) + 0.791] = 89.6$$
$$W' = [0.504(0.001) + 0.999] = 78.7$$

The vapor-liquid equilibrium data were recalculated to the new basis and the results are plotted in Fig. 7-21*a*.

To determine the minimum reflux ratio, it is necessary to locate the intersection of the operating line and the equilibrium curve. From page 155 the enthalpy of the feed is −690 cal. per g. mol and the enthalpy of saturated liquid of the feed composition is −970 cal. per g. mol (both values on original basis). Thus the excess enthalpy of the feed above saturated liquid is 100(280) = 28,000 cal. The latent heat on the new basis is 8,430 cal. per g. mol and the fraction vapor in the

feed is

$$\text{Fraction vapor} = \frac{28{,}000}{8{,}430(89.6)} = 0.037$$

The line of intersection of the operating line will cross the $y' = x'$ line at $z_F' = 0.1175$ and will have a slope equal to $-0.963/0.037 = -26$. This line is

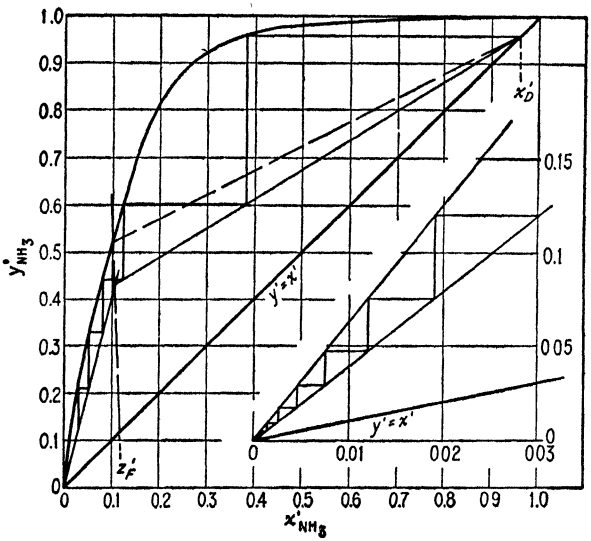


FIG. 7-21*a*.

shown in the figure. This line intersects the equilibrium curve at $x' = 0.102$. $y' = 0.517$ and the minimum reflux ratio corresponds to

$$\left(\frac{O'}{V'}\right)_{\min} = \frac{0.961 - 0.517}{0.961 - 0.104} = 0.517$$

$$\left(\frac{O_R'}{D'}\right)_{\min} = \frac{0.517}{0.483} = 1.07$$

Because the compositions of O_R' and D' are the same, the conversion factors to O_R and D will be the same and

$$\left(\frac{O_R}{D}\right)_{\min} = 1.07$$

This value is close to one obtained on page 156, and the two values probably agree within the accuracy of the calculation. For

$$\left(\frac{O_R'}{D'}\right)_{\text{act}} = 1.5\left(\frac{O_R'}{D'}\right)_{\min} = 1.605$$

$$\left(\frac{O'}{V'}\right)_n = \frac{1.605}{2.605} = 0.616$$

The corresponding operating lines are drawn on the diagram, and the theoretical

plates stepped off in the usual manner. The diagram indicates that a still and 11 theoretical plates are required. This checks the result obtained by the enthalpy-composition method.

This modified latent heat of vaporization method generally gives good results and would be only appreciably in error if (1) the heats of mixing were large or (2) the latent heats of vaporization of the component varied appreciably over the temperature range involved. In the latter case the results can be improved by using separate average values for stripping and enriching section.

Theoretically the enthalpy-composition method is more exact than the use of the modified latent heats of vaporization, but in most cases the two agree within the accuracy of the calculation. For binary mixtures, if the necessary enthalpy data are already available, the enthalpy-composition method is the easier to apply; if the data are not available and must be calculated, then the other method is the more convenient. For multicomponent mixtures the modified latent heat method is more convenient even if the complete enthalpy data are available.

HEAT ECONOMY

In the section on the Optimum Reflux Ratio it was pointed out that the operating costs, *i.e.*, the heating and cooling charges, were frequently the major cost of a distillation process and that fixed charges on the equipment were small. In such cases, it would appear desirable to decrease the heating and cooling requirement at the expense of additional equipment, and this section will consider a number of methods of accomplishing that result.

From a thermodynamic viewpoint the inefficiencies of a distillation operation can be grouped into two main categories: (1) those that are a function of the distillation process itself and (2) those that are related to supplying the necessary energy to the materials being separated.

Separation Efficiency of a Distillation Column. The minimum isothermal thermodynamic work required for separating 1 mol of a liquid binary mixture into its pure liquid constituents is given by the following equation:

$$\text{Minimum work} = \Delta F = -RT\left(x_1 \ln \frac{p_1}{P_1} + x_2 \ln \frac{p_2}{P_2}\right) \quad (7\text{-}41)$$

$$= -RT\left(x_1 \ln \frac{y_1\pi}{P_1} + x_2 \ln \frac{y_2\pi}{P_2}\right) \quad (7\text{-}42)$$

$$= -RT[x_1 \ln (\gamma_1 x_1) + x_2 \ln (\gamma_2 x_2)] \quad (7\text{-}43)$$

where ΔF = minimum work of separation (free-energy change) per mol of mixture
R = gas law constant
T = absolute temperature
x_1, x_2 = mol fractions of components in mixture
γ_1, γ_2 = activity coefficients of two components
π = total pressure
p = partial pressure, or fugacity of component in mixture
P = vapor pressure, or fugacity of pure saturated liquid
y_1, y_2 = mol fractions in equilibrium vapor

For an ideal solution, this expression has a maximum value at a mol fraction of 0.5, and for this condition the minimum work required is equal to $0.693RT$. Thus to separate 1 lb. mol of an ideal mixture of this composition at a temperature of 212°F. would require about 920 B.t.u.

In case the mixture is not completely separated, the minimum work required per mol is obviously less and can be calculated from the following equation:

$$\Delta F = -RT[(x_1 \ln \gamma_1 x_1 + x_2 \ln \gamma_2 x_2) - D(x_{1D} \ln \gamma_{1D} x_{1D} + x_{2D} \ln \gamma_{2D} x_{2D}) - W(x_{1W} \ln \gamma_{1W} x_{1W} + x_{2W} \ln \gamma_{2W} x_{2W})] \quad (7\text{-}44)$$

where D refers to distillate and W refers to bottoms.

Mixtures with positive deviations from Raoult's law, *i.e.*, solutions with activity coefficients greater than 1, require lower minimum work for separation than do ideal solutions; the reverse is true for those solutions with negative deviations. For example, consider the minimum work for separating a 3 mol per cent solution of ethanol and water at its normal boiling point into pure water and 87 mol per cent ethanol. The boiling point of such a solution is 173°F., and the activity coefficients are 4.4 and 1.01 for the 3 mol per cent solution for ethanol and water, respectively; the corresponding values for the 87 per cent solution are 1.01 and 2.2. On the basis of Eq. (7-44), the minimum work of separating 1 mol of this mixture into the desired product would be about 106 B.t.u. Separating an ideal solution of the same composition into the same products would require 153 B.t.u. The actual energy requirement is lower than the theoretical because ethyl alcohol and water have positive deviations from Raoult's law, indicating a tendency to immiscibility. An immiscible system requires essentially no work for separation. On the other hand, systems of negative devia-

tions from Raoult's law, *i.e.*, those that tend to maximum boiling azeotropes, would need more work for separation than an ideal solution.

The energy required for separating a mixture is supplied by adding heat to the fluid in the still and removing heat at a lower temperature level in the condenser. The available work energy, based on an isentropic process, in the heat supplied to the liquid in the still can be calculated on the basis of the following equation:

$$W_s = \text{available work} = Q\frac{T_W - T_o}{T_W} \tag{7-45}$$

where Q = heat added
T_W = absolute temperature of liquid in still
T_o = absolute temperature at which heat can be discharged, *i.e.*, temperature of cooling water

The available work equivalent to the heat removed from the condenser can be calculated by the following equation:

$$W_c = \text{available work} = Q_c\frac{T_c - T_o}{T_c} \tag{7-46}$$

where Q_c = heat removed from condenser
T_c = temperature of condensation of distillate

In order to simplify the following discussion, it will be assumed that the heat added to the still is equal to the heat removed in the condenser. This is essentially true when the feed enters as a liquid at its normal boiling point and when the distillate and bottoms leave as liquid at their boiling points. Other cases can be handled in a similar manner but are more involved. For a system in which $Q_s = Q_c$, the net available work supplied in the heat to the distillation process itself is equal to

$$\begin{aligned}\Delta W &= Q\frac{T_W - T_o}{T_W} - Q\frac{T_c - T_o}{T_c} \\ &= QT_o\left(\frac{1}{T_c} - \frac{1}{T_W}\right)\end{aligned} \tag{7-47}$$

The minimum heat that can be utilized in a distillation corresponds to the minimum reflux condition and, for a binary mixture, can easily be determined from the enthalpy-composition diagram.

It is interesting to compare the thermodynamic minimum work with that required by the actual distillation process at the minimum reflux condition. For ideal mixtures of close boiling compounds Eq. (7-47) can be combined with Eqs. (7-44) and (7-56), and approximations for

the relative volatility and latent heats as a function of temperature can be made to give simplified expressions, but they are misleading for most actual distillations. It is more instructive to study the ratio of Eq. (7-44) to Eq. (7-47) for actual cases. Such calculations for the systems benzene-toluene and ethanol-water at atmospheric pressure are given in Tables 7-5 and 7-6. In the case of the first system, it was assumed that complete separation was being obtained; in the second case, that the distillate was 87 per cent mol alcohol and the bottoms was pure water. In both cases, actual activity coefficients were employed, minimum heat requirements were estimated from enthalpy-composition diagrams, and pressure drop and heat losses were neglected.

TABLE 7-5. FRACTIONATION EFFICIENCY FOR ETHANOL-WATER MIXTURE (T_W = 672°R., T_c = 633°R., T_o = 546°R.)

Mol fraction ethanol in feed	Minimum heat requirement, B.t.u. per lb. mol of feed	Thermodynamic work equation (7-44), B.t.u. per lb. mol	Available work equation (7-47), B.t.u. per lb. mol of feed	Thermodynamic efficiency, per cent
0	—	0	—	0
0.03	2,620	106	131	81
0.1	8,740	195	437	45
0.2	17,500	261	875	30
0.3	26,200	310	1,310	24
0.4	34,900	288	1,745	17
0.5	43,600	283	2,180	13
0.6	52,400	234	2,620	9
0.7	61,200	195	3,060	6
0.8	69,600	90	3,480	3

The benzene-toluene system shows a maximum thermodynamic efficiency of about 80 per cent for a feed composition of 40 per cent benzene. The efficiency decreases for feeds both weaker and stronger, but in the range of feed compositions from 0.1 to 0.8 it is good. Equation (7-44) shows that the efficiency is zero both for x_F approaching 0 and 1.0. In the case of the ethanol-water system, the heat requirement per mol of distillate is essentially independent of the feed composition over the range shown because the minimum reflux ratio condition corresponds to a tangency with the equilibrium curve at about 84 mol per cent alcohol. Thus the reflux ratio is the same over the whole concentration region considered. This reflux ratio corre-

sponds closely to a pinched-in region for the 0.03 feed as well as to the pinched-in condition at the mol fraction of 0.84. Thus the operating line follows the equilibrium curve approximately, and the efficiency for the 0.03 feed concentration is high. For the higher strength feeds, the operating lines over most of the lower concentration regions are a considerable distance from the equilibrium curve. This leads to low efficiency.

TABLE 7-6. FRACTIONATION EFFICIENCY FOR BENZENE–TOLUENE MIXTURE (T_W = 692°R, T_c = 636°R., T_o = 546°R.)

Mol fraction benzene in feed	Minimum heat requirement, B.t.u. per lb. mol of feed	Eq. (7-43) thermodynamic work, B.t.u. per lb. mol	Eq. (7-47) net available work, B.t.u. per lb. mol	Thermodynamic efficiency, per cent
0	—	0	—	0
0.1	13,100	439	895	49
0.2	14,100	662	964	69
0.3	15,200	810	1,040	78
0.4	16,200	882	1,110	80
0.5	17,200	900	1,180	76
0.6	18,300	880	1,250	70
0.7	19,300	785	1,320	60
0.8	20,300	630	1,390	45
0.9	21,400	410	1,460	28
1.0	—	0	—	0

The values given in the tables were the maximum efficiencies and correspond to the minimum reflux ratio. In an actual tower, the heat supply would be greater and the efficiency values should be reduced. The reduction factor is approximately

$$\frac{1 + (O/D)_{\min}}{1 + (O/D)_{\text{act}}}$$

Efficiency of Supplying and Removing Energy from a Distillation Tower. In a simple distillation tower, the greatest inefficiency usually results from the methods employed in supplying energy to the system rather than in the separation process. For example, consider the benzene-toluene mixture of Table 7-6. Even allowing for the actual reflux ratio being greater than the minimum reflux ratio, a thermodynamic efficiency of 50 per cent or greater would be obtained over a wide range of feed compositions. However, in such a case it

would be common practice to use steam as a heating fluid with a condensation temperature of at least 250°F. This would give a temperature difference for heat transfer in the still of 18°F. There would then be a temperature drop through the distillation system corresponding to 56°F., and with cooling water available at 80°F. there would be temperature loss equivalent to 96°F. in going from the overhead vapor to the available heat sink. These temperatures and the corresponding losses in availability are given in Table 7-7. It is evident that the

TABLE 7-7

	Temp., °R.	Net available work, B.t.u. per B.t.u. of heat		Per cent of total
Steam	710	Steam to still,	0.02	8
Still	692	Still to distillate,	0.069	29
Distillate	636	Distillate to cooling water,	0.151	63
Cooling water	540			
Total	.....		0.24	100

major inefficiency is in adding and removing the heat. In this case over 70 per cent of the total available work in the heat was dissipated in these ways. In the case of a 3 per cent ethanol mixture distilled at atmospheric pressure, the loss in available energy of the steam due to heating and cooling could be over 80 per cent. These heat-transfer processes are the source of the major thermal inefficiencies in most industrial distillations. For these cases, the greatest improvement in efficiency will be obtained by reducing these losses. The most obvious way of accomplishing this result is by utilizing a higher fraction of the temperature difference between the source and sink temperatures for the actual distillation process and less for the heat transfer.

METHODS OF INCREASING EFFICIENCY

1. Separation Process. One method of reducing the irreversibility in the fractionating tower is to make the vapor stream entering a plate more nearly in equilibrium with the liquid on the plate. The extreme in this case is for this vapor and the liquid to be in equilibrium, but this obviously means no enrichment per plate. To accomplish this condition throughout the tower requires that the operating line coincide with the equilibrium curve, and this in turn involves a different reflux ratio for each plate, *i.e.*, heat must be added to or removed from each plate in the tower. It is obvious that such a system is impractical.

However, certain approaches have been made in this direction. For example, in most systems the vapor load is limited by the region around the feed plate. Actually a lower quantity of vapor would be suitable for the regions near the top or bottom of the tower, and it would be possible to operate a fractionating tower by supplying less heat at the bottom than corresponds to the required reflux ratio and then to supply additional heat at some point, or points, intermediate between the still and the feed region. This would be advantageous where an additional heat source was available which was not at a temperature level sufficient to operate the still but was suitable for the intermediate region. Likewise, above the feed plate, heat could be removed at some intermediate position and used for other heating purposes.

For example, in the ethanol separation given in Table 7-5 high feed concentrations gave low fractionating efficiency. This was because lower quantities of heat could have been used for the concentration region below a mol fraction of ethanol less than 0.8, and the high heat requirement resulted from the pinched-in region at the top of the tower. In this case, a high percentage of the heat could have been added at a temperature level only a few degrees above that of the condenser rather than at the higher temperature of the still. This would have given a much higher thermodynamic efficiency.

Such modifications result in a lower enrichment per plate and thus require more plates, but they might be attractive in certain cases. Actually, they are seldom advantageous.

2. Heat-transfer Process. In most cases, using a higher percentage of the available work in the heat supplied to the still is more practical than attempting to reduce the irreversibility in the distillation column. The available work utilized is relatively small because the difference in the absolute temperature in the still and the condenser is not large. If the heat could be employed over a wider temperature differential, the efficiency would be increased. The most common method of accomplishing this result is by the multieffect principle or a modification of it. For example, the mixture can be fractionated in two or more towers arranged with operating pressures such that the distillate condensing temperature of one tower is high enough to serve as the heating medium for the succeeding towers. This is entirely analogous to the use of multieffect evaporators. Figure 7-22 illustrates the multieffect system, and Figs. 7-23 to 7-26 show modifications of it.

Multieffect. This system reduces the heat required roughly in proportion to the number of columns employed. This is not quite true because there will be changes in the relative volatility with pressure

that may make some difference. It is possible to make further heat savings by taking the bottoms from the higher pressure columns and expanding them directly into the bottom of the succeeding columns, thereby obtaining a certain amount of sensible heat. The sensible heat of the condensate from a high-pressure stage can also be used in a low-pressure stage.

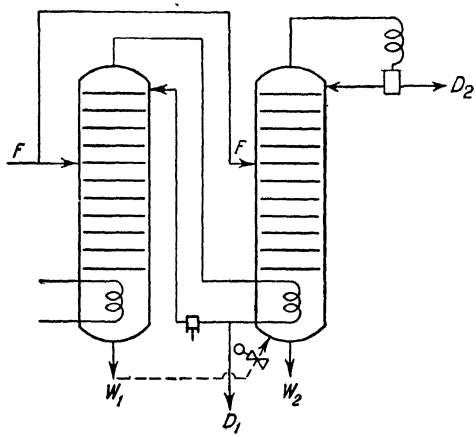


FIG. 7-22. Multitower system.

If the relative volatility does not change with pressure, the total volume of the distillation system will be essentially the same as for a single column operating at about the average pressure of the multieffect system. Thus the column costs will be of the same order for the single- and multieffect system. However, the heat-transfer surfaces required will be larger for the latter due to the lower temperature differences involved, and usually more cooling water will be required. The control problem will be greater than for a single column, but it would not be particularly difficult. Thus, the multieffect system should be attractive where the heating and cooling costs are large relative to the equipment costs.

The number of stages that can be employed is relatively limited because of the high temperature drop per stage. For example, in distilling the mixture ethanol and water, it would be difficult to operate without having each stage cover a temperature differential of the order of 60 to 80°F. Thus, a system having more than two stages would require a high-temperature heat source and would involve relatively high pressures.

In order to evaluate the heat requirement for the multitower system,

consider the case of the separation of a binary mixture in a single tower, for which the relative volatility is independent of the pressure and composition. Making the usual simplifying assumptions, the minimum vapor for a system with $V_n = V_m$ and $x_D = 1$, $x_W = 0$ is

$$V_{\min} = \frac{F[1 + (\alpha - 1)x_F]}{\alpha - 1} \tag{7-48}$$

where $V_{\min}$ = minimum vapor rate
F = feed rate
α = relative volatility
x_F = feed composition

For a multieffect system based on the same assumptions

$$\frac{V_1}{F} = \frac{1 + (\alpha - 1)x_F}{(\alpha - 1)n}$$

where V_1 = minimum vapor generation required for first effect
n = number of effects

Vapor Recompression. One method that has been proposed and utilized on a limited scale is vapor recompression, a schematic diagram of which is shown in Fig. 7-23. In this case, the overhead vapor is compressed to a pressure such that its condensation temperature will be suitable for heating the still. Theoretically, such a method appears attractive because the heat needs to be pumped through a relatively small temperature rise. However, in practice the system has not been particularly attractive due to the high cost of efficient vapor compressors of the size required for distillation units, and when the efficiency of the compressor and the efficiency for producing the power to drive the compressor are included, a great deal of the theoretical advantage is lost.

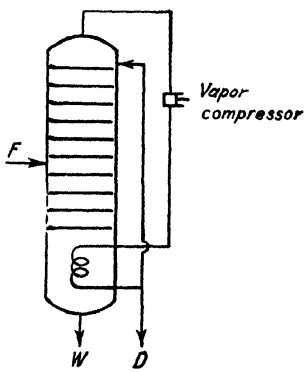


FIG. 7-23. Vapor recompression system.

Vapor Reuse. A modification of the multieffect system, shown in Fig. 7-24, has been termed the vapor reuse system (Ref. 12). In it, the feed is introduced into a stripping tower, and the vapor from it is used as the source of heat and the feed of the lower pressure column. The two columns may not be in balance; *i.e.*, the minimum heat required for the stripping section may be more or less than that

required for the fractionating column. This heat differential can either be added or be removed from the still of the lower pressure fractionating column. In case the heat requirement of the low-pressure tower is greater than for the stripper, it might be thought that the additional heat could be employed advantageously through the stripping column as well as through the fractionating column. However, this is not the case because this additional heat would require that more vapor leave the top of the stripping column and thus it must be a diluter vapor, which makes the work of the fractionating column more difficult. For the same idealized case considered in the multieffect section, the minimum vapor is

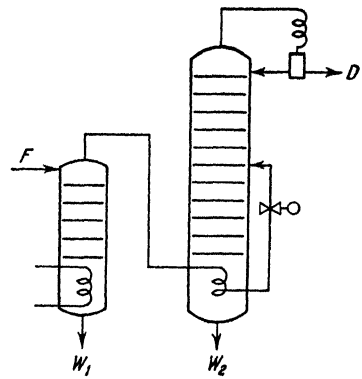


FIG. 7-24. Vapor reuse system.

For the stripping tower,

$$V_{1\,\min} = \frac{F}{\alpha}[1 + (\alpha - 1)x_F] \tag{7-49}$$

and, for the fractionating tower,

$$V_{2\,\min} = \frac{F[1 + (\alpha^2 - 1)x_F]}{\alpha(\alpha - 1)} \tag{7-50}$$

$$\text{If } x_F < \frac{\alpha - 2}{2(\alpha - 1)},\ V_{1\,\min} > V_{2\,\min}$$

$$\text{If } x_F = \frac{\alpha - 2}{2(\alpha - 1)},\ V_{1\,\min} = V_{2\,\min}$$

$$\text{If } x_F > \frac{\alpha - 2}{2(\alpha - 1)},\ V_{1\,\min} < V_{2\,\min}$$

Split Tower. Figure 7-25 shows a split-tower system which partly separates the feed in one fractionating column and completes the fractionation in the second column. It is similar to the previous case except that a fractionating column with reflux is employed instead of the stripping column. This system can be adjusted so that the two towers are in heat balance. The feed is shown entering the high-pressure tower. This makes relatively pure bottoms but impure distillate, which is then fractionated in the second tower. This arrangement is desirable for feeds with low concentrations of the more volatile component. If the feed concentration is high, it is more desirable to

fractionate the feed first into pure distillate and impure bottoms and refractionate the bottoms in the lower pressure column.

This system involves a lower over-all temperature drop than a two-stage multieffect system and thereby makes the design of the heat-transfer surfaces easier. However, the multieffect system has the

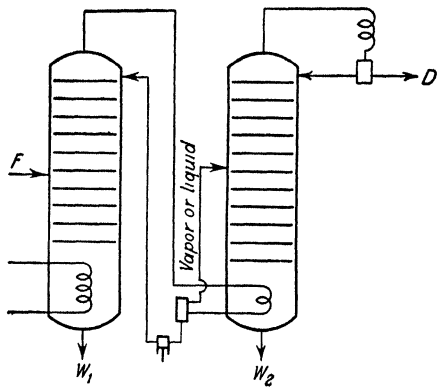


FIG. 7-25. Split-tower system.

advantage that it uses all the heat over the whole concentration region each time. This system utilizes the heat over a limited concentration region twice but over other regions only once. Thus, it tends to give a higher reflux ratio in the central portion of the column and lower reflux ratios at the ends. The minimum vapor requirement for this system for the assumptions made in the other cases is given by Eq. (7-51):

$$V_{\min} = \frac{F[1 + (\alpha - 1)x_F]^2}{(\alpha - 1)[2 + (\alpha - 2)x_F]} \tag{7-51}$$

This arrangement is very similar to that employed in the so-called double towers for the separation of oxygen and nitrogen. In this case the feed is relatively rich in the lower boiling component, nitrogen, and the first tower is used to produce an overhead that contains a high concentration of nitrogen and an impure bottoms containing 40 to 50 per cent oxygen. The liquid nitrogen overhead product from the high-pressure tower is added to the top of the low-pressure tower and serves as the only reflux for it. There is no other source of refrigeration to produce additional reflux. The impure bottoms from the high-pressure tower is introduced into the middle portion of the low-pressure tower. Such a two-tower system will give high-purity nitrogen and oxygen low in nitrogen although it will contain appreciable quantities

of noble gases. It is common practice in this case to build the low-pressure tower on top of the high-pressure tower, and the condenser-reboiler is a common unit of both columns.

A further modification of the split-tower system is given in Fig. 7-26 in which the feed is rectified into impure bottoms and an impure distillate, and these are then retreated in the lower pressure tower. In general, this system gives slightly lower heat requirements than the previous system, and it utilizes the same principle, namely, reusing the heat several times in the middle region concentrations where the heat requirements are the highest. The systems of Figs. 7-22 to 7-26 can be utilized with three or more towers to obtain still further heat reductions.

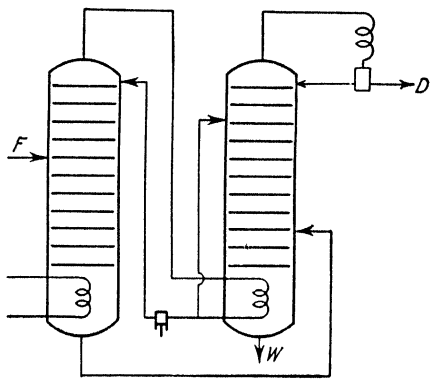


FIG. 7-26. Modified split-tower system.

In order to show the comparison between the different systems, the various equations have been plotted in Fig. 7-27 for the cases of feed concentrations equal to 0 and 1.0. The equation for the multieffect system has been plotted for $n = 1$, *i.e.*, a single tower. If a two-stage system is used, the values should be divided by 2, etc. For the vapor-reuse system the maximum vapor requirement for the two columns is given, and no credit has been applied for the low-temperature heat that could be withdrawn for the cases with the relative volatility greater than 2.0. It will be noted that none of the modifications is so effective in reducing the heat requirements as the multistage system, although some of them are equal to it for specialized conditions. Of the specialized arrangements, vapor reuse would not appear to be so attractive as the split-tower system shown although, in cases where the waste heat was of real utility, it could be attractive. The relative

attraction of the systems will be shifted somewhat as they are compared at reflux ratios lower than the minimum (or greater than total reflux). It still appears that, for a given number of towers, the multieffect system is the most attractive from the heat viewpoint. Likewise, for a given total quantity of heat supplied to the system and for the same number of towers, the total plate area required is less for the

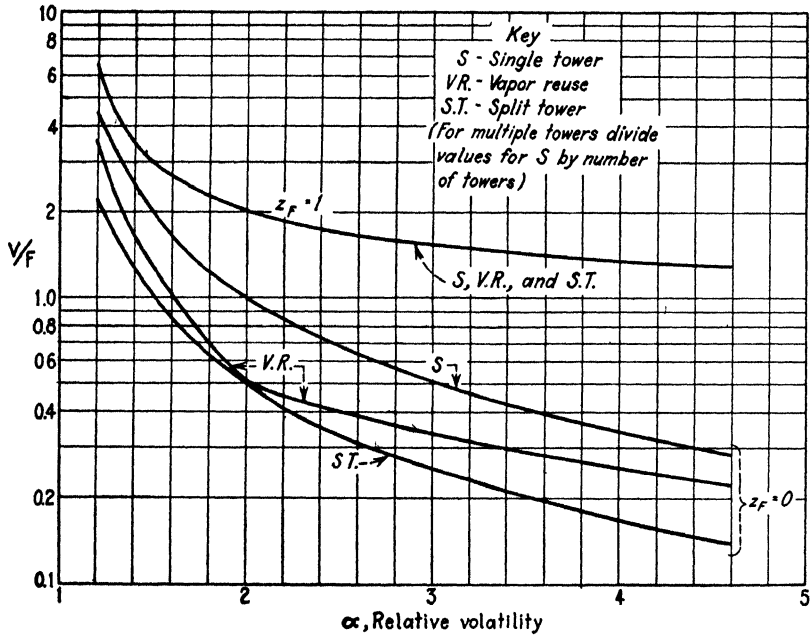


FIG. 7-27. Comparison of vapor requirements.

multieffect system than for the modifications. This greater efficiency is due to the more efficient utilization of the heat over a wide temperature range.

ANALYTICAL EQUATIONS

For a few special cases of limited applicability, it has been possible to develop mathematical solutions, some of the most useful of which are considered in this section.

Total Reflux. Fenske (Ref. 5) developed an algebraic method of calculating the minimum number of theoretical plates by utilizing the relative volatility together with the fact that at total reflux the operating line becomes the $y = x$ diagonal. Thus, considering the two

components x' and x'' and starting with the still,

$$\left(\frac{y'}{y''}\right)_W = \alpha_W \left(\frac{x'}{x''}\right)_W$$

and at total reflux the operating-line equation gives $y_W = x_1$, giving

$$\left(\frac{x'}{x''}\right)_1 = \alpha_W \left(\frac{x'}{x''}\right)_W \quad \text{and} \quad \left(\frac{y'}{y''}\right)_1 = \alpha_1 \alpha_W \left(\frac{x'}{x''}\right)_W$$

Continuing, in the same manner,

$$\left(\frac{x'}{x''}\right)_n = (\alpha_{n-1})(\alpha_{n-2}) \cdots \alpha_1 \alpha_W \left(\frac{x'}{x''}\right)_W$$

In some cases the relative volatility does not vary widely, and an average value for the entire column can be used, giving

$$\left(\frac{x'}{x''}\right)_N = (\alpha_{av})^N \left(\frac{x'}{x''}\right)_W$$

where N is the number of plates in the column. This can be changed to

$$N = \frac{\log (x'/x'')_N (x''/x')_W}{\log \alpha_{av}} \tag{7-52}$$

If a total condenser is employed, this becomes

$$N + 1 = \frac{\log (x'/x'')_D (x''/x')_W}{\log \alpha_{av}} \tag{7-53}$$

or, if a partial condenser equivalent to one theoretical plate is employed,

$$N + 2 = \frac{\log (y'/y'')_D (x''/x')_W}{\log \alpha_{av}} \tag{7-54}$$

These equations offer a simple and rapid means of determining the number of theoretical plates at total reflux and avoid the necessity of constructing the y,x diagram. Principally an arithmetic average of the relative volatility at the temperature of the still and the top of the tower is employed. This is a satisfactory average only if the relative volatility is reasonably constant over the concentration region involved. For larger variations the geometric average would be more satisfactory, *i.e.*, $\alpha_{av} = \sqrt{\alpha_t \alpha_W}$, or still better $\alpha_{av} = 1 + \sqrt{(\alpha_t - 1)(\alpha_W - 1)}$, where α_t is the relative volatility at the top of the column. In the cases of abnormal volatility such as are exhibited by ethyl alcohol and water,

the use of an average relative volatility is not satisfactory over an appreciable concentration range; however, the equation may be applied successively to small concentration ranges, but the operation becomes more time-consuming than constructing the y,x diagram and stepping off the plates. The use of the y,x diagram has the advantage that it gives a picture of the concentration gradient, and after the diagram has been constructed, the number of theoretical plates for other reflux ratios can be easily determined. This method is not applicable to conditions other than total reflux.

Minimum Reflux Ratio. The analytical equation for this case can be easily derived in terms of the coordinates, y_c and x_c, of the point of contact of the equilibrium curve and the operating line.

$$(V_n)_{\min} = \frac{D(x_D - x_c)[1 + (\alpha - 1)x_c]}{(\alpha - 1)(x_c)(1 - x_c)} = \frac{F(x_D - x_c)(z_F - x_W)[1 + (\alpha - 1)x_c]}{(\alpha - 1)(x_c)(1 - x_c)(x_D - x_W)} \tag{7-55}$$

$$\left(\frac{O_n}{D}\right)_{\min} = \frac{x_D[1 + (\alpha - 1)x_c] - \alpha x_c}{(\alpha - 1)(x_c)(1 - x_c)} \tag{7-56}$$

$$(V_m)_{\min} = \frac{W(x_c - x_W)[1 + (\alpha - 1)x_c]}{(\alpha - 1)(x_c)(1 - x_c)} = \frac{F(x_c - x_W)(x_D - z_F)[1 + (\alpha - 1)x_c]}{(\alpha - 1)(x_c)(1 - x_c)(x_D - x_W)} \tag{7-57}$$

when $V_n = V_m$ and x_D and x_W are approximately 1.0 and 0.0, respectively.

$$V_{min} = \frac{D[1 + (\alpha - 1)x_F]}{(\alpha - 1)x_F} = \frac{F[1 + (\alpha - 1)x_F]}{\alpha - 1} \tag{7-58}$$

and

$$\left(\frac{O}{D}\right)_{\min} = \frac{1}{(\alpha - 1)x_F} \tag{7-59}$$

These equations are exact for the case of constant molal flow rates where the value of the relative volatility is taken at the composition x_c. Equations (7-55) to (7-57) involve so many factors that it is usually easier to obtain the minimum reflux ratio values graphically or by using y_c and x_c with Eq. (7-10).

Theoretical Plates Required for Finite Reflux Ratios. The equation for the number of theoretical plates at total reflux is convenient for mixtures in which α is relatively constant, and it would be useful to

have a comparable method applicable at other reflux ratios. Two basic equations were used in the total reflux derivation:

$$\left(\frac{y_A}{y_B}\right)_n = \alpha_n \left(\frac{x_A}{x_B}\right)_n \qquad \text{and} \qquad \left(\frac{y_A}{y_B}\right)_n = \left(\frac{x_A}{x_B}\right)_{n+1}$$

The first of these two equations is true at any reflux ratio, but the latter is true only at total reflux. However, new variables may be defined such that

$$\left(\frac{y'_A}{y'_B}\right)_n = A_n \left(\frac{x'_A}{x'_B}\right)_n \tag{7-60}$$

and

$$\left(\frac{y'_A}{y'_B}\right)_n = \left(\frac{x'_A}{x'_B}\right)_{n+1} \tag{7-61}$$

It is obvious that the equation developed from these will be identical in form with Eq. (7-52). Thus, above the feed

$$N_n + 1 = \frac{\log\ (x'_A/x'_B)_D (x'_B/x'_A)_F}{\log\ (A_n)_{av}} \tag{7-62}$$

It remains to relate the new variables to the actual compositions and the usual operating variables. In addition it would be convenient, but not necessary, to have the following relation,

$$x'_A + x'_B = 1.0$$

A number of solutions for the new variables have been obtained (Refs. 16, 18), and one set is given here.

Above the feed,

$$x'_{An} = \frac{O}{V}\left[\frac{\left(\frac{\alpha - 1}{\alpha}\right)S}{\frac{S^2 O}{\alpha V} - 1}\right]\left(x_{An} - \frac{D}{O}\frac{x_D}{S - 1}\right) \tag{7-63}$$

$$x'_{Bn} = 1 - x'_{An}$$

Below the feed,

$$x'_{Am} = \frac{\left(\frac{O}{V}\right)\left(\frac{\alpha - 1}{\alpha}\right)S}{\frac{S^2 O}{\alpha V} - 1}\left(x_{Am} + \frac{W}{O}\frac{x_W}{S - 1}\right) \tag{7-64}$$

$$x'_{Bm} = 1 - x'_{Am}$$

Above the feed plate,

$$S - 1 = \frac{2(D/O)x_D(\alpha - 1)}{\left[\alpha\left(\frac{V}{O}\right) - 1 - \left(\frac{D}{O}\right)x_D(\alpha - 1)\right]\left\{1 - \sqrt{1 - \frac{4(D/O)x_D(\alpha - 1)}{[\alpha(V/O) - 1 - (D/O)x_D(\alpha - 1)]^2}}\right\}} \tag{7-65}$$

Below the feed the same equation is employed to calculate the value of S except that $-(Wx_W/O_m)$ is used instead of Dx_D/O_n. The value of A_n is calculated as follows:

$$A_n = \frac{S^2O}{\alpha V} \tag{7-66}$$

These equations are rather involved to use, and they become particularly difficult where the number of plates is large. The most effort is involved in evaluating the term S, and Fig. 7-28 is arranged to facilitate this calculation.

The equation above the feed plate should be employed down to the feed-plate conditions; *i.e.*, for minimum plates at a given O/D, it should be applied down to the conditions given by the intersection of the operating lines.

For special conditions found to apply in a great many design problems, it is possible to simplify the calculation of S. It is often found that the value of S below the feed plate is equal to $\alpha(V/O)$, which makes the calculation of S simple. It can be shown that this is the exact value of S for the case of $\frac{W}{O} x_W(\alpha - 1)$ equal to zero. For values of $\frac{W}{O} x_W(\alpha - 1)$ that are less than 1 per cent of $\alpha(V/O) - 1$, good results are obtained by using

$$S = \alpha\left(\frac{V}{O}\right) + \frac{W}{O} x_W(\alpha - 1) \tag{7-67}$$

and

$$A = \frac{S^2O}{\alpha V} = \alpha\left(\frac{V}{O}\right) + 2\frac{W}{O} x_W(\alpha - 1) \tag{7-68}$$

Above the feed plate similar approximations can be made giving,

$$S = \alpha\left[1 + \frac{D}{V}(1 - x_{AD})(\alpha - 1)\right] \tag{7-69}$$

$$A = \frac{S^2O}{\alpha V} = \frac{\alpha O}{V}\left[1 + 2\frac{D}{V}(1 - x_{AD})(\alpha - 1)\right] \tag{7-70}$$

Lewis Method. Lewis (Ref. 8) expresses the rate of increase of concentration of the liquid in the column from one plate to the next by the differential dx/dn; therefore,

$$x_{n+1} = x_n + \frac{dx}{dn} \tag{7-71}$$

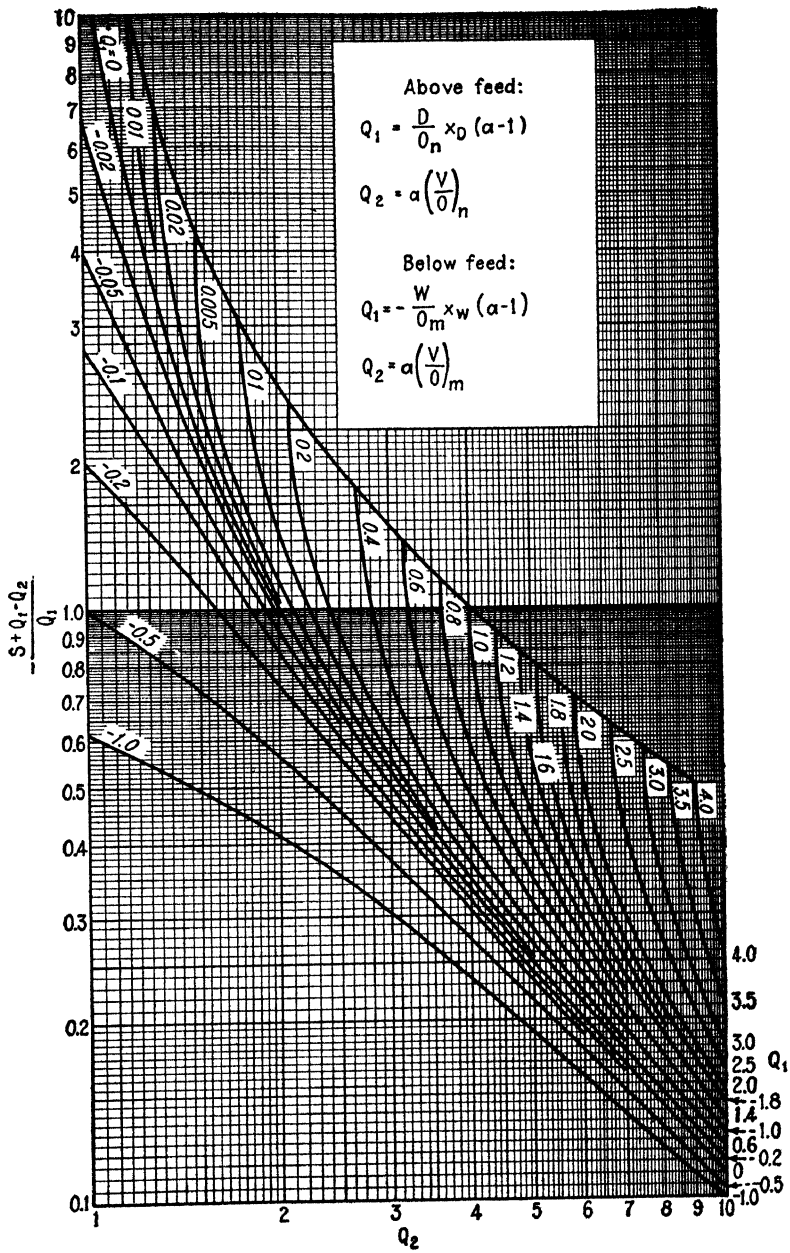


FIG. 7-28. Plot for analytical equation.

The material-balance equation

$$V_n y_n = O_{n+1} x_{n+1} + D x_D$$

can be written, using $V = O + D$,

$$y_n = x_{n+1} + \frac{D}{O}(x_D - y_n)$$

From Eq. (7-71),

$$\frac{dn}{dx} = \frac{1}{x_{n+1} - x_n} = \frac{1}{y_n - x_n - \frac{D}{O}(x_D - y_n)} \tag{7-72}$$

The integration of this equation gives the number of theoretical plates between the x limits chosen; thus, the number of theoretical plates above the feed N_n is

$$N_n = \int_{x_f}^{x_D} \frac{dx}{y_n - x_n - \frac{D}{O}(x_D - y_n)} \tag{7-73}$$

Similarly, below the feed the theoretical plates N_m become

$$N_m = \int_{x_W}^{x_f} \frac{dx}{y_m - x_m - \left(\frac{F - D}{O - pF}\right)(y_m - x_W)} \tag{7-74}$$

The equilibrium y,x curve gives the relation between y_n and x_n and y_m and x_m; thus by assuming values for x_n, values of y_n can be obtained from the equilibrium data, and

$$\frac{1}{y_n - x_n - \frac{D}{O}(x_D - y_n)}$$

can be calculated and plotted vs. the assumed values of x. The area under such a curve from x_f to x_D is the number of theoretical plates by the Lewis method.

Although this method is based on a continuous change of concentration instead of the actual stepwise concentration increase, the error involved is not serious when the change in concentration per plate is small. This latter condition is generally true when the number of plates involved is large.

When the relative volatility is reasonably constant over the range of concentrations involved, the equilibrium curve may be approximated by the relative-volatility relation (see page 30)

$$y = \frac{\alpha_{av}x}{1 + x(\alpha_{av} - 1)}$$

and the foregoing equation may be integrated directly, avoiding the necessity for the graphical integration. Thus, for total reflux at which $D/O = 0$ and $(F - D)/(O - pF) = 0$, the foregoing equations give

$$N_n + N_m + 1 = \left(\frac{1}{\alpha - 1}\right) \ln \frac{x_D}{x_W} \left(\frac{1 - x_W}{1 - x_D}\right)^{\alpha} \tag{7-75}$$

where $N_n + N_m + 1$ is the total number of steps including the still step and any condenser enrichment. Noting that $\ln \alpha$ for values of α near to 1 is approximately equal to $(\alpha - 1)$ makes the foregoing equation approach the equation for total reflux. The values at total reflux were calculated for an example with α equal to 1.07, $x_D = 0.96$, and $x_W = 0.033$. Equation (7-75) gave 97 theoretical plates, while Eq. (7-53) gave 94. Equation (7-53) is applicable only at total reflux, while the Lewis equation can be integrated for the case of finite reflux ratios and constant relative volatilities. Thus Eq. (7-73) can be integrated to give

$$N_n = \frac{1 + (b/2)}{\sqrt{b^2 - 4ac}} \ln \left[\left(\frac{x_D + A}{x_f + A}\right)\left(\frac{x_f + B}{x_D + B}\right)\right] - \frac{1}{2} \ln \frac{ax_D^2 + bx_D + c}{ax_f^2 + bx_f + c} \tag{7-76}$$

where $a = 1 - \alpha$

$b = (\alpha - 1)[1 - (D/O)x_D] + \alpha D/O$

$c = -(D/O)x_D$

$$A = \frac{b - \sqrt{b^2 - 4ac}}{2a} \quad \text{and} \quad B = \frac{b + \sqrt{b^2 - 4ac}}{2a}$$

A similar equation is obtained below the feed with $-W/O_m$ replacing D/O, $-(W/O_m)x_W$ replacing $(D/O)x_D$, and using x_f instead of x_D and x_W instead of x_f.

The integrated equations are most useful in cases where the number of plates is large and the graphical method would be long and tedious.

Example Illustrating the Use of Analytical Equations. As an example of the use of the analytical equations, consider the benzene-toluene rectification problem of page 122.

Total reflux [Eq. (7-53)]:

Using a relative volatility of 2.5,

$$N + 1 = \frac{\log \left(\frac{0.95}{0.05}\right)\left(\frac{0.95}{0.05}\right)}{\log 2.5} = 6.4$$

$$N = 5.4 \text{ plates}$$

Minimum reflux ratio [Eq. (7-56)]:

$$\left(\frac{O}{D}\right)_{\min} = \frac{0.95[1 + 1.5(0.5)] - 2.5(0.5)}{1.5(0.5)(0.5)} = 1.1$$

Theoretical plates at $(O/D) = 3.0$:

Above the feed plate, using Fig. 7-28,

$$Q_1 = \left(\frac{1}{3.0}\right)(0.95)(1.5) = 0.475$$

$$Q_2 = 2.5\ (\tfrac{4}{5}) = 3.333$$

$$-\frac{S + 0.475 - 3.333}{0.475} = 0.65$$

$$S = 3.333 - 1.65(0.475) = 2.55$$

$$A_n = \left(\frac{2.55}{2.5}\right)^2\left(\frac{3}{4}\right) = 1.95$$

$$x'_{AD} = \frac{3}{4}\left[\frac{(1.5/2.5)2.55}{1.95 - 1}\right]\left[0.95 - \frac{0.95}{3(2.55 - 1)}\right] = 0.9$$

$$x'_{BD} = 1 - 0.9 = 0.1$$

$$x'_{AF} = \frac{3}{4}\left[\frac{(1.5/2.5)(2.55)}{1.95 - 1}\right]\left[0.5 - \frac{0.95}{3(2.55 - 1)}\right] = 0.357$$

$$x'_{BF} = 1 - 0.357 = 0.643$$

$$N_n + 1 = \frac{\log\left(\frac{0.9}{0.1}\right)\left(\frac{0.643}{0.357}\right)}{\log 1.95} = 4.2$$

Below the feed plate, $W/O = 0.2$, $V/O = 0.8$, and using Fig. 7-28 and the equations gives $S = 2.03$, $A = 2.06$, $x'_{AF} = 0.731$, $x'_{BF} = 0.269$, $x'_{AW} = 0.086$, and $x'_{BW} = 0.914$.

$$N_m = \frac{\log\left(\frac{0.731}{0.269}\right)\left(\frac{0.914}{0.086}\right)}{\log 2.06} = 4.7$$

Thus the total number of steps including the still is 8.9, corresponding to 7.9 theoretical plates plus the still. This compares with $8\frac{1}{3}$ plates estimated by the stepwise method (page 123).

The values of S and A can be evaluated by the approximations, thus,

Above the feed plate,

$$S = 2.5[1 + \tfrac{1}{4}(0.05)(1.5)] = 2.55$$
$$A = 2.5(\tfrac{3}{4})[1 + \tfrac{3}{4}(0.05)(1.5)] = 1.95$$

Below the feed plate,

$$S = 2.5(\tfrac{4}{5}) + \tfrac{1}{5}(0.05)(1.5) = 2.02$$
$$A = 2.5(\tfrac{4}{5}) + \tfrac{2}{5}(0.05)(1.5) = 2.03$$

These values are so close to those obtained before that the result is essentially the same.

In certain cases the terminal compositions are small, and to obtain any accuracy by the usual y,x method requires expanding the diagram. However, in most of these cases, the number of steps between the operating line and the equilibrium curve can be easily calculated, utilizing the fact that the equilibrium curve and the operating line are straight in this region. The equilibrium curve can be expressed as $y = Kx$ and, for values of x near zero, K is equal to the relative volatility. The operating line in such a region will be straight for most cases, even on an enthalpy basis, because the variation of composition is so small that it makes essentially no difference in the enthalpy values.

For the bottom of the tower when the two lines are straight, the number of steps or theoretical plates required is given by

$$N_W = \frac{\ln\left[\dfrac{\left(\dfrac{VK}{O} - 1\right)\left(\dfrac{x_m}{x_W} - 1\right)}{(V/O)(K-1)} + 1\right]}{\ln\,(VK/O)} \tag{7-77}$$

where N_W = number of plates including plate m, but excluding the still
x = mol fraction of most volatile component

This relationship is similar to Eq. (7-62) for small values of x_W.

Above the feed plate, the corresponding relationship for a column and total condenser is obtained by using a similar analysis for the least volatile component,

$$N_n + 1 = \frac{\ln\left[\dfrac{\left(1 - \dfrac{O}{V}\right) + \dfrac{x_n}{y_T}\left(\dfrac{O}{V} - K'\right)}{1 - K'}\right]}{\ln\,(O/K'V)} \tag{7-78}$$

where N_n = plates above plate n
y, x = mol fractions of least volatile component
K' = equilibrium constant for least volatile component

Packed Towers. Packed towers can be used in fractional distillation as well as bubble-plate columns. Instead of bubbling through a pool of liquid as in a bubble-plate tower, the interaction between vapor and liquid can be obtained by causing the reflux to flow over the surface of the packing material while the vapor flows up through the voids. The use of packed towers is generally limited to towers of small sizes or to special distillations such as the concentration of nitric acid. In small laboratory and pilot-plant size, the packed tower necessary

for a given separation is, in general, less expensive than a corresponding bubble-plate tower; in large diameter, the reverse may be true. Aside from the economic aspects, packed towers are easily constructed and can be made of noncorrosive refractory earthenware, glass, and carbon as well as the usual metals used in bubble-plate tower construction. They have the disadvantage that it may be difficult to clean the tower without completely dismantling the unit, and often they channel badly; *i.e.*, the liquid and vapor segregate from each other, and the efficiency of contact between them is poor. The packed towers, in general, have very low pressure drops from top to bottom relative to an equivalent bubble-plate tower.

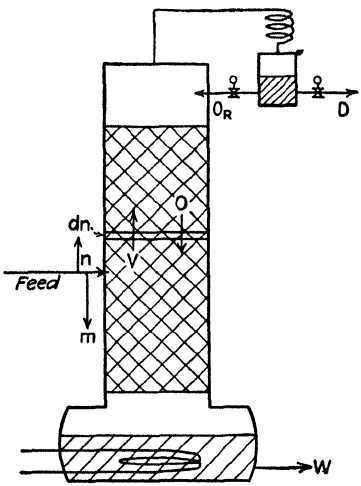


FIG. 7-29. Schematic diagram for packed tower.

For tower packing, a wide variety of materials have been used, *e.g.*, coke, stone, glass, earthenware, carbon and metal rings, wood grids, jack chain, carborundum, and metal and glass helices, as well as a large number of other packings including many manufactured packings of special shapes.

Design of Packed Tower. Ideally, the interaction between vapor and liquid in packed towers is true countercurrent rather than the stepwise-countercurrent process of a bubble-plate tower with theoretical plates. Instead of finite steps, the true countercurrent action should be treated differentially. Consider the schematic drawing of the packed tower in Fig. 7-29. Let O be the mols of overflow, V the mols of vapor, x and y the average mol fraction in the liquid and vapor, respectively, n distance above and m distance below the feed. Focusing on the differential section dn, $V(dy/dn)$ must equal $O(dx/dn)$ for each component, and this transfer must be due to an exchange of components back and forth between the liquid and vapor. This transfer is due to the fact that the vapor and liquid at a given cross section are not in equilibrium with each other, and the rate of transfer will be a function of the distance from equilibrium; thus,

$$V\frac{dy}{dn} = O\frac{dx}{dn} = kA(y^* - y) = k'A(x - x^*) \qquad (7\text{-}79)$$

where k, k' = proportionality constants
A = area per unit height
y^* = vapor in equilibrium with x
x^* = liquid in equilibrium with y

Integration of Eq. (7-79) is difficult because very little information is available on the values of and the factors involved in kA. Assuming that this product is constant and making the usual simplifying assumptions, equation can be arranged as follows:

$$n = \frac{V_n}{kA} \int_{y=y_{f'}}^{y=y_T} \frac{dy}{y^* - y} = \frac{O_n}{k'A} \int_{x=x_{f'}}^{x=x_T} \frac{dx}{x - x^*} \tag{7-80}$$

Below the feed,

$$m = \frac{V_m}{kA} \int_{y=y_s}^{y=y_{f'}} \frac{dy}{y^* - y} = \frac{O_m}{k'A} \int_{x=x_{W'}}^{x=x_{f'}} \frac{dx}{x - x^*} \tag{7-81}$$

where x'_f, y'_f are the liquid and vapor compositions in the tower at the level at which the feed is introduced, and x'_W is the liquid concentration at the bottom of the packed section.

A material balance above the feed gives

$$y = \left(\frac{O}{V}\right) x + \left(\frac{D}{V}\right) x_D \tag{7-82}$$

By assuming values of y, values of x can be calculated by Eq. (7-82), and these used in Eq. (7-80) together with equilibrium data to evaluate the integrals. A similar material balance below the feed can be used with Eq. (7-81). The equilibrium curve and the material-balance equation can be plotted on the y,x diagram, and $x^* - x$ or $y - y^*$ read directly.

Consider the separation of an equimolal mixture of benzene and toluene into a product containing 95 mol per cent benzene and a residue containing 5 mol per cent benzene. An O/D of 3 will be used, and the feed will enter heated such that the mols of vapor above and below the feed are the same. The usual simplifying assumptions will be made. The equilibrium curve is given in Fig. 7-30.

The operating lines are identical with those for the stepwise diagram. The vertical distance between the equilibrium line and the operating line is $y^* - y$, and the horizontal distance between the operating line and the equilibrium line is $x - x^*$. In general, the integration must be performed graphically, although in cases where the equilibrium curve can be expressed as an algebraic relation between y

and x the integration can be carried out algebraically, but the resulting equations are often complex and involved.

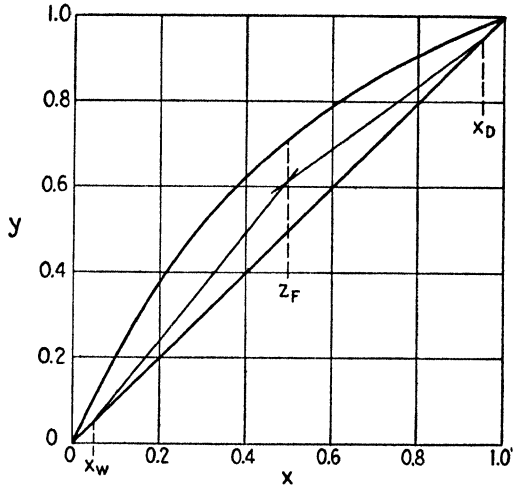


FIG. 7-30.

From Fig. 7-30, values of $y^* - y$ are read at various values of y. Such values are tabulated in Table 7-8.

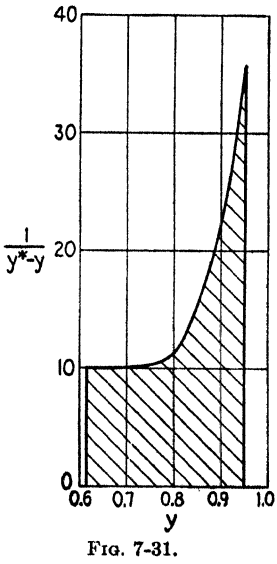


FIG. 7-31.

TABLE 7-8

y	$y^* - y$	$\frac{1}{y^* - y}$
0.615	0.098	10 2
0.7	0.100	10.0
0.8	0.090	11.1
0.9	0.043	23.2
0.95	0.028	35.7

Values of $1/(y^* - y)$ are then calculated and plotted vs. y. The area under this curve from $y = 0.615$ to $y = 0.95$ is equal to kAn/V; so that if kA is known, n can be calculated. The values $1/(y^* - y)$ vs. y are plotted in Fig. 7-31. The value of $dy/(y^* - y)$ is the shaded area, which is equal to 5.35. A similar procedure is used below the feed, and alternately the $x - x^*$ values may be used.

The difficulty in using this procedure is in evaluating kA and $k'A$.

There is a real question as to whether Eq. (7-79) is a proper formulation for the rate of transfer. This doubt arises from several factors:

1. There is no adequate proof that the rate of transfer is directly proportional to the difference in concentration, but there are theoretical considerations that would indicate this is not the proper driving force.
2. The distribution and ratio of the liquid and gas are not the same at all points of a given cross section resulting in differences of concentration, and it is doubtful whether a rate equation of this type is satisfactory with average values.
3. The wetted-area factor is a nebulous quantity because all the area of the packing is not wetted and because the wet areas are not all equivalent. It is a factor that varies widely with the system being distilled and with the column construction.

As a result of these factors, no satisfactory correlations have been presented for the kA and $k'A$. If data on a tower operating under essentially identical conditions to the one being designed are available, a reasonable extrapolation can usually be made. However, any major extrapolation will make the results questionable.

A number of attempts have been made to relate the values of kA obtained for one system with those for other systems. The coefficients involve resistances to mass transfer for both the vapor and the liquid phases, and it has been customary to apply relations based on the Lewis and Whitman two-film theory. It is doubtful that such a theory is applicable in this case since it is difficult to visualize the conditions inherent in this theory for a liquid phase in a packed tower. Further studies of the mechanism of mass transfer between the vapor and the liquid for systems approximating the conditions in a packed tower are needed to furnish a sound basis for correlating the over-all mass-transfer coefficients.

Height Equivalent to a Theoretical Plate. In general, the graphical calculation involved in the design of a packed tower is more tedious and time consuming than the stepwise procedure used for plate towers. Actually, the equilibrium curve and operating lines on the y,x diagram are identical for the two cases, and one of the most common methods of designing packed towers has been to determine the number of theoretical plates required for the separation by the usual stepwise method and then to convert to the height of the corresponding packed tower, by multiplying the number of theoretical plates by the height of packing equivalent to one theoretical plate. This is abbreviated to H.E.T.P. (Ref. 13) and is a height of packing such that the vapor leaving the top of the section will have the same composition as the

vapor in equilibrium with the liquid leaving the bottom of the section. The use of the H.E.T.P. substitutes a stepwise countercurrent procedure for the true countercurrent operation and is therefore theoretically unsound; but when the concentration change between plates is small and the number of plates is large, the error introduced by its use will be small. Values of H.E.T.P. are determined experimentally by calculating the number of theoretical plates necessary to be equivalent to some actual packed tower; the height of the packed tower divided by the number of theoretical plates is then the H.E.T.P. Values of H.E.T.P. will be considered in Chap. 17 on Column Performance (page 465).

Height of a Transfer Unit. Chilton and Colburn (Ref. 3) have proposed that the integrals of Eqs. (7-80) and (7-81) be termed the number of transfer units, N.T.U. The height of the packed section divided by the number of transfer units is termed the height of a transfer unit, H.T.U. This latter unit being defined above the feed plate as

$$\text{H.T.U.} = \frac{n}{\text{N.T.U.}} = \frac{V}{kA} = \frac{O}{k'A}$$

The transfer unit consists of a step on the operating line such that the change in y or x is equal to the average difference between the equilibrium curve and the operating line over the region of the step. If the equilibrium and operating lines are parallel, the step will be exactly equal to that for a theoretical plate, and the H.T.U. value will equal the H.E.T.P. value. If the slope of the equilibrium curve is less than that of the operating line, the two curves will tend to converge with increasing concentration, and the initial difference, which corresponds to the step taken for a theoretical plate, will be greater than the average difference corresponding to the transfer unit. Thus, in this case one equilibrium plate will give a greater concentration change than one transfer unit. If the two curves diverge with increasing concentration, the reverse is true.

Over the height of one transfer unit, the value of $y^* - y$ does not ordinarily vary widely, and the arithmetic average may be used. Baker (Ref. 1) has developed a relatively simple stepwise method for estimating the number of transfer units under these conditions. In the usual y,x diagram (Fig. 7-32), a line ab is drawn at the arithmetic mean of the equilibrium curve and the operating line. The H.T.U. corresponds to a step giving a change in y equal to the average value of

$* - y$ over the step. Starting at A, one proceeds not to B but to C, uch that $AD = DC$, and then steps from C to the operating line. f the curvature of the equilibrium curve is not too great, CG, the hange in y which is numerically equivalent to the EF, will be approxinately equal to the average value of $y^* - y$ between A and G; thereore, the steps correspond to one transfer unit. This stepwise procelure is continued to the terminals of the tower, giving the number of ransfer units in the tower. Values of H.T.U. are multiplied by the umber of transfer units required to determine the height of packing lesired.

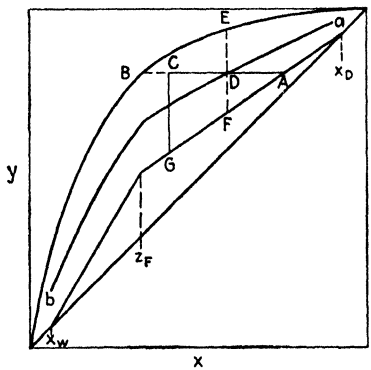


FIG. 7-32. Diagram for H.T.U.

Because the transfer unit is defined on a differential countercurrent basis, it is usually assumed to be more correct for the design of packed towers than the stepwise countercurrent procedure of the theoretical plate. This is probably true, but there is a serious question whether the transfer unit is on a sound theoretical basis. Most distillation operations are of a degree that requires a number of theoretical plates, and for such cases it is doubtful whether at the present stage of development the transfer-unit concept has any advantage over the theoretical-plate basis for the design of packed towers. The latter is easier to employ.

In practice the packed tower has been losing out relative to the bubble tower. The development of corrosion-resistant alloys and of bubble-plate columns made of ceramic, glass, and plastic has made it possible to rectify corrosive mixtures in such units. The development of efficient laboratory bubble-plate columns as small as 1 in. in diameter has made it possible to carry out such distillation in the laboratory, and experience has indicated that these columns give data that are

much more suitable for extrapolation in the design of large-scale bubble-plate towers than those obtained in packed towers. These small columns give plate efficiencies that are comparable to those of large towers, and their effectiveness is not a major function of the wetting characteristics of the liquid as it is in a packed tower. The one major remaining advantage of the packed tower is low pressure drop; even in this case, new types of columns are being developed which give definite and controlled contact between the liquid and the vapor and which have pressure drop as low as in packed towers. If large-sized packed towers can be developed to give efficiencies commensurate with those obtained in small laboratory packed towers and if their design can be made reliable and reproducible such that their performance can be predicted with reasonable accuracy, they could become a major factor in vapor-liquid interchange processes.

Nomenclature

α = relative volatility
C = specific heat
D = mols of distillate withdrawn as overhead products per unit of time
F = mols of mixture fed to column per unit of time
H = enthalpy, or heat content of vapor
h = enthalpy, or heat content of liquid
H.E.T.P. = height equivalent to a theoretical plate
H.T.U. = height of a transfer unit
m = number of plate under consideration, counting up from still
n = number of plate under consideration, counting up from feed plate
O = total mols of overflow from one plate to next, per unit of time
P = vapor pressure
p = $(O_{f+1} - O_f)/F$
Q = heat added or removed
$T,t,$ = temperature
W = mols of residue per unit of time
x = mol fraction of more volatile component in liquid
x' = pseudo mol fraction in liquid
y = mol fraction of more volatile component in vapor
y' = pseudo mol fraction in vapor
z = mol fraction in feed mixture
γ = activity coefficient

Subscripts

n refers to nth plate; *i.e.*, O_n and V_n refer to mols of liquid and vapor leaving nth plate, respectively
m refers to mth plate
f refers to feed plate; *i.e.*, x_f is mol fraction of more volatile component in overflow from feed plate
F refers to feed; *i.e.*, x_F is mol fraction of more volatile component in feed mixture

D refers to distillate
R refers to reflux
W refers to bottoms
L refers to liquid
V refers to vapor
t refers to top plate

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CHAPTER 8

SPECIAL BINARY MIXTURES

This chapter covers special fractional distillation systems for binary mixtures. The examples illustrate the flexibility of the fractional distillation process and the broad applicability of the design methods. The first section will consider operating conditions that lead to unusual operating lines, and the last section will consider the separation of binary azeotropic mixtures.

Special Operating Lines. The operating lines so far considered intersected the $y = x$ line at values between $x = 0$ and $x = 1.0$ and, with the exception of the bottom portion of the lower operating line for the steam distillation case, they were between the equilibrium curve and the $y = x$ diagonal. Although most operating lines lie in this region, it is not necessary that they do so. The operating line is a combination of the over-all material balance and a component balance. Consider the case of the section above the feed plate:

By over-all balance,

$$V_n = O_{n+1} + R$$

By component balance,

$$V_n y_n = O_{n+1} x_{n+1} + R x_R$$

where R is the net molal withdrawal from the section other than in V_n and O_{n+1}, and Rx_R is the net molal withdrawal of the component from the section other than in V_n and O_{n+1}.

In the cases considered in Chap. 7, it was assumed that there was a net withdrawal at the top of the column equal to D, but it may be that material is also added to the section such that R is positive, zero, or negative. If R is positive, O_{n+1}/V_n will be less than 1.0; if $R = 0$, O_{n+1}/V_n will equal 1.0; if R is negative, O_{n+1}/V_n will be greater than 1.0. In these cases x_R may be positive or negative. The following example will illustrate this case.

Leaky Condenser Example. An old ethyl alcohol distillation column has been tested, and it is concluded that there is a leak into the condensate in the condenser that amounts to 5 mols of water per 100 mols of feed. The tower is operating on a feed containing 3.5 mol per cent ethanol and 96.5 mol per cent water and produces

a distillate containing 70 mol per cent ethanol and a bottoms containing 0.001 mol per cent ethanol. The feed enters preheated such that $V_n = V_m$. Make the usual simplifying assumptions.

Solution. As a basis take 100 mols of feed. Then, by over-all material balance,

$$D + W = 105$$

By alcohol balance,

$$0.7D + 0.00001W = 3.5$$
$$D = 5.0$$
$$W = 100$$

For the upper section,

$$5 + V_n = O_{n+1} + D$$
$$V_n = O_{n+1}$$
$$R = 0$$

The alcohol-enriching line is

$$V_n y_n = O_{n+1}x_{n+1} + Dx_D$$
$$= O_{n+1}x_{n+1} + 3.5$$

Since $V_n = O_{n+1}$, this line intersects the $y = x$ line at $x = \infty$ and is parallel to the diagonal. With $V_n = V_m$, this line will intersect the lower operating line at the usual value, *i.e.*, at $x = 0.035$.

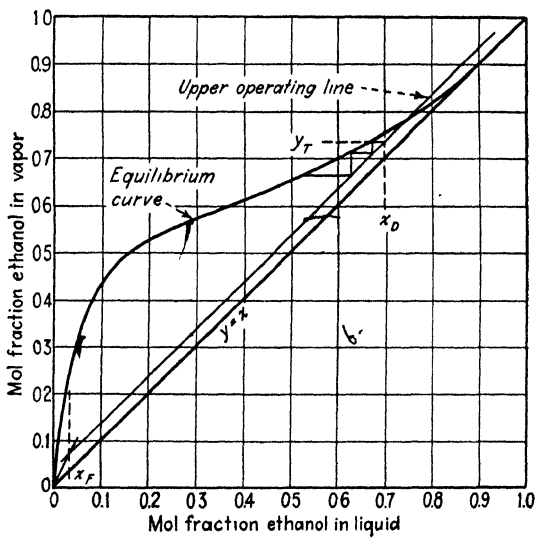


FIG. 8-1.

A possible position for the operating line is shown in Fig. 8-1. (The exact position is not known since the reflux ratio was not specified.) While the line extends outside of the diagram, it is utilized only in the region below the y,x equilibrium curve. The composition of the top vapor and the liquid reflux corresponds to a point on the operating line, and the step for the top plate should terminate at this point.

For the case just considered, $R = D$ − leak. If the leak is less than D, R would be positive, O/V would be less than 1.0, and the intersection with $y = x$ would be positive and greater than 0.7. As the size of the leak increased relative to D, O/V would become nearer to 1.0 and the intersection would increase and tend to infinity. If the leak became greater than D, R would become negative, O/V would be greater than 1.0, and the intersection with the $y = x$ line would be negative.

It appears that the leak makes the slope of the upper operating line more desirable (*i.e.*, nearer to 1.0), but a little consideration will show that, when this line keeps the same intersection with the lower operating line, the smaller the value of $(O/V)_n$, the fewer the plates required. Common sense also indicates that the leak is undesirable.

In this example the operating lines were above the $y = x$ diagonal but had intersections with the diagonal outside of the usual diagram. The following example illustrates a case for which the operating lines are also below the diagonal.

Isopropyl Alcohol Stripping Example. In the manufacture of isopropyl alcohol, propylene is dissolved in sulfuric acid to give an extract of mono-isopropyl sulfate. To avoid excessive decomposition this extract must be diluted until the ratio

$$\frac{\text{Lb. } H_2SO_4}{\text{Lb. } H_2O + \text{lb. } H_2SO_4} = 0.45$$

before the alcohol can be distilled. In this ratio the H_2SO_4 is the total acid, whether free or combined with propylene, and H_2O is the total water, free or combined with propylene as isopropyl alcohol. A typical extract containing H_2SO_4, propylene, and H_2O in equimolal proportions is first diluted with water, and is then stripped of isopropyl alcohol. Usually live steam is used in the stripping, and this results in dilute alcohol and very dilute bottom acid which must be reconcentrated The stripped acid contains negligible alcohol.

It has been proposed to modify this operation by diluting the extract in the stripping tower with the overflow and thereby produce more concentrated alcohol and at the time obtain 45 per cent H_2SO_4 as bottoms. To avoid polymerization during dilution, it is estimated that the overflow with which the extract is mixed must not contain over 10 mol per cent isopropyl alcohol. Isopropyl alcohol and water form an azeotrope containing 68 mol per cent alcohol. The accompanying diagram (Fig. 8-2) shows the flow sheet for the proposed modification to produce a 66 mol per cent alcohol product. The tower will operate with live steam and a total condenser. It is assumed that the feed will enter such that $V_n = V_m$, and the usual simplifying assumptions will be made. It is assumed that sulfuric acid is nonvolatile, and the calculations will be made on a "sulfuric acid-free" basis. It is also assumed that all of the propylene is in the solution as isopropyl alcohol and that the vapor-liquid equilibria for the isopropyl alcohol–water system will be used.

Solution. Basis: 1 mol of propylene in feed (also 1 mol each of H_2O and H_2SO_4).

By a sulfuric acid balance the water in the bottom equals

$$\frac{98}{18}\left(\frac{0.55}{0.45}\right) = 6.65 \text{ mols}$$

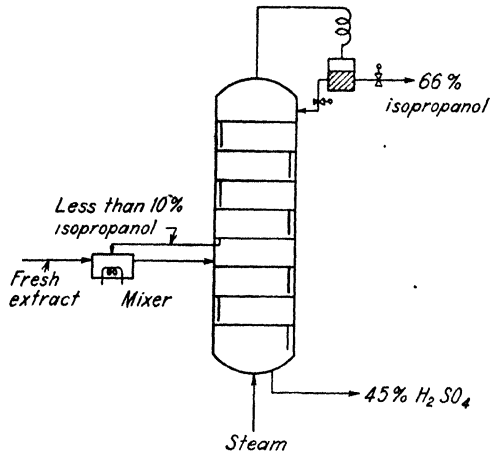


FIG. 8-2. Isopropyl alcohol distillation unit.

Uncombined water in distillate $= \dfrac{0.34}{0.66} = 0.515$ mol

Combined water as isopropyl alcohol in distillate = 1.0 mol

Water with feed = 1.0 mol

Mols of water added as steam $S = 6.65 + 1.515 - 1.0 = 7.165$ mols.

Operating lines:

By an alcohol balance,

$$V_n y_a = O_{n+1} x_a + D x_D = O_{n+1} x_a + 1.0$$

$$D = \frac{1}{0.66} = 1.515$$

$$V_n = V_m = S = 7.165$$

$O_m = 6.65$ (sulfuric acid-free basis)

$O_n = 5.65$

Operating line above feed plate,

$$y_a = \frac{5.65}{7.165} x_a + \frac{1.0}{7.165} = 0.789 x_a + 0.139$$

This line crosses the $y = x$ line at $0.66 = x_D$.

Operating line below feed plate,

$$6.65 x_a = 7.165 y_a + W x_W = 7.165 y_a$$

$$y_a = 0.928 x_a$$

The two operating lines intersect at $y = 0.928$, $x = 1.0$. These lines are shown in Fig. 8-3. The equilibrium curve shown is for water-isopropanol and should be suitable above the feed plate; below the feed plate, with the sulfuric acid present the separation should be easier than shown. The steps on the diagram would start at $x_D' = 0.66$ and continue down the upper operating line until the mol fraction of alcohol in the liquid is less than 0.10; then the shift to the lower operating line would

be made and the stepwise procedure carried on to the bottom. In the diagram as drawn, the first plate with an overflow containing less than 10 mol per cent alcohol has a concentration of 5 per cent alcohol. This would be mixed with the fresh feed, and the mixture would be the liquid to the feed plate. As drawn in Fig. 8-3, the liquid leaving the feed plate contains approximately 1 mol per cent alcohol, and from this concentration on down, the steps would be made between the equilibrium curve and the lower operating line which is below the $y = x$ line.

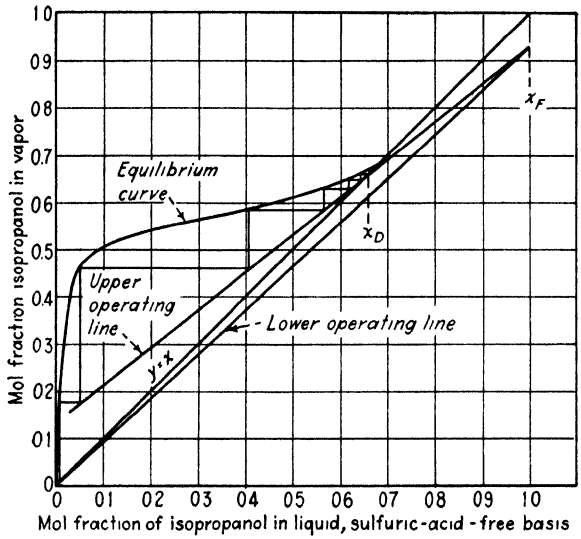


FIG. 8-3. y,x diagram for isopropyl alcohol example.

In this case the diagram is unusual in two respects: (1) The distillate has a lower ratio of alcohol to water than the feed and (2), the feed-plate composition is purposely fixed at a value different from that corresponding to the fewest plates.

Separation of Binary Azeotropic Mixtures. A large number of two-component systems form azeotropic mixtures, and it is frequently necessary to separate them into their components. Regular fractional distillation will not separate such mixtures into the components in high purity, but by suitable modifications it is frequently possible to obtain the desired separation. At the azeotropic composition the relative volatility is unity, and rectification is not possible. The methods employed for separating such systems involve using either (1) distillation plus other separation processes to get past the azeotropic composition or (2) a modification of the relative volatility.

1. *Distillation plus Other Separation Processes.* The techniques most commonly employed for moving by the azeotropic composition are decantation, extraction, crystallization, or absorption. A compo-

sition near the azeotrope can be produced by distillation and then separated into two fractions having compositions on each side of the azeotrope by one of these techniques. These two fractions can be fractionally distilled separately to give the essentially pure components and fractions of approximately azeotropic composition which can be recycled through the process.

The method of utilizing decantation to aid in the separation of the azeotrope is illustrated by the system phenol-water which at atmospheric pressure forms an azeotrope containing 1.92 mol per cent

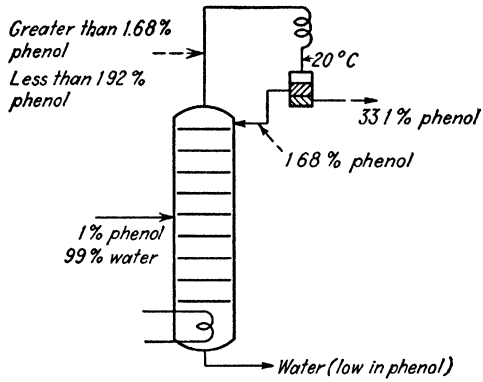


FIG. 8-4. Fractionating system to concentrate dilute aqueous phenol.

phenol. If a mixture of phenol and water is subjected to a continuous fractionation, the overhead will tend to the azeotropic composition and the bottoms will approach either phenol or water depending on the composition of the feed. Thus, if a feed containing 1 mol per cent phenol is given such a distillation, an overhead product approaching the azeotropic composition can be made with water, low in phenol, as bottoms. In this case, the azeotrope can be separated because phenol and water are only partly miscible. For example, at 20°C. the two saturated liquid phases contain 1.68 and 33.1 mol per cent phenol, respectively. Thus if the fractionation gives an overhead vapor containing more than 1.68 mol per cent phenol, it will break into two liquid layers on cooling to 20°C., the water layer containing 1.68 mol per cent phenol can be used as reflux, and the phenol layer can be withdrawn as product. This system of fractionation, cooling, and decantation is shown in Fig. 8-4. Such a system will separate dilute solutions of phenol into water and 33 per cent phenol. The condensate can be cooled to temperatures other than 20°C., but for the system to be effective two liquid phases must be formed, one of which must

have a composition less than the azeotrope and the other a composition greater. The system of Fig. 8-4 does not give complete separation of the two components, but by a similar arrangement concentrated solutions of phenol can be fractionated to give an overhead condensate that will separate into two liquid phases. Figure 8-5 shows a schematic flow sheet for a feed containing 50 mol per cent phenol. The column operates to produce an overhead vapor containing between 1.92 and 33.1 per cent phenol and, on cooling to 20°C., the condensate would give the same liquid compositions as obtained in Fig. 8-4. In this case the water layer would be the product and the phenol layer would be employed as reflux.

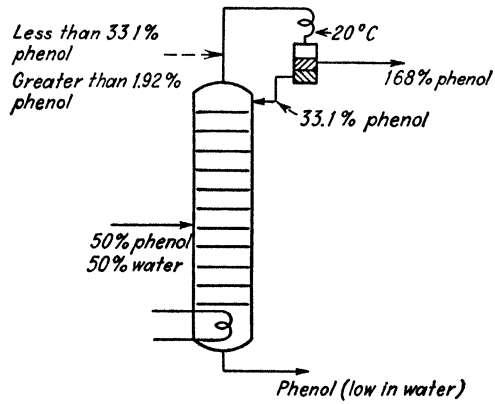


FIG. 8-5. Fractionating system to dehydrate aqueous phenol.

The systems shown in Figs. 8-4 and 8-5 can be combined to give complete separation. The arrangement of Fig. 8-6 shows a two-tower system for a dilute phenol feed. Both towers give the same condensate compositions, and the overhead vapors are fed to the same condenser and decanter. Tower 1 operates in the same manner as the single tower of Fig. 8-4 producing an overhead product containing 33.1 per cent phenol and a bottoms low in phenol. Tower 2 is only a stripping section because the reflux stream is its only feed. If the fresh feed contains less than 1.68 per cent phenol, it should be introduced into tower 1; from 1.68 to 33.1 per cent phenol, it should be added to the decantation system; if the feed contains more than 33.1 per cent phenol, it should be introduced into tower 2. The arrangement can give a high degree of separation between phenol and water. The quantitative calculations for such a system are illustrated by the following example.

Phenol-Water Rectification Example. A plant using phenol as a solvent desires to rectify a mixture containing 1.0 mol per cent phenol in water. As the bottoms are to be discarded in a nearby river, they must not exceed 0.001 mol per cent phenol. A system similar to that shown in Fig. 8-6 will be employed. The overhead vapors from the bubble-plate columns to be used are condensed and cooled to 20°C. Under these conditions the condensate separates into two saturated layers. The water layer is reheated to its boiling point and refluxed to column 1, and the

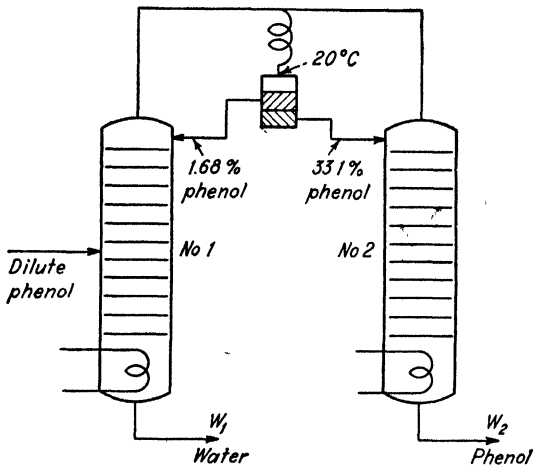


FIG. 8-6. Two-tower fractionating system to separate aqueous phenol.

phenol layer is reheated and sent to stripping tower 2, to recover a 99.99 per cent phenol as bottoms. At 20°C. the saturated water layer contains 1.68 mol per cent phenol, and the saturated phenol layer contains 33.1 mol per cent phenol. Assuming that $V_n = V_m$ and making the usual simplifying assumptions, determine:

1. The minimum mols of vapor per 100 mols of feed for each tower.
2. The number of theoretical plates required, using a vapor rate ⅔ times the minimum rate.
3. The minimum number of plates at total reflux. (Only the water layer is refluxed to the water tower.)

Solution of Part 1. Basis: 100 mols of fresh feed. Referring to Fig. 8-6,

$$1 = 0.00001W_1 + 0.9999W_2$$
$$W_1 + W_2 = 100; \qquad W_2 = 1.0; \qquad W_1 = 99.0$$

Operating lines for tower 1:

Above the feed plate, a balance between plates n and $n + 1$ and around tower 2,

$$V_n = O_{n+1} + W_2$$
$$V_n y_n = O_{n+1}x_{n+1} + 0.9999W_2$$

This line intersects the $y = x$ line at $x = 0.9999$.

Below the feed plate,

$$O_{m+1} = V_m + W_1$$
$$V_m y_m = O_{m+1} x_{m+1} - 0.00001 W_1$$

which intersects the $y = x$ diagonal at $x = 0.00001$.

VAPOR-LIQUID EQUILIBRIUM DATA FOR PHENOL-WATER AT 1 ATM. (Ref. 5)

x	y	x	y
0	0	0.10	0.029
0.001	0.002	0.20	0.032
0.002	0.004	0.30	0.038
0.004	0.0072	0.40	0.048
0.006	0.0098	0.50	0.065
0.008	0.012	0.60	0.090
0.010	0.0138	0.70	0.150
0.015	0.0172	0.80	0.270
0.017	0.0182	0.85	0.370
0.018	0.0186	0.90	0.55
0.019	0.0191	0.95	0.77
0.020	0.0195	1.00	1.00

Minimum vapor rate for tower 1:

The minimum vapor corresponds to the minimum reflux ratio, and there are two possibilities in this case: (1) the pinched-in region could occur at the feed plate, or (2) it could occur at the top of the tower.

If the feed plate is the limiting condition, then

$$0.0138(V_n)_{\min} = 0.01 O_{n+1} + 0.9999 W_2$$
$$= 0.01 V_n + 0.9899 W_2$$
$$(V_n)_{\min} = \frac{0.9899 W_2}{0.0038} = 260 W_2 = 260$$

(0.0138 is the vapor in equilibrium with a liquid of 0.01).

If the top plate is the limiting condition, then the concentration on this plate must be equal to the reflux concentration, and the top vapor will be in equilibrium with this composition, thus,

$$0.0181(V_n)_{\min} = 0.0168 O_{n+1} + 0.9999 W_2$$
$$= 0.0168 V_n + 0.9831 W_2$$
$$(V_n)_{\min} = \frac{0.9831 W_2}{0.0013} = 756 W_2 = 755$$

Since the top condition requires more vapor, it is the limiting condition and $(V_n)_{\min} = 755$.

Minimum vapor rate for tower 2:

Tower 2 will pinch at top, the liquid on the top plate will have a composition of 0.331, and the equilibrium vapor composition will equal 0.0403.

$$0.0403(V)_{\min} = 0.3310 - 0.9999W_2$$
$$= 0.331V - 0.6689W_2$$
$$V_{\min} = \frac{0.6689W_2}{0.2907} = 2.3W_2 = 2.3$$

Solution of Part 2

Tower 1:

$$(V_n)_{\text{act}} = \tfrac{4}{3}(755) = 1{,}007; \qquad O_{n+1} = 1{,}006$$
$$V_m = 1{,}007; \qquad O_{m+1} = 1{,}106$$

Above the feed plate,

$$1{,}007y_n = 1{,}006x_{n+1} + 0.9999$$
$$0.9999 - y_n = 0.999(0.9999 - x_{n+1})$$

Below the feed plate,

$$1{,}007y_m = 1{,}106x_{m+1} - 0.00001(99)$$
$$y_m - 0.00001 = 1.098(x_{m+1} - 0.00001)$$

Tower 2:

$$V_{\text{act}} = \tfrac{4}{3}(2.3) = 3.06$$

Operating line for phenol,

$$3.06y_m = 4.06x_{m+1} - 0.9999$$

Operating line for water,

$$3.06y_m = 4.06x_{m+1} - 0.0001$$

These operating lines are plotted in Figs. 8-7 and 8-8. Logarithmic plotting is used to facilitate the calculations at the low concentrations. In the case of tower 1, the operating lines for phenol are used; for tower 2, the operating line for water is used.

According to the diagram, tower 1 requires a still and 15 theoretical plates. Since the bottoms of this tower are essentially water, live steam could be used, but if the same phenol recovery (99.99 per cent) were obtained, a total of 20 theoretical plates would be required. The large increase in the number of plates is due to dilution by the large amount of vapor used. If the same bottoms composition had been maintained instead of the same recovery, 16 theoretical plates would be required and the recovery would be 98.9 per cent.

The steps for the region $x = 0.00001$ to 0.001 of this tower could be calculated by Eq. (7-77) since the equilibrium curve is $y = 2x$.

In the case of tower 2 using mol fractions of water instead of phenol, the plates are stepped up the operating line from $x_W = 0.0001$ to $x_F = 0.669$. In Fig. 8-8 a still and six theoretical plates would give a reflux composition of 0.54, and seven theoretical plates give 0.71. Thus a still and seven theoretical plates would give a slightly better separation than desired.

Solution of Part 3. At total reflux, the plates for tower 1 correspond to the steps between the equilibrium curve and the $y = x$ line from $x_W = 0.00001$ to the reflux composition, $x_R = 0.0168$. From the diagram it is found that a still and between 11 and 12 theoretical plates are needed.

For tower 2, the steps at total reflux go from $x = 0.0001$ to 0.669. In this case, a still and five theoretical plates are required.

It might be thought that the effectiveness of the fractionation would be improved by refluxing to tower 1 not only the 1.68 per cent phenol layer but also a portion of the 33.1 per cent layer. This would result in an increased overhead vapor composition but would require additional plates for the same vapor rate. Thus for the same separation and vapor rate, more plates are required, indicating that only

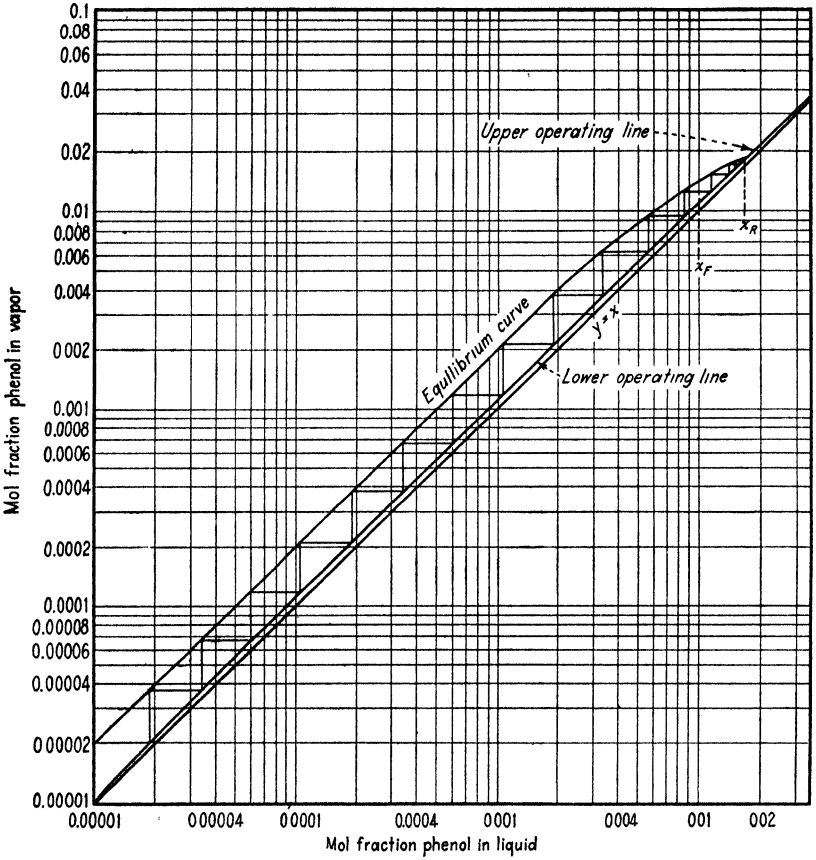


FIG. 8-7. Diagram for tower 1.

the 1.68 per cent layer should be refluxed. For compositions between 1.68 and 33.1 per cent phenol, decantation is a more efficient method of separation than distillation.

This two-tower system can be used to separate a number of binary systems, such as isobutanol-water, aniline-water, or benzene-water. In the last system the solubility of water in benzene is so low that a single-tower system is usually used for the dehydration of benzene,

and the water layer is discarded without treating it in a stripping tower.

Some partially miscible mixtures cannot be separated directly by this method. For example, methyl ethyl ketone and water are partially miscible and form an azeotrope at atmospheric pressure, but

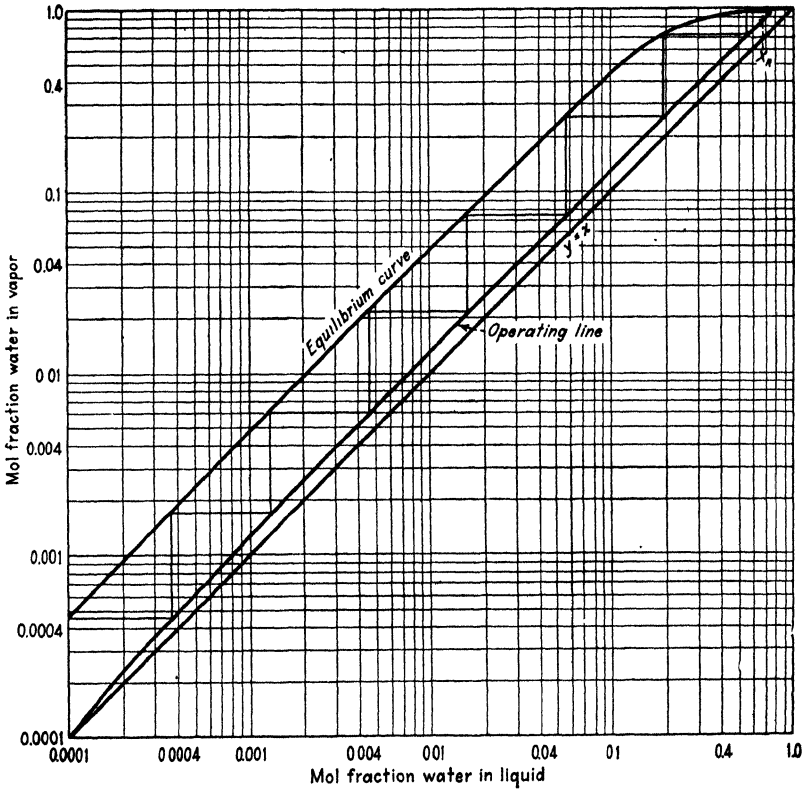


FIG. 8-8. Diagram for tower 2.

the compositions of the two liquid phases do not bracket the constant-boiling mixture composition. Cooling and decantation will not take the composition across the azeotrope. In this case, if salt is added to the decantation system, the solubility limits can be made to overlap the azeotrope and the fractionating-decantation system will make the separation.

2. *Modification of Relative Volatility.* The two most common methods of modifying the relative volatility of azeotropic mixtures involve (1) changing the total pressure and (2) adding other components to

the mixture. The effect of pressure on the azeotropic composition will be considered in the following section and the second method will be analyzed in Chap. 10.

The effect of pressure on the azeotropic composition is the result of (1) the change in the ratio of the vapor pressures and (2) the change in the activity coefficients. At a given composition the change in the activity coefficients is usually small in comparison to the effect of the vapor-pressure ratio. Thus, the qualitative effect of pressure on the azeotropic composition can be predicted from the vapor-pressure ratio. In the case of ethanol and water mixtures at atmospheric pressure, ethanol is the more volatile component for mixtures containing less than 89.5 mol per cent alcohol, and the less volatile component for more concentrated solutions. The ratio of the vapor pressure of ethanol to water decreases with increasing temperature and, assuming that the activity coefficients do not change, the azeotropic composition should decrease in alcohol content as the total pressure increases. This conclusion is in agreement with the experimental data.

A more quantitative prediction can be obtained by combining the Margules equation for the activity coefficients with equations for the vapor pressures.

At the azeotropic composition,

$$\gamma = \frac{\pi y}{Px} = \frac{\pi}{P}$$

and Eq. (3-34*a*) becomes

$$T^{0.25}(\ln \pi - \ln P_1) = x_2^2(b' + c'x_2) \tag{8-1}$$

$$T^{0.25}(\ln \pi - \ln P_2) = x_1^2[b' + c'(x_2 + 0.5)] \tag{8-2}$$

The variation of the azeotrope composition with temperature can be obtained by subtracting Eq. (8-1) from Eq. (8-2).

$$T^{0.25} \ln \frac{P_1}{P_2} = b'(2x_1 - 1) - c'(1 - 3x_1 + 1.5x_1^2) \tag{8-3}$$

If c' and b' have been determined for one temperature, the value of x_1 can be calculated as a function of the ratio of the vapor pressures. The total pressure can then be calculated by either Eq. (8-1) or (8-2).

Equations (8-1) and (8-2) can be combined with empirical equations for the vapor pressure as a function of the temperature to give a relation between the total pressure and the azeotropic composition, but the procedure outlined in the preceding paragraph will be found simpler in general.

Equation (8-3) was applied to the system ethanol-water, using T as degree Kelvin, $b' = 0.605$, and $c' = 6.01$. These values were obtained by fitting Eq. (8-1) and (8-2) to the azeotrope data for atmospheric pressure. The calculated results are compared with the experimental data (Ref. 2) in Fig. 8-9. Some of the difference shown in this figure is due to the fact that the constants used in the equation were based on

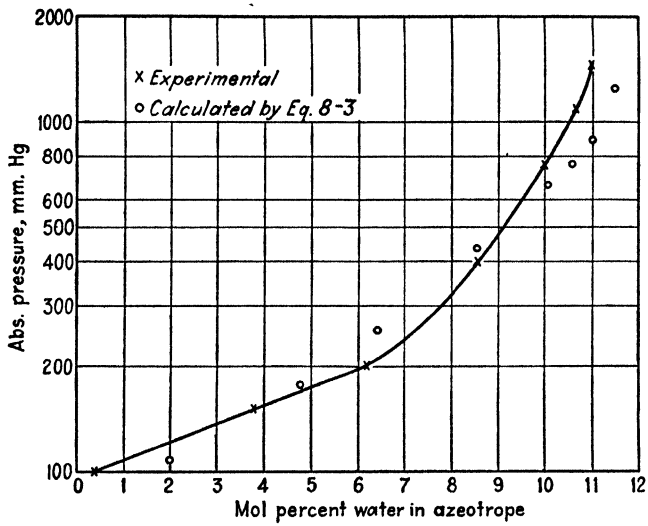


FIG. 8-9. Effect of pressure on azeotrope composition for system, ethanol-water.

an azeotropic composition at atmospheric pressure of 89.4 mol per cent alcohol (Ref. 4), while the experimental data plotted give 90 per cent alcohol.

Example of Fractionation at Two Pressures to Separate Azeotrope. Lewis (Ref. 3) suggested rectification at two different pressures to produce absolute alcohol from aqueous solutions. As an example of the use of this system, consider the production of 99.9 mol per cent alcohol from an aqueous feed containing 30 mol per cent alcohol. The azeotrope in this case increases in alcohol content as the pressure is reduced. Thus, by operating at reduced pressure, an overhead product can be produced which contains a higher percentage of alcohol than corresponds to the azeotrope at some higher pressure. By redistilling this overhead product at a higher pressure, it can be separated into a high-concentration alcohol as bottoms and an overhead which can be recycled to the low-pressure tower. Figure 8-10 shows such an arrangement. The 30 mol per cent feed is introduced into the low-pressure tower which operates at 95 mm. Hg abs. and produces an overhead containing 95 mol per cent alcohol and a bottoms containing 0.0001 per cent alcohol. The 95 per cent overhead product is pumped into the higher pressure tower which will operate at atmospheric pressure and produce an overhead containing 92.5

per cent alcohol and a bottoms containing 99.9 per cent alcohol. The overhead in this column will be returned to the low-pressure column for further rectification. This stream may be returned either as vapor or as liquid; however, the condensing temperature of the atmospheric column is sufficiently high that it will serve as the heat supply for the low-pressure column, and in such a case heat economy will be obtained by totally condensing the overhead and recycling the 92.5 per cent stream as a liquid. In order to simplify the calculations, it is assumed that all three feed

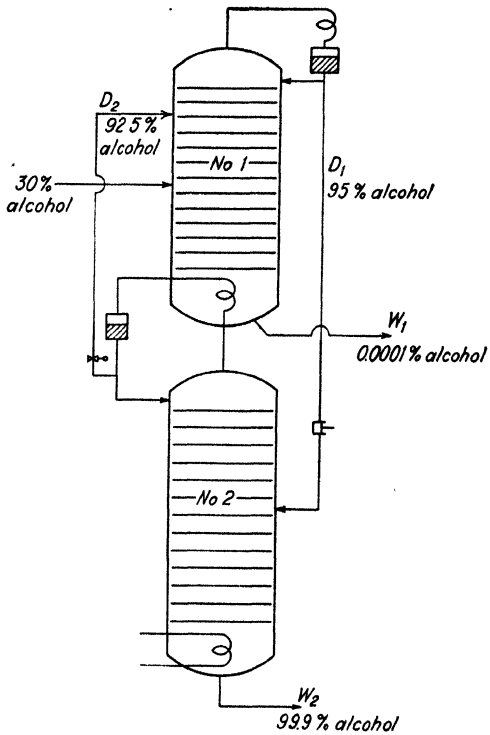


FIG. 8-10. Production of absolute alcohol.

streams enter such that there is no change in feed rate across the feed plates. The 95 per cent feed will be slightly below the temperature necessary for this condition, but it could be preheated by countercurrent heat exchange with the steam condensate from the reboiler of the atmospheric tower. The 92.5 per cent stream will be slightly superheated but will closely approximate the assumption made. The usual simplifying assumptions are made, and it is assumed that the vapor rates in the two towers are equal. The vapor rate will be calculated for each tower at a reflux ratio, O/D, equal to 1.5 times the minimum O/D. The larger vapor rate for the two towers will be employed.

The equilibrium data of Lewis and Carey (Ref. 4) will be used for the atmospheric conditions and the data of Beebee *et al* (Ref. 1) for 95 mm. Hg. The fractionation will be most difficult in the region containing more than 80 mol per cent

alcohol, and the relative volatilities for this range are shown in Fig. 8-11. The atmospheric pressure data were extrapolated past the azeotrope by the use of the Margules equation. The data for 95 mm. Hg were drawn to agree with the azeotrope composition reported in the literature (Ref. 2).

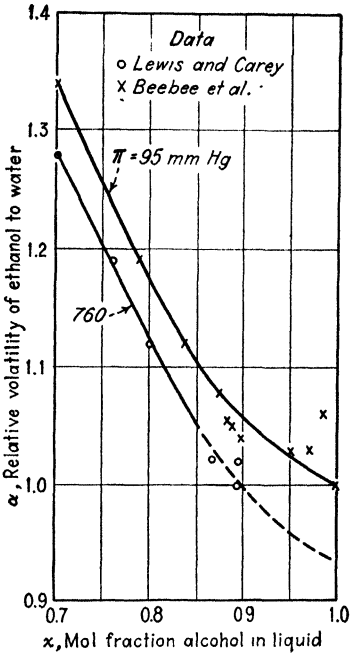


FIG. 8-11. Equilibrium data for system, ethanol-water.

Solution. Basis: 100 mols of original feed. (See Fig. 8-10 for nomenclature.)
By over-all alcohol balances,

$$30 = 0.000001W_1 + 0.999W_2$$

By total balance,

$$100 = W_1 + W_2$$
$$W_2 = 30, \qquad W_1 = 70$$

For tower 2:
By alcohol balance,

$$0.95D_1 = 0.999W_2 + 0.925D_2$$

By total balance,

$$D_1 = W_2 + D_2$$
$$= 30 + D_2$$

and

$$D_2 = 60, \qquad D_1 = 90$$

Minimum reflux ratios:

Tower 2: $V_n = V_m$ and, from a study of the equilibrium data, it is apparent that the pinched-in condition will occur at the feed plate. At $x = 0.95$, the equilibrium

vapor is 0.948 and by Eq. (7-10),

$$\left(\frac{O}{D}\right)_{\min} = \frac{0.925 - 0.948}{0.948 - 0.95} = 11.5$$
$$V_n = O + D = 12.5D = 750 \text{ mols}$$

Tower 1: The minimum reflux ratio in this case could be limited by either feed-plate condition or by a tangent contact between the equilibrium curve and the operating line. All three possibilities will be checked:

1. *Pinch at* 0.925 *feed.*

$$x = 0.925, \; y \text{ in equilibrium} = 0.9277$$
$$\left(\frac{O}{D}\right)_{\min} = \frac{0.95 - 0.9277}{0.9277 - 0.925} = 8.25$$
$$V_T = 9.25(90) = 832 \text{ mols}$$

2. *Pinch at* 0.30 *feed.*

$$x = 0.30, \; y \text{ in equilibrium} = 0.5875$$

Using the operating line below the feed plate,

$$\left(\frac{O}{V}\right)_m = \frac{0.5875 - 0.000001}{0.3 - 0.000001}$$
$$= 1.96$$
$$O_m = V_m + 70$$
$$V_m = 72.9 \text{ mols}$$

This is much less vapor than required for the feed at $x = 0.925$, and the minimum reflux ratio will not be determined by a contact at $x = 0.3$.

3. *Tangency.* For this case, the 832 mols of vapor required for $x = 0.925$ will be used to determine whether the operating line between $x = 0.3$ and 0.925 is below the equilibrium curve. In this section the overflow will be

$$O = 832 - 90 + 60 = 802$$
$$V = 832$$

and the equation of the operating line will be

$$\frac{O}{V} = \frac{802}{832} = \frac{0.9277 - y}{0.925 - x}$$

y values were calculated for a series of values of x and are given in Table 8-1.

TABLE 8-1

x	$y_{\text{op line}}$	$y_{\text{equilibrium}}$
0.925	0 9277	0 9277
0.92	0.9229	0 923
0 91	0 9132	0.9139
0 90	0.9036	0 9048
0.88	0.8843	0 887
0.86	0.8651	0.87
0.84	0.8458	0.854
0.82	0 8265	0 838

In all cases the equilibrium curve is above the operating line except at $x = 0.925$. Thus the minimum reflux ratio for tower 1 is determined by a pinched-in condition at $x = 0.925$. The minimum vapor corresponding to this condition is 832 mols which is greater than the 750 mols calculated for tower 2. This larger value will be taken as the minimum vapor rate for the system. Thus,

$$\left(\frac{O}{D}\right)_{\text{min}} = \frac{742}{90} = 8.25$$

Tower 1:

$$\left(\frac{O}{D}\right)_{\text{act}} = 8.25(1.5) = 12.38$$
$$O_R = 1{,}115$$
$$V_T = 1{,}205$$

Operating lines:

Above $x = 0.925$.

$$y_n = \frac{1{,}115}{1{,}205}x_{n+1} + \frac{90}{1{,}205}(0.95)$$
$$= 0.9254x_{n+1} + 0.071$$

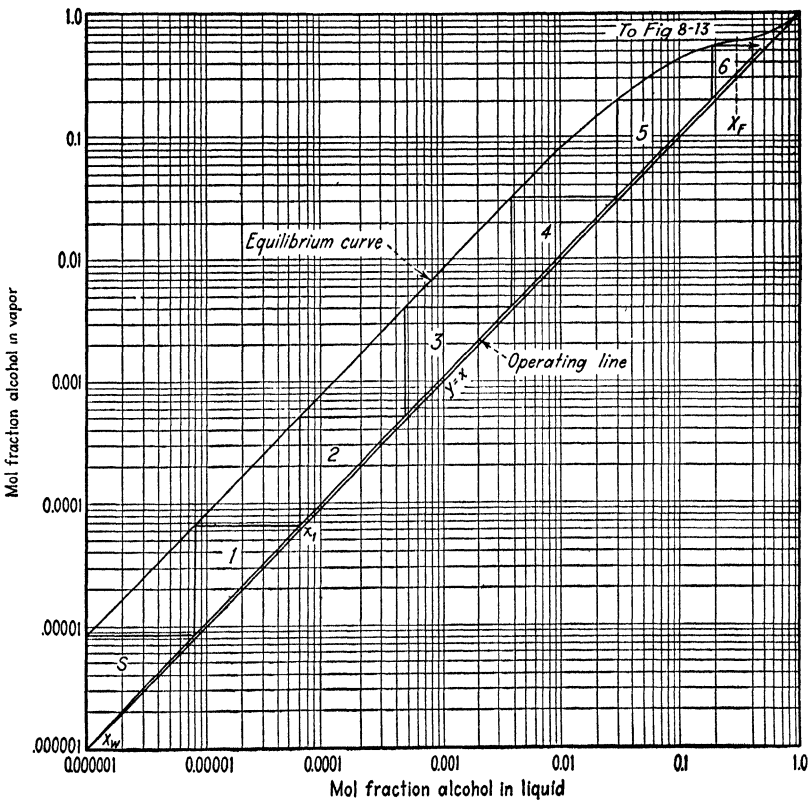


FIG. 8-12.

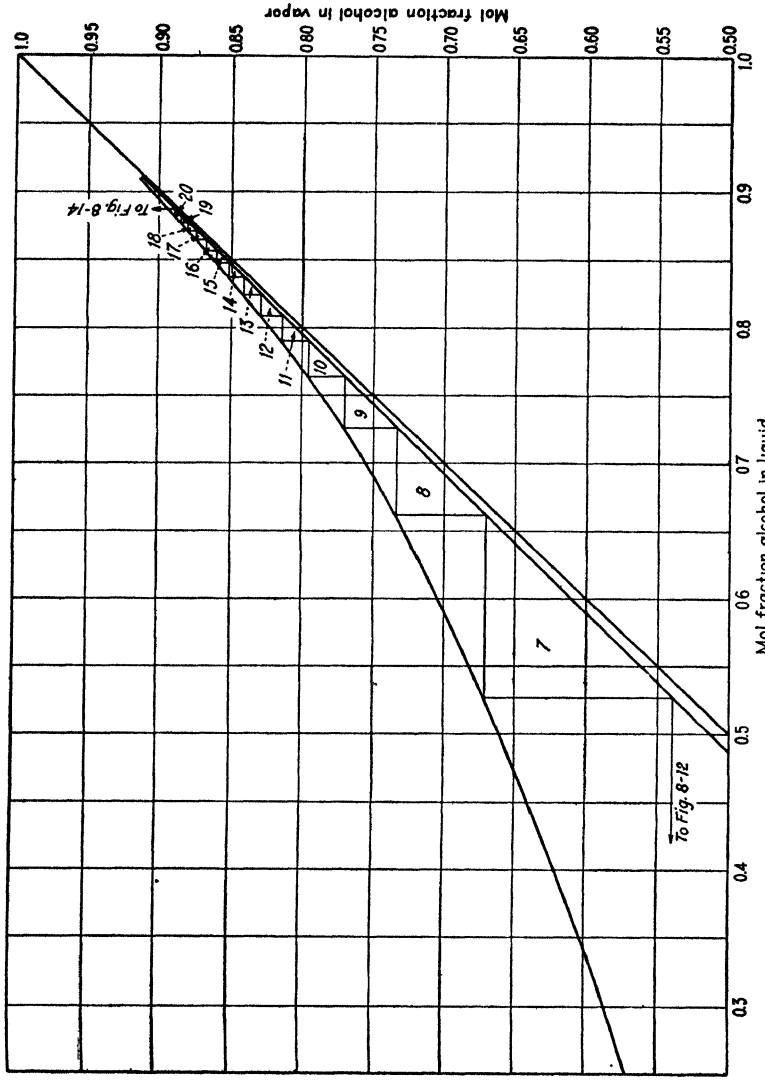

Mol fraction alcohol in vapor
1.0
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
Mol fraction alcohol in liquid
To Fig. 8-14
To Fig. 8-12
7
8
9
10
11
12
13
14
15
16
17
18
19
20

FIG. 8-13.

From $x = 0.3$ to $x = 0.925$,

$$y'_n = \frac{1{,}175}{1{,}205} x'_{n+1} + \frac{90(0.95) - 60(0.925)}{1{,}205}$$
$$= 0.9751x'_{n+1} + 0.0249$$

From $x = 0.000001$ to $x = 0.3$,

$$y_m = \frac{1{,}275}{1{,}205} x_{m+1} - \frac{70(0.000001)}{1{,}205}$$
$$= 1.0581x_{m+1} - 5.81 \times 10^{-8}$$

Tower 2:

$$V = 1{,}205$$
$$O_R = 1{,}145$$

Operating lines,

Above feed plate,

$$y_n = \frac{1{,}145}{1{,}205} x_{n+1} + \frac{60(0.925)}{1{,}205}$$
$$= 0.9502x_{n+1} + 0.0461$$

Below feed plate,

$$y_m = \frac{1{,}235}{1{,}205} x_{m+1} - \frac{30(0.999)}{1{,}205}$$
$$= 1.0249x_{m+1} - 0.0249$$

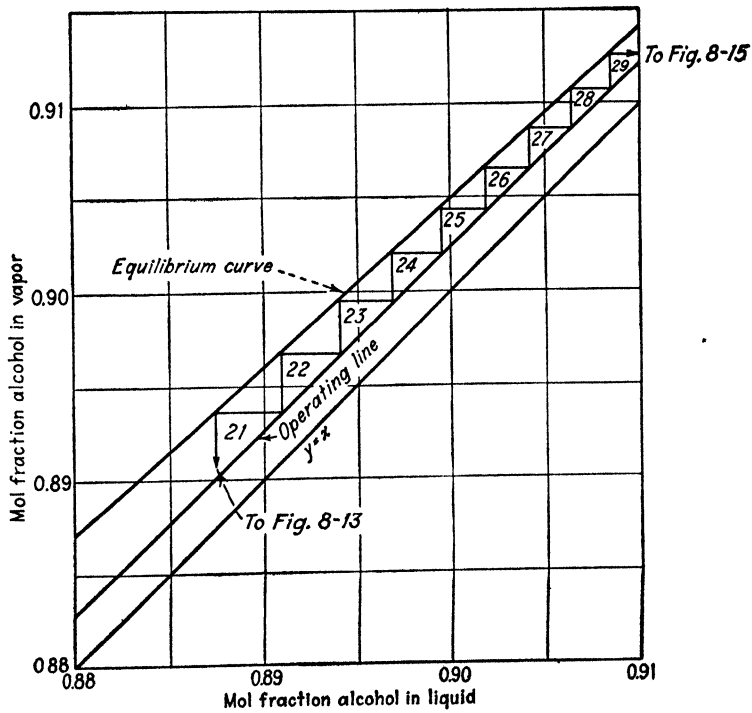


FIG. 8-14.

The various operating lines are plotted in Figs. 8-12 to 8-15. For the atmospheric pressure tower the plates in the bottom of the tower up to 1 per cent water were calculated by Eq. (7-77).

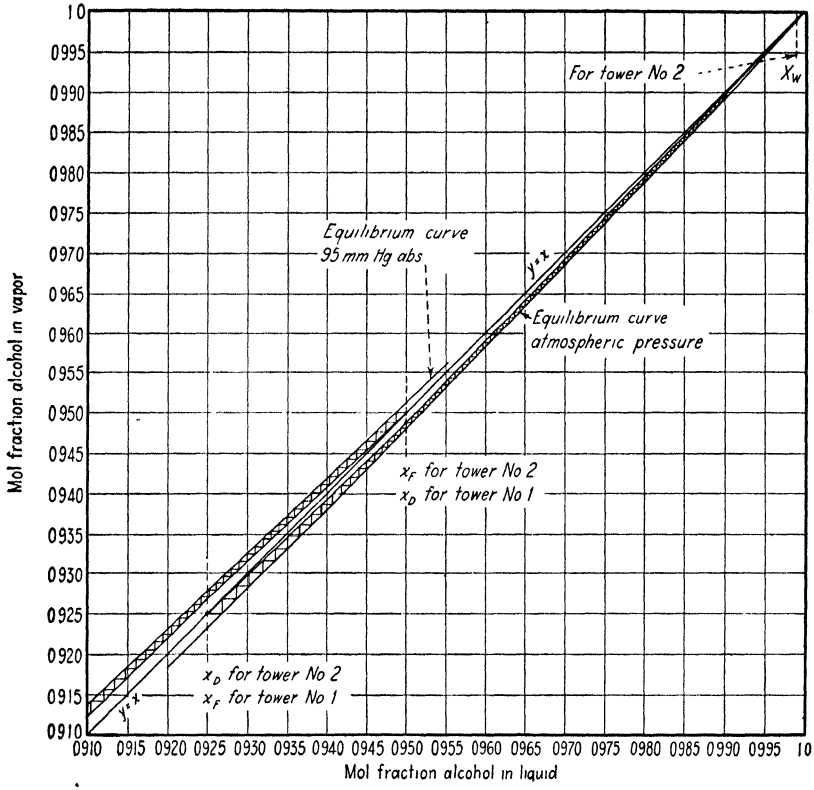


FIG. 8-15.

The low-pressure tower requires a still and 65 theoretical plates. The atmospheric pressure tower needs a still plus 120 theoretical plates. In view of the high heat consumption and the large number of plates required, other methods of producing absolute alcohol are more economical. Pressures above atmospheric would be advantageous for tower 2 and result in fewer theoretical plates.

Nomenclature

b', c' = constants in Margules equation
D = distillate rate, mols per unit time
O = overflow rate, mols per unit time
P = vapor pressure
R = net molal withdrawal rate from section other than V_n and O_{n+1}
S = steam rate, mols per unit time

T = temperature
V = vapor rate, mols per unit time
W = bottoms rate, mols per unit time
x = mol fraction in liquid
y = mol fraction in vapor
γ = activity coefficient
π = total pressure

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3. Lewis, U.S. Patent 1,676,700 (1928).
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CHAPTER 9

RECTIFICATION OF MULTICOMPONENT MIXTURES

Multicomponent mixtures are those containing more than two components in significant amounts. In commercial operations, they are encountered more generally than are binary mixtures, and as with binary mixtures, they can be treated in batch or continuous operations, in bubble-plate or packed towers. Since the continuous operation is much more amenable to mathematical analysis, owing to the steady conditions of concentration and operation, it will be considered first.

Fundamentally, the estimation of the number of theoretical plates involved for the continuous separation of a multicomponent mixture involves exactly the same principles as those given for binary mixtures. Thus, the operating-line equations for each component in a multicomponent mixture are identical in form with those given for binary mixtures (see page 119). The procedure is exactly the same; *i.e.*, starting with the composition of the liquid at any position in the tower, the vapor in equilibrium with this liquid is calculated; and then by applying the appropriate operating line for the section of the tower in question to each component, the liquid composition on the plate above is determined, and the operation repeated from plate to plate up the column. However, actually the estimation of the number of theoretical plates required for the separation of a complex mixture is more difficult than for a binary mixture. When considering binary mixtures, fixing the total pressure and one component in either the liquid or vapor immediately fixes the temperature and composition of the other phase; *i.e.*, at a given total pressure, a unique or definite relation between y and x allows the construction of the y,x curve. In the case of a multicomponent mixture of n components, in addition to the pressure, it is necessary to fix $(n - 1)$ concentrations before the system is completely defined. This means that for a given component in such a mixture the y,x curve is a function not only of the physical characteristics of the other components but also of their relative amounts. Therefore, instead of a single y,x curve for a given component, there are an infinite number of such curves depending on the relative amounts of

the other components present. This necessitates a large amount of equilibrium data for each component in the presence of varying proportions of the others, and, except in the special cases in which some generalized rule (such as Raoult's law) applies, these are not usually available, and it is very laborious to obtain them. One of the greatest uses of multicomponent rectification has been in the petroleum industry; for a large number of the hydrocarbon mixtures encountered in these rectifications, generalized rules have been developed which give multicomponent vapor-liquid equilibria with precision sufficient for design calculations. Such data are usually presented in the form $y = Kx$, where K is a function of the pressure, temperature, and component. The use of equilibrium data in such a form requires a trial-and-error calculation to estimate the vapor in equilibrium with a given liquid at a known pressure. This results from the fact that the temperature is not known, so a temperature is assumed, and the various equilibrium constants at the known pressure and assumed temperature are used to estimate the vapor composition. If the sum of the mol fractions of all the components in the vapor, so calculated, add up to 1, the assumed temperature was correct. If the sum is not equal to 1, a new temperature must be assumed, and the calculation repeated until the sum is unity. Such a procedure is much more laborious than that involved in a binary mixture where the composition of the liquid and the pressure together with equilibrium data immediately gives the vapor composition without trial and error.

In the foregoing discussion of multicomponent systems, it was assumed that the complete composition of the liquid at some position in the column was known as a starting point for the calculation. The determination of this complete composition as a starting point is often the most difficult part of the whole multicomponent design. This difficulty arises from the fact that there are a limited number of independent variables which will completely define the distillation process; therefore, it is not possible to select arbitrarily the complete composition of a liquid or vapor at some position in the distillation system. The degrees of freedom involved in a distillation system can be evaluated (Ref. 3) by applying (1) the law of conservation of matter, (2) the law of conservation of energy, and (3) the second law of thermodynamics. These laws together with the phase rule can be applied to each plate, the still, and the condenser in a distillation unit and the over-all degrees of freedom for the system determined. For the case of a rectifying column consisting of a total condenser, a reboiler, a feed plate, n theoretical plates above the feed plate, and m theoretical

plates below the feed plate, the degrees of freedom for a system involving C components is

$$C + 2m + 2n + 10 \tag{9-1}$$

The variables used for these degrees of freedom are usually chosen from the ones summarized in Table 9-1. Theoretically, the choice of variables is completely independent, but in practically all distillation calculations certain of those given in the tables are ordinarily fixed. For example, it is usual to define the composition and condition of the feed, the operating pressure of each plate, and the heat gain or loss to or from each plate and the condenser. Referring to the table, these four items add up to $C + 2m + 2n + 6$, leaving four variables that can still be assigned. In most cases, to facilitate the design calculations the reflux ratio is fixed, and in general it is desirable to carry out the separation specified with the minimum number of theoretical plates; *i.e.*, the ratio of n/m is such that the total number of plates shall be a minimum and this effectively fixes one additional variable. There are thus only two remaining variables which can be fixed, and

TABLE 9-1. RECTIFYING COLUMN VARIABLES

Type of Variable	No. of Variables Fixed
Complete composition of feed	$(C - 1)$
Condition of feed	2
Operating pressure over each plate and in still and condenser	$m + n + 3$
Operating temperature on each plate and in still and condenser	$m + n + 3$
Heat gain or loss to or from each plate and condenser	$m + n + 2$
Heat supplied to still	1
Composition of product streams	$2(C - 1)$
Relative quantity of two product streams	1
No. plates above feed	1
No. plates below feed	1
Relative quantity of liquid returned to top plate to overhead product	1

the choice of these is dictated by the essential nature of the operation to be performed in the column. In the case of a binary mixture, the choice of these two independent terminal concentrations obviously gives the complete compositions of the distillate and residue and makes the design calculations easy and straightforward. However, in the case of multicomponent mixtures, the problem is more complex and, in general, the complete composition of neither the residue nor the distillate can be determined by using the two additional factors to fix two terminal conditions. In this case, it is necessary to estimate the com-

plete composition of either the product or the residue and then proceed with the calculations as before until the desired degree of separation is attained. If, then, the calculated product and residue compositions satisfy a material balance for each component, the estimated composition was correct. However, if a material balance is not satisfied by any one of the components, it is necessary to readjust the composition and repeat the calculation until the material balances are all satisfied simultaneously. This estimation is often simplified because the degree of separation is so high that the heavier components will appear in the product in quantities so small as to be negligible. The same will be true for the lighter components in the residue.

In selecting the two terminal concentrations, it is desirable to choose components that will give a significant control of the separation desired and, at the same time, be components that appear in appreciable amounts in both the bottoms and the distillate. Because these controlling components are so important in determining the design calculations, they have been termed the "key components." In other words, they are the key to the design problem.

In the development of design equations, it has been found convenient to pick two key components: the light key component and the heavy key component. The former is the more volatile component whose concentration it is desired to control in the bottoms; the latter is the less volatile component whose concentration is specified in the distillate. Thus, in the stabilization of gasoline it is often desired to have only a small concentration of propane in the bottoms in order that the vapor pressure of the finished product will meet the desired specifications and also to limit the butane in the distillate so as to retain this component in the gasoline. In such a case, propane would be the light key component and butane the heavy key component.

The terminal concentrations of the two key components are important because most of the practical equations which have been developed for the minimum number of theoretical plates at total reflux, the optimum feed-plate location, and the minimum reflux ratio have involved these concentrations. However, certain difficulties are involved: (1) the design specifications may be such that the key components are not obvious and (2) these design equations often require the concentrations of both key components in the distillate and bottoms as well as the concentration of some of the other components. But as demonstrated in the foregoing analysis, only two of these terminal concentrations are independent and can be arbitrarily fixed as design conditions.

The difficulties of choosing the key components and estimating the complete distillate and bottoms compositions are often the most difficult parts of a multicomponent design calculation. The problem can generally be simplified if the design conditions are chosen with this problem in mind. Thus, in cases where the separation between adjacent components is essentially complete, the two independent variables can be chosen as the concentration of the more volatile of these two in the bottoms and as the concentration of the less volatile component in the distillate. These adjacent components then become the key components, and the composition of the distillate and bottoms can be determined completely enough for design calculations by simple material balances. Components more volatile than the light key component will be almost negligible in the bottom, and components heavier than the heavy key component will be negligible in the distillate. For rectifications in which there is an appreciable difference in volatility between adjacent components and in which a fairly high degree of separation is being carried out, the design condition can generally be specified in this manner and thereby simplify the problem. If the degree of separation is low and/or there are several components of nearly the same volatility in the range in which the separation is being made, the selection of the two key terminal concentrations will generally not give enough information to allow the complete terminal compositions to be calculated by simple material balances. In such a case, it is necessary to estimate the terminal concentration of the other distributed components and then check this estimation by proceeding with the usual stepwise plate-to-plate calculations. If such plate-to-plate calculations give a consistent over-all result, the estimated values are satisfactory; if the results are inconsistent, new values must be estimated and the calculation repeated. It should be emphasized that even in this latter case, although a large number of the terminal concentrations may not be known, only two of these are independent after the other variables selected have been fixed. All the other terminal concentrations are fixed when these two independent ones are chosen and therefore cannot be given values arbitrarily. The necessity of having the concentrations of these other components, that are fixed but not known, offers the main difficulty in setting up a multicomponent distillation example.

The above procedure will give the optimum design for the operating conditions chosen. However, occasionally it is desirable not only to obtain the desired separation between the two components but at the same time to control the amount of one of the other components in one of the products. Frequently, it is possible to accomplish this result

by shifting the feed-plate location. Thus the tower is not designed for the minimum number of plates to separate two key components but will employ a larger number of plates to accomplish a desired result.

Lewis and Matheson Method. Several methods have been proposed for the design of multicomponent mixtures, but fundamentally they are based on Sorel's method. One of the best is that due to Lewis and Matheson (Ref. 5). This is the application of Sorel's method together with the usual simplifying assumptions to multicomponent mixtures. The same operating lines as used on page 119 for binary mixtures are employed to determine the relation between the vapor composition and the composition of liquid on the plate above, this calculation together with vapor-liquid equilibrium data being sufficient for the determination of the number of theoretical plates for given conditions. The use of this method will be illustrated by the fractionation of a mixture of benzene, toluene, and xylene under conditions where the separation will be sufficiently good so that the determination of the terminal conditions will not be difficult.

Benzene-Toluene-Xylene Example. Consider the rectification of a mixture containing 60 mol per cent of benzene, 30 mol per cent of toluene, and 10 mol per cent of xylene into a distillate or product containing not over 0.5 mol per cent of toluene and a bottoms or residue containing 0.5 mol per cent of benzene. A reflux ratio O/D equal to 2 will be used, and the feed will enter preheated so that the change in mols of overflow across the feed plate will be equal to the mols of feed. The usual simplifying assumptions will be made, and Raoult's law will be used. The distillation will be carried out at 1 atm. abs. pressure.

Since the concentration of toluene in the distillate D is low, the xylene will be practically zero and therefore will be essentially all in the residue W. Taking as a basis 100 mols of feed, a benzene material balance, input equals output, gives the following:

$$\begin{aligned} 60 &= Dx_{DB} + 0.005W = (100 - W)x_{DB} + 0.005W \\ &= 100x_{DB} + (0.005 - x_{DB})W \\ x_{DB} &= 0.995 \\ 60 &= 99.5 - W(0.99) \\ W &= \frac{39.5}{0.99} = 39.9 \\ D &= 60.1 \end{aligned}$$

where D = mols of product
W = mols of residue
x_{DB} = mol fraction of benzene in liquid distillate

The terminal conditions are then

	Distillate		Residue	
	Mols	Mol per cent	Mols	Mol per cent
Benzene	59 8	99 5	0 20	0 5
Toluene	0 30	0 5	29 7	74 4
Xylene	0	—	10.0	25 1
Total	60 1	100.0	39.9	100 0

Since $O/D = 2$, in the top part of the tower

$$O_n = 2 \times 60.1 = 120.2,$$

and $V_n = O_n + D = 180.3$, and $O_m = O_n + F = 220.2$, giving $V_m = 180.3$.

For the part of the column below the feed plate, the operating lines are

For benzene:

$$y_{mB} = \left(\frac{O}{V}\right)_m x_{(m+1)B} - \left(\frac{W}{V}\right)_m x_{WB} = \left(\frac{220.2}{180.3}\right) x_{(m+1)B} - \frac{39.9}{180.3}(0.005)$$
$$= 1.221x_{(m+1)B} - 0.0011$$

For toluene:

$$y_{mT} = 1.221x_{(m+1)T} - 0.164$$

For xylene:

$$y_{mX} = 1.221x_{(m+1)X} - 0.0555$$

Beginning with the composition of the liquid in the still, a temperature is assumed, and the partial pressure of each component is calculated using Raoult's law. If the sum of the partial pressure is 760 mm. Hg (the total pressure), the assumed temperature was correct. The vapor pressure of these components is given in Fig. 9-1. Assume $T = 115°C$.

	x_W	P	x_WP	$y_W = x_WP/\Sigma x_WP$
C_6	0 005	1990	10	0 0135
C_7	0.744	850	632	0 854
C_8	0.251	390	98	0 1325
			740	1 0000

Since the total is 740 instead of 760, the assumed temperature was too low, but a more nearly correct temperature is easily found by determining the temperature from Fig. 9-1 at which the vapor pressure of toluene is $(^{760}/_{740})(850) = 873$, giving $T = 116.0°C$. The calculation is then repeated for 116°C.

	x_W	P	x_WP	$y_W = x_WP/760$ 4
C_6	0.005	2000	10	0 0131
C_7	0 744	873	650	0 855
C_8	0 251	400	100 4	0 132
			760 4	1 0000

With this assumed temperature, the sum of x_WP is seen to be very close to 760, and the temperature is satisfactory. Actually, such a recalculation is not necessary, since the values desired are y_W, and these values may be obtained from $y_W = x_WP/\Sigma x_WP$ where Σx_WP is the sum of the x_WP values. Thus, in the fourth column of the table for the first assumed temperature are given values of $y_W = x_WP/740$. These are seen to correspond closely to the values in the corrected table and agree well within the accuracy of such factors as the vapor pressures, the applicability of Raoult's law, etc. In general, such a simplified procedure is satisfactory when the sum of x_WP is within 10 per cent of the desired value; however, at times, such a simplification is not justified, and a preliminary check on the system in question should be made to determine the satisfactory limit of the sum of x_WP.

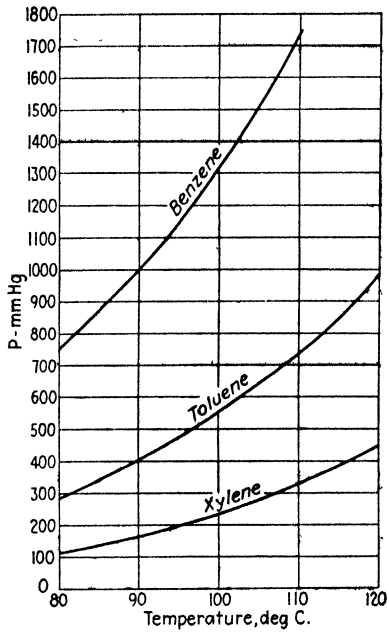


FIG. 9-1.

The value of x_1 is obtained from y_W by the use of the appropriate operating-line equation applied to each component. y_1 is then calculated using Raoult's and Dalton's laws at an assumed temperature of 115°C., and x_2 is obtained from the values of y_1 by the use of the operating-line equation. The operation is repeated, making adjustments of the assumed temperatures such that ΣxP stays between 700 and 820. In making these adjustments of temperature, it is desirable to continue using one temperature until the value of ΣxP is about as much greater than 760 as it was less than 760 on the first plate on which the temperature was used. Thus, in the following table, the values of

Component	T, °C. assumed	P_{mm}	x_w	x_wP	$y_w = x_wP/\Sigma x_wP$	x_1
C_6	115	1990	0.005	10	0.0135	
C_7	—	850	0.744	632	0.854	
C_8	—	390	0 251	98	0.1325	
				ΣxP = 740	Σy = 1.0000	
						x_1
C_6	116	2000	0 005	10	0.0131	0 0116
C_7	—	873	0.744	650	0.855	0.835
C_8	—	400	0.251	100.4	0 132	0 153
		-		ΣxP = 760.4	Σy = 1.0000	
			x_1	x_1P	y_1	x_2
C_6	115	1990	0.0116	23 1	0.0292	0 0248
C_7	—	850	0.835	709	0.895	0 868
C_8	—	390	0.153	59.7	0.0755	0 1065
				ΣxP = 791 8	Σy = 1	
			x_2	x_2P	y_2	x_3
C_6	110	1740	0.0248	43	0 0597	0 0498
C_7	—	740	0.868	642	0 892	0 865
C_8	—	330	0.1065	35	0.0486	0.085
				ΣxP = 720		
			x_3	x_3P	y_3	x_4
C_6	110	1740	0 0498	86.7	0 115	0 095
C_7	—	740	0 865	640	0 848	0 830
C_8	—	330	0.085	28	0.037	0.075
				ΣxP = 754 7		
			x_4	x_4P	y_4	x_5
C_6	110	1740	0 095	165	0.205	0.169
C_7	—	740	0 830	614	0 763	0.759
C_8	—	330	0.075	25	0.031	0.071
				ΣxP = 804		
			x_5	x_5P	y_5	x_6
C_6	105	1520	0.169	257	0.336	0.276
C_7	—	645	0.759	489	0.638	0.657
C_8	—	280	0.071	20	0.026	0.067
				ΣxP = 766		

110°C. were continued from $x_2P = 720$ to $x_4P = 804$, giving approximately an equal displacement on both sides of 760.

Component	T, °C. assumed	$K = P/760$	x_6	xK	$y_6 = xK/\Sigma xK$	x_7
C_6	100	1 745	0 276	0.482	0.49	0.402
C_7	—	0 735	0 657	0 482	0 49	0 535
C_8	—	0 316	0.067	0.021	0 021	0.063
				$\Sigma xK = 0.985$		
			x_7	x_7K	y_7	x_8
C_6	95	1 52	0.402	0.612	0.635	0.521
C_7	—	0 628	0 535	0 336	0 348	0 420
C_8	—	0.263	0.063	0 016	0.017	0.059
				$\Sigma xK = 0$ 964		
			x_8	x_8K	y_8	x_9
C_6	95	1 52	0 521	0 793	0 738	0 605
C_7	—	0.628	0 420	0.264	0 246	0 336
C_8	—	0.263	0 059	0 016	0 015	0.058
				$\Sigma xK = 1$ 073		

The table on page 222 carries these calculations up to the sixth plate.

As pointed out on page 215, the vapor-liquid data are more often given as $y = Kx$ rather than as Raoult's law. With equilibrium data in such form, the method of calculation is similar. Given the values of x in the liquid on any plate, the temperature is assumed, and a value of K for each component is obtained from equilibrium data at the assumed temperature and the operating pressure. The value of y in equilibrium with this liquid is given by Kx. If the sum of the values of y is equal to 1, the assumed temperature was correct, and the x values on the plate above may be obtained from the y values just calculated by using the operating-line equation. If the sum of the values of Kx does not equal 1, the temperature should be readjusted; but as in the previous case, this adjustment is usually unnecessary if the sum of Kx is within 10 per cent of 1, in which case the values of y are calculated by $y_a = K_a x_a / \Sigma Kx$.

The benzene-toluene-xylene calculations will be continued, using the K method. For this particular mixture, where Raoult's and Dalton's laws are assumed to apply, the equilibrium constant is equal to the vapor pressure divided by the total pressure; *e.g.*, $y_a\pi = x_aP_a$, or $y_a = (P_a/\pi)x_a$, giving $K_a = P_a/\pi$.

The ratio of x_{c6} to x_{c7} on plate 9 is approximately that in the feed, so this plate will be used as the feed plate. The proper feed-plate location for this column will be considered in a later section. Above the feed plate, the procedure is the same, except that the equation for the upper portion of the tower is utilized.

The operating-line equations above the feed are

For C_6,

$$y_{nB} = \left(\frac{O}{V}\right)_n x_{(n+1)B} + \left(\frac{D}{V}\right)_n x_{DB} = 0.667x_{(n+1)B} + 0.332$$

For C_7,

$$y_{nT} = 0.667x_{(n+1)T} + 0.0017$$

For C_8,

$$y_{nX} = 0.667x_{(n+1)X}$$

Proceeding as before:

Component	T, °C. assumed	K	x_9	xK	$y_9 = xK/\Sigma xK$	x_{10}
C_6	90	1 33	0 605	0 805	0 807	0 712
C_7	—	0 533	0.336	0.179	0.180	0 267
C_8	—	0.221	0 058	0 013	0 013	0 020
				$\Sigma xK = 0$ 997		
			x_{10}	$x_{10}K$	y_{10}	x_{11}
C_6	85	1.15	0 712	0.819	0.867	0 802
C_7	—	0 452	0.267	0 121	0 128	0.189
C_8	—	0 184	0.020	0 004	0 004	0.006
				$\Sigma xK = 0$ 944		
			x_{11}	$x_{11}K$	y_{11}	x_{12}
C_6	85	1 15	0 802	0 923	0.914	0 873
C_7	—	0 452	0 189	0 085	0 084	0 123
C_8	—	0.184	0.006	0 0012	0.0012	0.0018
				$\Sigma xK = 1.009$		
			x_{12}	$x_{12}K$	y_{12}	x_{13}
C_6	85	1.15	0.873	1.005	0.947	0.922
C_7	—	0 452	0.123	0.055	0 053	0.0765
C_8	—	0.184	0.0018	0.0004	0.0004	0.0006
				$\Sigma xK = 1.061$		

Component	T, °C. assumed	K	x_9	xK	$y_9 = xK/\Sigma xK$	x_{10}
			x_{13}	$x_{13}K$	y_{13}	x_{14}
C_6	80	0.995	0 922	0 917	0 968	0.953
C_7	—	0.379	0 0765	0 029	0.032	0.045
C_8	—	0.153	0.0006	0 0001	0.0001	0.00015
				$\Sigma xK = 0$ 946		
			x_{14}	$x_{14}K$	y_{14}	x_{15}
C_6	80	0 995	0 953	0 948	0 982	0 974
C_7	—	0 379	0 045	0 017	0 018	0.024
C_8	—	0 153	0 00015	0.00002	0 00002	0 00003
			x_{15}	$x_{15}K$	y_{15}	x_{16}
C_6	80	0 995	0 974	0 969	0 99	0.988
C_7	—	0 379	0 024	0 0091	0 0093	0 0114
C_8	—	0 153	0 00003	0 000005	0 000005	0.000007
			x_{16}	$x_{16}K$	y_{16}	
C_6	80	0 995	0 988	0 983	0 9956	
C_7	—	0.379	0.0114	0 0043	0 0044	
C_8	—	0.153	7×10^{-6}	10^{-6}	10^{-6}	

The vapor leaving the sixteenth plate, on being liquefied in the total condenser, will give a product containing slightly more than 99.5 per cent benzene. Thus, approximately 16 theoretical plates together with a total condenser and still or reboiler are required to effect the desired separation under the operating conditions chosen.

In general, it is instructive to plot the compositions vs. the plates. This type of figure is shown in Figs. 9-2 and 9-3 for the example just solved. The benzene is seen to rise on a smooth curve, and the concentration of toluene in the liquid passes through a maximum two plates above the still and then falls off in a smooth curve with the exception of a slight break at the feed plate; the xylene drops rapidly above the still and then flattens out until the feed plate is reached and then drops rapidly to a negligible value. The maximum in the toluene curve is a result of the fact that, in the still, toluene and xylene are the main components; and since toluene is the more volatile of the two, it

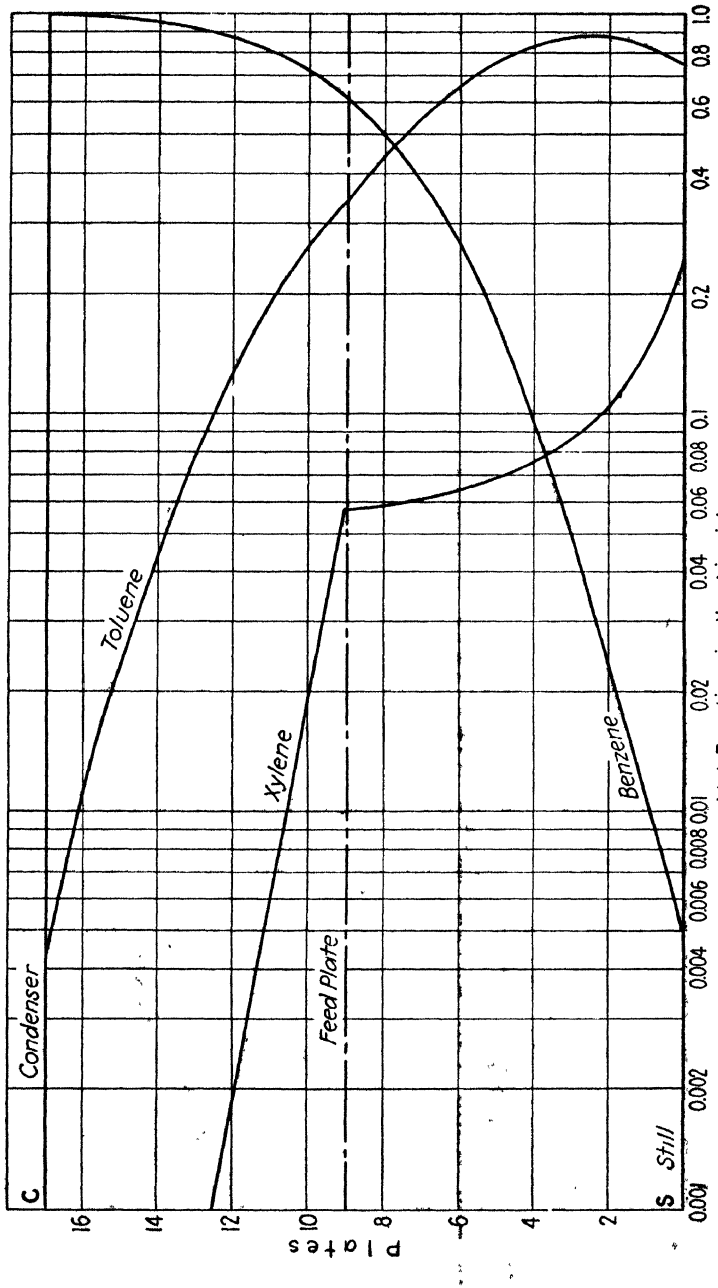

C Condenser
S Still
Toluene
Xylene
Benzene
Feed Plate
Plates
16
14
12
10
8
6
4
2
0.001
0.002
0.004
0.006
0.008
0.01
0.02
0.04
0.06
0.08
0.1
0.2
0.4
0.6
0.8
1.0
Mol Fraction in the Liquid

Fig. 9-2.

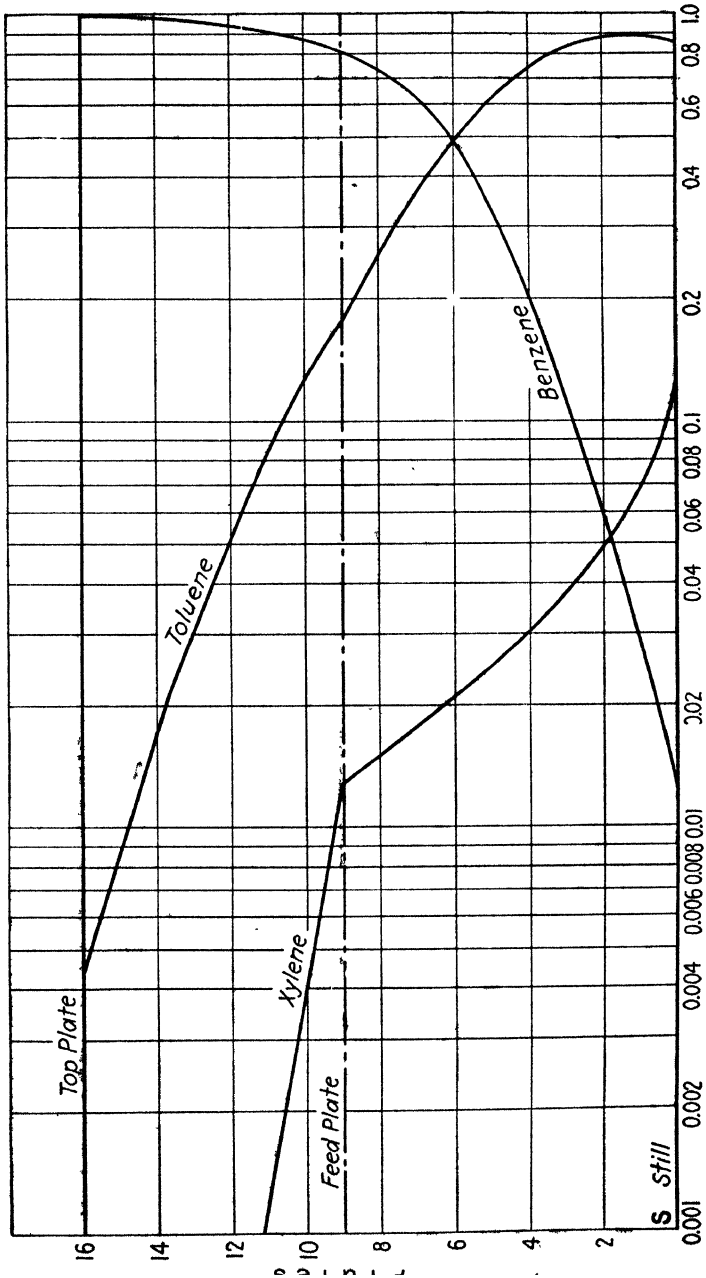

Top Plate
Toluene
Xylene
Feed Plate
Benzene
S Still
16
14
12
10
8
6
4
2
0.001
0.002
0.004
0.006
0.008
0.01
.02
0.04
0.06
0.08
0.1
0.2
0.4
0.6
0.8
1.0
Mol Fraction in Vapor

FIG. 9-3.

tends to increase, and the xylene tends to decrease. This increase in toluene concentration continues until the benzene concentration becomes appreciable, and since this latter component is very volatile, it increases rapidly and forces the toluene to decrease. This increase of benzene relative to the toluene continues up to the condenser. The xylene decreases up the column from the still because of its low volatility but cannot decrease below a certain value, since the 10 mols of xylene in the feed must flow down the column, and this sets a minimum limit on the concentration of

$$\frac{10}{O_m} = \frac{10}{220} = 0.0455$$

actually the value will be slightly higher, since the small amount of xylene that passes upward in the vapor must again pass down the column. This is due to the fact that essentially no xylene leaves the top of the column. Above the feed plate, the amount of xylene passing with the vapor to a plate must be equal to the xylene in the overflow from the plate, *i.e.*, $Vy_n = Ox_{n+1}$, since Dx_D is essentially zero. However, $y_n = Kx_n$, giving $x_{n+1} = (VK/O_n)x_n$; for a heavy component such as xylene which does not leave the top of the column in appreciable amount, the composition of the liquid on one plate is related to that on the plate below VK/O. In general, K is very small for such components and the concentration decreases rapidly as shown by the straight line in Fig. 9-2.

These concentration-gradient curves are typical of those generally obtained. The two main components between which the rectification is taking place tend to increase and decrease up the column, much as in a binary mixture. They are often called the key components. The concentrations of the components heavier than the heavier key component decrease rapidly as one proceeds from the still up the column, but they tend to become constant because of the necessity of their flowing down the overflows in order that they may be removed at the still. These components then decrease rapidly above the feed plate, usually dropping to negligible values a few plates above this plate. The concentrations of components lighter than the light key component give the same type of curves from the condenser down the column as the heavier components do from the still upward. Thus, the concentrations of these light components decrease rapidly for a few plates down from the condenser but then flatten out, since by material balance essentially all of the mols of these components that are in the feed must flow up through the upper part of the column to be removed

at the condenser, and this factor sets a lower limit on their concentration in this section. Below the feed plate, these light components decrease rapidly and generally become negligible a few plates below the feed plate.

Lewis and Cope Method. Lewis and Cope (Ref. 4) applied the same method graphically, by constructing a separate y,x plot for each com-

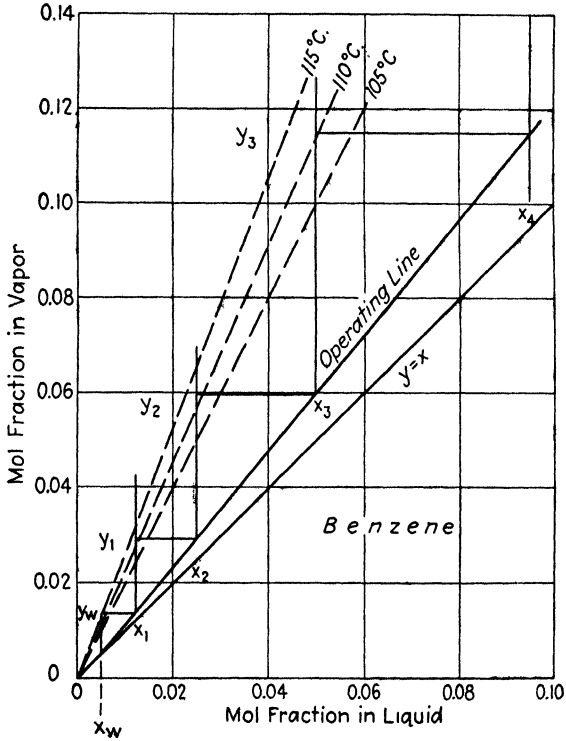


FIG. 9-4.

ponent. On these plots, the $y = x$ line and the operating lines are drawn the same as for a binary mixture. The three plots for the previous examples are given in Figs. 9-4 to 9-6. Only the lower portions of the benzene and xylene curves are given in order to increase the graphical accuracy. It is interesting to note that for xylene and toluene the intersection of the operating line, which occurs at x_F, just as in the case of a binary mixture, falls below the $y = x$ diagonal. This is due to the fact that x_W is greater than x_D, and the components are both of lower volatility than the benzene. If unique equilibrium

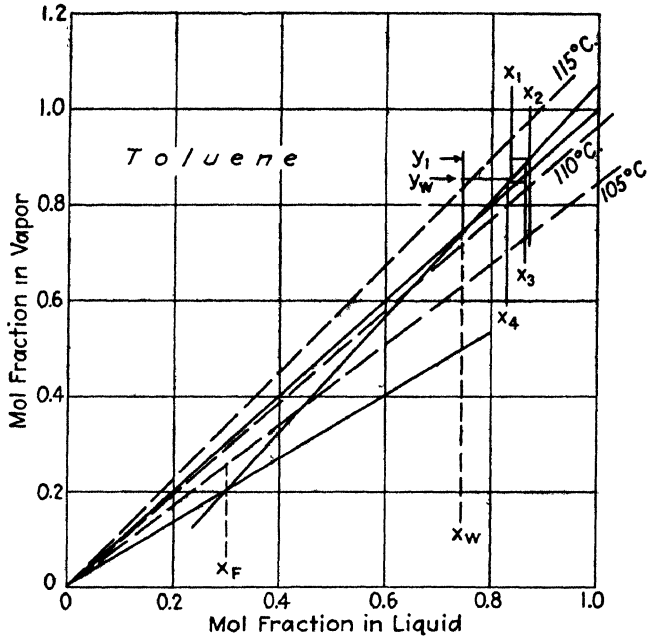

Toluene
Mol Fraction in Vapor
Mol Fraction in Liquid
115°C.
110°C.
105°C.
x_1
x_2
x_3
x_4
y_1
y_w
x_F
x_w
0
0.2
0.4
0.6
0.8
1.0
1.2

FIG. 9-5.

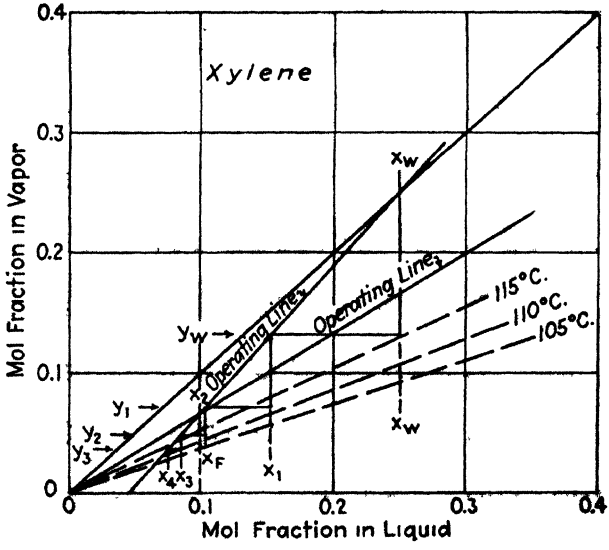

Xylene
Mol Fraction in Vapor
Mol Fraction in Liquid
Operating Line
Operating Line
115°C.
110°C.
105°C.
y_w
x_w
y_1
x_2
y_2
y_3
x_F
x_4
x_3
x_1
0
0.1
0.2
0.3
0.4

FIG. 9-6.

curves could be drawn on the diagrams, the problem would become similar to the stepwise procedure for a binary mixture. However, in general, such curves are not known. The Lewis and Cope method was to draw a series of equilibrium curves of the type $y = Kx$ which at constant temperature are in general straight lines through the origin of slope K. Thus, in the present example, $K = P/760$, where P of any one component is a function of the temperature only. Such equilibrium curves have been drawn in for the temperatures of 105, 110, and 115°C. Starting at x_W on each plot, vertical lines are drawn through this point cutting the equilibrium curves. By trial and error, temperatures are tried until the sum of the y values at the intersection of the vertical line through x_W and the equilibrium curve for the assumed temperature adds up to unity. Thus, if 115°C. is tried, the sum of the y values at the intersection of the 115°C. curve with the x_W lines is $0.013 + 0.837 + 0.13 = 0.98$, indicating that 115°C. is too low. By interpolation at 116°C., the sum becomes $0.013 + 0.855 + 0.132 = 1.00$, indicating that this is the correct temperature, and the y values give the composition y_W of the vapor in equilibrium with x_W. Horizontal lines are then drawn through the y_W values to the operating line, the abscissa of the intersection with the operating line being x_1. Vertical lines are drawn through the x_1's; and by using the same procedure as for x_W a temperature of 112.5°C. is found to give Σy equal to unity, and the step is then completed to the operating line. In a like manner, steps are taken up the column. The same operating line is used until the feed plate is reached, and then the change is made to the operating line for the upper portion of the column simultaneously for all three components.

A comparison of the values of these figures with those obtained in the previous algebraic calculation shows the close agreement. Actually, they have to give the same result, since they both are solutions of the same set of equations, one being algebraic and the other graphical. Both methods have their advantages; in the algebraic method, as a rule, higher accuracy can be obtained than in the graphical method this is especially true in the low-concentration region where the graphical diagram must be greatly expanded or replotted on logarithmic paper, such as was utilized in the binary mixtures. The advantage of the graphical method is that it gives a visual picture of the concentration gradients and operation of the tower. The amount of labor and time consumed is approximately the same for the two methods.

Numerous analytical methods based on the foregoing methods have been proposed to simplify the trial and error required in the Lewis and

Matheson method. Some of these methods will be considered in a later section, but generally the stepwise method outlined above is more satisfactory. By using $y = Kx/\Sigma Kx$ instead of making the Kx's add to exactly unity, the trial-and-error work of the Lewis and Matheson method is practically eliminated. In the example just solved, when ΣKx became larger than 1, the temperature was dropped, making ΣKx less than 1; and this temperature was used until ΣKx again became greater than unity, and then the temperature was again dropped. Thus, no actual trial and error was required, but merely successive drops of temperature of 5 to 10°. Such calculations require only a few hours more than the simplest of the approximate methods and only two or three such stepwise calculations at different reflux ratios together with the minimum number of plates at total reflux and the minimum reflux ratio are required to allow the construction of a curve of theoretical plates required vs. the reflux ratio. In general, the added confidence that may be placed in the stepwise calculations relative to the approximate methods more than justifies the extra work involved.

In using the stepwise method with the simplification that $y = Kx/\Sigma Kx$, the problem arises as to how much ΣKx can differ from unity and still not appreciably affect the values of y. The justification of this simplification is that for moderate changes in temperature the percentage change in the values of K for substances that do not differ too widely is approximately the same. A little consideration will show that if all the K values change the same percentage with temperature, then the values of y calculated by such a method will be independent of the temperature chosen. This relative variation in the K values is best expressed in the relative volatility. Thus, if $y_A = K_A x_A$ and $y_B = K_B x_B$, then $y_A/y_B = (K_A/K_B)(x_A/x_B)$, and (K_A/K_B) is the relative volatility of A to B, α_{AB} (see page 30). If the percentage change in both K_A and K_B is the same with temperature, α_{AB} will be a constant over this region, and a plot of α_{AB} vs. temperature will give immediately the region over which ΣKx can vary without appreciably altering the y value. Actually, the α's can be introduced into the equations, and the K's eliminated. Thus,

$$y_A + y_B + y_C + y_D + \cdots = 1$$

$$\frac{y_A}{y_B} + 1 + \frac{y_C}{y_B} + \frac{y_D}{y_B} + \cdots = \frac{1}{y_B}$$

using the relative volatility

$$\underline{\alpha_{AB}x_A} + 1 + \underline{\alpha_{CB}x_C} + \alpha_{DB}\underline{x_D} + \cdots = \frac{1}{\underline{\quad}}$$

which can be rearranged to give

$$y_B = \frac{x_B}{\alpha_{AB}x_A + x_B + \alpha_{CB}x_C + \alpha_{DB}x_D + \cdots} = \frac{x_B}{\Sigma \alpha x}$$

since

$$\frac{x_B}{y_B} = \alpha_{AB}\frac{x_A}{y_A}$$

$$y_A = \frac{\alpha_{AB}x_A}{\Sigma \alpha x}$$

Likewise,

$$y_C = \frac{\alpha_{CB}x_C}{\Sigma \alpha x}; \qquad y_D = \frac{\alpha_{DB}x_D}{\Sigma \alpha x} \tag{9-2}$$

A similar analysis starting with

$$x_A + x_B + x_C + \cdots = 1$$

leads to

$$x_A = \frac{y_A/\alpha_{AB}}{\Sigma y/\alpha}, \qquad x_B = \frac{y_B/\alpha_{BB}}{\Sigma y/\alpha}, \qquad x_C = \frac{y_C/\alpha_{CB}}{\Sigma y/\alpha} \tag{9-3}$$

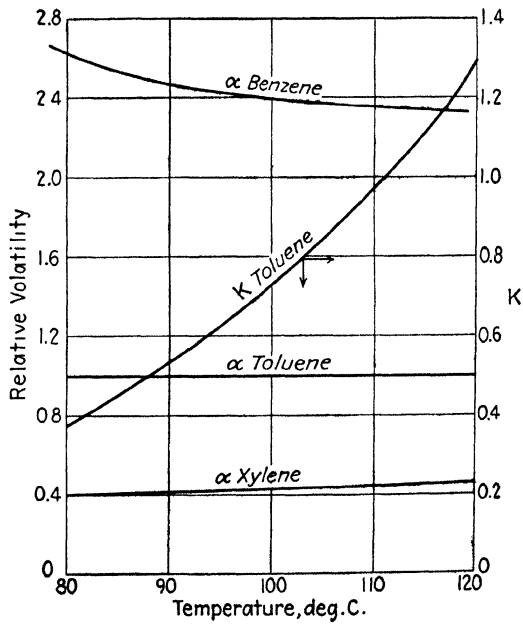


FIG. 9-7.

where all the relative volatilities are with respect to the B component; and in the case of the y_B equation, a relative volatility does not appear with x_B, since α_{BB} is 1. Given the liquid composition on any plate, the

values of x are multiplied by the α corresponding to the component in question, and the values of αx are totaled to give $\Sigma \alpha x$, then the value of y for any component is calculated by dividing αx for the component by $\Sigma \alpha x$. In general, it is desirable to take the volatilities relative to one of the key components; this will cause α to be greater than 1 for the components that are lighter and less than 1 for the heavier components. This method will be most clearly brought out by its application to actual problems. First it will be applied to the benzene, toluene, and xylene problem previously solved. Figure 9-7 shows the volatilities relative to toluene plotted as a function of temperature and also shows the K for toluene as a function of the temperature. It will be noticed that the variation in the relative volatilities with temperature is very small and that for xylene in the lower part of the column a constant value of α equal to 0.43 is well within the design accuracy. The benzene volatility relative to toluene varies more, but even here the variation is small. In the previous example, starting at the still:

	x_W	α_{110}	αx_W	$y_W = \alpha x/0.869$	x_1	$\alpha_{110} x_1$	$y_1 = \alpha x/0.932$
C_6	0.005	2.36	0.0118	0 0136	0 012	0 0283	0 030
C_7	0.744	1 0	0 744	0.856	0.835	0 835	0 896
C_8	0.251	0.45	0.113	0.130	0.152	0 0684	0 074
			0.8688			0.9317	

$K_T = 0.856/0.744 = 1.15$ $K_T = 0.896/0.835 = 1.07$
$T_W = 116°C.$ $T_1 = 113.4°C.$

	x_2	$\alpha_{110} x_2$	$y_2 = \alpha x/0.976$	x_3	$\alpha_{110} x_3$	$y_3 = \alpha x/1.02$
C_6	0.0254	0.06	0.061	0.0508	0.13	0.117
C_7	0.868	0.868	0.890	0 864	0.864	0.845
C_8	0.106	0.0477	0.049	0.086	0 039	0.038
		0.9757			1.023	

$K_T = 1/0.9757 = 1.025$ $K_T = 0.978$
$T_2 = 111.8°C.$ $T_3 = 110.2°C.$

	x_4	$\alpha_{110} x_4$	$y_4 = \alpha x/1.086$	x_5	$\alpha_{110} x_5$	$y_5 = \alpha x/1.192$
C_6	0.096	0.226	0.208	0.171	0.403	0.338
C_7	0.826	0.826	0.760	0.757	0.757	0.636
C_8	0.076	0.034	0.031	0.071	0.032	0.027
		1.086			1.192	

$K = 0.922$ $K = 0.84$
$T_4 = 108°C.$ $T_5 = 104.8°C.$

A comparison of the values calculated above with those previously obtained shows a very close agreement, as must be the case, since both calculations are fundamentally identical. In these calculations, the temperature has been determined on each plate by taking the K for toluene corresponding to the plate and determining the temperature from Fig. 9-7. Thus, K's were determined for the still and first plate by dividing the calculated y values by the value of x, $K_T = y_T/x_T$; thus for the still, x_T is 0.744, and y_T was calculated as 0.856, so that $K_T = 0.856/0.744 = 1.15$. From Fig. 9-7, the temperature is 116°C. at $K = 1.15$. A little consideration will show that K_T also is equal to $1/\Sigma\alpha x$, since $y = \alpha x/\Sigma\alpha x$; then $y/x = \alpha/\Sigma\alpha x$; but for the component relative to which the volatilities are taken, α is equal to 1, and $y/x = K = 1/\Sigma\alpha x$ for this component. This latter method was used for the second plate upward.

Continuing in this manner, the α's should probably be shifted when the temperature becomes about 100°C. Taking the new values of α at 90°C. should be satisfactory for finishing the column. Thus, no trial and error is needed, and only two sets of α values are employed. In order to speed computations, further modifications can be made. If, instead of calculating y_m, one calculates Vy_m, where V is the mols of vapor per mol of residue, then simply adding x_W to these values gives $O_m x_{m+1}$, where O_m is the mols of overflow per mol of residue. Then $O\alpha x_{m+1}$ is calculated, and $Vy_{m+1} = VO\alpha x_{m+1}/\Sigma O\alpha x_{m+1}$, which materially shortens the time necessary per plate but has the disadvantage that the actual x and y values do not appear. Continuing by this method, V per mol of bottoms is $180.3/39.9 = 4.52$, and $O = 220.2/39.9 = 5.52$.

The values of x_9 are essentially those obtained previously, indicating that the trial-and-error calculation to determine plate temperature is, in general, not necessary and that the Lewis and Matheson method when carried out in such a manner does not possess any great obstacles. The use of the relative-volatility method also offers other advantages than the ease of determining the plate composition. Consider the fractionation in a vacuum column in which the overhead pressure is fixed and the pressure drop per plate is an appreciable percentage of the total pressure causing the absolute pressure to vary widely. In general, the K values are approximately inversely proportional to the pressure and therefore would vary with the changes in pressure as well as with the changes in temperature. On the other hand, the relative volatility is often mainly a function of the temperature and only slightly affected by the moderate changes in pressure. In such cases,

	x_W	y_5	$4.52y_5$	$5.52x_6 = x_W + 4.52y_5$	$5.52\alpha_{110}x_6$	$4.52y_6 = (5.52\alpha x_6/7.411)(4.52)$
C_6	0 005	0.338	1 53	1 535	3 62	2 21
C_7	0.744	0 636	2.88	3.624	3.624	2 21
C_8	0.251	0 027	0.12	0.371	0 167	0.098
					7 411	

$K = 5.52/7.411 = 0.746$ $T_6 = 100.7$

	$5.52x_7$	α_{90}	$5.52\alpha x_7$	$4.52y_7 = (5.52\alpha x/8.56)4.52$	$5.52x_8$
C_6	2 215	2 47	5.46	2 89	2 895
C_7	2.954	1.0	2.954	1 56	2.304
C_8	0 349	0 42	0 147	0 078	0 329
			8 561		

$K = 5.52/8.56 = 0.646$ $T_7 = 95.8$

	$5.52\alpha x_8$	$4.52y_8$	$5.52x_9$
C_6	7 15	3 36	3 365
C_7	2 304	1 09	1 834
C_8	0 138	0.065	0 316
	9 592		

$K = 0.577$ $T_8 = 92.2$

	x_9
C_6	0 609
C_7	0 334
C_8	0 057

it is therefore possible to proceed by the α method, as in the constant-pressure calculations, without troubling with the pressure variation.

Tar Acid Fractionation. As another example of such calculations, consider the fractionation of a 35 mol per cent phenol, 15 mol per cent *o*-cresol, 30 mol per cent *m*-cresol, 15 mol per cent xylenols, and 5 mol per cent heavier. The overhead is to be 95 mol per cent phenol, and the phenol recovery is to be 90 per cent. The still pressure will be 250 mm. Hg abs., and 4 mm. Hg pressure drop will be allowed per theoretical plate. A reflux ratio O/D equal to 10 will be employed.

The equilibrium data obtained by Rhodes, Wells, and Murray (Ref. 7) for this type of system indicate that Raoult's law is followed, and thus the relative volatilities are independent of the pressure and a function of the temperature only. Thus, the relative-volatility

method will be most suitable for estimating the number of theoretical plates.

The result of over-all material balances is given in Fig. 9-8. The ratio of o-C_7 to m-C_7 in the distillate was assumed as 30 to 1.

Figure 9-9 gives the volatilities relative to o-cresol as well as the vapor pressure of o-cresol. In the calculations, the temperature is checked occasionally by determining the vapor pressure of o-cresol, P_o, on the plate. Since $y_o\pi = P_o x_o$, then

$$P_o = \frac{y\pi}{x} = \frac{\pi}{\Sigma \alpha x}$$

where π is corrected for pressure drop in the column. Below the feed, per mol of bottoms, the mols of vapor are

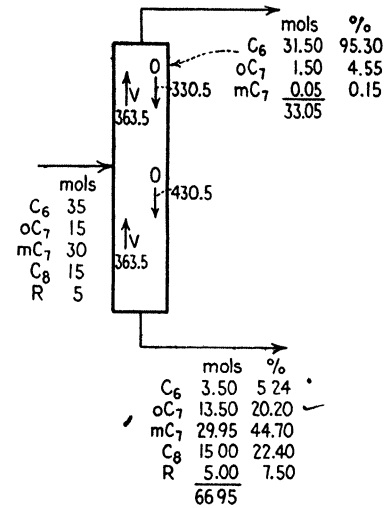


FIG. 9-8.

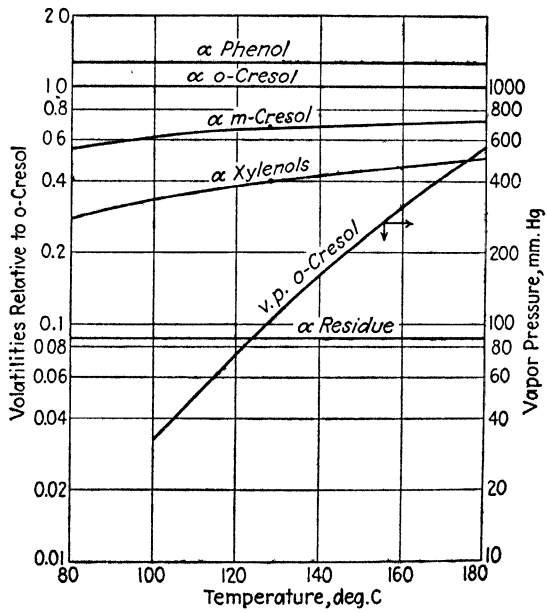


FIG. 9-9.

5.43, and the mols of liquid are 6.43; above the feed, the corresponding figures per mol of distillate are 11 and 10, respectively.

	x_W	α_{160}	αx_W	$5.43y_W = \alpha x_W(5.43)/0.685$	$6.43x_1$
C_6	0.0524	1 25	0 0656	0 521	0.573
o-C_7	0.202	1.0	0.202	1 60	1 80
n-C_7	0 447	0 7	0.312	2 48	2 93
C_8	0.224	0.44	0 099	0.79	1.01
R	0.075	0.087	0 006	0.048	0.123
			0 6846		

$P_o = 250/0.685 = 365$ mm. $T = 165$°C.

	$6.43\alpha x_1$	$5.43y_1$	$6.43x_2$	$6.43\alpha x_2$	$5.43y_2$
C_6	0.716	0.775	0 828	1 035	1 045
o-C_7	1 80	1 95	2.152	2 152	2 18
m-C_7	2.05	2 22	2.667	1 865	1 89
C_8	0 444	0 48	0 704	0 310	0 31
R	0 011	0.012	0.087	0 008	0 008
	5.021			5 370	

	$6.43x_3$	$6.43\alpha x_3$	$5.43y_3$	$6.43x_4$	$6.43\alpha x_4$
C_6	1.097	1.37	1 32	1 372	1.72
o-C_7	2 38	2 38	2.30	2 50	2 50
m-C_7	2 34	1 635	1 575	2 02	1 41
C_8	0.53	0.233	0 225	0 45	0 198
R	0.083	0 007	0 007	0 082	0 007
		5 625			5 835

	$5.43y_4$	$6.43x_5$	$6.43\alpha x_5$	$5.43y_5$	$6.43x_6$
C_6	1.60	1.652	2 07	1 87	1.92
o-C_7	2 33	2.53	2 53	2 28	2.48
m-C_7	1.31	1 76	1 23	1 11	1.56
C_8	0.184	0.41	0.18	0.16	0.38
R	0.006	0.081	0.007	0.006	0.081
			6.017		

$P_o = 230(6.43)/6.017 = 246$ $T_5 = 153$°C.

	$6.43\alpha x_6$	$5.43y_6$	$6.43x_7$	$6.43\alpha x_7$	$5.43y_7$
C_6	2.40	2.12	2 17	2 72	2.36
o-C_7	2.48	2.20	2.40	2 40	2 08
m-C_7	1.09	0 96	1.41	0 99	0.86
C_8	0.17	0 15	0 37	0 163	0.14
R	0 007	0 006	0.081	0 007	0.006
	6.147			6.280	

	$6.43x_8$	$\alpha_{1,10}$	$6.43\alpha x_8$	$5.43y_8$	$6.43x_9$	$6.43\alpha x_9$
C_6	2.41	1 26	3 04	2.61	2 66	3 35
o-C_7	2.28	1 0	2 28	1 95	2 15	2 15
m-C_7	1.31	0 675	0 88	0 76	1 21	0 82
C_8	0.36	0 392	0.14	0 12	0 34	0 13
R	0.081	0.087	0.007	0.006	0 081	0 007
			6 347			6 457

	$5.43y_9$	$6.43x_{10}$	$6.43\alpha x_{10}$	$5.43y_{10}$	$6.43x_{11}$	$6.43\alpha x_{11}$
C_6	2.82	2 87	3 62	3 01	3.06	3 86
o-C_7	1 81	2.01	2.01	1 67	1 87	1 87
m-C_7	0.69	1 14	0 77	0.64	1 09	0 74
C_8	0 112	0 34	0 13	0.11	0.33	0 13
R	0 006	0.081	0 007	0.006	0.081	0 007
			6.537			6 607

	$5.43y_{11}$	$6.43x_{12}$	$6.43\alpha x_{12}$	$5.43y_{12}$
C_6	3 17	3.22	4.06	3.32
o-C_7	1 54	1 74	1.74	1 42
m-C_7	0.61	1.06	0.71	0.58
C_8	0 11	0 33	0.129	0 105
R	0.006	0.081	0.007	0 006
			6.646	

$P_o = 202(6.43)/6.65 = 195$; $T_{12} = 146.5°C$.

	$6.43x_{13}$	$6.43\alpha x_{13}$	y_{13}
C_6	3.37	4.25	0 634
o-C_7	1.62	1 62	0 242
m-C_7	1.03	0.70	0.104
C_8	0.33	0.129	0.019
R	0.081	0.007	0.001
		6.706	

The ratio of phenol to *o*-cresol in the liquid on the thirteenth plate is essentially that in the feed, and this plate was used as the feed plate. The calculations are then completed using a basis of one mol of distillate. On such a basis, the operating line for each component $10x_n = 11y_{n-1} - x_D$ and the remainder of the table is set up in this manner.

	y_{13}	$11y_{13}$	$10x_{14}$	$10\alpha x_{14}$	$11y_{14}$
C_6	0 634	6 974	6 024	7 59	7 54
o-C_7	0 242	2 662	2 617	2.617	2.60
m-C_7	0.104	1 144	1 14	0.77	0 77
C_8	0.019	.209	.209	0 082	0 081
R	0.001	011	.011	0 001	0 001
				11 060	

	$10x_{15}$	$10\alpha x_{15}$	$10y_{15}$	$10x_{16}$	$10\alpha x_{16}$	$11y_{16}$	$10x_{17}$	$10\alpha x_{17}$	$11y_{17}$
C_6	6.59	8 3	8.0	7 05	8 89	8.38	7.42	9 36	8 73
o-C_7	2 55	2 55	2 46	2 41	2.41	2.27	2.22	2 22	2 07
m-C_7	0 765	0 516	0.498	0.493	0 333	0.314	0.31	0 209	0 195
C_8	0.081	0 032	0 031	0.031	0 012	0.011	0 011	0 004	0 004
R	0.001	9×10^{-5}	8×10^{-5}	8×10^{-5}	7×10^{-6}	7×10^{-6}	7×10^{-6}	6×10^{-7}	6×10^{-7}
		11.398			11.645			11 793	

	$10x_{18}$	$10\alpha x_{18}$	$11y_{18}$	$10x_{19}$	$10\alpha x_{19}$	$11y_{19}$	$10x_{20}$	$10\alpha x_{20}$	$11y_{20}$
C_6	7 78	9 81	9 02	8.07	10.2	9 3	8 35	10 55	9 53
o-C_7	2.02	2 02	1 86	1.81	1.81	1 65	1 60	1 6	1 44
m-C_7	0.19	0 128	0 118	0.113	0 076	0 069	0 064	0 043	0 0399
C_8	0.004	0 002	2×10^{-3}	2×10^{-3}	8×10^{-4}	7×10^{-4}	7×10^{-4}	3×10^{-4}	3×10^{-4}
		11.960			12.086			12.193	

$P_o = 178(10/11.96) = 149$ $\quad T_{18} = 138°C.$

	$10x_{21}$	$10\alpha x_{21}$	$11y_{21}$	$10x_{22}$	$10\alpha x_{22}$	$11y_{22}$	$10x_{23}$	$10\alpha x_{23}$	$11y_{23}$
C_6	8.58	10.8	9.74	8.79	11.08	9.91	8 96	11.30	10.1
o-C_7	1.39	1 39	1 25	1 20	1.20	1 07	1.02	1 02	0.91
m-C_7	0.035	0 024	0.022	0 018	0 012	0.011	0.007	$4\ 7 \times 10^{-3}$	4.2×10^{-3}
		12 214			12.292			12 32	

	$10x_{24}$	$10\alpha x_{24}$	$11y_{25}$	$10x_{25}$	$10\alpha x_{25}$	$11y_{25}$	$10x_{26}$	$10\alpha x_{26}$	y_{26}
C_6	9 15	11 52	10 24	9 29	11 70	10.37	9 42	11 88	0 952
o-C_7	0.86	0.86	0.76	0.71	0.71	0 63	0 58	0 58	0 047
		12 38			12 41			12 46	

$P_o = 154(10/12.38) = 124$ $T = 133°C.$

The concentration of *m*-cresol in the distillate is less than the assumed value, but a recorrection of this value would not make enough difference to be significant, and a material balance on this component is in essence satisfied. The results of the calculations are plotted in Fig. 9-10.

It is interesting to consider what would happen if the feed had not been introduced on the thirteenth plate. This calculation has been carried out and the results plotted in Fig. 9-11. Up to the thirteenth plate, the results are obviously identical with those given in Fig. 9-10; but above this plate, the change of concentration per plate is much less in Fig. 9-11. By the twenty-sixth plate, all the components have become almost asymptotic, and increasing the plates to an infinite number would make little difference in the concentrations from those for the twenty-sixth plate. Thus it is impossible to obtain the desired separation without having plates above the feed plate, since the asymptotic ratio of phenol to *o*-cresol is less than the desired ratio in the distillate. The limit to this asymptotic ratio is obvious from Fig. 9-11; since the *o*-cresol, *m*-cresol, xylol, and residue must all flow down the column, their concentrations cannot decrease below the value necessitated by material balance for their removal from the still. Although the concentration of the phenol is not limited by the same factor as the heavier components, it is limited by the fact that its value cannot exceed 1 minus the sum of the concentration of the heavier fractions; and since a minimum limit for the heavier components is fixed, a maximum for the phenol is likewise fixed. The condition illustrated in Fig. 9-11 around twentieth to twenty-sixth plate is termed "pinched in"; *i.e.*, conditions are so pinched that effective rectification is not obtained. As soon as the feed plate is passed, this pinched-in condition would be relieved, since the heavier components would decrease rapidly, as in Fig. 9-10, thereby allowing the phenol to increase.

At a lower reflux ratio, the enrichment per plate would be reduced, and more plates required for a given separation Figure 9-12 gives the

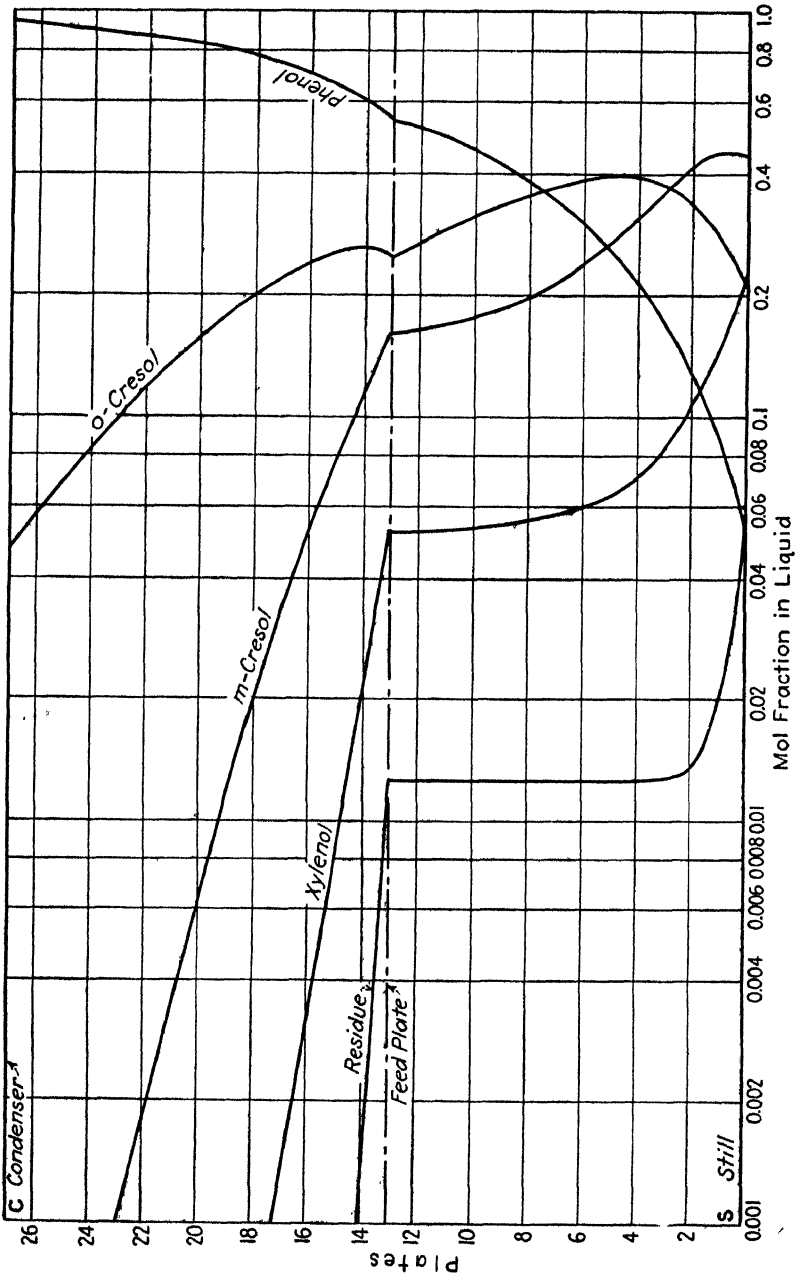

Phenol
o-Cresol
m-Cresol
Xylenol
Residue
Feed Plate
C Condenser
S Still
Plates
Mol Fraction in Liquid
26
24
22
20
18
16
14
12
10
8
6
4
2
0.001
0.002
0.004
0.006
0.008
0.01
0.02
0.04
0.06
0.08
0.1
0.2
0.4
0.6
0.8
1.0

FIG. 9-10.

results for the same design conditions as Fig. 9-10, except that O/D was 7 instead of 10. The number of plates increases from 26 to 35. It is to be noted that the asymptotic values of the concentrations of the heavier components in the lower part of the column also increase; this results from the fact that there is less overflow in this section of the tower.

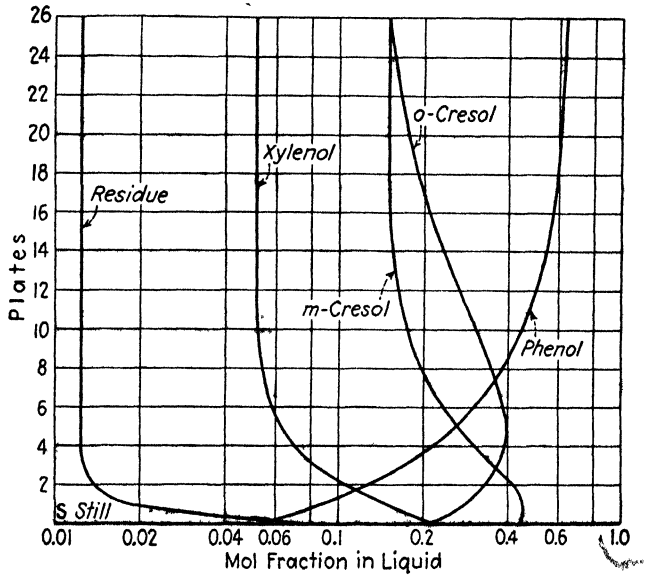


FIG. 9-11.

Minimum Theoretical Plates at Total Reflux. The minimum number of theoretical plates for a given separation is obtained at total reflux, the same as for a binary mixture. This minimum can be calculated by the stepwise method, using the operating line $y = x$ for each component for both sections of the column. Such a calculation will give the concentration and conditions through the tower. The assumptions made on page 175 for the calculation of the minimum number of plates in the development of Eq. (7-52) apply to any two of the components of a multicomponent mixture, and by its application this limiting condition can be calculated. In general, when applying the total reflux equation to a multicomponent mixture, it is desirable to use the two components whose concentrations are most accurately known in the distillate and residue, and most often these two components are the key components. However, the equation applies to

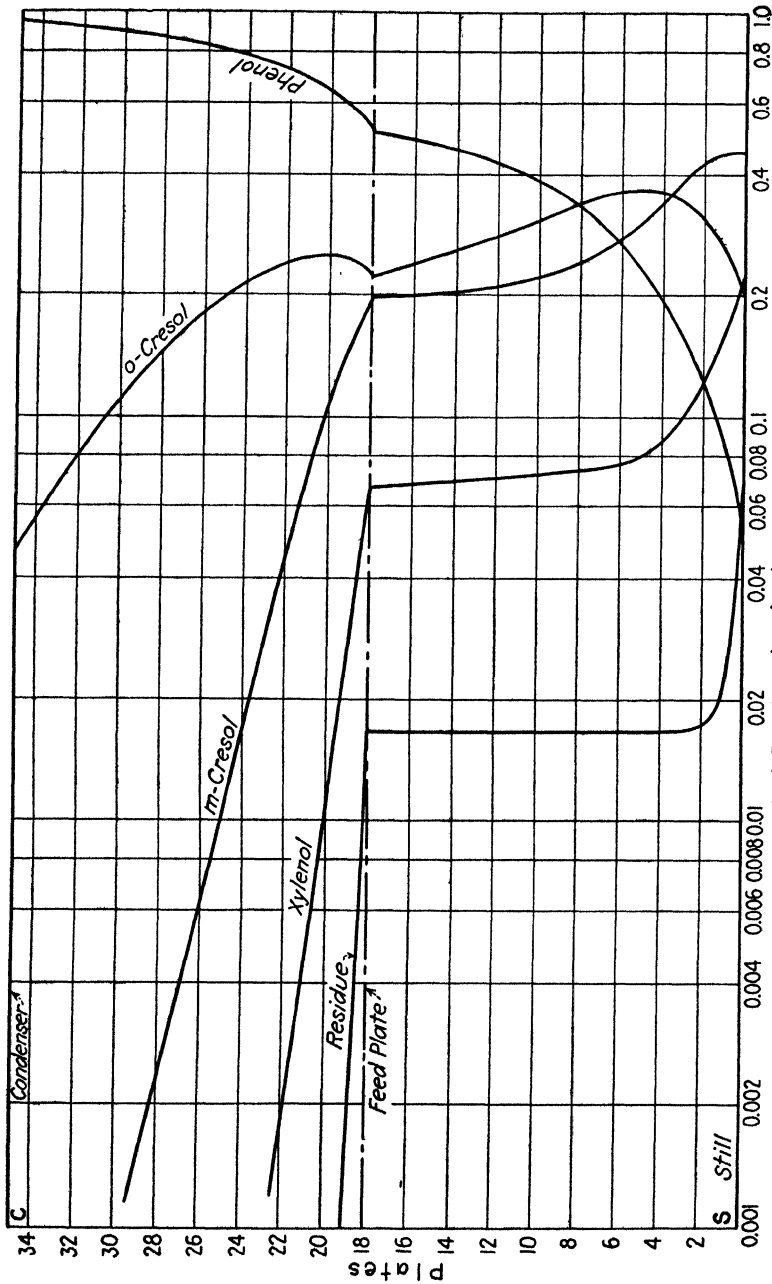

Phenol
o-Cresol
m-Cresol
Xylenol
Residue
Feed Plate
Condenser
Still
C
S
Plates
Mol Fraction in Liquid
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0.001
0.002
0.004
0.006
0.008
0.01
0.02
0.04
0.06
0.08
0.1
0.2
0.4
0.6
0.8
1.0

FIG. 9-12.

any two components in the mixture. The same limitations as to the constancy of relative volatility would apply as for the binary mixtures.

Feed-plate Location. The criterion for the optimum location of the feed plate is that the relative enrichment of the key components should be a maximum. As with binary mixtures, the feed plate corresponds to the step that passes from one operating line to the other. The change from one operating line to the other should be made just as soon as it will give a greater enrichment than continuing on the same operating line. In coming up from the still, the feed plate is the last step on the lower operating line; calling this the nth plate, and the key component vapors entering, $y_{lk(n-1)}$ and $y_{hk(n-1)}$, for the light, or more volatile, and heavy, or less volatile, components, respectively, the foregoing criterion states that if the nth plate is the optimum position for the feed, then the x ratio on this plate should be greater when calculated by the lower operating line from the y_{n-1} values than by the upper operating line, or

$$\left(\frac{x_{lk}}{x_{hk}}\right)_n = \frac{y_{lk(n-1)} + (W/V_m)x_{Wlk}}{y_{hk(n-1)} + (W/V_m)x_{Whk}} \geqq \frac{y'_{lk(n-1)} - (D/V_n)x_{Dlk}}{y'_{hk(n-1)} - (D/V_n)x_{Dhk}} \quad (9\text{-}4)$$

where y_{n-1} = mol fraction in vapor from plate $n - 1$ when feed is added to plate n

y'_{n-1} = mol fraction in vapor from plate $n - 1$ when feed is added to plate $n - 1$

For a binary mixture, y_{n-1}, would equal y'_{n-1}, assuming that the bottoms concentration is kept constant. However, the two values are not equal for multicomponent mixtures because of the presence of the components lighter and heavier than the key components. Owing to the presence of these components, the total vapor is not available for fractionating the key components. In order to reduce the interference of the components lighter than the light key component, it is desirable to utilize the lower operating line to a higher value of the ratio of the key components than would be the case for $y_{n-1} = y'_{n-1}$. Owing to the interference of the heavy components, it would be desirable to change to the upper operating line at a lower ratio of the key components. However, as a first approximation, it will be assumed that $y_{n-1} = y'_{n-1}$ and a correction for this assumption will be made later.

Combining Eq. (9-4) with

$$V_n = V_m + (p + 1)F$$

and

$$Wx_W + Dx_D = Fz_F$$

gives

$$\left(\frac{x_{lk}}{x_{hk}}\right)_n \leqq \frac{Fz_{Flk} + \left(\frac{V_n}{V_m} - 1\right) Wx_{Wlk}}{Fz_{Fhk} + \left(\frac{V_n}{V_m} - 1\right) Wx_{Whk}} \tag{9-5}$$

Also, by this criterion the x ratio on the $(n + 1)$th plate should be greater when calculated by the upper than by the lower operating line:

$$\left(\frac{x_{lk}}{x_{hk}}\right)_{n+1} = \frac{y_{nlk} - (D/V_n)x_{Dlk}}{y_{nhk} - (D/V_n)x_{Dhk}} \geqq \frac{y'_{nlk} + (W/V_m)x_{Wlk}}{y'_{nhk} + (W/V_m)x_{Whk}} \tag{9-6}$$

where y_n = mol fraction in vapor from plate n when feed is added to plate n

y'_n = mol fraction in vapor from plate n when feed is added to plate $n + 1$

Again using $y_n = y'_n$ gives

$$\left(\frac{x_{lk}}{x_{hk}}\right)_{n+1} \geqq \frac{z_{Flk} + (W/V_m)(p + 1)x_{Wlk}}{z_{Fhk} + (W/V_m)(p + 1)x_{Whk}} \tag{9-7}$$

The right-hand sides of Eqs. (9-5) and (9-7) are equivalent and equal to $(x_{lk}/x_{hk})_i$ as given by the intersection of the operating line; thus, since n is now the optimum feed plate, the subscript may be changed, and the criterion for the feed-plate step becomes

$$\left(\frac{x_{lk}}{x_{hk}}\right)_{f+1} \geqq \frac{z_{Flk} + (W/V_m)(p + 1)x_{Wlk}}{z_{Fhk} + (W/V_m)(p + 1)x_{Whk}} = \left(\frac{x_{lk}}{x_{hk}}\right)_i \geqq \left(\frac{x_{lk}}{x_{hk}}\right)_f \tag{9-8}$$

where $(x_{lk}/x_{hk})_i$ is the ratio of the key components as given by the intersections of the operating lines. However, it should be emphasized that the feed plate does not necessarily step across the intersection of the operating lines, as it does for a binary, but simply that the ratio of the keys for the optimum feed-plate step passes over the ratio of the values given by the operating-line intersections. The absolute value of both key components may be several times the values given at the intersection, provided the ratio satisfies Eq. (9-8).

The derivations of Eqs. (9-5) and (9-7) neglected the effect of the changing concentrations of the light and heavy components. The light components have a relative constant concentration above the feed plate, and this fact can be used to calculate their value. Thus,

$$V_n y_{ln} = O_{n+1} x_{l(n+1)} + D x_{Dl}$$

and, assuming

$$x_{ln} = x_{l(n+1)}$$
$$y_{ln} = K x_{ln}$$

giving

$$y_{ln} = \frac{Dx_{Dl}}{V_n - (O_n/K_l)}$$

As shown on page 228, the concentration of a light component changes approximately by a factor of O_m/V_mK_l per plate below the feed plate. Thus the change in the concentration of a light component per plate at the feed plate is

$$y_l\left(1 - \frac{O_m}{V_mK_l}\right) = \left(\frac{Dx_{Dl}}{V_n}\right)\frac{1 - (O_m/V_mK_l)}{1 - (O_n/V_nK_l)} \tag{9-9}$$

and for most cases $Dx_{Dl} = Fz_{Fl}$.

Let Δ_l equal the sum of the changes per plate for all light components, then

$$\Delta_l = \frac{1}{V_n}\sum_{lk+}\left(Fz_{Fl}\frac{1 - \dfrac{O_m}{V_mK_l}}{1 - \dfrac{O_n}{V_nK_l}}\right) \tag{9-10}$$

where $\sum_{lk+}$ is the sum of the term for all components more volatile than the light key components.

In a similar manner the sum of the changes in the vapor concentrations for the heavy components per plate at the feed plate, Δ_h, can be calculated.

$$\Delta_h = \frac{1}{O_m}\sum_{hk+}\left(K_hFz_{Fh}\frac{1 - \dfrac{K_hV_n}{O_n}}{1 - \dfrac{K_hV_m}{O_m}}\right) \tag{9-11}$$

where $\sum_{hk+}$ is the summation for all terms less volatile than the heavy key components.

The corrections due to these changes can be utilized (1) to calculate terms to be added to the intersection ratio $(x_{lk})/x_{hk})_i$ or (2) to modify the expression for the intersection ratio. The relations can be formulated so that both methods give essentially the same optimum ratio for the key components at the feed plate. The latter method is believed to be the more convenient, and using ϕ as the optimum ratio, an approximate expression is

$$\phi = \frac{Fz_{Flk} + \left[\dfrac{V_n(1 - \Delta_l)^2}{V_m(1 - \Delta_h)} - 1\right]Wx_{Wlk}}{Fz_{Fhk} + \left[\dfrac{V_n(1 - \Delta_l)^2}{V_m(1 - \Delta_h)} - 1\right]Wx_{Whk}} \tag{9-12}$$

In using this expression, it is recommended that K_l and K_h be calculated as (α_l/α_{lk}) and (α_h/α_{lk}), respectively. This expression is similar to that for the intersection ratio, but if Δ_l is large, ϕ will be larger than $(x_{lk})/(x_{hk})_f$; if Δ_h is large, ϕ will be smaller. Using these corrections, the optimum feed-plate location is such that

$$\left(\frac{x_{lk}}{x_{hk}}\right)_f \leqq \phi \leqq \left(\frac{x_{lk}}{x_{hk}}\right)_{f+1}$$

Optimum Feed-plate Location. The use of Eq. (9-12) will be illustrated by the examples already considered.

1. *Benzene-Toluene-Xylene* example

$$K_h = \frac{0.45}{2.5} = 0.18; \qquad O_n = 120.2; \qquad O_m = 220.2$$

$$V_n = V_m = 180.3$$

$$\Delta_l = 0$$

$$\Delta_h = \frac{0.18}{220.2}(10)\frac{1 - \dfrac{0.18(180.3)}{120.2}}{1 - \dfrac{0.18(180.3)}{220.2}} = 0.007$$

$$\phi = \frac{60}{30 + \left(\dfrac{1}{0.993} - 1\right)29.7} = 1.98$$

In this case ϕ is essentially the same as the intersection ratio of the operating line which was 2.0.

2. *Phenol-Cresol*

$$D = 33.05; \qquad O_n = 330.5; \qquad O_m = 430.5; \qquad V_n = V_m = 363.6$$

mC_7: $K_h = \dfrac{0.675}{1.26} = 0.54$

C_8: $K_h = \dfrac{0.392}{1.26} = 0.31$

R: $K_h = \dfrac{0.087}{1.26} = 0.07$

$$\Delta_l = 0$$

$$\Delta_h = \frac{1}{430.5}\left[0.54(30)\frac{1 - \dfrac{0.54(363.6)}{330.5}}{1 - \dfrac{0.54(363.6)}{430.5}} + 0.31(15)\frac{1 - \dfrac{0.31(363.6)}{330.5}}{1 - \dfrac{0.31(363.6)}{430.5}} + 0.07(5)\frac{1 - \dfrac{0.07(363.6)}{330.5}}{1 - \dfrac{0.07(363.6)}{430.5}}\right] = 0.039$$

$$\phi = \frac{35 + \left(\dfrac{1}{0.961} - 1\right)3.5}{15 + \left(\dfrac{1}{0.961} - 1\right)13.5} = 2.26$$

As compared to the intersection ratio of $^{8}5/_{15} = 2.33$. In the stepwise calculation, the ratio of the key components in the feed plate was 2.08 and 2.31 on the plate above. Thus the feed-plate composition utilized agrees with Eq. (9-12) satisfactorily.

In the foregoing derivations the feed could be vapor, liquid, or a mixture of the two, but it was assumed that the vapor and liquid leaving the feed plate were in equilibrium. In the case of an all-vapor feed that mixes with the vapor from the feed plate but does not react with the liquid on the plate, a similar derivation gives (Ref. 1)

$$\left(\frac{x_{lk}}{x_{hk}}\right)_{f+1} = \left(\frac{x_{lh}}{x_{hk}}\right)_{i} = \left(\frac{x_{lk}}{x_{hk}}\right)_{f+2}$$

This indicates the ratios of the concentrations of the key components on the plate above the feed plate, and the plate above that should straddle the intersection ratio for the key components. Or, if the nomenclature is changed such that the feed plate is the first plate with which this feed vapor reacts (*i.e.*, the plate above) and not the plate into which it enters, then the criterion becomes the same as before.

Minimum Reflux Ratio. As in the case of binary mixtures, there is a reflux ratio below which it is not possible to obtain the desired separation of a multicomponent mixture even when an infinite number of plates is used. The calculation of this minimum for a multicomponent mixture is much more involved than for the corresponding binary mixture. The condition of the minimum reflux ratio requires that to perform the given separation an infinite number of plates must be needed, which means that there must be a pinched-in region where there are a large number of plates having the same composition, but for multicomponent mixtures of normal volatility this region usually does not occur at the feed plate as it does in the case of binary mixtures. Under this condition usually a relatively few plates above the feed serve to reduce the concentrations of the components less volatile than the heavy key component to negligible values, and then a true pinched-in condition does occur with only the heavy key and more volatile components present. Likewise, below the feed plate a relatively few plates reduce the concentrations of the components more volatile than the light key component to negligible values, and a true pinched-in condition occurs with only the light key and less volatile components present. Thus the tower operating at the minimum reflux ratio might be considered as being composed of five sections (Ref. 2):

(1) Starting at the still the only components present in significant

amounts are the light key and the less volatile components, and in proceeding up the tower in this bottom section, the concentration of the light key component increases relative to the concentrations of the heavy key and heavier components.

2. Above section 1 is a pinched-in region where the concentrations of the light key and the less volatile components are all constant, and an infinite number of plates is required to produce a finite change in the plate composition.

3. Next there is an intermediate region where the concentrations of the components less volatile than the heavy key component decrease to negligible values and where the concentrations of the components more volatile than the light key component increase to significant values.

4. Above section 3 is another pinched-in region where the concentrations of the heavy key and the more volatile components are all constant, and an infinite number of the plates is required to produce a finite change in plate composition.

5. A section exists where the concentration of the heavy key component decreases relative to the concentration of the more volatile components until the overhead composition is obtained.

Actually there is no sharp line of demarcation between these five sections, but this division serves as a useful picture for considering the case of the minimum reflux ratio. The feed to the fractionating column would be introduced on some plate in intermediate section 3, and the true criterion for the minimum reflux ratio should be based on matching the ratio of the concentrations of the key components above and below the feed plate under conditions such that a pinched-in section occurs both above and below the feed plate. For mixtures of normal volatility, a pinched-in region in only one section does not necessarily mean that an infinite number of plates would be required to perform the desired separation at the reflux ratio under consideration, since by relocating the feed plate, such as to shift the ratio of the concentrations of the key components at this plate, the section that was not limited could be made to do more separation and thereby relieve the load on the pinched-in section. In other words, for mixtures of normal volatilities the condition of the minimum reflux ratio is not determined by either the fractionation above or below the feed plate alone, but is determined such that the separation is limited both above and below the feed.[1] The conditions in the intermediate feed section lead to

[1] For mixtures with abnormal volatilities the pinched-in condition may be due to

calculational difficulties because the concentrations are not constant in this region. Actually in this region the ratios of the concentrations of the key components generally change in the opposite direction from that desired for the separation; thus, proceeding up the column from the feed plate at the minimum reflux ratio, the ratio of the concentrations of the light key to the heavy key component decreases instead of increases. No satisfactory method of estimating the extent of this "retrograde" rectification has been developed. However, it is relatively simple to calculate the plate composition for a region where the concentrations are the same on successive plates, and such calculations can be made the basis for estimating the minimum reflux ratio.

Case I. It can be assumed that the concentrations of all components are constant for a number of plates above and below the feed plate. This requires that the pinched-in condition between the key components must occur with all the components present in significant amounts; actually, as pointed out before, only certain of the components are present at the pinched-in condition. The presence of these extra components makes the separation more difficult, and for that reason the minimum reflux ratio calculated on the basis of the assumptions of Case I will be equal to or greater than the true minimum reflux ratio.

Case II. Alternately it can be assumed that the ratio of the concentrations of the key components for the pinched-in region below the feed plate (section 2) can be matched with the same ratio for the pinched-in region above the feed plate (section 4), which amounts to neglecting the intermediate region (section 3). However, for the actual operation section 3 must be present and in this section the ratio of the concentrations of the key components changes in the opposite direction to that desired for the separation; for that reason, the assumptions of Case II correspond to an easier separation than the actual case, and the minimum reflux ratio calculated by these assumptions will be equal to or less than the true minimum reflux ratio.

Calculation of the minimum reflux ratio for these two cases will give limits for the true minimum reflux ratio. To evaluate these cases, it is necessary to calculate the concentrations of the various components for the pinched-in or constant composition regions. Such compositions are easily calculated by the use of the relative volatility, α, and the fact that the ratio of the concentrations of any two components are

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a tangent contact between the equilibrium curve and the operating line, and the separation will not be limited both above and below the feed plate.

the same on successive plates; thus for the volatile components above the feed plate,

$$\frac{\alpha_l}{\alpha_{hk}}\frac{x_l}{x_{hk}} = \frac{y_l}{y_{hk}} = \frac{(O/D)x_l + x_{Dl}}{(O/D)x_{hk} + x_{Dhk}} = \frac{\alpha_l}{\alpha_{hk}}\left[\frac{(V/D)y_l - x_{Dl}}{(V/D)y_{hk} - x_{Dhk}}\right]$$

giving

$$x_l = \frac{\alpha_{hk}x_{Dl}(D/O)}{\alpha_l - \alpha_{hk} + \alpha_l\,(x_{Dhk}/x_{hk})(D/O)} \tag{9-13}$$

and

$$y_l = \frac{\alpha_l x_{Dl}(D/V)}{\alpha_l - \alpha_{hk} + \alpha_{hk}(x_{Dhk}/y_{hk})(D/V)} \tag{9-14}$$

and, for less volatile components below the feed plate,

$$\frac{\alpha_{lk}x_{lk}}{\alpha_h x_h} = \frac{y_{lk}}{y_h} = \frac{(O_m/W)x_{lk} - x_{Wlk}}{(O_m/W)x_h - x_{Wh}} = \frac{\alpha_{lk}[(V_m/W)y_{lk} + x_{Wlk}]}{\alpha_h[(V_m/W)y_h + x_{Wh}]} \tag{9-15}$$

giving

$$x_h = \frac{\alpha_{lk}x_{Wh}(W/O_m)}{\alpha_{lk} - \alpha_h + \alpha_h\left(\dfrac{W}{O_m}\right)\dfrac{x_{Wlk}}{x_{lk}}}$$

and

$$y_h = \frac{\alpha_h x_{Wh}(W/V_m)}{\alpha_{lk} - \alpha_h + \alpha_{lk}\left(\dfrac{W}{V_m}\right)\dfrac{x_{Wlk}}{y_{lk}}} \tag{9-16}$$

In these equations the last term of the denominator is usually small relative to the other factors and can be neglected for the first estimations, making only the flow quantities, relative volatilities, and terminal concentrations necessary for the calculation of the asymptotic values. Corrections can then be made for the last term in the denominators, but usually this is not necessary.

These equations can be used to calculate the concentrations of the key components for evaluating the minimum reflux ratios for Cases I and II, which would involve matching the ratio of the concentrations of the key components above the feed plate with the same ratio below the feed plate. This leads to a quadratic solution for the minimum reflux ratio. Thus for Case I the ratio of the key components above and below the feed plate are equated, and allowance is made for all components at their asymptotic values in both sections.

$$\left(\frac{x_{lk}}{x_{hk}}\right)_m = \frac{1 - x_{hk} - \sum_h x_h - \sum_l x_l}{x_{hk}} = \left(\frac{x_{lk}}{x_{hk}}\right)_n = \frac{x_{lk}}{1 - x_{lk} - \sum_h x_h - \sum_l x_l}$$

On substituting the values of Eqs. 9-13 and 9-15 and rearranging,

$$\left(\frac{O}{D}\right)_m = \frac{\left(\frac{W}{D}I + J\right) + \sqrt{\left(\frac{W}{D}I + J\right)^2 - \frac{4W}{D}(IJ - GH)}}{2} \tag{9-17}$$

In Case II, below the feed plate only the light key and less volatile components are considered; above the feed plate, only the heavy key and more volatile components are considered:

$$\left(\frac{x_{lk}}{x_{hk}}\right)_m = \frac{1 - x_{hk} - \sum_h x_h}{x_{hk}} = \left(\frac{x_{lk}}{x_{hk}}\right)_n = \frac{x_{lk}}{1 - x_{lk} - \sum_l x_l}$$

The solution of this equation is the same as Eq. (9-17), but instead of I and J, I' and J', respectively, are used. Where

$$C^* = \frac{1}{x_{Dlk}}\left[\alpha_{lk} - \alpha_{hk} + \alpha_{lk}\left(\frac{x_{Dhk}}{x_{hk}}\right)\left(\frac{D}{O}\right)\right]$$

D = mols of distillate per unit time

$$E = \frac{1}{x_{Whk}}\left[\alpha_{lk} - \alpha_{hk} + \alpha_{hk}\left(\frac{x_{Wlk}}{x_{lk}}\right)\left(\frac{W}{O_m}\right)\right]$$

F = mols of feed per unit time

$$G = \frac{\alpha_{lk}}{E}$$

$$H = \frac{\alpha_{hk}}{C^*}$$

$$I = \frac{pF}{W} + \frac{\alpha_{lk}}{E} + (\alpha_{lk})\sum_h\left[\frac{x_{Wh}}{\alpha_{lk} - \alpha_h + \alpha_h\left(\frac{x_{Wlk}}{x_{lk}}\right)\left(\frac{W}{O_m}\right)}\right] + \alpha_{hk}\left(\frac{D}{W}\right)\left(\frac{O_m}{O_n}\right)\sum_l\left[\frac{x_{Dl}}{\alpha_l - \alpha_{hk} + \alpha_l\left(\frac{x_{Dhk}}{x_{hk}}\right)\left(\frac{D}{O}\right)}\right]$$

$$J = \frac{\alpha_{hk}}{C} + \alpha_{lk}\left(\frac{W}{D}\right)\left(\frac{O_n}{O_m}\right)\sum_h\left[\frac{x_{Wh}}{\alpha_{lk} - \alpha_h + \alpha_h\left(\frac{x_{Wlk}}{x_{lk}}\right)\left(\frac{W}{O_m}\right)}\right] + \alpha_{hk}\sum_l\left[\frac{x_{Dl}}{\alpha_l - \alpha_{hk} + \alpha_l\left(\frac{x_{Dhk}}{x_{hk}}\right)\left(\frac{D}{O}\right)}\right]$$

$$I' = \frac{pF}{W} + \frac{\alpha_{lk}}{E} + \alpha_{lk} \sum_h \left[\frac{x_{Wh}}{\alpha_{lk} - \alpha_h + \alpha_h \left(\frac{x_{Wlk}}{x_{lk}}\right)\left(\frac{W}{O_m}\right)} \right]$$

$$J' = \frac{\alpha_{hk}}{C} + \alpha_{hk} \sum_l \left[\frac{x_{Dl}}{\alpha_l - \alpha_{hk} + \alpha_l \left(\frac{x_{Dhk}}{x_{hk}}\right)\left(\frac{D}{O}\right)} \right]$$

(See nomenclature at the end of this chapter.)

These equations should not be applied to mixtures having minimum reflux ratios determined by a tangent contact in one section of the tower only. It is customary to use relative volatility values corresponding to approximately the feed-plate temperature. Actually some of the values correspond to the pinched-in region above the feed and the others to the lower section, but usually this refinement is not made although it can be done if necessary.

In addition to Eq. (9-17), it is possible to develop a large number of alternate relations. The most helpful of those are obtained by equating the ratio of the key components at the pinched-in region to the optimum feed-plate ratio.

Matching the optimum feed-plate ratio, ϕ, with the pinched-in region,

$$\phi = \frac{\alpha_{hk}}{\alpha_{lk}} \left(\frac{y_{lk}}{y_{hk}}\right) = \left[\frac{(O/D)x_{lk} + x_{Dlk}}{(O/D)x_{hk} + x_{Dhk}} \right] \frac{\alpha_{hk}}{\alpha_{lk}} \tag{9-18}$$

and solving for O/D,

$$\frac{O}{D} = \frac{(\alpha_{hk} x_{Dlk}/\phi) - \alpha_{lk} x_{Dhk}}{(\alpha_{lk} - \alpha_{hk}) x_{hk}}$$

Equation (9-18) is applicable to either binary or multicomponent mixtures, and the problem is one of evaluating x_{hk}.

For Case I:

$$x_{hk} = 1 - x_{lk} - \sum x_l - \sum x_h = \frac{1 - \Sigma x_l - \Sigma x_h}{1 + \phi} \tag{9-19}$$

For Case II:

$$x_{hk} = 1 - x_{lk} - \sum x_l = \frac{1 - \Sigma x_l}{1 + \phi}$$

or, in general,

$$x_{hk} = \frac{\beta}{1 + \phi}$$

where $\beta = 1$ for a binary
$= 1 - \Sigma x_l$ for Case II
$= 1 - \Sigma x_l - \Sigma x_h$ for Case I

The terms Σx_l and Σx_h can be evaluated by Eqs. (9-13) and (9-15) to give

$$\left(\frac{O}{D}\right)_{\min} = \frac{\frac{\alpha_{hk}x_{Dlk}}{\phi} - \alpha_{lk}x_{Dhk}}{\alpha_{lk} - \alpha_{hk}}(1 + \phi) + \alpha_{hk}\sum_{lk+}\left(\frac{x_{Dl}}{\alpha_l - \alpha_{hk}}\right) + \alpha_{lk}\frac{W}{D}\left(\frac{O_n}{O_m}\right)\sum_{hk+}\left(\frac{x_{Wh}}{\alpha_{lk} - \alpha_h}\right) \quad (9\text{-}20)$$

The first term is the minimum reflux ratio for a binary mixture with the same ratio of key components in the distillate and ϕ. Equation (9-20) can be written

$$\left(\frac{O}{D}\right)_{\min} = \left(\frac{O}{D}\right)_{B\min} + \alpha_{hk}\sum\left(\frac{x_{Dl}}{\alpha_l - \alpha_{hk}}\right) + \alpha_{lk}\left(\frac{W}{D}\right)\left(\frac{O_n}{O_m}\right)\sum\left(\frac{x_{Wh}}{\alpha_{lk} - \alpha_h}\right) \quad (9\text{-}21)$$

Equation (9-20) involves no trial and error if $O_n = O_m$, but it does for other cases. By equating the liquid-phase ratios instead of the vapor-phase ratios of Eq. (9-18), one obtains

$$\left(\frac{O}{D}\right)_{\min} + 1 = \left(\frac{\frac{\alpha_{hk}x_{Dlk}}{\phi} - \alpha_{hk}x_{Dhk}}{\alpha_{lk} - \alpha_{hk}}\right)\left(1 + \frac{\alpha_{lk}}{\alpha_{hk}}\phi\right) + \sum\left(\frac{\alpha_l x_{Dl}}{\alpha_l - \alpha_{hk}}\right) + \frac{W}{D}\left(\frac{V_n}{V_m}\right)\sum\left(\frac{\alpha_h x_{Wh}}{\alpha_{lk} - \alpha_h}\right) \quad (9\text{-}22)$$

This equation requires no trial and error for $V_n = V_m$. The first bracket again corresponds to the binary mixture case for the same ϕ and ratio of key components in the distillate.

Equations (9-20) and (9-22) are given for Case I, and for Case II the last term involving x_{Wh} is eliminated.

Similar equations can be derived by equating the ratio of key components below the feed plate to ϕ. Thus,

$$\left(\frac{O}{D}\right)_{\min} = \frac{W}{D}\left(\frac{O_n}{O_m}\right)\left[\frac{\alpha_{lk}x_{Whk} - \frac{\alpha_{hk}x_{Wlk}}{\phi}}{\alpha_{lk} - \alpha_{hk}}(1 + \phi)\right] + \alpha_{lk}\frac{W}{D}\left(\frac{O_n}{O_m}\right)\sum\left(\frac{x_{Wh}}{\alpha_{lk} - \alpha_h}\right) + \alpha_{hk}\sum\left(\frac{x_{Dl}}{\alpha_l - \alpha_{hk}}\right) \quad (9\text{-}23)$$

and

$$\left(\frac{O}{D}\right) + 1 = \left\{\frac{V_n W}{V_m D}\left[\alpha_{hk}\left(x_{Whk} - \frac{x_{Wlk}}{\phi}\right)\left(1 + \frac{\alpha_{lk}\phi}{\alpha_{hk}}\right)\right]\left(\frac{1}{\alpha_{lk} - \alpha_{hk}}\right)\right.$$
$$\left. + \frac{W}{D}\left(\frac{V_n}{V_m}\right)\sum\left(\frac{\alpha_h x_{Wh}}{\alpha_{lk} - \alpha_h}\right) + \sum\left(\frac{\alpha_l x_{Dl}}{\alpha_l - \alpha_{hk}}\right)\right\} \quad (9\text{-}24)$$

These two equations correspond to Case I; Case II is obtained by omitting the last term involving x_{Dl} in each equation. The bracketed terms are again the minimum reflux ratios for the binary for the same ϕ and ratio of key components.

If there are no components heavier than the heavy key component, Eqs. (9-20) and (9-22) should give essentially the true minimum reflux ratio; if there are no components lighter than the light key, Eqs. (9-23) and (9-24) should give the desired answer. In case both light and heavy components are present, the choice should be based on the relative size of the terms involving the heavy and light components. If the term involving the summation of the heavy terms is greater than the summation of the light terms, then Eqs. (9-23) and (9-24) are preferred to Eqs (9-20) and (9-22), and vice versa. The choice between Eqs. (9-20) and (9-22) and between Eqs. (9-23) and (9-24) is purely a matter of convenience.

In the use of Eqs. (9-17) to (9-24) the values of the concentration needed were calculated by difference. For example, in deriving Eq. (9-17), the concentration of the heavy key component was calculated as,

$$x_{hk} = 1 - x_{lk} - \Sigma x_l - \Sigma x_h$$

Instead of this relation, it is possible to use

$$x_{hk} = \frac{y_{hk}/\alpha_{hk}}{(y_{hk}/\alpha_{hk}) + (y_{lk}/\alpha_{lk}) + \Sigma(y_l/\alpha_l) + \Sigma(y_h/\alpha_h)}$$

and other equations would be obtained but they give essentially the same results (Ref. 8).

As a result of the various approximations involved, a large number of approximate equations can be derived. For the general case, none of them gives the exact answer. The ones given here have proved to be of real utility. Equation (9-17) is probably the most general and, using the proper relative volatility, it should give answers for Cases I and II that are above and below the true minimum reflux ratio. The other equations presented involve an approximate expression for the

ratio of the key components at the feed plate. It is therefore not so certain that the upper and lower values will bracket the true minimum reflux ratio but in most cases they do. Equations (9-20) to (9-24) are in general considerably easier to employ than Eq. (9-17) and, for that reason, are more commonly used. When it becomes possible to predict exactly the extent of the retrograde fractionation in the feed-plate section, it will be possible to develop exact equations for the minimum reflux ratio.

The foregoing derivations were made on the assumption that there were no components heavier than the heavy key components at the upper pinched-in region and no components lighter than the light key components at the lower pinched-in region. This is not completely true. If there are components only slightly heavier than the heavy key components or only slightly more volatile than the light key, it is possible for them to be present at the pinched-in region. This can be shown as follows:

Consider the pinched-in section below the feed plate, then $x_m = x_{m+1}$ for all components present and

$$\begin{aligned} V_m y_m &= O_{m+1} x_{m+1} - W x_W \\ y_m &= K x_m \\ x_m &= x_{m+1} \end{aligned}$$

and combining and solving for x_m the value at the pinched-in region,

$$x_m = \frac{(W/O_m) x_W}{1 - (V_m K/O_m)}$$

For the light key and the heavier components the value of x_m is positive and finite, which necessitates $V_m K/O_m$ being less than 1.0. For the light key components $W x_W/O_m$ is usually small in comparison to x_m which results from $V_m K/O_m$ being only slightly less than 1.0. If a more volatile component has a K value significantly larger than K_{lk}, then for that constituent $V_m K/O_m$ would be greater than 1.0 and the only solution for the above equation is $x_W = 0$ (assuming that this component is not being added below this region which could give negative values of x_W). The zero value for x_W was the condition assumed for the light components in the derivations of Eqs. (9-17) to (9-24), and in most cases it applies to all components having K values 20 per cent or more greater than K_{lk}. However, it is possible for a component to have a K value only slightly greater than K_{lk} and such that $V_m K/O_m$ is still less than 1.0. This type of component could appear at the lower pinched-in region in significant amounts, and its concen-

tration should be included in calculations for Case II. Case I equations have already included a provision for such a component.

The derivation of the minimum reflux ratio equations does not take into account the possibility of components intermediate in volatility to the two key components. When such components are present, they distribute themselves between the distillate and the bottoms, and distribution is a function of the reflux ratio; *i.e.*, the percentage of such a component that goes overhead will be different at total reflux than at the minimum reflux ratio. Such components can be included in the minimum reflux ratio equations either as light or heavy components but to do so requires their concentration in the distillate or bottoms. It is suggested that this distribution be made such that the values of their mol fraction as calculated by Eqs. (9-13) and (9-15) are equal.

These equations will be applied to some of the previous examples.

Minimum Reflux Ratio Examples. 1. *Benzene-Toluene-Xylene* (page 219). The key components are benzene and toluene, and the design conditions are given below. Since there are no components lighter than the light key and since $V_n = V_m$, Eq. (9-24) will be employed.

$$F = 100 \text{ mols}; \quad W = 39.9 \text{ mols}; \quad D = 60.1 \text{ mols}$$
$$\alpha_{lk} = 2.5; \quad \alpha_{hk} = 1.0; \quad \alpha_h = 0.45$$
$$\phi = 1.98 \text{ (see page 248)}$$

$$\left(\frac{O}{D}\right)_{\min} + 1 = \frac{39.9}{60.1}\left[\frac{1.0\left(0.744 - \frac{0.005}{1.98}\right)}{2.5 - 1.0}\right][1 + 2.5(1.98)] + \frac{39.9}{60.1}\left[\frac{0.45(0.251)}{2.5 - 0.45}\right] = 1.96 + 0.04$$

$$\left(\frac{O}{D}\right)_{\min} = 1.0$$

This value should be nearly exact because, in addition to the key components only heavy components were present and in small amounts. The value of ϕ used was for a reflux ratio $(O/D) = 2.0$ and should be rechecked.

$$\Delta_h = \frac{0.18}{160.1}(10)\frac{1 - \frac{0.18(120.2)}{60.1}}{1 - \frac{0.18(120.2)}{160.1}} = 0.008$$

$$\phi = \frac{60}{30 + \left(\frac{1}{0.992} - 1\right)29} = 1.98$$

so the assumed value was satisfactory.

As a comparison, use Eq. (9-17) and neglect the small correction terms. Assume $(O/D)_{\min} = 1.0$.

$$C = \frac{1}{0.995}(2.5 - 1.0) = 1.505$$

$$E = \frac{1}{0.744}(2.5 - 1.0) = 2.02$$

$$G = \frac{2.5}{2.02} = 1.24$$

$$H = \frac{1.0}{1.505} = 0.665$$

$$I = \frac{-100}{39.9} + 1.24 + 2.5\left(\frac{0.251}{2.5 - 1.0}\right) = -0.84$$

$$J = 0.665 + 2.5\left[\frac{39.9(60.1)}{60.1(160.1)}\right]\left(\frac{0.251}{2.5 - 1.0}\right) = 0.77$$

$$I' = -0.84$$

$$J' = 0.665$$

Case I:

$$\frac{W}{D} I + J = \frac{39.9}{60.1}(-0.84) + 0.77 = 0.213$$

$$IJ - GH = -0.84(0.77) - 1.24(0.665) = -1.47$$

$$\left(\frac{O}{D}\right)_m = \frac{0.213 + \sqrt{(0.213)^2 - 4\dfrac{39.9}{60.1}(-1.47)}}{2} = 1.09$$

The calculated value is close enough to the assumed value of 1.0, and the trial will not be repeated.

Case II:

The calculation is the same except that I' and J' are employed.

$$\left(\frac{O}{D}\right)_{\min} = 1.01$$

In this example, the two cases give approximately the same result, but the Case II value should be essentially correct because no light components were present.

Values obtained with the other equations are summarized in the following table:

	$(O/D)_{\min}$	
	Case I	Case II
Eq. (9-24)	1.0	1 0
Eq. (9-17)	1.09	1.01
Eq. (9-23)	1.02	1 02
Eq. (9-20)	1.07	0 97
Eq. (9-22)	1 0	0.96

2. *Phenol-Cresol* (page 236).

$$F = 100 \qquad W = 66.84 \qquad D = 33.16$$

$$V_n = V_m, \quad \alpha_{lk} = 1.26, \quad \alpha_{hk} = 1.0, \quad \alpha_{mC_7} = 0.66, \quad \alpha_{C_8} = 0.39$$

$$\alpha_R = 0.087; \quad \phi = 2.26 \left(\text{for } \frac{O}{D} = 10\right)$$

Using Eq. (9-24),

$$\left(\frac{O}{D}\right)_{\min} = \frac{66.84}{33.16}\left\{\frac{1.0\left(0.202 - \dfrac{0.052}{2.26}\right)[1 + 2.26(1.26)]}{1.26 - 1}\right\} - 1$$
$$+ \frac{66.84}{33.16}\left[\frac{0.66(0.444)}{1.26 - 0.66} + \frac{0.39(0.224)}{1.26 - 0.39} + \frac{0.087(0.075)}{1.26 - 0.087}\right] = 5.36 - 1 + 1.21 = 5.6$$

Rechecking ϕ at $(O/D) = 5.6$,

$$\Delta_h = \frac{1}{286}\left[0.54(30)\frac{1 - \dfrac{0.54(219)}{186}}{1 - \dfrac{0.54(219)}{286}} + 0.31(15)\frac{1 - \dfrac{0.31(219)}{186}}{1 - \dfrac{0.31(219)}{286}} + 0.07(5)\frac{1 - \dfrac{0.07(219)}{186}}{1 - \dfrac{0.07(219)}{286}}\right] = 0.05$$

$$\phi = \frac{35 + \left(\dfrac{1}{0.95} - 1\right)3.5}{15 + \left(\dfrac{1}{0.95} - 1\right)13.5} = 2.24$$

This is close enough to the value of 2.26 employed so that no recalculation is necessary. In other cases, such as an all vapor feed, the value of ϕ varies much more with the reflux ratio.

3. If, in the preceding example, the feed condition had been such that $O_n = O_m$, a higher reflux ratio would have been required. As a first assumption, $(O/D)_{\min}$ will be taken as 7.0

$$O_n = 232 = O_m; \qquad V_n = 265; \qquad V_m = 165$$

Calculating ϕ,

$$\Delta_h = \frac{1}{232}\left[0.54(30)\frac{1 - \dfrac{0.54(265)}{232}}{1 - \dfrac{0.54(165)}{232}} + 0.31(15)\frac{1 - \dfrac{0.31(265)}{232}}{1 - \dfrac{0.31(165)}{232}} + 0.07(5)\frac{1 - \dfrac{0.07(265)}{232}}{1 - \dfrac{0.07(165)}{232}}\right] = 0.06$$

$$\phi = \frac{35 + \left[\dfrac{265}{165(0.94)} - 1\right]3.5}{15 + \left[\dfrac{265}{165(0.94)} - 1\right]13.5} = 1.52$$

Using Eq. (9-23),

$$\left(\frac{O}{D}\right)_{\min} = \frac{66.84}{33.16}\left[\frac{1.26(0.202) - \dfrac{0.052}{1.52}}{1.26 - 1}\right](1 + 1.52)$$
$$+ 1.26\left(\frac{66.84}{33.16}\right)\left(\frac{0.447}{1.26 - 0.66} + \frac{0.224}{1.26 - 0.39} + \frac{0.075}{1.26 - 0.87}\right) = 6.9$$

This value is near enough to the original assumption and no additional retrials will be made.

Gasoline-stabilization Example. As a further illustration of the use of these methods, a gasoline-stabilization operation will be considered. The feed composition is given in the table on this page and the tower is to operate at 250 p.s.i.g. A reflux ratio of 2 will be used in the upper portion of the tower, and the feed will enter such that $(O/V)_m$ below the feed will be 1.5. It is desired to recover 96 per cent of the normal butane with the stabilized gasoline, but this bottoms product is to contain not over 0.25 mol per cent propane.

In preparing this table, it was assumed that the concentrations of all components lighter than propane were negligible in the residue and that all components heavier than n-C_4 were negligible in the distillate. The isobutane is intermediate to the propane and n-butane and therefore will appear in appreciable quantities in both the distillate and residue. Since the i-C_4 is more volatile than n-C_4, the following table was prepared on the assumption that 20 per cent of the i-C_4 in the feed would appear in the overhead. The volatilities relative to n-C_4 are given in Fig. 9-13. These relative volatilities are based on the fugacity data of Lewis and coworkers (Ref. 6). The equilibrium constant K

Feed		Residue		Distillate	
	Mol, per cent	Mols/100 feed	Mol, per cent	Mols/100 feed	Mol, per cent
CH_4	2.0	—	—	2.0	6 33
C_2H_6	10.0	—	—	10 0	31 60
C_3H_6	6.0	—	—	6 0	19 00
C_3H_8	12.5	0 0025W	0.25	12.5 − 0 0025W	39 00
i-C_4H_{10}	3 5	2 8	4 10	0 7	2 2
n-C_4H_{10}	15.0	14.4	21 10	0.6	1.9
C_5	15.2	15 2	22.20		
C_6	11.3	11 3	16.50		
C_7	9.0	9.0	13.20		
C_8	8.5	8 5	12.40		
360°F.	7.0	7.0	10.20		
		68.2 + 0.0025W		31.8 − 0.0025W	

$$68.2 + 0.0025W = W$$
$$W = 68.4; \quad D = 31.6.$$

for n-C_4 is also plotted in this figure. Since the overhead is very volatile, it will be removed as a vapor, only enough liquid being pro-

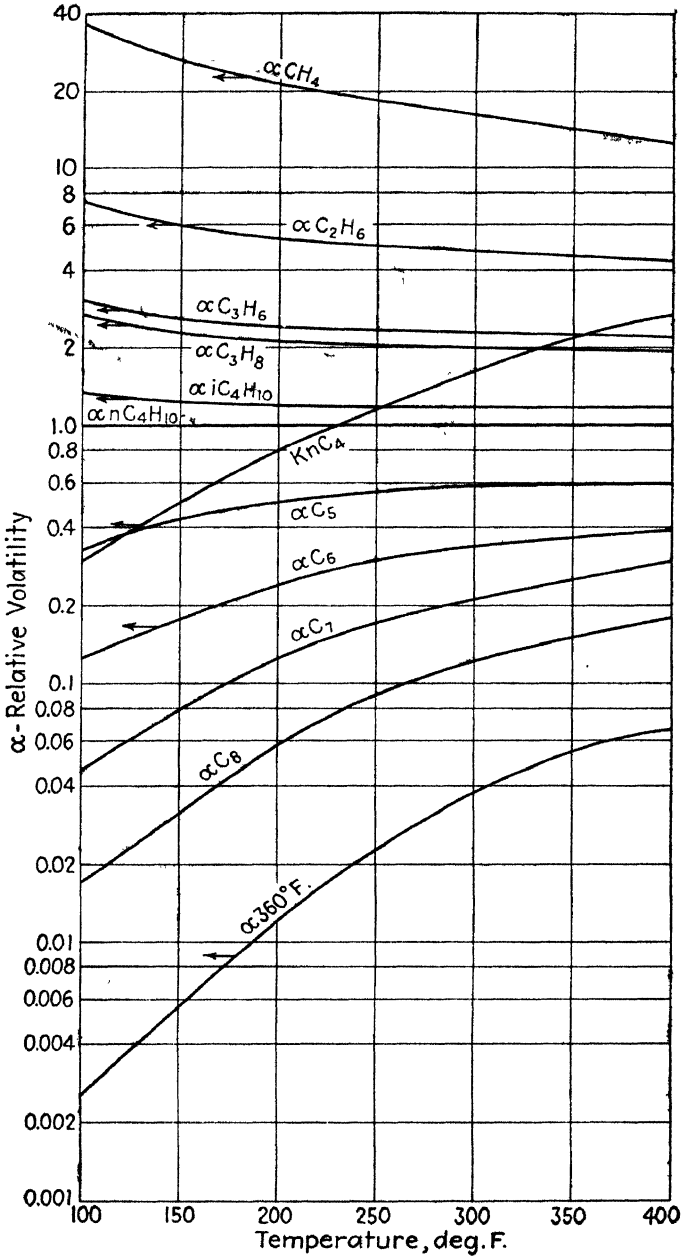

40
20
10
8
6
4
2
1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
0.008
0.006
0.004
0.002
0.001
α-Relative Volatility
αCH4
αC2H6
αC3H6
αC3H8
αiC4H10
αnC4H10
KnC4
αC5
αC6
αC7
αC8
α360°F.
100
150
200
250
300
350
400
Temperature, deg. F.

FIG. 9-13.

duced in the partial condenser to furnish reflux. It is assumed that the reflux from the condenser leaves in equilibrium with the product vapor.

Starting at the composition of the overhead vapor, the calculations are carried down the column by the use of the equations given on page 232 and the results are summarized in Table 9-2. The first coulmn of this table gives the components, the second column lists the vapor concentrations for the plate in question, and the third column gives the α values at the assumed temperature. The next column gives the values of the vapor concentrations divided by the relative volatility, and by using Eq. (9-3) on page 233, the liquid concentrations for this plate are obtained by dividing the values of the fourth column by the sum of all of the values in the fourth column. On the basis of 1 mol of overhead vapor or product, there are 2 mols of reflux, and for this reason the fifth column lists twice the concentrations obtained from column four and is therefore the actual mols of overflow for the basis chosen. There will be 3 mols of vapor to the plates, and the mols of each component in the vapor to any plate above the feed plate must equal the sum of the mols of that component in the product and in the overflow from that plate; *i.e.*, the sum of the values in column five plus the values in $y_{0\,\mathrm{H.}}$. These vapor values for the plate below are listed in the last column of the table. In Table 9-3, for the calculation beginning at the still, a similar procedure was used employing Eq. (9-2) on page 233 and using a basis of 1 mol of residue.

A temperature of 100°F. was assumed for the partial condenser, and the calculated temperatures based on $K_{n\text{-}C_4}$ are given for each plate. At the second plate below the top plate, the α values are shifted to 150°F. The liquid on the second plate below the top plate has a ratio of $C_3H_8/n\text{-}C_4$, a little higher than the feed ratio, and this plate will be made the last plate above the feed; *i.e.*, the feed plate will be the fourth from the top of the column. If an attempt is made to carry the calculations farther down the tower, a serious difficulty will be met in that no components heavier than $n\text{-}C_4$ have been considered, but they are much too large to be neglected below the feed plate. The most satisfactory solution to this difficulty is to carry out calculations starting at the still and continuing up to the feed plate. These calculations are presented in Table 9-3. Such calculations are continued until the ratio of $C_3H_8/n\text{-}C_4$ in the vapor from some plate is approximately the same as the ratio in the vapor calculated from the feed plate in Table 9-2. Thus, it is found that the vapor from plate 8 of Table 9-3 gives a ratio approximately equal to the ratio on the $T-3$ plate of Table 9-2.

TABLE 9-2
(Basis: 1 mol overhead vapor; $O/D = 2$)

	$y_{O.H.}$	α_{100}	$\frac{y_{O\,H}}{\alpha}$	$2x_R = \frac{2y_{O\,H}}{\alpha / \Sigma y/\alpha}$	$3y_T$
C_1	0.0633	36.5	0 00173	0.012	0.075
C_2	0.316	7.4	0 0427	0.296	0.612
C_3-	0.190	3.0	0 0633	0.440	0.630
C_3+	0 390	2.7	0 144	1.000	1 390
i-C_4	0.022	1.3	0 0169	0.117	0.139
n-C_4	0.019	1.0	0 019	0.132	0.151
			0 2876		

$K_{n\text{-}C_4} = 0.2876$ $T = 98°F.$

	$3y_T$	α_{100}	$3y_T/\alpha$	$2x_T$	$3y_{T-1}$
C_1	0.075	36 5	0.0021	0.004	0 067
C_2	0.612	7 4	0 0826	0 155	0 471
C_3-	0.630	3.0	0.210	0.394	0.584
C_3+	1.390	2 7	0 515	0.965	1 355
i-C_4	0.139	1 3	0 107	0.200	0 222
n-C_4	0.151	1.0	0 515	0 283	0 302
			1.067		

$K_{n\text{-}C_4} = 1.067/3 = 0.356$ $T = 120°F.$

	$3y_{T-1}$	α_{100}	$3y_{T-1}/\alpha$	$2x_{T-1}$	$3y_{T-2}$
C_1	0 067	36 5	0 0018	0 0029	0.066
C_2	0.471	7.4	0.0637	0.103	0.419
C_3-	0.584	3 0	0 195	0.316	0.506
C_3+	1.355	2.7	0.501	0.810	1.200
i-C_4	0.222	1.3	0 171	0.277	0.299
n-C_4	0.302	1.0	0.302	0.487	0.508
			1.2345		

$K_{n\text{-}C_4} = 0.41$ $T = 130°F.$

	$3y_{T-2}$	α_{150}	$3y_{T-2}/\alpha$	$2x_{T-2}$	$3y_{T-3}$
C_1	0.066	26	0 0025	0.003	0 066
C_2	0.419	6	0.070	0.091	0 407
C_3-	0.506	2.6	0.195	0.253	0.443
C_3+	1 200	2.3	0.522	0.678	1 068
i-C_4	0,299	1.23	0.243	0.315	p.337
n-C_4	0.508	1.0	0.508	0.660	0.679
			1.5405		

$K_{n\text{-}C_4} = 0.51$ $T = 150°F.$

Approximately eleven theoretical plates in addition to the still and partial condenser are required.

Feed-plate Matching. In the gasoline stabilization problem just considered, the vapor compositions obtained by calculating down from the condenser do not appear to match very satisfactorily with those obtained by calculations up from the still. This is due to the fact that, with the exception of propane, isobutane, and *n*-butane, the components involved in the two cases are different. In general, this condition is always encountered when there are components both more volatile than the light component and less volatile than the heavy component. In order to make the compositions match more exactly, it is necessary to introduce the light components into the calculations below the plate and the heavy components into the calculations above the feed plate. It is not necessary to repeat the calculations all the way from the still with all the light components. It is only necessary to drop back a sufficient number of plates such that the concentration of the component or components to be added will be small and can be added without altering the accuracy of the material balance.

Thus, in Table 9-4 the results of Table 9-3 are dropped back to the seventh plate and small concentrations of C_2 and C_3 are added; and then on the eighth plate the C_1 is introduced. It is obvious that the concentration of these light components should be added such that the vapor from the eighth plate will match the composition of these components as determined by the calculations for the top section.

This matching is complicated by the fact that the values of light components obtained for the top section of the tower in the first calculations will be reduced somewhat by the introduction of the heavy components into this section, and it is therefore a matter of successive approximations to obtain an exact match. The quantity of the components to be added on a given plate to obtain a desired value requires trial and error but can be simplified by the fact that for a light component below the feed plate the operating line is essentially $V_m y_m = O_{m+1} x_{m+1}$, since the value of $W x_W$ is negligible. This can be combined with the equilibrium constant to give $x_{m+1} = K_m (V/O)_m x_m$. Thus the increase in concentration per plate for a light component in the lower portion of the tower is essentially equal to the equilibrium constant times the V/O ratio. Instead of K the value of $\alpha/(\Sigma \alpha x)$ can be used. These relations make it relatively easy to estimate the number of plates that should be recalculated to obtain the desired values. Above the feed plate, a similar relationship can be developed for the heavy components, and the decrease in concentration of such a

component per plate is given by $K_m(V/O)_m$ or $(\alpha/\Sigma \alpha x)(V/O)_m$.

TABLE 9-3

Basis: 1 mol residue; $(O/V)_m = 1.5$

	x_W	α_{300}	αx_W	$2y_W = 2\alpha x_W/\Sigma\alpha x$	$3x_1$
C_3+	0 0025	2.0	0 005	0 020	0.0225
i-C_4	0 041	1 18	0 048	0 191	0.232
n-C_4	0 211	1 0	0 211	0.840	1.051
C_5	0 222	0 58	0.129	0.513	0 735
C_6	0.165	0.38	0 0627	0.249	0.414
C_7	0 132	0 215	0 0284	0 115	0 247
C_8	0 125	0.12	0.0150	0 060	0.185
360°F.	0.102	0.038	0.0039	0.016	0 118
			0.503		

$K_{n\text{-}C_4} = 1/0.503 = 1.99$ $T = 333$°F.

	$3x_1$	α_{300}	$3\alpha x_1$	$2y_1$	$3x_2$
C_3+	0 0225	2 0	0 045	0 044	0.0465
i-C_4	0.232	1.18	0 273	0.269	0 310
n-C_4	1 051	1.0	1 051	1.035	1 246
C_5	0 735	0.58	0 426	0.420	0 642
C_6	0 414	0 38	0 157	0 155	0.320
C_7	0.247	0 215	0 053	0 052	0 184
C_8	0.185	0 12	0 022	0 022	0.147
360°F.	0 118	0.038	0.005	0 005	0 107
			2 032		

$K_{n\text{-}C_4} = 3/2.032 = 1.48$ $T = 285$°F.

	$3x_2$	α_{300}	$3\alpha x_2$	$2y_2$	$3x_3$
C_3+	0.0465	2.0	0.093	0 082	0 0845
i-C_4	0.310	1 18	0 365	0 323	0 364
n-C_4	1.246	1 0	1 246	1 103	1 314
C_5	0.642	0 58	0.372	0.329	0 551
C_6	0.320	0 38	0.121	0 107	0 272
C_7	0.184	0 215	0.040	0.035	0 167
C_8	0.147	0 12	0 018	0 016	0.141
360°F.	0.107	0.038	0.004	0.004	0.106
			2.259		

$K_{n\text{-}C_4} = 3/2.259 = 1.33$ $T = 273$°F.

TABLE 9-3 (*Continued*)

	$3x_3$	α_{250}	$3\alpha x_3$	$2y_3$	$3x_4$
C_3+	0.0845	2.03	0 172	0 147	0 1495
i-C_4	0.364	1 18	0 430	0.367	0.408
n-C_4	1 314	1.0	1.314	1.120	1.331
C_5	0.551	0 55	0.302	0 258	0.480
C_6	0.272	0.30	0.082	0.070	0.235
C_7	0 167	0 172	0 029	0 025	0.157
C_8	0.141	0 090	0 013	0 011	0 136
360°F.	0.106	0.022	0 002	0 002	0 104
			2 344		

$K_{n\text{-}C_4} = 1.28$ $T = 265°F.$

	$3x_4$	α_{250}	$3\alpha x_4$	$2y_4$	$3x_5$
C_3+	0 1495	2 03	0 304	0 244	0 2465
i-C_4	0.408	1 18	0 481	0 386	0.427
n-C_4	1.331	1.0	1 331	1.070	1.281
C_5	0 480	0 55	0 264	0.212	0 434
C_6	0 235	0.30	0 071	0 057	0 222
C_7	0 157	0 172	0.027	0 022	0 154
C_8	0 136	0 090	0 012	0 010	0 135
360°F.	0 104	0.022	0.002	0 002	0.104
			2.492		

$K_{n\text{-}C_4} = 1.2$ $T = 256°F.$

	$3x_5$	α_{250}	$3\alpha x_5$	$2y_5$	$3x_6$
C_3+	0.2465	2 03	0 500	0 380	0 382
i-C_4	0 427	1.18	0.504	0.383	0 424
n-C_4	1.281	1.0	1.281	0.975	1 186
C_5	0.434	0.55	0.238	0 181	0 403
C_6	0.222	0.30	0 067	0 051	0 216
C_7	0.154	0 172	0.027	0 021	0.153
C_8	0.135	0.090	0 012	0 009	0 134
360°F.	0 104	0.022	0 002	0 002	0.104
			2.631		

$K_{n\text{-}C_4} = 1.14$ $T = 250°F.$

TABLE 9-3 (*Continued*)

	$3x_6$	α_{250}	$3\alpha x_6$	$2y_6$	$3x_7$
C_3+	0.382	2.03	0 776	0.556	0.558
i-C_4	0 424	1 18	0 501	0.359	0 400
n-C_4	1 186	1 0	1.186	0.850	1 061
C_5	0 403	0 55	0 222	0 159	0 381
C_6	0.216	0.30	0.065	0.047	0 212
C_7	0.153	0.172	0.026	0.019	0.151
C_8	0 134	0.090	0 012	0.009	0 134
360°F.	0.104	0 022	0 002	0.001	0 103
			2.790		

$K_{n\text{-}C_4} = 1.075$ $T = 241°F.$

	$3x_7$	α_{250}	$3\alpha x_7$	$2y_7$	$3x_8$
C_3+	0 558	2 03	1 135	0 762	0 764
i-C_4	0.400	1.18	0 472	0 317	0 358
n-C_4	1 061	1 0	1 061	0 713	0 924
C_5	0 381	0 55	0 210	0 141	0 363
C_6	0 212	0 30	0 064	0.043	0 208
C_7	0 151	0 172	0 026	0 018	0 150
C_8	0.134	0 090	0 012	0 008	0 133
360°F.	0 103	0 022	0.002	0 001	0 103
			2 982		

$K_{n\text{-}C_4} = 1.01$ $T = 232°F.$

	$3x_8$	α_{250}	$3\alpha x_8$	$2y_8$
C_3+	0.764	2 03	1.550	0 970
i-C_4	0 358	1 18	0 422	0 264
n-C_4	0 924	1 0	0.924	0 578
C_5	0.363	0 55	0.200	0 125
C_6	0.208	0.30	0 062	0 039
C_7	0.150	0 172	0 026	0.016
C_8	0 133	0 090	0 012	0 008
360°F.	0.103	0.022	0 002	0 001
			3 198	

$K_{n\text{-}C_4} = 0.94$ $T = 220°F.$

TABLE 9-4. REMATCHING FEED PLATE FROM BELOW

	$3x_7$	α_{225}	$3\alpha\lambda_7$	$2y_7$	$3x_8$
C_1	—	19 3	—	—	0 0045
C_2	0.036	5.1	0.181	0 100	0 100
C_3-	0.183	2.37	0.432	0 240	0 240
C_3+	0 559	2 07	1 155	0 642	0 644
i-C_4	0 400	1 18	0 472	0 262	0 303
n-C_4	1 061	1 0	1 061	0.590	0.801
C_5	0 381	0 53	0 202	0.112	0 334
C_6	0 212	0.27	0.057	0 032	0 197
C_7	0 151	0 15	0.023	0 013	0.145
C_8	0 134	0 072	0 010	0 006	0 131
360°F.	0 103	0 016	0 002	0 001	0 103
			3 595		

$K_{n\text{-}C_4} = 0.833$ $T = 205°F.$

	$3x_8$	α_{200}	$3\alpha x_8$	y_8
C_1	0 0045	21	0 094	0 024
C_2	0 100	5.3	0 530	0 134
C_3-	0 240	2.4	0.576	0 146
C_3+	0 644	2.1	1.350	0 341
i-C_4	0 303	1.2	0 364	0 092
n-C_4	0 801	1.0	0 801	0 203
C_5	0.334	0.5	0 167	0 042
C_6	0.197	0 24	0 047	0 012
C_7	0.145	0 125	0 018	0 004
C_8	0 131	0 057	0 007	0 002
360°F.	0.103	0 012	0 001	0 0003
			3 955	

$K_{n\text{-}C_4} = 0.76$ $T = 188°F.$

The rematching calculations for the gasoline-stabilizer problem for above the feed plate are given in Table 9-5.

By such rematching procedure, it is possible to obtain exact agreement at the feed plate for all the light components and all the heavy components because they are arbitrarily chosen in one portion of the tower. However, it may be impossible to obtain an exact match of the key components because an even number of theoretical plates will not be consistent with the design chosen. In this case, it is possible to bracket the required number of plates within a difference of one plate. While this rematching operation gives a more consistent set of

compositions, in most cases it does not alter the conclusion as to the number of theoretical plates required, and the first calculations of the type illustrated by Tables 9-2 and 9-3 are usually sufficient for determining the number of theoretical plates.

After such adjustments, it is noted that the vapor y_8 of Table 9-4 and the vapor y_{T-3} of Table 9-5 give a very satisfactory match. The i-C_4 from Table 9-5 is a little higher than in Table 9-4, indicating that a little less than 20 per cent of the i-C_4 would go overhead, but the difference is so small that it does not justify readjusting.

These concentrations given in the tables are plotted in Fig. 9-14.

TABLE 9-5. REMATCHING FEED PLATE FROM ABOVE

	$2x_{T-1}$	$3y_{T-2}$	A_{150}	$3y_{T-2}/\alpha$	$2x_{T-2}$	y_{T-3}
C_1	0 0029	0.066	26	0.0025	0.003	0 022
C_2	0.103	0.419	6	0 070	0.084	0.133
C_3-	0 316	0 506	2.6	0 195	0.233	0 141
C_3+	0.810	1.200	2.3	0 522	0 624	0 338
i-C_4	0 277	0 299	1 23	0 243	0 290	0 104
n-C_4	0 489	0 508	1 0	0 508	0.606	0.208
C_5	0.045	0 045	0 43	0 105	0.125	0 042
C_6	0.005	0 005	0.18	0.028	0.033	0.011
C_7	—	—	—	—	0 012	0 004
C_8	—	—	—	—	0.006	0 002
360°F.	—	—	—	—	0 0009	0 0003
				1 674		

$K_{n-C_4} = 0.56$ $T = 163$°F.

A heat balance around the feed plate indicates that the feed should enter as a liquid at about 130°F. to give the vapor and liquid flows assumed.

Optimum Feed-plate Location. The feed plate was chosen so that the ratio of the key components was approximately the same as in the feed. Equation (9-12) indicates the optimum feed-plate ratio for $C_3 + /n$-C_4 should be 1.14 as compared to 0.83 for the ratio in the feed. After rematching, the ratio of the key components for plate 8 in Table 9-3 is 0.803, and for plate 9 (plate $T-2$) in Table 9-4 the ratio is 1.03. The ratio for these two plates should bracket the value of 1.14. These values indicate that adding the feed to plate 9 would give more effective rectification than the plate that was employed.

Theoretical Plates at Total Reflux. The relative volatility of the key components does not vary too widely from the still to the condenser,

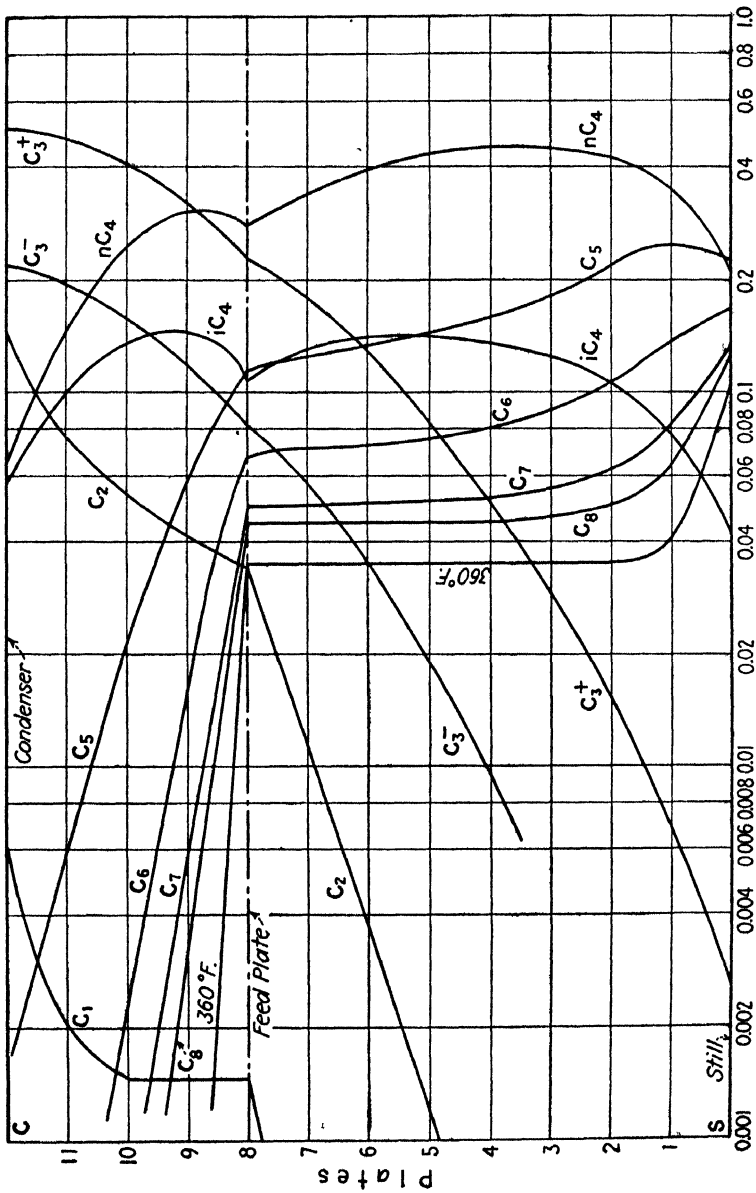

C
S
Condenser
Still
Feed Plate
360°F.
360°F
C_1
C_2
C_5
C_6
C_7
C_8
C_3^-
C_3^+
nC_4
iC_4
Plates
Mol Fraction in Liquid
0.001
0.002
0.004
0.006
0.008
0.01
0.02
0.04
0.06
0.08
0.1
0.2
0.4
0.6
0.8
1.0
1
2
3
4
5
6
7
8
9
10
11

FIG. 9-14.

and a satisfactory answer for the number of theoretical plates at total reflux can be obtained by the use of Eq. (7-54). Using an arithmetic average of the relative volatility at the still and condenser,

$$\alpha_{av} = \frac{2.0 + 2.7}{2} = 2.35$$

$$N + 2 = \frac{\ln\left[\left(\frac{0.390}{0.019}\right)\left(\frac{0.211}{0.0025}\right)\right]}{\ln 2.35} = 8.7$$

$$N = 6.7 \text{ (or 7) theoretical plates}$$

Minimum Reflux Ratio. The minimum reflux ratio will be calculated for this separation by Eq. (9-22).

Basis: 100 mols of feed. For actual case,

$$\left(\frac{O}{V}\right)_m = 1.5$$

$$O_m = 1.5V_m = V_m + W$$

$$V_m = 136.8$$

$$\frac{O}{D} = 2$$

$$V_n = 3D = 94.8$$

Therefore, assume $V_m - V_n = 42$ for minimum reflux conditions. Values of the relative volatility corresponding to the feed plate will be used.

	α		α
C_1	24 0	C_5	0 46
C_2	5 6	C_6	0 21
C_3-	2.5	C_7	0.11
C_3+	2.2	C_8	0.05
i-C_4	1.21	360°F.	0.01
n-C_4	1 0		

In calculating ϕ by Eq. (9-12), it is necessary to have values of V_n and V_m. As a first trial, assume $(O/D)_{min} = 0.9$.

$$V_n = 1.9(31.6) = 60 \qquad O_n = 28.4$$

$$V_m = 102 \qquad O_m = 170.4$$

By Eq. (9-10),

$$\Delta_l = \frac{1}{60}\left\{2.0\left[\frac{1-\frac{170.4}{102(15.8)}}{1-\frac{28.4}{60(15.8)}}\right]+10\left[\frac{1-\frac{170.4}{102(3.68)}}{1-\frac{28.4}{60(3.68)}}\right]+6.0\left[\frac{1-\frac{170.4}{102(1.66)}}{1-\frac{28.4}{60(1.66)}}\right]\right\}=0.148$$

K values at a temperature of 175°F. were employed.

By Eq. (9-11),

$$\Delta_h = \frac{1}{170.4}\left[0.30(15.2)\frac{1-\frac{0.30(60)}{28.4}}{1-\frac{0.30(102)}{170.4}}+0.14(11.3)\frac{1-\frac{0.14(60)}{28.4}}{1-\frac{0.14(102)}{170.4}}+0.07(9.0)\frac{1-\frac{0.07(60)}{28.4}}{1-\frac{0.07(102)}{170.4}}+0.03(8.5)\frac{1-\frac{0.03(60)}{28.4}}{1-\frac{0.03(102)}{170.4}}+0.007(7.0)\frac{1-\frac{0.007(60)}{28.4}}{1-\frac{0.007(102)}{170.4}}\right]=0.024$$

By Eq. (9-12),

$$\phi = \frac{12.5+\left[\frac{60(0.852)^2}{102(0.976)}-1\right]0.17}{15.0+\left[\frac{60(0.852)^2}{102(0.976)}-1\right]14.4}=1.8$$

Checking distribution of i-C_4 for assumed reflux ratio.

By Eq. (9-13),

$$x_{i\text{-}c_4} = \frac{1.0\,\frac{Dx_D}{28.4}}{1.21-1.0+1.21\left(\frac{0.019}{0.2}\right)\frac{1}{0.9}}=0.104Dx_D$$

By Eq. (9-15),

$$x_{i\text{-}c_4} = \frac{2.2\,\frac{Wx_W}{170.4}}{2.2-1.21+1.21\left(\frac{68.4}{170.4}\right)\left(\frac{0.0025}{0.27}\right)}=0.0131Wx_W$$

Equating these two values of $x_{i\text{-}C_4}$ and using $Wx_W + Dx_D = 3.5$,

$$Dx_D = 0.39$$
$$Wx_W = 3.11$$

About 11 per cent of the isobutane would go overhead. The calculations of D and W were based on the original assumption of 20 per cent i-C_4 overhead, but the difference is not large and no correction will be made. The values just calculated will be used in the minimum reflux ratio calculations.

By Eq. (9-22)

$$\left(\frac{O}{D}\right)_{\min} + 1 = \frac{1.0\left(\frac{0.39}{1.8} - 0.019\right)[1 + 2.2(1.8)]}{2.2 - 1.0}$$
$$+ \left[\frac{24.0(0.063)}{24.0 - 1} + \frac{5.6(0.316)}{5.6 - 1} + \frac{2.5(0.19)}{2.5 - 1} + \frac{1.21\left(\frac{0.39}{31.6}\right)}{1.21 - 1}\right]$$
$$+ \frac{60(68.4)}{102(31.6)}\left[\frac{0.46(0.222)}{2.2 - 0.46} + \frac{0.21(0.165)}{2.2 - 0.21} + \frac{0.11(0.132)}{2.2 - 0.11}\right.$$
$$\left. + \frac{0.05(0.124)}{2.2 - 0.05} + \frac{0.01(0.102)}{2.2 - 0.01}\right] = 0.81 + 0.83 + 0.11$$

$$\left(\frac{O}{D}\right)_{\min} = 0.75 \text{ for Case I}$$
$$= 0.75 - 0.11 = 0.64 \text{ for Case II}$$

The assumed value for O/D of 0.9 is close to the calculated value for Case I. A recalculation for Case II, assuming $O/D = 0.7$, gave a calculated value of 0.63.

Equation (9-22) was employed because the summation term for the light components was greater than for heavy components. The term for the isobutane was included with the light components, but it could equally well have been included with the heavy components, and the total would have been essentially the same.

It is interesting to note that a binary mixture of propane and butane of the same ratio as in the feed would have required only one-half as much vapor per mol of $C_3 + C_4$ separated as is necessary for this multicomponent mixture.

For a comparison, the minimum reflux ratio will also be calculated by Eq. (9-17).

By Eq. (9-17), assume

$$\frac{O}{D} = 0.9$$

By Eq. (9-15),

$$x_{hk} = \frac{2.2(14.4/170.4)}{2.2 - 1.0 + 1.0\left(\frac{68.4}{170.4}\right)\left(\frac{0.0025}{x_{lk}}\right)} = 0.155$$

By Eq. (9-13),

$$x_{lk} = \frac{1.0(12.33/28.4)}{2.2 - 1.0 + 2.2\left(\frac{1}{0.9}\right)\left(\frac{0.019}{0.155}\right)} = 0.290$$

For Eq. (9-17),

$$C = \frac{1}{0.39}(2.2 - 1.0 + 0.30) = 3.84$$

$$E = \frac{1}{0.211}(2.2 - 1.0) = 5.68$$

$$G = \frac{2.2}{5.68} = 0.387$$

$$H = \frac{1.0}{3.84} = 0.26$$

$$I = \frac{-142}{68.4} + 0.387 + 2.2\left[\frac{0.222}{2.2 - 0.46} + \frac{0.165}{2.2 - 0.21} + \frac{0.132}{2.2 - 0.11} + \frac{0.124}{2.2 - 0.05} + \frac{0.102}{2.2 - 0.01}\right] + 1.0\,\frac{31.6}{68.4}\left(\frac{170.4}{28.4}\right)\left[\frac{0.063}{24 - 1 + 0.12(24)} + \frac{0.316}{5.6 - 1 + 0.12(5.6)} + \frac{0.19}{2.5 - 1 + 0.12(2.5)} + \frac{0.39/31.6}{1.21 - 1 + 0.12(1.21)}\right]$$

$$= -2.08 + 0.387 + 0.825 + 0.617 = -0.251$$

$$J = 0.26 + \frac{68.4}{31.6}\left(\frac{28.4}{170.4}\right)(0.825) + 0.205 = 0.762$$

$$I' = -0.868$$

$$J' = 0.465$$

Case I:

$$\frac{W}{D}I + J = \frac{68.4}{31.6}(-0.251) + 0.762$$

$$= 0.218$$

$$\left(\frac{O}{D}\right)_{\min} = \frac{0.218 + \sqrt{(0.218)^2 - \frac{4(68.4)}{31.6}[(-0.251)(0.762) - (0.387)(0.26)]}}{2}$$

$$= 0.91$$

Case II:

$$\frac{W}{D} I' + J' = \frac{68.4}{31.6}(0.868) + 0.465$$
$$= -1.415$$

$$\left(\frac{O}{D}\right)_{\min}$$
$$= \frac{-1.415 + \sqrt{(-1.415)^2 - \frac{4(68.4)}{31.6}[-0.868(0.465) - (0.387)(0.26)]}}{2}$$
$$= 0.55$$

These values were not recalculated for a new assumed value of O/D since both are reasonably close to the first value assumed.

Constancy of Molal Flow Rates. The design calculations presented have been based on the use of constant molal overflow and vapor rates. Enthalpy balances similar to Eqs. (7-13) and (7-27) can be written for each of the components of a multicomponent mixture and, if the data are available, they can be applied plate by plate in the stepwise calculations. This procedure usually requires trial and error because, in calculating up or down the tower, the temperature on the next plate is needed to complete the enthalpy balance, and it must be assumed and checked in a later calculation. The most serious difficulty is the lack of the necessary enthalpy data, but in most cases these can be approximated by the methods on pages 139 to 142.

The same general considerations relative to the constancy of flow rates apply to multicomponent and binary mixtures. Thus the latent heat of vaporization at various positions in the column should serve as the principal criterion, although in multicomponent systems there is more possibility of large sensible heat effects changing the overflow and vapor rates.

The modified latent heat method (M.L.H.V.) given on page 158 is applicable to multicomponent mixtures, and it probably is the most satisfactory procedure for handling such calculations. It should give good results for the examples considered in this chapter, because the heats of mixing for the mixtures involved would be small, even though the latent heats of vaporization of individual components for the gasoline stabilization problem differ several fold. In this latter example, there is undoubtedly considerable variation in the molal flow rates, and the M.L.H.V. method will give more satisfactory results than the method employed. The calculations were repeated by the M.L.H.V. method using arithmetic average values of latent heats

of vaporization at the still and the condenser to calculate the values of β for each component. Table 9-6 gives the latent heat values and the β terms based on the latent heat of *n*-butane. The values of β are used to calculate βz_F, $\beta y_{\text{o.h.}}$, βx_W, and $z'_F = \beta z_F / \Sigma(\beta z_F)$, $y'_{\text{o.h.}} = \beta y_{\text{o.h.}} / \Sigma(\beta y_{\text{o.h.}})$, and $x'_W = \beta x_W / \Sigma(\beta x_W)$. The values of the terminal flow quantities are given below:

$$\begin{aligned} W' &= 68.4(1.467) = 100 \\ D' &= 31.6(0.650) = 20.5 \\ F' &= 100(1.205) = 120.5 \end{aligned}$$

Table 9-7 presents the plate-to-plate calculations; the values of $y'_{\text{o.h.}}$ are taken from Table 9-6, and the values of $y_{\text{o.h}}$ and $2x_R$ are taken from Table 9-2. The calculations will be made for $O/D = 2.0$ and for $V_m - V_n = 42$ which are the same as the values used in Tables 9-2 and 9-3. For $F = 100$, $D = 31.6$, $O_R = 63.2$, and the fourth column of Table 9-7 gives $\beta x_R = 0.751$ making $O'_R = 0.751(63.2) = 47.5$, and $O'_R/D' = 47.5/20.5 = 2.32$. The remaining columns of Table 9-7 are based on $D' = 1.0$, $O' = 2.32$, $V' = 3.32$. The values of the fifth column are $2.32x'_R = 2.32 \dfrac{\beta x_R}{\Sigma(\beta x_R)}$; the values of $3.32y'_T$ are equal to $2.32x'_R + y'_{\text{o.h.}}$. In order to go to y_T, the values of $3.32y'_T$ are divided by the corresponding β terms and $y_T = (y'_T/\beta)/\Sigma(y'_T/\beta)$. The y_T values are used to calculate x_T, using the relative volatilities of Table 9-2, and these are converted to x'_T.

The general flow quantities are shown in Fig. 9-15 which gives both the normal and modified values. For $F = 100$, the value of V'_n is 68 throughout the top section, but the value of V_n will vary from plate to plate. Thus $V_T = 94.8$, but $V_{T-1} = V'_{T-1}\Sigma(y_{T-1}/\beta) = 91$, and this value decreases further for the next plate. This decrease in vapor rate is due to the fact that the average latent heat of vaporization is increasing from plate to plate down the column, resulting in lower vapor and liquid rates and making the separation more difficult.

The calculations are carried in the same manner down to y_{T-3}. The calculations were given in detail to show the values of y and x as well as those for y' and x', but this is not necessary because it is possible to go from y' to x' directly by $x' = (y'/\alpha)/\Sigma(y'/\alpha)$ in which the normal α values are employed.

The calculations for the lower section of the tower are given in Table 9-8 on the basis $W' = 1.0$, $O'_m = 2.186$, and $V'_m = 1.186$. The value of V_W for $F = 100$ is calculated from $V'_m/\Sigma(\beta y_W) = 101$. This

represents a large decrease in vapor from the top of the tower where $V_T = 94.8$. With $V_m - V_n = 42$, the vapor from the still would have been 136.8 on the usual basis. The decrease of 136.8 − 101 = 35.8 is due to variation in the latent heats of vaporization. The calculations up to x'_5 are given in Table 9-8. The calculations up to x'_3 were made in detail, but from x'_3 to x'_5 the values of $1.186y'$ were calculated from

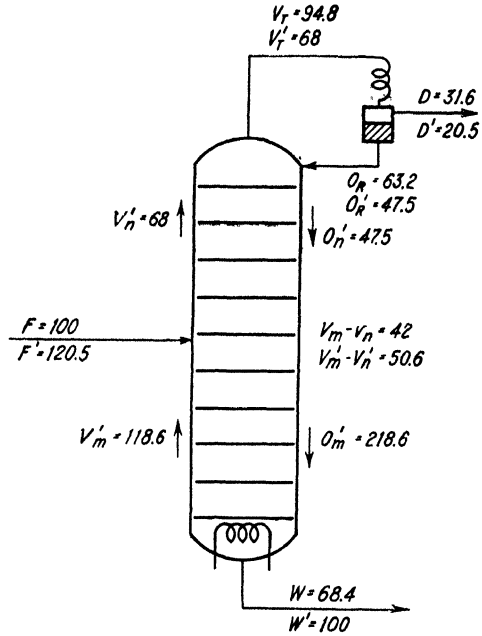


FIG. 9-15. Comparison of flow quantities for gasoline-stabilization example.

$1.186(2.186\alpha x')/\Sigma(2.186\alpha x')$. This method requires only three columns per plate, and the calculations are as simple as the normal type of calculations given in Table 9-3. The calculations were continued, and y'_9 gave a good match with y'_{T-3} of Table 9-7, indicating that 12 theoretical plates would be required as compared to 11 plates for constant flow rate conditions. The difference would be greater for reflux ratios nearer the minimum.

The minimum reflux ratio can be calculated on the modified latent heat basis using any of the equations derived for constant molal flow rates with the x' and y' values.

The calculations for $(O'_R/D')_{\min}$ by Eq. 9-22 were made in an analogous manner to calculations on page 274. The values are summarized

below:

$$\Delta_1' = 0.069; \qquad \Delta_h' = 0.026; \qquad \phi' = 1.055$$

For isobutane,

$$D'x_D' = 0.3$$
$$W'x_W' = 2.96$$

By Eq. (9-22),

$$\left(\frac{O_R'}{D'}\right)_{\min} = 1.0, \text{ Case I}$$
$$= 0.93, \text{ Case II}$$

TABLE 9-6

	Latent heat of vaporization, B.t.u./lb. mol			β	z_F	βz_F	z_F'
	98°F.	333°F.	Av				
C_1	1,100	200	650	0.113	0.02	0.002	0.0016
C_2	3,500	2,200	2,850	0.496	0.10	0.0494	0 0413
C_3-	4,700	3,500	4,100	0 713	0.06	0 0425	0 0354
C_3+	5,200	4,000	4,600	0 80	0.125	0.10	0 0826
i-C_4	5,800	4,900	5,350	0.93	0 035	0.0321	0 027
n-C_4	6,200	5,300	5,750	1.0	0.150	0.150	0 124
C_5	7,300	6,600	6,950	1.21	0.152	0.182	0 152
C_6	8,500	7,700	8,100	1.41	0.113	0.159	0.131
C_7	10,000	9,100	9,550	1.66	0.090	0.150	0.124
C_8	11,900	10,700	11,300	1.97	0 085	0.166	0.139
360°F.	14,900	13,500	14,200	2.47	0.070	0 172	0 143
						1.205	

	x_D	βx_D	x_D'	x_W	βx_W	x_W'
C_1	0.0633	0.007	0.011	—	—	—
C_2	0 3160	0.157	0.242	—	—	—
C_3-	0.1900	0.135	0 208	—	—	—
C_3+	0.3900	0.312	0.480	0.0025	0.002	0 0014
i-C_4	0 022	0.020	0.031	0.0410	0.038	0.026
n-C_4	0.019	0.019	0.029	0.2110	0.211	0 144
C_5	—	—	—	0.2220	0.268	0.183
C_6	—	—	—	0.1650	0.233	0.152
C_7	—	—	—	0.1320	0.219	0 149
C_8	—	—	—	0.1240	0.244	0 166
360°F.	—	—	—	0.1020	0.252	0.172
		0.650			1.467	

TABLE 9-7

	$y'_{O.H.}$	$y_{O.H.}$	$2x_R$	$2\beta x_R$	$2.32x'_R$	$3.32y'_T$	$\frac{3.32y'_T}{\beta}$	y_T
C_1	0 011	0 0633	0 012	0.0014	0.0022	0 0132	0 117	0 025
C_2	0.242	0.316	0.296	0 147	0.227	0.469	0.945	0 204
C_3-	0.208	0.190	0.440	0.314	0 484	0.692	0 970	0.210
C_3+	0.480	0 390	1.0	0 80	1.232	1.712	2 14	0 463
i-C_4	0.031	0 022	0.117	0.109	0.168	0.199	0 214	0 046
n-C_4	0.029	0.019	0.132	0 132	0 2035	0 2325	0 2325	0 050
				1 503			4.618	

$V_T = 94.8$

	$\frac{y_T}{\alpha_{100}}$	x_T	βx_T	$2.32x'_T$	$3.32y'_{T-1}$	$\frac{3.32y'_{T-1}}{\beta}$	y_{T-1}	$\frac{y_{T-1}}{\alpha_{150}}$
C_1	0.00068	0 00191	0 00022	0 0006	0 0116	0 102	0 023	0 00089
C_2	0.0276	0 0777	0 0385	0 112	0 354	0.714	0 161	0 027
C_3-	0.070	0 197	0.141	0 409	0 617	0.866	0 195	0 075
C_3+	0 172	0 484	0 387	1 12	1.60	2 0	0 45	0 196
i-C_4	0 035	0.0985	0.0915	0 266	0.297	0.319	0 072	0 059
n-C_4	0 050	0.141	0 141	0 409	0 438	0.438	0.099	0 099
	0 3553		0 799			4 439		0 4569

$V_{T-1} = 91$

	x_{T-1}	βx_{T-1}	$2.32x'_{T-1}$	$3.32y'_{T-2}$	$\frac{3.32y'_{T-2}}{\beta}$	y_{T-2}	$\frac{y_{T-2}}{\alpha_{150}}$
C_1	0 00195	0 00022	0 00062	0 0116	0 102	0 023	0 00088
C_2	0 059	0.0293	0.082	0.324	0 653	0 150	0 025
C_3-	0 164	0.117	0 328	0 536	0 753	0 173	0 0665
C_3+	0 430	0.344	0 965	1 445	1 81	0 416	0 181
i-C_4	0 129	0 120	0.336	0 367	0 395	0 091	0 074
n-C_4	0.217	0 217	0 608	0 637	0 637	0 147	0 147
		0 8275			4.350		0.4944

$V_{T-2} = 89$

	x_{T-2}	βx_{T-2}	$2.32x'_{T-2}$	$3.32y'_{T-3}$
C_1	0 0018	0.0002	0 00054	0 0115
C_2	0 051	0.025	0.068	0.31
C_3-	0.135	0.096	0 260	0.468
C_3+	0 366	0.296	0 803	1.283
i-C_4	0 150	0 140	0 380	0 411
n-C_4	0 298	0 298	0 808	0 837
		0 855		

TABLE 9-8

	x'_W	x_W	$1.186y_W$	$1.186\beta y_W$	y'_W	$1.186y'_W$	$2.186x'_1$
C_3+	0.0014	0.0025	0 0118	0 0095	0 0068	0 0081	0.0095
i-C_4	0.026	0 041	0.113	0 105	0.0755	0.090	0.116
n-C_4	0.144	0.211	0.497	0.497	0.357	0.424	0.568
C_5	0.183	0.222	0.304	0 368	0.265	0.315	0 498
C_6	0 152	0 165	0 148	0 209	0 150	0.178	0 330
C_7	0.149	0.132	0 067	0.111	0 080	0 095	0.244
C_8	0 166	0.125	0.035	0 069	0 050	0.059	0 225
360°F.	0 172	0.102	0 009	0 022	0.016	0 019	0.191
				1.390			

$V_W = 101$

	$\frac{2.186x'_1}{\beta}$	x_1	$\alpha_{300}x_1$	y_1	βy_1	$1.186y'_1$	$2.186x'_2$
C_3+	0.0119	0 0071	0 0142	0.0215	0 0172	0 0186	0.02
i-C_4	0 1245	0.074	0.087	0.132	0 123	0 133	0 159
n-C_4	0.568	0.338	0 338	0.512	0 512	0 552	0 696
C_5	0 411	0 244	0 141	0.214	0 259	0.280	0 463
C_6	0 234	0 139	0 053	0.080	0 113	0 122	0 274
C_7	0.141	0.084	0 018	0 027	0.045	0.049	0 198
C_8	0 114	0.068	0.008	0 012	0 024	0.026	0 192
360°F.	0 077	0.046	0 002	0.003	0.007	0.007	0.179
	1.681		0.661		1.101		

$V = 108$

	$\frac{2.186x'_2}{\beta}$	x_2	$\alpha_{300}x_2$	y_2	βy_2	$1.186y'_2$	$2.186x'_3$
C_3+	0 025	0 014	0.028	0 0384	0.0307	0 034	0.035
i-C_4	0.171	0.097	0.114	0.156	0.145	0.161	0 187
n-C_4	0.696	0.396	0.396	0.543	0.543	0.602	0 746
C_5	0.383	0.218	0.126	0.173	0.210	0 232	0 415
C_6	0.194	0.110	0.042	0 058	0.082	0 091	0 243
C_7	0.119	0.068	0.015	0 021	0.035	0 039	0 188
C_8	0 097	0.055	0.007	0.010	0 019	0 021	0 187
360°F.	0.072	0.041	0.002	0.002	0 005	0.006	0 178
	1.757		0.730		1.070		

$V = 111$

TABLE 9-8 (*Continued*)

	$2.186\alpha_{300}x'_3$	$1.186y'_3$	$2.186x'_4$	$2.186\alpha_{250}x'_4$	$1.186y'_4$	$2.186x'_5$
C_3+	0.070	0.058	0.059	0.120	0.098	0.099
i-C_4	0.221	0.182	0.208	0.246	0.200	0.226
n-C_4	0 746	0.616	0 760	0.760	0.619	0.763
C_5	0.241	0.199	0.381	0 210	0.171	0.354
C_6	0.092	0.076	0.228	0 068	0.056	0.208
C_7	0 040	0 033	0.182	0 031	0.025	0.174
C_8	0.022	0.018	0.084	0.017	0.014	0.180
360°F.	0.007	0.006	0.178	0.004	0.003	0.175
	1.439			1.456		

In calculating these values, the same relations used on pages 277 to 278 were employed with the same relative volatilities. Converting the values of $(O'_R/D')_{min}$ to $(O_R/D)_{min}$ by the factors given in Table 9-7 gives

$$\left(\frac{O_R}{D}\right)_{min} = 0.86, \text{ case I}$$
$$= 0.8, \text{ case II}$$

These compare with 0.75 and 0.64, respectively, obtained on page 274, indicating that the variation of the flow rates results in a value of $(O_R/D)_{min}$ about 20 per cent greater than would be estimated on the basis of constant molal flow rates. However, the mols of vapor that would need to be generated in the still are approximately the same by both methods.

In this example, the use of the modified values did not make a large difference in the results, but if the design conditions had been nearer the optimum, *e.g.*, $(O_R/D) = 1.25(O_R/D)_{min} = 0.94$, then calculations based on the constant molal rates would be seriously in error. When the average latent heats of vaporization at the bottom and top of the column differ appreciably, calculations based on the modified basis are to be preferred.

Another method of handling unequal molal overflow rates for multicomponent mixtures is to make the calculations on the constant molal flow rates and then to calculate the heat load required to give these rates for a few positions in the column. If the heat input to the still is made equal to the largest requirements, and the condenser and tower cross section correspondingly corrected, a conservative design will be obtained. The check points most commonly employed are (1) around the still, (2) the entire section below the feed plate, (3) the feed

plate and section below, and (4) around the entire column. In general, the modified latent heat of vaporization method is a more satisfactory procedure.

Nomenclature

C = number of components
C^* = factor in Eq. (9-17)
D = distillate rate, mols per unit time
E = factor in Eq. (9-17)
F = feed rate, mols per unit time
G = factor in Eq. (9-17)
H = factor in Eq. (9-17)
H_L = molal enthalpy of liquid
H_V = molal enthalpy of vapor
I = factor in Eq. (9-17)
I' = factor in Eq. (9-17)
J = factor in Eq. (9-17)
J' = factor in Eq. (9-17)
K = equilibrium constant = y/x
m = number of plates below feed plate (including feed plate)
N = number of plates in column
n = number of plates above feed plate
O = overflow rate, mols per unit time
P = vapor pressure
p = $(O_{f+1} - O_f)/F$
Q = heat input
T = temperature
V = vapor rate, mols per unit time
W = bottom product rate, mols per unit time
x = mol fraction in liquid
y = mol fraction in vapor
z = mol fraction
α = relative volatility
ϕ = optimum ratio of key components on feed plates
π = total pressure

Subscripts:

B refers to benzene
D refers to distillate
F refers to feed
f refers to feed plate
h refers to heavy component
hk refers to heavy key component
l refers to light component
lk refers to light key component
m refers to conditions below feed plate
n refers to conditions above feed plate
R refers to reflux

T refers to toluene
W refers to bottom product
X refers to xylene

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CHAPTER 10

EXTRACTIVE AND AZEOTROPIC DISTILLATION

The design engineer frequently must separate mixtures for which normal distillation methods are not practical due either to the formation of azeotropes or to a very low relative volatility over a wide concentration region. In the first case the separation is impossible unless some special method of by-passing the azeotrope is employed (page 196), and in the second case excessive heat consumption and equipment size are involved. For a large number of such mixtures, it has been found possible to modify the relative volatility of the original components by the addition of another component (or components). This technique has been classified into two categories: *extractive distillation* and *azeotropic distillation.*

In essentially all separations carried out to date by these techniques the effect of the added component is in the liquid phase, although it is possible to modify the vapor-phase properties for systems operating at high pressure.

The added component by being present in the liquid phase can alter the activity coefficient of the various components, and unless the components already present are identical in physical and chemical properties, the percentage change in the activity coefficients will be different for each component, thereby altering their relative volatility. This technique is effective only when the components in the original mixture *do not obey* Raoult's law, and in general the greater the deviation from Raoult's law, the easier it becomes to alter the relative volatility significantly by the addition of another component. Thus a consideration of the deviations from Raoult's law is essential for an understanding of extractive and azeotropic distillation. While no exact relationship has been developed for the predictions of such deviations, the Van Laar equation does give a qualitative picture that is useful.

As the simplest case, consider a binary mixture of components 1 and 2 which is to be modified by the addition of component 3.

The relative volatility of component 1 to 2 is

$$\alpha = \frac{y_1}{x_1}\frac{x_2}{y_2} = \frac{\gamma_1 P_1}{\gamma_2 P_2}$$

By Eq. (3-58), page 73,

$$T \ln \gamma_1 = \frac{(x_2 \sqrt{B_{12}} + x_3 A_{32} \sqrt{B_{13}})^2}{(x_1 A_{12} + x_2 + x_3 A_{32})^2}$$

$$T \ln \gamma_2 = \frac{(x_1 A_{12} \sqrt{B_{21}} + x_3 A_{32} \sqrt{B_{23}})^2}{(x_1 A_{12} + x_2 + x_3 A_{32})^2}$$

Over moderate temperature ranges the ratio of the vapor pressures of the pure components does not change appreciably. The main possibility of modifying the relative volatility lies in altering the ratio of the activity coefficient. By subtracting the two activity coefficient equations, it is possible to obtain the ratio,

$$T \ln \frac{\gamma_1}{\gamma_2} = \frac{(x_2 \sqrt{B_{12}} + x_3 A_{32} \sqrt{B_{13}})^2 - (x_1 A_{12} \sqrt{B_{21}} + x_3 A_{32} \sqrt{B_{23}})^2}{(x_1 A_{12} + x_2 + x_3 A_{32})^2} \quad (10\text{-}1)$$

Consider the case in which compounds 1 and 2 are similar, *i.e.*, *almost* obey Raoult's law, *e.g.*, ethanol and isopropanol. For this case, B_{12} will be small and A_{12} will be approximately equal to unity. Equation (10-1) can be simplified for these conditions to the approximate relationship,

$$T \ln \frac{\gamma_1}{\gamma_2} = \frac{(\sqrt{B_{12}})(\sqrt{B_{13}})(2x_3 A_{32}) \left(x_1 + x_2 + x_3 \frac{A_{32}}{A_{12}} \right)}{(x_1 A_{12} + x_2 + x_3 A_{32})^2} \quad (10\text{-}2)$$

$$= 2 \sqrt{B_{12} B_{13}} \, (V_3) \quad (10\text{-}3)$$

where V is the effective volume fraction of the component in the mixture.

The significance of this equation can be better shown by comparing it with the activity coefficient ratio, $(\gamma_1/\gamma_2)_o$, for the binary mixture without the added agent. By Eqs. (3-44) and (3-45)

$$T \ln \left(\frac{\gamma_1}{\gamma_2} \right)_o = B_{12}(V_{20}^2 - A_{12} V_{10}^2)$$

where V_{10}, V_{20} are the volume fractions of components 1 and 2, respectively, without agent present, and

$$T \ln \frac{\gamma_1/\gamma_2}{(\gamma_1/\gamma_2)_o} = B_{12} \left[2 \sqrt{\frac{B_{13}}{B_{12}}} \, (V_3) - V_{20}^2 - A_{12} V_{10}^2 \right] \quad (10\text{-}4)$$

For any effective addition agent the first term of the right-hand side of the equation will be large in comparison to the last term and, approximately,

$$T \ln \frac{\gamma_1/\gamma_2}{(\gamma_1/\gamma_2)_o} = 2\sqrt{B_{12}}\sqrt{B_{13}}\,V_3 \qquad (10\text{-}5)$$

For a given binary mixture, the effectiveness of the added component is indicated by how much the activity coefficient group of Eq. (10-5) can be made to differ from unity, and the effectiveness is increased by large absolute values of V_3, and $\sqrt{B_{13}}$. The derivation of Eq. (10-5) was for A_{12} approximately equal to unity and for small values of B_{12}. A more detailed analysis of Eq. (10-1) for the general case leads to essentially the same conclusions; *i.e.*, the ratio of the activity coefficients is changed the most when (1) $\sqrt{B_{12}}$ is large, (2) $\sqrt{B_{13}}$ is large, and (3) V_3 is large. However, in this case it will make a greater difference whether $\sqrt{B_{13}}$ and $\sqrt{B_{12}}$ are of the same or opposite sign.

A high value of V_3 is obtained by using a large quantity of the added agent, but it is usually not economically feasible to use a value greater than 0.8 to 0.9. To obtain these values for V_3 requires a 4 to 9 volume of the addition agent per volume of the components to be separated, and to obtain a value of V_3 equal to 0.95 would require a ratio of 19. For most cases, the small increase in the relative volatility obtained by increasing V_3 from 0.9 to 0.95 does not justify utilizing twice as much of the added agent. In some cases, values of V_3 as low as 0.4 to 0.5 may be sufficient, but higher values are usually required.

It should be noted that, for low values of $\sqrt{B_{12}}$, the effective change in the ratio of the activity coefficient will be small. Thus this technique would not be effective for ideal solutions ($B_{12} = 0$, $A_{12} = 1$), and the larger the value of $\sqrt{B_{12}}$, the easier it would be to obtain large effects.

The value of the $\sqrt{B_{13}}$ is probably the most important variable under the control of the designer. To obtain a large modification of the activity coefficient ratio, it is desirable that the absolute value of the term be as large as possible. However, there is an upper limit because a value of B from 1,200 to 1,800 corresponds to immiscibility. While it is necessary for the agent to dissolve only 10 to 20 volume per cent of the mixture, it is doubtful whether the value of B_{13} can exceed 2,000 to 3,000. Qualitatively, the value of B is a function of the difference in polarity of the two compounds under consideration. Thus a large value of B is associated with a large difference in polarity, and for the case in question it would be desirable to add an agent which

differed as much as possible in polarity from component 1. This difference could be either a compound with greater polarity or one with a lower polarity. In the first case, the $\sqrt{B_{13}}$ would be negative and in the second case positive. Assuming that the $\sqrt{B_{12}}$ is positive, *i.e.*, compound 1 more polar than 2, a positive value of $\sqrt{B_{13}}$ would increase the relative volatility while a negative value would decrease it. It is therefore possible either to decrease or to increase the relative volatility by adding another component. The general rule is (1) if the added material is more polar than the components of the original mixture, it will increase the relative volatility of the less polar component relative to the more polar, and (2) if the added material is less polar, the reverse will be true. For example, consider a mixture of acetone and methanol, which forms an azeotrope at atmospheric pressure. In this mixture methanol is more polar than acetone, and by adding a more polar component such as water, it is possible to increase the relative volatility of acetone to methanol to such a degree that an azeotrope no longer exists. However, if a material of low polarity, such as a hydrocarbon, is added to the mixture, the volatility of methanol will be increased relative to that of acetone. Water would probably be preferred to a hydrocarbon, not only because of cheapness and ease of separation from the components, but also because the vapor pressure of acetone at a given temperature is greater than that of methanol. Thus water will act to aid the natural difference in vapor pressure while a hydrocarbon will work against it.

For large values of V_3, components 1 and 2 behave as if they were each in a binary mixture with component 3, and there is essentially no interaction between 1 and 2. For these two "binary" systems, Eq. (3-44) can be applied; for V_3 approximately equal to unity, they reduce to

$$T \ln \frac{\gamma_1}{\gamma_2} = B_{13} - B_{23} \tag{10-6}$$

This equation can be modified to give

$$T \ln \frac{\gamma_1}{\gamma_2} = \sqrt{B_{12}} \left(\sqrt{B_{13}} + \sqrt{B_{23}}\right) \tag{10-6a}$$

Equation (10-6) is equivalent to Eq. (10-5) for small values of B_{12} and A_{12} approaching unity, but it is not limited to these conditions. The use of the binary principle for each component with the added agent is a useful guide, both for selecting effective agents and for estimating the quantitative vapor-liquid relationships. For example,

data are available on the vapor-liquid equilibria for the systems acetone-water and methanol-water. The activity coefficients for acetone and methanol can be calculated for a low concentration, and these values will be close to the values for a dilute mixture of acetone and methanol in water, thus allowing their relative volatility to be calculated for these conditions. Frequently, it is easier to determine the vapor-liquid equilibria for the two binaries with the added agent than it is to investigate the three-component system.

While theoretically it is possible to add a material of either higher or lower polarity, both cases are not usually equally attractive or practical. For example, in separating a binary mixture of a paraffin and an olefin of the same number of carbon atoms, it is difficult to find practical agents of lower polarity, and the only real possibility is to use a material of higher polarity. Such an agent will increase the volatility of the paraffin relative to that of the olefin, and it is unfortunate that the natural volatility of the olefin is often greater than that of the paraffin. Thus, adding small quantities of the agent actually makes the separation more difficult, and large enough quantities must be used to reverse the normal volatility completely. Obviously, the reversal must be sufficient to make the separation by distillation appreciably easier than without the agent. For example, aqueous acetone has been used for the separation of butadiene 1,3 from butylenes. In this case, the solvent added is of high polarity and increases the volatility of the olefines relative to the diolefine. Normally the relative volatility of *cis*-butene-2 (one of the constituents of the mixture) to butadiene is 0.78, and the value increases to 1.3 with 80 volume per cent of aqueous acetone. A relative volatility of 1.3 gives an ease of separation about equal to a value of 0.78, and the use of less than 80 volume per cent of aqueous acetone would make the separation of these components more difficult than for the hydrocarbons alone.

Extractive and azeotropic distillations both employ this technique of adding a component to modify the volatilities. They differ chiefly in the fact that the agent added in the case of extractive distillation is relatively nonvolatile as compared to the other components in the mixture, while in azeotropic distillation the volatility is essentially the same as that of the other components; it, therefore, forms an azeotrope with one or more of them due to the differences in polarity. In extractive distillation the agent is usually added near the top of the column, and most of it is removed with the liquid at the bottom. In azeotropic distillation the agent is also added near the top of the column,

but in this case most of it is removed with the overhead vapor. The distinction is not sharp. In the separation of pentane and amylenes using acetone as the added agent, most of the acetone is removed from the still, but it forms an azeotrope with the pentane and a small portion is carried overhead. For the purposes of this text, the term extractive distillation will be applied to those cases in which the agent is appreciably less volatile than the components to be separated and in which the concentration of the agent is relatively constant from plate to plate except as affected by additions or withdrawals from the column. Azeotropic distillation will be used to define those operations in which the added material has a high concentration in the upper portion of the column and then decreases to a relatively low value in the lower portion of the unit.

In any given case there are usually a number of compounds that are effective as azeotropic- or extractive-distillation agents, and the choice depends on a number of factors:

1. Effectiveness for modifying normal volatility.
2. Solubility relationships with system in question.
3. Cost of agent.
4. Stability of agent.
5. Volatility of agent.
6. Corrosiveness of agent.
7. Ease of separating agent from original components.

Extractive distillation will be considered first because the mathematical analysis for it is simpler than for azeotropic distillation.

EXTRACTIVE DISTILLATION

This type of operation has been used for several important separations, and it is one of the most valuable techniques in fractional distillation. Its earliest use probably was in the distillation of nitric and hydrochloric acids using sulfuric acid as the added agent to aid in the separation. It is extensively used, and some of the separations that have been carried out commercially are given in Table 10-1.

The general arrangement normally used is shown in Fig. 10-1. The feed is introduced into the main extractive distillation tower, and the extractive agent is introduced a few plates below the top of the column. These top plates serve to remove the agent from the overhead product. In certain cases, such as the isoprene-amylene separation with acetone, the agent cannot be completely eliminated from the overhead product by this method owing to azeotrope formation. In such cases, other

TABLE 10-1. COMMERCIAL EXTRACTIVE DISTILLATION OPERATIONS

System	Extractive Agent
$HCl–H_2O$	H_2SO_4
$HNO_3–H_2O$	H_2SO_4
Ethanol–H_2O	Glycerine
Butene–butane	Acetone, furfural
Butadiene–butene	Acetone, furfural
Isoprene–pentene	Acetone
Toluene–paraffinic hydrocarbons	Phenol
Acetone–methanol	Water

means, such as extraction, must be employed to separate the agent. The bottoms from the tower are treated to separate the agent and the bottoms product. Occasionally, a portion of the agent is added with the feed in order to maintain its concentration essentially the same above and below the feed.

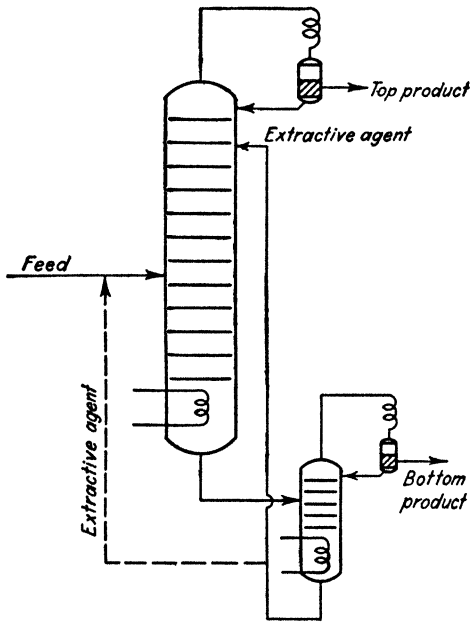


FIG. 10-1. Schematic diagram of extractive distillation system.

The design calculations for such systems are straightforward, assuming that the physical-chemical data on the systems are available. In the limiting case of an essentially nonvolatile extractive agent, the problem reduces to a standard binary or multicomponent problem depending on the feed to the unit, except for the modification of the

volatilities. In case the agent is volatile, the problem is more complicated, but it can be handled by methods analogous to those used for regular distillations.

Total Reflux. This limiting condition is not equivalent to that for regular rectification because to maintain a given concentration of the extractive solvent in the liquid phase would require the addition of an infinite amount per unit of feed. Thus the concentration of the components being separated would approach zero in the bottoms from the

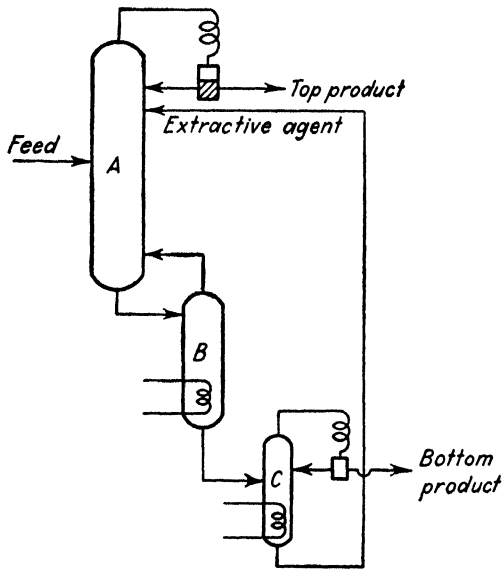


FIG. 10-2. Extractive distillation diagram for total reflux.

extraction tower. It would require an infinite number of plates to reduce the concentrations from the finite values in the upper part of the column to zero at the bottom, except for the case where the solvent was nonvolatile. This limit of an infinite number of plates and infinite heat consumption does not aid in orienting the design calculations. A useful limit for orientation purposes can be based on the desired separation of the key components from the overhead to bottoms. Thus the calculations should be carried down the column until the desired bottoms ratio of the key components is obtained. Actually the system can be considered as shown in Fig. 10-2. Column *A* is the usual extractive distillation unit, which obtains the desired degree of separation of the key components, and produces a bottoms containing

a finite concentration of the key components in the desired ratio. B is some type of unit that produces the vapor for column A and reduces the concentration of the key components without changing their ratio. Column C is the tower that separates the solvent from the bottom product. In case the solvent is nonvolatile, unit B is a still. The number of theoretical plates for tower A is the desired answer. The minimum number of plates at total reflux will therefore be calculated on the basis of the desired ratio of the key components in the overhead and bottoms. If the relative volatility is reasonably constant over the concentration range involved, Eq. (7-52) should be satisfactory. In any case, the plate-to-plate calculation methods of Chap. 9 can be applied.

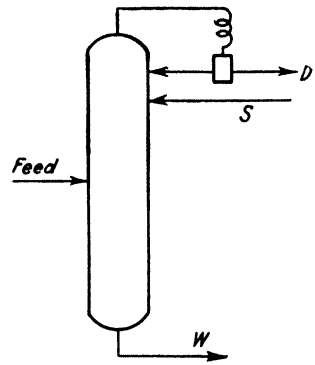


FIG. 10-3. Extractive distillation diagram.

Minimum Reflux Ratio. The calculation for this case is similar to that for the usual multicomponent mixture, but with the extractive agent included at both the pinched-in regions. The asymptotic value is calculated in the same manner as Eqs. (9-13) and (9-15). Thus for Fig. 10-3, the asymptotic concentration above the feed is

$$x_{Sn} = \frac{\alpha_{hk}\left(\dfrac{Sx_S - Dx_{DS}}{O_n}\right)}{\alpha_{hk} - \alpha_S - \alpha_S\,(Dx_{Dhk}/O_n x_{hk})} \tag{10-7}$$

and, below the feed,

$$x_{Sm} = \frac{\alpha_{lk}(Wx_{WS}/O_m)}{\alpha_{lk} - \alpha_S + \alpha_S(Wx_{Wlk}/O_m x_{lk})} \tag{10-8}$$

where x_{Sn}, x_{Sm} = asymptotic values of solvent above and below the feed plate respectively

Sx_S = solvent added to system at top of column

In many cases, the mixture to be separated is a binary, since it is usually desirable to separate all but two components by regular distillation and then subject them to the extractive operation. Generally, the amount of solvent added at the top of the tower is varied with the reflux ratio in order to maintain a constant mol fraction of solvent in the total liquid returned to the top region of the column. An alternative method of operation is to employ a given solvent rate independent

of the reflux ratio, which would give a solvent concentration in the tower that varied widely with the reflux ratio. The first method of operation appears to be more desirable for most cases, in order to obtain a relative constant concentration of solvent in the tower that approximates the desired value. The equations for the minimum reflux ratio have therefore been derived to be most convenient for the first method of operation. For the general case in which the feed contains light and heavy components in addition to the key components, it is recommended that the minimum reflux ratio be calculated by

$$O_R = \frac{Q + T + \sqrt{(Q + T)^2 - 4(QT - AH)}}{2} \tag{10-9}$$

where $A = \dfrac{\alpha_{lk} D x_{Dlk}}{(\alpha_{lk} - \alpha_{hk})E}$

$$H = \frac{\alpha_{lk} W x_{Whk}}{(\alpha_{lk} - \alpha_{hk})G}$$

$$E = \frac{1 - x_{DS} - \dfrac{\alpha_{hk}}{\alpha_{hk} - \alpha_S}(x_{RS} - x_{DS})}{1 - x_{RS}}$$

$$G = \frac{1 - x_{DS} - \dfrac{\alpha_{lk}}{\alpha_{lk} - \alpha_S}(x_{RS} - x_{DS})}{1 - x_{RS}}$$

$$Q = \frac{\alpha'_{lk}\left[\dfrac{W x_{Whk}}{\alpha'_{lk} - \alpha_{hk}} + \sum\left(\dfrac{W x_{Wh}}{\alpha'_{lk} - \alpha'_h}\right) + \dfrac{F_S - D x_{DS}}{\alpha'_{lk} - \alpha'_S}\right] + pF}{G}$$

$$T = \frac{\alpha_{hk}\left(\dfrac{D x_{Dlk}}{\alpha_{lk} - \alpha_{hk}} + \dfrac{D x_{Dl}}{\alpha_l - \alpha_{hk}} - \dfrac{D x_{DS}}{\alpha_{hk} - \alpha_S}\right)}{E}$$

O_R = reflux from condenser before solvent is added at top

x_{DS}, x_{RS} = mol fraction of solvent in distillate and total liquid added to the top of tower, including reflux and solvent

F_S = solvent added with feed

α, α' = relative volatilities for solvent concentrations above and below feed, respectively

If the feed is binary mixture, the terms involving x_{Dl} and x_{Wh} are dropped. For certain special cases, simpler equations can be employed. For example, if solvent is added with the feed such that its concentration is the same above and below the feed plate, the minimum vapor required can be calculated on a solvent-free basis by the regular minimum reflux equations, and then this vapor requirement is

increased to allow for the solvent in the vapor. In case the solvent is so high boiling that its concentration in the vapor is negligible, no correction to the solvent-free calculation is necessary. In making the calculation for the solvent-free conditions, the relative volatilities employed are those for the pinched-in region with the solvent present. By equating Eqs. (10-7) and (10-8) it is possible to calculate the amount of solvent that must be added with the feed to obtain equal concentrations above and below the feed plate. For simplification, the last terms in the numerator can be neglected because they are usually small.

$$S_F = \frac{x_{Sn}\left[\Delta\left(1 - \frac{\alpha_S}{\alpha_{lk}}\right) + \left(\frac{\alpha_S}{\alpha_{lk}}\right) O_n \left(\frac{\alpha_{lk}}{\alpha_{hk}} - 1\right)\right]}{1 - x_{Sn}\left(1 - \frac{\alpha_S}{\alpha_{lk}}\right)} \tag{10-10}$$

where S_F = mols of solvent added with feed

$\Delta = O_m - O_n - S_F$ = increase in overflow due to feed to tower

The value of x_{Sn} can be obtained from Eq. (10-7), and O_n can be obtained from a balance on the upper portion of the tower. For the case in which the solvent rate is maintained proportional to the reflux rate,

$$O_n = \frac{O_R(1 - x_{DS})}{1 - x_{RS}} \tag{10-11}$$

Feed-plate Location. In case solvent is added with the feed to maintain the same concentration in the upper and lower sections, the optimum key ratio can be calculated by the same method as for a regular distillation. If the solvent concentration is not the same in the two sections, there are usually two main factors tending to modify the optimum ratio. If the solvent concentration is lower below the feed plate than above, then (1) the relative volatility for the key components may be less favorable in the lower section and (2) the mol fraction of the solvent in the vapor is greater in the upper section. The first factor would make it desirable to use a low key component ratio for the feed plate to take advantage of the better relative volatility. Owing to the higher solvent vapor concentration above the feed plate, it would be desirable to use a higher key ratio than normal. The safest method is to calculate the feed-plate ratio for a regular distillation, and in the plate-to-plate analysis test several plates in the region to determine the optimum condition.

Concentration of Nitric Acid by Extractive Distillation. The concentration of nitric acid by the use of sulfuric acid will be used as an example of extractive distillation employing a nonvolatile agent. A typical flow sheet of a commercial unit is shown in Fig. 10-4. By the oxidation of ammonia and the absorption of the nitrogen oxides a 62 weight per cent nitric acid is made. A portion of this feed acid is mixed with 92 weight per cent sulfuric acid and added to the top of the tower. The remainder of the feed is vaporized and introduced into the middle region of the column. Direct steam is added at the

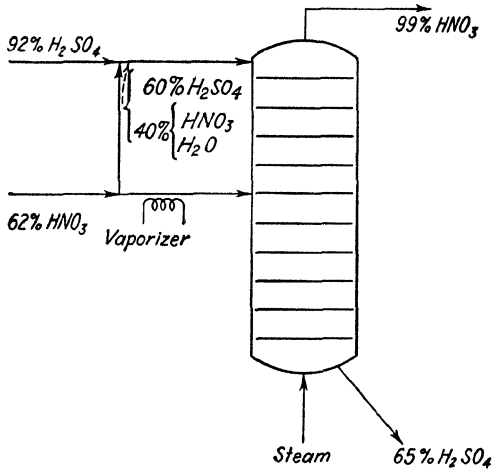


FIG. 10-4. Concentration of nitric acid

bottom. The overhead vapors are 99 weight per cent HNO_3, and an over-all recovery of nitric of 99 per cent is obtained. The sulfuric acid removed from the bottom is 65.0 weight per cent. The addition of the feed to the top of the tower is unusual and, in general, is not good distillation practice, but in this case the strong sulfuric acid would cause decomposition of concentrated nitric acid and is therefore diluted by the feed. The feed to the middle region is vapor so that there will be less dilution of the sulfuric acid. 1.2 lb of 92 per cent sulfuric is used per pound of 62 per cent nitric concentrated. The mixed acid added at the top is colder than the tower temperature, and the condensate produced in the column to heat it serves as reflux.

The operation of this nitric acid system will be analyzed to determine the number of theoretical plates involved. An analysis of the enthalpy values indicates that the usual simplifying assumptions will

not be satisfied, but the deviations are not large and the assumptions will be used to simplify the calculations. The problem can be solved more exactly on an enthalpy-composition diagram. In general such a diagram is not suitable for a three-component mixture, but due to the negligible volatility of the sulfuric acid, a modified form of the diagram can be used. Equilibrium data (Refs. 2, 4) are given in Fig. 10-5.

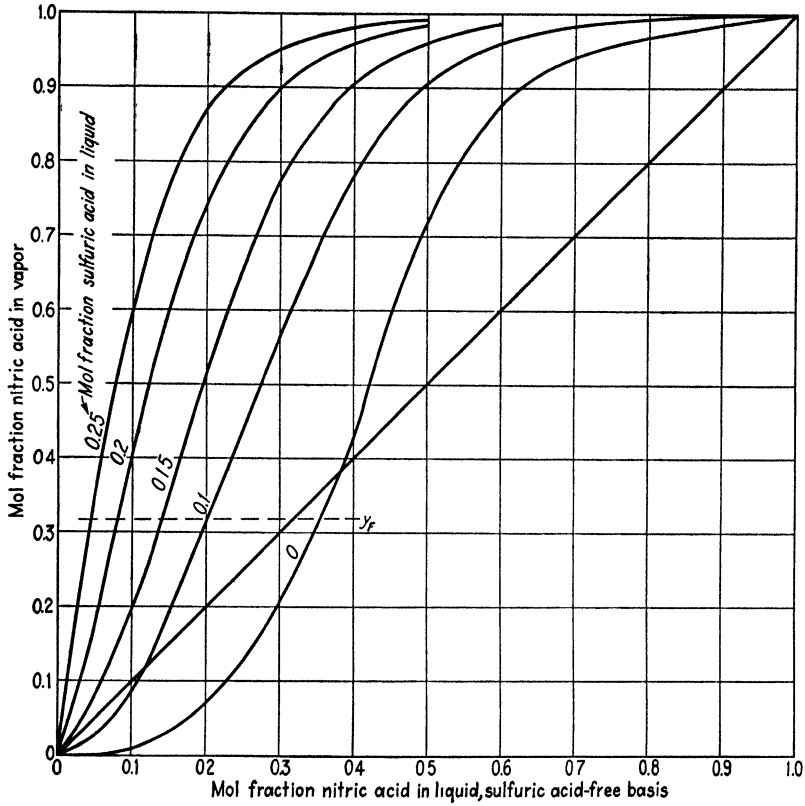


FIG. 10-5. Vapor-liquid equilibrium system, nitric acid–water–sulfuric acid.

These equilibrium data illustrate the effect of the added agent on the relative volatility. With no sulfuric acid present, nitric acid and water form a maximum boiling azeotrope containing 38 mol per cent acid. The 62 weight per cent feed available is 31.8 mol per cent nitric acid. It is therefore impossible to make 99 weight per cent nitric acid from this feed unless some method of passing the azeotrope is available. The addition of sulfuric increases the volatility of nitric acid relative to

water, and the equilibrium curves for liquid phases containing various mol fractions of sulfuric acid are given in Fig. 10-5. The units of the ordinates are expressed on a sulfuric acid-free basis. When the liquid phase contains 10 mol per cent sulfuric acid, the volatility of nitric acid is increased and the azeotrope composition becomes 12 mol per cent nitric acid. This sulfuric acid strength could be employed in a two-tower system to give the desired separation. The 31.8 mol per cent acid could be treated to extractive distillation with 10 mol per cent H_2SO_4 in the liquid to give the desired concentrated product and a bottoms containing about 15 mol per cent nitric acid. These bottoms would be fractionated without sulfuric acid being present to give water overhead and 31.8 per cent HNO_3 as bottoms which would be recycled. Instead of this two-tower arrangement, it is found more practical to use more sulfuric acid and make the complete separation in one step. In order to obtain a satisfactory relative volatility of nitric acid to water at the low end of the curve requires 20 to 25 mol per cent sulfuric acid in the liquid phase. The actual acid consumption for 25 mol per cent sulfuric acid is approximately the same as for 20 mol per cent, because the lower relative volatility for the latter requires more stripping steam which increases the acid requirement.

Solution. Basis: 100 mols of 62 weight per cent nitric acid.

$$x_F = \frac{62/63}{62/63 + 38/18} = 0.318$$

$$x_D = 0.965$$

$$D = \frac{31.8(0.99)}{0.965} = 32.6$$

Pounds of 62 per cent HNO_3 = 31.8(63) + 68.2(18) = 3,225

Pounds of 92 per cent H_2SO_4 = 1.2(3,225) = 3,870

$$\text{Mols } H_2SO_4 = \frac{3{,}870(0.92)}{98} = 36.4$$

$$\text{Mols } H_2O \text{ in with } H_2SO_4 = \frac{3{,}870(0.08)}{18} = 17.2$$

$$\text{Mols } H_2O \text{ in bottoms} = \frac{3{,}870(0.92)(0.35)}{0.65(18)} = 106.5$$

Mols H_2O in feed = 68.2

Mols H_2O in overhead = 32.6(0.035) = 1.14

Calculating the steam rate, S, by over-all water balance,

$$S = 106.5 + 1.14 - 17.2 - 68.2 = 22.2$$

It is assumed that sufficient nitric acid will be mixed with the sulfuric acid at the top of the tower so that the combined stream contains 60 weight per cent sulfuric acid.

Let x_N = weight fraction of HNO_3 in top mixture and $0.4 - x_N$ = weight fraction of H_2O in top mixture.

H_2O balance:

$$\frac{0.92(0.4 - x_N)}{0.60} = 0.08 + \frac{(0.92)x_N}{0.62(0.6)}0.38$$

$$x_N = 0.215$$
$$0.4 - x_N = 0.185$$

62 per cent HNO_3 added at top $= \dfrac{3{,}870(0.92)(x_N)}{0.62(0.60)}$

$= 9{,}570x_N$ lb. $= 2{,}060$

$= 297x_N$ lb. mols

$= 64$(20.35 mols 100 per cent HNO_3)

Vapor and liquid rates on H_2SO_4-free basis:

$$V_n = 22.2 + 36 = 58.2$$
$$O_n = 58.2 - 32.6 + 64 + 17.2 = 106.8$$
$$V_m = 22.2$$
$$O_m = 106.8$$
$$x_D = 0.965$$
$$x_W = \frac{31.8(0.01)}{106.8} = 0.003$$

It is interesting to note that for $S = 22.2$ an enthalpy balance gives V_n to the top plate of 53.2 as compared to the 58.2 obtained on the basis of constant O and V rates.

The mol fraction of sulfuric acid in the liquid phase is

$$\frac{36.4}{36.4 + 106.8} = 0.254$$

For vapor-liquid equilibria the curve for a mol fraction of sulfuric acid equal to 0.25 given in Fig. 10-5 will be used. This curve is replotted in Fig. 10-6, and the operating lines for the calculated flow rates are given.

The upper operating line for nitric acid is

$$58.2y_n = 106.8x_{n+1} + 31.5 - 20.35$$
$$= 106.8x_{n+1} + 11.15$$

The lower operating line is

$$22.2y_m = 106.8x_{m+1} - 0.32$$
$$y_m = 4.8x_{m+1} - 0.0144$$

The plates are stepped off starting at $y_T = 0.99$ and continuing down to $x = 0.003$ at $y = 0$. Approximately eight theoretical plates are required.

A more conventional extractive distillation would be to add all of the feed in the middle region of the tower and to return a portion of the overhead product as reflux with the sulfuric acid. Figure 10-7 shows such a system.

An exact comparison with the system of Fig. 10-4 can not be made, but several cases will be evaluated using 25.4 mol per cent H_2SO_4 in the liquid phase, and the same (O/V) ratio below the feed plate.

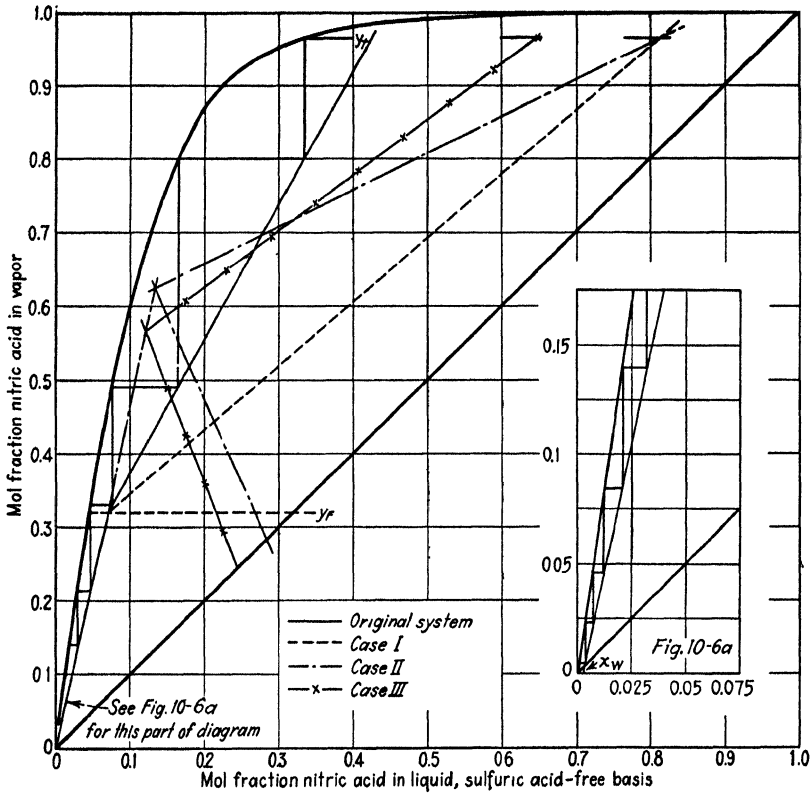


FIG. 10-6. Design diagram for nitric acid concentration.

Case I:

Feed all vapor and using 92 per cent H_2SO_4 at top. Basis: 100 mols of feed.

$$V_n = 122.2 \qquad O_n = 106.8$$
$$V_m = 22.2 \qquad O_m = 106.8$$

Composition of acid mixture refluxed to tower, 3,870 lb. 92 weight per cen H_2SO_4 + 89.6 lb. mols 96.5 mol per cent HNO_3

	Lb.	Weight per cent	Mol per cent
H_2SO_4	3,560	38.0	25.4
H_2O	366	3.9	14.2
HNO_3	5,430	58.1	60.4
	9,356		

Lower operating line, same as before.

Upper operating line,

$$122.2y_n = 106.8x_{n+1} + 31.5$$
$$y_n = 0.873x_{n+1} + 0.2575$$

The upper operating line is shown on Fig. 10-6. It requires about one less theoretical plate, but the heat requirements would be greater because of the necessity of vaporizing all of the feed.

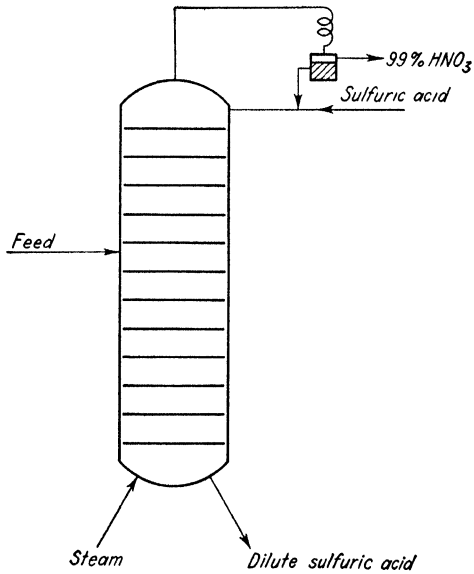


FIG. 10-7. Concentration of nitric acid.

Case II:

Feed 36 per cent vapor and using 92 per cent H_2SO_4 at top. Basis: 100 mols of feed. In order to maintain the sulfuric acid concentration constant, 72 per cent of it will be added at the feed plate.

$$V_n = 58.2 \qquad O_n = 30.4$$
$$V_m = 22.2 \qquad O_m = 106.8$$

Lower operating line, same as before but extends up the diagram farther because of the part liquid feed.

Upper operating line,

$$58.2y_n = 30.4x_{n+1} + 31.5$$
$$y_n = 0.522x_{n+1} + 0.541$$

This case requires the same heat and acid consumption as the original example but needs one additional theoretical plate. With the feed partly vaporized it would have been better to separate the liquid and vapor and introduce each at its

optimum location. If this change is made, the system reduces to the original system of Fig. 10-4, because the optimum feed-plate composition for the liquid portion of the feed is approximately the same as the top plate composition.

Case III:

Feed 36 per cent vapor and using 85 weight per cent H_2SO_4 at top. Basis: 100 mols of feed. The sulfuric acid will be split as for Case II.

For 85 per cent acid,

$$\text{Mol fraction } H_2SO_4 = 0.51$$

For bottom acid strength,

$$0.254 = \frac{H_2SO_4}{H_2SO_4 + (0.49/0.51)H_2SO_4 + (100 - 32.5) + S}$$

and, for same slope of lower operating line,

$$\frac{106.8}{22.2} = \frac{(0.49/0.51)H_2SO_4 + (100 - 32.6) + S}{S}$$

$$S = 30.2 \text{ mols}$$

$$H_2SO_4 = 49.4 \text{ mols } (17 \text{ mols at top, } 32.4 \text{ mols at feed})$$

H_2SO_4-free basis,

$$V_n = 30.2 + 36 = 66.2 \qquad O_n = 49.95$$
$$V_m = 30.2 \qquad O_m = 145.1$$

Lower operating line, same as before but the intersection of the two lines will be at a different position.

Upper operating line,

$$66.2y_n = 49.95x_{n+1} + 31.5$$
$$y_n = 0.755x_{n+1} + 0.476$$

These operating lines are shown in Fig. 10-6. This case requires fewer plates than Case II but requires more steam. It requires both more plates and steam than the original example. The use of additional steam is objectionable both because of the increased steam consumption and because it must be removed from the sulfuric acid in the concentrator.

The original system is more desirable than any of the three cases. It is instructive to analyze the possibilities of improving the original distillation system. Below the feed plate it would be desirable to reduce the steam consumption as much as possible, but for the 25 mol per cent sulfuric acid, Fig. 10-6 indicates that the ratio of O/V for this section cannot be increased significantly without increasing the difficulty of fractionation excessively. Using this same slope ($O/V = 4.8$), the steam consumption is

$$S = \frac{H_2O \text{ (with } H_2SO_4) + 67.4 \text{ (from feed)}}{3.8}$$

For the same strength nitric acid feed and the given acid recovery and overhead concentration, the only way to reduce S is by reducing the water brought in by the sulfuric acid. Higher strength sulfuric acid would reduce S but increase the difficulty of reconcentrating the acid. A higher mol per cent sulfuric acid in the

liquid phase would make it possible to reduce S but would increase the acid recirculation. None of these alternatives for the lower section appears to offer any great advantage over the original system. The concentration change per plate is less below the feed plate than above, and it is desirable to shift to the upper operating line at a low concentration. The original system accomplishes this result by using an all-vapor feed. If all the feed is added as a vapor (see Case I), the fractionation in the enriching section is very easy but requires vaporizing all of the feed. The original system reduces the heat consumption by vaporizing only a portion of the feed and adding the remaining feed as liquid at the top which is approximately the optimum feed-plate location for the liquid feed. This still gives the favorable intersection of the operating lines and reduces the heat required for vaporizing the

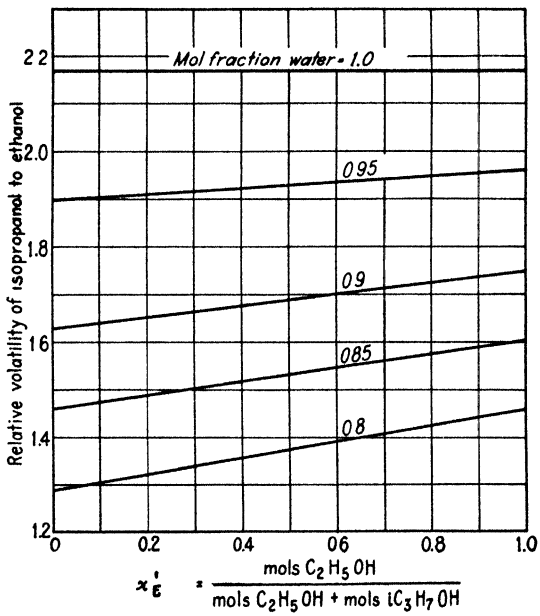


FIG. 10-8. Relative volatility of isopropanol to ethanol in presence of water.

feed. It makes the separation a little more difficult than using all of the feed as vapor, but it is obvious that the extra theoretical plate required is well justified by the savings of heat. On the basis of Fig. 10-6, it would appear that it might be advantageous to add more of the feed as liquid at the top and thereby reduce the amount to be vaporized. This would necessitate preheating the mixed acid added at the top by an amount equal to the reduced heat input with the vapor feed, but low-pressure waste steam might be used for this purpose. Such a change would need to be carefully analyzed on an enthalpy basis in order to determine whether a pinched-in condition was being encountered at the top of the column. In the case of the original system, one portion of the feed was vaporized and the other added as liquid at the top. Some improvement would be obtained by vaporizing under

equilibrium conditions such that the vapor feed would be more dilute in nitric acid and the liquid stronger. These two fractions could then be added as in Fig. 10-4, and the operating lines would be more favorable.

In most extractive distillation cases the added component is volatile. The following example will illustrate the application of general equations developed in this chapter when using an extractive agent of appreciable volatility.

Separation of Ethanol and Isopropanol by Extractive Distillation. A mixture containing 20, 4, and 76 mol per cent of water, isopropyl alcohol, and ethyl alcohol, respectively, is to be separated into an ethyl alcohol product containing not over

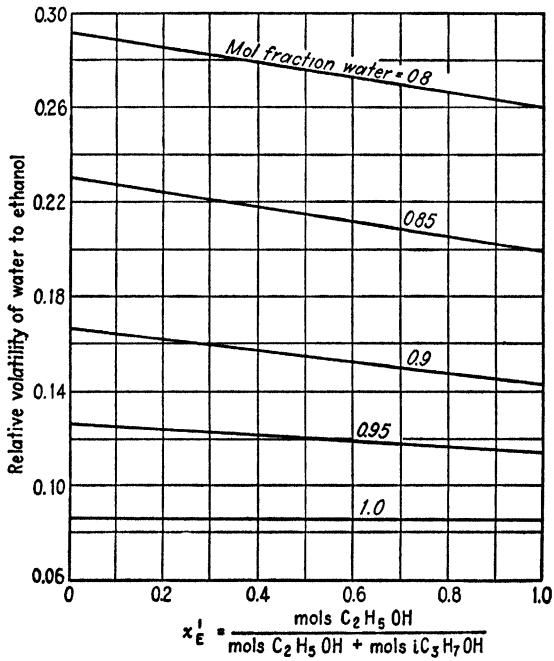


FIG. 10-9. Relative volatility of water to ethanol.

).2 mol per cent isopropyl alcohol on a water-free basis with an ethanol recovery of)8 per cent. It has been decided that water will be used as an extractive distillation agent, and enough water will be added to the reflux to make the liquid added to the tower 85 mol per cent water. The feed will be diluted to 85 mol per cent water before it is added to the tower, and it will be heated such that $V_n = V_m$. Making the usual simplifying assumptions, calculate:

1. The minimum number of plates at total reflux.
2. The minimum reflux ratio, O/D.

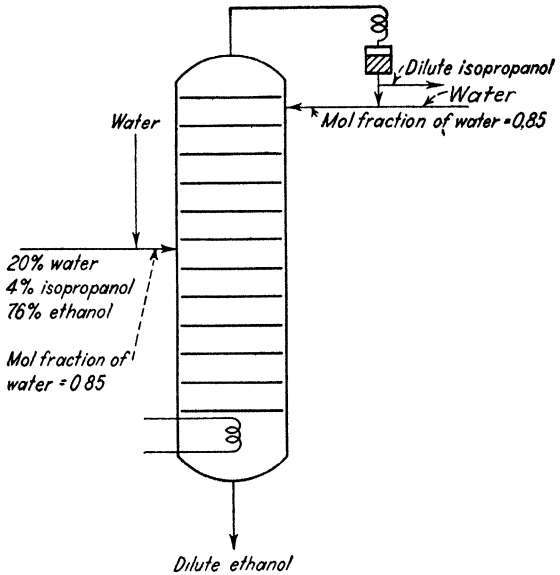


FIG. 10-10. Extractive distillation system for isopropanol-ethanol.

3. The number of theoretical plates required for O/D equal to 1.5 minimum O/D.

The equilibrium data (Refs. 5, 6) for this system are given in Figs. 10-8 and 10-9. A schematic diagram is shown in Fig. 10-10.

Solution:

Let I = isopropyl alcohol
E = ethyl alcohol
H = water

Basis: 100 mols of undiluted feed.

Since, in the presence of water, isopopanol is more volatile than ethanol, the latter will be largely in the bottoms. By an ethanol balance

$$76(0.98) = Wx_E = 74.48$$

For design conditions,

$$\frac{Wx_I}{Wx_I + Wx_E} = 0.002; \qquad Wx_I = 0.149$$

and, by difference,

$$Dx_E = 1.52; \qquad Dx_I = 3.85$$

The water in the distillate cannot be determined until the composition of the top plate is known, and this calculation is complicated by the fact that the water concentration on the top plate is not known. The water content of the reflux to the tower is 0.85, but there will be some change of this on the top plate; however, as a first approximation, a mol fraction of water equal to 0.85 will be assumed for

this plate. Then using the relative volatilities from Figs. 10-8 and 10-9 a balance is applied to the top plate.

Component	y_{top}	α	$\frac{y}{\alpha}$
E	$\frac{1.52}{D}$	1.0	$\frac{1.52}{D}$
I	$\frac{3.85}{D}$	1.49	$\frac{2.58}{D}$
H	$\frac{D - 5.37}{D}$	0.22	$\frac{4.54D - 24\ 4}{D}$
			$\sum \frac{y}{\alpha} = \frac{4.54D - 20.3}{D}$

$$x_H = 0.85 = \frac{4.54D - 24.4}{4.54D - 20.3}; \qquad D = 10.5$$

Water in distillate equals $10.5 - 5.37 = 5.13$, and for the distillate $x_E = 0.145$,

$$x_I = 0.367 \qquad x_H = 0.488$$

The mols of water added to dilute the feed $= (80/0.15) - 100 = 433$. Mols of water added at top of tower $= O_R\left(\frac{0.512}{0.15} - 1.0\right) = 2.41O_R$

Solution of Part 1. For the condition of total reflux the operating lines for the alcohols are $y = 3.41x$, and for water $y = 3.41x - 2.41$. The water concentration at the top of the tower will be approximately 0.85 and will increase slightly down the tower because the relative volatility of water to the alcohols increases as the ethanol concentration increases. The concentration at the bottom of the tower is assumed as 0.86.

For these water concentrations the relative volatility of isopropanol to ethanol is 1.5 at the top and 1.64 at the bottom. Thus,

$$N + 1 = \frac{\log (0.367/0.145)(0.998/0.002)}{\log 1.57} = 16$$

Therefore, approximately 15 theoretical stages are required.

It has been pointed out in the discussion that this case is inconsistent in actual bottoms concentration, but the answer just calculated gives a valuable limit for orientation, and the actual theoretical plates for $O/D = 1.5(O/D)_{min}$ will be about 50 per cent greater.

Solution of Part 2. The minimum reflux ratio will be calculated by three methods:

Method 1. Since the amount of water in both the liquid and vapor phases is relatively constant from plate to plate, the system may be treated as a binary to

find $(O/D)_{min}$. Using the mol fractions of the alcohols on a water-free basis, which will be indicated by primes, with $V_n = V_m$, at the feed plate, the concentration of isopropyl alcohol in the feed is $x_I' = 4/80 = 0.05$ and $\alpha_{IE} = 1.6$ (mol fraction water = 0.85).

$$y_I' = \frac{1.6(0.05)}{1 + 0.6(0.05)} = 0.0776$$

on this basis,

$$x_D' = \frac{3.85}{3.85 + 1.52} = 0.716$$

$$\left(\frac{O'}{V'}\right)_{min} = \frac{0.716 - 0.0776}{0.716 - 0.050} = 0.959$$

$$\left(\frac{O'}{D'}\right)_{min} = \frac{0.959}{0.041} = 23.2$$

$$D' = 5.37$$

and

$$(O_n')_{min} = 23.2(5.37) = 125 \text{ mols of alcohol in overflow to feed plate}$$

$$(V_n')_{min} = 125 + 5.37 = 130.4 \text{ mols of alcohol in vapor}$$

$$(O_n)_{min} = \frac{125}{0.15} = 833 \text{ (assume } x_H \text{ at feed plate} = 0.85)$$

$$O_R = \frac{833}{3.41} = 244$$

By Eq. (10-7) the asymptotic concentration of the solvent is

$$x_{Sn} = \frac{1.0\left[\dfrac{2.41(244) - 5.1}{833}\right]}{1.0 - 0.2} = 0.875$$

as compared to 0.85 assumed.

This value is essentially independent of the value of O_n, since the numerator of the bracket is $2.41O_R - 5.1$, the denominator is $3.41O_R$, and the 5.1 is only a small correction.

Thus, with $x_{Sn} = 0.875$

$$(O_n)_{min} = \frac{125}{0.125} = 1{,}000$$

$$(O_R)_{min} = \frac{1{,}000}{3.41} = 293$$

$$\left(\frac{O_R}{D}\right)_{min} = \frac{293}{10.5} = 27.9$$

The value of x_{Sm} is a little lower than x_{Sn}, and Eqs. (10-7) and (10-8) indicate that, for this reflux ratio, approximately 530 mols of water should be added with the feed to make them equal instead of the 453 mols used to make the mol fraction of water in the feed equal to 0.85.

Method 2. By Eq. (10-9) using same values for relative volatilities above and below the feed plate,

$$x_{RS} = 0.85; \qquad x_{DS} = 0.49$$

$$E = \frac{(1 - 0.49) - \dfrac{1.0}{1.0 - 0.2}(0.85 - 0.49)}{1 - 0.85} = 0.4$$

$$G = \frac{(1 - 0.49) - \frac{1.6}{1.6 - 0.2}(0.85 - 0.49)}{1 - 0.85} = 0.667$$

$$A = \frac{1.0(3.85)}{(1.6 - 1.0)(0.4)} = 16$$

$$H = \frac{1.6(74.48)}{(1.6 - 1.0)(0.667)} = 298$$

$$Q = \frac{1.6\left(\frac{74.48}{1.6 - 1.0} + \frac{453 - 5.1}{1.6 - 0.2}\right) - 533}{0.667} = 0.268$$

$$T = \frac{1.0\left(\frac{3.85}{1.6 - 1.0} - \frac{5.1}{1.0 - 0.2}\right)}{0.4} = 0$$

$$O_R = \frac{268 + \sqrt{(268)^2 + 4(16)(298)}}{2} = 285$$

$$\frac{O_R}{D} = \frac{285}{10.5} = 27.1$$

Using this value of the reflux ratio it is possible to calculate the ratio of the key components at the feed plate. In this case, the value of the ratio is 0.055 or only slightly higher than the ratio in the feed.

Method 3. A third method is equating the pinched-in ratio for the key components to the intersection ratio, ϕ. This is not a general method because the intersection ratio may be considerably different from the optimum matching ratio.

$$\phi = \frac{0.04}{0.76} = 0.0526 = \frac{x_{lk}}{1 - x_{lk} - x_{Sn}}$$

calculating x_{lk} by Eq. (9-13) and x_{Sn} by Eq. (10-7).

$$0.0526 = \frac{\frac{1.0\,(3.85/O_n)}{1.6 - 1.0}}{1 - \frac{1.0\left(\frac{3.85}{O_n}\right)}{1.6 - 1.0} - \frac{1.0\,\frac{Sx_S - Dx_{DS}}{O_n}}{1.0 - 0.2}}$$

$$O_n = O_R \frac{1 - x_{DS}}{1 - x_{RS}} = 3.410_R$$

$$Sx_S = O_R \frac{x_{RS} - x_{DS}}{1 - x_{RS}} = 2.41O_R$$

$$0.0526 = \frac{6.41}{3.41O_R - 6.41 - 3.01O_R + 6.41}$$

$$O_R = \frac{6.41}{0.0526\,(0.4)} = 305$$

$$\frac{O_R}{D} = 29$$

The value for O_R by Method 3 is higher because the optimum key component ratio is greater than that used.

A value of ϕ equal to 0.055 instead of 0.0526 would make the reflux ratio calculated by Method 3 equal to those of the other two methods.

Solution of Part 3. Using a value of 27.5 for $(O_R/D)_{min}$ gives

$$\left(\frac{O_R}{D}\right)_{act} = 1.5(27.5) = 41.3$$

and

$$O_R = 41.3(10.5) = 433 \text{ mols}$$

Water added at top = 2.41(433) = 1,042 mols
Water out with bottom = 1,042 + 453 − 5 = 1,490 mols
O_n = 433 + 1,042 = 1,475 mols
$V_n = V_m$ = 433 + 10.5 = 443 mols
O_m = 1,475 + 533 = 2,008 mols

TABLE 10-2

	Bottoms		α	αx_W	$0.22y_W$	$\frac{Wx_W}{2{,}008}$
	Mols	Mol fraction				
E	74.5	0 0476	1 0	0 0476	0 067	0 037
I	0 149	0 0000955	1 96	0.000187	0 000263	0 00007
W	1,490.0	0.952	0.114	0.1085	0.1525	0 742
	1,564 6			0 1563		

	$x_1 = 0.22y_S + \frac{Wx_W}{2{,}008}$	α	αx_1	$0.22y_1$	x_2	α	$0.22y_2$
E	0 104	1 0	0.104	0 0966	0 1335	1 0	0 101
I	0 000333	1 62	0 00054	0 0005	0 00057	1.65	0 000715
W	0 895	0.148	0.1325	0 123	0 865	0 18	0 118
			0 237				

	x_3	α	$0.22y_3$	x_4	x_5	x_6	x_7
E	0.138	1.0	0.101	0.138	0.138	0.138	0 137
I	0 000785	1.635	0.000935	0.0010	0.00127	0 0016	0 00196
W	0 86	0.188	0.1185	0.86	0.860	0.860	0.860

	x_8	x_9	x_{10}	x_{11}	x_{12}	x_{13}	x_{14}
E	0.137	0.137	0 1365	0.136	0 1355	0.135	0.134
I	0.0024	0.00293	0.00355	0.0042	0.00505	0.006	0 0071
W	0.860	0.860	0.859	0.859	0.859	0.859	0.859

Operating lines:

Above feed plate for alcohols,

$$443y_n = 1{,}475x_{n+1} + Dx_D$$

$$0.3y_n = x_{n+1} + \frac{Dx_D}{1{,}475}; \qquad \frac{Dx_D}{1{,}475} = 0.00261 \text{ for isopropanol}$$

$$= 0.00103 \text{ for ethanol}$$

Above feed plate for water,

$$0.3y_n = x_{n+1} + \frac{5.13 - 1042}{1{,}475}$$

$$= x_{n+1} - 0.703$$

Below the feed plate for alcohols,

$$443y_m = 2{,}008x_{m+1} - Wx_W$$

$$0.22y_m = x_{m+1} - \frac{Wx_W}{2{,}008}$$

where $Wx_W/2{,}008$ equals 0.037 for ethanol, 0.00007 for isopropanol, and 0.742 for water.

The calculations are carried up from the still in the usual manner, with relative volatility values from Figs. 10-8 and 10-9. The results are summarized in Table 10-2.

The intersection ratio of the key components is 0.0526, and the actual ratio on the thirteenth plate is 0.0444 and 0.053 on the fourteenth plate. In this case, the optimum ratio is slightly higher than the intersection ratio, and the fourteenth plate will be used as the feed plate. The calculations are then continued using the enriching line equations. The results are presented in Table 10-3.

TABLE 10-3

	x_{15}	x_{16}	x_{17}	x_{18}	x_{19}	x_{20}	x_{21}
E	0.130	0.126	0.123	0.118	0.1105	0.101	0.0886
I	0 0087	0 0113	0.0154	0 0215	0.0301	0.042	0 0563
W	0.861	0.862	0.862	0.860	0 859	0 857	0 855

	x_{22}	x_{23}	y_{23}	x_{24}	y_{24}	x_D
E	0.0744	0.060	0 1575	0.0463	0 119	0.145
I	0.0723	0 0889	0.354	0.104	0.401	0 367
W	0.853	0.851	0.488	0.849	0 480	0 488

The x and y values are given for plates 23 and 24. It will be noted that y_{23} is not quite up to x_D, but that y_{24} exceeds it. Thus between 23 and 24 theoretical plates in addition to the still are required. The water concentration on the top plate is close to the assumed value of 0.85. If this assumption had not checked with the calculated value, it would be necessary to estimate whether the error would materially affect the result. If the correction was large, the calculations might need to be repeated to obtain a satisfactory result.

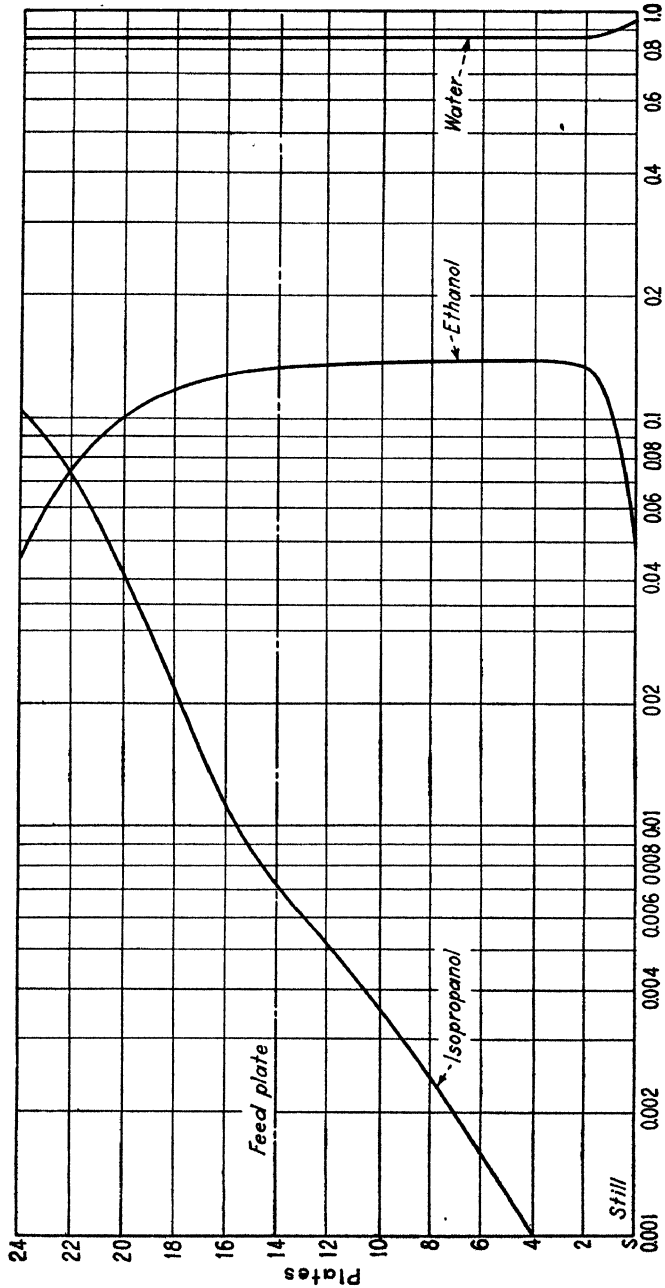

Plates
24
22
20
18
16
14
12
10
8
6
4
2
S
Still
Feed plate
Isopropanol
Ethanol
Water
0.001
0.002
0.004
0.006
0.008
0.01
0.02
0.04
0.06
0.08
0.1
0.2
0.4
0.6
0.8
1.0
Mol fraction in liquid

FIG. 10-11.

The calculated values for the liquid phase are plotted in Fig. 10-11. There is a rapid decrease in the water concentration from the still to the first few plates, and then the value is relatively constant in the remainder of the tower. The decrease through the tower is small because (1) the relative volatility of water relative to the alcohols decreases as the ratio of isopropanol to ethanol increases and (2) the water concentration in the still is high. The concentration of water in the bottoms is higher because the vapor removed from the still contains a much higher ratio of alcohol to water than the liquid to the still.

Because the water concentration is relatively constant, approximate calculations could be made on a water-free basis. The total available vapor and liquid should be decreased by an amount equal to that required for the water, and the remaining vapor and liquid used to separate the alcohols as a binary mixture using relative volatility from Fig. 10-8 at the assumed water concentration. For this case, the result should be reasonably close to the more rigorous method employed in this section, but it is doubtful whether the calculation is much simpler or less time-consuming.

AZEOTROPIC DISTILLATION

The first commercial application of azeotropic distillation was the use of benzene by Young (Ref. 7) for the azeotropic dehydration of aqueous alcohol, which is still one of the most important applications of this type of operation.

It has been pointed out that this system differs from extractive distillation chiefly in the behavior of the agent. For example, consider the continuous dehydration of ethyl alcohol by the use of benzene as the azeotropic agent, as shown in Fig. 10-12. Tower 1 serves to remove the water from the alcohol, and tower 2 serves to recover the alcohol and benzene. Essentially anhydrous alcohol is produced as bottoms in tower 1, and sufficient plates are used above the feed plate to produce an overhead vapor that will give two liquid layers on condensation. The benzene-alcohol layer is used as reflux for tower 1, and the water layer containing small amounts of alcohol and benzene is stripped to recover these constituents. In such an operation, the agent, benzene, must vary from essentially zero in the still to a relatively high concentration in the tower. Thus there is a wide variation in the solvent concentration in the tower, and some of the approximations made for extractive distillation would lead to serious errors.

The benzene-alcohol-water system can produce an overhead vapor that will give two liquid phases on condensation which makes it possible to by-pass the azeotrope in a manner analogous to that which was shown for partly miscible binary distillations, and the same type of two-tower system is applicable. It should be noted that the system does not produce the ternary azeotrope as the overhead composition,

but it is essential that the condensate is two layers. With some azeotropic systems the overhead will not give two liquid layers, and some other type of operation must be used to split the overhead, such as extraction or dilution.

In order to illustrate the phenomena involved in azeotropic distillation, an example will be considered first and then the various limiting

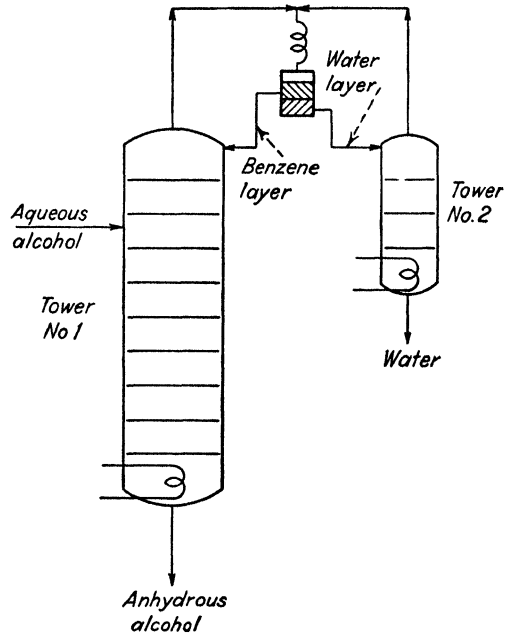


FIG. 10-12. Azeotropic system for the production of absolute ethanol using benzene.

conditions will be reviewed. Consider the production of anhydrous ethanol using benzene as the azeotroping agent. In such cases, it is found most economical to concentrate the alcohol by normal distillation to almost the binary azeotrope concentration before it is introduced into the azeotropic system.

Production of Absolute Alcohol by Azeotropic Distillation with Benzene. For the purposes of this example it is assumed that the feed to the dehydration system contains 89 mol per cent alcohol and 11 mol per cent water A two-tower system will be employed similar to that illustrated in Fig. 10-12, and only a single liquid layer will be refluxed to each tower. Both towers will be designed for an overflow rate below the feed plate of 125 mols per 100 mols of vapor, and the usual simplifying assumptions will be made. The feed to the alcohol tower will be such that $V_n = V_m$, and it is assumed that any condensation due to the reflux liquids

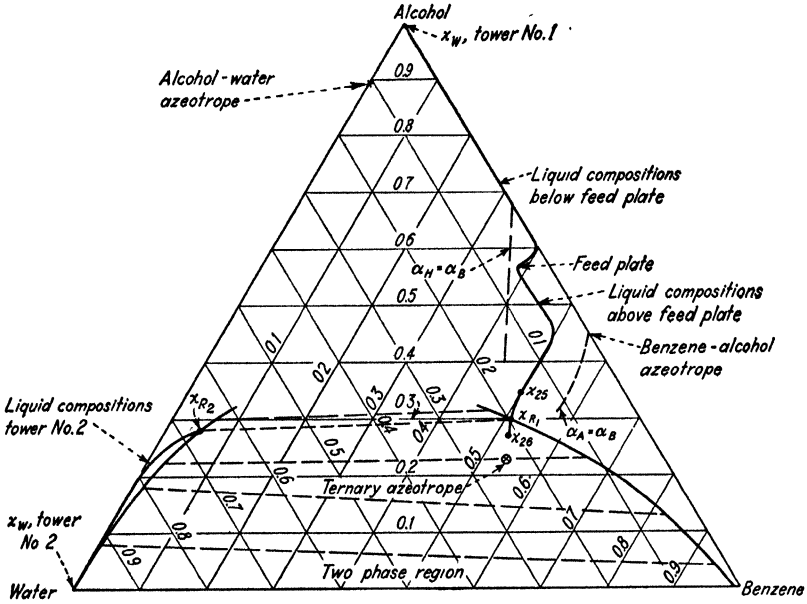


FIG. 10-13. Diagram for system, ethanol-benzene-water.

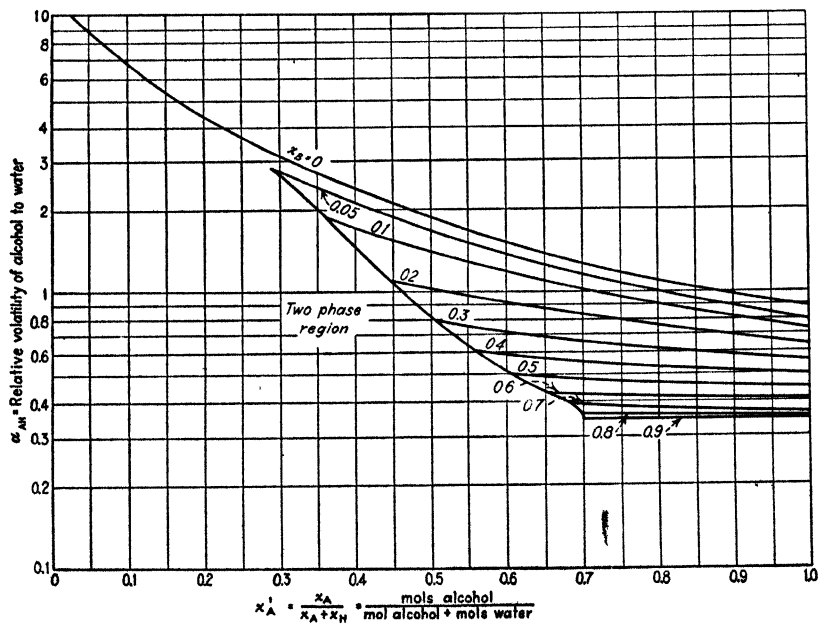


FIG. 10-14. Equilibrium data for system, ethanol-benzene-water.

being at a lower temperature than their boiling point is negligible. The bottoms from the water tower are to contain not over 0.01 mol per cent alcohol, and the anhydrous alcohol is to contain not over 0.01 and 0.1 mol per cent benzene and water, respectively. Theoretically, it is not possible to set the exact bottoms concentration because the composition of the refluxes is limited by the solubility relationships; however, it is found that rather wide latitude is possible in selecting the composition of the bottoms product. For this example it is assumed that the bottoms are 99.9, 0.01, and 0.09 mol per cent alcohol, benzene, and water, respectively.

The physical-chemical data for this system are taken from Cook (Ref. 3) and Barbaudy (Ref. 1). The solubility data for 25°C. are given in Table 10-4 and plotted in Fig. 10-13. The vapor-liquid equilibrium data for the system at atmospheric pressure are presented in Figs. 10-14 and 10-15.

It should be noted that equilibrium data available were not so complete or so consistent as would be desired, and that these two figures represent a smoothing, extrapolation, and interpolation of the data.

Solution. Basis: 100 mols of feed.

Alcohol balance,

$$0.999W_1 + 0.0001\,W_2 = 89$$

Over-all balance,

$$W_1 + W_2 = 100$$

$$W_1 = 89.1$$

$$W_2 = 10.9$$

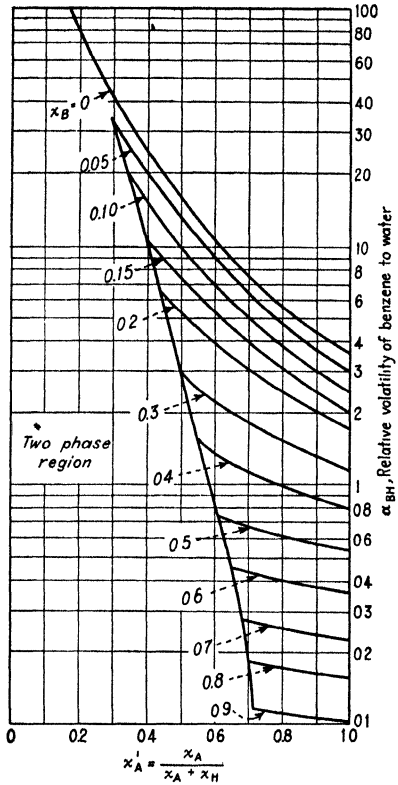


FIG. 10-15. Equilibrium data for system, ethanol-benzene-water.

TABLE 10-4. PAIRS OF TIE-LINE COORDINATES

Alcohol.....	0.3 and 0.315	0.225 and 0.23	0.18 and 0.13	0.08 and 0.04
Benzene.....	0.068 and 0.465	0.025 and 0.655	0.015 and 0.82	0.007 and 0.94
Water.....	0.632 and 0.22	0.75 and 0.115	0 805 and 0.05	0.914 and 0 02

Tower 1:

$$\frac{O_m}{V_m} = 1.25$$

$$O_m = V_m + 89.1 = 125V_m$$

$$V_m = 356 \qquad O_m = 445$$

$$V_n = 356 \qquad O_n = 345$$

The calculations will be started from the still, using a basis of $O_m = 1.0$, $V_m = 0.8$, and $W = 0.2$. The results are given in Table 10-5.

The feed ratio of the key components is $^{11}/_{89} = 0.123$, and the change from the lower to the upper section should be made at about this ratio. The ratios for plates 20, 21, and 22 are 0.075, 0.0935, and 0.114, respectively, from which it would

TABLE 10-5

(B = Benzene, A = Alcohol, H = Water)

	x_W	$0.2x$	α	αx_W	$0.8y_W$	x_1
B	0.0001	0.00002	3.6	0.00036	0 00032	0.000344
A	0.999	0.1998	0.89	0.89	0.7989	0.9987
H	0.0009	0.00018	1.0	0 0009	0.00081	0.00099
				0.89126		

	α	αx_1	$0.8y_1$	x_2	αx_2	$0.8y_2$	x_3
B	3 6	0 00124	0.00111	0.00113	0.00406	0.00364	0.00366
A	0 89	0.899	0.798	0.9978	0.888	0 7954	0.9952
H	1.0	0.00099	0.00089	0.00107	0.00107	0.00096	0 00114
		0.89123			0.89313		

	αx_3	$0.8y_3$	x_4	α	αx_4	$0.8y_4$	x_5	α
B	0.0132	0.0117	0.01172	3.4	0.0398	0.0354	0.03542	3 2
A	0.886	0.7873	0.9871	0.87	0.859	0.764	0 9638	0 82
H	0.00114	0.00101	0.00119	1.0	0.00119	0.00106	0.00124	1.0
	0.89934				0.89999			

	αx_5	$0.8y_5$	x_6	α	αx_6	$0.8y_6$	x_7
B	0.113	0.10	0.10	2 5	0 25	0.22	0.22
A	0.79	0.70	0.8998	0.73	0.657	0.579	0.7788
H	0.00124	0.0011	0.00129	1.0	0.00129	0.00114	0.00132
	0.90424				0.90829		

	α	αx_7	$0.8y_7$	x_8	α	αx_8	$0.8y_8$
B	1.58	0.348	0.335	0.335	0.98	0.328	0.382
A	0.62	0.483	0.464	0.664	0.54	0.358	0.417
H	1.0	0.00132	0.00127	0.00145	1.0	0.00145	0.00169
		0.83232				0.68745	

TABLE 10-5 (*Continued*)

	x_9	α	αx_9	$0.8y_9$	x_{10}	α	αx_{10}	$0.8y_{10}$
B	0.382	0.82	0.313	0 396	0.396	0.76	0 301	0.398
A	0.617	0.515	0.317	0.402	0.602	0.5	0.301	0.398
H	0.00187	1.0	0.00187	0.00237	0 00255	1.0	0.00255	0.00337
			0 63187				0.60455	

	x_{11}	αx_{11}	$0.8y_{11}$	x_{12}	αx_{12}	$0.8y_{12}$
B	0.398	0 302	0 400	0 400	0 304	0.400
A	0 598	0 299	0 396	0.596	0 298	0 393
H	0.00355	0 00355	0 0047	0.0049	0 0049	0 00645
		0 60455			0.6069	

	x_{13}	αx_{13}	$0.8y_{13}$	x_{14}	αx_{14}	$0.8y_{14}$	x_{15}
B	0.400	0.304	0 400	0 400	0 304	0.399	0.399
A	0 593	0.297	0 392	0.592	0 296	0 389	0 589
H	0.0066	0.0066	0 0087	0.0089	0 0089	0.0117	0.0119
		0.6076			0 6089		

	αx_{15}	$0.8y_{15}$	x_{16}	αx_{16}	$0.8y_{16}$	x_{17}	α	αx_{17}
B	0 303	0.398	0.398	0 302	0.395	0 395	0.76	0.301
A	0 295	0 387	0.587	0 294	0.384	0.584	0 51	0.298
H	0.0119	0.0156	0.0158	0.0158	0.0206	0.0208	1.0	0.0208
	0.6099			0.6118				0 6198

	$0.8y_{17}$	x_{18}	αx_{18}	$0.8y_{18}$	x_{19}	α	αx_{19}	$0.8y_{19}$
B	0 389	0.389	0.296	0.382	0.382	0 82	0 314	0 385
A	0 385	0.585	0.298	0.384	0.584	0.52	0.304	0 373
H	0.0268	0.027	0.027	0.0348	0.035	1 0	0.035	0.0429
			0.621				0.653	

	x_{20}	αx_{20}	$0.8y_{20}$	x_{21}	α	αx_{21}	$0.8y_{21}$	x_{22}
B	0.385	0.316	0.385	0.385	0.82	0.316	0.38	0.38
A	0.573	0.298	0.363	0.563	0.53	0.298	0 358	0.558
H	0.0431	0 043	0.0524	0.0526	1.0	0.0526	0.063	0.0632
		0 657				0 6666		

appear that plate 22 would be the best feed plate. By trial it is found that plate 21 is more desirable. This is largely because, below the feed plate, the benzene liquid-phase concentration is asymptotic at a value less than 0.4, but above the feed plate, this composition rises rapidly to above 0.5. This increased concentration increases the relative volatility of water to ethanol making the fractionation easier, and it is advantageous to do more of the fractionation above the feed plate.

The plate-to-plate calculations (Table 10-6) are carried above plate 21 in a similar manner. A basis of 1 mol of liquid is used, making $D = 1\frac{1}{345} = 0.032$ and $V = 1.032$.

TABLE 10-6. FEED PLATE 21

	$1.032y_{21}$	$0.032x_D$	x_{22}	α	αx_{22}	$1.032y_{22}$	x_{23}	α	αx_{23}
B	0.49	—	0.49	0 52	0.255	0.507	0.507	0.475	0.241
A	0.462	—	0.462	0.465	0 215	0.428	0 428	0.46	0.1965
H	0 0815	0.032	0.0495	1 0	0 0495	0 0985	0.0665	1.0	0 0665
					0.5195				0 5040

	$1.032y_{23}$	x_{24}	α	αx_{24}	$1.032y_{24}$	x_{25}	α	αx_{25}	$1.032y_{25}$	x_{26}
B	0.493	0 493	0 55	0.271	0.495	0.495	0 69	0 343	0.52	0.52
A	0.402	0.402	0.475	0.191	0.348	0.348	0.52	0 181	0.273	0.273
H	0.136	0 104	1 0	0 104	0 190	0 158	1 0	0 158	0 239	0 207
				0 566				0 682		

The top plate of the tower is determined by the fact that the reflux to it must correspond to the benzene layer of the two-phase region. In order to illustrate this condition, the liquid compositions are plotted on the triangular diagram in Fig. 10-13. The liquid composition x_{25} is in the single-phase region while x_{26} is in the two-phase region; thus neither of them satisfies the condition. This means that the exact design conditions are not fulfilled by an even number of theoretical plates and that between 24 and 25 theoretical plates are required since x_{25} would be the reflux to plate 24 and x_{26} the reflux to plate 25. Theoretically, the exact conditions could be satisfied by using a different reflux ratio, feed-plate location, or bottoms composition, but the trial-and-error procedure involved does not justify the effort. It is sufficient to know that between 24 and 25 theoretical plates are required. The x_{26} value could be satisfied exactly if a mixture of two liquid layers was refluxed, but this is not advantageous.

While it is not necessary to obtain an even number of theoretical plates in the calculations, it is essential to have a reasonably accurate estimate of the composition of the overhead vapor and the reflux in order to make the balances on the condenser. A satisfactory method of evaluating these compositions is to plot the compositions, as in Fig. 10-13, and use the composition where the curve cuts the two-phase boundary as the composition of the reflux to the alcohol tower, x_{R_1} and the reflux (or feed) to the water tower, x_{R_2}, will be the liquid in equilibrium with x_{R_1}. From Fig. 10-13,

	x_{R_1}	x_{R_2}	$1.032y_{T_1}$
B	0 51	0.053	0.51
A	0 298	0.282	0.298
H	0.192	0.665	0.224

As would be expected, the values of x_{R_1} are intermediate between x_{25} and x_{26}.

Using as basis an overflow rate of 1 mol of liquid per unit time for the water tower, $W_2 = 0.2$ and $V = 0.8$. The mols of each component in the overhead vapor from the water tower are equal to the difference between the mols in the reflux and the bottoms. Thus,

	x_{R_2}	$0.2x_W$	$0.8y_T$
B	0.053	—	0.053
A	0 282	0 00002	0.282
H	0.665	0.2	0.465

While both $1.032y_{T_1} - x_{R_1}$ and $x_{R_2} - 0.8y_T$ have been made equal to the bottoms from the water tower, they are on different bases and it is interesting to consider the relative quantity of the two refluxes.

For tower 1:

$$V_T = O_R + W_2$$

$$O_{R_1} = \frac{W_2}{0.032}$$

For tower 2:

$$O_{R_2} = V_T + W_2$$

$$= \frac{W_2}{0.2}$$

Therefore,

$$O_{R_1} = 6.25O_{R_2} \qquad \text{and} \qquad V_{T_1} = 8.06V_{T_2}$$

or, on the basis of 100 mols of feed,

$$O_{R_1} = 345 \qquad \text{and} \qquad O_{R_2} = 55.2$$

The plate-to-plate calculations for tower 2 are given in Table 10-7.

The mol fraction of alcohol in x_{T-3} is 1.5 times the maximum value specified while in x_{T-4}, the concentration is much lower, and between four and five theoretical plates are required. Due to the high volatility of benzene in water, its concentration in the bottoms of this tower would be quite low.

If two liquid layers had been refluxed to match x_{26} for tower 1, the composition of the two layers would be the terminal points of the solubility tie line through the composition of x_{26}. The reflux to the water tower would have the composition of the water-layer end of the tie line. In this case this latter layer would have been lower in benzene and alcohol, thereby making the fractionation in the water

TABLE 10-7

	$0.8y_T$	α_T	$\frac{0.8y_T}{\alpha}$	x_T	$0.8y_{T-1}$	α	$\frac{0.8y_{T-1}}{\alpha}$	x_{T-1}	$0.8y_{T-2}$	α
B	0 053	150	0.00035	0.0007	0 0007	200	0.0000035	5×10^{-6}	5×10^{-6}	200
A	0 282	8.0	0.035	0 070	0.07	9.7	0.0072	0 0097	0.0097	10
H	0.465	1.0	0.465	0.93	0 73	1.0	0.73	0.99	0.79	1
			0 50035				0.737			

	$\frac{0.8y_{T-2}}{\alpha}$	x_{T-2}	$0.8y_{T-3}$	α	$\frac{0.8y_{T-3}}{\alpha}$	x_{T-3}	$0.8y_{T-4}$	$\frac{0.8y_{T-4}}{\alpha}$	x_{T-4}
B	$2\ 5 \times 10^{-8}$	3×10^{-8}	3×10^{-8}	200	1.5×10^{-10}	2×10^{-10}	2×10^{-10}	10^{-12}	10^{-12}
A	0 00097	0 0012	0.0012	10	0 00012	0.00015	0 00013	0 000013	0 000016
H	0 79	0 999	0.799	1	0 799	0 99985	0 79984	0 79985	0.99998
	0.79				0 799			0.79986	

tower easier. The reflux to tower 1 would be two layers, but the liquid from the top plate would be a single phase of composition x_{25}. However, it is possible to operate with two liquid phases on a plate, provided the mechanical design is satisfactory. Thus in the present case the calculations can be carried past x_{25}, but allowance must be made for the two liquid phases. For example, the compositions of the two phases corresponding to x_{26} are as follows:[1]

	$(x_{26})_1$	$(x_{26})_2$	α_1	$\alpha(x_{26})_1$	$1.032y_{26}$	x_{27}
B	0.56	0 04	0.54	0.302	0.527	0.527
A	0.275	0.26	0.45	0.124	0.217	0.217
H	0.165	0.7	1.0	0.165	0.288	0.256
				0 591		

The composition of the vapor was calculated on the basis of $(x_{26})_1$ because it is believed that the equilibrium data are more reliable in the high benzene region than in the high water region. If 26 theoretical plates were employed and two liquid layers were refluxed to match x_{27}, then plate 26 would have two liquid layers present. Usually only one liquid layer is refluxed.

The tables of data and the liquid compositions plotted on Fig. 10-13 illustrate the factors involved. Starting at the bottom of tower 1, the system behaves like a mixture of benzene and alcohol, and the benzene concentration increases rapidly. The relative volatility of water is low and does not increase significantly until the benzene concentration has built up enough to increase the volatility of the water.

[1] These calculations are not exact, because the solubility data given in Fig. 10-13 are for 25°C., while the temperature on plate 26 is about 66°C. The solubilities are somewhat different at the two temperatures, but the 25°C. data are used to illustrate the principle.

The water concentration then increases rapidly until the feed plate is reached. Above the feed plate the heavy key component (alcohol) decreases rapidly, and the benzene and water attain values that result in two-layer formation. It will be noted that the liquid compositions are heading for ternary azeotrope composition as reported by Young (Ref. 7). The composition of the mixed vapors to the condenser is a point on the tie line through x_{R_1} and x_{R_2}, and the relative distances from this composition to x_R and x_{R_2} are inversely as O_{R_1} and O_{R_2}.

The limiting conditions for azeotropic conditions are not easily expressed in analytical equation, but they can be evaluated for each specific case.

Minimum Number of Theoretical Plates at Total Reflux. Owing to the wide variation of the relative volatility, equations of the type of (7-53) are not applicable. The number of theoretical plates required is calculated best by the plate-to-plate method using $y = x$ as the operating line for each component. For the benzene-alcohol-water system considered in the preceding section, this plate-to-plate method indicates that between 12 and 13 theoretical plates are required at total reflux.

Minimum Reflux Ratio. This limit corresponds to a pinched-in position, or positions, in the tower. Because of the wide variation in relative volatilities with composition, this limit frequently corresponds to a tangent condition of the operating lines and equilibrium values rather than an intersection. In such cases it is difficult to calculate the exact tangent condition, and each system is essentially a new problem. However, in a number of cases, the minimum reflux ratio is determined by intersections of the operating lines and the equilibrium values, and these often occur near the feed plate, because the mixture to be treated is usually a binary and the azeotrope agent is approximately constant above and below the feed plate. For these cases, the general principles employed for multicomponent mixtures can be applied. As an example, consider the benzene-alcohol-water system already studied, which has this type of limiting condition. The asymptotic concentrations below the feed plate are given by equations of the type of (9-15). Solving for the values between water and benzene,

$$x_H = \frac{\alpha_B x_{WH}(W/O_m)}{\alpha_B - \alpha_H + \alpha_H(W/O_m)(x_{WB}/x_B)} \tag{10-12}$$

The concentration of benzene in the bottoms, x_{WB}, is much smaller than the asymptotic value, x_B, and the last term of the denominator

will be neglected. The value of x_H is much larger than the numerator of the right-hand side of the equation, and this necessitates α_B being essentially equal to α_H. Thus, for this case where x_{WH} and x_{WB} are very small, the pinched-in condition corresponds to the relative volatility of benzene to water being unity; *i.e.*, $\alpha_{BH} = 1.0$. A study of Fig. 10-15 indicates that $\alpha_{BH} = 1$ for only a limited concentration range for benzene. Above the feed plate the net alcohol and benzene removals are very small, and the same type of analysis leads to the conclusion that $\alpha_B = \alpha_A$. The conditions $\alpha_{BH} = 1$ below the feed plate and $\alpha_{AB} = 1.0$

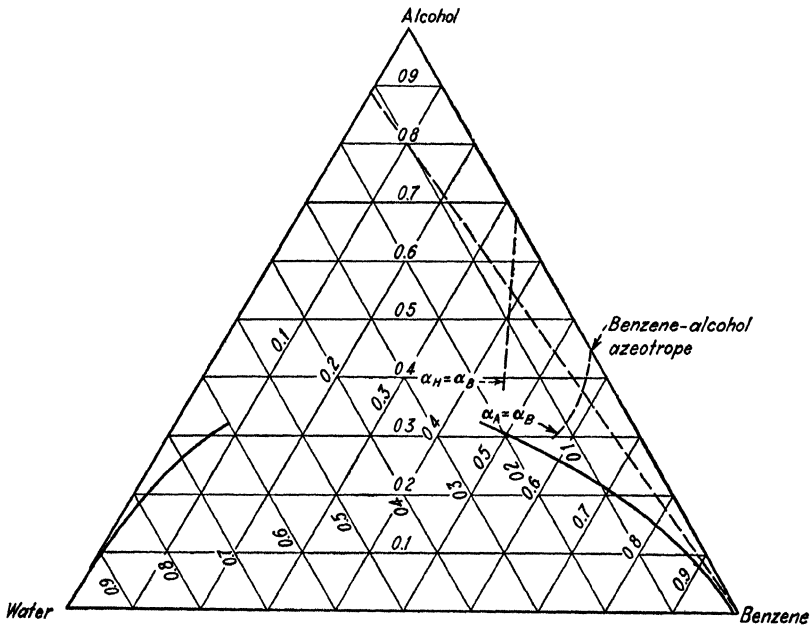


FIG. 10-16.

above the feed plate can be used to evaluate the minimum reflux ratio. One approximation for this limit can be obtained by equating the concentration ratio of alcohol to water for $\alpha_B = \alpha_H$ to the feed ratio. The composition for this condition can be obtained by drawing a line through $x_A = 0.89$, $x_H = 0.11$, and the benzene corner of the diagram. Where this line cuts the $\alpha_H = \alpha_B$ line gives the desired values. This construction has been carried out in Fig. 10-16, and the intersection gives $x_A = 0.55$, $x_H = 0.07$, and $x_B = 0.38$. From Figs. 10-14 and 10-15, $\alpha_{AH} = 0.54$ and $\alpha_{BH} = 1.0$. By Eq. (9-15),

$$x_A = \frac{\alpha_H(W/O_m)x_{WA}}{\alpha_H - \alpha_A + \alpha_A(W/O_m)(x_{WH}/x_H)} \qquad (10\text{-}13)$$

$$0.55 = \frac{(W/O_m)(0.999)}{1 - 0.54}$$

$$\frac{W}{O_m} = 0.253$$

$$O_m = 352 \qquad \text{and} \qquad V_m = 263$$

$$\left(\frac{O_m}{V_m}\right)_{\max} = \frac{352}{263} = 1.34$$

or, taking the net distillate, D', as 11 mols,

$$O_n = 252 \qquad V_n = 263$$

$$\left(\frac{O_{R_1}}{D'}\right)_{\min} = 22.8$$

The value of $O_m/V_m = 1.25$ employed in the plate-to-plate calculations corresponds to

$$\frac{O_{R_1}}{D'} = \frac{345}{11} = 31.4$$

A similar calculation can be made above the feed plate using $\alpha_A = \alpha_B$, and the value obtained is $O_{R_1}/D' = 17.5$. This difference is due to the fact that the ratio of the key components was taken the same as in the feed. It has already been pointed out that the optimum feed-plate composition corresponds to a higher ratio of alcohol to water than in the feed.

Another method of calculating the minimum reflux ratio is to equate the ratio of the key components for the two pinched-in regions. This involves a trial-and-error procedure to find a composition on the $\alpha_H = \alpha_B$ line that gives the same O_{R_1}/D' value as a composition on the $\alpha_B = \alpha_A$ line when the ratio of x_A/x_H is the same at both. This calculation gave $O_{R_1}/D' = 21$ for a key component ratio of 11 to 1 as compared to 8 to 1 in the feed. This last answer for the minimum reflux ratio should be near the true value.

The minimum reflux ratios for other cases can be handled in a similar manner.

Nomenclature

A,B = constants in Van Laar equation
F = feed rate
O = overflow rate
P = vapor pressure

$p = (O_n - O_m)/F$
T = temperature
V = vapor rate
x = mol fraction in liquid
y = mol fraction in vapor
α = relative volatility
γ = activity coefficient

Subscripts:

A refers to alcohol
B refers to benzene
D refers to distillate
E refers to ethanol
F refers to feed
H refers to water
h refers to heavy component
hk refers to heavy key component
I refers to isopropanol
l refers to light component
lk refers to light key component
m refers to below feed plate
n refers to above feed plate
R refers to reflux
S refers to extractive agent
T refers to top plate
1,2,3, refer to component or plate number

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CHAPTER 11

RECTIFICATION OF COMPLEX MIXTURES

The design methods considered for multicomponent mixtures in Chap. 9 were based on a limited number of definitely known components. In some cases, the mixtures are so complex that the composition with reference to the pure component is not known. This is particularly true of the petroleum naphthas and oils which are mixtures of many series of hydrocarbons, many of the substances present having boiling points so close together that it is practically impossible to separate them into the pure components by fractional distillation or any other means. Even if it were possible to determine the composition of the mixture exactly, there are so many components present that the methods of Chap. 9 would be too laborious. It has become customary to characterize such mixtures by methods other than the amount of the individual components they contain, such as simple distillation or true-boiling-point curves, density, aromaticity (or some other factor related to types of compounds), refractive index, etc.

The simple distillation curve is the temperature as a function of the per cent distilled in a simple or Rayleigh type of distillation. This type of distillation is approximated by the laboratory A.S.T.M. distillation which is widely used to characterize petroleum fractions. The A.S.T.M. procedure gives some reflux and rectification, and the results are not exactly equal to the simple batch distillation, although the difference is not large. The temperature normally measured is the condensation temperature of the vapor flowing from the still to the condenser. Curve *A* of Fig. 11-1 is typical for the simple distillation of a complex mixture. The temperature at any point is the averaged result of a large number of components and includes all the effects of nonideality in the solutions. Thus in most cases it is impossible to relate such a curve to the volatility of the individual components involved. As a result, such simple distillation curves are not of much direct value for the solution of rectification problems.

The true-boiling-point curve is an attempt to separate the complex mixture into its individual components. Actually it is a batch dis-

tillation carried out under rectification conditions. Usually a laboratory distillation column equivalent to a large number of plates is employed, and the separation is made at a high reflux ratio to obtain efficient fractionation. Because it is a batch operation, low liquid holdup in the column is important, and packed columns are generally employed. Ideally a true-boiling-point curve for a mixture corresponding to the simple distillation curve A of Fig. 11-1 might be represented by curve B of this figure, showing individual horizontal lines for each component with sharp increases in temperature in going from one constituent to the next. In most petroleum mixtures the curve obtained is similar to B of Fig. 11-2, and no definite steps are obtained.

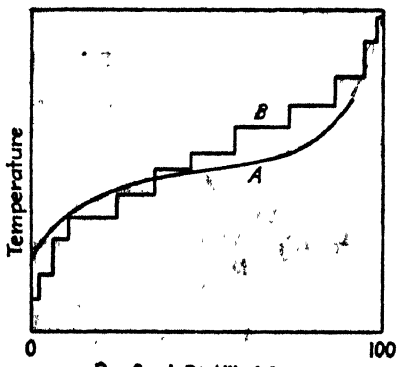


FIG. 11-1.

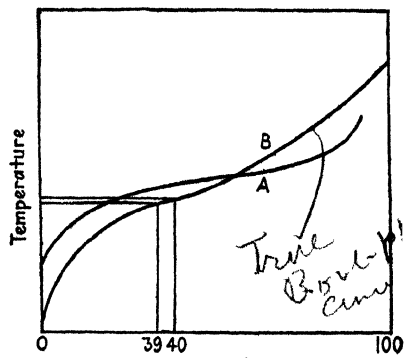


FIG. 11-2.

This result is obtained because (1) the number of components is very large and no single step would be very significant and (2) the degree of fractionation usually employed is not sufficient to give the sharp breaks in the curve. The sharpness of the fractionation between the different components is also lowered by the formation of azeotropes and by other solution abnormalities. However, the true-boiling-point curve probably represents a fairly high degree of separation in most cases. It is interesting to compare curves A and B of Fig. 11-2. The true-boiling-point curve begins at a lower and ends at a higher temperature than the simple distillation curve because the latter gives an averaging effect. Actually a simple distillation should give the same final temperature as the true-boiling-point distillation, because the last material to be vaporized should be the pure highest boiling component in both cases, but in general the distillations cannot be carried to 100 per cent distilled. A number of methods have been proposed for calculating

the true-boiling-point and simple distillation curves from each other, and they are useful in some cases, but if solution abnormalities are involved, they can be in error.

It has been found possible to use true-boiling-point curves to define the compositions for distillation calculation. A fraction distilling over a narrow range is taken as an individual component. Thus the fraction coming over as distillate between 39 and 40 per cent in curve *B* of Fig. 11-2 might be considered as a component, the boiling point of which, at the pressure at which the distillation was carried out, being

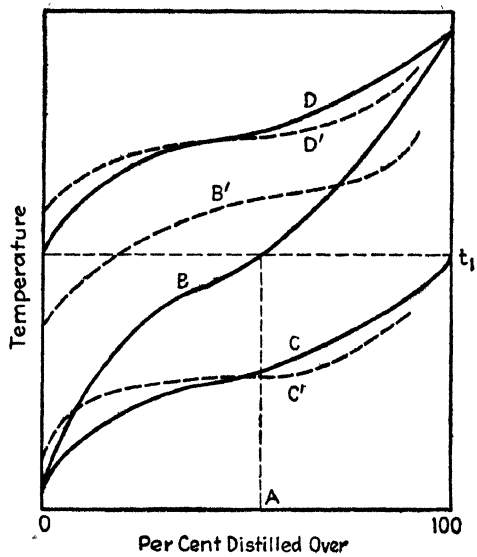


FIG. 11-3.

the average of the two temperatures corresponding to 39 and 40 per cent. In this manner the curve can be divided into any desired number of "components" with estimated vapor-liquid characteristics corresponding to their distillation temperature. These components can then be employed in the distillation calculations using the various methods given in Chaps. 9 and 12. The components in the various fractions can be recombined to give the true-boiling-point curve of the products.

If the distillate during a true-boiling-point distillation were to be divided into two fractions at some convenient point, *A*, corresponding to the temperature t_1, and simple distillation and true-boiling-point curves obtained for the two fractions, the results would resemble the

curves shown in Fig. 11-3 where curve B is the original true-boiling-point curve and B' the A.S.T.M. distillation curve for the same mixture. The true and the A.S.T.M. curve of the two fractions are shown as C and D curves for the more volatile and the less volatile fractions, respectively.

It will be noted that the initial temperature of curve D' is considerably higher than the final boiling point of curve C'. This difference,

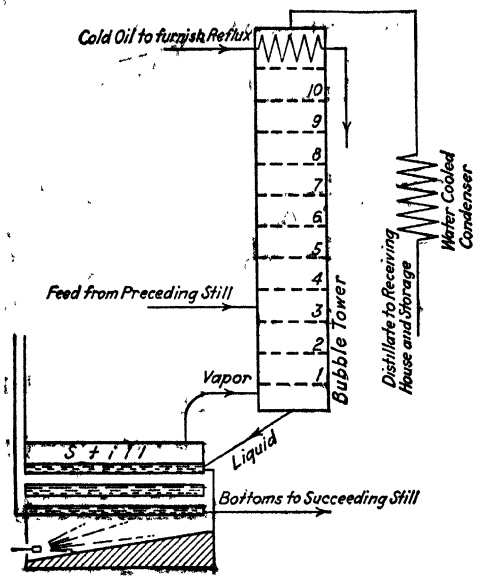


FIG. 11-4. Flow sheet of still and tower used in test.

the so-called "gap," is frequently used as design specification for the separation desired. The averaging effect of the simple distillation technique tends to give large temperature gaps even though the lower boiling fraction may have components that boil higher than some of those in the less volatile fraction. The fractionation in actual cases will not be so good as assumed for Fig. 11-3, and there will always be some of each component in each fraction. Thus, theoretically, the true-boiling-point curve of all fractions in a given system would begin and end at the same temperature. However, with reasonably good rectification it is possible to obtain fractions that will give considerable temperature gaps by an A.S.T.M. distillation. In the case of a low degree of separation, the A.S.T.M. curves for two successive or adjacent fractions may give initial and final temperatures that overlap.

Lewis and Wilde Method. These authors (Ref. 2) applied the Sorel-Lewis method described in Chap. 9 to complex petroleum fractions employing the true-boiling-point curves combined with Raoult's law. Data were obtained in a test on a fractionating column used in a petroleum refinery. The plates in the column were 9 ft. in diameter and fitted with the usual type of bubble caps. A schematic diagram of the unit is shown in Fig. 11-4, and some of their data are summarized in Table 11-1. In the table, the column called "Average boiling point" is the temperature at which the fraction as a whole boils and not the average that would be obtained during an A.S.T.M. distillation.

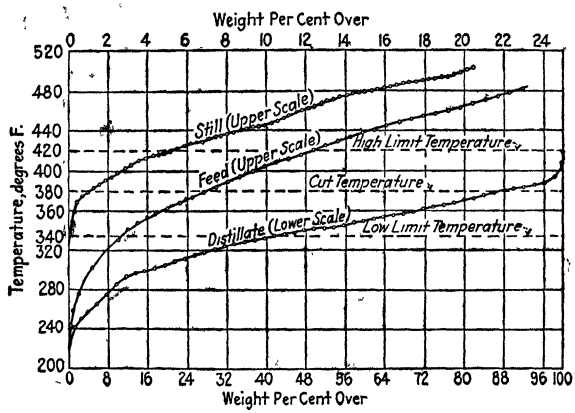


FIG. 11-5. True-boiling-point curves of feed residuum distillate.

The true-boiling-point curves for the feed, the distillate, and the residue are given in Fig. 11-5. The curves for the liquids sampled from the plates are given in Fig. 11-6.

Lewis and Wilde's method consists of breaking the true-boiling-point curve of the feed up into fractions boiling within narrow temperature limits. Thus the feed is divided into 10 or 20°F. fractions and expressed as a component boiling between definite temperature limits, such as 420 to 430°F. fraction which is present to the extent of 1.5 weight per cent. Such cuts are then used as individual components by the methods given in Chap. 9. The true-boiling-point curve on any plate in the tower is constructed from the calculations for that plate, by simply recombining the cuts in the proportion that the calculations indicate.

The vapor above the plate of an actual column is not in equilibrium with the liquid leaving the plate owing to inadequate contact. In

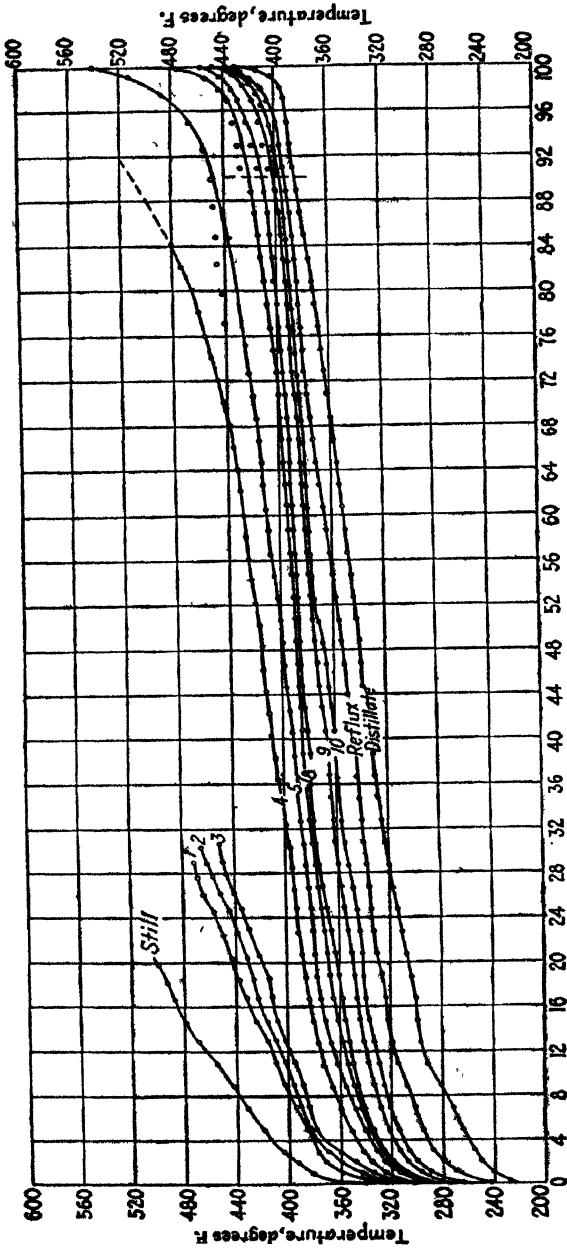


FIG. 11-6. True-boiling-point curves of liquids on plates.

TABLE 11-1. SUMMARY OF DATA OBSERVED AT BATTERY AND IN LABORATORY

Item	Column temp., °F.	Gravity, °A.P.I.	Average boiling point, °F.	Molecular weight	Rate, gal. per hr.
Feed to battery	—	38.6	—	—	28,920
Total gasoline produced	—	58.4	—	—	10,200
Gasoline from still 4	330	50.6	320	112	1,585
Feed to still 4	446	30.8	460	230	
Residuum from still 4	490	29.2	515	250	
Kerosene from still 5	—	45.3	405	—	2,000
Liquid on plate 1	447	32.7	463		
Liquid on plate 2	442	32.6	457		
Liquid on plate 3	438	34.0	444	212	
Liquid on plate 4	391	44.8	402	141	
Liquid on plate 5	373	46.9	388	140	
Liquid on plate 6	370	47 5	380		
Liquid on plate 7	360	47 8	377		
Liquid on plate 8	358	48.1	372		
Liquid on plate 9	343	48.8	360		
Liquid on plate 10	340	49.0	357		
Reflux to top plate	—	49.4	340		
Vapor from still to bottom of tower	485	43.2	419	150	

Gravity of cold oil through partial condenser	38.6° A.P.I.
Average rate of cold oil through partial condenser	10,600 gal. per hr.
Average temperature of oil into partial condenser	77°F.
Average temperature of cold oil out of partial condenser	181°F.
Total steam in vapor from tower	100 gal. per hr.
Steam used in heating feed to tower	26 gal. per hr.
Barometric pressure	758 mm. of Hg
Pressure at bottom of tower	16 mm. Hg above barometer
Pressure at top of tower	23 mm. Hg below barometer

analyzing the behavior of an actual column, this plate efficiency must always be included. Using a plate efficiency of 65 per cent, Lewis and Wilde estimated the proportion of the 420 to 430°F. component on the several plates above the bottom, and compared it with the actual amounts found in the test as a measure of the accuracy of their calculations. This comparison is given in Fig. 11-7 where the curve represents the calculated concentration and the points the actual ones as found. It will be noted that very satisfactory agreement was obtained, indicating the utility of this method.

Graphical Method. An alternate method (Refs. 1, 3, 4) has been proposed by which the complex mixture is treated as a binary mixture

of components, consisting of the fraction above and below the temperature at which the cut is being made. The vapor-liquid equilibria are constructed from the characteristics of the true-boiling-point analysis or A.S.T.M. distillation curves, and the calculation is carried out as in the McCabe-Thiele method.

Laboratory Studies of Complex Mixtures. Where laboratory space and facilities are available, it is very wise to design petroleum equipment on the basis of laboratory experiments, using the data thus obtained as a starting point in calculations of the sort just indicated.

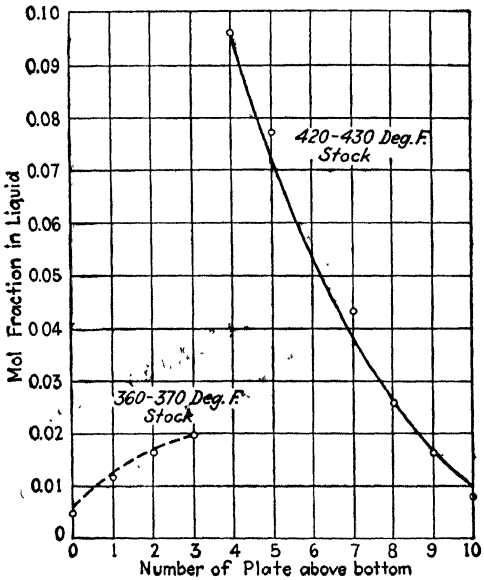


FIG. 11-7.

It is believed that a rational analysis of laboratory data collected with a thorough understanding of the requirements for subsequent calculations offers the safest method for the study of commercial problems.

An illustration of such laboratory data, taken by Smoley (Ref. 5), is given in the following pages.

A large-scale laboratory column with 10 plates was operated with total reflux, so that all of the distillate was returned to the top of the column. Under this condition, with total reflux and no distillate, the column was operating with maximum separation per plate.

A mixture of benzene and toluene was distilled in this apparatus, and the composition of the liquid on the several plates determined, with the results shown by the solid line in Fig. 11-8. The effect of the

efficiency of the actual plate as contrasted with the theoretical plate is shown in the same figure. The dotted line was obtained by plate-to-plate calculations at total reflux using theoretical plates. Thus, to produce a 90 mol per cent distillate requires about 10 steps in the actual column, whereas the same effect is obtained in 6 steps in the perfect column, indicating a plate efficiency of around 60 per cent.

The same column was then operated in the same way but using a mixture of benzene, toluene, and xylenes so as to produce as high a concentration of benzene as possible in the condenser and to segregate the xylenes in as concentrated a form as possible at the bottom. The

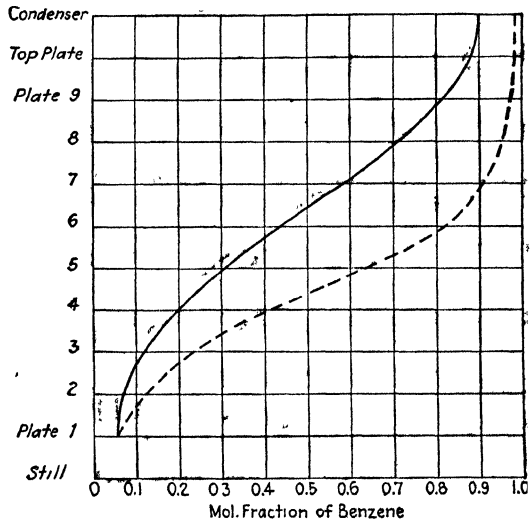


FIG. 11-8. Operation of benzene-toluene column.

results are shown in Fig. 11-9. The amount of xylenes was small so that a large proportion of toluene was present on the bottom plate. The highest concentration of toluene occurred on the fifth plate, this component thus tending to segregate in the column. Under ordinary conditions, a column would be operated at a lower temperature level so that the benzene at the top would have contained less toluene, thus delivering the toluene and xylene together from the bottom for subsequent separation in a second column. This experimental column had insufficient plates to do this.

The column was then operated with total reflux on a cracked petroleum distillate obtained from a Winkler-West Texas crude oil. The liquid samples from the several plates in the column were then analyzed in a true-boiling-point still, being separated into components of 5°C.

boiling-point range. Each of these components was indicated by its mid-temperature. Thus a component boiling on the true boiling-point apparatus between 75 and 80°C. was called the 77.5°C. component. The results of this experiment are given in Fig. 11-10, where each component is indicated by a concentration curve.

It will be noted that each component tends to segregate in the column, the segregation point depending on its boiling point. This segregation of a component in a continuous column is the basis for the type of still frequently found in petroleum refineries where streams or cuts

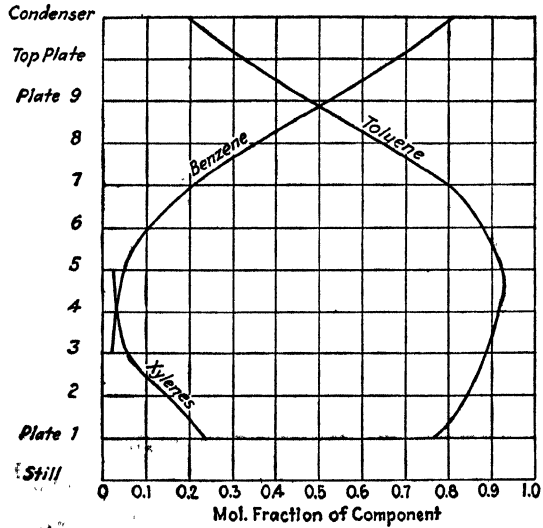


FIG. 11-9. Operation of column on benzene-toluene-xylenes mixture.

are taken from the central portions of the column as well as from the top and bottom. It is evident from Fig. 11-10 that such side cuts cannot be all pure or free from other components; in the commercial column, where total reflux is not employed, the segregation is much less pronounced than is indicated in Fig. 11-10.

The maxima in concentrations of the fractions shown in Figs. 11-9 and 11-10 are definitely related to the volatility of the component in question and the temperature in the distillation column. These curves were obtained at total reflux, and for this condition the composition of the vapor entering a plate is equal to the liquid leaving the plate for all components, *i.e.*,

$$y_n = x_{n+1}$$

and

$$y_n = K_n x_n$$

giving

$$K_n = \frac{x_{n+1}}{x_n}$$

For the position in the tower at which a component is going through a maximum concentration, the value of the liquid composition on suc-

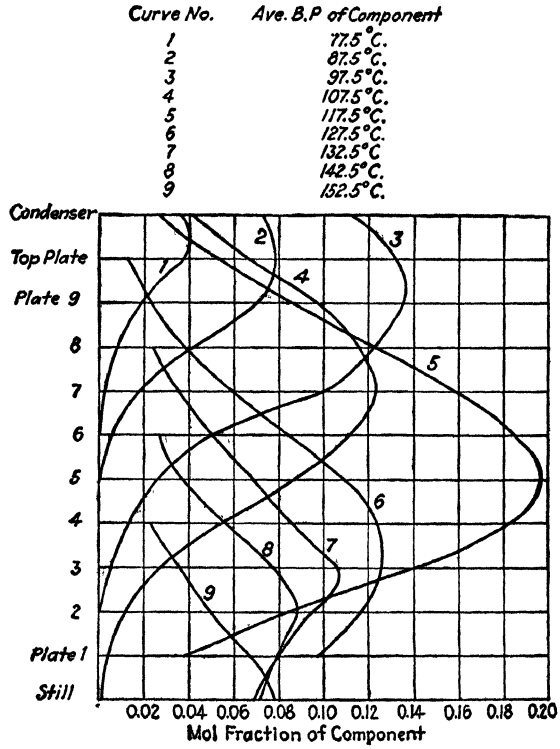


FIG. 11-10. Operation of column on petroleum distillate.

cessive plates is approximately the same, making $K_n = 1.0$. Thus the maximum occurs at the position in the column where the temperature is such that the equilibrium constant of the component is equal to 1.0.

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CHAPTER 12

ALTERNATE DESIGN METHODS FOR MULTICOMPONENT MIXTURES

In Chap. 9 the Lewis and Matheson procedure for Sorel's plate-to-plate method was presented. Many other design methods have been proposed based on alternate methods of analysis or approximations. None of them illustrates the phenomena involved in multicomponent rectification so well as the Lewis and Matheson method. A number of the methods require less effort to obtain certain design factors than the stepwise procedure and are useful in cases where similar systems are to be analyzed repeatedly. When a new type of problem is to be considered, the information obtained by the plate-to-plate method is well worth the effort involved. Actually a detailed analysis by methods of Chap. 9 does not usually require over a few hours, and the confidence in the result and the insight obtained of the operation justify the effort involved.

The space available in this text does not allow a detailed analysis of these various design methods, but a brief review will be given of some of them. A number of the methods involve assumptions that are not justified in many cases, and the design engineer must appreciate these limitations or misleading results will be obtained.

PLATE-TO-PLATE METHODS

In addition to the Lewis and Matheson, and Lewis and Cope methods given in Chap. 9, plate-to-plate procedures have been given by Thiele and Geddes (Ref. 14) and Hummel (Ref. 9).

The Thiele and Geddes method is a stepwise procedure based on using a ratio of the concentration of a component to its terminal concentration. Starting at the top of the column, for any component,

$$x_T = \frac{y_T}{K_T} = \frac{x_D}{K_T} \text{ (for total condenser)}$$

and

$$\frac{y_{T-1}}{x_D} = \frac{O_T}{V_{T-1}}\left(\frac{x_T}{x_D} - 1\right) + 1 \tag{12-1}$$

$$= \frac{O_T}{V_{T-1}}\left(\frac{1}{K_T} - 1\right) + 1,$$

$$\frac{x_{T-1}}{x_D} = \frac{y_{T-1}}{K_{T-1}x_D}$$

In general,

$$\frac{y_n}{x_D} = \frac{O_{n+1}}{V_n}\left(\frac{x_{n+1}}{x_D} - 1\right) + 1 \tag{12-2}$$

and

$$\frac{x_n}{x_D} = \frac{y_n}{K_n x_D} \tag{12-3}$$

Thus, if the values of the equilibrium constants and the ratios of O/V are known for each plate, it is possible to calculate the ratio x_n/x_D for any plate above the feed plate without knowing the value of x_D.

Below the feed plate a similar analysis can be made.

$$\frac{y_W}{x_W} = K_W$$

and, from the operating line,

$$\frac{x_1}{x_W} = \frac{V_W}{O_1}\left(\frac{y_W}{x_W} - 1\right) + 1 \tag{12-4}$$

in general,

$$\frac{y_m}{x_W} = K_m \frac{x_m}{x_W} \tag{12-5}$$

$$\frac{x_{m+1}}{x_W} = \frac{V_m}{O_{m+1}}\left(\frac{y_m}{x_W} - 1\right) + 1 \tag{12-6}$$

The calculations can be carried up from the still and down from the condenser to the feed plate, giving values of y_m/x_W and y_n/x_D. Assuming that the feed plate is such that the vapor and liquid leaving are in equilibrium, then the values of the vapor composition in the two ratios must be equal and the value of x_D/x_W can be calculated for each component. This ratio can be used to calculate D and W.

Thus, for each component,

$$Dx_D + Wx_W = Fz_F$$

$$Wx_W = \frac{Fz_F}{1 + \frac{F - W}{W}\left(\frac{x_D}{x_W}\right)} \tag{12-7}$$

$$Dx_D = \frac{Fz_F}{1 + \frac{F - D}{D}\left(\frac{x_W}{x_D}\right)} \tag{12-8}$$

Summing the Wx_W and Dx_D terms for all components,

$$1 = \sum\left[\frac{z}{\frac{W}{F}\left(1 - \frac{x_D}{x_W}\right) + \left(\frac{x_D}{x_W}\right)}\right] = \sum\left[\frac{z}{\frac{D}{F}\left(1 - \frac{x_W}{x_D}\right) + \left(\frac{x_W}{x_D}\right)}\right] \tag{12-9}$$

where Σ indicates the sum of the terms for all components. With the value of x_D/x_W for each component, W/F or D/F can be evaluated.

As compared to the Lewis and Matheson method, this method has the advantage that it is easier to calculate the separation to be obtained for a given number of theoretical plates at a specified reflux ratio. In case the separation and reflux ratio are specified, the Lewis and Matheson method is the easier to apply.

Thiele and Geddes Calculation for Benzene-Toluene-Xylene Separation. To illustrate the application of this method, consider the separation of the benzene-toluene-xylene mixture of page 219 in a tower having five theoretical plates with the feed entering the middle plate. The reflux ratio O/D will be 2.0, $V_n = V_m$; the vapor leaving the feed plate will be in equilibrium with the liquid leaving, and the usual simplifying assumptions will be made.

Solution. Basis: 100 mols feed. $O/D = 2$, $(O/V)_n = 0.667$.

	x_F	Mols feed	Distillate comp.	Assume T = 85°C. K_T	$\frac{x_T}{x_D} = \frac{1}{K_T}$	$\frac{y_{T-1}}{x_D} = 0.667\left(\frac{x_T}{x_D} - 1\right) + 1$
Benzene....	0.60	60	x_{DB}	1.15	0.87	0.913
Toluene....	0.30	30	x_{DT}	0.452	2.21	1.807
Xylene.....	0.10	10	x_{DX}	0.184	5.44	3.96

	Assume $T = 85°C.$ K_{T-1}	$\frac{x_{T-1}}{x_D} = \frac{1}{K_{T-1}}\left(\frac{y_{T-1}}{x_D}\right)$	$\frac{y_{T-2}}{x_D}$	Assume $T = 90°C.$ K_{T-2}	$\frac{x_{T-2}}{x_D}$	$\frac{y_{T-3}}{x_D}$
C_6	1.15	0.793	0.862	1.38	0.649	0.766
C_7	0.452	3.99	3.0	0.533	5.63	4.09
C_8	0.184	21.5	15.35	0.221	69.4	46.6

From still up, assume $D = 66$; then $V_n = 198 = V_m, O_m = 232, (V_m/O_m) = 0.853$.

	Assume $T = 115°C.$ $K_W = \frac{y_W}{x_W}$	$\frac{x_1}{x_W} = 0.853\left(\frac{y_W}{x_W} - 1\right) + 1$	Assume $T = 110°C.$ K_1	$\frac{y_1}{x_W}$	$\frac{x_2}{x_W}$	Assume $T = 110°C.$ K_2
C_6	2.62	2.38	2.29	5.45	4 8	2.29
C_7	1.12	1.102	0.975	1.075	1 064	0.925
C_8	0.513	0 587	0.435	0 255	0.365	0.435

	$\frac{y_2}{x_W}$	$\frac{x_3}{x_W}$	Assume $T = 100°C.$ K_3	$\frac{y_3}{x_W}$
C_6	11.0	9.53	1.745	16.65
C_7	1 038	1.032	0.735	0.76
C_8	0.159	0.282	0 316	0.104

Equating $y_3 = y_{T-3}$ gives

	$\frac{x_D}{x_W} = \frac{y_3/x_W}{y_{T-3}/x_D}$
C_6	21.8
C_7	0.186
C_8	0.0022

By Eq. (12-9),

$$1 = \frac{0.6}{-20.8(W/F) + 21.8} + \frac{0.3}{0.814(W/F) + 0.186} + \frac{0.1}{0.9978(W/F) + 0.0022}$$

$$\frac{W}{F} = 0.334$$

The section below the feed was calculated on the basis $W/F = 0.34$ compared to the calculated value of 0.334, and it will not be rechecked. This is one of the difficulties with the Thiele and Geddes method, *i.e.*, specifying the reflux ratio and feed condition still leaves trial and error for both the plate temperatures and the ratio of O/V below the feed plate.

The temperature assumptions will now be reviewed.

	x_D, by Eq. (12-8)	x_T	y_{T-1}	x_{T-1}	x_{T-2}
C_6	0.88	0.765	0.803	0.698	0.571
C_7	0.12	0.265	0.217	0.479	0.676
C_8	0.00065	0.0035	0.0025	0 014	0.045
		1.0335	1.0225	1.191	1.292

The fact that the sum of x_T is greater than 1.0 indicates that the actual temperature is slightly higher than 85°C. The assumed temperatures for both plates $T-1$ and $T-2$ are considerably low as indicated by the sums of x_{T-1} and x_{T-2} being greater than 1.0, and the results should be recalculated for a satisfactory design.

Below the feed plate,

	x_w	y_w	y_1	y_2	y_3
C_6	0.042	0.11	0.229	0.462	0.699
C_7	0.658	0 737	0.707	0.693	0.50
C_8	0.300	0.153	0.076	0.048	0.031
		1.000	1.012	1.203	1.230

The assumed temperatures for the still and first plate are satisfactory, but the assumed temperature of plate 2 is too high. The sum of y_3 is larger than 1.0, and this would appear to indicate that the assumed temperature was much too high, actually most of the excess is from plate 2. The fact that $\Sigma_{y2} > 1.0$ made $\Sigma x_3 > 1.0$ and, even if the assumed temperature for plate 3 were correct, Σy_3 will be greater than 1.0. Thus an error in the assumed temperature for one plate carries through succeeding plates. It is obvious that the calculation requires considerable trial and error.

A method similar to the Thiele-Geddes method has been proposed by Hummel (Ref. 9). In this method plate-to-plate calculations are made for a few plates at each end and around the feed plate to establish the temperatures. With the values and the known number of theoretical plates the temperature gradient in the tower is drawn. This then gives the temperatures to employ in a Thiele-Geddes type of calculation. For a given number of plates and a given reflux ratio, this method requires an estimation of the distillate, bottoms, and feed-plate compositions. Basically, Hummel's method furnishes a systematic method of successive approximations for the plate temperatures to be used in evaluating the equilibrium constants.

REDUCED RELATIVE VOLATILITY METHODS

Underwood (Ref. 15) and Gilliland (Ref. 5) have proposed design methods for applying a total reflux type equation with a reduced relative volatility. For the enriching section of the tower,

$$\left(\frac{y_A}{y_B}\right)_T = \alpha_T \left(\frac{x_A}{x_B}\right)_T$$

where T refers to top plate. For a total condenser,

$$\left(\frac{x_A}{x_B}\right)_D = \alpha_T \left(\frac{x_A}{x_B}\right)_T$$

and, by the operating material balances,

$$\left(\frac{y_A}{y_B}\right)_{T-1} = \frac{1 + (D/O)(x_{AD}/x_{AT})}{1 + (D/O)(x_{BD}/x_{BT})} \left(\frac{x_A}{x_B}\right)_T = \beta_{T-1} \left(\frac{x_A}{x_B}\right)_T \tag{12-10}$$

and

$$\left(\frac{x_A}{x_B}\right)_D = \frac{\alpha_T}{1} \left(\frac{\alpha_{T-1}}{\beta_{T-1}}\right) \left(\frac{\alpha_{T-2}}{\beta_{T-2}}\right) \cdots \left(\frac{\alpha_{f+2}}{\beta_{f+2}}\right) \left(\frac{\alpha_{f+1}}{\beta_{f+1}}\right) \left(\frac{\alpha_f}{\beta_f}\right) \left(\frac{x_A}{x_B}\right)_f \tag{12-11}$$

where

$$\beta_n = \frac{1 + (D/O_n)(x_{AD}/x_{An+1})}{1 + (D/O_n)(x_{BD}/x_{Bn+1})} \tag{12-12}$$

and below the feed plate,

$$\left(\frac{x_A}{x_B}\right)_f = \frac{\alpha_{f-1}}{\beta_{f-1}} \left(\frac{\alpha_{f-2}}{\beta_{f-2}}\right) \cdots \left(\frac{\alpha_2}{\beta_2}\right) \left(\frac{\alpha_1}{\beta_1}\right) \left(\frac{\alpha_W}{1}\right) \left(\frac{x_A}{x_B}\right)_W \tag{12-13}$$

where

$$\beta_m = \frac{1 - (W/V_m)(x_{AW}/x_{Am+1})}{1 - (W/V_m)(x_{BW}/x_{Bm+1})} \tag{12-14}$$

To simplify the calculation, average values of α and β are employed,

$$\left(\frac{x_A}{x_B}\right)_D = \left(\frac{\alpha}{\beta}\right)_{n\,\mathrm{av}}^{N_n+1} \left(\frac{x_A}{x_B}\right)_f \tag{12-15}$$

$$\left(\frac{x_A}{x_B}\right)_f = \left(\frac{\alpha}{\beta}\right)_{n\,\mathrm{av}}^{N_m} \left(\frac{x_A}{x_B}\right)_W \tag{12-16}$$

where N_n = number of theoretical plates above feed plate
N_m = number of theoretical plates below feed plate including feed plate

Arithmetic averages have been employed for α and β

$$\left(\frac{\alpha}{\beta}\right)_{n\ av} = \frac{\alpha_T + (\alpha/\beta)_f}{2} \tag{12-17}$$

$$\left(\frac{\alpha}{\beta}\right)_{m\ av} = \frac{\alpha_W + (\alpha/\beta)_{f-1}}{2} \tag{12-18}$$

The values of β_f and β_{f-1} involve the composition on the feed plate and the plate above. The feed-plate composition is determined by assuming that the components more volatile than the key components are negligible in the bottoms, that those less volatile are negligible in the distillate, and that the concentration of both the light and heavy components are asymptotic at the feed plate.

Thus, for the more volatile components,

$$Vy_f = Ox_{f+1} + Dx_D$$

Using $y_f = K_f x_f$ and $x_{f+1} = x_f$,

$$VK_f x_f = Ox_f + Dx_D$$

$$x_f = \frac{(D/O_n)x_D}{(K_f V_n/O_n) - 1} \tag{12-19}$$

Similarly, for the less volatile components,

$$x_f = \frac{(W/O_m)x_W}{1 + (K_{f-1}V_m/O_m)} \tag{12-20}$$

The values of x_{f+1} needed for the calculation of β_f are obtained by stepwise calculation from x_f. For approximate values, β_f can be calculated with x_f instead of x_{f+1}.

Reduced Relative Volatility Calculations for Benzene-Toluene-Xylene Separation. The benzene-toluene-xylene example of page 219 will be solved by this method.

Solution. Basis: 100 mols of feed. (See page 220 for design quantities.)

Estimation of feed-plate composition. By Eq. (12-20) the mol fraction of xylene in the feed plate is

$$x_{fX} = \frac{(W/O_m)x_W}{1 - (K_{f-1}V_m)/O_m)} = \frac{10/220.2}{1 - K_{f-1}\,(180.3/220.2)}$$

Assuming $K_{f-1} = K_f = 0.22$ ($t = 90°$C.),

$$x_{fX} = 0.0555$$

This compares with a value of 0.058 obtained by the stepwise calculations, page 223. A better check would be obtained using K_{f-1}.

By mol fraction balances,

$$x_{fB} + x_{fT} = 1 - 0.0555 = 0.9445$$
$$y_{fB} + y_{fT} = 1 - 0.22(0.0555) = 0.988$$

Using $K_{fB} = 1.33$, $K_{fT} = 0.533$ ($t = 90°C.$),

$$1.33x_{fB} + 0.533x_{fT} = 0.988$$
$$x_{fB} = 0.609 \quad \text{and} \quad x_{fT} = 0.336$$

By plate-to-plate calculation,

	x_f	K_f	y_f	x_{f+1}
C_6	0.609	1.33	0 811	0.718
C_7	0.336	0.533	0.179	0.267
C_8	0 0555	0 22	0 011	0.016
			1 001	

For benzene relative to toluene

$$\beta_f = \frac{1 + \dfrac{0.995}{2(0.718)}}{1 + \dfrac{0.005}{2(0.267)}} = 1.69$$

$$\beta_{f-1} = \frac{1 - (39.9/180.3)(0.005/0.609)}{1 - (39.9/180.3)(0.744/0.336)} = 1.9$$

From page 223,

$$\alpha_D = 2.63$$
$$\alpha_W = 2.36$$
$$\alpha_f = 2.49$$
$$\left(\frac{\alpha}{\beta}\right)_f = \frac{2.49}{1.69} = 1.47$$
$$\left(\frac{\alpha}{\beta}\right)_{f-1} = \frac{2.49}{1.9} = 1.31$$
$$\left(\frac{\alpha}{\beta}\right)_{n\ av} = \frac{1.47 + 2.63}{2} = 2.05$$
$$\left(\frac{\alpha}{\beta}\right)_{m\ av} = \frac{1.31 + 2.36}{2} = 1.84$$

By Eq. (12-15),

$$N_n + 1 = \frac{\log (0.995/0.005)(0.336/0.609)}{\log 2.05} = 6.6$$

By Eq. (12-16)

$$N_m = \frac{\log (0.609/0.336)(0.744/0.005)}{\log 1.84} = 9.2$$

$N = N_n + N_m = 14.8$ theoretical plates vs. 16 found on page 225 by stepwise calculation. Because $(\alpha/\beta)_f$ and $(\alpha/\beta)_{f-1}$ are near to 1.0, the geometric mean should be more conservative.

By Eq. (12-21),

$$\left(\frac{\alpha}{\beta}\right)_{n\ av} = 1 + \sqrt{0.47(1.63)} = 1.87$$

and

$$\left(\frac{\alpha}{\beta}\right)_{m\ av} = 1 + \sqrt{0.31(1.36)} = 1.65$$

$$N_n + 1 = 7.5$$

$$N_m = 11.2$$

$$N_n + N_m = 17.7 \text{ theoretical plates}$$

The xylene in the distillate can be estimated by Eq. (12-15).

For toluene relative to xylene,

$$\beta_f = \frac{1 + \dfrac{0.005}{2(0.267)}}{1 + \dfrac{x_{DX}}{2(0.0555)}} = 1.0$$

$$\left(\frac{\alpha}{\beta}\right)_{n\ av} = \frac{\alpha_T + \alpha_f}{2} = \frac{2.48 + 2.42}{2} = 2.45$$

$$7.5 = \frac{\log\ (0.005/x_{DX})(0.0555/0.336)}{\log 2.45}$$

$$x_{DX} = \frac{0.005(0.0555)}{830(0.336)} = 10^{-6}$$

An approximate check on the assumed feed-plate temperature can be obtained by assuming that the temperature gradient is linear from the still to the condenser.

From pages 222 and 225, $t_W = 116°C.$ and $t_D = 80°C.$

$$t_f = \frac{7.5}{18.7}(116 - 80) + 80$$

$$= 94.4°C.$$

as compared to the assumed temperature of 90°C.

The results given by these equations are only approximate, and their accuracy increases as the reflux ratio, O/D, increases. For reflux ratios near the minimum value, β_f becomes equal to α, and the equations should be applied with caution because they give too few theoretical plates under these conditions. In fact, owing to the method of obtaining $(\alpha/\beta)_{av}$, they can indicate a finite number of plates at values of the reflux ratio less than the true minimum. For values of (α/β) near to 1.0 a better average is obtained by

$$\left(\frac{\alpha}{\beta}\right)_{n\ av} = 1 + \sqrt{\left[\left(\frac{\alpha}{\beta}\right)_f - 1\right](\alpha_T - 1)} \qquad (12\text{-}21)$$

$$\left(\frac{\alpha}{\beta}\right)_{m\,av} = 1 + \sqrt{\left[\left(\frac{\alpha}{\beta}\right)_{f-1} - 1\right](\alpha_W - 1)} \qquad (12\text{-}22)$$

These averages force the equation to give an infinite number of plates for $(\alpha/\beta) = 1.0$.

ABSORPTION FACTOR METHOD

Brown and Souders (Ref. 3) suggested the use of the absorption factor method of Kremser (Ref. 11) as a design procedure for multicomponent mixtures.

By a material balance on one component starting at the bottom of the column,

$$y_1 = K_1 x_1$$

$$x_2 = \frac{V}{O} y_1 - \left(\frac{V}{O} y_W - x_1\right)$$

$$= S_1 \frac{V}{O} y_W - \left(\frac{V}{O} y_W - x_1\right)(S_1 + 1)$$

where $S = KV/O$.

$$x_3 = \frac{V}{O} y_2 - \left(\frac{V}{O} y_W - x_1\right)$$

$$= S_2 S_1 \frac{V}{O} y_W - \left(\frac{V}{O} y_W - x_1\right)(1 + S_2 + S_1 S_2)$$

and

$$x_m = (S_{m-1} S_{m-2} \cdots S_3 S_2 S_1) \frac{V}{O} y_W - \left(\frac{V}{O} y_W - x_1\right)(1 + S_{m-1} + S_{m-1} S_{m-2} + \cdots + S_{m-1} S_{m-2} \cdots S_{m-1})$$

Assuming S is a constant and letting N_m equal the number of theoretical plates below feed,

$$x_f = S^{N_m} \frac{V}{O} y_W - \left(\frac{V}{O} y_W - x_1\right)(1 + S + S^2 + \cdots + S^{N_m}) \qquad (12\text{-}23)$$

$$x_f - x_1 = x_1 S(1 + S + S^2 + \cdots + S^{N_m - 1}) - \frac{V}{O} y_W + (1 + S + S^2 + \cdots + S^{N_m - 1})$$

$$= \left(S x_1 - \frac{V}{O} y_W\right)(1 + S + S^2 + \cdots + S^{N_m - 1})$$

$$x_f - \frac{y_W}{K_1} = x_1(1 + S + S^2 + \cdots + S^{N_m}) - \frac{V}{O}\frac{y_W}{S}(1 + S + S^2 + \cdots + S^{N_m})$$

$$= \frac{x_1 S - \frac{V}{O} y_W}{S}(1 + S + S^2 + \cdots + S^{N_m})$$

$$\frac{x_f - x_1}{x_f - \frac{y_W}{K_1}} = \frac{S(1 + S + S^2 + \cdots + S^{N_m - 1})}{1 + S + S^2 + \cdots + S^{N_m}} \tag{12-24}$$

Multiplying the numerator and denominator of the right-hand side by $1 - S$ gives

$$\frac{x_f - x_1}{x_f - (y_W/K_1)} = \frac{S^{N_m+1} - S}{S^{N_m+1} - 1} \tag{12-25}$$

A similar analysis above the feed plate gives

$$\frac{y_f - y_T}{y_f - K_T x_R} = \frac{A^{N_n+1} - A}{A^{N_n+1} - 1} \tag{12-26}$$

where x_R = composition of reflux to top of tower
$A = O/KV$

Equation (12-26) is applied to the heavy key component above the feed plate, and Eq. (12-25) to the light key component below the feed plate.

An average value of K is employed and, above the feed,

$$K_{av} = \frac{K_T + K_{f+1}}{2}$$

below feed plate,

$$K_{av} = \frac{K_W + K_{f-1}}{2}$$

Absorption Factor Calculation for Benzene-Toluene-Xylene Separation. This method will be applied to the benzene-toluene-xylene example (data from pages 220 and 343).

	$y_T = x_R$	K_T	K_{f+1}	y_f	y_W	x_1	x_f	K_W	K_{f-1}
C_6	—	—	—	—	0.0131	0.0116	0.605	2.63	1.52
C_7	0.005	0.38	0.48	0.180	—	—	—	—	—

Above feed plate for toluene,

$$K_{av} = \frac{0.38 + 0.48}{2} = 0.43$$

$$A = \frac{O}{KV} = \frac{2}{3(0.43)} = 1.55.$$

By Eq. (12-26),

$$\frac{0.18 - 0.005}{0.18 - 0.38(0.005)} = \frac{1.55^{N_n+1} - 1.55}{1.55^{N_n+1} - 1}$$

$$N_n + 1 = 7.95$$

$$N_n = 6.95$$

Below feed plate for benzene,

$$K_{av} = \frac{2.63 + 1.52}{2} = 2.07$$

$$S = 2.07\ (^{18}\%_{20}) = 1.7$$

By Eq. (12-25),

$$\frac{0.605 - 0.0116}{0.605 - (0.0131/2.63)} = \frac{1.7^{N_m+1} - 1.7}{1.7^{N_m+1} - 1}$$

$$N_m + 1 = 9.3$$

$$N_m = 8.3$$

Total plates = 7 + 8.3 + 1 = 16.3.

Edminster (Ref. 4) has presented a modified absorption factor method that determines the molal quantities for each component as a fraction of their values in the distillate and bottoms in a manner somewhat similar to the Thiele and Geddes equations. The geometric mean of the absorption and stripping factors at the ends of the section under consideration is employed, and empirical correction terms are applied to these averages.

GRAPHICAL CORRELATIONS

When the number of theoretical plates is plotted as a function of reflux ratio, the curve is hyperbolic in type with asymptotes at N_{min} and $(O/D)_{min}$. These two limiting conditions as asymptotes are useful in drawing such a curve, but they would be more helpful as definite points on the diagram. By modifying the variables, they can be made definite points; in fact they can be made the same points for all cases. There are many ways in which the variables can be modified, and one that has been useful (Ref. 6) is shown in Fig. 12-1. The ordinate is $(S - S_m)/(S + 1)$, where S is the total theoretical steps including any enrichment in the still and condenser, and S_m is the value of S for total reflux, $O/D = \infty$. The abscissa is $\left[\frac{O}{D} - \left(\frac{O}{D}\right)_{min}\right] \Big/ \left(\frac{O}{D} + 1\right)$.

At total reflux the ordinate is 0.0 and the abscissa is 1.0, while at the minimum reflux ratio the ordinate is 1.0 and the abscissa is 0.0. As the reflux ratio is increased from the minimum to total reflux, a given design problem will give a curve that goes from 1,0 to 0,1. It was expected that a series of curves between these two points would be obtained, depending on (1) the degree of separation, (2) the relative

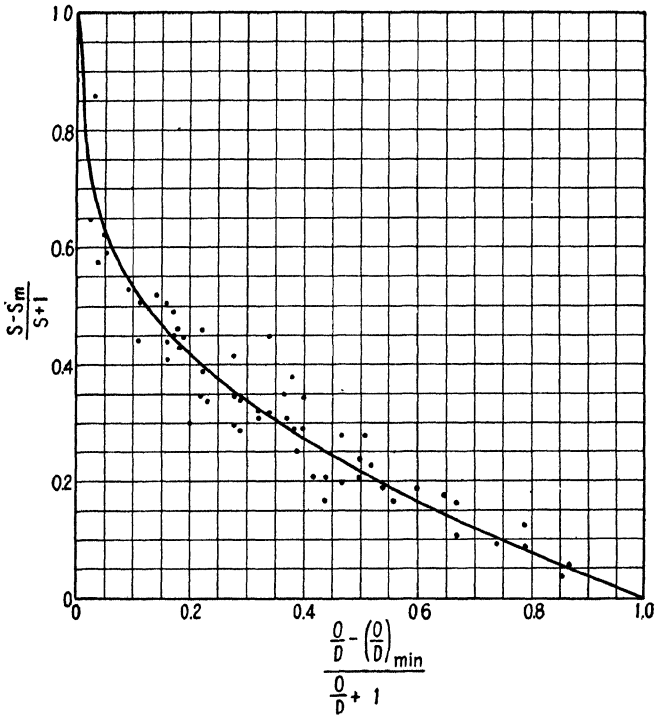


FIG. 12-1. Graphical correlation for design calculations.

volatilities, and (3) the components lighter and heavier than the key components. The results of plate-to-plate calculations were plotted and gave a narrow band which could be reasonably represented by a single line. It can be shown theoretically that a single line cannot represent all cases exactly, and the correlation can be improved by using more than one line. For example, the position of the line is a function of the fraction of the feed that is vapor. The best line drawn through the all-vapor feed cases on a plot such as Fig. 12-1 is lower than the corresponding line for all-liquid feeds. It is also possible to

improve the correlation by changing the variable groups, but it is doubtful whether the increased accuracy justifies the added complications. The accuracy of such a correlation will always be limited by the errors in S_m and $(O/D)_{min}$. It is believed that it is of real value when it is applied as (1) a rapid but approximate method for preliminary design calculation or (2) a guide for interpolating and extra-

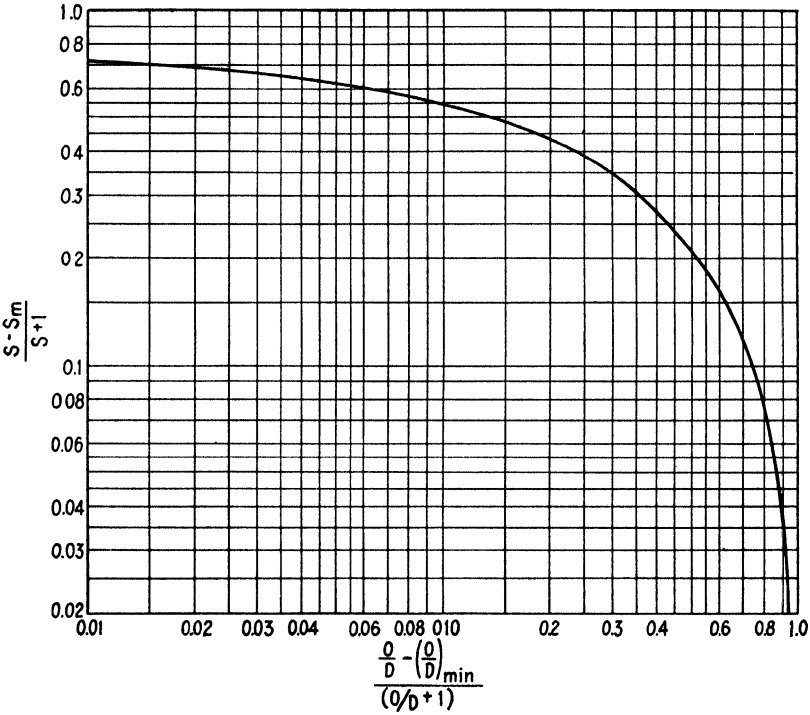


FIG. 12-2. Graphical correlation for design calculation.

polating plate-to-plate calculations. In this latter case, if only one plate-to-plate result is available at a reflux ratio from 1.1 to 2.0 times $(O/D)_{min}$, this point can be plotted on the diagram and a curve of similar shape to the correlation curve fitted to it. Such a method should give good results for other reflux ratios, assuming the values of S_m and $(O/D)_{min}$ are reasonably accurate.

Use of Graphical Correlation for Benzene-Toluene-Xylene Separation. Applying this correlation to the benzene-toluene-xylene example:

From page 259, $(O/D)_{min} = 1.0$.

Calculation of S_{min}. From Fig. 9-7, page 233, for benzene relative to toluene,

$$\alpha_D = 2.6, \quad \alpha_W = 2.3$$

$$\alpha_{av} = \sqrt{2.6(2.3)} = 2.45$$

$$S_m = N + 1 = \frac{\log \left(\frac{0.995}{0.005}\right)\left(\frac{0.744}{0.005}\right)}{\log 2.45} = 11.4$$

$$\frac{(O/D) - (O/D)_{min}}{(O/D) + 1} = \frac{2.0 - 1.0}{2.0 + 1.0} = 0.333$$

From Fig. 12-1,

$$\frac{S - S_m}{S + 1} = 0.32$$

$$S = 17.2$$

$N = 16.2$ theoretical plates

This compares with 16 plates as determined by the stepwise procedure.

An interesting fact is that the commonly used design reflux ratios of 1.2 to 1.5 times $(O/D)_{min}$ usually correspond to values of $(S - S_m)/(S + 1)$ from 0.4 to 0.6, and because S is usually large in comparison to 1.0, a rough working rule is that the number of theoretical steps required at the optimum reflux ratio will be twice the number needed at total reflux. This is a rule that can be applied for orientation purposes and requires only an estimation of the number of theoretical plates at total reflux.

The correlation also illustrates why the economic reflux ratio is usually so close to $(O/D)_{min}$. A small initial increase in the reflux ratio group above 0.0 makes a large decrease in the theoretical plate group, but further increases become less effective.

A modification of the above correlation has been suggested by Schiebel (Ref. 12), and a somewhat different graphical correlation has been published by Brown and Martin (Ref. 2).

MODIFIED EQUILIBRIUM CURVES AND OPERATING LINES

Several methods have been given which treat a multicomponent mixture as a modified binary mixture of the key components that can be analyzed graphically on a y,x type diagram.

Jenny (Ref. 10) published a graphical method for multicomponent design calculation. A few plate-to-plate calculations are made at the top and bottom of the column and above and below the feed plate. For the section below the feed plate, a y,x diagram is made for the light key component using the calculated values to place the effective equilibrium curve for this component on the diagram. The operating line is drawn in the usual manner and the plates determined by the stepwise

procedure. Above the feed plate a diagram is constructed for the heavy key component in the same manner.

Hengstebeck (Ref. 8) developed a graphical method for multicomponent mixtures which employed the key components on a binary-type diagram. The mol fractions for the distillate and bottoms were calculated on a key component basis

$$x'_{wlk} = \frac{x_{wlk}}{x_{wlk} + x_{whk}}$$

and the equilibrium curve for a binary mixture of the key components is employed. The operating lines are corrected for the quantity of the light and heavy components present.

Schiebel and Montross (Ref. 13) developed a method for making multicomponent design calculations on the basis of a pseudobinary mixture. A modification of this method by Bailey and Coates (Ref. 1) will be reviewed.

The analysis is made on a key component basis, and plate-to-plate calculations are made above and below the feed plate to determine x'_{f+1}, t_{f+1}, y'_f, x'_f, t_f, and y'_{f-1}. The feed-plate composition is obtained by the method given on page 342. The operating line in the stripping section is drawn as a straight line through $y'_{wlk} = x'_{wlk} = \frac{x_{wlk}}{x_{wlk} + x_{whk}}$ and $x'_{flk} = \frac{x_{flk}}{x_{flk} + x_{fhk}}$, $y'_{(f-1)lk} = \frac{y_{(f-1)lk}}{y_{(f-1)lk} + y_{(f-1)hk}}$, and similar procedures are used to calculate x'_{Dlk}, y'_{flk}, and $x'_{(f+1)lk}$, where the primed mol fractions are on a key component basis. The relative volatility of the key components is plotted vs. x' using the values α_t, x'_D and α_{f+1}, x'_{f+1} to give a curve for volatility above the feed plate and α_W, x'_W and α_f, x'_f to give a curve below the feed plate. These relative volatility curves are used to calculate the y' vs. x' equilibrium curves by

$$y' = \frac{\alpha x'}{(\alpha - 1)x' + 1}$$

In general, the equilibrium curves calculated from the two curves do not match exactly, and each is used for its respective portion of the column. Plates are stepped off between the operating lines and equilibrium curves in the usual manner.

Bailey and Coates (Ref. 1) also modified the Schiebel and Montross method of calculating the minimum reflux ratio for a multicomponent

mixture. They give

$$\left(\frac{O}{D}\right)_{\min} = (x_{Dlk} + x_{Dhk})\left(\frac{O}{D}\right)'_M + \frac{W}{D}\sum\left(\frac{\alpha_h x_{hF}}{\alpha_{lk} - \alpha_h}\right) + \frac{F}{D}\sum(x_{lF})\left[\frac{\alpha_{hk}(\alpha_{lk} + \alpha_{lk})}{\alpha_l^2}\right] \quad (12\text{-}27)$$

where $(O/D)'_M$ is the pseudo-minimum reflux ratio.

This equation appears somewhat similar to Eq. (9-21), and the nomenclature is the same. $(O/D)'_M$ is calculated by

$$\left(\frac{O}{D}\right)'_M = \frac{1}{\alpha_{av} - 1}\left(\frac{x'_D}{x'_i} - \alpha_{av}\frac{1 - x'_D}{1 - x'_i}\right) \quad (12\text{-}28)$$

where x'_D, x'_i = mol fractions on key component basis for distillate and at intersection of pseudo operating lines

α_{av} = average relative volatility

$$x'_i = \frac{z'_F(1 + m)[(O/D)'_M + 1] - x'_D}{(O/D)'_M(1 + m) + m} \quad (12\text{-}29)$$

where $m = \dfrac{M_L - \Sigma M_{hF}}{M_V - \Sigma M_{lF}}$

z'_F = mol fraction on key component basis for feed

M_L = mols of liquid in feed

M_V = mols of vapor in feed

ΣM_{hF} = mols of components heavier than heavy key component in feed

ΣM_{lF} = mols of components lighter than light key component in feed

Values of x'_D are calculated from the terminal conditions, and x'_i and $(O/D)'_M$ obtained by simultaneous solution of Eqs. (12-28) and (12-29).

The calculation of $(O/D)'_M$ is frequently laborious, and Eq. (9-21) is easier to use.

Solution of Benzene-Toluene-Xylene Example by Modified Equilibrium Curve Method. The use of this method will be illustrated by the benzene-toluene-xylene example. Benzene and toluene are the key components and the necessary feed-plate calculations were made for this example on page 343.

The results are summarized for the key components:

	x_f	y_f	x_{f+1}	y_{f-1}
C_6	0 609	0.811	0.718	0.739
C_7	0.336	0.179	0.267	0.246

t_f = 90°C. t_{f-1} = 95°C.

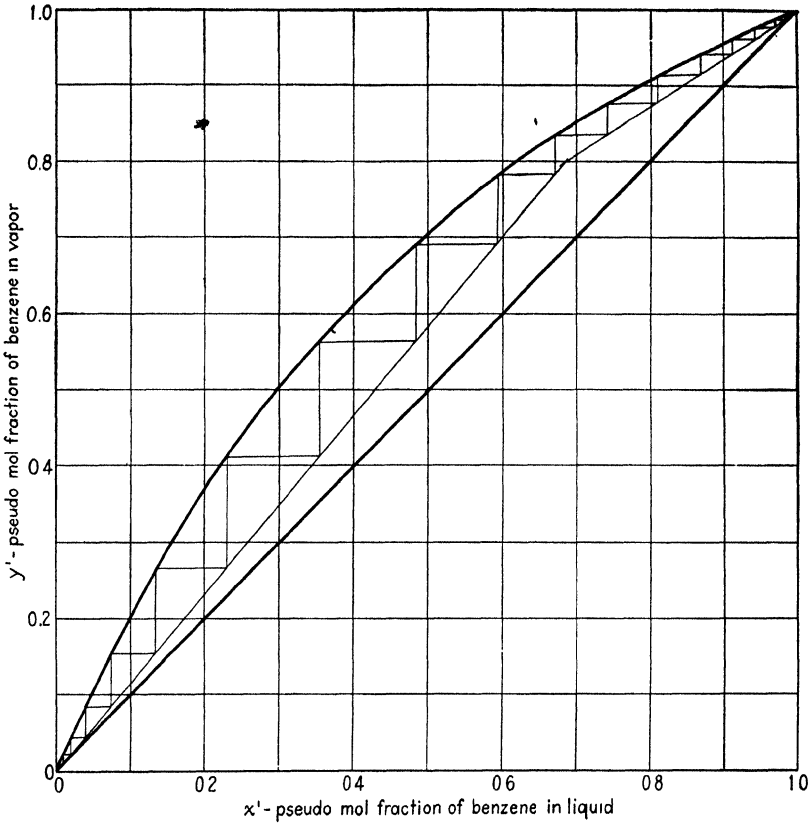


FIG. 12-3.

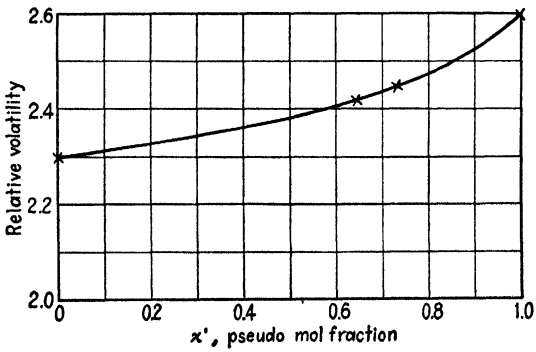


FIG. 12-4.

Coordinates for benzene for lower operating line,

$$y'_W = x'_W = \frac{0.005}{0.749} = 0.0067$$

$$y'_{f-1} = \frac{0.739}{0.985} = 0.75$$

$$x'_f = \frac{0.609}{0.945} = 0.645$$

Coordinate for enriching line,

$$y'_D = x'_D = \frac{0.995}{1.0} = 0.995$$

$$y'_f = \frac{0.811}{0.98} = 0.828$$

$$x'_{f+1} = \frac{0.718}{0.985} = 0.73$$

Straight lines are drawn through these points on Fig. 12-3. The relative volatility values corresponding to α_t, α_{f+1}, α_f, and α_W were plotted as a function of x' in Fig. 12-4. These values were used to calculate the equilibrium curve of Fig. 12-3. The steps are made on this diagram in the usual manner, and the procedure gives between 16 and 17 theoretical plates. This method is particularly good in this case because the components other than the key components are present only in small quantities.

The minimum reflux ratio by this method is obtained as follows. By Eq. (12-28),

$$\left(\frac{O}{D}\right)'_M = \frac{1}{2.45 - 1}\left(\frac{0.995}{x'_i} - 2.45\,\frac{0.005}{x'_i}\right)$$

By Eq. (12-29),

$$m = \frac{100 - 10}{0} = \infty$$

$$x'_i = \frac{0.6}{0.9} = 0.667 \qquad \text{and} \qquad \left(\frac{O}{D}\right)'_M = 1.01$$

By Eq. (12-27),

$$\left(\frac{O}{D}\right)_{\min} = 1.01 + \frac{39.4}{60.6}\left[\frac{0.4(0.1)}{2.34 - 0.4}\right]$$

$$= 1.02$$

This compares closely with the values given on page 259.

ANALYTICAL EQUATIONS

Exact mathematical equations for the case of constant molal overflow rate and constant relative volatilities have been presented by Harbert (Ref. 7) and Underwood (Ref. 16). Underwood's equation for a three-component mixture can be arranged as follows:

Above feed plate,

$$\frac{X_{D_1}}{X_{D_2}} = \left(\frac{\phi_1}{\phi_2}\right)^{N_n+1} \frac{X_{F_1}}{X_{F_2}}$$
$$\frac{X_{D_2}}{X_{D_3}} = \left(\frac{\phi_2}{\phi_3}\right)^{N_n+1} \frac{X_{F_2}}{X_{F_3}} \qquad (12\text{-}30)$$
$$\frac{X_{D_3}}{X_{D_1}} = \left(\frac{\phi_3}{\phi_1}\right)^{N_n+1} \frac{X_{F_3}}{X_{F_1}}$$

Similar ratio equations can be written for any two components of a multicomponent mixture where

$$X_{D_1} = \frac{\alpha_A x_{DA}}{\alpha_A - \phi_1} + \frac{\alpha_B x_{DB}}{\alpha_B - \phi_1} + \frac{\alpha_C x_{DC}}{\alpha_C - \phi_1} + \cdots$$

x_D = distillate composition

X_{D_2}, X_{D_3} = X_{D_1} with ϕ_1 replaced by ϕ_2 and ϕ_3, respectively

X_F = X_D with x_{DA}, x_{DB}, x_{DC} replaced by x_{FA}, x_{FB}, and x_{FC}, respectively

x_F = feed-plate composition

N_n = number of plates above feed plate

ϕ_1, ϕ_2, ϕ_3 = roots of the equation

$$\frac{\alpha_A \frac{D}{V_n} x_{DA}}{\alpha_A - \phi} + \frac{\alpha_B \frac{D}{V_n} x_{DB}}{\alpha_B - \phi} + \frac{\alpha_C \frac{D}{V_n} x_{DC}}{\alpha_C - \phi} + \cdots = 1 \qquad (12\text{-}31)$$

The roots will be bracketed by the relative volatilities; thus, for a three-component mixture,

$$\alpha_A > \phi_1 > \alpha_B, \qquad \alpha_B > \phi_2 > \alpha_C, \qquad \alpha_C > \phi_2 > 0$$

Below the feed plate similar equations are obtained.

$$\frac{X'_{F_1}}{X'_{F_2}} = \left(\frac{\phi'_1}{\phi'_2}\right)^{N_m} \frac{X'_{W_1}}{X'_{W_2}} \qquad (12\text{-}32)$$

Similar relations can be written for the other components where

X'_F = X_F except ϕ' used instead of ϕ

X'_W = X_D with x_{DA}, x_{DB}, x_{DC} replaced by x_{WA}, x_{WB}, x_{WC}, respectively, and using ϕ' instead of ϕ

N_m = number of theoretical plates, feed plate and below

ϕ'_1, ϕ'_2, ϕ'_3 = roots of the equation

$$\frac{\alpha_A \frac{W}{V_m} x_{WA}}{\alpha_A - \phi'} + \frac{\alpha_B \frac{W}{V_m} x_{WB}}{\alpha_B - \phi'} + \frac{\alpha_C \frac{W}{V_m} x_{WC}}{\alpha_C - \phi'} + \cdots = -1 \qquad (12\text{-}33)$$

In many cases, the use of these equations is complicated by the fact that a trial-and-error procedure is involved. If the terminal compositions are known, the trial-and-error operation involves matching at the feed plate. Usually the terminal conditions are not completely known, and additional trial and error may be required. In most cases a three-component problem can be solved just as rapidly by the usual stepwise procedure, and variations in the relative volatility can be included.

Underwood has used these equations to calculate the minimum reflux ratio.

$$\left(\frac{O}{D}\right)_{\min} + 1 = \frac{\alpha_{lk}}{\alpha_{lk} - \theta} \tag{12-34}$$

where θ is the root of the equation.

$$\frac{\alpha_A x_{FA}}{\alpha_A - \theta} + \frac{\alpha_B x_{FB}}{\alpha_B - \theta} + \frac{\alpha_C x_{FC}}{\alpha_C - \theta} + \cdots = 1 + p \tag{12-35}$$

where $p = (O_n - O_m)/F$.

This equation has several roots. The one employed in Eq. (12-34) is the value lying between α_{lk} and α_{hk}.

Solution of Benzene-Toluene-Xylene Example by Analytical Equations. These equations will be applied to the benzene-toluene-xylene example. Relative volatilities for the three components will be used as $\alpha_B = 2.45$, $\alpha_T = 1.0$, and $\alpha_X = 0.4$.

By Eq. (12-31),

$$\frac{2.45(0.995/3)}{2.45 - \phi} + \frac{0.005/3}{1 - \phi} = 1$$

$$2.45 > \phi_1 > 1.0, \qquad 1.0 > \phi_2 > 0$$

The term for xylene is neglected because its concentration in the distillate is unknown, and it will make little difference in the values of ϕ_1 and ϕ_2. Solution of this equation gives

$$\phi_1 = 1.64, \qquad \phi_2 = 0.9963$$

By Eq. (12-33),

$$\frac{2.45(0.005)(39.9/180.3)}{2.45 - \phi'} + \frac{1.0(0.744)(39.9/180.3)}{1 - \phi'} + \frac{0.4(0.251)(39.9/180.3)}{0.4 - \phi'} = -1$$

$$\phi_1' > 2.45, \qquad 2.45 > \phi_2' > 1.0, \qquad 1.0 > \phi_3' > 0.4$$

$$\phi_3' = 0.4173, \qquad \phi_2' = 1.169, \qquad \phi_1' = 2.45308$$

Using these values for the key components,

$$X'_{F_1} = \frac{2.45x_{FB}}{2.45 - 2.45308} + \frac{x_{FT}}{1 - 2.45308} + \frac{0.4x_{FX}}{0.4 - 2.45308}$$

$$= -795x_{FB} - 0.688x_{FT} - 0.195x_{FX}$$

It is obvious that the first term will be the important factor.

$$X'_{W_1} = -795(0.005) - 0.688(0.744) - 0.195(0.251)$$
$$= -4.64$$
$$X'_{F_2} = \frac{2.45x_{FB}}{2.45 - 1.169} + \frac{x_{FT}}{1 - 1.169} + \frac{0.4x_{FX}}{0.4 - 1.169}$$
$$= 1.915x_{FB} - 5.92x_{FT} - 0.519x_{FX}$$
$$X'_{W_2} = -4.53$$

By Eq. (12-32),

$$\frac{-795x_{FB} - 0.688x_{FT} - 0.195x_{FX}}{1.915x_{FB} - 5.92x_{FT} - 0.519x_{FX}} = \left(\frac{2.45}{1.169}\right)^{N_m}\left(\frac{-4.64}{-4.53}\right)$$

By a similar procedure for X'_{F_1} and X'_{F_3},

$$\frac{1.915x_{FB} - 5.92x_{FT} - 0.519x_{FX}}{1.203x_{FB} + 1.718x_{FT} - 23.1x_{FX}} = \left(\frac{1.169}{0.4173}\right)^{N_m}\left(\frac{-4.53}{-4.514}\right)$$

With $x_{FB} + x_{FT} + x_{FX} = 1.0$, there are three equations and four unknowns. By using two similar equations for the section above the feed, only one additional unknown, N_n, is introduced, and the equation can be solved. However, with x_{DX} unknown, only one equation is available. x_{DX} is small, and to satisfy Eq. (12-31) it can be shown that $\phi_3 = 0.4 - 0.334x_{DX}$, and the correction term $-0.334x_{DX}$ can be neglected in all cases except the $(\phi_3 - 0.4)$ term. This introduces an additional unknown, and an additional specification can be added such as the ratio of the key components on the feed plate or that $N_n + N_m$ is to be a minimum. The trial-and-error solution for the latter case is time-consuming; instead, the feed-plate compositions obtained by the stepwise procedure on page 223 will be employed; $x_{FB} = 0.605$, $x_{FT} = 0.336$, and $x_{FX} = 0.058$.

For ratio of 1 to 2, the relation reduces to

$$\left(\frac{2.45}{1.169}\right)^{N_m} = \frac{-4.53}{-4.64}\left(\frac{481}{-0.86}\right)$$
$$N_m = 8.5 \text{ theoretical plates}$$

For ratio of 2 to 3,

$$\left(\frac{1.169}{0.4173}\right)^{N_m} = \frac{4.514}{4.53}\left(\frac{0.86}{0.044}\right)$$
$$N_m = 2.9$$

The last value for N_m is very sensitive to the value employed for x_{FX}, and a value of 0.0562 for xylene at the feed plate instead of 0.058 would make the last equation give $N_m = 8.5$. This value of $N_m = 8.5$ compares with nine plates by the stepwise procedure. The difference is due to the fact that the relative volatility in the lower section of the tower averaged less than 2.45.

A similar calculation for the upper section using the same feed composition gave $N_n + 1 = 8.6$, $N_n = 7.6$ or total plates,

$$N = N_n + N_m = 8.5 + 7.6 = 16.1$$

as compared to 16 plates by the Lewis and Matheson method.

For the minimum reflux ratio, by Eq. (12-33),

$$\frac{2.45(0.6)}{2.45 - \theta} + \frac{1(0.3)}{1 - \theta} + \frac{0.4(0.1)}{0.4 - \theta} = 0$$

The desired θ is between 1 and 2.45.

$$\theta = 1.25$$

$$\left(\frac{O}{D}\right)_{\min} + 1 = \frac{2.45}{2.45 - 1.25}$$

$$= 2.02$$

$$\left(\frac{O}{D}\right)_{\min} = 1.02$$

This compares closely with the values given on pages 259 and 354.

SUMMARY

The Lewis and Matheson method appears to be the most satisfactory method of handling the general multicomponent design problem. In most cases, it requires relatively little trial and error and will handle cases of normal and abnormal vapor-liquid equilibria. It is especially well suited to the cases in which the reflux ratio and the separation of the key components are specified and the problem is to determine the number of theoretical plates and the component concentrations in the column. In some specific cases, other methods may have advantages, but unless a number of problems of the same type are to be handled, it is more desirable to have one method that will apply to essentially all cases.

The Thiele and Geddes method is advantageous when the number of theoretical plates and the reflux ratio are specified and the calculation of the separation is desired. Even in this case, the trial and error involved in obtaining the proper equilibrium constants for each plate is formidable.

The reduced relative volatility and absorption factor methods are rapid but can be appreciably in error because of the approximations involved. If the design engineer understands their limitations, they can be useful. In cases involving abnormal vapor-liquid equilibrium conditions or at reflux ratios near to the minimum, these methods may be so in error that the results are of little value.

The methods based on modified equilibrium curves and operating lines are simple to use and can give satisfactory results for many cases. They do not give information on the light and heavy components without considerable additional effort. In general, they are not satisfactory for mixtures with abnormal vapor-liquid equilibria.

The analytical solutions for the case of constant molal overflow and constant relative volatility are a mathematical accomplishment, but they do not appear to be well suited for the average design problem. The greatest contribution of these methods will probably be as an aid in studying the process of rectification, particularly the minimum reflux ratio condition.

The graphical correlations are useful in obtaining approximate answers rapidly. They are not applicable to all cases and can be seriously in error under some conditions.

The various approximate methods are helpful for orientation purposes, but the greater confidence that the design engineer can place in the rigorous plate-to-plate calculation justifies any greater effort involved.

Nomenclature

A = absorption factor = O_n/KV_n
D = molal distillate rate
F = molal feed rate
K = equilibrium constant = y/x
m = ratio, see page 352
M_L = mols of liquid in feed
M_V = mols of vapor in feed
ΣM_{hF} = mols of components heavier than heavy key component in feed
ΣM_{lF} = mols of components lighter than light key component in feed
N_n = number of theoretical plates above feed plate
N_m = number of theoretical plates feed plate and below
O = molal overflow rate
S = stripping factor = KV_m/O_m
t = temperature
V = molal vapor rate
W = molal bottoms rate
x = mol fraction in liquid
X = composition factor in Eq. (12-30)
x' = mol fraction in liquid based on key components only
y = mol fraction in vapor
y' = mol fraction in vapor based on key components only
α = relative volatility
β = relative operability
ϕ,ϕ' = roots of Eqs. (12-32) and (12-33)
θ = root of Eq. (12-35)

Subscripts:

A refers to component A
B refers to benzene or component B
D' refers to distillate
F refers to feed

f refers to feed plate
h refers to heavy component
hk refers to heavy key component
l refers to light component
lk refers to light key component
n refers to section above feed plate
m refers to section below feed plate
T refers to toluene or to top plate
W refers to bottoms
X refers to xylene

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CHAPTER 13

SIMULTANEOUS RECTIFICATION AND CHEMICAL REACTION

In most rectification systems, chemical reactions among the components to form new stable compounds do not usually occur, but in a few special cases sueh a condition is involved. In some cases, the combination of rectification and reaction is beneficial as in the preparation of esters; while in other cases, it may be detrimental in that it decreases the effectiveness of the separation or the yield of the desired component.

In the preparation of esters such as ethyl acetate from acetic acid and ethanol, the equilibrium is such that only a moderate conversion is obtained. If the reaction mixture is brought to equilibrium and then fractionally distilled to remove the ethyl acetate, leaving water, unreacted acetic acid, and ethanol, it would give only a low conversion on further reaction. The reaction can be carried out in a fractionating column with the esterification occurring in the liquid on the plates. The acetic acid is added to the upper portion of the column, and the alcohol is introduced in the lower portion. The plates below the alcohol addition are used to strip the alcohol out of water. The middle section between the plates where the alcohol and acetic acid are added is the chief esterification section. The upper portion of this middle section has a high ratio of acetic acid to alcohol and gives good cleanup of the ethanol. The lower portion is high in alcohol and gives a rapid reaction of the acetic acid. The top part of the column fractionates the ethyl acetate out of the acetic acid. A small amount of acid catalyst is added at the top of the column. The unit produces the ethyl acetate and water and, by separating them, carries the reaction almost to completion.

In the esterification system, if the liquid level on the plates is low and a normal vapor rate is employed, the amount of reaction per unit time will be small relative to the vapor rate and a high reflux ratio will be necessary. This will result in a high heat consumption per gallon of ethyl acetate produced. If a very deep liquid level is employed on the plate to increase the amount of reaction relative to the vapor rate, it may be that the rate at which the ethyl acetate is removed is so low that the liquid on the plates is near equilibrium and the reaction rate

will be retarded. Thus the large volume of column required because of the deep liquid level will be used ineffectively. The volume of the liquid should be proportioned to the vapor rate such that there is an adequate supply of ester for separation but not to the extent that it seriously retards further reaction.

The large liquid volume required can be obtained by using a deep liquid level on the plates or by having the overflow from a plate pass through a holding tank for the chemical reaction before it is added to the plate below. Deep liquid levels give undesirable action with normal-type bubble plates, but tall caps and risers can be used to obtain satisfactory operation.

In other cases, the chemical reaction may be undesirable. For example, in the distillation of an aqueous solution of alcohols and aldehydes, aldols can form in the upper portion of the column and, being of lower volatility, go down the column and be hydrolyzed by the water at the bottom. This cycling action is undesirable. Polymerization and thermal decomposition occur in some cases and are usually objectionable. In most of these cases, the undesirable reactions take place in the liquid phase and can be minimized by using low liquid depth on the plates and by keeping the temperatures as low as practical. Frequently inhibitors can be added to the fractionating system to reduce the amount of reaction. For example, in the fractionation of styrene from ethyl benzene or of butadiene from butylene, the polymerization of the styrene and butadiene can be reduced by adding inhibitors such as sulfur or tertiary butyl catechol with the reflux. The styrene rectification is also carried out under vacuum to reduce the temperature. The separation of styrene from ethyl benzene requires a large number of plates, and even with specially designed bubble-cap plates the pressure drop would be so great that the still temperature would be excessive. To avoid this difficulty the rectifying column is made in two sections. The vapor from the section that serves as the bottom portion of the tower is liquefied under vacuum in a condenser and then pumped, vaporized, and added at the bottom of the other section. The liquid from the bottom of the top section is added to the top of the lower section. A vacuum condenser is also employed for the top section. In this manner the average pressure and temperature in the column can be made lower than for the single tower.

The design calculations for these systems can be made by the usual stepwise procedure making allowance for the chemical reaction on each plate. The calculations frequently require trial-and-error methods,

because the terminal conditions and flow rates are a function of the chemical reaction. The method of calculation will be illustrated by the fractional distillation of cyclopentadiene.

Example on Preparation of Cyclopentadiene. Cyclopentadiene is obtained in high-temperature vapor-phase petroleum cracking operations. It is mixed with other hydrocarbons, and its separation is complicated by the fact that it will dimerize and the dimer will depolymerize at about normal distillation conditions. One method of operating is to dimerize the pentadiene and then remove all remaining constituents below C_7. The residue is then given a thermal treatment which will depolymerize the dimer, and the mixture is distilled to obtain the cyclopentadiene. A unit is to be designed for this final fractional distillation, and an estimate is to be made of the amount of polymerization that will be obtained.

As a basis for the estimate, it is assumed that the feed is a binary mixture containing 20 mol per cent cyclopentadiene and 80 mol per cent C_7. The overhead product is to contain 98 mol per cent cyclopentadiene, and the cyclopentadiene content of the bottoms is to be 0.5 mol per cent. The column will operate with a still and total condenser at atmospheric pressure. A reflux ratio, O/D, three times the minimum reflux ratio for the separation of the binary mixture with no polymerization will be used.

Data and Notes

1. Holdup in the condenser is negligible.
2. Holdup per plate is equivalent to a liquid depth of 3 in. on the superficial area.
3. Holdup in the still is equivalent to one plate.
4. Superficial vapor velocity is equivalent to 1.0 f.p.s. (S.T.P.)
5. The liquid on each plate is well mixed, and the plate efficiency is 100 per cent.
6. The feed enters such that $V_n = V_m$.
7. Neglect polymerization in vapor.
8. For simplification assume the relative volatilities of cyclopentadiene and dicyclopentadiene to C_7 are 6.0 and 0.1, respectively.
9. The rate of depolymerization at the temperature of distillation is negligible.
10. The rate of polymerization in the liquid phase is a function of temperature, but for simplification an average value of the rate constant will be employed in the equation $-(dr/d\theta) = Kr^2$, where r = g. mol of cyclopentadiene per liter, θ = sec., $K = 6 \times 10^{-5}$ l./sec.-g. mol.
11. Assume that liquid volumes are additive. Densities of C_5, C_7, and C_{10} average 0.80, 0.68, and 0.92, respectively.
12. Assume that the same number of mols of vapor enters each plate per unit of time.

Solution. Minimum reflux ratio for binary mixture: Because cyclopentadiene is the more volatile component, the mol fractions for the binary mixture will be used on the basis of this component. With $V_n = V_m$, the intersection of the operating lines will be at $x = x_F = 0.2$.

With a constant relative volatility of 6.0, the pinched-in condition will occur at the intersection of the operating lines. The y coordinate of the intersection is

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} = \frac{6(0.20)}{1 + (6 - 1)(0.20)} = 0.60$$

From these coordinates and because $x_D = 0.98$, the slope of the enriching line and the reflux ratio are found.

$$\left(\frac{O}{V}\right)_{\text{min.}} = \frac{0.98 - 0.60}{0.98 - 0.20} = \frac{0.38}{0.78}$$

$$\left(\frac{O}{D}\right)_{\text{min.}} = \frac{0.38}{0.78 - 0.38} = 0.95$$

Design case:

For this case, $O/D = 3(O/D)_{\text{min.}}$

$$\frac{O}{D} = 2.85 \qquad \text{and} \qquad \frac{V}{D} = 3.85$$

Because the amount of polymerization is unknown and because the complete composition of neither the distillate nor the bottoms is known, the calculations are a series of trial-and-error calculations.

Basis: 1 sq. ft. of plate area and 1 sec. of time.

The volume of liquid on a plate = ¼ cu. ft. = ¼(28.32) = 7.08 l.

The molal volumes of each of the three components may be found by dividing their respective molecular weights by their densities.

$$C_5: \quad v = 66.1/0.80 = 0.0826 \text{ l./g. mol}$$
$$C_7: \quad v = 100.2/0.68 = 0.1475 \text{ l./g. mol}$$
$$C_{10}: \quad v = 132.2/0.92 = 0.144 \text{ l./g. mol}$$

$$r = \frac{x_5}{0.0826x_5 + 0.1475x_7 + 0.144x_{10}} = \frac{1}{0.0826 + (0.1475x_7/x_5) + (0.144x_{10}/x_5)}$$

$$-\frac{dr}{d\theta} = (6)10^{-5}r^2$$

or the number of mols of C_5 that polymerize on any plate in 1 sec. is given by

$$p = 6(7.08)10^{-5}\,r^2 = (4.25)10^{-4}\,r^2$$

From the superficial vapor rate of 1 f.p.s. at standard temperature and pressure, the conversion factor of 454 g./lb., and the fact that the pound molal volume of a gas is 359 cu. ft. (S.T.P.), the vapor rate V may be found.

$$V = \frac{454}{359} = 1.265 \text{ g. mols/sec.}$$

$$D = \frac{V}{V/D} = \frac{1.265}{3.85} = 0.328 \text{ g. mols/sec.}$$

$$O_R = V - D = 1.265 - 0.328 = 0.937 \text{ g. mols/sec.}$$

Top plate:

Because the conditions at the top of the tower are much better known than are those at the bottom of the tower, the calculations will be started at the top. The volatility of C_{10} is so low that it is assumed first that the C_{10} in the distillate is negligible.

To calculate the amount of polymerization on the top plate, the ratios x_7/x_5 and x_{10}/x_5 must be known.

$$\frac{x_7}{x_5} = \frac{y_7}{y_5}(\alpha_5) = \frac{0.02}{0.98}(6) = 0.1225$$

The value of x_{10}/x_5 is not known until the amount of polymerization is known, so it is assumed as 0.0252.

$$\frac{1}{r} = 0.0826 + 0.1475(0.1225) + 0.144(0.0252) = 0.104$$

$$p = \frac{(4.25)10^{-4}}{(0.104)^2} = 0.0389; \qquad \frac{p}{2} = 0.01945$$

With $V_{t-1} = V_t$ (subscript t, $t-1$ refer to top plate and plate below, respectively), the polymerization will make O_t less than O_R by the decrease in mols, $p/2$.

$$O_t = O_R - \frac{p_t}{2} = 0.936 - 0.0195 = 0.916$$

Assuming that 0.00082 more mols of C_{10} enter the top plate in the vapor than leave it in the distillate,

$$Ox_{10} = \frac{p}{2} + 0.00082 = 0.02027$$

$$Ox_5 + Ox_7 = O_t - Ox_{10} = 0.916 - 0.020 = 0.896$$

$$Ox_5 = \frac{0.896}{1.1225} = 0.798$$

$$Ox_7 = \frac{0.896}{1.1225}(0.1225) = 0.0976$$

$x_{10}/x_5 = 0.02027/0.798 = 0.0254$, which checks the assumption satisfactorily.

$$y_{10} = \frac{x_{10}}{x_7} y_7 \alpha_{10}$$

$$= \frac{0.020}{0.0976}(0.02)(0.10) = 0.00041$$

which checks the assumption that it is negligible.

The following table may now be constructed for the top plate:

Comp.	y_t	$O_t x_t$	Dx_D
5	0 98	0.798	0 3215
7	0.02	0 0976	0.00656
10	0 00041	0.02027	0.000134

Plate $t-1$:

Calculations may proceed downward to the next plate by making material balances on components C_5 and C_7 and by assuming, and later checking, vapor values for C_{10}.

For C_5,

$$Vy_{t-1} = Dx_D + Ox_t + p_t = 0.3215 + 0.798 + 0.0389 = 1.159$$

For C_7,

$$Vy_{t-1} = Dx_D + Ox_t = 0.00656 + 0.0976 = 0.1042$$

Knowing the ratio of the y's, the ratio of the x's may be found, using α

$$\frac{x_7}{x_5} = 6\,\frac{0.1042}{1{,}159} = 0.540$$

and assuming $x_{10}/x_5 = 0.0495$,

$$\frac{1}{r} = 0.0826 + 0.1475(0.540) + 0.144(0.0495) = 0.1694$$

$$p_{t-1} = \frac{(4.25)\ 10^{-4}}{(0.1694)^2} = 0.0148; \qquad \frac{p}{2} = 0.0074$$

Assuming that 0.0006 more mols of C_{10} enter plate $(t-1)$ in the vapor than leave in the vapor,

$$Ox_{10} = 0.02027 + 0.0074 + 0.0006 = 0.0283$$

$$O_{t-1} = O_t - \frac{p_{t+1}}{2} = 0.916 - 0.0074 = 0.909$$

$$Ox_5 + Ox_7 = 0.909 - 0.028 = 0.881$$

$$Ox_7 = \frac{0.54}{1.54}\,0.881 = 0.309 \qquad \text{and} \qquad Ox_5 = 0.572$$

These calculated values may now be tabulated.
Tabulating for $t-1$:

Comp.	Vy	Ox
5	1.159	0.572
7	0.1042	0.309
10	0.00095	0 0283

The value of Vy_{10} is calculated using α.

$$Vy_{10} = \frac{Ox_{10}}{Ox_7}\,(Vy_7)\alpha_{10} = \frac{0.0283}{0.309}\,(0.1042)(0.10) = 0.00095$$

Thus, 0.00095 − 0.00013 = 0.00082, which checks the assumptions made for the top plate. $x_{10}/x_5 = 0.0283/0.572 = 0.0495$, which checks the assumption used to calculate r.
Plate $t-2$:

For C_5,

$$Vy_{t-2} = 0.3215 + 0.0389 + 0.0148 + 0.572 = 0.947$$

For C_7,

$$Vy_{t-2} = 0.00656 + 0.309 = 0.3155$$

$$\frac{x_7}{x_5} = 6\,\frac{0.3155}{0.947} = 1.998$$

Assume that $x_{10}/x_5 = 0.0986$.

$$\frac{1}{r} = 0.0826 + 0.1475(1.998) + 0.144(0.0986) = 0.391$$

$$p_{t-2} = \frac{(4.25)\ 10^{-4}}{(0.391)^2} = 0.00278; \qquad \frac{p}{2} = 0.00139$$

Assume that 0.0008 more mols of C_{10} are in the vapor from plate $(t-2)$ than in the vapor to this plate. Therefore,

$$Ox_{10} = 0.0283 + 0.0014 - 0.0008 = 0.0289$$
$$O_{t-2} = 0.909 - 0.0014 = 0.908$$
$$Ox_5 + Ox_7 = 0.908 - 0.029 = 0.879$$
$$Ox_5 = \frac{0.879}{2.998} = 0.293 \qquad \text{and} \qquad Ox_7 = 0.586$$

Tabulating for $t-2$:

Comp.	Vy	Ox
5	0.947	0.293
7	0 3155	0 586
10	0.00155	0.0289

$$Vy_{10} = \frac{0.0289}{0.586}(0.10)(0.3155) = 0.00155$$

The C_{10} condensing on plate $(t-1) = 0.00155 - 0.00095 = 0.0006$, which checks the assumption used in finding Ox_{10} for plate $(t-1)$.

$x_{10}/x_5 = 0.0289/0.293 = 0.0986$, which checks the value used to calculate r_{t-2}.

Plate $t-3$ = feed plate:

The ratio of x_5/x_7 is approaching that in the feed, and trial calculations show that plate $(t-3)$ should be the feed plate. To calculate O values for this plate, the value of F must be known. To find F, assume that 0.0571 mol of the C_5 fed to the tower polymerizes. Over-all balances give

$$F = W + D + \frac{0.0571}{2} = W + 0.357$$

By C_5 balance, assuming $x_W = 0.004$,

$$0.20F = 0.3215 + 0.004W + 0.057 = 0.004W + 0.3786$$

Solving,

$$F = 1.915 \qquad \text{and} \qquad W = 1.56$$

For $C_5 + 2C_{10}$,

$$Wx_W = 1.915(0.20) - 0.3215 = 0.0615$$

For C_7,

$$Wx_W = 1.915(0.80) - 0.00656 = 1.526$$

Calculations for plate $(t-3)$, the feed plate:

For C_5,

$$Vy_{t-3} = 0.3215 + 0.293 + 0.0389 + 0.0148 + 0.0028 = 0.671$$

For C_7,

$$Vy_{t-3} = 0.00656 + 0.586 = 0.5925$$

$$\frac{x_7}{x_5} = 6\,\frac{0.5925}{0.671} = 5.30$$

Assume

$$\frac{x_{10}}{x_5} = 0.0661; \qquad \frac{1}{r} = 0.0826 + 0.1475(5.30) + 0.144(0.0661) = 0.875$$

$$p_{t-3} = \frac{(4.25)10^{-4}}{(0.875)^2} = 0.000555; \qquad \frac{p}{2} = 0.000277$$

Assume that 0.002 mol of C_{10} condenses on $t-3$, then

$$Ox_{10} = 0.0289 + 0.00027 + 0.0002 = 0.0293$$

$$O_{t-3} = 0.908 - 0.0003 + 1.915 = 2.823$$

$$Ox_5 + Ox_7 = 2.823 - 0.029 = 2.794$$

$$Ox_5 = \frac{2.794}{6\ 30} = 0.443 \qquad \text{and} \qquad Ox_7 = 2.351$$

Tabulating for $t-3$:

Comp.	Vy	Ox
5	0 671	0 443
7	0 5925	0.351
10	0 00074	0 0293

$$Vy_{10} = \frac{0.0293}{2.351}(0.5925)(0.10) = 0.000739$$

Mols C_{10} vaporizing from $t-2 = 0.00155 - 0.00074 = 0.0008$
Checking the assumption used in calculating Ox_{10} for plate $(t-2)$,

$$\frac{x_{10}}{x_5} = \frac{0.0293}{0.443} = 0.0661$$

which checks the assumption used to find r_{t-3}.

The calculations for the succeeding plates are carried out in the same manner and the results are given in the following table:

Comp.	$(Vy)_{t-4}$	$(Ox)_{t-4}$	$(Vy)_{t-5}$	$(Ox)_{t-5}$	$(Vy)_{t-6}$	$(Ox)_{t-6}$
5	0.439	0.227	0.222	0.0956	0.0912	0.0357
7	0.825	2 567	1.041	2 697	1 171	2.757
10	0 00095	0 0295	0 00114	0.0296	0.0013	0.0306
p	0.00013		Neglected		Neglected	

Comp.	$(Vy)_{t-7}$	Wx_W	x_W
5	0.0313	0.00646	0.004
7	1.231	0 526	0.978
10	0 0023	0 0283	0.018

The value of 0.057 mol polymerized is approximately correct, and the per cent of cyclopentadiene polymerized is

$$\frac{0.057(100)}{1.915(0.20)} = 1.49 \text{ per cent}$$

The number of plates required is seven.

The solution required a large amount of trial and error. An approximate value could be obtained by treating the mixture as a binary of C_5 and C_7 on the usual y,x

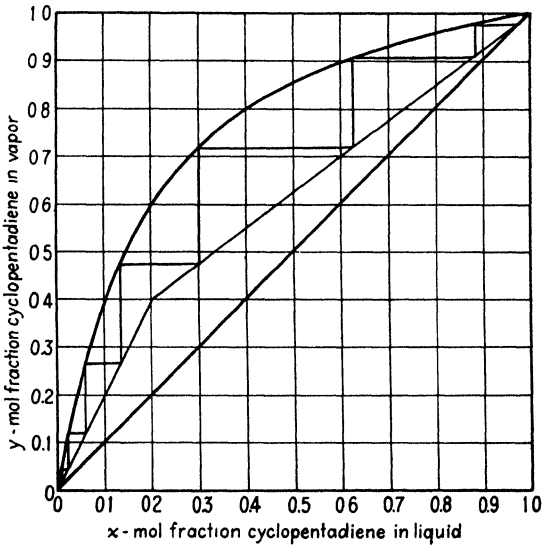


FIG. 13-1. Fractionation of cyclopentadiene.

diagram and then calculating the amount of polymerization from the plate composition so obtained. Such a diagram is shown in Fig. 13-1, and six plates are required. The plates are fewer because in the actual case the polymerization decreases the effective reflux ratio for the $C_5 + C_7$. The polymerization was calculated neglecting the C_{10} in the liquid and was found 0.057 mol of C_5. This value agrees well with the value found by the plate-to-plate calculations.

CHAPTER 14

BATCH DISTILLATION

Continuous operation is normally employed when the material to be distilled is large in quantity and is available at a reasonably uniform rate. Under such conditions, it is usually cheaper than batch distillation, but there are a large number of cases which are not suited to continuous operation and which are handled on the batch basis.

A batch distillation with rectification involves charging the still with the material to be separated and carrying out the fractionation until the desired amount has been distilled off. The overhead composition will vary during the operation, and usually a number of cuts will be made. Some of the cuts will be the desired products, while others will be intermediate fractions that can be recycled to subsequent batches to obtain further separation.

The equipment employed and the method of operation are similar for batch and continuous distillation, but in the latter the mathematical analysis is based on the assumption that in all portions of the system the compositions and flow rates are independent of the time of distillation. These conditions do not apply to a batch distillation, and because of the continuous variations involved, it must be analyzed on a differential basis. As a result, the calculations are much more difficult, and satisfactory design methods have been developed for only a few simple cases.

BINARY MIXTURES

The batch distillation of binary mixtures will be considered for the cases of (1) no rectification, (2) rectification without liquid holdup in the column, and (3) rectification with holdup.

No Rectification. Batch distillation without rectification corresponds to the simple distillations of Chap. 6, and the calculations of the concentrations as a function of the amount distilled can be made by Eqs. (6-3) and (6-7).

Rectification without Liquid Holdup in Column. *Finite Reflux Ratio.* In this case, it is assumed that the distillation is carried out with a fractionating column, that the holdup of liquid in the column is negligi-

ble in comparison to the liquid in the system, and that the rate of change of the holdup of a component on a plate is negligible in comparison to the rate of flow of that component through the plate. Thus the change in the quantity of each component in the column can be neglected in the differential material balances.

Consider the system shown in Fig. 14-1. On the basis of the assumptions made, an over-all differential material balance gives

$$dD = -dL$$

where L represents the mols of liquid in still, and a component balance gives

$$\begin{aligned} x_D\,dD &= -d(Lx_L) \\ &= -L\,dx_L - x_L\,dL \\ &= -L\,dx_L + x_L\,dD \\ \frac{dD}{L} &= \frac{dx_L}{x_L - x_D} \end{aligned} \qquad (14\text{-}1)$$

This equation is equivalent to the Rayleigh equation but differs in that the denominator is $x_L - x_D$ instead of $x_L - y_L$. The integration of Eq. (14-1) involves determining a relation between x_L and x_D. Neglecting the rate of change of holdup of a component on the plates and in the condenser, a balance between the n and $n + 1$ plates gives

$$\begin{aligned} V_n &= O_{n+1} + D \\ V_n y_n &= O_{n+1}x_{n+1} + Dx_D \end{aligned}$$

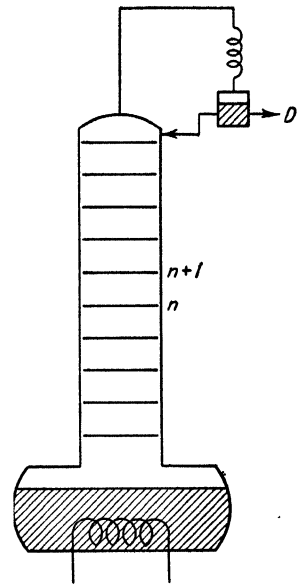


FIG. 14-1. Schematic diagram of batch distillation system.

At any time these equations are identical to those for the continuous distillation and can be applied to determine the relation between x_L and x_D for that instant. By applying the equations repeatedly, the value of $x_L - x_D$ can be obtained as a function of x_L and the integration of Eq. (14-1) performed. There are a number of ways such a distillation can be made, but the two most common cases involve (1) operating at constant reflux ratio and taking cuts that average the desired composition and (2) operating at variable reflux ratio to give a constant product composition while making the desired product. In the first case the value of (O_n/V_{n+1}) will remain constant during the distillation, and a series of lines of this slope can be drawn on the usual y,x diagram for various assumed values of x_D, and the value of x_L can be determined by stepping down each line the number of theoretical

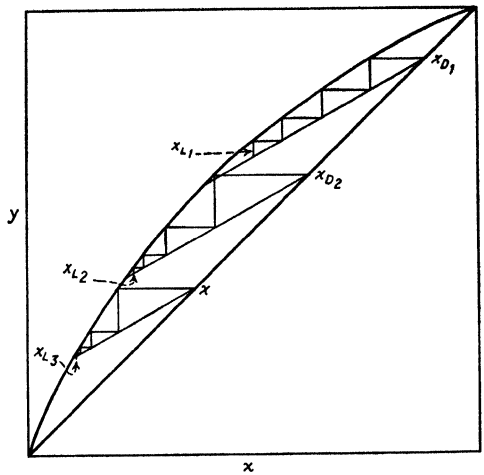


FIG. 14-2. Constant reflux ratio case.

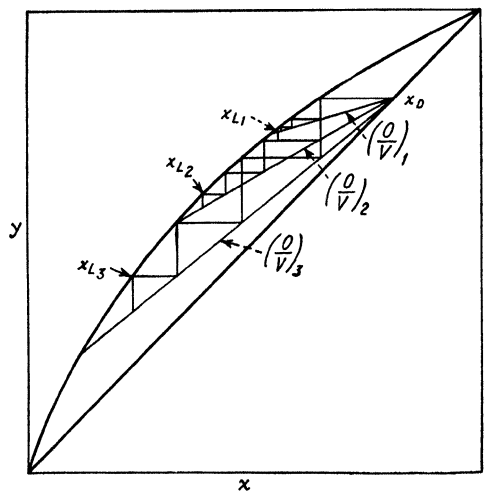


FIG. 14-3. Constant distillate composition case.

plates equivalent to the column. This procedure is illustrated in Fig. 14-2 for a column and still equivalent to four theoretical plates. In the second case the value of x_D is fixed, a series of operating lines of different slopes is drawn through it, and the plates are stepped off on each line to determine the value of x_L. This procedure is illustrated in Fig. 14-3. By these procedures, Eq. (14-1) can be integrated, giving the relation between the amount distilled and the composition of the

liquid remaining in the still. In the second case with x_D constant, the integration of Eq. (14-1) amounts to only simple material balance, and the data from Fig. 14-3 are not needed for this purpose. In addition to the information obtained by integration of Eq. (14-1), it is frequently necessary to have data on the vapor required or the average composition of a fraction produced.

For the constant reflux case, the calculation of the vapor requirement can be made as follows:

$$V = \left(\frac{O}{D} + 1\right) D \tag{14-2}$$

and the average composition of any fraction is

$$x_{av} = \frac{L_1 x_1 - L_2 x_2}{L_1 - L_2} \tag{14-3}$$

For the variable reflux case,

$$dV = dO + dD$$
$$dD = \left(1 - \frac{dO}{dV}\right) dV$$

and, by material balance,

$$Lx_L = L_o x_o - (L_o - L)x_D$$
$$L = \frac{L_o(x_o - x_D)}{x_L - x_D}$$

where L_o = original mols in still
x_o = original composition of liquid in still
Substituting these values in Eq. (14-1) gives

$$dV = \frac{L_o(x_o - x_D)\, dx_L}{(x_L - x_D)^2 \left(1 - \frac{dO}{dV}\right)} \tag{14-4}$$

Form Fig. 14-3 the relation between x_D, x_L, and the slope of the operating line, dO/dV, can be obtained and Eq. (14-4) integrated to give the vapor requirement.

The use of these methods will be illustrated by the following example.

Batch Fractionation of a Binary Mixture. An equimolal mixture of A and B is to be fractionated in a batch column equivalent to three theoretical plates plus a still. The still will operate at atmospheric pressure, with a total condenser, and the

holdup in the column and condenser is negligible. The company desires to obtain an overhead A product containing 95 mol per cent A, and two methods of operation have been suggested: (1) Operate the column at a constant reflux ratio (O/D) equal to 5.0 and continue the distillation until the average composition of the distillate is 95 per cent A; (2) Operate the column at a variable reflux ratio to give a distillate of constant composition.

Using data and notes given below, calculate:

1. For Method 1,
   - *a.* The mol per cent of the original charge to the still that can be obtained as the 95 per cent distillate.
   - *b.* The mols of vapor per 100 mols of original charge to obtain the distillate of Part *a*.

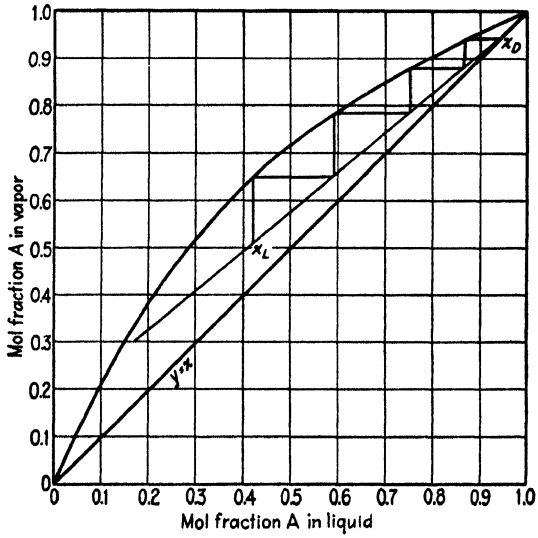


FIG. 14-4.

2. For Method 2, the mol per cent of the original charge to the still that can be obtained as the 95 per cent distillate, using a total vapor-to-charge ratio equal to that of Part 1, *b*.

Assume α_{AB} is constant at 2.5.

Solution. By trial and error the relations between x_L and x_D could be determined analytically by Eq. (7-62) because the relative volatility is constant and the usual simplifying assumptions apply. However a y,x diagram is probably simpler and will be employed. The mol fractions of component A will be used in the calculations.

The equilibrium curve was calculated from the relative volatility and is given in Fig. 14-4.

Method 1. The slope of the operating line $= O/V = \frac{5}{6} = 0.833$. The relation between any x_L and the corresponding x_D is found by taking four steps from

x_D on the operating line. The case for $x_D = 0.94$ is shown in Fig. 14-4 and gives $x_L = 0.41$. The values for other cases are given in Table 14-1.

TABLE 14-1

x_D	x_L	$\frac{1}{x_L - x_D}$	$\ln \frac{L_o}{L}$	$\frac{L}{L_o}$	$(x_D)_{av}$
0 98	0 658	−3 11	—	—	—
0.96	0.490	−2 13	0 022	0 978	0.962
0 94	0.410	−1 89	0.182	0 834	0 955
0 92	0.344	−1 73	0 299	0 742	0 948
0.90	0.293	−1.65	0 379	0.678	0 937

The values of $1/(x_L - x_D)$ are plotted as a function of x_L, and the graphical integration is performed from $x_L = 0.5$ to x_L. The resulting values of the integral are equal to $\ln (L_o/L)$ and are tabulated in the fourth column of the table. The fifth column gives the values of L/L_o and the average composition of all of the distillate from the start of the distillation as calculated by Eq. (14-3). By plotting the average value of x_D vs. (L/L_o), it is found that $(x_D)_{av} = 0.95$ for $(L/L_o) = 0.82$. Therefore, mol per cent of original charge recovered as 95 per cent distillate is 18.0.

For

$$L_o = 100 \text{ mols}, \quad D = 18$$

and

$$V = \text{total vapor} = O + D = 6D = 6(18)$$
$$= 108 \text{ mols}$$

Method 2. In this case it is necessary to calculate the per cent recovery of the original charge as 95 per cent distillate for a total heat supply equal to 108 mols of vapor when operating on the variable reflux basis. This result can be evaluated by integrating Eq. (14-4). For various assumed values of the slope of the operating line dO/dV, the lines were drawn through $x_D = 0.95$ and the plates stepped down to obtain x_L. The values are summarized in Table 14-2 for $L_o = 100$.

TABLE 14-2

$\frac{dO}{dV}$	x_L	$\frac{100(0.5 - 0.95)}{(0.95 - x_L)^2\left(1 - \frac{dO}{dV}\right)}$	V
1.0	0.330	∞	∞
0.95	0 360	−2,590	176 2
0 90	0.390	−1,430	121.5
0 85	0.435	−1,130	65.7
0.80	0.480	− 968	19.1
0.75	0.510	− 937	—

The values given in the third column of Table 14-2 were plotted vs. x_L, and the area under the curve from $x_L = 0.5$ to x_L is equal to the total vapor necessary to reduce the still concentration to x_L. A plot of x_L against V gives $x_L = 0.398$ at $V = 108$ and

$$0.398L + 0.95(L_o - L) = 0.5L_o$$

$$\frac{L}{L_o} = 0.815$$

Recovery as 95 per cent distillate = 18.5 per cent of original charge. This would indicate that Method 2 gave a slightly better recovery for the same heat consumption, but the accuracy of the calculations is not sufficient to make the difference significant. Method 1 would be more practical from an operating viewpoint.

Total Reflux. Limiting conditions can be calculated for batch distillation that are useful for orientation purposes. The total reflux limit applies to the constant reflux category and can be used to determine the minimum number of theoretical plates necessary to give the desired product recovery or to determine the maximum possible recovery for a given number of plates. Consider an equimolal mixture of A and B having constant relative volatility of 2, and make the usual simplifying assumptions. The desired distillate is to contain 95 mol per cent A, and the limits to be estimated are (1) the number of theoretical plates for a 50 per cent recovery of A in the distillate and (2) the maximum per cent recovery of A with a tower equivalent to five theoretical plates.

For total reflux and constant relative volatility, by Eq. (7-53),

$$\frac{x_D}{1 - x_D} = \alpha^{N+1} \frac{x_L}{1 - x_L}$$

$$x_D = \frac{\alpha^{N+1} x_L}{(\alpha^{N+1} - 1)x_L + 1} \tag{14-5}$$

Substituting this value in Eq. (14-1),

$$\frac{dL}{L} = \frac{dx_L}{\dfrac{\alpha^{N+1} x_L}{(\alpha^{N+1} - 1)x_L + 1} - x_L} \tag{14-6}$$

This equation is identical with Eq. (6-5) except that α^{N+1} has replaced α, and by integration from x_o, L_o to x, L,

$$\ln \frac{L}{L_o} = \frac{1}{\alpha^{N+1} - 1} \ln \frac{x(1 - x_o)}{x_o(1 - x)} + \ln \frac{1 - x_o}{1 - x} \tag{14-7}$$

for 50 per cent recovery of A,

$$(L_o - L)0.95 = 0.5L_o(0.5)$$
$$\frac{L}{L_o} = 0.737$$
$$x = \frac{0.25}{0.737} = 0.339$$

Using these values with Eq. (14-7) gives $N = 3.8$ theoretical plates.

For maximum per cent recovery with five theoretical plates,

$$\ln \frac{L}{L_o} = \frac{1}{2^6 - 1} \ln \frac{x(0.5)}{0.5(1 - x)} + \ln \frac{0.5}{1 - x}$$

and

$$Lx + 0.95(L_o - L) = 0.5L_o$$
$$\frac{L}{L_o} = \frac{0.45}{0.95 - x}$$

Solving these equations simultaneously gives

$$\frac{L}{L_o} = 0.492, \qquad x = 0.0352$$
$$\text{Recovery} = \frac{0.5L_o - 0.0352L}{0.5L_o} \times 100$$
$$= 96.3 \text{ per cent}$$

It will be noted that the per cent recovery increases rapidly as the theoretical plates are increased in number.

If the relative volatility is not constant, the total reflux condition can be solved using the $y = x$ line as the operating line and determining x_L as a function of x_D graphically.

Minimum Vapor Requirements. Another limit that is instructive is the minimum vapor requirement for a given separation and recovery. This limit will correspond to the minimum reflux ratio condition for continuous distillation and will require an infinite number of theoretical plates. For this case, the operating line must contact the equilibrium curve at some point. For the general case, the limit can be determined graphically, for either the constant or variable reflux conditions, by drawing such operating lines and obtaining x_L as a function of x_D or dO/dV and integrating Eqs. (14-1) and (14-4).

The general principles can be illustrated analytically for the case of constant relative volatility. For the constant reflux method, the operating line will intersect the equilibrium curve at either $x_D = 1$ or

at $x = x_L$. The overhead product will be pure volatile component, $x_D = 1$, until x_L decreases to a value such that the operating line through $x_D = 1$ intersects the equilibrium curve at the composition of the still; for smaller values of x_L, the intersection will be at x_L. This limiting value of x_L can be calculated by

$$\frac{O}{V} = \frac{1 - y_L^*}{1 - x_L^*}$$

where x_L^* = value of x_L such that operating line intersects equilibrium curve at $x_D = 1$ and x_L^*
y_L^* = vapor in equilibrium with x_L^*

For constant relative volatility,

$$x_L^* = \frac{1 - (O/V)}{O/V(\alpha - 1)} \tag{14-8}$$

for values of x_L equal to or greater than x_L^*, x_D will be equal to unity. For values less than x_L^*,

$$\frac{x_D - y_L}{x_D - x_L} = \frac{O}{V}$$

With constant relative volatility, substituting for y_L gives

$$x_D = \frac{x_L\left[\dfrac{\alpha}{(\alpha - 1)x_L + 1} - \dfrac{O}{V}\right]}{1 - (O/V)} \tag{14-9}$$

$$x_D - x_L = x_L \frac{(\alpha - 1)(1 - x_L)}{[(\alpha - 1)x_L + 1]\left(1 - \dfrac{O}{V}\right)} \tag{14-10}$$

This relation can be combined with Eq. (14-1) and integrated from x_L^* to x and L^* to L to give

$$\ln \frac{L}{L^*} = \left(1 - \frac{O}{V}\right)\left[\frac{1}{\alpha - 1} \ln \frac{x(1 - x_L^*)}{x_L^*(1 - x)} + \ln \frac{1 - x_L^*}{1 - x}\right] \tag{14-11}$$

which is the same as Eq. (6-5) except for the $(1 - O/V)$ term. This equation can be rewritten

$$\frac{L}{L^*} = \left\{\frac{1 - x_L^*}{1 - x}\left[\frac{x(1 - x_L^*)}{x_L^*(1 - x)}\right]^{1/(\alpha-1)}\right\}^{1-\frac{O}{V}} = \phi \tag{14-12}$$

The average composition for the distillate from L_o to L is

$$(x_D)_{av} = \frac{x_o - \phi x(L^*/L_o)}{1 - \phi(L^*/L_o)} \tag{14-13}$$

and the total vapor generated from L_o to L,

$$\frac{V}{L_o} = \left(\frac{O}{D} + 1\right)\left(1 - \phi\frac{L^*}{L_o}\right) = \left(\frac{O}{D} + 1\right)\left(1 - \frac{L}{L_o}\right) \tag{14-14}$$

By a similar procedure an equation can be developed for the variable reflux case.

$$\frac{V}{L_o} = \frac{x_o - x_D}{2(\alpha - 1)}\left[\frac{2(\alpha - 1) + (1 + x_D)}{x_D - 1}\ln\frac{(1 - x)(x_o - x_D)}{(1 - x_o)(x - x_D)} - \ln\frac{x^2(x_o - x_D)(1 - x_o)}{x_0^2(x - x_D)(1 - x)}\right]$$

Minimum Vapor Requirements for Batch Distillation. Consider the batch distillation of an equimolal mixture of A and B. The relative volatility, α_{AB}, is constant at 2; and the average distillate is to be 95 mol per cent A. Calculate the minimum mols of vapor for 50 mol per cent recovery of A in the distillate for both the constant reflux ratio and the variable reflux ratio cases.

Solution

$$0.95(L_o - L) = 0.25L_o$$
$$\frac{L}{L_o} = 0.737$$

Final liquid composition, $xL = 0.25/0.737 = 0.339$. For the constant reflux method, assume that the value of O/D is such that x_L^* will be less than 0.5; then by Eq. (14-8)

$$x_L^* = \frac{1 - O/V}{O/V} = \frac{D}{O}$$

By over-all material balance

$$\frac{L^*}{L_o} = \frac{1 - x_o}{1 - x_L^*} = \frac{0.5}{1 - D/O}$$

For the portion of the distillation when the liquid in the still is decreasing from x_L^* to 0.339, Eq. (14-12) gives

$$\frac{L}{L^*} = 0.737\left(\frac{L_o}{L^*}\right) = 1.474\left(1 - \frac{D}{O}\right) = \left\{\frac{1 - D/O}{0.661}\left[\frac{0.339(1 - D/O)}{D/O(0.661)}\right]\right\}^{1-O/V}$$

Solution of this relation by trial and error gives $O/D = 2.12$. This value gives $x_L^* = 0.472$, indicating that the assumption made was correct. Then, by

Eq. (14-14),

$$\frac{V}{L_o} = (2.12 + 1)(0.263) = 0.82$$

For variable reflux operation,

$$\frac{V}{L_o} = \frac{-0.45}{2}\left[\frac{2 + 1.95}{-0.05}\ln\frac{0.661(-0.45)}{0.5(-0.611)} - \ln\frac{(0.339)^2(-0.45)(0.5)}{(0.5)^2(-0.611)(0.661)}\right] = 0.767$$

As was found in the example page 376, the variable reflux method requires less vapor for a given separation than the constant reflux method.

Rectification with Liquid Holdup in Column. In continuous distillation holdup does not harm the degree of separation obtainable; in some cases it may be an advantage in that it gives "flywheel" action and tends to smooth out the operation. The effect of column holdup in batch distillation is not completely clear because a satisfactory method of analyzing the operation has not been developed. Rose, Welshans, and Long (Ref. 3) present approximate equations for total reflux, and Colburn and Stern (Ref. 1) have discussed the case of finite reflux. Rose *et al.* concluded that holdup was detrimental at total reflux, and Colburn and Stern indicated that holdup in some cases improved the sharpness of separation as compared to no holdup. In order to investigate this difference of opinion, a number of cases were studied analytically, and holdup was not advantageous in any of them. For the same number of theoretical plates, reflux ratio, and total mols vaporized, the no-holdup system was superior in all the cases tried. It is believed that the improved results reported with column holdup were due to the fact that, for the starting condition, a concentration gradient was already established in the rectifying column which had required the expenditure of considerable vapor which should be but was not included in the evaluation. The amount of vapor required to establish this concentration gradient can be estimated from Fig. 18-3. For a system with a relative volatility of 2.0, the "prerun" vapor would be about eight times the column holdup. Thus a column holdup equal to 15 per cent of the charge to still would require a prerun vapor generation of approximately 1.2 times the charge to the still. If the column holdup was obtained by charging it with the fresh still liquid and including all vapor from the beginning of the distillation, the holdup results would have been less favorable. Alternately, if the no-holdup case was given the extra vapor corresponding to the "tune-up" period for the holdup case, it would be more favorable. It is concluded that in general holdup in the rectifying column is undesirable in batch distillation.

There is an intermittent type of batch operation for which column holdup has an apparent advantage. In this case the column is run at total reflux, and the top plates are filled with liquid rich in the more volatile component. Product is then withdrawn at a high rate for a short time after which the column is put back on total reflux to reestablish a concentration gradient. Most of the product withdrawn during the short time interval comes from the accumulation of volatile component on the top plates. For this type of operation, improved results would be obtained without liquid holdup in the column, but with a reservoir in the reflux line. The column would operate at total reflux until the liquid in the reservoir was rich in the volatile component. This liquid would then be withdrawn completely, and the column returned to total reflux operation to prepare the next fraction. This type of operation is frequently convenient for laboratory distillations but is not often advantageous for large-scale operation.

A detailed differential stepwise integration for a batch distillation with holdup can be made, but the time and effort involved are usually not justified by the value of the result. The method is useful in developing the principles of batch distillation with holdup. The following section will consider the basic differential equations which are helpful in obtaining a qualitative picture of the process. By an analysis similar to that for Eq. (14-1),

$$x_D\,dD = -d(Lx_L) - d(Hx_H) \tag{14-15}$$

where H = holdup in column

x_H = average composition of holdup

The integration of this equation requires a relationship between Hx_H and L and x_L. This relationship is very complex and has not been expressed in a form suitable for direct integration. It has been customary to simplify this equation by assuming that H is constant. In some cases this may be a reasonable assumption, but on a molal basis it could be greatly in error. For example in the distillation of an isopropanol-water mixture, a given volume of holdup could give a fourfold variation in molal holdup. If Eq. (14-15) is applied on a weight and weight fraction basis, the variation of holdup during the distillation will be less, but it can still be large. Analysis based on the constancy of H will be only approximate for most cases.

An operating line for this case can be written by taking a material balance on one of the components,

$$y_n\,dV_n = x_{n+1}\,dO_{n+1} - d(Lx_L) - d(H_m x_{Hm}) \tag{14-16}$$

or

$$y_n\,dV_n = x_{n+1}\,dO_{n+1} + x_D\,dD - d(H_n x_{Hn}) \qquad (14\text{-}17)$$

where $H_m x_{Hm}$ and $H_n x_{Hn}$ equal holdup of component for plates from still to plate n, and for plate $n + 1$ to top of column, respectively.

Because the last terms, $d(H_m x_{Hm})$ and $d(H_n x_{Hn})$, vary from plate to plate, the operating line is curved and cannot be evaluated without a knowledge of the variation of these terms. At total reflux, these terms are negligible in comparison to the first two terms, and the operating line is the $y = x$ diagonal with holdup the same as it was for no holdup, but for finite reflux ratio the operating line with holdup is curved and difficult to establish on the y,x diagram.

When a batch distillation is carried out by the variable reflux ratio method to give a constant value of x_D, and the distillation is continued until the reflux ratio is essentially total reflux, the amount of holdup in the column at the end of the distillation can be easily calculated by using the $y = x$ line as the operating line. Such a procedure gives the composition of the liquid on each plate, and a correction can be applied for effect of the holdup on the percentage yield of a given fraction.

Batch Rectification of Binary Mixture. Assume that the equimolal mixture already considered, page 376, is to be distilled in this manner, and it is desired to evaluate the effect of the column holdup.

Solution. Basis: 100 mols liquid charged to still, no liquid in column at start.

At the end of the distillation the results will correspond to total reflux and, by Eq. (14-5),

$$\frac{x_D}{1 - x_D} = 2^6 \frac{x_L}{1 - x_L}$$

$$x_L = \frac{0.95}{2^6(0.05) + 0.95} = 0.229$$

By material balance,

$$0.5(100) = 0.95D + 0.229L + \sum_1^5 (hx)$$

$$100 = D + L + \sum_1^5 h$$

where $\sum_1^5 (hx)$ = total mols of A in the holdup on the plates at total reflux

$\sum_1^5 (h)$ = total mols of holdup on the plates

For the case in which the total holdup per plate is constant, the value $h\sum_{1}^{5} x$ can be obtained approximately in a mathematical form (Ref. 2), but it is just as easy in most cases to evaluate it plate by plate. In the present case, assuming the holdup per plate is constant,

$$h\sum_{1}^{5}(x) = h(x_1 + x_2 + x_3 + x_4 + x_5)$$
$$= h(0.371 + 0.541 + 0.701 + 0.823 + 0.903)$$
$$= 3.35h$$

and

$$50 = 0.95D + 0.229(100 - D - 5h) + 3.35h$$
$$27.1 - 2.205h = 0.721D$$
$$D = \frac{27.1 - 2.205h}{0.721}$$

If the holdup per plate were 2 per cent of the original charge to the still, then

$$h = 2$$

and the mols of the distillate would be

$$D = \frac{27.1 - 2.205(2)}{0.721}$$
$$= 31.5$$

as compared to $D = 37.5$ for no holdup. If the value of holdup per plate was as high as 12.3 per cent of the charge, no 95 per cent distillate could be produced in the 5-plate column. If the percent of A in the original feed had been smaller, the effect of holdup would have been even more serious.

A similar analysis has been applied by some writers to the case where the distillation has been discontinued at a finite reflux ratio. The usual straight operating line was employed to determine the plate composition at the end of the distillation, but in view of the fact that the operating line is curved for such a case, the calculations are probably of little value. If the operating lines corresponding to Eq. (14-16) or (14-17) could be evaluated for the end of the distillation, then an analysis of the effect of holdup could be made.

MULTICOMPONENT MIXTURES

The state of the art for the batch distillation of multicomponent mixtures is even less satisfactory than for binary mixtures, and except for total reflux, no accurate and practical method is available even without liquid holdup in the column. This difficulty arises from the fact that, starting with a given liquid composition in the still, it is possible to calculate the equilibrium vapor leaving the still, but the composition of the overflow to the still from the first plate cannot be calculated without knowing the composition of the distillate leaving the system. In a binary system, it is possible to choose the composi-

tion of the distillate arbitrarily and calculate back to the liquid in the still, and the liquid composition in the actual distillation must pass through this condition. However, in a multicomponent mixture, the still composition calculated in that manner for an assumed overhead product will probably not occur in an actual distillation. For example, consider the distillation of a mixture of components A, B, and C and assume an overhead composition of x_{DA}, x_{DB}, and x_{DC}. For these assumed values, the calculations can be carried down the column for a given reflux ratio assuming no holdup, and values of x_{LA}, x_{LB}, and x_{LC} will be obtained. However, in the actual distillation when component A has the value x_{LA}, it is very improbable that the ratio of B to C will be the same as calculated on the basis of the assumed overhead composition. By a laborious trial-and-error procedure, a consistent calculation could be made, but it is doubtful that it would justify the effort. A laboratory distillation would probably give a better and cheaper evaluation.

As a guide to the characteristics of multicomponent batch distillation, the case of (1) total reflux with no liquid holdup in the column and (2) finite reflux ratio with no liquid holdup by an approximate method, will be considered.

Rectification without Liquid Holdup in Column. *Total Reflux.* For the case of no liquid holdup, Eq. (14-1) applies to each of the components, but the difficulty involves the evaluation of x_D as a function of x_L.

In this case the stepwise calculations can be carried out starting at the still, because the composition of the distillate does not affect the operating line. Thus for a given x_L the value of x_D can be calculated, but the calculation is still difficult for the general case because the concentration pattern followed by the liquid in the still is unknown. The pattern can be approximated by a stepwise integration, but the calculations are tedious. The general principles will be developed for the case in which all the relative volatilities remain constant, because in this case direct integration is possible. It is simpler to apply the relative volatility form of the simple distillation of Eq. (6-6) than to use Eq. (14-1). Thus, for any two components of a multicomponent mixture at total reflux,

$$\left(\frac{y_A}{y_B}\right)_L = \alpha_{AB}\left(\frac{x_A}{x_B}\right)_L$$

$$= \left(\frac{x_A}{x_B}\right)_1$$

and, for a column with a total condenser,

$$\left(\frac{x_A}{x_B}\right)_D = \left(\frac{y_A}{y_B}\right)_T = \alpha_{AB}^{N+1}\left(\frac{x_A}{x_B}\right)_L \tag{14-18}$$

Let a differential amount, dV, be vaporized and set

$$y_{AT}\,dV = -dA$$
$$y_{BT}\,dV = -dB$$

where A, B are mols of A and B in still, respectively.

$$\frac{-dA}{-dB} = \alpha_{AB}^{N+1}\left(\frac{A}{B}\right) \tag{14-19}$$

integrating from A_o to A, B_o to B

$$\ln\frac{A}{A_o} = (\alpha_{AB}^{N+1})\ln\frac{B}{B_o}$$
$$\frac{A}{A_o} = \left(\frac{B}{B_o}\right)^{\alpha_{AB}{}^{N+1}} \tag{14-20}$$

Likewise,

$$\frac{A}{A_o} = \left(\frac{C}{C_o}\right)^{\alpha_{AC}{}^{N+1}}$$

and the same for the other components.

For a given fraction of A vaporized, it is possible to calculate (1) the fraction of all components vaporized, (2) the composition of the liquid remaining in the still, (3) the instantaneous composition of the distillate, and (4) the average composition of all of the distillate.

Batch Rectification of Multicomponent Mixture at Total Reflux. As an example, consider the fractionation of an equimolal mixture of A, B, C, and D at total reflux with relative volatility $\alpha_{AB} = 2.0$, $\alpha_{AC} = 4.0$, and $\alpha_{AD} = 8.0$. The column is equivalent to three theoretical plates and holdup of liquid will be neglected.

Solution. Basis: 100 mols originally charged to still.

a. First distillate composition:

$$\frac{y_A}{y_B} = 2^4 = 16$$
$$\frac{y_A}{y_C} = 4^4 = 256$$
$$\frac{y_A}{y_D} = 8^4 = 4{,}096$$
$$y_A + y_B + y_C + y_D = 1.0$$
$$y_A = \frac{4{,}096}{4{,}096 + 256 + 16 + 1} = 0.938$$
$$y_B = 0.0586$$
$$y_C = 0.00366$$
$$y_D = 0.00023$$

b. 50 per cent of A distilled:

$$\frac{B}{B_o} = 0.5^{1/6} = 0.958$$

$$\frac{C}{C_o} = 0.5^{1/256} = 0.9973$$

$$\frac{D}{D_o} = 0.5^{1/4,096} = 0.99983$$

The compositions of (1) liquid remaining in still, (2) average distillate, and (3) instantaneous distillate are given in Table 14-3.

TABLE 14-3

	Mols	(1) x_L	(2) $x_{D(av)}$	(3) x_D
A	0.125	0 145	0.922	0.900
B	0.24	0.278	0.074	0.0931
C	0.2494	0.288	0.004	0.0061
D	0.25	0.289	—	0.004
	0.864			

By repeating this type of calculation, the values of the instantaneous distillate composition given in Fig. 14-5 were obtained.

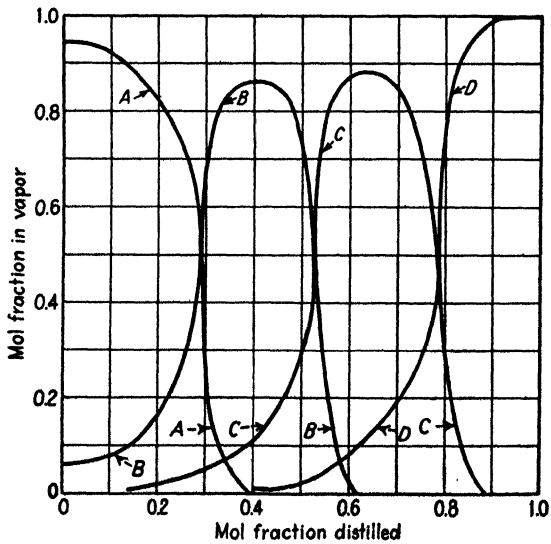


FIG. 14-5. Fractionation curves for multicomponent mixture at total reflux.

In the example on page 385, about 60 per cent of the original charge could be obtained as fractions containing one of the components in at least 85 concentration. It will be noted that the least volatile material can be obtained in the highest purity because it is taken over when the still contains the least amount of other components. By operating an inverted batch column as shown in Fig. 14-6, it is possible to remove the less volatile components and obtain the most volatile material in high purity. In this case, the batch is charged to the reservoir, and

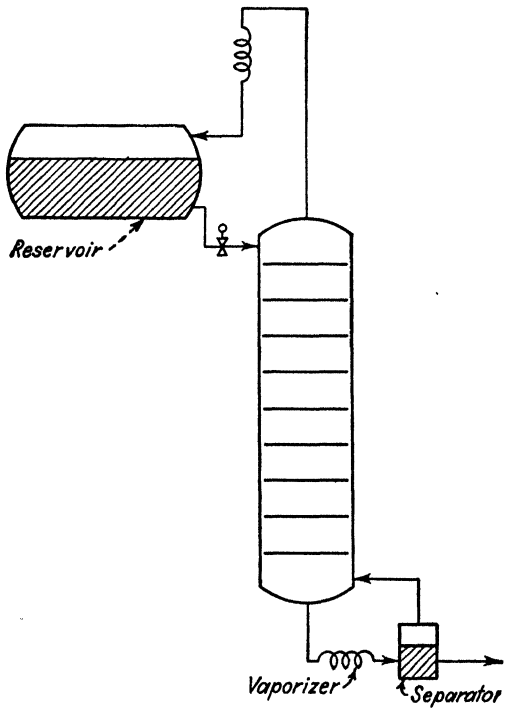


FIG. 14-6. Inverted batch distillation system.

liquid is continuously added to the top of the column from this tank. The liquid from the bottom of the column is partly vaporized, and the unvaporized portion is removed as product. The vapor is passed back up the column to strip out the more volatile components, and the overhead vapor is condensed and returned to the reservoir. The most volatile component collects in the reservoir and is obtained as the last fraction after essentially all the other components have been eliminated. An intermediate fraction can be increased in concentration

by fractionating first in a normal batch operation to remove the lighter components and then in an inverted batch unit to remove the heavy constituents; or both operations can be combined simultaneously taking the lighter components overhead and the heavier components out the bottom with the reservoir between. This combined operation can save heat but requires additional equipment.

Finite Reflux Ratio. It was pointed out on page 384 that this case was difficult because, if the plate-to-plate calculations were carried down from the top for an assumed overhead product, the still composition would probably not correspond to any liquid composition encountered in the actual distillation. Starting with a given liquid composition in the still, it is possible to make calculations for an assumed overhead composition. If the calculated overhead composition checks the assumed value, this gives one set of corresponding distillate and still compositions. Thus a laborious trial-and-error procedure is necessary to obtain this one set of values, but the design calculation requires a number of such sets for liquid compositions that follow a definite pattern. Thus the overhead vapor corresponding to the original charge could be calculated by the above trial-and-error procedure and a small increment of this composition removed, leaving a new liquid composition. By a large number of such small steps, the distillation curve can be established, but making the trial-and-error plate-to-plate calculation for each step is almost prohibitive.

The total reflux analysis of the preceding section was relatively simple, and an approximate method for finite reflux ratios can be developed in an analogous manner. For the operating lines for any two components, the liquids on a plate are related to the vapors from below by

$$\frac{(y_A)_n}{(y_B)_n} = \frac{(x_A)_{n+1}}{(x_B)_{n+1}} \left[\frac{1 + \dfrac{D}{O_{n+1}} \dfrac{(x_A)_D}{(x_A)_{n+1}}}{1 + \dfrac{D}{O_{n+1}} \dfrac{(x_B)_D}{(x_B)_{n+1}}} \right] \tag{14-21}$$

$$= (\beta_{AB})_n \left(\frac{x_A}{x_B}\right)_{n+1}$$

$$\left(\frac{x_A}{x_B}\right)_n = \frac{(\beta_{AB})_n}{(\alpha_{AB})_n} \left(\frac{x_A}{x_B}\right)_{n+1} \tag{14-22}$$

Thus, for a batch distillation,

$$\left(\frac{y_A}{y_B}\right)_T = \frac{\alpha_T}{1} \left(\frac{\alpha_{T-1}}{\beta_{T-1}}\right) \cdots \left(\frac{\alpha_2}{\beta_2}\right) \left(\frac{\alpha_1}{\beta_1}\right) \left(\frac{\alpha_L}{\beta_L}\right) \left(\frac{x_A}{x_B}\right)_L \tag{14-23}$$

for a total condenser,

$$\left(\frac{x_A}{x_B}\right)_D = \frac{\alpha_T}{1}\left(\frac{\alpha_{T-1}}{\beta_{T-1}}\right) \cdots \left(\frac{\alpha_2}{\beta_2}\right)\left(\frac{\alpha_1}{\beta_1}\right)\left(\frac{\alpha_L}{\beta_L}\right)\left(\frac{x_A}{x_B}\right)_L \tag{14-24}$$

These equations are the same as some of those presented in Chap. 12, page 341, for the approximate design of continuous columns.

Using an average value of α/β gives

$$\left(\frac{x_A}{x_B}\right)_D = \left(\frac{\alpha_{av}}{\beta_{av}}\right)^{N+1}\left(\frac{x_A}{x_B}\right)_L \tag{14-25}$$

For the average value it is possible to use either

$$\left(\frac{\alpha}{\beta}\right)_{av} = \frac{\alpha_T + (\alpha_L/\beta_L)}{2}$$

or the ratio of (α_{av}/β_{av}) calculated as

$$\alpha_{av} = \frac{\alpha_T + \alpha_L}{2}$$

$$\beta_{av} = \frac{1 + \beta_L}{2}$$

Equation (14-25) is analogous to Eq. (14-18) and the resulting integrated form is equivalent to Eq. (14-20) except that α is replaced by (α/β).

The evaluation of β_L requires a trial-and-error procedure that can be best illustrated by the following example.

Batch Rectification of Multicomponent Mixture at Finite Reflux Ratio. The example given on page 385 will be repeated for a constant reflux ratio, O/D, equal to 5.0. The tower will operate with a total condenser, and the usual simplifying assumptions are made. The calculation for the initial vapor overhead is given in Table 14-4.

TABLE 14-4

Comp.	Assumed x_D	β_L (relative to component D)	α (relative to component D)	β_{av}	$\left(\frac{\alpha}{\beta}\right)_{av}$	$\left(\frac{\alpha}{\beta}\right)^4 x_L$	$x_{D\,calc}$
A	0 85	1 68	8	1 34	5 96	315	0.851
B	0.14	1.112	4	1.06	3.78	50.8	0 138
C	0.01	1.008	2	1 00	2.0	4 0	0.011
D	0.0	1.0	1	1.00	1.0	0.25	0 0006

The second column Table 14-4 gives the assumed values of the overhead composition, and the third column is the β_L relative to component D calculated from the assumed x_D values, for example, for component A,

$$\beta_L = \frac{1 + \frac{D}{O}\frac{(x_A)_D}{(x_A)_L}}{1 + \frac{D}{O}\frac{(x_D)_D}{(x_D)_L}}$$

This is not the correct value of β_L which should be calculated using x_{L+1} values instead of x_L values. For purposes of simplification this concentration in the still was employed.

The fifth column gives the values of β_{av}, which divided into the relative volatilities are presented in the sixth. These values of (α/β) can be used with the liquid composition to calculate the distillate concentrations. The procedure used in column seven is the same as Eq. (9-3). The individual values of $(\alpha/\beta)^4 x_L$ are divided by $370.05 = \Sigma(\alpha/\beta)^4 x_L$ to give x_D. The calculated values are close enough to the assumed value, and no retrial is necessary.

Equation (14-20) using $(\alpha/\beta)_{av}$ instead of α cannot be applied over a wide range due to the variation of the exponent as the distillation proceeds, but it can be used over a limited region averaging the values of $(\alpha/\beta)_{av}$ for the two ends of the range. For example, assume that the first increment is to remove 40 per cent of the A, *i.e.*, at the end of the step, $F_A = A/A_o = 0.6$. In order to carry out the calculations, the values of $(\alpha/\beta)_{av}$ corresponding to this final condition are assumed. These calculations are summarized in Table 14-5.

TABLE 14-5

Comp.	Assumed $(\alpha/\beta)_{av}$	F	Mols remaining in still $= 0.25F$	x_L	$\left(\frac{\alpha}{\beta}\right)^4_{av} x_L$	x_D	β_L	β_{av}	$\left(\frac{\alpha}{\beta}\right)_{av}$
A	5.5	0.6	0.15	0.171	155.5	0 762	1 89	1.445	5.53
B	3.6	0.915	0.229	0.261	43.8	0.215	1 165	1.083	3.68
C	1.95	0.993	0.248	0.283	4.1	0.020	1.014	1.007	1.98
D	1.0	1.0	0 25	0.285	0.285	0.001	1.001	1.0	1.0
			0.877		203.69				

The assumed values of $(\alpha/\beta)_{av}$ are given in the second column, and averaging these with those of Table 14-4 gives values that are used to calculate the values of F by Eq. (14-20). At the start of the distillation $(\alpha/\beta)_{av}$ for component A was 5.96, and the assumed value is 5.5 giving an arithmetic value of 5.73 over the increment. The corresponding value for component B is 3.69 and

$$\frac{A}{A_o} = 0.6 = \left(\frac{B}{B_o}\right)^{(5.73/3.69)^4}$$

$$\frac{B}{B_o} = 0.915$$

A similar procedure is employed for the other components. The composition of the liquid in the still is calculated from the values of the fractions unvaporized, F, and is given in the fifth column of the table. The following column contains the values of $(\alpha/\beta)_{av}$ of the second column raised to the fourth power and multiplied by the mol fraction in the liquid. The x_D, β_L, β_{av}, and $(\alpha/\beta)_{av}$ values are calculated in the same manner as in Table 14-4. The calculated values of $(\alpha/\beta)_{av}$ are in good agreement with the assumed values. The calculations for the next increment are made in a similar manner using F' as the fraction unvaporized for the increment. The results are given in Table 14-6.

TABLE 14-6

Comp.	Assumed $(\alpha/\beta)_{av}$	F'	F	Mols remaining in still $= 0.25F$	x_L	$\left(\frac{\alpha}{\beta}\right)_{av} x_L$	x_D	β_L	β_{av}	$\left(\frac{\alpha}{\beta}\right)_{av}$
A	5.0	0.5	0 3	0.075	0.098	60.6	0 58	2.19	1.595	5.01
B	3.5	0.86	0.786	0 197	0 257	38.9	0.372	1.29	1.145	3.49
C	1.97	0 986	0.98	0 245	0 320	4.77	0 0456	1.028	1.014	1.97
D	1.0	0.999	0 999	0 25	0 325	0.325	0 003	1 002	1.001	1.0
				0.767						

In this case the values of $(\alpha/\beta)_{av}$ were assumed, and F' for A was taken as 0.5. This latter value indicates that the increment is to reduce the mols of A in the still left after the step of Table 14-5 by one-half. The values of F' for the other components were calculated from $F'_A = 0.5$ and the average of the assumed value of $(\alpha/\beta)_{av}$ of Table 14-6 and the calculated values given in the last column of Table 14-5. The values of F were obtained by multiplying F' by the corresponding F value of the preceding table. The rest of the calculations are made in the same manner as those of Table 14-5.

The values of y_T calculated by this method are plotted in Fig. 14-7 as a function of mol fraction of the original charge distilled. The total reflux results of Fig. 14-5 are also included in the dotted curves for comparison. As would be expected, the separation with the finite reflux ratio is not so sharp as for total reflux. This decrease in the degree of separation is particularly marked for the intermediate fraction and is least serious in the case of the least volatile fraction. The inverted and split-towers systems discussed for total reflux would be effective in increasing the purity of any given fraction.

This approximate method is most accurate for high values of (O/D) and relatively few total plates. It reduces to the total reflux method for $(O/D) = \infty$. When the number of plates is large, they tend to pinch at the equilibrium curve and the arithmetic average for β is not satisfactory.

Finite Reflux Ratio with Column Holdup. The conditions in this case are similar to those discussed on page 380 for binary mixtures. The operating lines for each component are curved except for total

reflux, and it is very difficult to evaluate the position of these lines. The total reflux relations given on page 382 for a binary mixture do not apply exactly in this case because it was assumed that the unit was operating with a variable reflux ratio, producing a constant overhead composition. In the case of a multicomponent mixture, it is generally

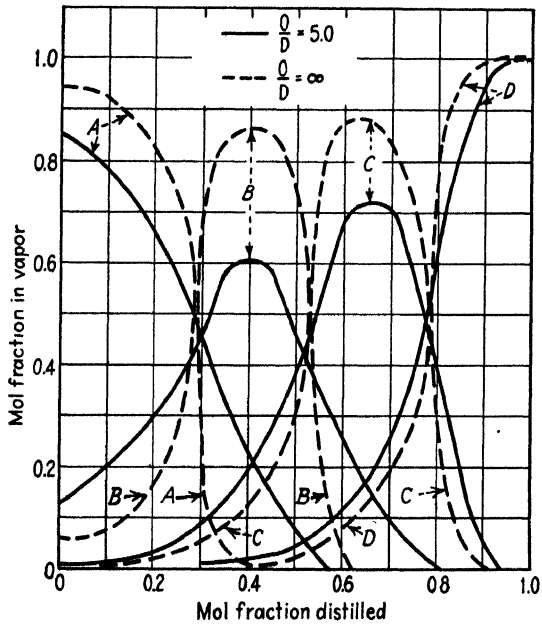


FIG. 14-7. Fractionation curve for multicomponent mixture at finite reflux ratio.

impossible to keep the overhead composition constant for all components as product is withdrawn. In certain cases, the distillate may be reasonably constant, and a similar analysis can be made.

The design methods for batch distillation allowing for liquid holdup in the column are very unsatisfactory, and it is a field that should be actively studied in view of the importance of the operation. Improvements in the design calculations for multicomponent mixtures with no liquid holdup in the column are also needed.

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CHAPTER 15

VACUUM DISTILLATION

Reduced pressures are frequently used in distillation processes for the purpose of lowering the temperature required. This is frequently important in the distillation of organic substances that are thermally unstable and would decompose if boiled at normal pressures. In addition to the reduced thermal degradation, the lower temperature often modifies the relative volatility or the degree of separation involved.

In the design methods considered in the preceding chapters, vapor-liquid equilibrium was used as a basic criterion. The equilibrium condition between a vapor and a liquid is a dynamic condition in which equal numbers of molecules of each species enter and leave the liquid per unit time. Langmuir (Ref. 5) derived an expression for the rate of this interchange based on kinetic theory considerations. The number of molecules striking a unit of surface per unit time for a perfect gas is

$$n = \frac{Pu}{4RT} \tag{15-1}$$

where P = pressure
u = average velocity of molecules
R = gas-law constant
T = temperature
n = number of molecules striking a unit area per unit time

The arithmetical average velocity of the molecules is

$$u = \sqrt{\frac{8RT}{\pi M}} \tag{15-2}$$

where M is the molecular weight, and the mass, m, striking a unit area per unit time is

$$m = nM = P\sqrt{\frac{M}{2\pi RT}} \tag{15-3}$$

Langmuir has investigated the fraction of the molecules striking a surface that rebound, and his results would indicate that essentially all the molecules striking the surface would enter and not be reflected.

Assuming that none are reflected, Eq. (15-2) can be used to calculate the rate of evaporation from a liquid at equilibrium with a vapor. The same relation has been used to predict the rate of evaporation from a liquid even when the vapor is not in equilibrium with a liquid. This may be approximately true for the nonequilibrium case, but there is undoubtedly some interference of the molecules in the vapor with those evaporating, and the use of Eq. (15-3) to calculate the absolute rate of evaporation probably gives results that are somewhat low. For the purposes of this discussion, Eq. (15-3) will be used as the basis of estimating the absolute evaporation rate from a liquid.

A consideration of Eq. (15-3) indicates that the vapor pressure is the most important factor in determining the rate of evaporation. Molecular weight and temperature are of less importance. The same reasoning that was used to develop this equation can be applied to each component in a mixture, giving for component A,

$$m_A = p_A \sqrt{\frac{M_A}{2\pi RT}} \tag{15-4}$$

It is instructive to compare this absolute rate of evaporation with the rate of mass transfer obtained in an atmospheric pressure distillation of benzene and toluene. Assume that the liquid phase is equimolal in benzene and toluene and that a vapor bubble ½ in. in diameter changes 10 mol per cent in composition for a 0.1-sec. contact with the liquid. This liquid composition corresponds to an equilibrium temperature of 92.4°C. and an equilibrium vapor composition of 0.71 mol fraction benzene. By Eq. (15-3) the rate of evaporation of benzene is

$$m_B = 0.71(1)(1.01 \times 10^6) \sqrt{\frac{78}{2(3.1416)(8.316 \times 10^7)(365.4)}}$$

$$= 14.5 \text{ g. per sq. cm. per sec.}$$

$$= 53.5 \text{ tons per sq. ft. per hr.}$$

A similar calculation for toluene gives 6.4 g. per sq. cm. per sec. In the actual experiment it is assumed that the exchange is equimolar, and the rate of exchange is

$$m' = \left[\left(\frac{2.54}{2}\right)^3 \frac{\pi}{6}\right]\left[\frac{273}{22{,}400(365.4)}\right]\left(\frac{0.1}{0.1}\right)$$

$$= 3.5 \times 10^{-5} \text{ g. mols per sq. cm. per sec.}$$

$$= 2.7 \times 10^{-3} \text{ g. benzene per sq. cm. per sec.}$$

$$= 3.2 \times 10^{-3} \text{ g. toluene per sq. cm. per sec.}$$

The actual rates of mass transfer are about 0.03 per cent of the theoretical evaporation rates. Under the conditions of mass transfer, the true vapor-liquid equilibria do not exist at the interface because molecules are leaving the liquid phase at a different rate than they are returning. In the case of benzene, more molecules are leaving than return while for toluene the reverse is true. In the case just considered, the net removal from the interface is so small in comparison to the interchange rate that equilibrium should be closely attained at the interface. If the net removal is made a large percentage of the interchange rate, normal vapor-liquid equilibrium will not be obtained. In the extreme case all the molecules that evaporate could be removed, and the relative rate for two components would be

$$\frac{m_A}{m_B} = \frac{p_A}{p_B}\sqrt{\frac{M_A}{M_B}} \tag{15-5}$$

If an equilibrium vapor were removed, the ratio of the components would be p_A/p_B, and the relative evaporation rate differs by the molecular weight term. Thus, the composition of an equilibrium vapor and the one obtained by removing all the molecules that evaporate will generally be different unless the molecular weights are the same. It should be possible in some cases to separate normal azeotropic mixtures by the evaporative technique, while other mixtures that would give no separation by this method could be handled by equilibrium vaporization. The azeotrope for the system ethanol-water should give a vapor by the evaporative method of considerably different composition than the liquid due to the high ratio of the molecular weights.

It should be possible to obtain a vapor composition anywhere between the true equilibrium value and that given by Eq. (15-5) by adjusting the net removal rate relative to the evaporation rate. A system with a net removal rate equal to the evaporation rate has been termed "molecular distillation" by Fawcett (Ref. 2) and "unobstructed-path distillation" by Hickman (Ref. 3). Hickman has used the term "molecular distillation" for systems having mean free path for the vapor molecules comparable to the distance between the evaporating and condensing surfaces. In this text the term *molecular distillation* will be applied to those cases in which the net removal rate is a high percentage of the absolute evaporation rate.

The benzene-toluene example gave low rates of transfer relative to the absolute evaporation rate, because (1) the interchange process introduces diffusional resistance and (2) the vapor approaches equilib-

rium with the liquid thereby decreasing the net rate of transfer. In order to approach molecular distillation conditions, it is necessary to increase the net rate at which molecules are removed relative to the rate at which they evaporate. This can be accomplished by increasing the removal rate and decreasing the evaporation rate.

For either type of vaporization, the general consideration of solution laws apply and can be used to predict the results of modifying the liquid phase. Thus it would be possible to modify the composition of the vapor removed in molecular distillation just as in azeotropic or extractive distillation.

VACUUM AND STEAM DISTILLATION

For pressures down to about 1 mm. Hg abs., the distillation operation can be carried out in a manner similar to those at higher pressures, and the problems relate to reducing the pressure drop for vapor flow through conventional equipment. The pressure drop of bubble-cap plates can be reduced to the order of 2 mm. Hg per plate (see page 404), and special spray-type plates can give pressure drops as low as 0.5 mm. Hg per plate. With such contacting units it is obvious that even a few plates will necessitate a still pressure of several millimeters even with a high vacuum at the condenser. Packed towers can give low pressure drops, and still pressures of the order of 5 to 10 mm. Hg are obtainable with reasonable tower sizes and rates of distillation. However, owing to the poor vapor-liquid contact, they are not widely used for such operations. The contact is particularly poor in this case because of the low volumetric ratio of liquid to vapor.

Lower distillation temperatures can be obtained by the use of steam. In this case the steam does not usually condense in the tower, and the plates contain only the high boiling organic material. The steam acts as an inert carrier that is easily condensed and does not have to pass through the vacuum pump. In some cases the temperature gradient in the distillation column may be so great that the steam will condense in the upper portions, and it should be withdrawn. If too much water collects on a plate, it may seriously interfere with the fractionation; if the water runs down the tower, it will vaporize on the lower plates and this steam recycle in the tower can overload the unit and seriously interfere with the fractionation. Theoretically it is possible to fractionate a material with a very low vapor pressure by the use of steam distillation, but the steam consumption increases as the vapor pressure on the component decreases. Reduction of the total pressure reduces the steam consumption, but if the vapor pressure of the com-

ponent at the distillation temperature becomes less than 0.1 mm. Hg, the steam consumption becomes excessive for most cases. The rectification calculation for such distillations can be made in the usual plate-to-plate manner.

The vapor-liquid equilibria at pressures down to 1 mm. Hg are not greatly different from those at higher pressure. The relative volatility of a binary system may either increase or decrease as the pressure is reduced. For example, in a mixture of oleic and stearic acids, oleic is the more volatile at temperatures above 100 to 110°C., while below these temperatures it is the less volatile. For mixtures that obey Raoult's law the relative volatility generally increases as the temperature is decreased because the less volatile constituent has the higher latent heat resulting in a high temperature coefficient of vapor pressure.

The calculations of the separation to be expected as a function of the reflux ratio and the number of theoretical plates for vacuum distillation are completely analogous to those for higher pressure operation. The difficult design problems are those related to obtaining efficient contact between the liquid and vapor with the low pressure drops available.

MOLECULAR DISTILLATION

This type of operation has been applied to the distillation of materials that have very low vapor pressures at the maximum operating temperature. The available pressure drops in such cases would be too low to obtain practical production rates in conventional equipment, but by operating such that the rate of distillation is approximately equal to the absolute evaporation rate of the liquid reasonable capacities can be obtained. The most common method of obtaining the molecular distillation conditions is to carry out the operation at a high vacuum (0.01 mm. Hg or less) and to place the condensing surface so that it is parallel to the evaporating surface and in close proximity to it. The condenser is operated at a low temperature to limit the reevaporation. In order to obtain satisfactory absolute rates of evaporation, it has been found that as an approximate rule the temperature should not be lower than 100°C. below the temperature at which the vapor pressure of the substance being evaporated is 1 to 5 mm. Hg abs.

Even with molecular distillation, the rates of evaporation obtained are low when the vapor pressure is less than 0.01 mm. Hg abs. Thus for a material having a molecular weight of 400 and a vapor pressure of 0.01 mm. Hg at 100°C., the absolute evaporation rate by Eq. (15-3)

would be only 0.02×10^{-3} g. per sec. per sq. cm. This is much lower than the rate estimated on page 394 for normal vapor-liquid interchange. High-molecular-weight polymers would have low evaporation rates regardless of the vacuum.

It should be possible to obtain results similar to molecular distillation at higher total pressures by a high degree of turbulence in the space between the condenser and the evaporating liquid in order to obtain rapid mass transfer.

In the high-vacuum method of operating, it is usually suggested that the distance between the condenser and the evaporating surface should be of the order of the mean free path of the molecules in the vapor. Jeans (Ref. 4) gives the following equation for the mean free path (M.F.P.) of a molecule:

$$\text{M.F.P.} = \frac{1}{\sqrt{2}\pi\rho d^2} \tag{15-6}$$

where M.F.P. = mean free path, cm.
ρ = molal density = molecules, cu. cm.
$= 1.75 \times 10^{19}(P/T)$ for a perfect gas
d = diameter of molecule, cm. (As an approximate rule use cube root of $6/\pi$ times the liquid volume per molecule)
P = absolute pressure, mm. Hg
T = absolute temperature, °R.

Thus for a material that has a molecular weight of 500 and a liquid density of 0.9, the mean free path at a pressure of 10^{-3} mm. Hg and 400°F. would be

$$\text{M.F.P.} = \frac{1}{\sqrt{2}\,\pi\left[(1.75 \times 10^{19})\,\dfrac{10^{-3}}{860}\right]\left[\dfrac{(500/0.9)6}{(6.06 \times 10^{23})\pi}\right]^{2/3}}$$

$$= 0.77 \text{ cm.}$$

However, it does not appear to be necessary to make the mean free path as large as the distance between the condenser and the evaporating surface to obtain molecular distillation conditions. Brönsted and Hevesy (Ref. 1) obtained separations of mercury isotopes that corresponded closely to molecular distillation rates under conditions where the condenser was separated from the evaporating mercury surface by a distance approximately 100 times the mean free path. Taylor (Ref. 7) distilling petroleum fractions found the rate of evaporation to be independent of the total pressure over a range corresponding to mean

free paths of 0.01 to 10 times the clearance between the condenser and the evaporating surface. He also found that noncondensable residual gas at pressures up to the vapor pressure of the liquid being distilled did not materially lower the distillation rate. Higher residual gas pressure can cause appreciable lowering of the rate.

The most common type of high vacuum molecular distillation still is the vertical-tube falling-film unit, a schematic diagram of which is shown in Fig. 15-1. The liquid to be distilled is first degassed. This is essential if splashing in the distillation unit is to be avoided. This liquid then flows down in a film on the outside of the inner tube which is internally heated. The inner surface of the outer tube is the condenser which can be air- or water-cooled. For a high rate of distillation, the clearance between the two surfaces should be relatively small, but if they are too close, any noncondensable gas released at the bottom of the still will have difficulty flowing out of the unit. A clearance of 0.4 to 1.0 in. appears to be about optimum for a unit 2 to 4 ft. long.

In such a falling-film unit a molecule moving from the evaporating liquid to the condenser encounters a number of resistances: (1) diffusional resistance from the interior to the surface of the liquid, (2) evaporational resistance, (3) resistance to transfer in the vapor, (4) resistances in condensation.

The resistance to condensation is small, and the resistance to vapor transfer is made small by the use of low pressure and by keeping the condenser close to the evaporating surface. The evaporating rate of the molecules in the surface is chiefly a function of temperature which should be kept as high as possible without thermal degradation or bubbling of the liquid which throws unvaporized material over to the condenser. In most cases, the limiting rate is diffusion in the liquid phase. Owing to the large size of the molecules and the viscosity of the liquid, the mass-transfer rate is very low. The outer surface of the liquid is depleted of the more rapidly evaporating molecules a short distance from the top of the unit, and the surface then has a higher concentration of the less volatile molecules than the average composition of the liquid. This reduces both the evaporation rate and the degree of separation obtained. A small amount of large-size, essentially nonvolatile, material in the liquid can give a serious blocking of the surface. Owing to this effect, increasing the length of the apparatus does not give a proportional increase in the amount of evaporation. For this reason, the falling-film units are seldom made over 2 to 4 ft. high. Several methods can be used to reduce the effect of this surface blocking: (1) Various mechanical devices have been proposed to cause mix-

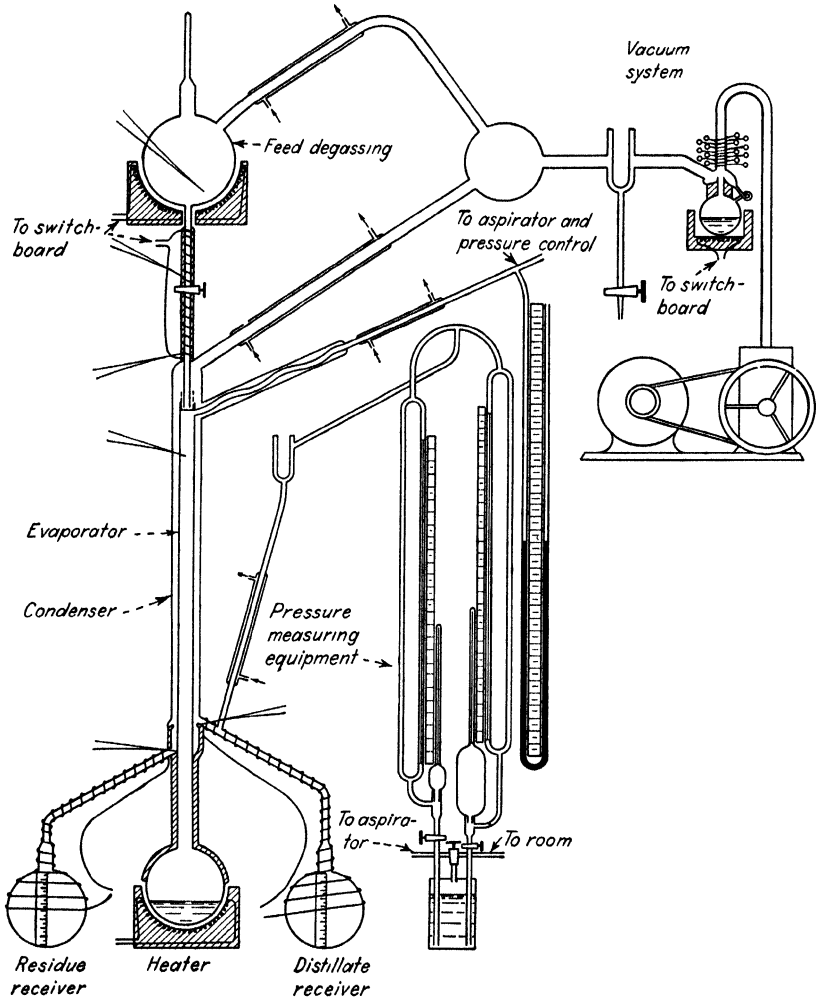


FIG. 15-1. Diagram of falling-film unit.

ing of the falling film. (2) The liquid circulation rate can be increased, resulting in a lower percentage evaporation per pass through the unit. A high percentage evaporation can be obtained either by recirculating the liquid or by using several units in series with mixing between each unit. (3) A high liquid flow rate can be used to cause the outer portion of the falling film to be in turbulent rather than laminar flow. This type of operation may also necessitate recirculation or series

operation to obtain a high percentage of the liquid distilled. (4) The unit may be modified to give a continually increasing surface. For example, the inner tube can be made conical with the small end at the top. As the liquid flows down, it must increase in area which will present fresh surface for evaporation. Hickman (Ref. 3) has developed a spinning-plate type of film unit in which the liquid is fed at the center and flows across the spinning plate due to centrifugal force. The plate is heated, and the condenser is placed parallel to it. Because of the high centrifugal force, it is possible to obtain thin films which mean large surface area per unit volume of liquid, and the increasing diameter of the plate requires the formation of new surface as the liquid flows outward. The spinning-plate unit is effective for the purpose of increasing evaporation rate, but other methods would appear to be simpler for large-scale units.

Besides keeping the temperature at a low level, molecular distillation holds only a small volume of the liquid at the evaporation temperature and thereby reduces the thermal degradation. The spinning-plate type of still is particularly effective in this respect because of the thin film obtained.

The thermal efficiency of a molecular distillation is low. Fawcett (Ref. 2) has given a heat balance on a unit distilling triolein at 240°C. with the condenser at 25°C. The data are summarized in the following table:

	Per Cent
Preheat of liquid..	8
Radiation...	59
Latent heat of evaporation	9
Conduction..	24

Only 17 per cent of the total heat is usefully employed, the other 83 per cent is lost by heat transfer. The loss by radiation could be reduced somewhat by increasing the temperature of the condenser, but this might reduce the effectiveness of the distillation.

Another drawback to molecular distillation is the fact that an effective rectification system has not been developed. Greater separations than are equivalent to a single distillation stage have been obtained by repeated distillations in the manner described on page 102, but they are tedious and difficult to perform.

Schaffner, Bowman, and Coull (Ref. 6) have described a vertical falling-film multiple distillation column that can be employed for fractionation under vacuum. The wall is made up of short sections with

alternate sections being heated and cooled. Vapor condenses on the cooled section and flows down to the heated section below where it is partially vaporized, and the action is repeated on succeeding sections. By this series of partial condensations and vaporizations, an enrichment of the vapor in the more volatile component is obtained. Because vapor must flow between sections, molecular-type distillation is not possible. Such a unit is very sensitive to operating conditions, and the heat added and removed in the successive sections must be well balanced or the vapor will all condense or the liquid will all vaporize. Owing to the temperature changes during distillation, the heat supplies will need frequent readjustments to obtain optimum operation.

The very low pressures involved almost preclude an effective contact similar to that obtained in normal rectification. It would appear that the use of higher pressures with a high degree of turbulence to obtain the necessary rate of distillation at the low temperatures involved would offer better possibilities for rectification than the use of high vacuum. By the use of a low molecular weight gas, such as hydrogen, to maintain the pressure, it should be possible to obtain high transfer rate with a moderate degree of gas turbulence.

Because of the high cost per unit of product distilled, the use of molecular distillation has been limited in its application to the separation of relatively expensive materials that are sensitive to thermal degradation.

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CHAPTER 16

FRACTIONATING COLUMN DESIGN

The design calculations given in the previous chapters involved the mathematical problem of determining the number of theoretical plates and did not consider whether or not such performance could be obtained. This chapter will consider the mechanical design problems encountered in attempting to attain the desired degree of contact between the vapor and liquid and the necessary fluid and vapor flow. The fractionating column must bring the liquid and vapor into countercurrent contact (or some approximation of this type of flow), and it must be constructed to furnish the necessary pressure drops (or liquid heads) to give the desired flow conditions.

The liquid gradients and the pressure drops encountered by the liquid and the vapor are important for several reasons:

1. The conditions may be such that the liquid will not flow down the column, countercurrent to the upflow of the vapor. Such action preventing rectification is termed "flooding" or "priming." Any column has a maximum operating capacity, above which this condition will be encountered, but the capacity of a column of given diameter with fixed plate spacing will be a function of the design.

2. The contact between the vapor and liquid is a function of the liquid gradients and the gas pressure drops.

3. The pressure drop per plate is of vital importance in vacuum rectification.

BUBBLE-CAP PLATES

The bubble-cap plate is the most common vapor-liquid contacting device employed for fractional distillation. Its purpose is to bring the vapor and liquid into intimate contact so that the necessary mass transfer can be effected. This requires means for bringing the liquid down the column from plate to plate, across the plates, and into contact with the vapor. The design of such a unit involves obtaining the desired flow conditions of the liquid and vapor and the contact between the two. Figure 16-1 gives a schematic drawing of the cross section of a bubble-cap plate. The liquid flows onto a plate from the down pipes, flows across the plate contacting the vapor, flows over the outlet weir

and through the down pipe to the plate below. The vapor flows up through the liquid on the plate and to the space above. For these flows to follow the desired pattern, the necessary pressure drops and hydraulic heads must be available.

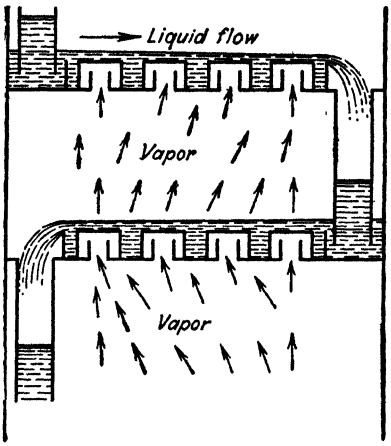


FIG. 16-1. Schematic cross-sectional diagram of bubble-cap plate column.

The liquid meets resistance in the down pipes, in flowing across the plate, and in flowing over the weirs. The frictional resistance in the down pipes is handled by making them of adequate cross section and height to take the liquid load. For a given cross section, in general the liquid-handling capacity of the down pipes will increase with increasing height but it is desirable to keep the height low in order to reduce the plate spacing. On the other hand, down pipes of large cross section reduce the available plate area for vapor liquid contact. In flowing across the plate the liquid decreases in depth owing to the frictional and kinetic effects giving the so-called hydraulic gradient. An overflow weir is employed

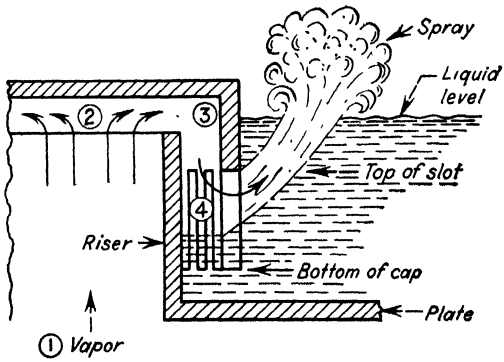


FIG. 16-2. Cross section of bubble cap.

to maintain the liquid level at approximately the desired level. These various factors are considered in detail in later paragraphs.

Pressure Drop for Vapor Flow. The vapor meets its main resistance in passing through the bubble cap and the liquid on the plate. Consider the section of a cap shown in Fig. 16-2. The vapor from the plate

below enters the riser at (1) and encounters a pressure drop due to the reduction in cross section. There is a frictional drop in the riser from (1) to (2), a reversal loss (2) to (3) between the top of the riser and the cap, and then a frictional drop against the cap from (3) to (4). The vapor then passes through the slot and up to the vapor space above the liquid. It is convenient to group these into three pressure drops: the pressure drop through the riser and cap, h_c; the loss in pressure in flowing through the slots, h_s; and the pressure drop due to the liquid head above the slots, h_L.

Pressure Drop through Risers and Cap. This loss is chiefly a kinetic velocity effect due to the changing cross-sectional areas. The pressure drop in inches of the liquid equivalent to the kinetic head is

$$h_H = \frac{12V_R^2}{2g_c}\frac{\rho_V}{\rho_L} \tag{16-1}$$

where h_H = kinetic head, inches of liquid of density ρ_L
V_R = maximum velocity in riser, between top of riser and cap, or in annulus between riser and cap, f.p.s.
g_c = conversion constant
= 32.2[(ft.)(lb force)]/[(sec.^{2})(lb. mass)]
ρ_V = density of gas, same units as ρ_L

The actual loss in pressure, h_c, from (1) to (4) should be a function of h_H. The data of Mayer (Ref. 24), Schneider (Ref. 28), and Dauphiné (Ref. 5) on several 3-, 4-, and 6-in.-diameter caps with risers from 2 to 4 in. in diameter gave ratio of h_c/h_H from 4.7 to 6.3. Souders (Ref. 34) gave results indicating a ratio of 2.9, Kirkbride (Ref. 20) recommended 3.2, and Edminster (Ref. 7) suggested 7.8 but included the pressure drop through the slots. In view of the extensive data by the first three investigators, a value of the ratio equal to 6.0 will be used giving

$$h_c = 1.1V_R^2\frac{\rho_V}{\rho_L} \tag{16-2}$$

Pressure Drop through Slots. The pressure drop through the slot, h_s, is evidenced by the liquid level in the cap being lower than the top of the slots. The value of h_s will be taken as equal to the difference in the pressure of the vapor in the cap at position (4) and the liquid outside the cap at the top of the slot. The slot action varies with the rate of flow. At low rates of flow an intermittent type of bubbling action is obtained. Owing to the surface tension, the pressure within the cap rises until the liquid under the cap is depressed an appreciable distance below the top of the slots. When the pressure is sufficient to overcome

the surface tension, there is a rapid flow of vapor reducing the pressure, and the cycle is then repeated. Thus a pressure drop across the plate greater than the height of the liquid above the slots is necessary to initiate vapor flow. At higher rates of vapor flow, bubbling becomes continuous, and the pressure drop through the slots becomes greater than that necessary to initiate flow. At still higher vapor rates, the vapor blows open channels through the liquid. For all cases, the pressure drop through the slots is greater than for flow through the slots on a dry plate. The calculation of h_s is also complicated because the velocity of the vapor in the cap approaching the slots may be equal to or greater than the slot velocity, and a simple orifice-type equation is not applicable.

A definite value of h_s is necessary to initiate flow. It then increases slowly with the rate of vapor flow as the slot opening increases, and when the slots are completely open, the pressure drop increases rapidly with increase in vapor rate through the slots.

For values of h_s less than the height of the slot, the data of Carey (Ref. 3), Griswold (Ref. 14), Mayer, Schneider, and Dauphiné can be correlated by

$$h_s = 0.12\frac{\gamma}{\rho_L} + K\left(h_o^* V_s \sqrt{\frac{\rho_V}{\rho_L - \rho_V}}\right)^{0.67} \tag{16-3}$$

where h_s = slot opening or pressure drop through slots, in.
γ = surface tension, dynes/cm.
ρ_L = liquid density, lb. per cu. ft.
ρ_V = vapor density, lb. per cu. ft.
h_o^* = slot height, in.
V_s = velocity based on total slot area, f.p.s.
K = see Table 16-1
$\frac{h_o^* V_s}{12}$ = cu. ft. per sec. per total ft. of slot width

The variation in the values of K is believed to be due mainly to the effect of the ratio of velocity in the cap to slot velocity. In the case of the small caps, this ratio was high, and it is suggested that for other cases the following relation be employed.

$$K = 1 - \left(\frac{V_R}{2.0V_s}\right)^2 \tag{16-4}$$

The pressure-drop values for a number of different caps are plotted in Fig. 16-3 on the basis of the groups of Eq. (16-3). The data for the large caps are higher than for the small caps, and the slope of the best

TABLE 16-1

Cap	K
6-in.-diameter galvanized-iron cap:	
Slots, ⅛ by (0.5, 1.0, 1.5, and 2.0) in. Slots, 3/16 by (0.5, 1.0, and 1.5) in.	0.8
6-in.-diameter cast-iron cap:	
Slots, ¼ by (0.5 and 1.0) in	1.0
4-in.-diameter copper cap:	
Slots, 5/32 by ½ in	0.6
4-in.-diameter cast-iron cap:	
Slots, 3/16 by (0.5 and 1.0) in	0.7
Tunnel cap, slots 3/16 by 0.875 in. 4-in. caps, tangential slots ⅛ by 0.75 in.	0.55

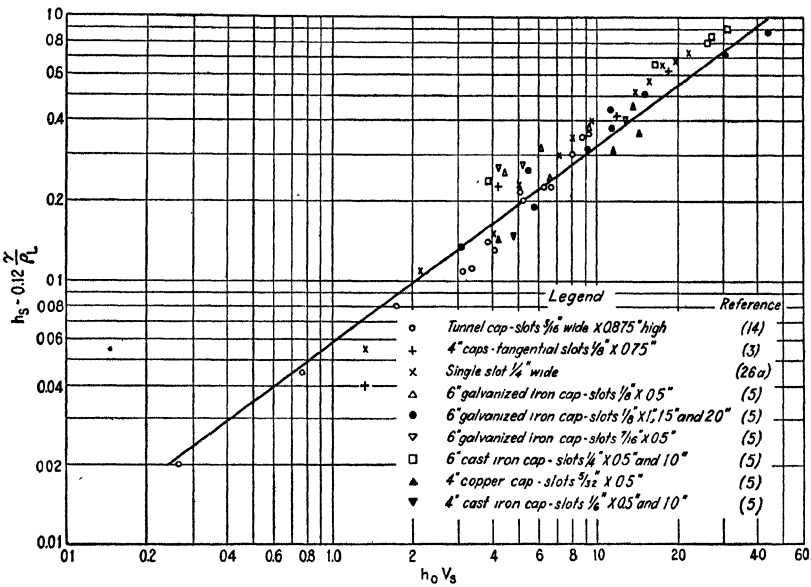


FIG. 16-3. Pressure drop through bubble-cap slots.

line through the data for any one cap is approximately ⅔ for most cases. The line drawn for all the caps is

$$h_s = 0.12\frac{\gamma}{\rho_L} + 0.058(h_o^* V_s)^{0.75} \tag{16-5}$$

and, including the square root of the density terms, Eq. (16-5) becomes

$$h_s = 0.12\frac{\gamma}{\rho_L} + 0.72\left(h_o^* V_s \sqrt{\frac{\rho_V}{\rho_L - \rho_V}}\right)^{0.75} \tag{16-6}$$

It is believed that Eq. (16-3) with a value of K by Eq. (16-4) gives better results for specific cases, but that Eq. (16-6) is helpful for general cases.

With the usual plate design the slots become completely open for vapor flow at values of h_s less than h_o^* due to the fact that the average density of the vapor-liquid mixture around the cap is only $\frac{1}{3}$ to $\frac{1}{2}$ that of the liquid. For studies of single caps this lowered-density effect is of less importance. At vapor rates higher than those corresponding to complete opening of the slots, the relation between h_s and V_s should be modified. In some cases the bottoms of the caps are raised above the plate to allow excess vapor to escape. With this arrangement, high capacities can be obtained without excessive pressure drops, although the vapor-liquid contact for such operation is probably of low effectiveness. In other cases, the bottoms of the caps are sealed to the plates, and any excess vapor is forced through the slots. For this condition the following equation is suggested for h_s greater than h_s^*:

$$h_s = h_s^* \left(\frac{V_s}{V_s^*}\right)^2 \tag{16-7}$$

where V_s^* is vapor velocity in Eq. (16-3) for h_s equal to h_s^* and h_s^* is the value of h_s for slots completely open. For conventional plate arrangements it is suggested that h_s^* be taken equal to $\frac{1}{2}h_o^*$.

Pressure Drop Due to Liquid Head above Slots. The pressure drop due to the liquid head above the top of the slot is customarily taken as equal to the actual liquid depth above the slots. This liquid depth is frequently taken as weir height, h_w, plus the weir crest, h_{cr}, minus the height of the top of the slot, h_{sp}, thus

$$h_L = h_w + h_{cr} - h_{sp} \tag{16-8}$$

In some cases a correction is added for the additional liquid head at the cap in question owing to the liquid gradient. This method of evaluating h_L is simple, but the data of Seuren (Ref. 29), Ghormley (Ref. 11), and Kesler (Ref. 19) show that the actual liquid head in the aerated section of a plate can be considerably less than that at the weir. This effect is the result of liquid flow from a nonaerated section to an aerated section and back to a nonaerated section. This condition will be discussed in the section on Hydraulic Gradient. The use of Eq. (16-8) with a correction for the hydraulic gradient will give high values for the liquid head.

The over-all pressure drop for a plate, h_p, is calculated by

$$h_p = h_c + h_s + h_L \tag{16-9}$$

Liquid Flow. *Weirs and Down Pipes.* The liquid depth on a plate is controlled by exit overflow weirs. The action of the liquid flowing over the weir is complicated by the action of the caps and by the restrictions due to the wall. The last row of caps may blow a con-

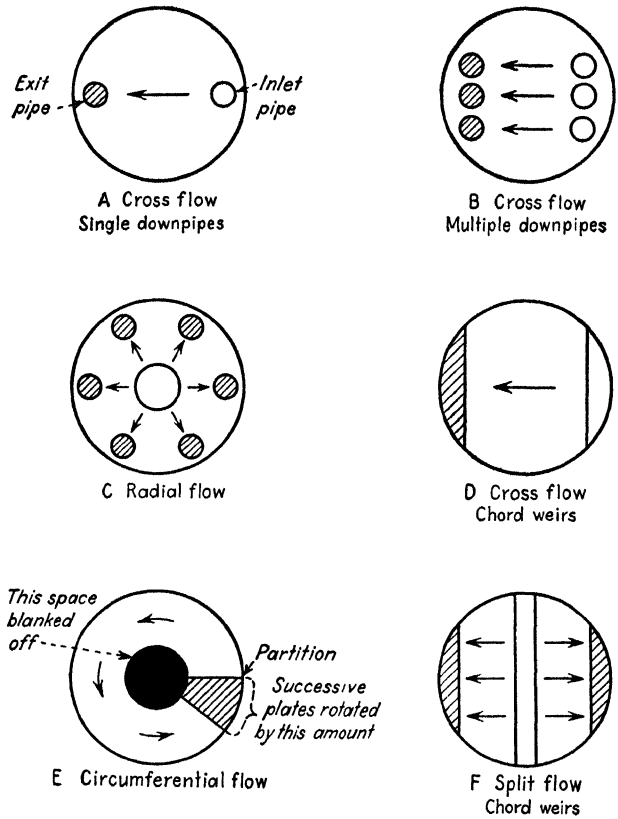


FIG. 16-4. Downflow pipe arrangements on bubble-cap plates.

siderable quantity of liquid over the weir as spray and in surges. The walls may be so close to the downstream side of the weir that they interfere with the liquid flow.

A variety of different weir and down-pipe arrangements are employed (see Fig. 16-4).

In small columns, the overflow from plate to plate is usually carried in pipes, the upper end of the pipe projecting above the plate surface to form an overflow weir and maintain a liquid seal on the plate. The lower end extends into a well on the plate below, thereby sealing the

pipe so that the vapor may not pass upward through it. In larger columns, straight overflow weirs placed on a chord across the tower are often used.

Locke (Ref. 22) from a study of circular down pipes with the tops acting as weirs concluded that at least three types of liquid flow were possible in circular down pipes with liquid seals at the bottom. At low rates of liquid flow, the top of the pipe acted as a weir, and the liquid flowed down in a film. As the liquid head was increased, the pipe became full and sucked vapor bubbles down with it; at still higher liquid rates, the pipe ran full but did not entrap vapor. The first type flow occurred for liquid head less than one-sixth to one-fifth of the pipe diameter, and this type of flow could be represented by the familiar Francis weir formula:

$$h_{cr} = k\left(\frac{Q}{L}\right)^{2/3} \tag{16-10}$$

where Q = cu. ft. of liquid per sec.
L = perimeter of inside surface of pipe, ft.
h_{cr} = head of liquid above top of pipe, in.
k = constant, increasing from 3.9 to 4.3 as pipe size was increased from 0.87 to 2.07 in.

Rowley (Ref. 27) recommends the following equation for the last two types of flow:

$$h' = \left(\frac{18}{2g_c} + \frac{24fl}{g_c D}\right) V_o^2 \tag{16-11}$$

where h' = head of liquid necessary to overcome down-pipe friction and entrance and exit losses, in.
g_c = proportionality constant, 32.2
D = inside diameter of pipe, ft.
V_o = linear velocity of liquid in pipe, f.p.s.
f = proportionality constant of Fanning friction equation (See Walker, Lewis, McAdams, and Gilliland, "Principles of Chemical Engineering," 3d ed., p. 78.)

For large straight weirs when the downspouts are not running full, the Francis weir equation may be used. This weir formula is frequently employed neglecting the approach velocity, and in some cases this may not be a satisfactory approximation. The equation for zero approach velocity is

$$h_{cr} = 5.4\left(\frac{Q}{L}\right)^{2/3} \tag{16-12}$$

Units same as for Eq. (16-10).

To allow for the approach velocity, a correction factor is given in Fig. 16-5, as a function of Q/L and $h_{cr} + h_w$, where h_w is the height of the weir. This correction was calculated on the basis that the liquid approaching the weir had a velocity corresponding to the unaerated depth of $h_{cr} + h_w$. The actual velocity of approach is probably higher owing to the caps and vapor. The correction factor is multiplied into the right-hand side of Eq. (16-12) to calculate h_{cr}.

When the head on the weir becomes high, the liquid carries past the dam a considerable distance, and the wall may interfere with the flow. In circular pipes, Locke reported that the streams from the various sides interfered with each other when the head on the weir at the top of the pipe was 0.2 of the pipe diameter. This would indicate an over-

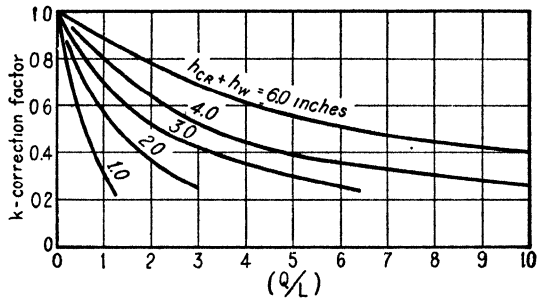


FIG. 16-5. Correction factor for Eq. (16-12).

shoot of over twice the head. The effect for straight weirs is probably less, and Edminster (Ref. 7) has suggested neglecting the portion of the weir that is closer to the wall than the value of h_{cr}. This would appear to be a reasonable assumption.

For large downspouts running full, it is recommended that Eq. (16-11) be used, employing for D four times the hydraulic radius, which is equal to the cross-sectional area of the downspout divided by the perimeter.

When the liquid head over the weir is low, the discharge from one side to the other will vary if the top edge is not level. This variation can be reduced by using a V-notched top which reduces the effective weir length at low rates of flow. In general, it is desirable to keep the head over the weir low because this reduces the variation of liquid depth on the plate for different operating rates. Values of h_{cr} of 1.0 in. are common, but they seldom exceed 3 in.

In some cases, under- and overweirs are used at the outlet to handle

two liquid layers on a plate. Such an arrangement can also be used to hold back foam from the down pipe. The clearance between the underweir and the plate must be adequate to handle the liquid load.

The bottoms of downflow pipes must have enough clearance to allow the liquid to flow easily, but they should not allow vapor to by-pass up through them. This vapor by-passing is usually prevented by a positive seal which holds liquid above the bottom of the down pipe (see Fig. 16-1). In large columns, this seal is often made an inlet weir which serves to distribute the liquid as well as seal the down pipe.

For the reversal loss at the bottom of the down pipe, it is recommended that a loss equal to one kinetic head be used with a coefficient of 0.6.

$$h_D = \frac{12}{2g_c}\left(\frac{V_D^2}{0.6^2}\right) = 0.5V_D^2 \tag{16-13}$$

where h_D = loss in head at bottom of down pipe, in.

V_D = maximum velocity at bottom of down pipe, f.p.s.

Liquid Gradient. One of the important factors that must be considered in the design of a bubble plate is the liquid gradient across the plate. It is obvious that the liquid level will normally be higher at the liquid inlet than at the outlet. In small towers, this difference in level offers no serious difficulties, but in towers of moderate and large diameters it can become so great that the vapor distribution is poor and the overflow may by-pass the plate by dumping through the caps.

The gradient is due to the resistance to liquid flow across the plate and results from (1) friction with the caps and the plate, (2) eddy losses in the liquid due to repeated acceleration and deceleration, and (3) resistance due to the effects of vapor flow.

Experimental data on this gradient have been published by several investigators (Refs. 10, 11, 12, 13, 18, 19, 29). Gonzales and Roberts (Ref. 12) studied a plate with 4⅜-in.-diameter caps which were 6¼ in. tall using air and water. Their column was rectangular in shape with 12 rows of caps in the direction of liquid flow. Based on liquid flow around staggered pipes, they developed the following equation for the gradient as a function of the number of rows of caps:

$$h^{2.8} = A - Bn \tag{16-14}$$

where h = liquid depth on plate

A,B = constants

Their data were taken at liquid levels less than the top of the caps

and agreed well with the equation for both aerated and unaerated conditions. A and B were functions of both the water and air rates.

Bijawat (Ref. 2) reviewed the data obtained by Gonzales and Roberts and, on the basis of orifice-type flow of the liquid between the caps, suggested

$$h^3 = A' - B'n \tag{16-15}$$

This equation correlated the data about as well as Eq. (16-14). Seuren (Ref. 29), Ghormley (Ref. 11), and Kesler (Ref. 19) obtained data on a rectangular plate with 10 rows of 4-in. caps in the direction of liquid flow. Good, Hutchinson, and Rousseau (Ref. 13) investigated the liquid gradient on a rectangular plate having 12 rows of 3-in. caps for a number of operating conditions.

Klein (Ref. 20*a*) has investigated the factors that cause the loss in head of the liquid flowing across the plate. His data indicate that with no vapor flow there is essentially no hydraulic gradient even at liquid rates considerably greater than those normally employed. It was concluded that the loss in head was due to high frictional losses for the flow of the vapor-liquid mixture. The drag per unit area was determined by measuring the force on a plate suspended in the aerated liquid, and values ten times as large as for unaerated liquid flowing at the same linear velocity were found. Abnormally high frictional losses have also been reported for the flow of mixtures of vapor and liquids in pipes.

Klein confirmed the observation of Ghormley and Kesler that the hydrostatic head of the liquid in the aerated section was frequently less than that at either the inlet or outlet to the plate. Klein, Kesler, and Bloecher (Ref. 2*a*) measured the potential head of the liquid by determining the hydrostatic head as a function of depth and then integrating up from the bottom of the plate. The potential head is equal to the number of inches above the tray at which all the water present would give the same total potential energy as the aerated liquid. For a nonaerated liquid the potential head, according to this definition, is equal to one-half the liquid depth. It was shown that the potential head decreases progressively across the plate. It is this head, and not the hydrostatic head, which is the driving force for liquid flow. The flow across a bubble plate can be considered in terms of five zones. (1) There is the inlet unaerated section in which the potential head is twice the hydrostatic head. (2) There is the transition section from the first zone to the aerated region. This transition occurs a short distance upstream from the first row of caps to about

the second row of caps. In this region (*a*) the apparent depth of liquid rises sharply owing to the aeration, (*b*) the hydrostatic pressure drops abruptly, and (*c*) the potential head remains almost constant. For the potential head to remain constant the hydraulic head must decrease because some of the liquid is at a higher level. Near the plate the pressure in the liquid in Zone 1 is higher than in the transition section and liquid flows towards the caps, but at higher levels the reverse is true and the liquid flows back (against the normal flow). (3) The third zone is the main aerated section in which the hydrostatic head remains essentially constant and there is a progressive decrease in the potential head. (4) The fourth zone is the outlet transition zone which extends from the last two rows of caps to the calming section before the outlet weir. The phenomena are similar to those for the inlet transition zone, *i.e.*, (*a*) the apparent depth of the liquid drops sharply, (*b*) the hydrostatic head increases abruptly, and (*c*) the potential head remains almost constant. In this case there is a flow of liquid back toward the caps near the plate and toward the outlet section at the higher levels. (5) The final region is the unaerated calming section before the outlet weir. These effects are illustrated in Fig. 16-6. At low air rates there is a decrease in hydrostatic head in the aerated zone, but a clear liquid layer on the plate extends from the inlet to the outlet. At higher vapor rates the liquid becomes "completely aerated," and no apparent clear liquid layer remains. This condition is shown in diagram *A* of Fig. 16-6. Data on the hydrostatic and potential head for a completely aerated condition are shown in diagram *B*. The sharp drop and rise in the hydrostatic head at the two ends of the plate are clearly shown, but there is essentially no change in the aerated section. The value of twice the potential head is plotted so that it will be numerically equal to the hydrostatic head in the two nonaerated sections. The potential head decreases regularly across the plate.

Referring again to diagram *B*, Fig. 16-6, the hydrostatic head given is the value at the bottom of the plate. If values are determined in planes parallel to, but above, the plate, it is found that the hydrostatic head decreases more rapidly with height in the nonaerated sections than in the bubbling zone owing to the lower density of the vapor-liquid mixture. Eventually, at a height less than h_o, the hydrostatic head in the outlet transition zone (Zone 4) becomes equal to that in Zone 5, and at higher heights above the plate the aerated section has the higher head. Thus, the hydrostatic head is a complicated function of the position and the distance above the plate.

Klein found that for a given liquid rate the hydraulic gradient

increased with increasing vapor rate until the liquid-vapor mixture in the aerated section had an apparent density approximately one-third that of the liquid but further increases in vapor rate did not appreciably change the loss in head. He termed the condition for the mixture density equal to one-third the liquid density "complete aeration."

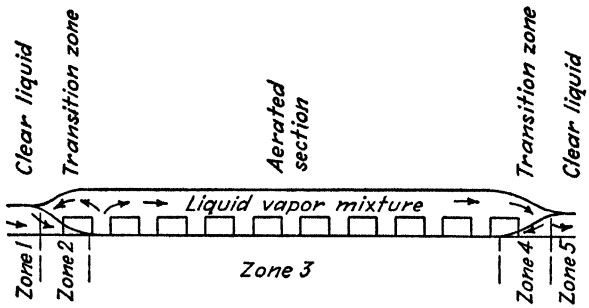


Diagram *A*

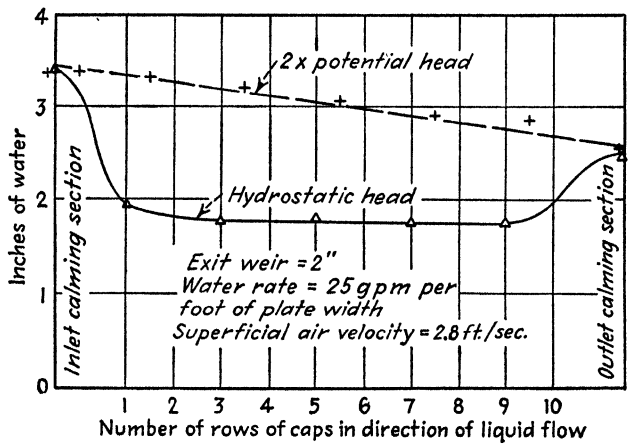


Diagram *B*

FIG. 16-6.

Higher air rates or foaming agents increased the apparent liquid height, but static pressure probes indicated that for these cases the density was approximately one-third that of the liquid for the main region of fluid flow just above the plate and on top of this layer there was a light froth containing essentially no liquid. Practically all the liquid flow was accounted for in the layer with the one-third normal density. The light froth did not appear to have a significant effect on the hydraulic gradient.

Klein correlated his data and that of other investigators on the basis of a Fanning-type friction equation.

$$F = \frac{f' V_f^2 B}{g_c r_h} \tag{16-16}$$

$$r_h = \frac{bL_o}{b + 2L_o} \tag{16-17}$$

where F = loss in head from inlet to exit calming sections, ft.
f' = friction factor
V_f = velocity of liquid in foam, f.p.s.
$= Q_W/(\rho_f L_o b)$
Q_W = liquid rate, lbs. per sec.
ρ_f = density of foam, lbs. per cu. ft.
L_o = foam height, ft.
b = width of plate, ft.
B = length of bubbling section, ft.
g_c = conversion constant = 32.2
r_h = mean hydraulic radius, ft. $= \dfrac{bL_o}{b + 2L_o}$

The values of f' were calculated from the experimental data and correlated as a function of a modified Reynolds number, $Re' = (r_h V_f \rho_f)/\mu_f$, where μ_f = viscosity of foam. In making the correlation it was assumed (1) that the average foam density was one-third the density of the normal liquid, (2) that the viscosity of the foam, μ_f, was one-third the true viscosity of the liquid, and (3) that L_o was equal to two times the hydrostatic head in the outlet calming section. Thus,

$$Re' = \frac{r_h V_f \rho_L}{\mu_L} \tag{16-18}$$

$$V_f = \frac{3Q_W}{\rho_L L_o b} \tag{16-19}$$

and

$$L_o = 2h_o \tag{16-20}$$

where ρ_L = normal density of liquid, lbs. per cu. ft.
μ_L = normal viscosity of liquid, lbs. per f.p.s.
h_o = hydrostatic head in outlet calming section, ft.

Klein found that the value of f' was a function of the exit-weir height relative to height of the slot and used an empirical relation to allow for this effect. He correlated $f'\left(\dfrac{h_{sp}}{h_o - h_{sp}}\right)^{3/5}$ as a function of Re', where h_{sp} = height of top of slot above plate.

The hydraulic gradient results of several investigators are plotted in Fig. 16-7. In view of the number of factors and assumptions involved, the correlation is reasonably good. Most of the results

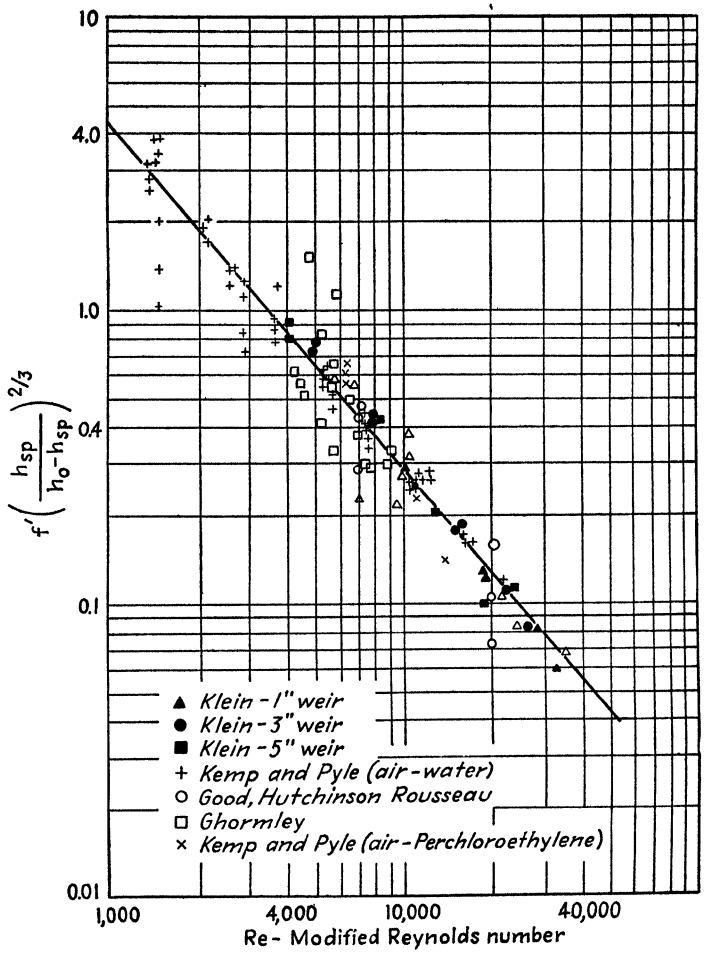


FIG. 16-7.

correlated were for essentially standard caps and plate arrangements, and the relation should be used with caution for plate layouts that differ significantly.

It will be noted for Fig. 16-7 that f' is essentially inversely proportional to the value of Re'. Combining this relationship with the fact

that for large plates $2L_e$ is small in comparison with b gives

$$F = k\left(\frac{Q_W}{b}\right)\left(\frac{1}{h_o^3}\right)\left(\frac{\mu_L}{\rho_L^2}\right)B \qquad (16\text{-}21)$$

This relation would indicate that the hydraulic gradient is directly proportional to the liquid flow rate per foot of plate width and to the length of the bubbling section. The outlet hydrostatic head is probably the most important factor determining the hydraulic gradient, and high outlet weirs should be an effective method of reducing the loss in head.

Equation (16-21) indicates that the gradient is approximately proportional to the liquid viscosity. The liquid viscosities studied ranged from that of water at room temperature to glycerine. Gardner (Ref. 10) studied the hydraulic gradient on a plate with tunnel caps using water at different temperatures and concluded that the liquid viscosity was not a factor. The plate design was unusual in that the liquid flow was across rather than along the tunnel caps. However, until additional data are available it is recommended that μ_L be taken equal to 0.00067 pounds per f.p.s. for all liquids of lower viscosity and equal to the actual viscosity for those having higher values.

Liquid Head. As shown in Fig. 16-6 the hydrostatic head in the bubbling section can be less than at the outlet weir. However, the liquid head above the top of the slots may be greater or less than the difference in the height of the outlet liquid and the top of the slots owing to the increased depth of the vapor-liquid mixture. The value of the liquid head calculated by Eq. (16-8) should be satisfactory for most cases, but the actual value may differ somewhat due to the aeration effects.

Plate Stability. The term "plate stability" has been used to describe the vapor and liquid distribution on a plate. A stable plate has been defined as one in which all the caps are handling vapor, although the quantity of vapor per cap may vary widely from one side of the plate to the other. The plate is stable in the sense that liquid is flowing across the plate and not by-passing by "dumping" through the cap risers, but the distribution of vapor may be quite poor.

The term "stable plate" does not differentiate between the various types of plate action and in this text the following terms will be used.

Uniform vapor distribution—will indicate the condition when each cap on the plate handles the same amount of vapor per unit time.

Active cap—will indicate that vapor is passing through the cap.

Inactive cap—will indicate that vapor is not passing through the cap.
Completely active plate—will indicate that all caps are active.
Partly active plate—will indicate that only part of the caps are active.
Plate dumping—will indicate that liquid is flowing to the plate below through some of the cap risers.

The distribution of the vapor among the various caps is a function of the pressure drops involved. The lateral pressure difference in the vapor space above a plate is usually small and, when this condition is true,

$$h_p = h_c + h_s + h_L = \text{constant}$$

Because h_L varies across the plate, $h_c + h_s$ must vary. Substituting the values from Eqs. (16-2) and (16-3) in the above equation gives

$$1.1V_R^2\left(\frac{\rho_V}{\rho_L}\right) + 0.12\frac{\gamma}{\rho_L} + K\left(h_o V_s \sqrt{\frac{\rho_V}{\rho_L - \rho_V}}\right)^{\frac{3}{5}} + h_L = h_p \quad (16\text{-}22)$$

and, for a given plate, this can be condensed to

$$k_1V^2 + k_2V^{\frac{3}{5}} + h_L = h_p - 0.12\frac{\gamma}{\rho_L} \quad (16\text{-}23)$$

The right-hand side of Eq. (16-23) would be constant for all parts of the plate on the basis of the assumptions made, and if the value of h_L varies across the plate, then the vapor flow per cap must vary. This relation indicates that a given cap will become inactive when h_L at that point is equal to $h_p - 0.12(\gamma/\rho_L)$; *i.e.*, when the liquid head over a slot becomes equal to the total pressure drop minus the pressure drop necessary to initiate bubbling against the surface tension.

Consider the case for the caps at the inlet side just inactive. By Eq. (16-23),

$$h_L^i = h_p - \frac{0.12\gamma}{\rho_L} \quad (16\text{-}24)$$

where h_L^i is the head of liquid above the slots at the inlet row of caps where the pressure drop is just sufficient to cause bubbling.

Assuming that the plate is rectangular and that the two terms involving velocity can be combined,

$$k_1V^2 + k_2V^{\frac{3}{5}} = k_3V^m \quad (16\text{-}25)$$

where V = vapor rate per row of caps perpendicular to direction of liquid flow
m = constant between $\frac{2}{3}$ and 2.0

Then, for any row of caps,

$$k_3 V^m = h_p - h_L - 0.12\frac{\gamma}{\rho_L} \tag{16-26}$$

Equation (16-26) could be used to evaluate the vapor distribution if the variation in h_L across the plate were known. It has already been shown that the variation of the hydrostatic head across the plate where the liquid is aerated is a function of the height above the plate at which the head is determined, and the relation for the plane corresponding to the top of the slots could vary significantly depending on the height of the slots relative to the hydrostatic heads in the inlet and outlet calming sections. However, as a first approximation it will be assumed that

$$h_L = \frac{(h_L^i - h_L^o)n}{N} + h_L^o \tag{16-27}$$

where h_L^i, h_L^o = liquid head above top of slots at inlet and outlet of plate
N = rows of caps on plate
n = number of rows of caps from outlet weir

When the inlet row of caps is just inactive, the condition for the outlet row of caps can be obtained by combining Eqs. (16-24) and (16-26), giving

$$k_3 V_o^m = h_L^i - h_L^o \tag{16-28}$$

where V_o is the vapor rate at the outlet row of caps. Thus the pressure drop due to vapor flow for the outlet row of caps is equal to the hydraulic gradient when the inlet row of caps is just inactive. Equations (16-27) and (16-28) can be combined to evaluate the pressure drop and the vapor distribution. In order to simplify the analysis, it is assumed that the number of rows of caps is large enough that conditions vary approximately continuously across the plate so that integration instead of stepwise summation can be employed. Thus, for the total vapor flow,

$$\begin{aligned} V_T &= -\int_N^o V\,dn = -\left(\frac{h_L^i - h_L^o}{k_3}\right)^{1/m} \int_N^o \left(1 - \frac{n}{N}\right)^{1/m} dn \\ &= \left(\frac{h_L^i - h_L^o}{k_3}\right)^{1/m} \frac{N}{(m+1)/m} \\ h_L^i - h_L^o &= \left(\frac{m+1}{m}\right)^m k_3 \left(\frac{V_T}{N}\right)^m \end{aligned} \tag{16-29}$$

where V_T equals total vapor through plate.

Combining this relation with Eq. (16-28) gives

$$k_3 V_o^m = \left(\frac{m+1}{m}\right)^m k_3 \left(\frac{V_T}{N}\right)^m \tag{16-30}$$

If there were uniform vapor distribution, V_o would equal (V_T/N), and the above relation indicates that the pressure drop is increased by the liquid gradient. Where the inlet row of caps is just inactive, the pressure drop due to velocity is greater by the factor $[(m+1)/m]^m$, and this term varies only from 1.84 to 2.25 for m from $\frac{2}{3}$ to 2. A value of 2.0 is within the accuracy of the assumption made.

The plate pressure drop when the inlet caps just become inactive, h_p'', is

$$h_p'' = k_3 V_o^m + h_L^o + 0.12\frac{\gamma}{\rho_L} \tag{16-31}$$

while, for a plate with uniform vapor distribution, it would be

$$h_p' = k_3 \left(\frac{V_T}{N}\right)^m + h_L^o + 0.12\frac{\gamma}{\rho_L} \tag{16-32}$$

and using the factor of 2.0 obtained for Eq. (16-30) gives

$$\begin{aligned} h_p'' &= 2k_3 \left(\frac{V_T}{N}\right)^m + h_L^o + 0.12\frac{\gamma}{\rho_L} \\ &= 2h_p' - \left(h_L^o + 0.12\frac{\gamma}{\rho_L}\right) \end{aligned}$$

In cases where the value of the bracketed term is small, the pressure drop for a plate with caps just becoming inactive is equal to approximately twice the pressure drop for the same plate with the same total vapor load uniformly distributed. If the last terms are not small, the pressure drop will be increased by a factor less than 2.0. This increased pressure drop is one of the objections to hydraulic gradient.

The relations given in Eqs. (16-24) to (16-32) were based on the condition that the inlet row of caps was just inactive. Similar analysis can be made for other conditions. Thus, all caps on a plate will be active if

$$\begin{aligned} h_p &> (h_L^i - h_L^o) + h_L^o + 0.12\frac{\gamma}{\rho_L} \\ &> h_L^i + 0.12\frac{\gamma}{\rho_L} \end{aligned} \tag{16-33}$$

For an active plate, with $k_3 V_o^m > h_L^i - h_L^o$, it is frequently desirable

to estimate the actual pressure drop in terms of that for a plate with uniform vapor distribution. By the same type of integration employed for Eq. (16-29), an approximation can be obtained for V_o and the value of h_p. Thus,

$$V_o = \frac{2(V_T/N)}{2 - \dfrac{h_L^i - h_L^o}{2\left(h_p' - h_L^o - 0.12\dfrac{\gamma}{\rho_L}\right)}} \tag{16-34}$$

and, by Eq. (16-23),

$$h_p = k_1 V_o^2 + k_2 V_o^{3/4} + h_L^o + 0.12\frac{\gamma}{\rho_L} \tag{16-35}$$

The term $\left(h_p' - h_L^o - 0.12\dfrac{\gamma}{\rho_L}\right)$ is equal to $k_1(V_T/N)^2 + k_2(V_T/N)^{3/4}$ and will be termed the velocity head for uniform vapor distribution, h_V. It is equal to the pressure drop due to the vapor flow in the riser, cap, and slots for a plate operating with a uniform velocity distribution.

For a plate with the inlet row of caps just inactive, $2h_V$ is equal to $(h_L^i - h_L^o)$ and Eq. (16-34) reduces to the previous criterion. When $(h_L^i - h_L^o)$ is small in comparison to $2h_V$, the equation gives $V_o = \dfrac{V_T}{N}$; *i.e.*, the vapor distribution is uniform. To use these equations, h_p' is calculated using V equal to (V_T/N) and $h_L = h_L^o$, and V_o is obtained from Eq. (16-34). The pressure drop for the plate is then calculated by Eq. (16-35).

The distribution of the vapor among the caps is important, and an approximation can be obtained by the following relation:

$$\frac{V_n}{V_o} = 1 - \frac{(h_L^i - h_L^o)(n/N)}{2h_V} \tag{16-36}$$

where V_n = vapor rate through inflow cap.

In order to obtain a velocity through the first row of caps equal to one-half that through the last row would require that $2h_V$ be twice the hydraulic gradient, and this would appear to be about the minimum ratio of velocities that should be considered for design purposes.

Plate Dumping. This condition can occur in extreme cases. When the upstream row of caps becomes inactive owing to an increase in the hydraulic gradient, the liquid level in the caps will be depressed below the top of the slots by an amount equal to the surface tension effect. If the gradient is increased further, the liquid level under the inactive caps rises and the pressure drop for the same rate of vapor flow

increases. Eventually a condition is reached where the liquid level under some of the inactive caps reaches the top of the riser and liquid spills to the plate below. In extreme cases, essentially all of the liquid flowing to a plate will dump down through the risers of the first few rows of caps, and very little will flow across the plate. Under these conditions, there is frequently an abrupt drop in liquid level on the plate between the section of inactive and active caps. The momentum of the vapor issuing from the active caps acts as dam for the liquid giving a "Red Sea" effect. Plate dumping is undesirable because with the usual column, with liquid flowing in opposite directions on successive plates, the liquid that spills through the risers by-passes the vapor on two plates.

Equations for the condition of plate dumping, similar to those for inactive caps, can be derived but, because it is an undesirable condition, it is better to control conditions such that all the caps are active. This will ensure against plate dumping. Plate dumping conditions in a large commercial tower have been described by Harrington *et al.* (Ref. 15).

General Design Considerations. It is usually desirable to have a bubble plate that gives (1) a low pressure drop and (2) a reasonably uniform vapor distribution. These two conditions are partly incompatible because a high pressure drop usually gives more uniform vapor distribution.

The vapor distribution relation of Eq. (16-36) indicates that the two main factors involved in obtaining a low variation in (V/V_o) across the plate are (1) low value of the hydraulic gradient and (2) a high value of h_V. Equation (16-16) shows that a low liquid gradient will be obtained for a given liquid flow rate by increasing h_o, or decreasing N.

Increasing the liquid depth should be very effective in lowering the gradient due to the increase in r_h and the decrease in V_f. A deep liquid level above the top of the caps is not desirable because it allows surges and wave action to occur. Raising the caps to allow liquid flow below the skirts is probably one of the most effective ways of reducing the hydraulic gradient. It does introduce the possibility that part of the liquid will cross the plate without intimate contact with the vapor. This condition would be most serious when the column is operating at reduced capacity. This method has the advantage that it reduces the gradient without increasing the pressure drop.

The space above the caps should be as unobstructed as possible to allow free passage of the liquid. Hold-down bars for the caps or other mechanical devices should be arranged in the direction of liquid flow.

Decreasing the value of N is a common method of improving vapor distribution, and this result is obtained by the use of split plates or multiple downspouts. This shortened path may be accomplished by having the inlet downspout on one plate in the center and the exit downspouts placed uniformly around the circumference (Fig. 16-4*C*). Thus, the liquid flows out radially and crosses only half of the plate. On the next plate below, the liquid would flow radially into the center. Other designs bring the liquid in at opposite sides and flow across half the tower to central weirs that extend across the tower perpendicular to the direction of flow (Fig. 16-4*F*). On the plate below, the liquid flow is outward. This latter method can be arranged to give any fractional distance across to plate desired, such as $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, or $\frac{1}{5}$.

These arrangements tend to decrease the hydraulic gradient, but they may lower the plate efficiency by reducing the cross flow effect, and they offer difficulties in properly proportioning the overflow between the different sections.

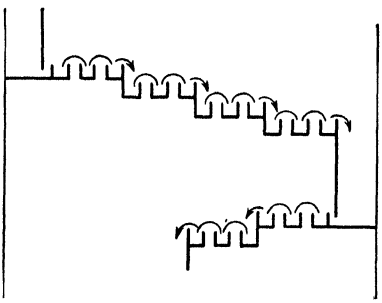


FIG. 16-8. Cascade plate.

Another arrangement that attempts to obtain complete cross flow, but reduced hydraulic gradient, is the staggered plate illustrated in Fig. 16-8. In this case, the plate is broken up into narrow segments, each with its own overflow weir. If the segments are narrow and the weirs are all adjusted to the proper height, the level at the caps can be kept uniform. The plate also has the advantage of complete cross flow. The main difficulty is the constructional complexity.

Increasing the value of h_V by increasing the pressure drop will be effective in improving vapor distribution. The use of excessive pressure drops to obtain this result is not desirable, although it may be the simplest method of correcting a column that has already been built. In this latter case, some of the caps can be removed, or constrictions can be placed in the risers to increase the pressure drop. This increase in pressure drop increases the possibility of flooding the column by liquid backing up the down pipes. Good original design should give low pressure drop and good vapor distribution.

Entrainment. Entrainment is the carrying of the liquid from one plate to the plate above by the flow of the vapor. It is usually defined

as the weight of liquid entrained per weight of vapor. Entrainment is undesirable, since it reduces plate efficiency by tending to destroy the countercurrent action of the tower, and it also may affect the distillate adversely from the standpoint of color or other nonvolatile impurities.

The entrainment of the liquid is due to two main causes: (1) the carrying of liquid droplets due to the mass velocity of the gas and (2) the splashing of the liquid on the plate. These depend on the slot-vapor velocity, the superficial column velocity, and the plate spacing.

Several investigators have published quantitative data on the amount of entrainment in bubble-plate columns. Most of their investigations have been on systems involving air and water.

The data of Volante (Ref. 36) are given in Fig. 16-9 where the entrainment, expressed as pounds of liquid per pound of vapor, is plotted as a function of the superficial velocity, V_c, in feet per second, multiplied by the square root of the vapor density in pounds per cubic foot. The entrainment increases rapidly with the vapor throughput and with a decrease in plate spacing. An entrainment of 0.01 lb of liquid per pound of vapor does not seriously lower the plate efficiency (see page 454), although it may give contamination. The superficial vapor velocity for these data is lower than commercial practice, and values of the abscissa of 0.3 and 0.7 would be more comparable. Other data are given in Fig. 16-10. The curves labeled *A* are based on the data of Peavy and Baker (Ref. 26) for the entrainment in an 18-in.-diameter column with ten 3-in.-diameter caps per plate. They investigated the entrainment when distilling an alcohol-water mixture for plate spacings of 12 and 18 in.

Curves *B* are based on the air-water results of Sherwood and Jenny (Ref. 31). The tower contained two plates and was 18 in. in diameter. Four-inch caps were employed having 33 notched-type slots. The slots were $\frac{3}{4}$ in. high and tapered from $\frac{3}{16}$ in. at the bottom to $\frac{1}{8}$ in. at the top.

Holbrook and Baker (Ref. 16) studied entrainment in an 8-in. bubble-plate column using steam and water. Curves *C* are based on a portion of their data. They conclude that the plate spacing and vapor velocity were the main factors in determining the amount of entrainment and that the amount of liquid flow and slot-vapor velocity were of less importance.

Curve *E* is based on the data of Ashraf, Cubbage, and Huntington (Ref. 1) for the entrainment in a 7- by 30-ft. commercial absorber. The tower contained 10 trays, 22 in. apart. The tower was operating

on a gas oil–natural gas system at 45 p.s.i.a. The investigators obtained a maximum entrainment of 0.0017 at a mass velocity of 23.4 lb. per min. per sq. ft.

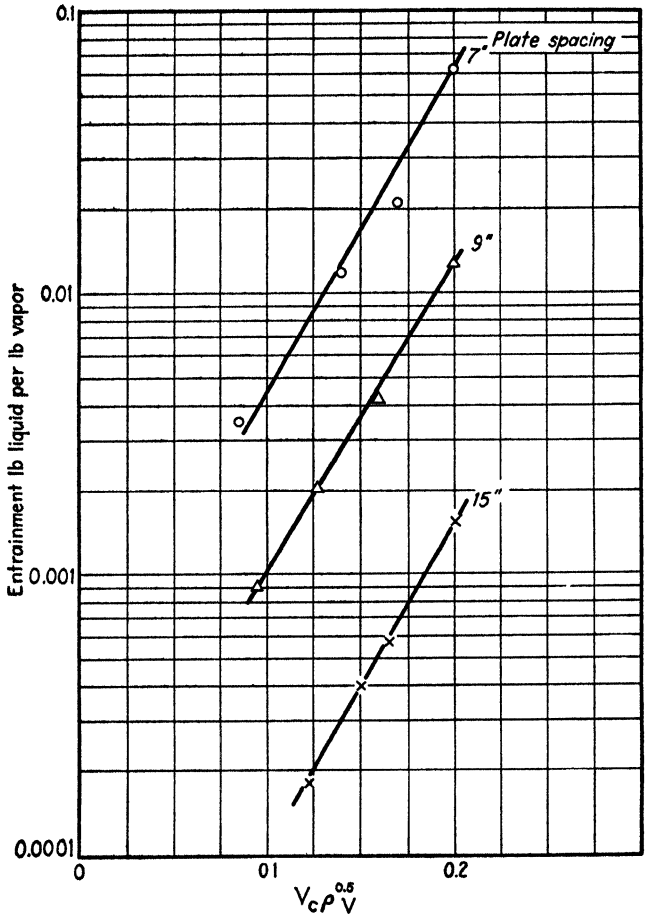


FIG. 16-9. Entrainment of water by air.

Entrainment separators and baffles have been suggested, and tests of various arrangements have shown that they are effective in reducing the amount of liquid carried by the vapor, but they have not been used to any extent in industrial rectifying towers.

Plate Spacing. Rectifying columns are built with the plates spaced as close as 6 in. to as much as 4 to 6 ft. There are a numbersr of facto

that influence this spacing, such as the proper flow of vapor and liquid in the column and the necessity of a man working between the plates.

To obtain the proper flow of liquid down the column, it is essential

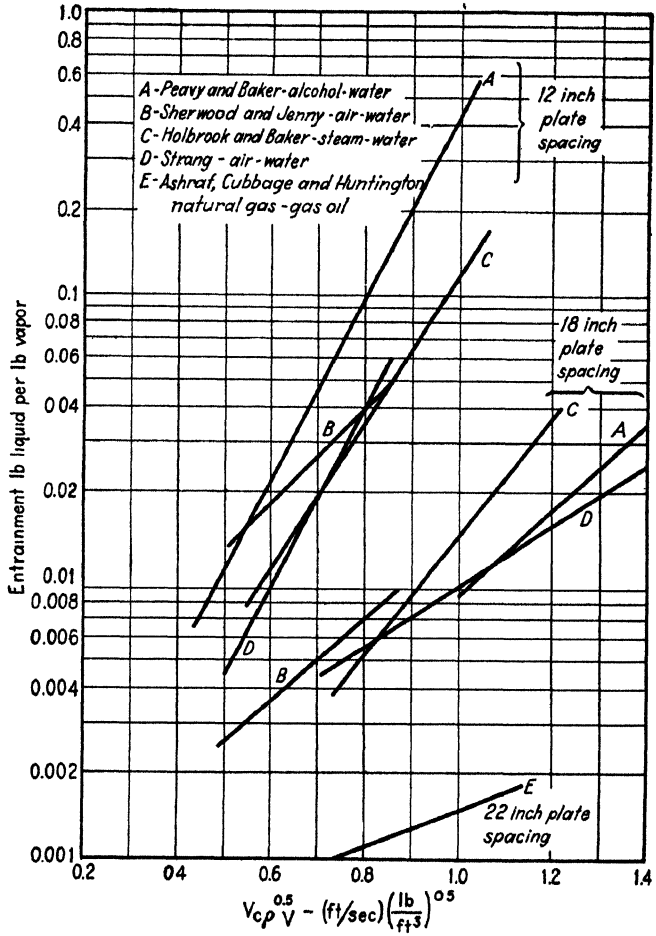
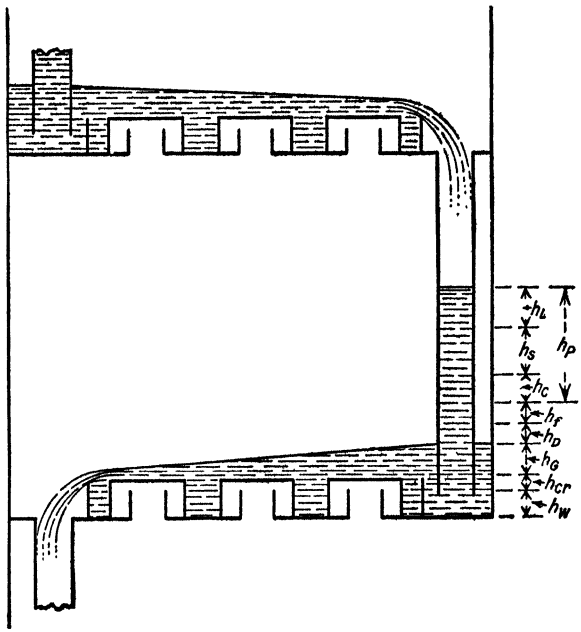


FIG. 16-10. Entrainment in bubble-cap plate columns.

that there be sufficient liquid head in the down pipes. Figure 16-11 shows schematically the liquid head in the down pipes and its causes. The plate spacing must be great enough to allow for the sum of these heads plus some extra height to handle short periods of excess flow. Values of h_p normally range from 2 to 4 in. of fluid; the various liquid heads on the plate ($h_w + h_{cr} + h_d$) amount to 3 to 4 in. A plate

spacing of 6 in. leaves little margin of safety and requires the use of low liquid heads on the plate and low vapor velocities to give low pressure drop and reasonable entrainment. A plate spacing of 12 to 24 in. would appear to be more feasible.

In addition to the items included in Fig. 16-11, there are the factors of foaming and cross flow of the vapor. Foaming of the liquid may be



h_w = height of exit weir
h_{cr} = height of crest on weir
h_G = liquid gradient
h_D = reversal loss in down pipe
h_f = friction in down pipe
h_c = pressure drop through riser and inside cap
h_s = pressure drop through slot
h_L = liquid head above slot
h_p = pressure drop through plate

FIG. 16-11. Schematic drawing of the liquid heads in a bubble-plate column.

so great that it extends from one plate to the next and results in high pressure drop and entrainment, but it is usually not that serious. However, a relatively small amount of foam may cause difficulties by filling the upper part of the down pipe and hindering the liquid flow. In many cases, foam blocking the down pipes is the limiting factor in column capacity. The foam is produced largely by the vapor on the plate, and its plugging effect in the down pipes can be reduced by including a short calming section before the down pipes or by baffles

that will hold the foam back on the plate and prevent it from flowing into the down pipes. If relatively stable foams are produced, it may be necessary to add some foam-breaking agent to the column. Experimental data indicate that the average density of the liquid and entrained vapor mixture is about one-half that of the liquid itself. For design purposes, it is therefore desirable to have a downspout height equal to approximately twice the value of the calculated liquid head.

Vapor flow across the column in the vapor space results from the nonuniform vapor distribution and from the usual reverse direction of liquid flow on succeeding plates. On a given plate ⅔ to ¾ of the total vapor may flow up the downstream half of the plate. This necessitates from ⅓ to ½ of the vapor flowing across the center of the plate to enter the other half of the plate above. Using the factor of ½, for purposes of illustration,

$$V_{CF}H_S D = \frac{V_c}{2}\frac{\pi D^2}{4} \tag{16-37}$$

where V_{CF} = cross-flow velocity
V_c = superficial velocity
H_S = free clearance between plates
D = column diameter

$$V_{CF} = \frac{\pi}{8}\frac{D}{H_S}V_c \tag{16-38}$$

In small-diameter columns, D/H_S is usually so small that the effect of cross flow is negligible, but in large columns it may become so great that the kinetic head equivalent to V_{CF} may be significant in terms of liquid head. Under these conditions, the pressure in the vapor space is not constant across the cross section, and its variation is such that it forces an increase in the hydraulic gradient. In order to make H_S as large as possible, any beams or projection on the bottom of a plate should be positioned to aid the vapor cross flow. Good vapor distribution on the plate will eliminate the effect of vapor cross flow.

An effect equivalent to the action of vapor cross flow is frequently obtained when the vapor is introduced through the side of the fractionating column. For example, the vapor from the reboiler is normally introduced into the side of the column near the bottom. If this vapor pipe terminates at the column wall, the kinetic energy of the vapor may be so great that it will cause a high impact pressure on the opposite side of the column. This type of action can result in very

poor vapor distribution for plates up the column, and some type of distributor should be employed. These frequently take the form of baffles which serve to direct the vapor over the whole cross section.

Allowable Vapor Velocity. A factor closely related to plate spacing is the allowable superficial vapor velocity that can be employed. The limiting factor can be either the liquid-handling capacity of the down pipes or the loss of rectification efficiency due to entrainment. The limiting capacity in the first case is calculated on the basis of the pres-

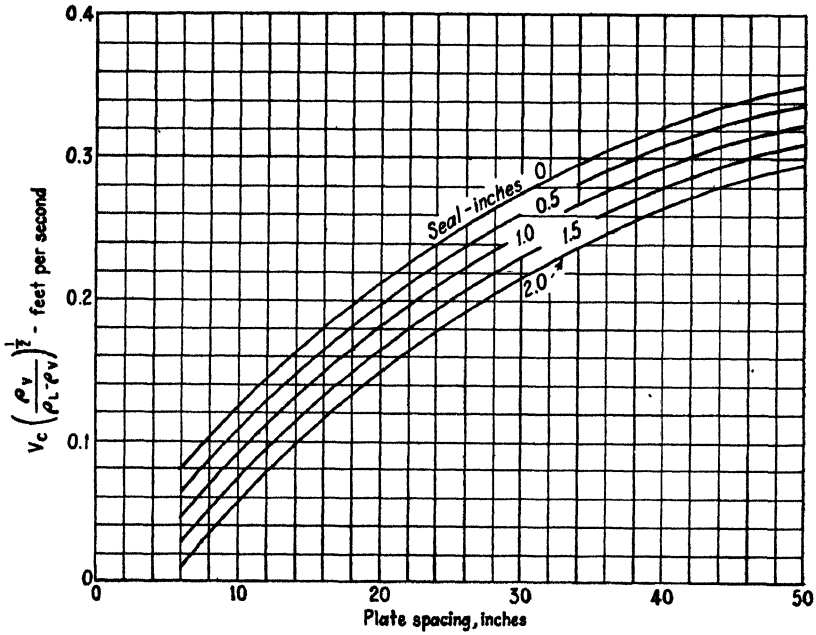


FIG. 16-12. Allowable superficial velocity.

sure drops and the liquid heads as outlined in the preceding sections. For the capacity limited by entrainment, correlations have been presented by Souders and Brown (Ref. 33) and Peavy and Baker (Ref. 26). Their results plus other data have been used to construct Fig. 16-12. The superficial vapor velocity, V_c, in feet per second multiplied by the square root of the density ratio is plotted as a function of the plate spacing, taken as the distance from the liquid surface to the plate above. Lines for different values of liquid seals above the top of the slots are given. High liquid levels above the slots give increased splashing and entrainment. The values given by this figure are reasonable design factors for most cases.

Plate Layout. A large number of types of bubble caps have been employed, but in most cases circular caps 4 to 6 in. in diameter are used. The slots are usually rectangular, although triangular and trapezoidal shapes are also employed. In some cases, the slots have been cut through the caps shell tangentially, but in the majority of cases they are cut radially. Tunnel caps are employed in some cases, but long caps of this type are sensitive to hydraulic gradient because the corrective action of the pressure drop through the risers is less effective. Hexagonal caps have been used but do not appear to have any advantage over circular ones.

Caps are usually arranged on triangular centers, and they are most commonly placed so that the liquid flow is at right angles to the rows of caps. This requires the liquid to follow a staggered path across the plate, and it has been assumed that this gave good contact of the liquid with the vapor.

Small-diameter caps can give more slot area and more free space for liquid flow than large caps. Caps larger than 6 in. in diameter are seldom employed and, except in small laboratory columns, caps less than 3 in. are not used because of the mechanical problem of handling the large number of them needed even for plates of moderate diameter. With the usual cap design and plate layout, the ratio of total slot area to superficial area generally falls between 0.1 to 0.2.

The caps should not be placed too near the weirs or walls. A clearance of 2 to 3 in. between the caps and the weirs and 1 to 2 in. at the walls is usually adequate. Clearances of 1 to 2 in. between caps are employed; *i.e.*, 4-in.-diameter caps might be placed with centers at the corners of equilateral triangles with sides 5½ to 6 in.

OTHER TYPES OF PLATES

Bubble-cap plates are the most common plate type of contacting device, but other arrangements are used. Perforated or sieve plates are effective vapor-liquid contacting devices and are frequently used for liquids containing suspended solids, such as the beer mashes in alcohol production. At their rated capacity, their efficiency is equal to that of bubble-cap plates, but they have two disadvantages that have limited their utility. (1) Because the pressure drop through the openings of the perforated plate is proportional to the square of the vapor velocity, it varies more rapidly with changes of vapor rate than a bubble-cap plate, and this reduces its flexibility. (2) The liquid on the plate can dump if the vapor rate is momentarily stopped. Various arrangements have been proposed to make the opening of the perfora-

tions vary with the vapor in a manner similar to the slot action of a bubble cap, but their use has been limited.

The design problems of the weirs and downflow pipes for perforated plates are the same as those for bubble-cap plates. However, the pressure drop due to vapor flow through the perforation will be considerably different than for a bubble cap. The small holes behave like a submerged orifice, but their cross section will not vary with the vapor rate in a manner similar to the slot action of a cap. For the pressure drop through these perforations, the following equation is suggested,

$$h_\pi = 0.04 \frac{\gamma}{d\rho_L} + \frac{\rho_V}{\rho_L} V_\pi^2 \qquad (16\text{-}39)$$

where h_π = pressure drop through perforation, in. of liquid
γ = surface tension, dynes per cm.
ρ_V = vapor density, lb. per cu. ft.
ρ_L = liquid density, lb. per cu. ft.
V_π = velocity based on total perforation area, f.p.s.
d = diameter of perforation, in.

The total pressure drop across the plate will be equal to h_π plus the liquid head on the plate. The problem of calculating the liquid head is similar to that for a bubble-cap plate, and the actual depth at the exit weir is a good approximation in most cases. The hydraulic gradient would increase the liquid head, but the aeration effect would reduce it.

The allowable vapor velocities for perforated plates should be comparable to those for bubble-plate trays, and Fig. 16-12 should give suitable design values. Perforations from 0.1 to 0.5 in. are employed, and they are usually placed on triangular centers spaced such that the total area of the openings is 0.10 to 0.15 times the tower cross-sectional area. The larger openings have more of a tendency to by-pass liquid and give plate dumping but are less likely to become plugged. Except for the reduction of liquid head due to aeration, dumping should occur when h_π for the downstream row of perforations is equal to the hydraulic gradient. Actually the dumping will occur before the gradient is this great, owing to aeration effects and surges.

Spray-type plates have been described for low-pressure operations. In order to obtain high rates of mass transfer, the liquid is collected periodically and resprayed. Kraft (Ref. 21) has described shower-type trays in which the liquid is allowed to rain down from one plate to the next through small perforations, and the vapor flows across the shower but does not bubble through the liquid. These plates are reported to give pressure drops of 0.75 mm. Hg per plate at practical operating

rates. This is about one-half the pressure drop of the best bubble-cap plates. Disk and doughnut-type plates have also been used, and these also pass the vapor through a liquid shower.

PLATE DESIGN EXAMPLE

As an example of the use of the methods outlined in this chapter, consider the design of a bubble plate for a column to handle a benzene-toluene mixture. For the separation 20 actual plates will be used, and the plate design will be based on the bottom plate. This plate will handle essentially pure toluene, and the liquid and vapor rates will be 480 and 400 lb. mols per hr., respectively.

Data and Notes.

The pressure at the bottom plate will be 2.5 p.s.i.g.
Use chord overflow weir.
Cap, 4 in. O.D. by 3½ I.D. by 4$\frac{3}{16}$ in. high cast iron.
Caps placed on equilateral triangle centers of 6 in., 3-in. minimum clearance at weirs and 1-in. minimum clearance at walls.
Slots, 33 per cap, ⅛ by 1½ in.
Minimum seal on slots at no flow, ¼ in.
Minimum liquid depth at no flow, 2 in.
Minimum down-pipe seal, 1¼ in.
Plate will have cross flow with only one down pipe per plate.
Plate spacing, 24 in.

Solution. The seal on the caps at no flow is ¼ in., and the head on the weir at operating conditions will be taken as 1.0 in., making a total liquid seal at the outlet of 1¼ in. A hydraulic gradient of 0.1 in. is assumed, making the inlet seal 1.35 in. An average seal of 1.3 in. will be used with Fig. 16-12, to determine the allowable superficial velocity. The plates are spaced 24 in. apart, but this will be reduced to 20.5 in. to allow for liquid level and plate thickness.

From Fig. 16-12,

$$V\left(\frac{\rho_V}{\rho_L - \rho_V}\right)^{1/2} = 0.164$$

At 2.5 p.s.i.g. the boiling point of toluene is 694°R., and $\rho_L = 52.8$ lb. per cu. ft. Assuming the perfect gas laws apply to toluene vapor,

$$\rho_V = \frac{92}{359(694/492)(14.7/17.2)} = 0.212 \text{ lb. per cu. ft.}$$

Allowable vapor velocity,

$$V = 0.164\left(\frac{52.8}{0.212}\right)^{1/2} = 2.6 \text{ f.p.s.}$$

$$\text{Vapor rate} = \frac{400 \times 92}{0.212(3{,}600)} = 48.2 \text{ cu. ft. per sec.}$$

$$\text{Net area of plate} = \frac{48.2}{2.6} = 18.6 \text{ sq ft.}$$

Allow 2 sq. ft. for the two down-pipe areas

$$D = \sqrt{\frac{20.6}{0.7854}} = 5.2 \text{ ft.}$$

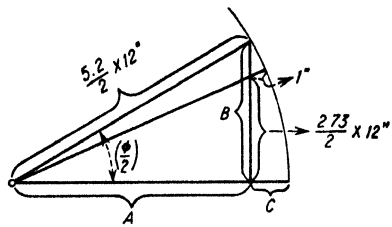
Weir Length. By Eq. (16-12),

$$1.0 = 5.4\left[\frac{480(92)}{53(3{,}600)L}\right]^{2/3}$$

and, using a factor of 0.96 from Fig. 16-5,

$$L = [5.4(0.96)]^{1.5}\frac{480(92)}{53(3{,}600)}$$
$$= 2.73 \text{ ft.}$$

In the text it was suggested that the weir within a weir head of the wall should be neglected, and the actual weir length will be longer than just calculated. The following sketch shows these conditions:



$$A^2 + \left(\frac{2.73}{2} \times 12\right)^2 = \left(\frac{5.2}{2} \times 12 - 1\right)^2$$
$$A^2 + 26.8 = 912$$
$$A = 25.8 \text{ in.}$$
$$C = 5.4 \text{ in.}$$
$$A^2 + B^2 = \left(\frac{5.2}{2} \times 12\right)^2 = 974$$
$$B^2 = 974 - 644$$
$$B = 18.2 \text{ in.}$$
$$\text{Length of weir} = 2\left(\frac{18.2}{12}\right) = 3.03 \text{ ft.}$$

Let ϕ = angle subtended by weir chord

$$\sin\frac{\phi}{2} = \frac{3.03}{5.2} = 0.582$$
$$\phi = 71.2°$$
$$\text{Area of downcomer} = \frac{\pi}{4}(5.2)^2\left(\frac{71.2}{360}\right) - \frac{3.03(5.2/2)\cos(\phi/2)}{2}$$
$$= 1.0 \text{ sq. ft.}$$

Total area of downcomers on each side of plate equals 2 sq. ft., which is the assumed value.

A schematic plate layout is shown in Fig. 16-13. The center line of the row of caps nearest the weir is 25.8 − 5 in. from the center with a length of 46.6 in. The number of caps in this row will be 46.6/6, or 7 caps. The distance between the inlet and outlet rows of caps is 41.6 in., and this will allow 9 rowsof caps with 1.6 in. over which will be used for the inlet weir. The total number of caps is 77.

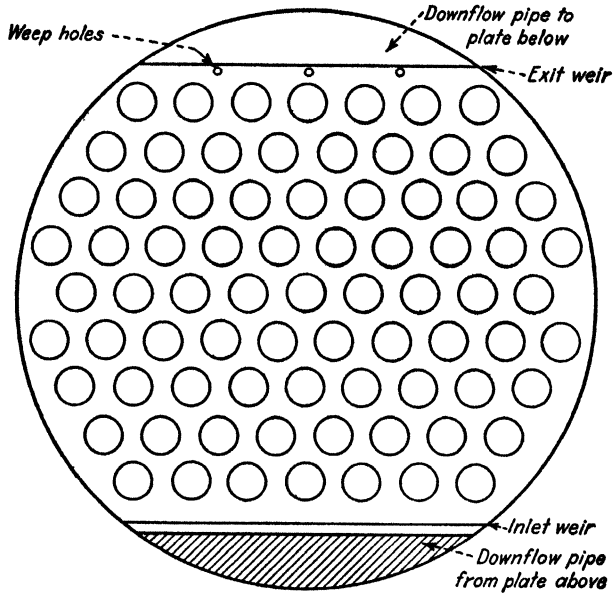


FIG. 16-13. Layout of bubble-cap plate.

Hydraulic Gradient. The section with the bubble caps approximates a rectangular section, and Eq. (16-16) will be employed for the calculation of the hydraulic gradient.

The average foam velocity by Eq. (16-19) is

$$V_f = \frac{3(480)(92)}{3600(53)(0.5)(4.6)} = 0.30 \text{ f.p.s.}$$

The value of $b = 4.6$ feet was taken as the average of the diameter of the column and the width at the first row of caps.

By Eq. (16-17),

$$r_h = \frac{4.6(0.5)}{4.6 + 1} = 0.41 \text{ ft.}$$

and from Eq. (16-18), using the viscosity of the liquid equal to 0.00067 (see p. 418),

$$Re' = \frac{0.41(0.3)(53)}{0.00067} = 9730$$

Using this value with Fig. 16-7 gives

$$f'\left(\frac{h_{sp}}{h_o - h_{sp}}\right)^{2/3} = 0.3$$

$$f' = \left(\frac{3 - 1.75}{1.75}\right)^{2/3}(0.3) = 0.24$$

The loss in head is calculated from Eq. (16-16)

$$F = \frac{(0.24)(0.30)^2(3.7)}{32.2(0.41)}$$
$$= 0.0061 \text{ ft. of toluene}$$
$$= 0.073 \text{ in. of toluene}$$
$$= 0.062 \text{ in. of water}$$

The gradient for this plate is somewhat smaller than the assumed value of 0.1 in. of toluene. However, the difference is not large and no corrections will be made.

Pressure Drop through Caps.

1. Assume uniform vapor distribution with no gradient,

$$\text{Cu. ft. vapor per second per cap} = \frac{48.2}{77} = 0.626$$

a. Pressure drop through risers and inside cap

$$V_R = \frac{0.626(144)}{2.35^2(0.7854)} = 20.8$$

By Eq. (16-2),

$$h_c = 1.1(20.8)^2\left(\frac{0.212}{53}\right)$$
$$= 1.9 \text{ in. of toluene}$$

b. Pressure drop through slots

At 694°R., γ for toluene = 18 dynes/cm.

$$V_s = \frac{0.626(144)}{6.2} = 14.5$$

By Eq. (16-4),

$$K = 1 - \left[\frac{20.6}{2(14.5)}\right]^2 = 0.5$$

This compares with a value of 0.7 for a slightly different 4-in. cap given on page 407. To be conservative use 0.7.
From Eq. (16-3),

$$h_s = 0.12(18\tfrac{2}{3}53) + 0.7\left[1.5(14.5)\sqrt{\frac{0.212}{53 - 0.2}}\right]^{2/3}$$
$$= 0.04 + 0.86$$
$$= 0.90 \text{ in. of toluene}$$

c. Liquid head above slots = 1.25 in. of toluene.

d. Pressure drop for ideal plate with no liquid gradient,

$$h_p' = 1.9 + 0.90 + 1.25$$
$$= 4.05 \text{ in. of toluene}$$

2. Pressure drop for actual plate,

$$h_V = 4.05 - 0.04 - 1.25$$
$$= 2.76 \text{ in. of toluene}$$

The value of the gradient is so small relative to h_V that Eq. (16-34) indicates essentially uniform vapor distribution, and the pressure drop will be the same as calculated for an ideal plate.

Height of Liquid in Down Pipe.

1. Loss in head at bottom of downpipe. Assume the chord down pipe comes within 1.0 in. of plate. For Eq. (16-13),

$$V_D = \frac{0.231}{\frac{1}{12}(3)} = 0.92 \text{ f.p.s.}$$
$$h_D = 0.5(0.92)^2$$
$$= 0.42 \text{ in. of toluene}$$

2. Friction loss in down pipe. Because the velocity in the down pipe is only 0.23 f.p.s., the friction will be negligible.

3. Head of liquid in down pipe above plate level (see Fig. 16-11).

$$h_{Dp} = 2.0 + 1.0 + 0.07 + 0.42 + 0 + 4.05$$
$$= 7.54 \text{ in. of toluene}$$

The plate spacing of 24 in. should be adequate unless foaming is excessive.

General Consideration. The general arrangement of the plate is shown in Fig 16-13. Weep holes have been added to allow the column to drain when shut down. Three $\frac{3}{8}$-in. weep holes were placed in the plate before the exit weir. These should allow the column to drain in about 5 hr. At rated load, the weep holes handle about 2.5 per cent of the total liquid, but even this amount does not short-circuit because it flows down on the proper side. These weep holes can be placed in the inlet and outlet weirs instead of the plate.

PACKED TOWERS

Pressure Drop. Although the pressure drop through packed towers is usually small at atmospheric pressure, it may become a limiting factor in vacuum distillations.

Chilton and Colburn (Ref. 4) have published a method for predicting such pressure drop for solid packings, based on the Fanning equation for friction in pipes. They modify the friction equation to

$$\Delta p = \frac{2fA_w A_L \rho_V u^2 h}{gd^*} \qquad (16\text{-}40)$$

where Δp = pressure drop in height h
A_w = correction factor for wall effect
A_L = correction factor for wetting of the packing, by the liquid
ρ_V = density of the vapor
g = conversion factor for consistent units
u = superficial gas velocity, *i.e.*, linear gas velocity based on the total cross section of the tower
d^* = size of packing, nominal
μ = viscosity of vapor
f = function of $(d^*u\rho/\mu)$ as given in Eqs. (16-41) and (16-42)

Chilton and Colburn gave a plot of f as a function of the Reynolds number $(d^*u\rho/\mu)$. The data of this plot may be approximated by the following equations:

For $(d^*u\rho/\mu)$ less than 40, use

$$f = \frac{850}{d^*u\rho/\mu} \tag{16-41}$$

For $(d^*u\rho/\mu)$ greater than 40,

$$f = \frac{38}{(d^*u\rho/\mu)^{0.15}} \tag{16-42}$$

All these equations are dimensionally sound, and any consistent set of units may be used. The following table contains values of the factor A_w:

Packing diameter / Tower diameter	A_w	
	$\left(\frac{d^*u\rho}{\mu}\right) < 40$	$\left(\frac{d^*u\rho}{\mu}\right) > 40$
0	1.0	1 0
0.1	0.83	0 72
0.2	0.74	0.65
0.3	0 71	0.57

The correction for the wetting of the packing, A_L, is 1.0 for dry packing and is greater than 1.0 for wet packing because the liquid decreases the free volume. The factor is greater than 1.0 for wet packing even without liquid flow, and it increases with the liquid rate. As an approximation, the following relation is suggested for A_L for wet

packing,

$$A_L = 1.4 + 0.0005Y \tag{16-43}$$

where Y = liquid rate, lb. per hr. per sq. ft.
Liquid rates above 5,000 to 10,000 lb. per hr. per sq. ft. give values of A_L so large that the tower may flood.

The pressure drop with hollow packings is less than given by the equation for solid packings. The data on this effect are not very conclusive as to absolute magnitude but do indicate that, for hollow packing, the smaller the packing size the larger the pressure drop. For a detailed discussion of this factor, the reader is referred to Sherwood's summary (Ref. 30).

Allowable Gas and Liquor Velocities. The capacity of packed towers is limited by the tower's becoming flooded with liquid. The flooding can be caused by increasing either the liquid or the gas flow. This flooding is a result of the pressure drop through the tower exceeding the gravity head of the liquid flowing down.

These pressure drops per foot of height are given by the modified Fanning equation:

$$\Delta p_G = \frac{f_G V_G^2 \rho_V}{2gm} \qquad \Delta p_L = \frac{f_L V_L^2 \rho_L}{2gm}$$

where f = proportionality factor, a function of $mu\rho/\mu$
V_G = actual linear gas velocity = u_G/FA_G, f.p.s.
V_L = actual linear liquid velocity = u_L/FA_L, f.p.s.
ρ = density, lb. per cu. ft.
g = conversion factor—32.2(lb. force)(ft.)/(lb. mass)(sec.^{2})
μ = viscosity, poises
F = fraction of tower that consists of voids[1]
S = surface of packing,[1] sq. ft. per cu. ft. of packing
m = hydraulic radius = free volume/contact area = F/S, ft.
A_G, A_L = fraction of free cross section occupied by gas and liquid, respectively
u = superficial velocity, f.p.s.

The flooding occurs when $\Delta p_L = \rho_L - \Delta p_G$ is a small fraction of Δp_G, since under such conditions a slight increase in the rate of flow of either stream or an uneven surge in the tower will increase A_L and decrease A_G, because of increased liquid holdup. This decrease in A_G will increase V_G and thereby Δp_G. If Δp_L is large relative to Δp_G, this

[1] For data on the values of S and F for various packings, the reader should consult Refs. 9 and 30 at the end of the chapter.

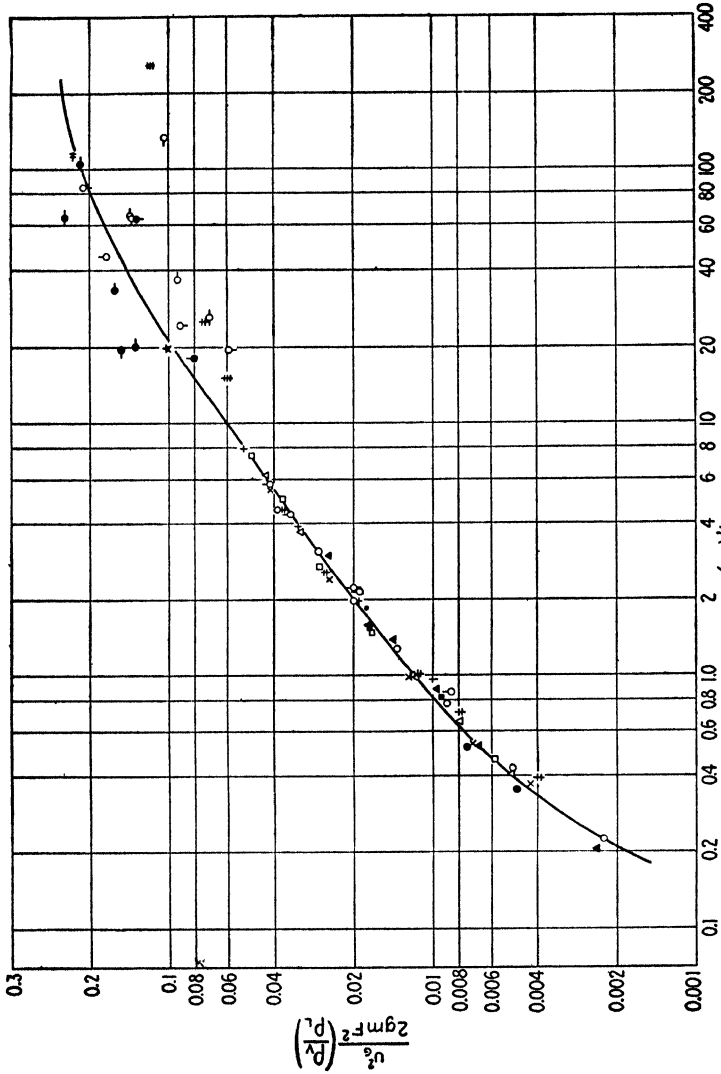


FIG. 16-14. Flooding velocities in packed towers.

increase in Δp_G will affect the liquid flow only slightly; however, if Δp_L is small compared to Δp_G, a small increase in Δp_G will make a large percentage decrease in Δp_L, causing the holdup to increase and the tower to flood.

Combining the pressure-drop equations,

$$\frac{A_G}{A_L} = \frac{A_G}{1 - A_G} = \sqrt{\frac{f_G u_G^2 \rho_V}{f_L u_L^2 \rho_L}} \sqrt{\frac{\rho_L - \Delta p_G}{\Delta p_G}}$$

Setting the ratio $(\rho_L - \Delta p_G)/\Delta p_G$ equal to b and noting that at flooding Δp_G becomes approximately equal to ρ_L modifies the previous equation to give

$$\frac{u_G^2 \rho_V}{2gm\rho_L F^2} = \frac{b(u_G/u_L)^2 \rho_V/\rho_L f_L}{[1 + b^{1/2}(u_G/u_L)(\rho_V f_G/\rho_L f_L)^{1/2}]^2} \tag{16-44}$$

At low values of $(u_G/u_L)^2 \rho_V/\rho_L$, the denominator of the right-hand side becomes 1, and the limiting gas velocity is a function of $(u_G/u_L)(\rho_V/\rho_L)$, the tower dimensions, and f_L, the latter term being chiefly a function of μ_L. It is interesting to note that in this region the gas viscosity is not a factor; but when the last term of the denominator is not negligible, the viscosity of the gas becomes a factor in the limiting gas velocity.

At very high values of this group, the right-hand side reduces to f_G.

TABLE 16-2

Packing	System	Reference
No. 19 aluminum jack chain	Heptane-methyl cyclohexane	8
1-in. Raschig rings	Air-water	23
1-in. Berl saddles	Air-water	23
8-mm. Raschig rings	Air-water	23
½-in. Raschig rings	H_2-water	32
½-in. Raschig rings	Air-water	32
½-in. Raschig rings	CO_2-water	32
½-in. Berl saddles	Air-water	32
½-in. Raschig rings	Air-methanol	32
½-in. Rachig rings	Air-(50% H_2O + 50% CH_3OH)	32
½-in. Raschig rings	Air-glycerin	32
½-in. Raschig rings	Water + butyric acid-air	32
7/32-in. carding teeth	Benzene-carbon tetrachloride	9
¼-in. bent carding teeth	Benzene-carbon tetrachloride	9
0.23- by 0.27-in. glass rings	Benzene-carbon tetrachloride	9
0.18-in. glass rings	Ethanol-water	17
0.47-in. glass rings	Quinoline (distillation at 10 mm. Hg abs.)	17

This would be the case when a very low liquid rate was employed and the gas occupied essentially the whole free cross section of the tower. For convenience in plotting, the right-hand side will be taken as a function of $(u_G/u_L)(\rho_V/\rho_L)^{1/2}/\mu_L^a$. The data of a number of investigators are correlated in this way in Fig. 16-14 using a value of $a = 0.21$. The systems involved are given in Table 16-2.

The data are seen to correlate well except at high values of the abscissa. This deviation may be due to the fact that the f_G factor in the denominator is neglected in the method of plotting of this figure.

Nomenclature

A_L = correction factor for liquid on packing in packed tower
A_u = area under skirt of caps for liquid flow
A_w = correction factor for wall effect in packed towers
B = length of bubbling section, ft.
b = width of plate, ft.
C = pressure recovery factor for orifice
D = inside diameter, ft.
d = diameter, in.
d^* = size of packing, nominal
F = loss in head from inlet to exit calming sections, ft.
f = friction factor for fluid flow
f' = friction factor
g,g_c = conversion constant = 32.2 [(ft.)(lb. force)]/[(sec.^{2}) (lb. mass)]
h = liquid depth above surface of plate
h_c = pressure drop through riser and undercap, in. of liquid
h_{cr} = height of liquid above top of weir, in.
h_D = pressure drop for reversal of flow at bottom of down pipe, in. of liquid
h_{Dp} = liquid level in down pipes above surface of plate, in.
h_H = kinetic head, in. of liquid
h_i = liquid depth above surface of plate at inlet weir
h_L = liquid depth above top of slots, in.
h_L^i = value of h_L at inlet row of caps
h_L^o = value of h_L at outlet row of caps
h_o = liquid depth above surface of plate at outlet weir, in.
h_s^* = slot height, in.
h_s^* = value of h_s for slots completely open
h_p = over-all pressure drop for plate, in. of liquid
h_p' = over-all pressure drop for uniform vapor distribution, in. of liquid
h_p'' = over-all pressure drop when inlet row of caps is just inactive, in. of liquid
H_s = free clearance between plates, ft.
h_s = pressure drop through slots, in. of liquid
h_{sp} = height of top of slot above surface of plate
h_V = velocity head for uniform vapor distribution, in. of liquid
h_w = height of weir above surface of plate
h_π = pressure drop through perforations, in. of liquid
K,k = constants

L = perimeter of weir, ft.
L_o = foam height, ft.
m = exponent
N = number of rows of caps from outlet to inlet weir
n = number of rows of caps, counting from the overflow weir
Q = liquid flow rate, cu. ft. per sec.
Q_W = liquid rate, lbs. per sec.
q = liquid flow rate, g.p.s.
$Re' = \frac{(r_h V_f \rho_f)}{\mu_f}$
r_h = mean hydraulic radius, ft. $= \frac{bL_o}{b + 2L_o}$
u = superficial velocity in packed tower, f.p.s.
u_G = superficial velocity of gas
u_L = superficial velocity of liquid
V = vapor flow rate
V_c = superficial vapor velocity, f.p.s.
V_{CF} = cross flow velocity, f.p.s.
V_D = maximum velocity at bottom of down pipe, f.p.s.
V_f = velocity of liquid in foam, f.p.s. $= Q_W(\rho_f L_o b)$
V_G = linear gas velocity in packed tower, f.p.s.
V_L = linear liquid velocity in packed tower, f.p.s.
V_o = liquid velocity in down pipe, f.p.s.
V_R = maximum velocity under cap, f.p.s.
V_s = slot velocity based on total slot area, f.p.s.
V_s^* = slot velocity for h_s equal to h_o^*
V_T = total vapor flow rate for plate
V_π = velocity based on total perforation area
γ = surface tension, dynes per cm.
ρ_f = density of foam, lbs. per cu. ft.
ρ_V = vapor density
ρ_L = liquid density
μ = viscosity
μ_f = viscosity of foam
μ_L = normal viscosity of liquid, lbs. per f.p.s.

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CHAPTER 17

FRACTIONATING COLUMN PERFORMANCE

The design calculations considered in the preceding chapters were based on theoretical plates. In order to complete the design, it is necessary to have the relationship between these idealized values and the actual performance of the contacting device. The vapor and liquid brought into contact with each other in the tower are not at equilibrium, and the rate of mass transfer determines the effectiveness of the unit. This chapter will consider the methods of predicting the effectiveness of the vapor-liquid contact for the various types of units.

PLATE-TYPE COLUMNS

Plate Efficiency Definitions and Relations. *Over-all Column Efficiency.* The relation between the performance of actual and theoretical plates is expressed as plate efficiencies. A number of different plate efficiencies have been proposed, but the two most commonly used are the "over-all column efficiency" which was proposed by Lewis (Ref. 20) and "plate" or "point" efficiencies suggested by Murphree (Ref. 24). The over-all column efficiency, E^o, is the number of theoretical plates necessary for a given separation divided by the number of actual plates required to perform the same separation; *i.e.*, it is the factor by which the number of theoretical plates is divided to give the actual number of plates. This efficiency has no fundamental mass-transfer basis, but it serves as an easily applied and valuable design factor and is therefore widely used.

Murphree Efficiencies. The Murphree efficiencies are based on more fundamental concepts than E^o, but even in this case the basic relations employed are more qualitative than quantitative. Murphree developed two cases: one employing vapor-phase relations and the other liquid-phase conditions. For the vapor-phase derivation he assumed that a bubble of vapor in rising through the liquid on a plate was in contact with a liquid of constant composition, and that the composition

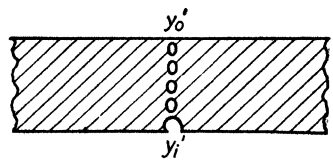


FIG. 17-1.

in the bubble changed continuously by mass transfer. Consider the bubbles shown in the simplified schematic diagram of Fig. 17-1. These bubbles enter with a composition y'_i pass up through a liquid of composition x, and leave with a composition y'_o. Using a simplified expression for the instantaneous mass transfer to one of the bubbles,

$$-G\,dy' = PK_Ga(y' - y_e)\,d\theta \tag{17-1}$$

where G = mols of gas in bubble
y' = mol fraction of component in bubble
y_e = vapor in equilibrium with liquid
P = total pressure
K_G = over-all mass-transfer coefficient, (mols)/(unit time) (unit pressure difference) (unit interfacial surface)
a = interfacial area of bubble
θ = contact time of bubble with liquid

Assuming G, P, y_e, and K_Ga are constant, this equation can be integrated to give

$$\frac{PK_Ga\theta}{G} = \ln\frac{y' - y_e}{y'_o - y_e} \tag{17-2}$$

Murphree applied the relation to the whole plate, assuming that conditions were the same at all points. In this case (G/θ) is replaced by the vapor rate, and a becomes the average total interfacial area of all the bubbles on a plate at any instant.

This equation can be rearranged to

$$E_{MV} = \frac{y'_i - y'_o}{y'_i - y_e} = 1 - e^{-m} \tag{17-3}$$

where $m = \dfrac{PK_Ga\theta}{G}$

In many cases there are considerable differences in the compositions of the liquids at various points on a plate, and the conditions assumed in the derivation are not satisfied for the whole plate. However, for convenience, the value of the Murphree plate efficiency is defined as

$$E^o_{MV} = \frac{y_i - y_o}{y_i - y^*_e} \tag{17-4}$$

where y_i, y_o = average composition of vapor entering and leaving plate, respectively
y^*_e = composition of vapor in equilibrium with liquid flowing to plate below

Equations (17-3) and (17-4) appear similar, but the former uses the values for a small region of the plate, while the latter uses average values for the various streams entering and leaving a plate. E°_{MV} is not equal to $1 - e^{-m}$.

The derivation of Eq. (17-3) should apply to a limited region of the plate, and this has been termed the Murphree point efficiency, E^{*}_{MV}. In this case

$$E^{*}_{MV} = \frac{y'_i - y'_o}{y'_i - y_e} \tag{17-5}$$

where y', y_o = vapor compositions entering and leaving the local region

y_e = vapor composition in equilibrium with the liquid in the local region

The Murphree plate efficiency is the integrated effect of all the Murphree point efficiencies on the plate.

The derivation of the Murphree equation is based on a very qualitative picture of the mass transfer. At low vapor rates individual bubbles are obtained, but a study of mass transfer for such systems indicates that it cannot be expressed as a simple rate equation involving a constant multiplied by a driving force in mol fraction units. The experimental data indicate that mass transfer is very rapid while the bubble is being formed and then is relatively slow while the bubble is rising through the liquid. At higher vapor rates channels are blown through the liquid, and a large quantity of spray is thrown up into the vapor space giving additional mass transfer. The simple rate Eq. (17-1) cannot be any more than a crude expression of the phenomena involved, and $K_G a$ must be a complicated function of a large number of variables including Δy and θ.

The value of E°, E°_{MV}, and E^{*}_{MV} are the most commonly used design factors for plate efficiencies. The over-all tower plate efficiency is simpler to apply than the Murphree efficiencies because only terminal conditions are required; whereas in the calculation of the Murphree plate efficiency, plate-to-plate compositions are required, and for the Murphree point efficiency, complete liquid- and vapor-composition traverses are required on each plate. However, the Murphree efficiencies are probably on a more fundamental basis than the over-all efficiencies.

By definition, a theoretical plate is one on which the average composition of the vapor leaving the plate is the equilibrium value for the liquid leaving the plate. If the vapor and liquid upon a plate were

completely mixed, it would be impossible to obtain better separation than that given by a theoretical plate. However, when there is a concentration gradient in the liquid across the plate, the average concentration of the more volatile component in the liquid on the plate may be appreciably greater than the concentration of the liquid leaving the plate; as a result of this greater concentration, the vapor actually leaving the plate may exceed the concentration of the vapor in equilibrium with the liquid leaving. It is thus possible for the concentration-gradient effect to give over-all and Murphree plate efficiencies greater than 100 per cent; but since such gradients do not apply to the Murphree point efficiency, this latter efficiency should never exceed 100 per cent. The theoretical effect of the concentration gradient has been studied by a number of investigators (Refs. 15, 19, 21). Three cases were considered by W. K. Lewis, Jr.: Case I, vapor completely mixed, liquid unmixed; Case II, vapors do not mix, and the overflows are arranged such that the liquid flows in the same direction on all plates; Case III, the vapor rises from plate to plate without mixing, and the liquid flows in the opposite direction on successive plates.

Lewis assumed that (1) E^*_{MV} was constant over all of the plate, (2) the equilibrium curve is a straight line over the concentration range involved, $y_e = Kx + b$, and (3) the liquid flows across the plate without mixing.

The results of this analysis for the three cases are given in Fig. 17-2 in which the ratio (E^o_{MV}/E^*_{MV}) is plotted as a function of E^*_{MV} and the ratio of the slope of equilibrium curve, K, to the slope of the operating line, (O/V). The slope of the equilibrium curve, K, should be the average slope, dy_e/dx, over the concentration region involved. These calculated values indicate that it should be possible to obtain high plate efficiencies by preventing the liquid from mixing. The usual bubble-cap plates probably fall between Cases I and III as far as the vapor is concerned, but they give considerable liquid mixing which would lower the value of (E^o_{MV}/E^*_{MV}) as compared to the values given by the plot. Case II has the possibility of giving higher plate efficiencies than the other two cases, but in practice it is difficult to arrange the downflow pipes such that the liquid flows in the same direction on all plates. The circumferential flow plate, Fig. 16-4*E*, gives essentially this type of flow, but it is not a desirable construction in most cases.

The relationship between the over-all column efficiency and E^o_{MV} can be derived in a similar manner and assuming

1. Constant O/V

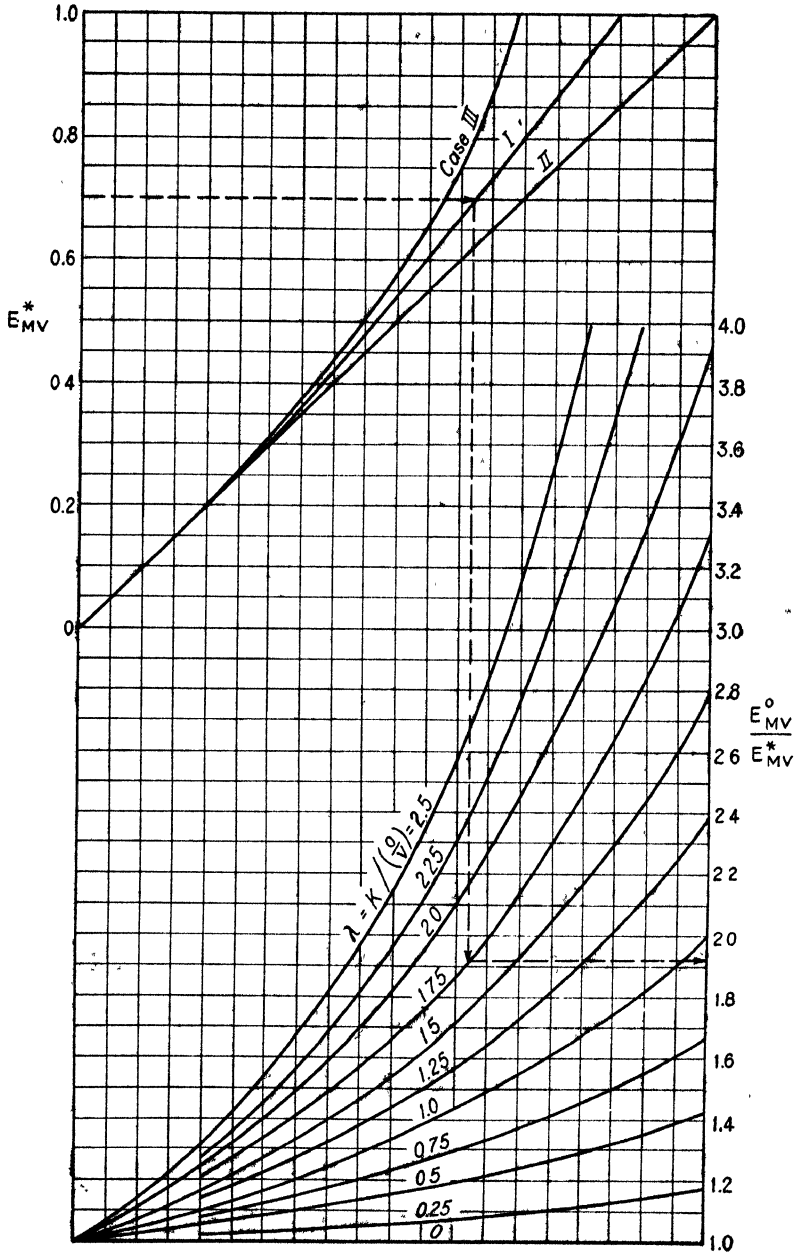


FIG. 17-2. Relation between $E_{MV}{}^\circ$ and $E_{MV}{}^*$.

2. Constant slope of the equilibrium curve, *i.e.*, $dy_e/dx = K$
3. E^o_{MV} same for all plates considered.

Lewis (Ref. 21) obtained

$$E^o = \frac{\ln \{1 + E^o_{MV}[K/(O/V) - 1]\}}{\ln [K/(O/V)]} \tag{17-6}$$

This equation is plotted in Fig. 17-3. It will be noted that in general E^o/E^o_{MV} is close to 1.0. In cases where the rectifying system

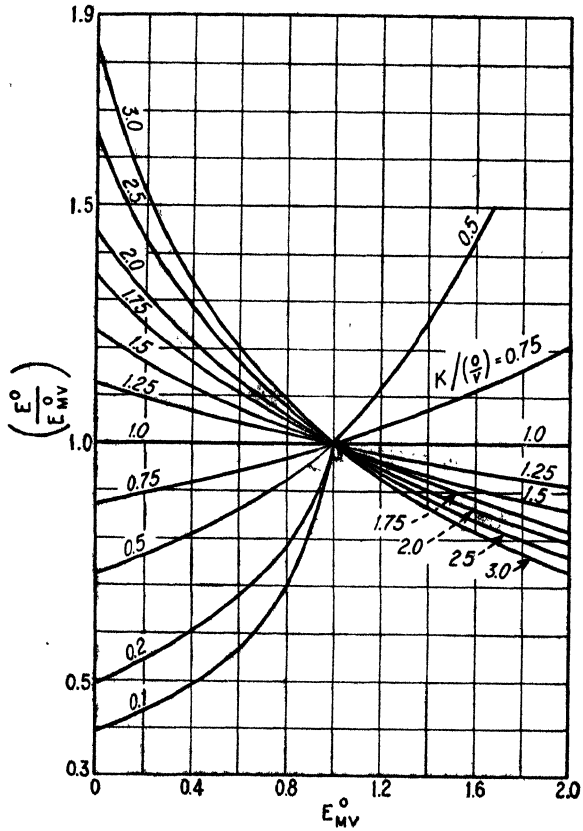


FIG. 17-3. Relation between E^o and $E_{MV}{}^o$.

operates from low to high concentrations, the value of $K/(O/V)$ will average out to around 1.0, making E^o approximately equal to E^o_{MV}.

For cases where $K/(O/V)$ is widely different from 1.0 and E^o_{MV} is low, the ratio of E^o can be either much larger or smaller than E^o_{MV}.

Thus Fig. 17-4 illustrates a case where $K/(O/V)$ is very small, and one theoretical plate would go from y_n to a composition of almost 1.0. If the over-all column efficiency for this region were 0.5, two actual plates would give the same increase, but the diagram indicates that about five plates with $E^o_{MV} = 0.5$ would be required. Actually the efficiencies employed were incompatible, and if $E^o_{MV} = 0.5$ then E^o

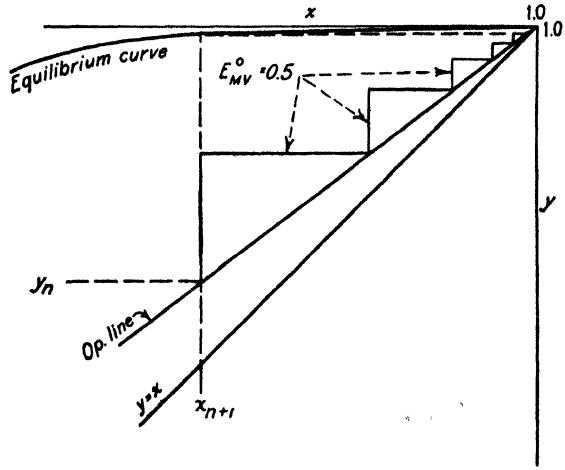


FIG. 17-4.

would be small for the low value of $K/(O/V)$. The first step with $E^o_{MV} = 0.5$ does make a change in the vapor composition equal to one-half of that for a theoretical plate but, because of the convergence of the equilibrium curve and the operating line, the available potential decreases and the succeeding plates do not make so large a change in the vapor composition.

Murphree also gave a derivation for a plate efficiency based on liquid-phase compositions. The basic differential equation was

$$-L'\,dx = K_L a(x - x^*)\,d\theta \tag{17-7}$$

where x = mol fraction in liquid
x^* = liquid in equilibrium with vapor leaving
K_L = mass-transfer coefficient
L' = liquid in slug under consideration

The equation was integrated with K_L, a, L', and x^* constant to give

$$E^o_{ML} = \frac{x_o - x_i}{x^* - x_i} = 1 - e^{-(K_L a\theta/L')} \tag{17-8}$$

where x_o, x_i = liquid composition to and leaving plate, respectively
E^o_{ML} = liquid-phase plate efficiency
L'/θ = liquid rate

It is difficult to picture any mass-transfer process on a bubble-type plate that corresponds to the derivation of Eq. (17-8). For example, consider the application of these equations to a local section of the plate. The liquid flowing across this section contacts the vapor rising through it, but the vapor composition varies with the liquid depth while the integration assumed that x^* was constant. The mol fraction ratio of Eq. (17-8) will be used as the definition of E_{ML}, but the mass-transfer portion of the equation does not apply to bubble-cap plate conditions.

Equations (17-3) and (17-8) can be related by the operating line and the equilibrium curve. Assuming that the equilibrium curve is such that $K_e = y_o/x^* = y^*/x_o$ (K_e is equal to K if the equilibrium curve is a straight line through the origin) gives

$$\frac{K_e}{O/V} = \frac{E^o_{ML}(1 - E^o_{MV})}{E^o_{MV}(1 - E^o_{ML})} \tag{17-9}$$

The assumptions made in the derivation of Eq. (17-3) appear to be on a somewhat sounder mass-transfer basis than Eq. (17-8). If this is true, E^*_{MV} depends on the operating conditions only to the extent that they affect the mass-transfer conditions while E_{ML} in addition is a function of the ratio $K_e/(O/V)$.

TABLE 17-1

	Location in column			
	Bottom	Just below feed plate	Just above feed plate	Top
O/V	1.2	1.2	0.7	0.7
K	2.5	1.0	1.0	0.4
$K/(O/V)$	2.08	0 883	1.43	0 57
E^o_{MV}/E^*_{MV}	1.9	1.38	1.67	1.18 (Fig. 17-2)
E^o_{MV}	1 14	0.83	1.0	0.71
E^o/E^o_{MV}	0.96	0.98	1.0	0 91 (Fig. 17-3)
E^o	1 09	0.81	1.0	0.65
K_e	2.5	1.5	1.5	1.0
E^o_{ML}	1.06	0.86	1.0	0.78

The vapor efficiency E^o_{MV} is much more commonly used than E^o_{ML}. This preference is justified in view of the derivation of the latter.

As an illustration of these relationships, consider the separation of a benzene-toluene mixture with $(O/V)_n = 0.7$ and $(O/V)_m = 1.2$ for $E^*_{MV} = 0.6$. The flow conditions correspond to Case III.

The feed-plate region was arbitrarily chosen to make $K = 1.0$. This corresponds to a liquid composition of about 40 per cent benzene.

The values given for E^o_{MV} would be higher than actually obtained because of the liquid mixing on the plate. It is interesting to note that E^o/E^o_{MV} is near to 1.0 at all positions, and the use of $E^o = E^o_{MV}$ would be a reasonable approximation. The values of K_e are larger than K except at the bottom of the column. For usual cases, $K_e/(O/V)$ is greater than 1.0, and E^o_{ML} will be between E^o_{MV} and 1.0.

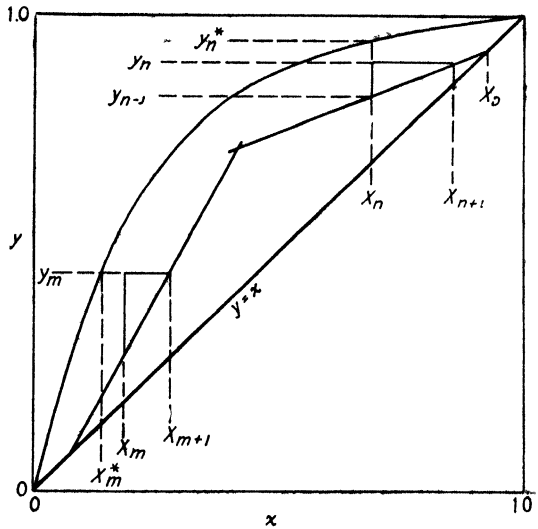


FIG. 17-5. Application of Murphree plate efficiencies.

From the calculational viewpoint, E^o is the easiest to apply, but E^o_{MV} and E^o_{ML} can be used without much additional effort either in algebraic or graphical design calculations. Thus in algebraic calculations, the usual theoretical plate calculations will give y^*_n for a known y_{n-1}, and $y_n = y_{n-1} + E^o_{MV}(y^*_n - y_{n-1})$. Thus the values of y_n can be calculated, if E^o_{MV} is known and the calculation is repeated for the next plate. The efficiencies can also be applied to the graphical calculation for binary or multicomponent mixtures. This is illustrated in Fig. 17-5. The use of E^o_{MV} is illustrated on the upper operating line: y_{n-1} is the actual vapor composition entering plate n and by material balance the composition x_n is fixed on the operating line; the vapor in equilib-

rium with x_n is y_n^* and the actual increase in vapor composition is $y_n - y_{n-1}$, which is obtained by a vertical step of a height equal to $E_{MV}^{\circ}(y_n^* - y_{n-1})$; *i.e.*, a fraction of the theoretical plate increase equal to E_{MV}° is taken. The use of E_{ML}° for plate m is shown on the lower operating line. In this case a fractional horizontal step equal to E_{ML}° times the theoretical plate change is used.

Effect of Entrainment on Efficiency. Entrainment can lower the apparent plate efficiency because the vapor-liquid mixture carried to the plate above will have a lower average concentration of the more volatile components than the vapor alone. Colburn (Ref. 6) has given an equation relating the measured efficiency with entrainment to that for a plate giving the same change in vapor composition but without entrainment.

$$E_{MT}^{\circ} = \frac{E}{1 + \dfrac{eE}{O/V}} \tag{17-10}$$

where E_{MT}° = apparent efficiency with entrainment
E = efficiency for same change in vapor composition
e = mols of entrained liquid per mol of vapor

For most cases the effect of entrainment does not become serious until e is 0.1 or greater. Referring to Fig. 16-10, it will be noted that $e = 0.1$ corresponds to $V_c\rho_G^{0.5}$ of about 0.9 or for atmospheric pressure a velocity of 2 to 4 f.p.s. with 12-in. plate spacing and to several fold higher velocities for 24-in. spacing. Equation (17-10) is normally used with E taken as the expected value of E_{MV}°, but this is in error due to

TABLE 17-2

	Bottom	Just below feed plate	Just above feed plate	Top
E_{MT}°	1.04	0.77	0.87	0.65

the mass transfer that takes place between the vapor and liquid droplets above the main liquid body on the plate. The composition of the liquid employed was that of overflow to the plate below while the actual composition will be different because of mass transfer and concentration gradients. This equation will give a too high value for E_{MT}° when E_{MV}° is used for E. For a value of $e = 0.1$ and using $E_{MV}^{\circ} = E$, these values of E_{MT}° corresponding to Table 17-1 are given in Table 17-2.

In this case the loss in efficiency for $e = 0.1$ is relatively small, and

larger values of e are not commonly found in commercial practice because the operation of the column becomes unstable before the corresponding velocities are obtained.

Experimental Data on Plate Efficiencies. A considerable number of investigations of plate efficiencies have been reported, but it is difficult to obtain a coherent picture from the data because of the number of unknown factors usually involved. Thus some of the results are reported on an over-all column basis while others are given on a plate basis. They involve unknown amounts of entrainment, unknown amounts of liquid mixing in the plate, unknown hydraulic gradients, unknown vapor distribution, unknown interface temperatures, and in some cases unknown degrees of liquid by-passing or dumping. As a result, most of these data are not suitable for correlation purposes but are useful for giving a general picture of the results obtained. The following discussion reviews some of these data for orientation purposes, but it is not intended to be a comprehensive survey.

TABLE 17-3

System	Average Murphree plate efficiency, E°_{MV}				
Average superficial vapor velocity, f.p.s. . .	1	2	3	4	5
Methanol–water. . .	99	96	90	82	73
n-Propanol–water.	83	85	88	88	80
Isobutanol–water.	98	95	90	84	75
Methanol–*n*-propanol.	90	88	87	87	87
Methanol-isobutanol.	75	71	75	76	73
Benzene–carbon tetrachloride	82	88	89	84	74

Gadwa (Ref. 12) has studied the plate efficiency in the fractionation of mixtures of (1) benzene-carbon tetrachloride, (2) methanol-isobutanol, (3) methanol-*n*-propanol, (4) isobutanol-water, (5) *n*-propanol-water, and (6) methanol-water. A small four-plate column containing one bubble cap per plate was employed. The bubble caps were 3½ in. in diameter and 2 in. high containing 38 slots ⅛ in. wide by ⅝ in. high per cap. A vapor space of 5 by 5 in. was partitioned off from the overflow pipes, giving a ratio of slot area to superficial area of 0.12. The plates were spaced 11 in. apart, and overflow weirs were employed. Plate samples were taken so that the Murphree plate efficiencies could be calculated. Some of these results are given in Table 17-3. The efficiencies in this table were calculated for the vapor phase.

Gadwa concluded that, for the mixtures he studied, the Murphree plate efficiency was substantially independent of the concentration and of the vapor velocity so long as foaming and entrainment were not appreciable but that, when foaming and entrainment did occur, the efficiency decreased with increasing velocity.

Brown *et al.* (Ref. 4) and Gunness (Ref. 14) both report Murphree plate efficiencies of 100 per cent or greater for large commercial gasoline stabilizers. The tower studied by Gunness, operated at 250 p.s.i.g., was 4 ft. 8¼ in. in diameter, and contained 28 plates each having 27 cast-iron bubble caps. The bubble caps were 6¼ in. in diameter and contained 32 1- by ½-in. rectangular slots per cap. The plate spacing was 18 in. In these columns, there were a number of bubble caps per plate, and the liquid flowed in opposite directions on successive plates. Gunness analyzed his data by Lewis's cross-flow enrichment method (page 448) and concluded that the Murphree point efficiency was between 70 and 80 per cent.

Lewis and Smoley (Ref. 22) studied the plate efficiency in the rectification of mixtures of (1) benzene-toluene, (2) benzene-toluene-xylene, and (3) naphtha and mixtures of pinene and aniline in naphtha. An experimental column 8 in. in diameter with 10 plates spaced 16 in. apart was used. The bubble cap was rectangular, being 2 in. high and 2 in. wide, and extended across the column. There were 24 slots ⅞ by 3/16 in. on each side of the cap, giving a ratio of slot area to superficial area of about 0.16. The investigators found average plate efficiencies of 60 per cent for the benzene-toluene mixture, 75 per cent for the ternary mixture, and 80 to 95 per cent for the naphtha mixtures.

In the same tower, Carey, Griswold, Lewis, and McAdams (Ref. 5) found an average Murphree efficiency of 70 per cent when fractionating benzene-toluene. They found the efficiency substantially constant for superficial velocities from 0.2 to 4.5 f.p.s. and independent of liquid composition. The same investigators report efficiencies of 50 to 99.75 per cent for the fractionation of an ethanol-water mixture in a 6-in.-diameter tower containing one plate. The logarithm of 100 minus the plate efficiency was found to be a linear function of the depth of submergence of the slots. A benzene-toluene mixture in the same one-plate tower gave an average Murphree efficiency of 58 per cent. A distillation of an aniline-water mixture in the 10-plate tower gave an average plate efficiency of 58 per cent at a vapor velocity of 2.77 f.p.s.

Lewis and Wilde (Ref. 23) found an average plate efficiency of 65 per cent at a vapor velocity of 2.8 f.p.s. for the rectification of naphtha in a

10-plate column 9 ft. in diameter. There were 115 bubble caps per plate containing slots ¼ by 1 in. The ratio of slot area to superficial area was 0.10, and the plate spacing was 2 ft.

Brown (Ref. 3) reports efficiencies as high as 120 per cent for a commercial beer column using perforated plates. The same efficiency was reported for the rectification of an ethanol-water mixture in a special laboratory column. The same investigator reports efficiencies of about 20 per cent for naphtha-absorption towers.

Atkins and Franklin (Ref. 1) found an over-all column efficiency of 18 per cent for a natural gasoline absorber using gas oil as the absorbing liquid. Walter (Ref. 30) obtained Murphree vapor plate efficiencies from 80 to 95 per cent in a 2-in. laboratory column for air humidification. Data taken in the same unit on the absorption of propylene and isobutylene in gas oil, heavy naphtha, and mixtures of gas and lube oil, gave plate efficiencies on the vapor basis of 5 to 36 per cent.

Horton (Ref. 16) studied the absorption of carbon dioxide and ammonia in water on a single 18-in.-diameter plate and reported values of E^{o}_{MV} about 3 per cent for CO_2, and 70 per cent for ammonia. Fairbrother (Ref. 9) studied the absorption of carbon dioxide in aqueous solutions of glycerine and obtained values of the Murphree plate efficiency of 0.65 to 4 per cent.

Peavy and Baker (Ref. 27) investigated the rectification of ethanol-water mixtures in an 18-in.-diameter column, and obtained plate vapor efficiency from 80 to 120 per cent for superficial vapor velocities between 1 and 3 f.p.s. For other data on plate efficiency, see Refs. 7, 8, 13, 18, 25, 26, 28.

The values of the plate vapor efficiency vary from less than 1 to over 100 per cent. The absorption systems with gases of low solubility and liquids of high viscosity have low efficiencies; while most of the distillation systems give values of 60 to 100 per cent. In most cases the efficiency is relatively independent of vapor rate until appreciable foaming and entrainment are encountered. For the distillation systems there does not appear to be any significant effect of liquid composition.

Plate Efficiency Correlations. It has been pointed out that the correlation of the plate efficiency data is difficult because of the large number of unknown conditions involved in most cases. However, some correlations have been developed that are helpful in estimating the plate efficiency.

Gunness (Ref. 14) analyzed the data for several columns and concluded that the liquid-film resistance was a major factor, and he sug-

gested that the plate efficiency be correlated with the viscosity of the liquid, because this characteristic is a major factor in liquid-phase mass transfer. He plotted the efficiency as a function of the operating pressure, on the basis of the fact that the viscosities of liquids are approximately the same at a given vapor pressure. This correlation on a viscosity basis is given in Fig. 17-6.

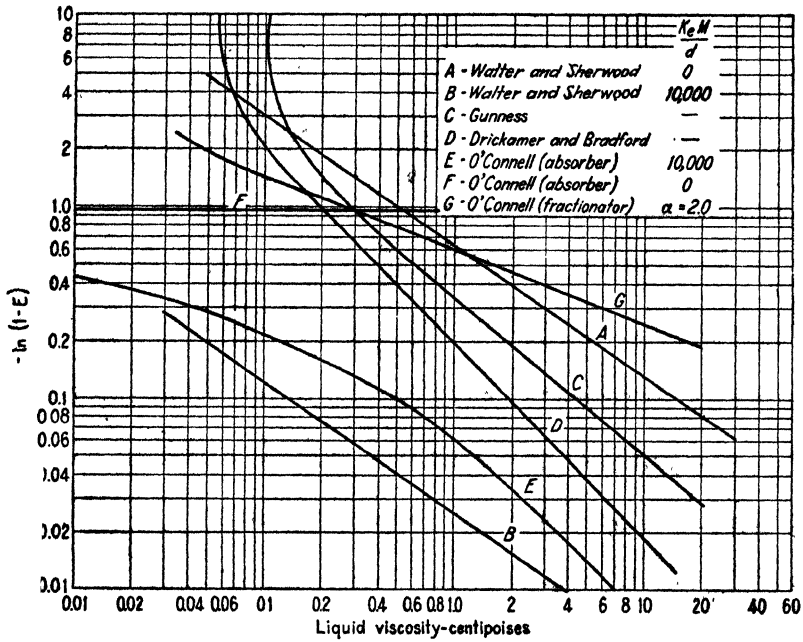


FIG. 17-6. Comparison of plate efficiency correlations.

Walter and Sherwood (Ref. 31) gave a correlation for the plate efficiency based on the derivation of Eq. (17-3). Using the two-film absorption concept (Ref. 33), they separated the over-all mass-transfer resistance into a liquid- and vapor-film resistance.

$$\frac{1}{K_G a} = \frac{1}{k_G a} + \frac{1}{H k_L a} \tag{17-11}$$

where $K_G a$ = same as for Eq. (17-1)
$k_G a$ = gas-film transfer coefficient
$k_L a$ = liquid-film transfer coefficient
H = Henry's law constant

The basic assumptions of the two-film theory are not satisfied by the action of a bubble-cap plate, but Eq. (17-11) is probably a reasonable approximation for the division of the resistance between the two phases, indicating that solubility is a major factor in the relative resistances.

Walter and Sherwood assumed (1) that K_G was proportional to G/θ, (2) that the total interfacial area of all the bubbles, a, was proportional to the liquid depth from the center of the slots to the top of the overflow weir, (3) on the basis of the data of Carey, Griswold, Lewis, and McAdams (Ref. 5), that $K_G a$ was proportional to the cube root of the slot width, and (4) that both $k_G a$ and $k_L a$ were proportional to the 0.68 power of the liquid viscosity. Their equation for the value of m in Eq. (17-3) is

$$m = \frac{h}{\left(2.5 + \frac{0.37}{HP}\right)\mu^{0.68} w^{0.33}} \tag{17-12}$$

where H = Henry's law constant, lb. mols per cu. ft. per atm.
P = pressure, atm.
μ = viscosity of liquid, centipoises
w = slot width, in.
h = height from center of slots to top of weir, in.
$E^*_{MV} = 1 - e^{-m}$

Equation (17-12) can be made more suitable for distillation calculations by replacing Henry's law constant by the equilibrium constant K_e, $(= y/x)$, giving

$$m = \frac{h}{\left(2.5 + \frac{0.0059 K_e M}{d}\right)\mu^{0.68} w^{0.33}} \tag{17-13}$$

where K_e = equilibrium constant $= y/x$
M = molecular weight of the liquid
d = specific gravity of liquid relative to water

The terms 2.5 and $0.0059 K_e M/d$ are the relative resistances of the vapor and liquid phases, respectively.

K_e and μ are properties of the system and, for a given mixture, it is difficult to make any major changes. In distillation, the values of K_e for the key components usually range from 1.0 to a maximum of approximately 5, but for the absorption of relatively insoluble gases, K_e may be as large as 1,000. The latter systems give small values of m and low E_{MV}. By increasing the total pressure, the values

of K_e for the absorption cases can be reduced, but the values for distillation cases remain about the same.

The viscosity term plays a major part in determining the value of m, and it is subject to some control. In the case of distillation systems, the liquids are essentially at their boiling points under the pressure involved. Under such conditions most common liquids have viscosities of the same order of magnitude. However, raising the operating pressure increases the temperature and lowers the viscosity. Thus, high-pressure towers tend to give high plate efficiencies, but the gain is usually not great enough to justify such operation for this purpose only. In the case of absorption towers, the operating temperature can often be varied independently of the pressure, and at a given operating pressure a high temperature gives a larger value of K_e and a lower value of μ. These two counterbalancing effects usually work to produce an optimum operating temperature.

In most distillation systems, the value of the viscosity is from 0.15 to 0.5 centipoise, and with slots $\frac{1}{8}$ to $\frac{1}{4}$ in. wide they give point efficiencies of 60 to 95 per cent. However, in the case of absorption, the liquid viscosities may be as high as 20 centipoises, and the point efficiencies may be 10 per cent or lower.

For a binary mixture it can be shown that the value of E_{MV} must be the same for both components in order to make the mol fractions in the liquid and the vapor add up to unity. In the case of multicomponent mixtures, each of the components can have a different value of E_{MV} for a given plate. On the basis of Eq. (17-13) it might be assumed that the heavier components with lower values of K_e would have the highest efficiency. There are no data which prove conclusively the relative efficiencies in a multicomponent mixture on a given plate. The inaccuracies of the measurements are such that they leave the trend in doubt. However, they do indicate that for the mixtures so far tested the difference in the value of E^o_{MV} between components is not large. On the basis of diffusion theory, it would be expected that the heavier components would approach equilibrium more slowly and therefore have lower values of E_{MV}.

The values calculated from these equations are given in Fig. 17-6, for $h = 1.0$, $w = 0.25$, and various values of KM/d.

Drickamer and Bradford (Ref. 7) analyzed the test data for a number of rectifying towers separating hydrocarbons and gave a plot of E^o as a function of the molal average liquid viscosity. The data presented by these investigators correlated reasonably well over a considerable variation in liquid viscosity. They did not include systems

that would have large values of $K_e = y/x$, and the correlation would probably not be suitable for such cases. Their relation is given in Fig. 17-6.

A correlation similar to that of Drickamer and Bradford was developed by O'Connell (Ref. 26), but in this case the plate efficiency was plotted as a function of $\alpha\mu$ (α = relative volatility) for fractionating towers and of μ/HP or $K_eM\mu/d$ for absorption towers. These correlations include both of the main factors, solubility and liquid viscosity, found to be important by Walter and Sherwood. The inclusion of the solubility factor directly with the viscosity is probably not so sound as the type of grouping used in Eq. (17-13). It would be expected that O'Connell's correlation would break down for extreme or unusual variations in the solubility factor.

Geddes (Ref. 13) has presented a semitheoretical method for the estimation of plate efficiency. The method is complicated to apply, and several of the assumptions made in the derivation are questionable. He obtained good results by the method in cases involving widely differing conditions. For the present state of the art, it is believed that the Walter and Sherwood equation gives as satisfactory results and is easier to apply.

A more detailed analysis of the mechanism of the mass transfer between the two phases of a bubble-cap plate has been made by Etherington (Ref. 8). He presented correlations for both k_Ga and k_La. These values would then be combined with Eq. (17-11) to give K_Ga which would be used to calculate E^*_{MV}. The method has been tested on only a few mixtures, and a more detailed evaluation is needed to determine whether the added complications are justified.

The correlations proposed by Gunness, Walter and Sherwood, Drickamer and Bradford, and O'Connell are compared in Fig. 17-6. The ordinate is $-\ln(1 - E)$, and the abscissa is the viscosity of the liquid in centipoises. The correlations are not all comparable. Walter and Sherwood's relation was based on small laboratory units and probably corresponds to point conditions, while the other relations were based on plate or over-all column efficiencies. For Eq. (17-13) h was taken = 1.0, $w = 0.25$, and two curves are given with $K_eM/d = 0$ being used to approximate fractionating conditions and $K_eM/d = 10{,}000$ to correspond to absorber conditions. Three curves are given for O'Connell's relations; curves E and F are for the absorber correlation with $K_eM/d = 0$ and 10,000, respectively; and curve G is for the fractionator correlation with $\alpha = 2.0$. The curves for Gunness and Drickamer and Bradford agree with the $K_eM/d = 0$

curve of Walter and Sherwood at low viscosities and approach the $K_e M/d = 10{,}000$ curve at high viscosities. This is because the data used in these correlations for the high efficiencies were for fractionating columns having low values of liquid viscosities and of $K_e M/d$, while the low efficiency points were for absorbers with high values of liquid viscosity and $K_e M/d$. While in many cases the solubility and viscosity factors tend to parallel each other, it is possible to vary the viscosity widely for the same value of the solubility. Etherington's data indicate that the viscosity and solubility factors should be separated. The curves based on O'Connell's correlation for absorbers with $K_e M/d = 10{,}000$ are in reasonable agreement with curve B, but the values for high solubilities ($K_e M/d$ near 0) do not appear to represent the data. At higher values of $K_e M/d$, the curves agree approximately with those of Walter and Sherwood.

From a review of the available data, it is recommended that Walter and Sherwood's equation be used for values of E^*_{MV}. In using this equation, it is suggested that for fractionating towers the relative volatility of the light key to heavy key components be used instead of K_e to calculate the Murphree point vapor efficiency for the light key component and that this value of the efficiency be used for all components in the mixture. The experimental data for fractionation systems do not vary with compositions to the extent that would be indicated by the use of K_e values. The viscosity term can be taken as molal average viscosity of the liquid. In the case of absorbers, it is suggested that $K = dy/dx$ be used instead of $K_e = y/x$, since the former is more consistent with the derivation of Eq. (17-11). The efficiency should be calculated for the key component, and it is suggested that the same value be employed for the other components. The value of h should be a function of the liquid depth instead of the "fixed" value given for the correlation. It is suggested that this term be replaced by $(h')^{0.5}$, where h' is the distance from the center of the slot opening to the top of the liquid level over the weir. With these changes, the relations become

$$E^*_{MV} = 1 - e^{-m'}$$

where

$$m' = \frac{(h')^{0.5}}{\left(2.5 + \dfrac{0.00594KM}{d}\right)\mu^{0.68}w^{0.33}} \qquad (17\text{-}14)$$

h' = distance from top of liquid level at weir to center of slot opening

K = use relative volatility of key components for fractionating

columns, and $K = (dy/dx)$ for equilibrium curve for absorbers

μ = viscosity, centipoises

w = slot width, in.

For values of the Murphree plate vapor efficiency in commercial size towers, the following equation is recommended:

$$E^{o}_{MV} = \left[1 + \frac{K}{6(O/V)}\right](1 - e^{-m''}) \tag{17-15}$$

where

$$m'' = \frac{(h')^{0.5}}{\left(3.5 + \dfrac{0.005KM}{d}\right)\mu^{0.68}w^{0.33}} \tag{17-16}$$

The units are the same as those of Eq. (17-14).

Plate Efficiency Example. As an example of the use of these equations, the plate efficiency for the plate design example of Chap. 16, page 433 will be calculated. The values of the various terms from this previous example are summarized below:

K = relative volatility = 2.4

M = 92

d = 52.8/62.4 = 0.85

w = 1/8 in.

O/V = 1.2

At 694°R. viscosity of toluene = 0.24 centipoise.

The liquid depth at the outlet weir is $h_w + h_{cr} = 2.0 + 1.0 = 3.0$ in.

The top of the slots is 1.75 in. above the plate and the slot opening, $h_s = 1.13$, giving the center of the slot opening at $1.75 - \frac{1.13}{2} = 1.2$ in. above the plate.

The value of h' is $3.0 - 1.2 = 1.8$ in.

By Eq. (17-14).

$$m' = \frac{(1.8)^{0.5}}{\left[2.5 + \dfrac{0.00594(2.4)(92)}{0.85}\right]0.24^{0.68}\left(\frac{1}{8}\right)^{0.33}}$$

$$= 1.75$$

$$E^{*}_{MV} = 1 - e^{-1.75}$$

$$= 0.83$$

By Eq. (17-16),

$$m'' = \frac{(1.8)^{0.5}}{\left[3.5 + \dfrac{0.005KM}{d}\right]0.24^{0.68}\left(\frac{1}{8}\right)^{0.33}}$$

$$= 1.47$$

$$E^{o}_{MV} = \left(1 + \frac{2.4}{7.2}\right)(1 - e^{-1.47})$$

$$= 1.02$$

EFFICIENCY OF PACKED TOWERS

The efficiency of packed towers is generally expressed as the height equivalent to a theoretical plate. Most of the reported values of H.E.T.P.'s are for small laboratory columns, since this is one of the largest uses of packed columns. H.E.T.P. is a function of the packing dimension and construction, tower size, vapor velocity, and system being rectified. The efficiency of packed towers may be seriously impaired by the liquid's tending to pass down one side while the vapor flows up the other. This channeling of vapor and liquid prevents effective interaction between the vapor and liquid.

Baker, Chilton, and Vernon (Ref. 2) report the results of tests on the distribution of water over various packing materials with air flowing up through the packing. The water rate was 500 lb. per hr. per sq. ft. in all tests. They found that a ratio of tower diameter to packing size greater than 8 to 1 gave a fairly uniform liquid distribution. At values of the ratio less than 8, the liquid tended to run down the tower walls and leave the center of the column nearly dry. A multiple-point liquid distributor at the top improved the liquid distribution at the top portion of the tower. The results of these investigators indicate the desirability of having the tower diameter over eight times the size of the packing material and of using multiple-point liquid distributors; this latter is most important in short towers.

Fenske, Tongberg, and Quiggle (Ref. 11) give the results of a large number of tests on packed laboratory towers. A comparison of some of their results for the distillation of a carbon tetrachloride-benzene mixture is given in Table 17-4.

The investigators conclude that (1) the best packings are one-turn and two-turn wire or glass helices, carding teeth, and No. 19 jack chain, (2) the efficiency of the packing decreases when the tower diameter is increased or when the height of the packed section is increased, and (3) different hydrocarbon mixtures give approximately the same value for H.E.T.P.

Weimann (Ref. 32) has published results on the fractionation of ethanol-water mixtures in packed towers. Using a superficial velocity of 1 f.p.s. at $O/D = 1.0$ with 8- by 8-mm. porcelain Raschig rings in a 0.11-m. (4⅓-in.) diameter tower, H.E.T.P. values of 6 to 8.5 in. were obtained for packing heights of 3.5 to 13 ft. A larger tower, approximately 1 ft. in diameter, using a 7-ft. depth of the same packing gave an H.E.T.P. of 8.5 in. at a superficial vapor velocity of 1¼ f.p.s.

Jantzen (Ref. 17) has presented the results of fractionating an

ethanol-water mixture in a 13.5-cm. (1.37-in.) tower packed to a depth of 1 m. with either 1- or 0.46-cm. Raschig rings. The values of H.E.T.P. calculated from his data range from about 3 to 6 in., for superficial vapor velocities ranging from 0.15 to 2 f.p.s. The H.E.T.P. values increased as the 0.2 power of the vapor velocity and were about 50 per cent larger for the large than for the small rings. These values were found to be independent of the liquid concentration and of the reflux ratio (experimental values of O/D ranged from 4 to 10).

TABLE 17-4

Packing	Tower dimensions, in.	H.E.T.P., in.
Straight $\frac{7}{32}$-in. carding teeth	0 76 by 27	1.5
Straight $\frac{5}{32}$-in. carding teeth	0 76 by 27	1.7
Bent $\frac{1}{4}$-in. carding teeth	0.76 by 27	1.7
Miscellaneous carding teeth	0 76 by 27	2.2
Double-cross wire form	0.76 by 27	2.1
Hollow-square wire form	0.80 by 55	5.4
No. 20 single-link iron jack chain	2.0 by 53	5.2
No. 2 cut tacks	0 8 by 55	2.4
6-turn No. 24 Lucero wire helix	0.8 by 66	8.0
No. 18 single-link iron jack chain	2 0 by 53	6.5
Glass tubes	0 78 by 27	5 5
No. 16 single-link iron jack chain	0.76 by 27	4.2

Fenske and coworkers (Ref. 10) have also made an extensive study of the efficiency of packings when used for the separation of a *n*-heptane-methyl cyclohexane mixture in a 2-in.-diameter glass tower at total reflux. The tower was 114 in. high and was operated at atmospheric pressure. A few of their results are summarized in Table 17-5.

These data indicate that H.E.T.P. values as low as 1.5 in. have been obtained, making it possible to obtain the equivalent of a large number of theoretical plates in a relatively short height. Because of their efficiency and simplicity, packed towers are widely used for laboratory columns. However, when larger packed towers are used, the efficiency in general decreases, and H.E.T.P. values of a few feet are more common for columns of commercial size.

The cause of the poor results in large-diameter columns is apparently poor liquid distribution. The use of liquid redistributor plates every few feet can increase the effectiveness of the units, but they increase the pressure drop. With a number of such liquid distributors, the values

of H.E.T.P. can be made reasonably low and reproducible, but the tower has become almost equivalent to a perforated plate column.

The values of H.E.T.P. for large columns are so random that any correlation gives only a qualitative idea of what might be expected. The following equation is presented as a rough guide only, and it would not be surprising if actual values in some cases were several fold different.

$$\text{H.E.T.P.} = \frac{d_t}{M_G}\left[12G^{0.2} + \frac{G}{HPD\left(\frac{L}{\mu'}\right)^{0.75}\left(\frac{\mu'}{\rho D}\right)^{0.5}}\right] \qquad (17\text{-}17)$$

where H.E.T.P. = feet, for nominal packing size less than one-tenth tower diameter
d_t = tower diameter, ft.
M_G = average molecular weight of vapor phase
G = superficial mass velocity of vapor, lb. per hr. per sq. ft.
P = absolute pressure, atm.
D = diffusivity of solute gas in liquid, sq. cm. per sec.
L = liquid rate, lb. per hr. per sq. ft. tower cross section
μ' = liquid viscosity, poises
ρ = liquid density, g. per cu. cm.
H = Henry's law constant (lb. mols/cu. ft.) per atm.
HP = 0.016 (KM_L/ρ), where $K = y/x$, M_L = molecular weight of liquid

The individual film coefficients are based mainly on the results of Sherwood and Holloway (Ref. 29), but they have been combined with other factors and the equation should be considered purely empirical. If the values obtained from Eq. (17-17) are greater than the distance between distributor plates, it is suggested that this latter difference be employed.

Packed Tower Example. Equation (17-17) will be used to estimate the H.E.T.P. values for the atmospheric distillation of a benzene-toluene mixture in a packed tower 5 ft. in diameter. The liquid and vapor rates are 480 and 400 lb. mols per hr., respectively. The calculation will be made for the section near the bottom of the column where the liquid and vapor are essentially toluene.

Solution

Area of column = $5^2(0.7854) = 19.6$

$$G = \frac{400(92)}{19.6} = 1{,}880 \text{ lb. per hr. per sq. ft.}$$

$$L = \frac{480(92)}{19.6} = 2{,}250 \text{ lb. per hr. per sq. ft.}$$

$$M_G = 92$$

$$d_t = 5.0$$

$$HP = 0.016\left(\frac{KM_L}{\rho}\right) = 0.016\left[\frac{2.4(92)}{0.85}\right] \text{ (see page 463 for values)}$$

$$= 4.15$$

The diffusivity for the system was estimated to be 1.0×10^{-5} sq. cm./sec. at °C., and it was corrected to the higher temperature assuming that the diffusivity aried inversely as the 1.5 power of the liquid viscosity.[1] This calculation gave) = 3.5×10^{-5} sq. cm. per sec.

$$\left(\frac{L}{\mu}\right)^{0.75} = \left(\frac{2{,}250}{0.0024}\right)^{0.75} = 30{,}200$$

$$\left(\frac{\mu}{\rho D}\right)^{0.5} = \left[\frac{0.0024}{0.85(3.5 \times 10^{-5})}\right]^{0.5} = 9$$

By Eq. (17-15),

$$\text{H.E.T.P.} = \frac{5}{92}\left[12(1{,}880)^{0.2} + \frac{1{,}880}{(3.5 \times 10^{-5})(4.15)(30{,}200)(9)}\right] = 5.5 \text{ ft.}$$

The pressure drop for this tower can be estimated from Eq. (16-40). It will be ssumed that the packing size is 3.0 in.

$$\frac{\Delta P}{h} = \frac{2fA_w A_L \rho u^2}{g d_p}$$

$$\text{The Reynolds number, } \frac{d_p u \rho}{\mu'} = \frac{\frac{1}{4}(1{,}880)}{0.0024(242)} = 810$$

By Eq. (16-42),

$$f = \frac{38}{810^{0.15}} = 14$$

From the table on page 438, $A_w = 0.86$.
By Eq. (16-43), $A_L = 1.4 + 0.0005(2{,}250) = 2.5$
The superficial gas velocity, assuming that absolute pressure is 1.0 atm.,

$$u = \frac{400(359)(385)}{19.6(3{,}600)(273)}$$

$$= 2.87 \text{ f.p.s.}$$

$$\frac{\Delta P}{h} = \frac{2(14)(0.86)(2.5)(0.21)(2.87)^2}{32.2(\frac{1}{4})}$$

$$= 12.9 \text{ p.s.f. per ft.}$$

$$= 2.9 \text{ in. of liquid toluene per ft. of length}$$

This pressure drop is high indicating that the tower is operating near the flooding ondition. Figure 16-4 would give a flooding velocity of about 4 f.p.s. for these onditions.

[1] See ARNOLD, Sc.D. thesis in chemical engineering, M.I.T., 1931.

TABLE 17-5

Packing	Vapor velocity, f.p.s.	H.E.T.P., in.
Open tower	0.25 to 1.7	25.5 to 29.2
½- by ½-in. carbon Raschig rings	0.25 to 1.45	6.0 to 11.3
½- by ½-in. stoneware Raschig rings	0.8 to 1.55	5.0 to 8.5
⅜- by ⅜-in. stoneware Raschig rings	0.3 to 1.1	3.8 to 7.3
¼- by ¼-in. carbon Raschig rings	0.15 to 0.5	4.7 to 6.0
¼- by ¼-in. glass Raschig rings	0.4 to 0.9	4.3 to 6.8
No. 19 aluminum jack chain	0.1 to 1.65	4.2 to 8.9
½- in. clay Berl saddles	0.05 to 1.6	5.8 to 7.0
½-in. aluminum Berl saddles	0.3 to 1.75	4.1 to 7.0
6-mesh carborundum	0.1 to 0.35	1.6 to 5.1
¼-in. aluminum single-turn helices	0.7 to 2.1	5.0 to 10.7
3/16-in. aluminum single-turn helices	0.1 to 1.8	3.7 to 6.2
5/32-in. single-turn stainless-steel helices	0.3 to 1.25	4.0 to 5.4
5/32-in. single-turn nickel helices	0.55 to 1.65	2.9 to 5.5
⅛-in. single-turn nickel helices	0.1 to 1.0	2.9 to 5.5
3/32-in. single-turn stainless-steel helices	0.15 to 0.95	1.5 to 2.3
⅛- by 7/32-in. carding teeth	0.4 to 1.35	2.0 to 4.2

Nomenclature

a = interfacial area of bubble or total contact area per plate
D = diffusivity, cm.²/sec.
d = specific gravity, relative to water
d_p = diameter of packing, ft.
d_t = tower diameter, ft.
E = plate efficiency
E^o = over-all plate efficiency
E^o_{MV} = Murphree vapor-phase plate efficiency
E^*_{MV} = Murphree point efficiency
E^o_{ML} = Murphree liquid-phase plate efficiency
E^o_{MT} = apparent plate efficiency with entrainment
e = mols of liquid entrained per mol of vapor
G = mols of gas in bubble or superficial mass velocity of vapor, lb./(hr.) (sq. ft.)
H = Henry's law constant, (lb. mols)/(cu. ft.) (atm.)
h = height from center of slots to top of weir, in.
h' = distance from top of liquid level to center of slot opening
K = slope of equilibrium curve = dy/dx
K_e = y/x
K_G = over-all mass-transfer coefficient
$k_G a$ = gas-film mass-transfer coefficient
K_L = over-all mass-transfer coefficient
$k_L a$ = liquid-film mass-transfer coefficient
L' = liquid in slug

L = liquid rate, lb./(hr.)(sq. ft. of tower cross section)
M = molecular weight of liquid
M_G = average molecular weight of vapor phase
P = total pressure, atm.
w = slot width, in.
x = mol fraction in liquid
x^* = equilibrium with vapor leaving
x_o = liquid leaving plate
x_i = liquid entering plate
y = mol fraction in vapor
y' = mol fraction in bubble
y_e = equilibrium with liquid
y_i = entering plate
y_o = leaving plate
y_o^* = equilibrium with liquid leaving plate
μ = viscosity of liquid, centipoise
μ' = viscosity of liquid, poise
ρ = liquid density, g./cu. cm.
θ = contact time of bubble

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CHAPTER 18

FRACTIONATING COLUMN AUXILIARIES

In addition to the fractionating column, there are certain auxiliaries necessary for its operation. These include the condenser, reboiler, pumps, instruments, valves, and receivers.

Condensers. The condensers are tubular heat exchangers used to liquefy the overhead vapor to produce the necessary reflux. For small columns, the condensers are mounted above the column, and the condensate returns to the system by gravity. For larger installations, the condensers are generally mounted below the top of the column, and the reflux is pumped back to the system. Placing the condensers at the lower level reduces the size of the supporting structure and makes them more accessible for cleaning. The design of condensers is largely a problem of heat transfer, and the reader is referred to "Heat Transmission" by McAdams (Ref. 1). In addition to the heat removal problems, the various pressure drops should be evaluated to determine whether the vapor and condensate will flow properly.

Reboilers. In small units the reboiler is frequently mounted directly below the column and consists of a large kettle containing a steam coil. In large installations it is customary to build the reboiler as a separate unit. This allows easier servicing of the heat-transfer surface. Where fouling of the heating tubes is rapid, two reboilers are often included to allow a spare that can be used while the other is being cleaned. The design of a reboiler is also mainly a heat-transfer problem, but pressure drops and adequate settling space above the liquid should be considered. Where separate reboilers are employed, the vapor is piped to the column, and the pressure drop may be such that it hinders the liquid flow to the reboiler. Considerable splashing of the liquid in the still is often encountered due to the deep liquid level, and a settling space of at least 2 ft. should be employed with a cross-sectional area two to three times that of the column. In order to obtain a large cross-sectional area, horizontal drums are frequently used for reboilers, and these units can be arranged to give longitudinal flow of the liquid. This can give additional separation by a Rayleigh-type distillation. The reboiler should be designed to obtain the desired

vapor production, and any extra rectification in the still should be a secondary consideration.

When live steam is employed, it can be added directly under the bottom plate of the column, or a still can be used and the steam introduced under the liquid through some type of distributor. Steam is the most common medium for the stills, but in some cases it is not desirable because (1) the still temperature is too high, (2) the leakage of water into the system may be undesirable and hazardous, or (3) the still temperature may be so low that freezing may be encountered. In some cases, organic liquids or vapors, such as Dowtherm, are used as the heating medium, or the liquid at the bottom of the column may be pumped through a direct-fired heater and partly vaporized. In this last case, the liquid-vapor mixture from the heater is passed through a separator, with the vapor going to the column and the liquid being removed as bottoms, although it may be recycled through the heater to obtain additional vaporization.

Fractionating Column Control. In order to obtain satisfactory performance from a fractional distillation unit, it is necessary to control the operating conditions. In the case of a continuous rectification system, it is desirable, and almost essential, to introduce a feed of relatively constant composition and temperature at a reasonably constant rate. In general the system is to make a specified separation with the given column and a given feed plate, and this leaves two main variables to be controlled: (1) the reflux ratio and (2) the heat supply to the still. For example, consider the separation of a binary mixture and assume that the desired separation is not being obtained. The reflux ratio can be increased which should increase the degree of separation, but if the same heat supply to the still is maintained, the overhead product rate will decrease. To obtain the desired percentage of the feed as overhead product, it may be necessary either to decrease the feed rate or to increase the heat supply if the column will handle the added load. The problem of fractionating tower control becomes one of maintaining the proper balance of the feed rate, reflux ratio, and heat supply to the still. Manual control can be used, but automatic control instruments generally do a better job because operators tend to overcorrect. The problem of overcorrecting is especially serious in rectification because the large liquid holdup introduces long time lags. In columns with a large number of plates, the mols of liquid held up in the system may be the same order of magnitude as the vapor or liquid throughput per hour and may correspond to several times the feed rate per hour. This large quantity of liquid acts like a flywheel and smooths out the

operation, but it makes the response to corrective action very slow and leads to overcorrection.

Instrumentation. One method of instrumentation of a fractionating column is shown in Fig. 18-1. The feed rate to the column is held constant by the feed-flow controller. The overhead vapor is condensed

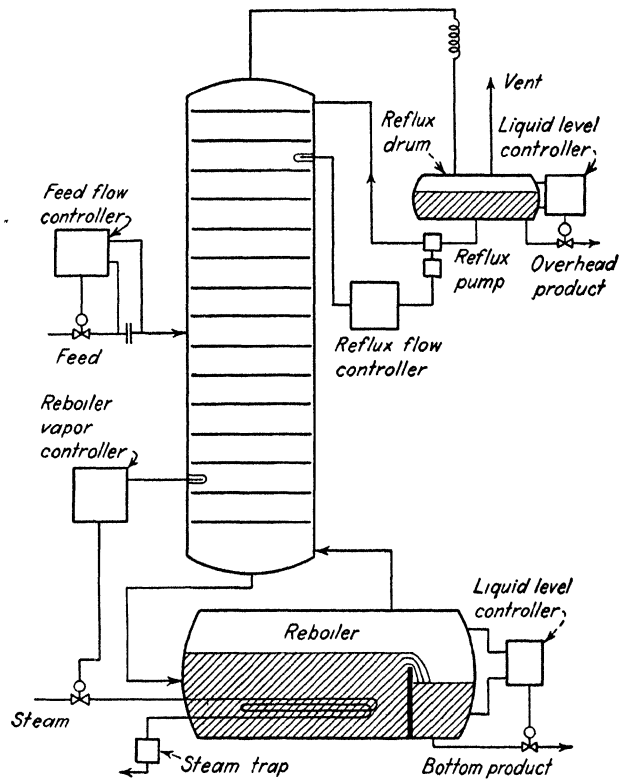


FIG. 18-1. Diagram of instrumentation for continuous rectification system.

and runs to a reflux drum accumulator, and a portion of the condensate is pumped back to the column for reflux. The excess condensate is the overhead product and is removed from the drum by the liquid level controller. The reflux rate is regulated by the reflux-flow controller which attempts to hold the temperature near the top of the column at a fixed value. The steam rate to the still is controlled by a reboiler vapor controller operating on a temperature indicator, and the unvaporized liquid is removed from the still by a liquid-level controller.

In the operation of the system illustrated in Fig. 18-1, the feed-flow,

reflux-flow, and reboiler vapor controllers would be set at the desired values. If the temperature at the top control point became lower than the desired value, the reflux-flow controller would reduce the reflux rate which would increase the product withdrawal rate and raise the temperature. If the temperature were too high, the controller would take the opposite action. If the temperature at the reboiler control point becomes lower than desired, the controller will increase the steam supply to the still, resulting in a higher vapor rate. This will give better stripping of the light components and will raise the temperature at the control point. This action of the reboiler vapor controller will lower the reflux ratio by increasing the overhead product rate and will probably require the reflux-flow controller to increase the reflux rate to hold the top temperature down. In this system the reboiler vapor controller operates to give the desired temperature at the bottom control point which presumably gives the specified bottom product. The reflux-flow controller operates to give the desired temperature difference between the two control points. The system is operable because for a given number of plates the degree of separation can be varied by changing the reflux ratio. The feed rate and the temperature values that are fixed must obviously be within the fractionating capabilities of the system.

A number of alternate control systems can be employed. Thus a fixed reflux ratio could be used with the top control point regulating the feed rate to the column with the bottom control operating the same as before. In case the overhead product is difficult to liquefy, a partial condenser may be employed, and this requires a different method of control. A typical case of this type is gasoline stabilization where a small amount of C_2, C_3, and C_4 hydrocarbons are removed to obtain the desired volatility of the bottoms product. For this case, the system of Fig. 18-1 could be modified as shown in Fig. 18-2 by removing the overhead product through the vent line. This vent line would be equipped with a pressure controller which would adjust the vapor removal rate to maintain the desired operating pressure. The liquid-level controller would be used to adjust the cooling water rate to the condenser instead of the product withdrawal rate. The reflux-flow controller would operate to maintain the top temperature as before, and the liquid-level controller would decrease the cooling water rate if the level became too high, thereby decreasing the rate of condensate production and increasing the overhead vapor rate.

Control Variables. One of the difficult problems in the automatic control of fractionating towers is finding an easily measured charac-

teristic that will ensure the desired separation. Temperature is the most commonly used factor, but it is not always a satisfactory criterion. Thus, if the product is of high purity and contains only a small amount of other constituents, these can vary several fold without significantly changing the equilibrium temperature. This is particularly serious in the separation of close boiling constituents. In the case of multicomponent mixtures, temperature is not a good criterion of composition, but it can be a satisfactory indication of volatility. The problem

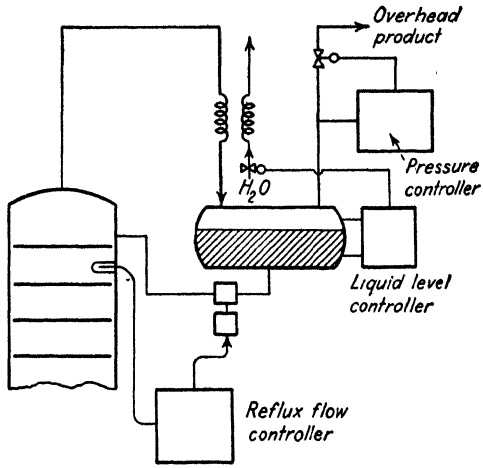


FIG. 18-2. Diagram for partial condenser operation.

is particularly difficult in extractive distillation systems where the presence of the large quantity of solvent masks the effect of composition of the key components on the temperature. Temperature control is also sensitive to the column pressure.

In some of these cases, the effectiveness of temperature can be improved by proper location of the temperature control point. For example, in the case of high product purity, the temperature control point can be placed several plates from the end of the column at a point where the minor constituents have higher concentrations. This results in a larger temperature variation which makes the instrumentation easier, but it removes the direct control on the product.

Other control factors besides temperature have been used, such as density of the liquid, refractive index of the liquid, infrared or other spectrographic types of analysis, and freezing point. The factor should be one which gives an indication of product composition and which can be easily and rapidly determined by a relatively inexpensive, stable

instrument capable of operating electronic or pneumatic equipment. The spectographic type of instruments should be very useful because they can frequently be adjusted to indicate the amount of an impurity present in extremely small amounts. Unfortunately they are somewhat delicate and need frequent adjustment, but these defects can undoubtedly be eliminated.

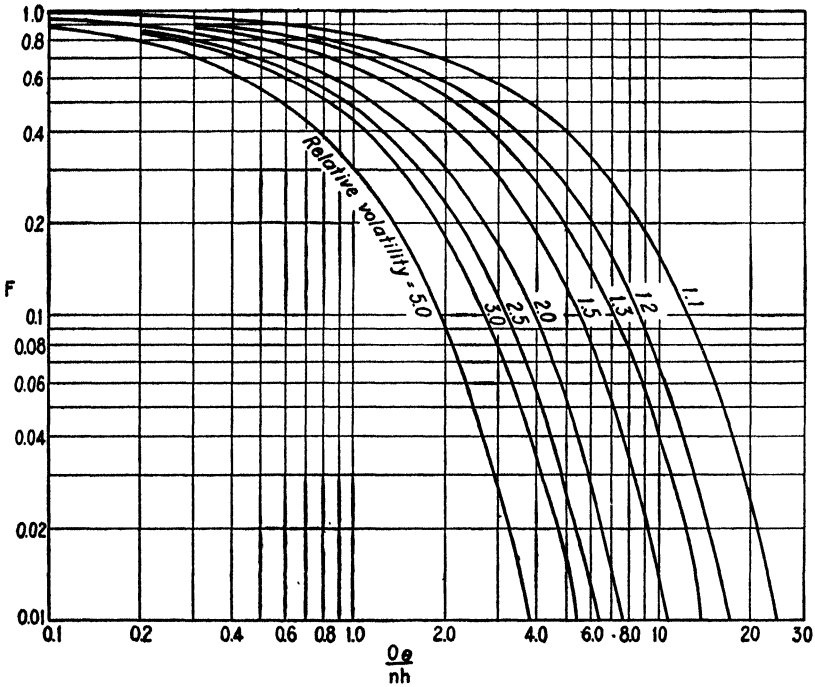


FIG. 18-3.

Rate of Approach to Equilibrium. Corrective action or other changes in the operating conditions introduce a transient condition into the system. Consider a section of a column operating at steady-state conditions. Assume that a change is made on one of the plates (such as a change in the feed composition to the feed plate), and the problem is to determine how rapidly other plates will approach their new equilibrium condition. The exact mathematical solution of the general case is very complex, but solutions based on certain approximations can be obtained. The curves given in Fig. 18-3, based on a number of stepwise integrations, should be helpful in obtaining approximate results. In this figure the ordinate, F, is the fractional approach

to the new equilibrium conditions of a plate which is n plates from the one on which the change in composition was made. The value of F is defined as,

$$F = \frac{(y_n)_\infty - y_n}{(y_n)_\infty - y_n^\circ} \quad (18\text{-}1)$$

where y_n = vapor leaving plate at time θ
$(y_n)_\infty$ = new equilibrium value of y_n, *i.e.*, value of y_n at $\theta = \infty$
y_n° = equilibrium vapor composition before change in conditions were made

The abscissa is the dimensionless ratio of liquid flow through the section to liquid holdup in the section. This group is

$$\frac{O\theta}{nh}$$

where O = overflow rate, mols per unit time
θ = time
n = number of plates in section between where conditions were modified at $\theta = 0$ and plate n
h = holdup per plate, mols

The value of F decreases rapidly as $(O\theta/nh)$ increases, indicating that the section approaches the new equilibrium after a change, more rapidly for large values of the overflow rate, small values of holdup per plate, and a small number of plates. Lines are given on Fig. 18-3 for different relative volatilities between the key components, and for multicomponent mixtures the value of F should be applied to the light key component. For a change in condition that affects all plates almost simultaneously, such as a change in reflux ratio, it is suggested that the correlation of Fig. 18-3 be employed with $n = 2.0$.

To bring a section of a column to a reasonable approach to the new equilibrium would require, according to Fig. 18-3, a liquid throughput of two to ten times the liquid holdup in the section. For usual design conditions, a tower operating at atmospheric pressure will have a liquid throughput per minute equal to about the holdup per plate. For high-pressure towers the ratio of liquid holdup to liquid flow per plate may be as low as 0.1; for vacuum towers it may be as high as 5.0. Thus an atmospheric pressure column with 20 plates above the feed plate may require from 0.5 to 3 hr. to steady down after a change in feed composition, while a high-pressure tower would adjust itself much more rapidly.

Figure 18-3 indicates that a change in the vapor composition entering a section will make a difference in the plate just above much sooner

than on plates farther removed, while a change in the reflux ratio would change $(y)_\infty$ for all the plates almost simultaneously. Thus changes in feed composition will be noticeable much sooner at plates just above and below the feed plate, and instruments located in these positions would be able to correct for such changes in composition much more rapidly. However, in multicomponent mixtures it may be very difficult to relate conditions at these locations to the desired separation. While the instruments can be set to control the temperature at the feed plate region, this may not give control of the product compositions. Control points near the ends of the columns are less affected by changes in feed compositions but do not anticipate variations so rapidly and are generally less sensitive. Changes due to reflux ratio or vapor rate are most apparent where the change in composition of the key components per plate is greatest. This usually occurs in the intermediate section somewhat above and below the feed plate.

In most cases with temperature regulation, the control point for the top should be down enough plates from the top to gain the amplified temperature difference and the anticipatory effect of being closer to the feed plate, but it should not be so close to the feed plate that it is appreciably affected by the components heavier than the heavy key component. Similar considerations apply to the section below the feed plate.

Reference

1. McAdams, "Heat Transmission," 2d ed., McGraw-Hill Book Company, Inc., New York, 1942.

APPENDIX

TABLE OF ENTHALPIES, OR LATENT HEATS OF VAPORIZATION

Substance	Boiling point, °C.	Molecular weight	Latent heat in calories per gram at boiling point
Acetal	104.0	118.1	66 2
Acetaldehyde	20 8	44.0	134.6
Acetic acid	118 7	60.0	89.8
Acetic anhydride	136 4	102.1	66.1
Acetone	56.6	58.1	125.3
Acetyl chloride	55 6	78.5	78.9
Ammonia	− 34 7	17.0	341 0
Aniline	183.9	93.1	109 6
Benzaldehyde	178 3	106.1	86.6
Benzene	80.2	78.1	93.5
Benzyl alcohol	205 0	108.1	98 5
Brombenzene	155.5	157.0	57.9
Butyl alcohol (*n*)	117.6	74.1	143 3
Butyl alcohol (iso)	107 9	74.1	138 9
Butyric acid (iso)	162.2	88.1	114 0
Carbon tetrachloride	76.8	153.8	46 4
Chlorbenzene	131.8	112.5	75.9
Chloroform	61.2	119.4	58 9
Cresol (*m*)	200 5	108.1	100 5
Ethyl bromide	38.2	109.0	60 4
Ethyl iodide	72.3	155.9	47 6
Formic acid	100.8	46.0	120 4
Glycol	197.1	62.1	190 9
Heptane	98.4	100.2	74.0
Hexane	69.0	86.1	79 2
Iso amyl alcohol	130.1	88.1	125 1
Iso propyl alcohol	82.9	60.1	161.1
Methyl alcohol	64.7	32.0	261.7
Methyl chloride	− 24.1	50.5	96.9 (at 0°C.)
Methyl iodide	42.4	141.9	46.0
Methyl ethyl ketone	81.0	72.1	103.5
Methyl aniline	193.8	107.1	95 5
Nitrobenzene	208.3	123.1	79.2 (at 151.5°C.)
Octane	125.8	114.2	71.1
Pentane	36.3	72.1	85.8
Propyl alcohol (*n*)	97 4	60.1	162.6
Toluene	110.4	92.1	86.8
o-Toluidene	203.3	107.1	95.1
Water	100.0	18.0	536.6
o-Xylene	144 0	106 1	82.5

APPENDIX

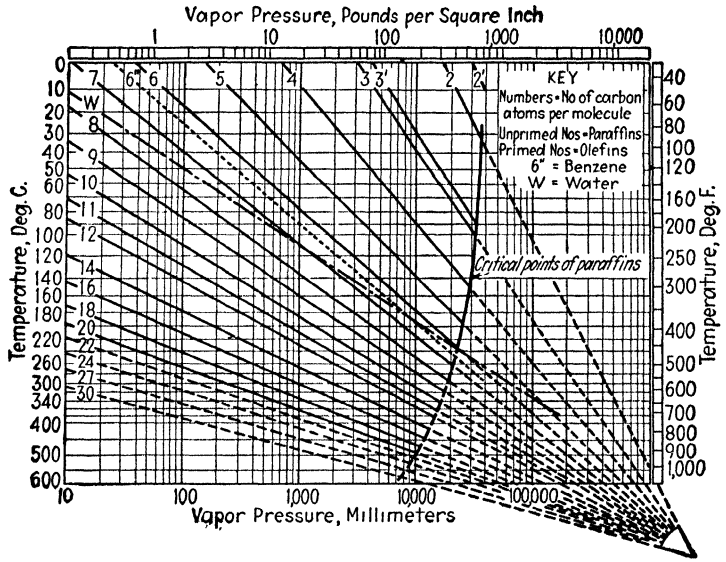


FIG. 1. Cox chart for extrapolating vapor-pressure temperature curves. (*Walker, Lewis, McAdams, and Gilliland, "Principles of Chemical Engineering," 3d ed., McGraw-Hill Book Company, Inc., New York,* 1937.)

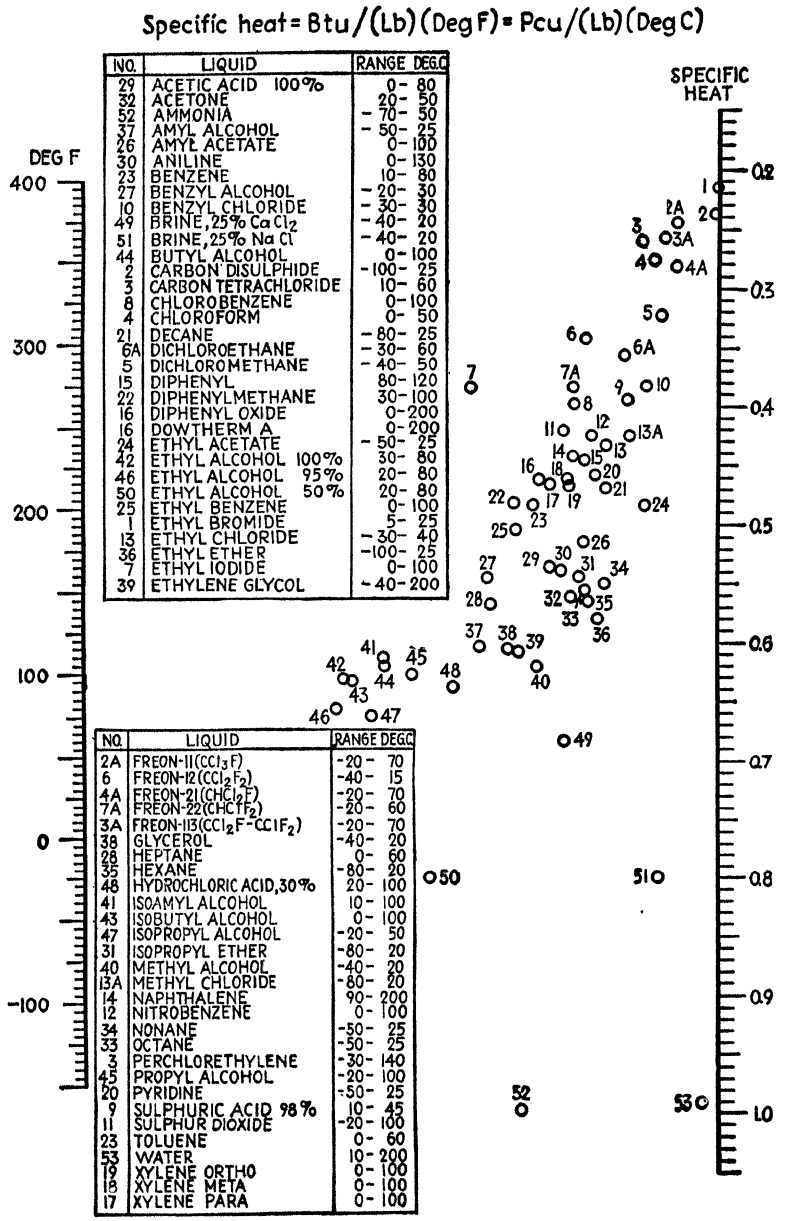


FIG. 2. True specific heats of liquids. (*Chilton, Colburn, and Vernon, based mainly on data from "International Critical Tables," McGraw-Hill Book Company, Inc., New York*, 1926–1930.)

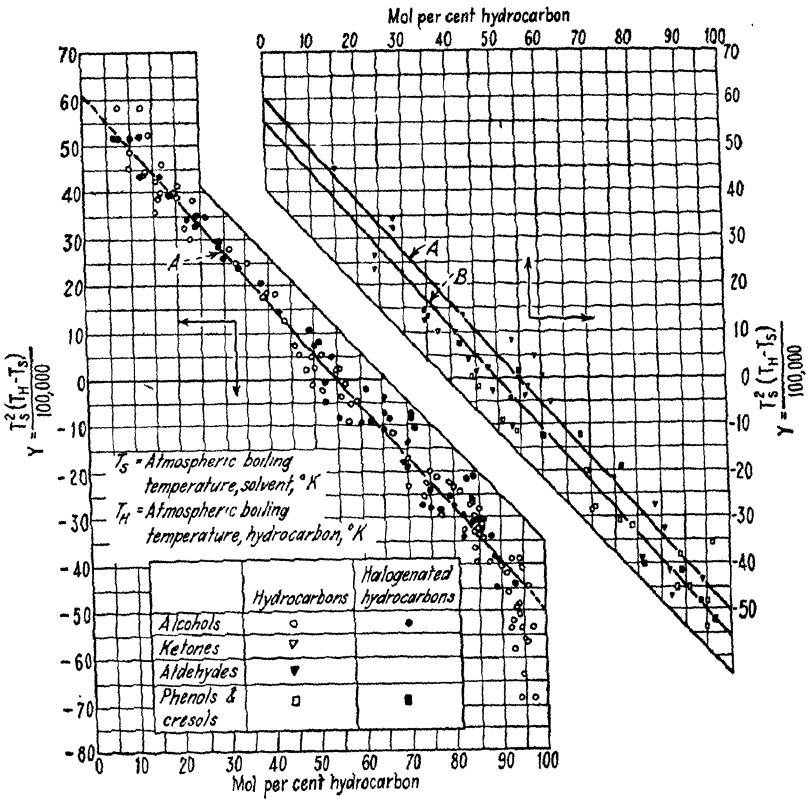
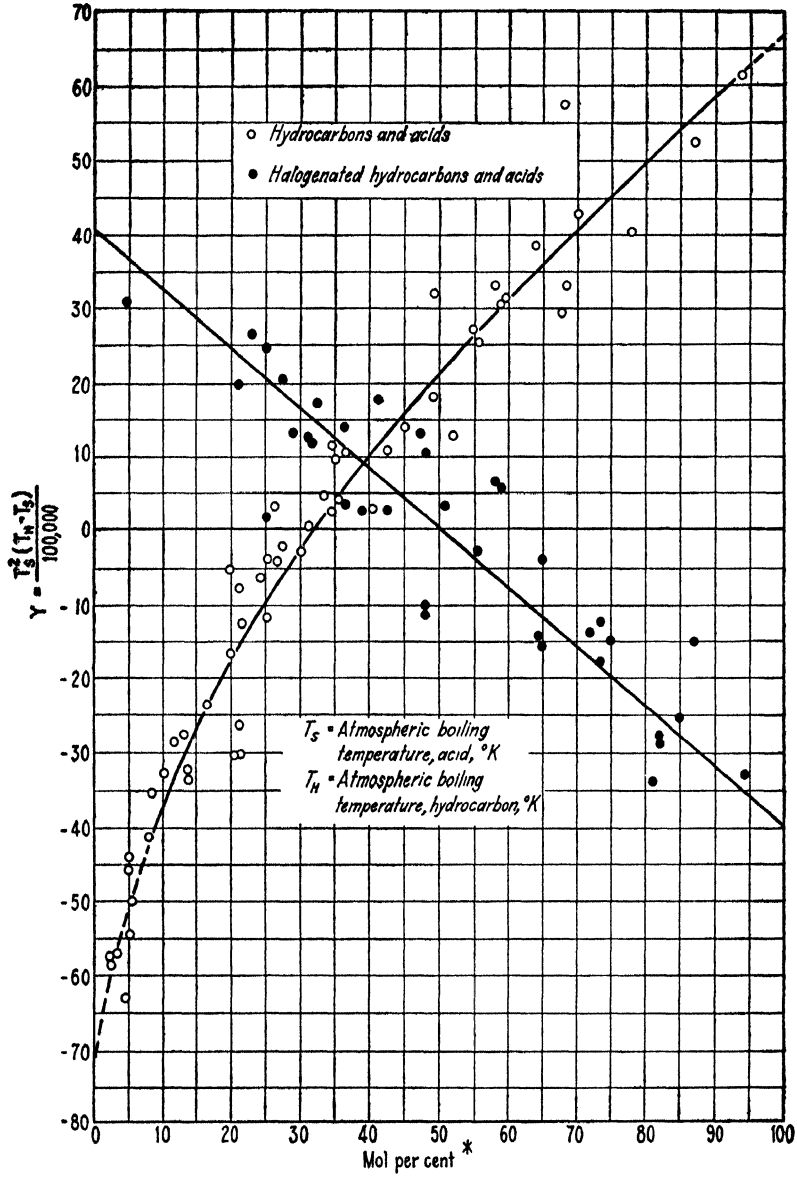


FIG. 3. Composition of binary azeotropes—hydrocarbons and various solvents. [*Courtesy of Meissner and Greenfield, Industrial and Engineering Chemistry*, **40**, 438 (1948).]



* Abscissa is mol per cent halogenated hydrocarbons for halogenated hydrocarbons-acids systems and mol per cent acids in hydrocarbons-acids systems.

FIG. 4. Composition of binary azeotropes—hydrocarbons and carboxylic acids [*Courtesy of Meissner and Greenfield, Ind. Eng. Chem.*, **40**, 438 (1948).]

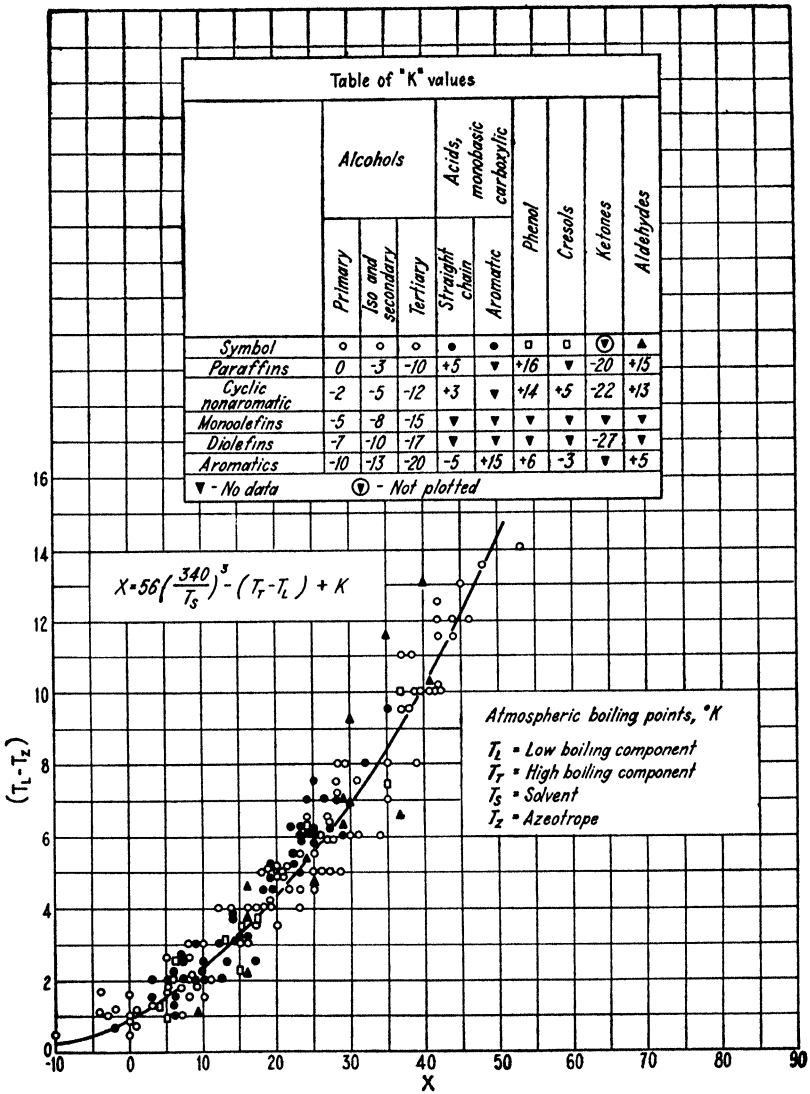


FIG. 5. Atmospheric boiling points of binary azeotropes—hydrocarbons and various solvents. [*Courtesy of Meissner and Greenfield, Ind. Eng. Chem.*, **40**, 438 (1948).]

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