Theoretical Aspects of Stagewise Operations in Chemical Engineering

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by

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HEMICAL ENGINEERING

To the Faculty of the Graduate School of Arts and Sciences
University of Cincinnati
Cincinnati, Ohio

Gentlemen:

I respectfully submit the following dissertation entitled "Theoretical Aspects of Stagewise Operations in Chemical Engineering" in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

This investigation was originally undertaken solely for the study of the difference equations arising in binary and multicomponent distillation. Later the topic was enlarged and generalized to include the other stagewise processes of gas absorption and extraction. It is the primary purpose of this work to present the principles underlying the graphical and analytical solutions of the equations which arise in the stagewise processes of chemical engineering.

Any claim that this research contributes to the advancement of knowledge in the field of engineering lies in the method of attack rather than in any particular results. The specific formulas that have been derived are simply the results of a considerable amount of drudgery. Anyone who masters the fundamental concepts presented herein can multiply the contents of the pages within this binder many fold. It is sincerely hoped that this scratch which has been made on the surface of stagewise processes will be steadily enlarged by future investigators in the years to come.

Respectfully submitted,

Frank M. Tiller

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ABSTRACT

This dissertation is divided into four parts consisting of (1) an introduction to stagewise processes; (2) a summary of investigations appearing in the literature; (3) the detailed application of finite calculus to the stagewise operations of extraction, gas absorption and fractionation; and (4) an appendix containing the elements of the finite calculus and a few numerical solutions of problems presented in part (3).

In the introduction emphasis is placed upon the importance and fundamental nature of stagewise processes. The natural relationship existing between the finite calculus and stagewise operations is indicated, and a discussion is presented concerning the contrast with differential processes as treated with infinitesimal calculus. In part II, the literature pertaining to stagewise operations is taken up briefly. Particular emphasis is placed on the types of equations which have arisen in stepwise operations and their graphical or analytical solutions. In general, it will be seen that few investigators recognized the connection between the equations resulting from material balances in stagewise equipment and difference equations. The union between the material balances of stagewise operations and the mathematical methods of treating difference equations forms the chief subject of this research.

In part III a detailed application of finite calculus to chemical engineering stagewise operations is given. The chief objective of this third section is to illustrate the power of the methods of the difference calculus for solving the stagewise equations. Both graphical and analytical methods are presented.

The appendix contains the fundamental elements of differences, sums and finite integrals, and the graphical and analytical solutions of difference equations. For the reader who is not familiar with the difference calculus, it is recommended that the section be studied prior to reading Chapter III. In addition part V of the appendix contains examples of both graphical and analytical solutions of problems arising in extraction, washing, gas absorption, and distillation.

GENERAL REMARKS CONCERNING STAGEWISE PROCESSES

Chapter I

Among the natural and mathematical processes involving interrelated variables, those in which the independent variable exists solely for integral values are termed stagewise. These stagewise processes are characterized in that their graphical representation consists simply of a series of points with abscissas equally spaced along the axis of the independent variable. Although the independent variable is restricted to integral values, the values of the dependent variables are determined only by physical limitations. In the more common stagewise processes, there is usually but one discrete independent variable. In general, a stagewise or stepwise process may be considered as one in which the variables are incapable of mutually continuous variation. These processes are in contrast to the differential processes in which the variables are continuous functions of one another.

Distance and time are truly continuous variables of nature. In moving body problems, the related length and time may take on infinitesimal increments, and the processes are classed as differential. The flow of mass or energy on a macroscopic scale is treated as a differential process, although, when the fundamentally discontinuous nature of mass and energy is considered, it is seen that certain processes which appear to be differential are actually stepwise in nature. From the practical viewpoint any stepwise process may be treated as though it were differential if the magnitude of the unit variations in the discrete variables are less than the limit of accuracy of the physical measurements involved in the quantitative measurement of these variables or if the magnitudes are very small. In general, a stagewise process can accurately be treated as differential in nature if the values of the first difference and first derivative lie in the neighborhood of one another.

Many experiments are carried out in a stagewise manner. The observation of data at equally spaced intervals gives rise to a series of isolated points, although if the process is differential by nature, a smooth curve is drawn intuitively through the points. Even though such processes may be differential, they can sometimes be handled mathematically more easily by stepwise means. This is particularly true in the case of the rectification of certain kinds of experimental data.

Many examples of stagewise processes arise in pure and applied mathematics. The value of the sum of the terms of a finite series is determined by the integral number of terms involved. The sum of an arithmetic or geometric series varies in steps as the number of terms is changed. In games of chance various problems of stepwise nature are encountered. Where a series of games are played the fortunes of the players vary in a discontinuous and stepwise manner from game to game. The probability that a player will win or lose a certain amount of money falls into a doubly stepwise process, in that the probability is a function of both the player's fortune and the number of games to be played. These latter two variables are both characteristically stepwise quantities. The installment payment of loans and compound interest problems fall into the category of stagewise processes.

In chemical engineering, two essentially different types of operations arise as considered from the standpoint of the relationship of the variables. In the first type the variables change continuously and differentially, and material balances lead to differential equations. The second type is characterized by a lack of continuity in the variables. The independent variable is discrete, and consequently the dependent variable is defined only at isolated points. This latter type is stepwise by nature, and material balances lead to difference equations.

Many examples of differential processes are found among the unit operations. In the flow of fluids, the transfer of heat, and the absorption of gases, liquid-liquid extraction, or fractionation in packed towers, infinitesimal changes of the mutually dependent variables are possible, and the processes are classed as differential. In such operations, the laws of continuity dictate the mathematical processes to be used.

In contrast to these operations, which are characterized by differential[*] changes in the variables, are the stagewise processes of chemical engineering. The processes termed stagewise are those in which two or more phases are contacted in some portion of the process, and after an interphase transfer of material and energy has resulted, are then separated for further contactings. In these operations the contacting of phases is accomplished in successive stages of the process. The stages form an arithmetic sequence, and the discrete number associated with any stage becomes the independent variable. Only whole stages exist physically, and consequently the independent variable is defined solely for integral values. In general the concentrations in the phases of the various components are the most important dependent variables. For a given set of external conditions and a given mode of operation, the concentration variables are uniquely determined by the stage number. Except for

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[*] The term "differential" is applied rather than its confusing analog "continuous", because many processes, stagewise or differential, are operated continuously. Thus a stagewise process may be continuous with respect to time. In this dissertation the term continuous will usually be employed to indicate that the process is operated continuously, while the term differential will be reserved for indicating the relationships that exist between the fundamental process variables.

certain limiting conditions, the theoretical values of the dependent variables change in finite jumps from one stage to the next. Stagewise processes are not ruled by the laws of continuity, and the branches of mathematics based on continuous variables are of little use in the solutions of the fundamental equations that arise.

In stagewise processes, difference equations usually arise through the application of the laws of conservation of mass and energy; and various schemes have been proposed for solving these equations. Dodge and Huffman[23] suggested for binary fractionation with constant relative volatility that, if the change in concentration per stage were small, $\Delta x/\Delta n$ could be replaced by dx/dn and the resulting differential equation solved. However, the substitution of infinitesimals for finite increments is at best an approximation and in addition can only be used where the number of stages is large. Solving the corresponding difference equation is generally no more difficult and has the advantage of giving exact solutions.

In the past, it has frequently been the practice in chemical engineering to use algebraic iteration[55,82,86,88] for solving the difference equations that have arisen. While the algebraic iterative method yields exact solutions to the difference equations, it is sometimes tedious and frequently requires considerable ingenuity and intuition on the part of the investigator. In the past, the calculus of finite differences, though a well known and old branch of mathematics, has not often been used in the solution of the fundamental problems arising in chemical engineering even though difference equations have been freely sprinkled through chemical engineering literature. In the chapters that follow, the application of finite differences to chemical engineering is presented.

The invention of the stagewise processes is intimately associated with the early history of chemical engineering. The development, near the beginning of the 19th century, of countercurrent leaching of black ash in the LeBlanc process[47] for production of sodium carbonate was among the first stepwise processes applied to a prominent industrial process. One of the first plate fractionating towers was developed by Pistorius in 1817.[9] The apparatus was employed for distilling and concentrating alcohol in a single operation. Condensation was effected by cooling water. The modern continuous column was developed by Savalle in France. His ideas were drawn partially from the stills of Coffey and Champonnois.[9] In 1885 Lunge and Rohrman[63] patented a device for scrubbing gases which consisted of a tower with a series of internal plates. At a later date Lunge[64] described the scrubber in detail and termed it a "plate tower." The apparatus was probably inspired by the rectifying apparatus of that day and was similar to the Coffey still. The stagewise equipment of today, while reflecting modern techniques, is fundamentally the same as that developed in the last century.

INVESTIGATIONS CONCERNED WITH STAGEWISE OPERATIONS

A Review of the Literature

Chapter II

Part I Extraction

In extraction processes the separation of chemically different substances is accomplished by selective liquid treatment. The scope of extraction processes is broad and in different respects is similar to gas absorption, distillation, and crystallization. The term extraction generally includes solvent extraction, washing, and leaching. Recently a combined operation of extraction and distillation called "extractive distillation" has been described.[7] In this process a simultaneous extraction and distillation are carried on by adding a third component at the top of the column. The effect of adding this third component for extractive purposes is to change the effective value of the relative volatility.

The partial separation of a liquid mixture into its component parts by a selective solvent which is immiscible or partially miscible with at least one component of the liquid mixture is termed solvent extraction. The use of solvents in this manner for refining petroleum fractions has had a marked effect on the petroleum industry in recent years. Edeleanu[27] was among the first to advocate the use of sulfur dioxide for removing certain elements of petroleum fractions rather than destroy them. He showed that aromatic and unsaturated hydrocarbons which were the cause of undesireable behavior in illuminating oil could be eliminated with sulfur dioxide. Many other solvents including propane[98], nitrobenzene[32], chlorex[80], and phenol have been used in the refining of petroleum. Propane is of particular value as it is cheap and readily available in petroleum fields. It has the advantage that by using it at different temperatures and pressures, it is possible to remove wax, napthenic bodies, asphaltic substances, heavy ends, and color bodies. Other solvent extraction processes such as the use of ethyl acetate for extracting acetic acid from water are in common use.

The removal of soluble substances from the surface of insoluble materials by solution in a liquid is termed washing. If the solute must be removed by a slow diffusional process from within the solid, as in the beet sugar industry, the operation is termed leaching. This latter operation will not be discussed in this dissertation. The operation of washing in Dorr[25] countercurrent decantation processes is common in the chemical industries. In the preparation of sodium hydroxide from the interaction of lime and soda ash, a fine precipitate of chalk is produced and the caustic soda must be washed from the surface of the calcium carbonate in a countercurrent process.[34] Other washing operations including the production of phosphoric acid through the use of sulfuric acid,[3] the separation of wax from paper, and the extraction of oil from fish livers[74] are well known.

Ham and Coe[40] were among the first to discuss problems allied to washing in successive stages. Their work was later taken up by MacMullin and Weber[65] who solved a number of difference equations by successive approximations. Among the difference equations which arose are the following:

$$F\ c_{n-1} = F\ c_n + k\ V\ c_n^2 \tag{1}$$

$$F\ c_{n-1} = F\ c_n + k\ V\ c_n^3 \tag{2}$$

in which

c_n = concentration in n(th) unit
F = rate of flow
k = specific reaction rate
V = volume of each unit

Hawley[43] was a pioneer in the mathematical treatment of washing processes. He indicated that there was a profuseness in the use of such terms as lixiviation, leaching, percolation, decoction, and decantation all of which were loosely used as synonyms for washing. The problem of washing a soluble substance (NaCl) from the surface of an insoluble, impermeable, wettable solid (glass beads) was treated in detail in his earliest work. Such terms as solvent ratio and solvent retained were clearly recognized and defined. No formal difference equations were introduced, but the solutions of a number of different cases were obtained by algebraic iteration. The problem of batch countercurrent extraction without movement of solids was adequately treated in Hawley's work of 1921. Hunter and Nash[50] also discussed the mechanism of batch countercurrent extraction, and Ravenscroft in a private communication to Baker[5] presented a relationship between the number of units required for countercurrent extraction both with and without pumping of the solids.

Mathematical formulas for washing have been given in papers by Baker[5] and Sanders[79]. The latter author presented the following second order difference equation

$$W\,x_n + W\,S\,x_{n-2} = (1 + S)W\,x_{n-1} \tag{3}$$

where W = pounds of water per pound of inert sludge, S = solvent ratio, and x_n = concentration in n(th) stage. In Sanders' paper a series of equations similar to (3) were solved simultaneously to obtain the value of x_n as a function of n. Graphical plots which could be employed for obtaining solutions of the resultant equations were presented. Baker followed an identical procedure but did not set up any formal difference equations. He suggested graphical solution of his equations.

Ravenscroft[74] was among the first to present a graphical solution for the number of stages when the solvent ratio is not constant. If the density and viscosity of the solution are appreciably affected by the solute concentration, the solvent retained by the inert solids may vary from stage to stage resulting in a changing solvent ratio. Generally it might be expected that this sort of variation would occur when the solute concentration undergoes a large change. Data on solvent retained is meager both for cases of constant and variable solvent ratio, and, consequently, it would generally be necessary to obtain experimental data for most systems. Ravenscroft's method is rather involved and Elgin[28] presented another solution based upon triangular coordinates which is similar to the method suggested by Evans[30] for liquid-liquid extractions. Improvements on the techniques for solution of such problems were given by Tiller[89] and Armstrong and Kammermeyer.[1] These latter authors developed simplified procedures based upon a modification of the McCabe-Thiele method using a curved operating line.

While relatively few publications concerning washing have appeared, the past several years have witnessed a great increase in the number of researches dealing with liquid-liquid extraction. This is partially due to the wider utility of solvent extraction in the chemical industries and also partially because of the large amount of phase data required for the necessary calculations with ternary systems. The general theory of both cocurrent and countercurrent extraction has been dealt with by various authors. In general it has been necessary to employ triangular coordinates (equilaterial or right triangular) with weight percentages for the most general case of solvent extraction.[82] Simplified procedures have been developed for cases in which two of the components are immiscible, and analytical solutions obtained for those systems having a constant distribution coefficient.[89] As in washing, the analytical solutions of the difference equations have been obtained by algebraic iteration.

Evans[30] developed the concept of minimum concentration and relative efficiency for cocurrent extraction. Tiller extended the ideas to countercurrent operation and produced formulas which were similar to those of Kremser.[55] Evans and Tiller have both shown that for constant distribution coefficient the ratio of the actual amount of solute extracted to the maximum amount which could be extracted is dependent upon the numbers of stages and the solvent ratio for a given system and not upon the initial concentrations of the solvent or solution being treated. The relative efficiency as defined by Evans and Tiller represents the ratio of the actual overall efficiency (ratio of solute removed to solute present) to the maximum overall efficiency. It is of value in that it shows how closely the efficiency of an actual process approaches the theoretical maximum efficiency. The effect on efficiency of adding additional stages is forcefully shown by relative efficiency calculations. Evans has pointed out that after five stages are in use, little increase in efficiency can be expected from adding additional stages. In cocurrent extraction no less than 94 per cent of extractable material will be removed if five stages are employed while in countercurrent extraction at least 83 per cent of the extractable material will be removed with five stages. These percentages represent operation under the most unfavorable conditions, and in countercurrent extraction it would be expected that at least 95 per cent of the extractable material would normally be removed under reasonable operating conditions with five stages.

In recent years emphasis has been placed upon the operation of packed extraction columns and a considerable amount of data has appeared on the variables affecting the tower capacities.[18,29,77,85] Row, Koffolt, and Withrow[77] investigated the effect of various types of packing, bubble caps, and perforated plates on the system toluene-benzoic acid-water. These authors correlated their data by plotting H.T.U.'s against certain of the operating variables. They found that Raschig rings and Berl saddles gave the best results while a spray column with large drops gave the poorest results. In between these extremes were spray columns with small drops, knitted cloth packing, and bubble caps.

Comings and Briggs[18] carried out solvent extraction involving the transfer of benzoic acid, aniline, and acetic acid between benzene and water layers. Wetted wall and packed towers were used for the experimental work. Mass transfer coefficients were given as functions of the velocities of both dispersed and continuous phases. In general it was found that the velocity of the dispersed film had the greater affect on the capacity coefficient.

Determination of accurate equilibrium data is essential both for performing calculations and for predicting applicability of a given solvent for extraction purposes. The International Critical Tables, the Science of Petroleum, and other publications,[6,46,62,95,99] contain a large amount of phase data for various systems. For complex petroleum mixtures, Dean and Davis[20] and Hill and Coats[45] have developed simple and useful methods for representing phase data. Tie lines are equally as important as solubility data and several methods of interpolation have been presented.[82,89] Othmer, White, and Trueger[72] presented a considerable amount of data on various ternary liquid systems and discussed correlation and interpolation of the distribution data.

Part II Gas Absorption

In the unit operation of gas absorption, the soluble components of a gas mixture are dissolved in suitable solvents. The gas and liquid phases are intimately contacted in either packed or plate columns so that there will be ample interfacial area for mass transfer. The reverse process in which a soluble substance passes from a liquid mixture into a gas is termed stripping. Mathematically, the two processes are identical. By far the greatest amount of work in the literature has been devoted to packed tower operation.

Lewis[57] was among the first to focus attention on the mathematical treatment of gas absorption in packed towers. He utilized the fundamental viewpoint that the rate of solution of a soluble gas is proportional to the partial pressure driving potential. Based upon this concept, Lewis developed equations relating the gas concentration to tower height. The solutions as developed by Lewis are essentially the same as those presented by later authors. Donnan and Masson[24] continued along lines similar to those used by Lewis in the development of theoretical equations using a slightly different nomenclature and more thoroughly discussing the limitations.

Lewis and Whitman[58] introduced the two film concept which has since served as the fundamental basis for the development of theoretical formulae in gas absorption. The definitions and relations of individual and overall gas and liquid film coefficients were presented by these authors. Fundamentally it was assumed that the rate of mass transfer was proportional to the concentration gradient expressed as partial pressures in the gas phase and mass per unit volume in the liquid phase. Although a tremendous quantity of work based upon the two-film concept has appeared in the literature, no direct experimental data has been offerred to confirm the validity of the assumptions. A similar situation existed in the field of drying of solids in which a great deal of theoretical work was done before the fundamental assumptions were experimentally tested. Sherwood[83] and others assumed that the rate of moisture flow was proportional to the concentration gradient and derived theoretical equations for moisture distribution curves. Later, other authors[14,90] obtained experimental data and found that the proposed fundamental assumption governing the rate of moisture flow could not be justified and consequently that the theoretical conclusions were unsound. It would appear that the two film theory of gas absorption should be subjected to the same searching analysis.

Cantelo,[12] Cantelo, Simmons, Giles, and Brill,[13] and Garber[35] also have treated the problem of determining the height of a column as a function of the concentration variables and other parameters. These authors followed procedures similar to those of Lewis[57] and Donnan and Mason[24] but were more rigorous in their treatments. Cantelo[12] took into account the vapor pressure of the liquid and Garber used mol fraction units for expressing the equilibria. This latter procedure led to a rather involved expression requiring tedious calculations. Greenberg[39] continued the work of Garber and applied his formulas to experimental data for the calculation of transfer coefficients.

A number of authors[41,59,82] utilized the procedures originally developed for diffusional processes by Maxwell for application to gas absorption. The original equations presented by Maxwell for the true diffusion of one gas through another were utilized for mass transfer through the films postulated in the Lewis-Whitman two film theory. A number of equations were derived showing the effects of different variables on the mass transfer coefficients. Gilliland and Sherwood[38] described a wetted wall tower and gave experimental data supporting the deductions drawn from the diffusion equations.

Chilton and Colburn[16] introduced the concept of transfer units and height equivalent to a transfer unit (H.T.U.). The relationship between the H.T.U. and the mass transfer coefficients was developed. The methods presented by these authors have been an extension of the two film theory and are almost exclusively utilized by present day experimentors. It has become common practice to correlate data in the form of plots of H.T.U.'s against operating variables.

Very little published work has appeared on the subject of gas absorption in plate towers. Graphical procedures have been based upon the McCabe-Thiele method[67] used in determining the number of theoretical plates in fractionating columns. Kremser[55] obtained an expression relating the concentration to the number of plates for cases in which the equilibria may be expressed by y = Hx where x and y are liquid and vapor concentrations expressed in mass ratio units. Souders and Brown[88] defined a quantity known as the absorption factor and which is given by

$$\text{absorption factor} = \frac{y_o - y_N}{y_o - Hx_o}$$

where x_O, y_O, y_N, and H are entrance liquid composition, entrance gas concentration, exit gas concentration, and Henry's coefficient as defined above. This absorption factor is similar to the efficiencies defined by Evans[30] and Tiller.[89] Tiller and Tour[91] treated two problems in gas absorption illustrating the use of the calculus of finite differences. Garber and Lerman[36] were among the first to recognize the value of finite differences in solving problems in stripping. They obtained and solved a Riccati difference equation for stripping in plate towers. They also solved certain equations graphically for which no analytical solutions could be obtained.

Part III Distillation

Whereas virtually all of the work in absorption has been confined to packed towers, the reverse is true in fractionation where the majority of investigations have been concerned with plate towers. As far back as 1893, Sorel[87] proposed a method for obtaining the number of equilibrium stages in an alcohol column. While he suggested a stepwise algebraic procedure, his method can easily be adapted to graphical calculations as will be shown in the chapter on distillation. Contrary to some prevalent impressions, Sorel's procedure readily adapts itself to graphical computations without the so-called "usual simplifying assumptions" in which the molal overflow is assumed constant. With Sorel's equation, a curved operating line must be used in conjunction with the equilibrium curve for graphical calculations. Hausbrand[42] introduced the assumption of constant molal overflow and this concept coupled with Sorel's work forms the basis for the modern theory of fractionation calculations.

Lewis[60] was the first to develop a graphical procedure for obtaining the number of plates by replacing the first difference by the first derivative. Lewis failed to realize that the procedure was not sound except for large numbers of plates and stated that the equations involving derivatives were exact as they depended solely upon material balances. Dodge and Huffman[23] recognized the limitations of the Lewis equations and obtained analytical solutions utilizing relative volatilities. These methods in which derivatives are substituted for differences have not produced any simplifications and should be avoided.

Graphical solutions were proposed by Ponchon and Savarit[75], Fouche and Thorman,[67] and Rodebush.[76] The method of Ponchon and Savarit is the best among these authors and is recognized as a standard procedure. In order to utilize this method it is necessary to have enthalpy data, and unfortunately as these data are seldom available, the method is not often employed. The most popular graphical method is that of McCabe and Thiele[67] in which a straight operating or material balance line is plotted on the equilibrium diagram and the number of stages stepped off.

The first analytical solution for binary fractionation was obtained by Fenske[31] for infinite reflux ratio. Later Smoker[86] solved the binary equations with finite reflux ratio for the case of constant relative volatility. By translating the axes so that the origin of coordinates coincided with the intersection of the operating and equilibrium curves, Smoker was able to simplify the difference equations and solve them by algebraic iteration.

In multicomponent fractionation, Lewis and Matheson[56] revised the Hausbrand equations and obtained solutions by trial and error subject to Raoult's law representing the equilibria. Lewis and Cope[19] presented a trial and error graphical procedure which was equivalent to the method of Lewis and Matheson. Underwood[92] derived simplified equations for plate to plate calculations based upon constant relative volatilities. His equations possessed the advantage of eliminating the trial and error calculations and in not requiring determination of the vapor concentrations. Robinson and Gilliland[75] modified Underwood's method and took changing relative volatilities into account improving the accuracy of the method.

Brown and Souders[11] set up a second order difference equation based on a material balance for a single component of a multicomponent system. With the simplifying assumptions that the absorption and stripping factors were constant, Brown and Souders produced linear difference equations and solved them by algebraic iteration. The simplifications were such that the resulting equations were not trustworthy and this method has been abandoned.

Many other authors[37,44,48,52] have proposed approximate solutions and methods for obtaining feed plate compositions in multicomponent systems. While the various methods yield correct results, there is no method which is free of the usual objections to approximate solutions.

EXTRACTION OPERATIONS

Chapter III

Extraction processes are defined as those processes in which separation of different substances is accomplished by selective liquid treatment. The term extraction generally includes solvent extraction, washing, and leaching. The separation of a liquid mixture into its component parts by a selective solvent which is immiscible or partially miscible with at least one component of the liquid mixture is called solvent extraction. The removal of soluble substances from the surface of insoluble materials by solution in a liquid is termed washing. If the soluble material must be removed from the interior of the inert substance by a slow diffusional process, the term leaching is applied.

In solvent extraction, a liquid mixture is treated with a solvent which preferentially dissolves one or more of the components of the mixture. The solvent is recovered by evaporation, fractionation, steam distillation, decantation, or other separatory processes. Solvent extraction may be valuable where ordinary fractional distillation is impractical because of close volatilities of the substances to be separated. In general, solvent extraction is employed to separate molecules of similar chemical type while distillation finds use in the separation of different sized molecules. In some cases where both distillation and extraction are practical, cost economics determine which process should be used.[94] Even though extraction must generally be followed by a distillation process to remove the solvent, extraction may prove more economical.

Solid precipitates, formed in liquid solutions, are usually wet after filtration or decantation and must be dried. If the adhering solution contains large concentrations of undesirable soluble impurities, they must be removed prior to the drying operation. By treating the solids with pure liquid in a washing process, the impurities may be reduced to any desired concentration. In many cases, however, the soluble substance is the valuable material. The adhering liquid should then be removed by washing with the optimum amount of wash liquid so that final concentration of the solution is not too costly and too much soluble substance is not lost. Leaching operations involving diffusional processes will not be treated in this dissertation.

In any stagewise extraction operation, the essential units are (1) a mixer and (2) a separator. Numerous methods are available for contacting or mixing the liquids or liquids and solids. Operation may be batch or continuous, multiple or differential contact, countercurrent or cocurrent. In batch or multiple contact processes, mixing may be accomplished by mechanical agitation, compressed air, or other means. In countercurrent towers, where the light layer rises through the heavy layer, mixing may be brought about by various types of tower packing, special types of bubble caps, or by spraying one liquid into the other. Phase separation is frequently effected in settling chambers but may also be brought about be centrifuging.

Extraction may be carried out in a number of different ways as outlined in the next paragraphs. Included in the outline are differential contact extraction operations which are best treated by the methods of the differential calculus.

Cocurrent Operation

1. Single batch contact. The solvent and material to be treated are brought together and allowed to remain in contact until the single batch treatment is completed.

2. Continuous single contact. Two streams of material are brought together and separated continuously.

3. Multiple batch contact with fresh solvent in each treatment. In this type of operation, the solvent is divided into a number of portions, each of which is used for only one batch treatment and is then discarded.

4. Continuous multiple contact with fresh solvent in each treatment. This operation differs from the previous one in that the contacting and separation processes are continuous.

5. Differential contact.[94] Solvent is added in a

continuous stream to a fixed amount of material, and the extract is removed continuously and differentially.

Countercurrent Operation

1. Batch countercurrent multiple contact. In this system the material to be treated and the solvent pass through the process in a countercurrent fashion. Operation is batch in the sense that the solvent and material to be treated are not brought together in continuous streams. The materials are contacted for a sufficient length of time and are then separated for further treatment.

2. Continuous countercurrent multiple contact. This process differs from the previous one in that there is a continuous flow of material from one stage to the next.

3. Countercurrent differential contact.[77] The two liquid phases pass each other in opposite directions. Flow depends upon the difference in density of the two phases, and pumping is impossible. The extraction may be carried out in either spray or packed towers.

4. Countercurrent operation with reflux.[78,94] The degree of separation may be greatly improved if reflux is employed in the extraction process. It is more difficult to produce reflux in an extraction column than in a fractional distillation column. In changing an extract to reflux at the top of a column, it is necessary to obtain a reflux with both proper concentration and proper density. Otherwise

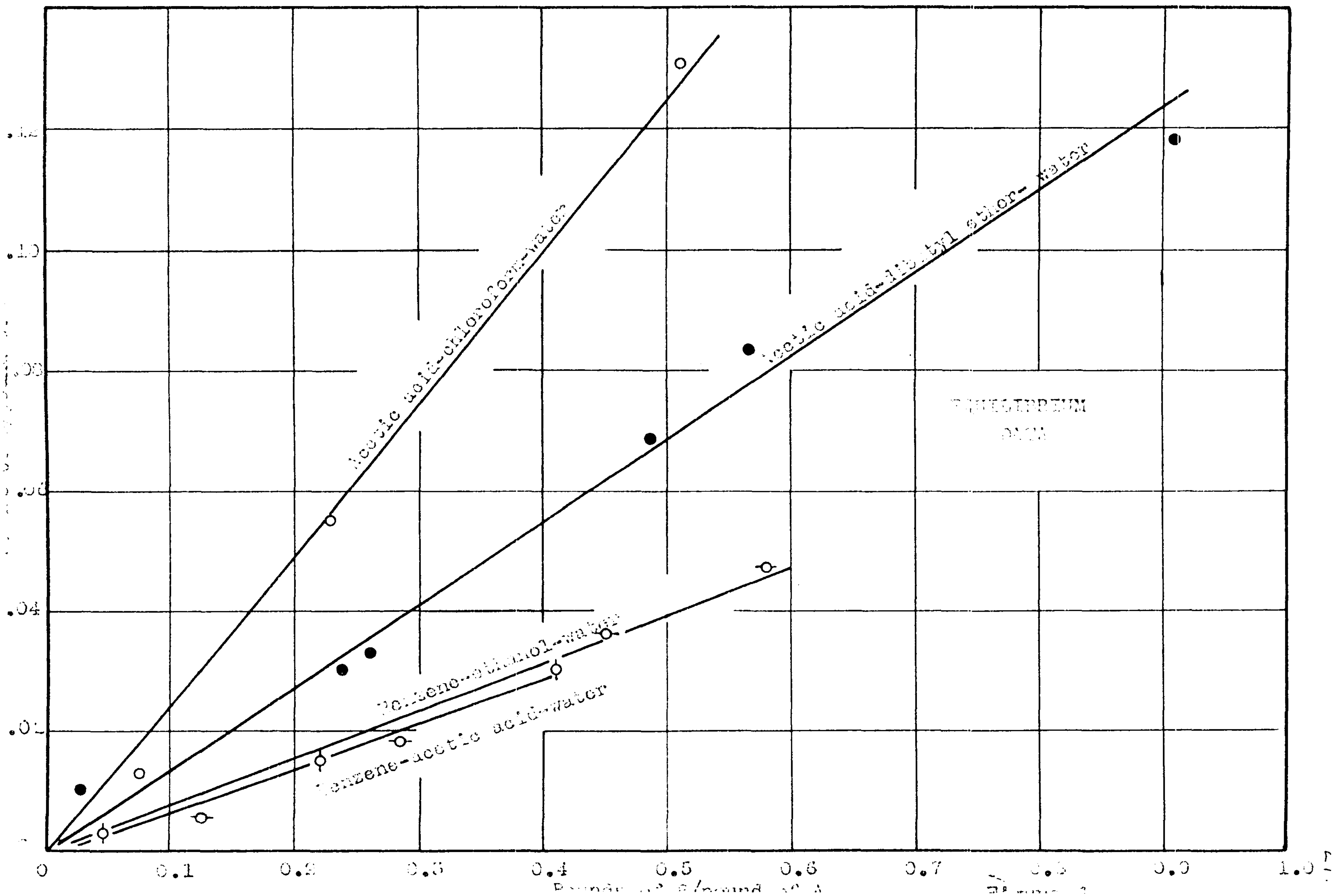
impossible extractions become feasible with the use of reflux.

Cocurrent Extraction

The term, cocurrent, is applied to extraction operations in which fresh solvent is employed in each stage. The original solution is treated with fresh batches of solvent as it passes from contactor to contactor, and after each treatment, the extracts are discarded. Compared with countercurrent extraction, greater masses of solvent are required to effect a given decrease in concentration.

It is essential to the success of a solvent extraction process that on addition of solvent to the solution to be treated that (1) at least two phases be formed and (2) a change be accomplished in the relative proportions of the substances to be separated. Thus if a two component mixture is to be separated by the action of a third component, the addition of the third component must produce a mixture lying in a two-liquid phase region; and the equilibrium must provide for a change in the relative concentrations of the mixture.

The essential variables involved in extraction operations are the inlet and exit concentrations, number of stages, and relative amounts of solution and solvents. In the general case involving three component systems, it is necessary to use a graphical method on triangular coordinates.


Acetic acid-chloroform-water
Acetic acid-dibutyl ether-water
Toluene-ethanol-water
Benzene-acetic acid-water
EQUILIBRIUM DATA
.02
.04
.06
.08
.10
.12
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Pounds of S/pound of A

For the special case in which two of the components are immiscible, the graphical treatment can be simplified, and under special conditions, analytical solutions may be obtained.

Immiscible Solvents.[82] Published data dealing with three component systems indicates that virtually all of them have regions of miscibility. However, in a great many cases two of the components are nearly immiscible over a substantial portion of the solubility curve. Examples of typical systems and the regions of immiscibility (solubility less than 2% by weight) along with the distribution coefficients are given in the following table:

Table I

System			Region of Immiscibility			
A	B	C	% B in A	% B in C	Dist. Coef.	Temp.
Water	Ethanol	Benzene[93]	35	15	.076	25°C
Water	Acetic Acid	Isopropyl Ether[29]	20	6	.28	20°C
Water	Acetic Acid	Chloroform[94]	30	20	.21	18°C
Water	Ethanol	Trichlorethylene[60]	30	10	.07	25°C
Water	Acetic Acid	n-butyl ether[72]	60	20	.14	25°C

For these systems it is possible to carry out simplified graphical calculations.

Consider the system comprising components A, B, and C in which A and C are completely immiscible irrespective of the presence of B. Suppose C is the solvent that is used to extract B from the solution containing A and B. The phase data can be conveniently represented on rectangular coordinates as indicated in Figure I. with concentrations expressed in mass ratio units. In the process to be considered, b lbs./hr. of A (B-free basis) containing x_o lbs. B/lb. of A is treated in successive contacts with w lbs./hr. of C(B-free basis) containing y_o lbs. B/lb. of C. If the point (x_o, y_o) lies below the equilibrium curve, a transfer of B from the A to the C phase must take place. In Figure 2, a schematic diagram of the process is shown. The amounts of component B flowing from one stage to the next are shown. A material balance over the (n+1)st stage yields

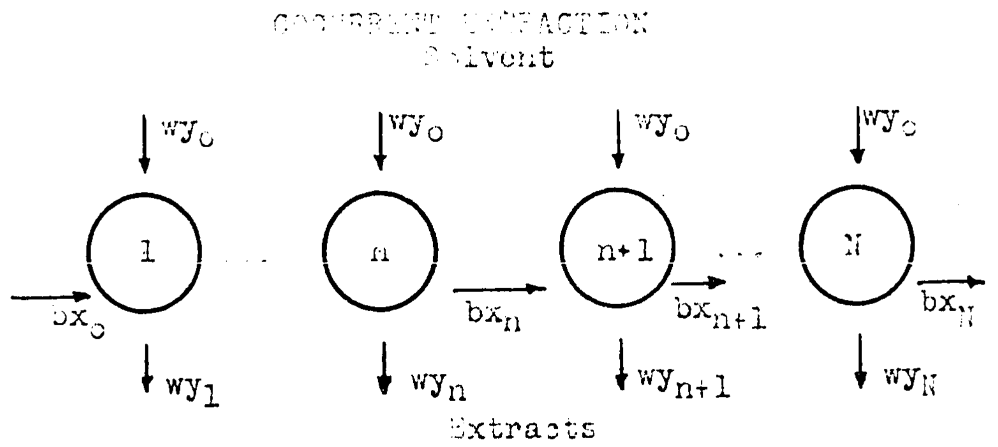


Figure 2

$$w(y_{n+1}-y_o) = b(x_n-x_{n+1}) \tag{1}$$

Defining w/b as the solvent ratio, a, and rearranging terms gives

$$(y_{n+1}-y_o)/(x_{n+1}-x_n) = -1/a \qquad (2)$$

Equation (2) is a difference equation which is exact as it is solely the result of a material balance. Because three variables, x, y, and n, are involved, the difference equation can not be solved unless there is a known relation between x and y. If it is assumed that the stages are theoretical, i.e. extract and raffinate are in equilibrium in each stage and the point (x_n, y_n) for each stage lies on the equilibrium curve, a procedure for relating the number of stages to the parameters and dependent variables can be deduced.

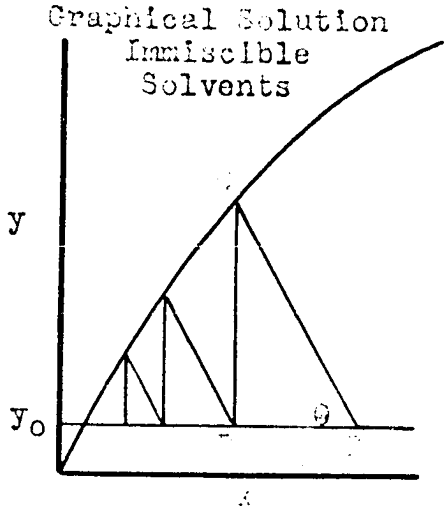


Figure 3

To locate the point (x_1,y_1) representing the first stage and successive points (x_n,y_n), first construct a line through the point (x_o,y_o) having a slope -1/a. According to Equation (2), this line must intersect the equilibrium curve at (x_1,y_1). This is evident from the triangle PQR in which

$$(y_1-y_o)/(x_1-x_o) = \tan \theta = -1/a \qquad (2b)$$

Having obtained x_1, the same procedure may be used to obtain (x_2,y_2) and in general (x_n,y_n) from (x_{n-1},y_{n-1}). The number of units necessary to produce the desired reduction in concentration is given by the number of points on the equilibrium curve.

The above method can be modified if the equilibrium relationship is expressed by $y_n = k_n x_n$ where k_n is the distribution coefficient for the nth stage. Eliminating y_{n+1} from (2a) yields

$$a(k_{n+1} x_{n+1} - y_o) = x_n - x_{n+1} \tag{3a}$$

or

$$x_n = (ak_{n+1} + 1)x_{n+1} - ay_o \tag{3b}$$

The solution of this difference equation falls under case 3 of section A in Part IV of the Appendix. The operating line x_n vs x_{n+1} can be plotted as indicated in Figure 4. The points (x_o,x_1), (x_1,x_2), (x_n,x_{n+1}) all lie on the line represented by (3b) while the points (x_1,x_1), (x_2,x_2), (x_n,x_n) lie on the 45° line. If x_o is given, x_1 can be found as the corresponding point on the operating line as shown in Figure 4. After crossing horizontally to the 45° line to the point (x_1,x_1), the point (x_1,x_2) can then be found on the operating line. The total number of steps necessary to reduce x_o to x_1 is given by the steps or

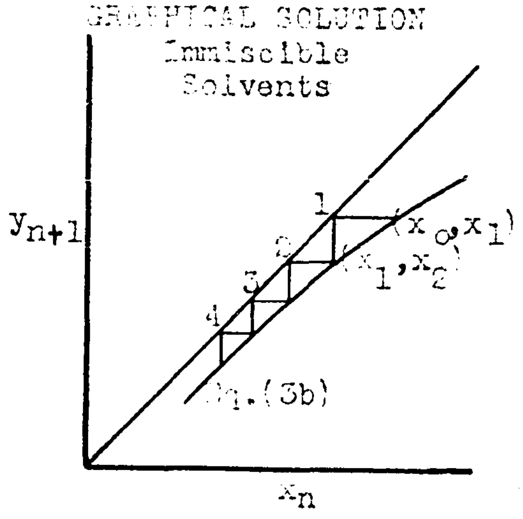


Figure 4

preferably by the points 1, 2, 3, ..., etc., on the 45° line.

Constant Distribution Coefficient[30,82] If the concentration data for the systems in Table I are plotted, it will be observed that the data can be approximated by straight lines as shown in Figure I. For these systems in which the equilibrium curve is straight, and the distribution coefficient in Equation (3b) is constant, an analytical solution relating the variables can be obtained. Equation (3b) may be rearranged to give

$$x_{n+1} - \left[1/(ak+1)\right] x_n = ay_0/(ak+1) \tag{4}$$

Equation (4) is a first order linear difference equation with constant coefficients. Placing this equation in standard form gives (See Part III of Appendix)

$$\left[E - 1/(ak+1)\right] x_n = ay_0/(ak+1) \tag{5}$$

The solution of the reduced equation is $C/(ak+1)^n$, and a particular solution of the complete equation is y_0/k (Equation (33), Part III of Appendix). The sum of these two solutions is then the complete solution of (4), i.e.

$$x_n = C/(ak+1)^n + y_0/k \tag{6}$$

If the initial concentration is x_0, C may be determined by placing n = 0 and solving the resulting equation. Determination of C leads to

$$x_n = (x_0 - y_0/k)/(ak+1)^n + y_0/k \tag{7}$$

It is usually desired to know how many contactings are necessary to reduce the initial concentration x_o to the final concentration x_N. Letting N be the total number of units and solving for N gives

$$N = \frac{\log(x_o - y_o/k)/(x_N - y_o/k)}{\log\,(ak+1)} \tag{8}$$

A differentiation between n and N is made on the basis that N refers specifically to the total number of units while n may refer to any unit between zero and N. If the number of units is fixed, the solvent ratio may be determined from (8) as follows

$$\alpha+1 = (1/k)\left[\frac{x_o - y_o/k}{x_N - y_o/k}\right]^{1/N} \tag{9}$$

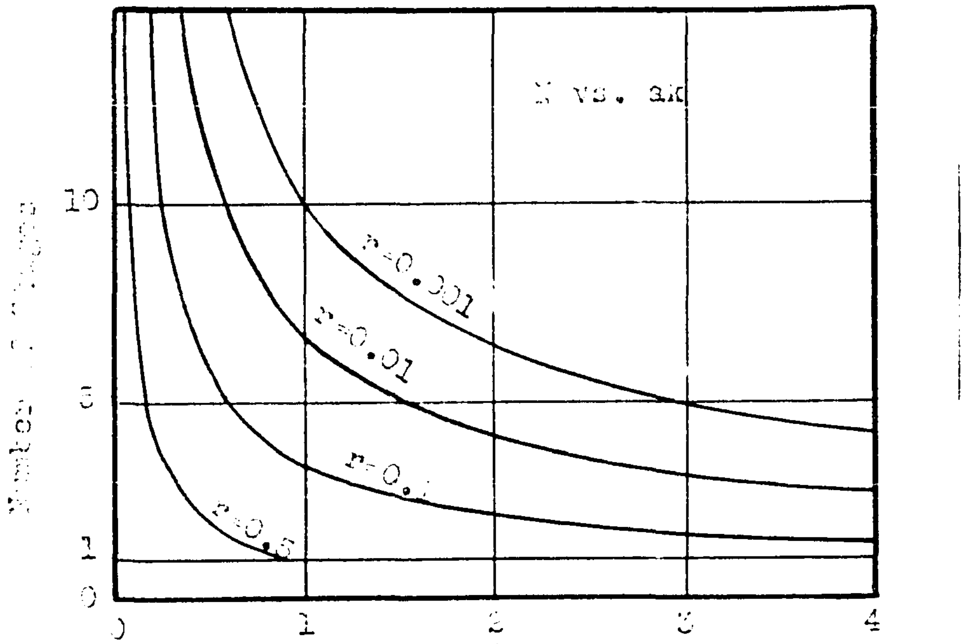


Figure 5

The effect of the solvent ratio and distribution coefficient on the number of required units is shown in Figure 5. The product ak is plotted against N for constant values of the raffinate ratio, r = $(x_n - y_0/k)/(x_0 - y_0/k)$, which is defined as the ratio of the material remaining after N treatments that may be removed by further extraction to the maximum amount of material that could possibly be extracted with an infinite amount of solvent. It is apparent that for small values of ak, a large number of contactings are required.

<u>Decrease in Concentration per Contact</u>. The decrease in concentration from the nth to the (n+1)st contacting is simply $x_n - x_{n+1} = -\Delta x_n$. Taking the first difference of x_n in (7) and rearranging yields

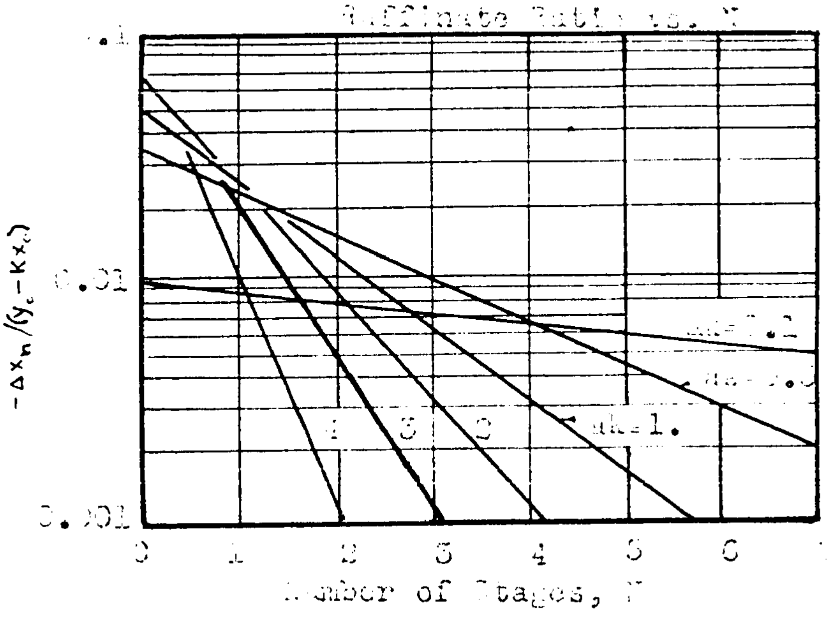


Figure 6

$$-\Delta x_n/(x_0-y_0/k) = ak/(ak+1)^{n+1} \qquad (10)$$

The quantity on the left side of the equation represents the ratio of the decrease in concentration per contacting to the maximum possible decrease. In Figure 6 the logarithm of this ratio is plotted against n for various values of ak. With very small values of ak, the decrease in concentration per contacting does not drop very much with increasing number of units. On the other hand, for large values of ak, the concentration drops off very rapidly, and the change in concentration decreases to a low value in the first few treatments.

Multiple Contact Washing With Fresh Solvent in Each Contacting. In washing processes, soluble substances are removed from the surfaces of insoluble materials by liquid treatment. In the simplest type of process the wet solids are treated with fresh solvent, agitated and settled, and the supernatant liquid drawn off. If the treatment is repeated, the operation becomes multiple contact in nature and is similar to the solvent extraction processes previously discussed.

In batch processes, the wash liquid and solids are mixed; and after the concentration of solute has become uniform, the inert material is allowed to settle. The height to which the suspension settles determines the amount of clear liquid that may be drawn off and the amount of water held in the interstices of the inert solid.

The ratio of the mass of liquid on a solute-free basis drawn off from the clear layer in a particular contacting to the mass of pure liquid retained by the solid is designated as the solvent ratio for washing.

In a series of thickeners in which the solids are pumped continuously from one unit to another, the ratio of the (mass or volume) rate of clear liquid overflow(solute free basis) to the rate of flow of liquor (solute free basis) retained by the solids (underflow) pumped through the system becomes the solvent ratio. The solvent retained by the solids is determined by the method of operation and the physical properties of suspended material and wash liquid. While it is desirable to have a low liquor retention in batch settlers, enough liquid must be left in the solids in continuous thickeners to permit pumping.

If mixing is efficient, the solute is uniformly distributed through the solvent; and the concentration, y, of solute in the overflow is equal to the concentration, x, of solute in the underflow. This corresponds to having a distribution coefficient of unity, i.e., $y = x$. Graphically this corresponds to having a 45° equilibrium curve in Figure I.

Constant Solvent Ratio. If the solids and adhering liquid are separated in a similar manner in each treatment and the solute concentration does not appreciably affect the physical properties of the solution, the pounds of solvent (solute free basis) retained per pound of inert solid will be the same in each contacting. Under normal operation, equal quantities of liquid are added in each step of the process; and, as a consequence, the ratio, a, of solvent introduced and subsequently drawn off to the solvent retained is a constant. This condition of constant solvent ratio permits an easy graphical or analytical solution of the equation. The schematic diagram shown in Figure 2 may be used for washing provided b represents the pounds of water (on a solute free basis) adhering to the surface of one pound of inert material; x and y_o represent respectively the concentrations of solution and solvent in pounds of solute per pound of water; and w is the pounds of wash water added per pound of inert in each stage. Since $y = x$, the material balance corresponding to Equation (1) becomes

$$w(x_{n+1}-y_o) = b(x_n-x_{n+1}) \tag{11}$$

Rearranging

$$x_{n+1} = \frac{1}{a+1}\,x_n + \frac{a\,y_o}{a+1} \tag{12}$$

This equation can be solved graphically by the methods presented in Figures 3 and 4. Equation (4) is identical with Equation (12) if k is placed equal to unity. The solutions and discussion of Equation (4) are applicable to (12) provided k is placed equal to unity.

While the previous formulas are of limited application for solvent extraction because of the assumption of constant k, no such limitations are involved in washing. The equations may be used with confidence. The assumption that the solids enter the process containing exactly the amount of solvent retained in succeeding stages should be carefully examined before employing the formulas. The solids may enter with other than this amount of moisture, in which case the first stage must be treated separately from the others.

Variable Solvent Ratio. If the solvent retained by the solids varies with the solute concentration, the solvent ratio will not be constant. The graphical solution must then be modified for the variation in slope of the construction lines. Consider a system in which the variation of solvent retained with concentration is known experimentally as indicated by the b vs x curve in Figure 7. The zero line for this b vs x curve is constructed along the line $y = y_o$. As x increases, the value of b also increases, and the amount of liquid retained is different in each stage. The solids enter the process containing b_c (solute free basis) pounds of liquid per pound of inert with a concentration x_o. The solvent initially added is equivalent to w_o (solute free basis) pounds of liquid per pound of inert with a concentration y_o. The operation will usually be carried out so that the total amount of solvent is constant in each stage, i.e., $w_n + b_n = V$. A material balance over the first contacting yields

$$(x_1-y_0)/(x_1-x_0) = -b_0/w_0 \qquad (13)$$

to obtain x_1, a line of slope $-b_0/w_0$ is drawn from the point (x_0,y_0) to the equilibrium line. To obtain a line through (x_0,y_0) having a slope $-b_0/w_0$, the following procedure is followed. Point P is used as a center for striking an arc of radius w_0 that intersects a horizontal line through P at Q. A line from Q to (x_0,y_0) then has the desired slope and intersects the 45° line at x_1. For the second stage, the construction line has a slope $-b_1/w_1$ where b_1 is obtained as a point on the solvent retained

GRAPHICAL SOLUTION, VARIABLE SOLVENT RATIO

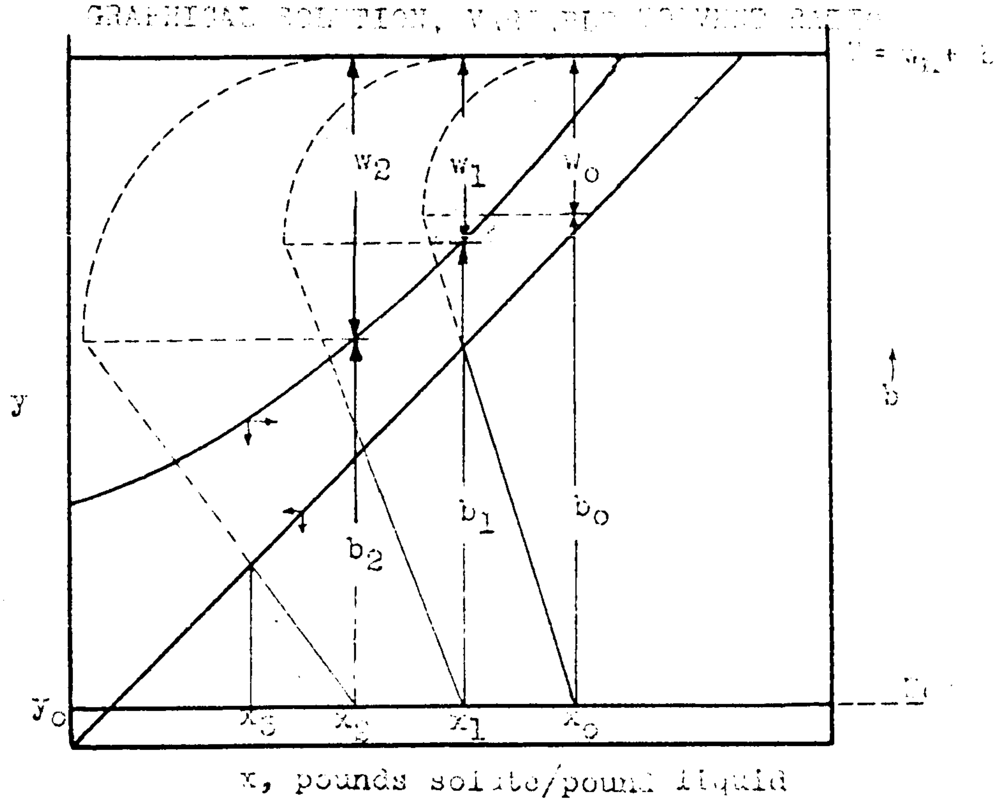


Figure 7

curve corresponding to x_1, and w_1 is given by the difference ($V-b_1$). A line having slope $-b_1/w_1$ is drawn from the point (x_1,y_0) to the 45° line which it intersects at x_2. This graphical process may be carried out until the desired concentration has been reached. Should the process be carried out so that the total mass of liquid per stage is not constant, the V line will not be horizontal. When a constant amount of solvent is added in each contacting, the total solvent line will be parallel to and above the b vs x curve.

When the insoluble material enters the washing process containing undissolved solute, the graphical procedure must be further modified. If X represents the undissolved dry salt per pound of inert, define x' as follows

$$x' = X/b+x \tag{14}$$

where b represents the pounds of pure liquid retained per pound of inert and x is the concentration of solute in the liquid. When undissolved salts are present x will equal the saturation concentration x_s and x' will equal $X/b + x_s$. After all the undissolved solute is removed, x' reduces to x.

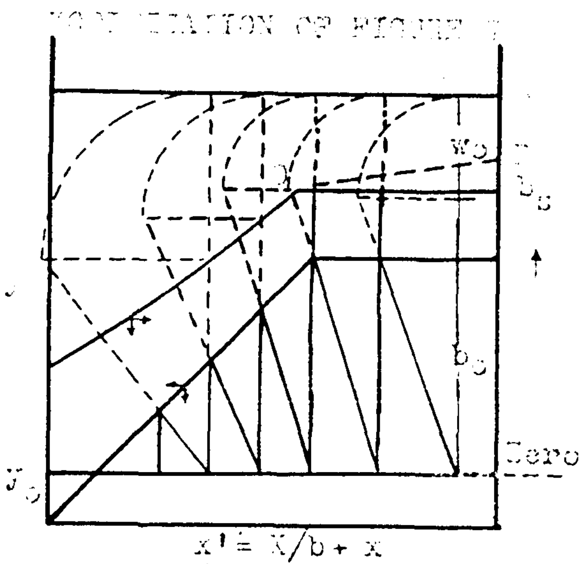


Figure 8

The equilibrium curve passes from a 45° line to a straight horizontal line at $y = x_s$ as the extract has a saturated composition regardless of the presence of undissolved salt. At saturation the liquid retained, b_s, per pound of inert does not change with changing x' and the b vs x curve changes shape at x_s. If the undissolved salt has no effect on the retained solvent, the b vs x curve becomes a horizontal line. Should the undissolved salt also retain solvent, the retained liquid line must be modified as indicated by the line OP. Suppose an inert solid containing X_o pounds of undissolved salt per pound of inert and wet with b_o (solute free basis) pounds of saturated liquid per pound of inert is washed in a multiple contact process in which the total liquid per pound of inert in each stage is constant and equal to V. If undissolved salt remains and the liquid adhering to the undissolved salts is neglected, a material balance gives

$$w_o\, y_o + b_o\, x_s + X_o = X_1 + (w_s + b_s)x_s \tag{15}$$

Rearrangement gives

$$\frac{x_s - y_o}{X_1/b_o - X_o/b_o} = \frac{x_s - y_o}{x_1' - x_o'} = -\frac{w_o}{b_o} \tag{16}$$

$$(y_{n+1} - y_o)/(x'_{n+1} - x'_n) = -b_n/w_n \tag{17}$$

in which y_{n+1} equals x_s while undissolved salt is present and x_{n+1} when all solute is dissolved.

Second Graphical Solution For Variable Solvent Ratio. The graphical solution illustrated in Figure 7 is essentially a modification of the method shown in Figure 3. A second method representing a modification of the method presented in Figure 4 can be developed. Consider a material balance around an (n+1)st unit as indicated in Figure 9. A solvent balance yields

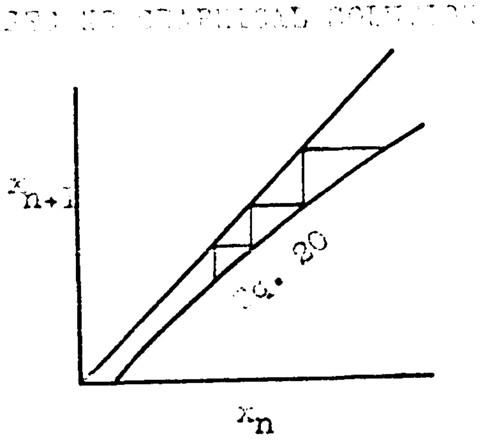


Figure 9

$$b_n + w_{n+1} = b_{n+1} + W_{n+1} \tag{18}$$

where W_{n+1} represents the pounds of extract removed per pound of inert. A solute balance gives

$$x_n b_n + y_o w_{n+1} = x_{n+1}\, b_{n+1} + x_{n+1}\, W_{n+1} \tag{19}$$

If the operation is carried out so that $b_n + W_{n+1} = V$, then (18) and (19) can be combined to give

$$x_{n+1} = \frac{b_n}{V} x_n + \frac{V - b_n}{V} y_o \tag{20}$$

Since b_n is a function of x_n, the solution of this equation falls under case II of section A in Part IV of the Appendix. A plot of x_{n+1} vs x_n is made resulting in a curved operating or material balance line corresponding to the straight line in Figure 4. After this operating line has been plotted, the procedure is identical with the method illustrated in Figure 4 of this chapter.

If the amount of solvent, w_n, added to each stage is constant, Equation (20) must be modified as follows

$$x_{n+1} = \frac{b_n}{w + b_n} x_n + \frac{w y_0}{w + b_n} \qquad (22)$$

A slightly different operating line results from plotting this equation.

Minimum Concentration. From Equation (7) it can be seen that the minimum concentration obtainable is y_0/k which corresponds to the concentration of a solution in equilibrium with the extracting liquid. To obtain this concentration the term $(ak + 1)^N$ must become infinite. Thus, either ak or N must be infinite; in either case an infinite amount of solvent is required. As a finite amount of solvent is always employed, it is natural to inquire what minimum concentration is obtainable with some definite quantity of solvent. Suppose b pounds of A containing bx_0 pounds of B are treated with a total of W pounds of C containing Wy_0 pounds of B. Let the solvent be divided into N equal parts for contacting so that W/N pounds of solvent will be used in each treatment. Defining the overall solvent ratio as A = W/b, Equation (7) becomes on replacing a by A/N

$$x_N = \frac{(x_0 - y_0/k)}{(Ak/N + 1)^N} + y_0/k \qquad (23)$$

The limit of this expression as N approaches infinity gives the minimum concentration x_i. To find this limit, place (23) in the following form

$$\log \frac{x_n - y_o/k}{x_o - y_o/k} = - \frac{\log \frac{Ak}{N+1}}{1/N} \tag{23a}$$

Allowing N to become infinite in (23a) leads to the indeterminate form 0/0 which may be evaluated by L'Hospital's rule to give

$$x_i = (x_o - y_o/k)e^{-kA} + y_o/k \tag{24}$$

This is the concentration that would result if the solution were treated continuously with solvent while the extract was removed simultaneously. This infinite stage process corresponds to a differential process and must have the same solution that results from solving the equations of differential batch extraction.

To show that this is true, consider a mixture containing b pounds of A and bx_o pounds of B which is treated differentially with a solvent consisting of W pounds of C and Wy_o pounds B. A differential material balance yields (x and y in mass ratio units)

$$-bdx = (y - y_o)dW \tag{25}$$

Rearranging and integrating gives

$$\int_{x_o}^{x} \frac{dx}{y - y_o} = - \frac{W}{b} = -A \tag{26}$$

If the distribution law holds and $y = kx$, integration produces

$$x = (x_0 - y_0/k)e^{-kA} + y_0/k \tag{27}$$

This is the same expression as derived for the minimum concentration in equation (24). For washing it is simply necessary to place $k = 1$. If the same total solvent is used in both a multiple contact process using fresh solvent and a differential extraction, the ratio of the extractable material removed in the first case to the material removed in the latter is identical with the relative efficiency as given in Equation (28).

Relative Efficiency.[30] If the overall solvent ratio is A, the maximum reduction in concentration is $x_0 - x_i = (x_0 - y_0/k)(1 - e^{-kA})$ and the actual reduction for N total units is $x_0 - x_N$. The ratio of these two quantities is a measure of the relative efficiency of the extraction process. The relative efficiency, E_n, is defined mathematically by

$$E_N = (x_0 - x_N)/(x_0 - x_i) \tag{28a}$$

$$= \left[1 - \left[N/(N + kA)\right]^N\right] /(1-e^{-kA}) \tag{28b}$$

A plot of relative efficiency vs kA for constant values of N is shown in Figure 10. E_N undergoes a minimum when kA has a value of 1.6. This may be shown by setting the derivative $dE_N/d(kA)$ equal to zero and solving for kA. Investigation of Figure 10 leads to the conclusion that the use of more than five units should be carefully considered as no less than 94 per cent of the extractable material is extracted, and little improvement is obtained by adding more stages.

Overall Efficiency. The relative efficiency affords an insight into the approach to perfection of a given operation but sheds no light on overall recovery. The overall efficiency, e_N, is defined as the ratio of material recovered to the total material originally present. Thus

$$e_N = (x_0 - x_N)/x_0 = (1 - y_0/kx_0)\left[1 - N/(N + kA)\right]^N \qquad (29)$$

and hence, the overall efficiency is not independent of x_0 and y_0. The maximum overall efficiency, e_i, is obtained when N becomes infinite and is

$$e_i = (1 - y_0/kx_0)(1 - e^{-kA}) \qquad (30)$$

From the definitions of e_N and E_N it may be shown that

$$e_n = e_i E_n \qquad (31)$$

In addition to E_N, e_i is also plotted on Figure 10 for various values of y_0/kx_0. This curve shows a sharp rise for the region in which kA is less than 4. It is obvious that operation with more than five contactings and a value of kA greater than four should be carefully investigated since the efficiency approaches a maximum in this region.

Dilution Ratio. The ratio of the pounds of extractable material removed to the total pounds of solvent used is a measure of the efficiency with which the solvent is employed.

MAXIMUM OVERALL AND RELATIVE EFFICIENCY VS. ka

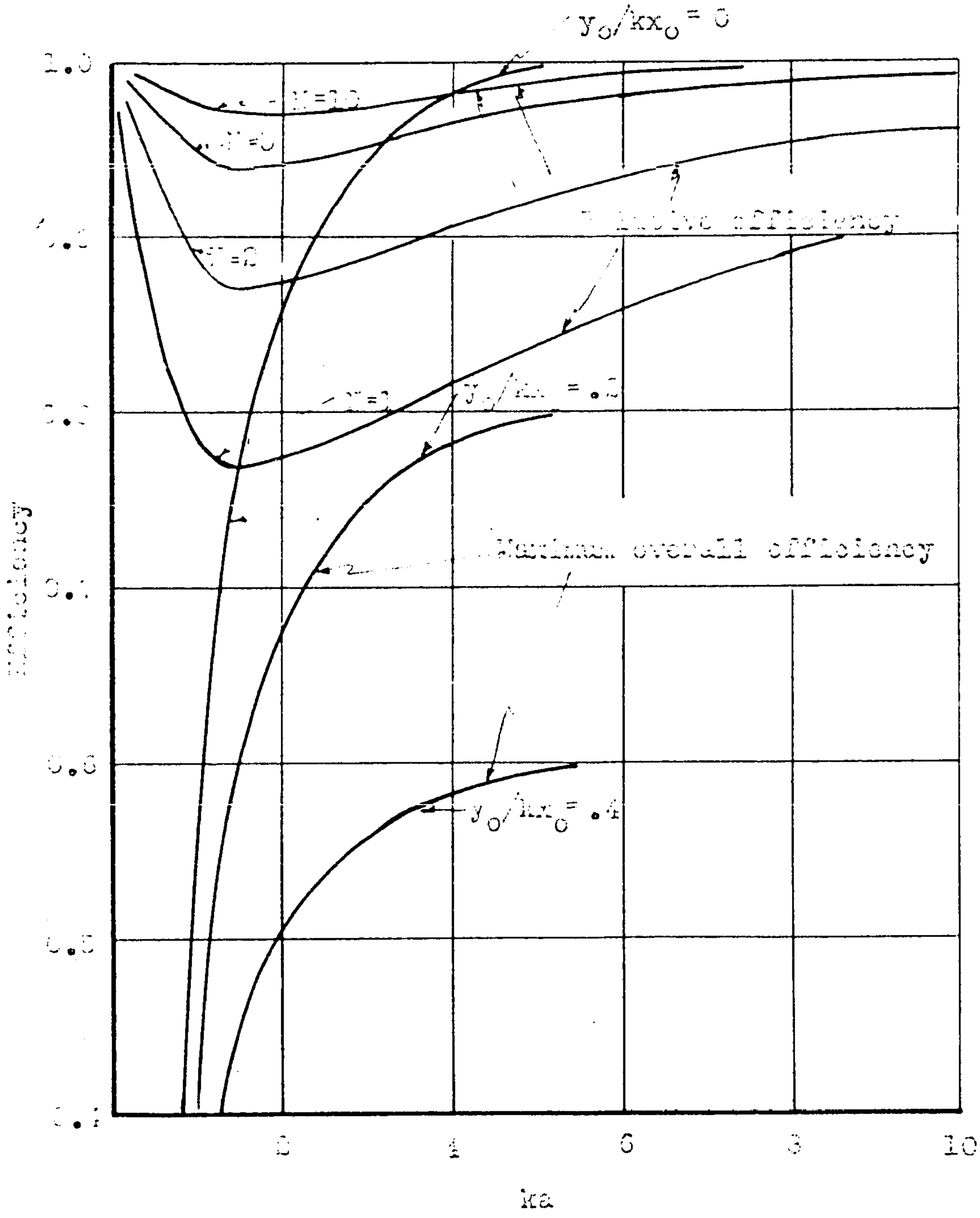


Figure 10

If all the extracts are combined, the concentration of extractable material in this total extract is defined as the dilution ratio D.

$$D = b(x_o - x_N)/Nw = (x_o - x_N)/Na = (x_o - x_N)/A \qquad (32)$$

Countercurrent Extraction

In cocurrent extraction relative large volumes of solvent are required for effective separation as compared with countercurrent extraction. Extracts with low concentrations result; and if evaporation or distillation of the extract is necessary, excessive amounts of heat may be required. Cocurrent extraction may be of importance when the solvent is cheap, and the soluble substances are of no value. The extract may then be discarded without economic loss. If the weak extracts are used for further extraction in countercurrent operation, a considerable saving of solvent results.

In the general case of three component countercurrent[30,49,82] extraction where the solvents are partially miscible, the triangular diagram must be employed to obtain the relationship between the number of stages and the other variables. If two of the components are immiscible it is possible to obtain graphical and analytical solutions similar to those carried out for cocurrent operations.

Immiscible Solvents. Consider a system having the three components A, B, and C in which A and C are completely immiscible. Component B distributes itself between the A and C phases being at least partially miscible with each of the components A and C. Suppose that C is used as a solvent for extracting B from the A phase. It is unnecessary to consider material balances for components A and C because of their immiscibility. While the problem may be solved on triangular coordinates, it is easier to employ mass ratio units on Cartesian coordinates.

In the countercurrent process shown in Figure 11, w pounds per hour of C containing wy_o pounds of B are introduced as solvent at one end of the process and b pounds per hour of A containing bx_o pounds of B is introduced at the opposite end. The raffinates and extracts are pumped continuously through the process in a countercurrent fashion. Three useful material balances may be written for

COUNTERCURRENT EXTRACTION

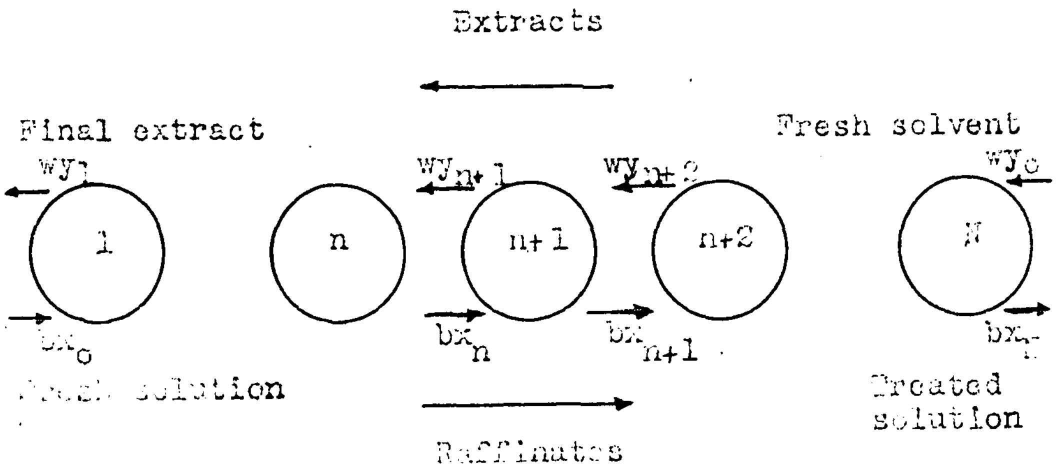


Figure 11

this process: (1) a material balance around the (n+1)st unit and adjoining stages; (2) a material balance over the first n units or from the (n+1)st to the Nth stage and (3) a material balance around the entire process. If w/b is defined as the solvent ratio, the following equations are obtained:

a. Material balance around (n+1)st unit

$$ay_{n+1} + x_{n+1} = ay_{n+2} + x_n \tag{33}$$

or

$$a(y_{n+2} - y_{n+1}) = x_{n+1} - x_n = a\Delta y_{n+1} = \Delta x_n \tag{34}$$

b. Material balance around first n units

$$ay_1 + x_n = ay_{n+1} + x_o \tag{35}$$

$$y_{n+1} = (1/a)x_n + (y_1 - x_o/a) \tag{36}$$

c. Material balance around entire process

$$ay_1 + x_N = ay_o + x_o \tag{37}$$

In general, x_o and y_o are independent of process operation and, hence, fixed. Two of the three remaining quantities must then be specified in order that all variables in (34) be determined.

Equation (33) can be integrated to give $y_{n+1} = (1/a)x_n + C$ which is of exactly the same form as (36). It is obvious that the above constant of integration is simply $(y_1 - x_o/a)$. A material balance around an (n+1)st and adjoining stages leads to a second order difference equation, and the first integral of this second order equation is necessarily of the same form as the equation obtained directly from a material balance over the first n units or over the portion of the process including the (n+1)st and N(th) stages.

Graphical Solutions. The number of theoretical stages required to reduce the initial concentration, x_o, to some predetermined value can be obtained from Equation (36). This equation, which belongs to the case considered in section D in Part IV of the Appendix, contains the three variables x_n, y_n and n. Before a solution can be obtained, it is necessary to have a relationship between x_n and y_n. If it is assumed that the stages are theoretical, x_n and y_n will be in equilibrium. From Equation (36), it can be seen that y_{n+1} is a linear function of x_n. The plot of this linear function in Figure 12 is termed the operating or material balance line. The points (x_o,y_1), (x_1,y_2), (x_2,y_3), etc., lie on this line while the points (x_1,y_1), (x_2,y_2), (x_3,y_3), etc., lie on the equilibrium curve. If x_o is specified, the point (x_o,y_1) can be located on the material balance line. With y_1, the point (x_1,y_1) is found

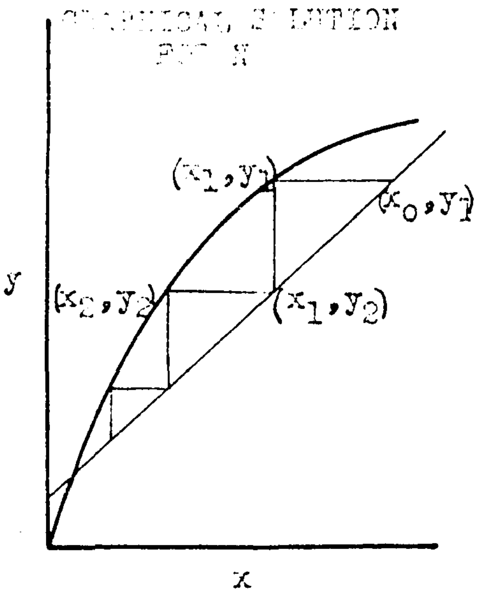


Figure 12

on the equilibrium curve. This procedure can be continued until the final concentration is reached. The number of theoretical stages is obtained by counting the points (x_1,y_1), (x_2,y_2), ... (x_n,y_n) on the equilibrium curve as each of these points corresponds to a stage.

<u>Minimum Solvent Ratio</u>. Under usual conditions, the concentrations of the feed, x_o, and solvent, y_o, are fixed. If it is desired to reduce the concentration to some particular value x_N, there is a minimum solvent ratio with which the desired separation may be accomplished. If x_N and y_o are specified, the point (x_N,y_o) corresponding to P in Figure 12 is determined. Another point on the operating line is (x_o,y_1). As x_o is predetermined, y_1, must be so determined that the solvent ratio will be a minimum. As the slope of the operating line is the reciprocal of the solvent ratio, y_1 must be so placed that the slope will have its largest possible value. This value is determined as the intersection, Q, of the line $x = x_o$ and the equilibrium curve. With this value of y_1, there will be

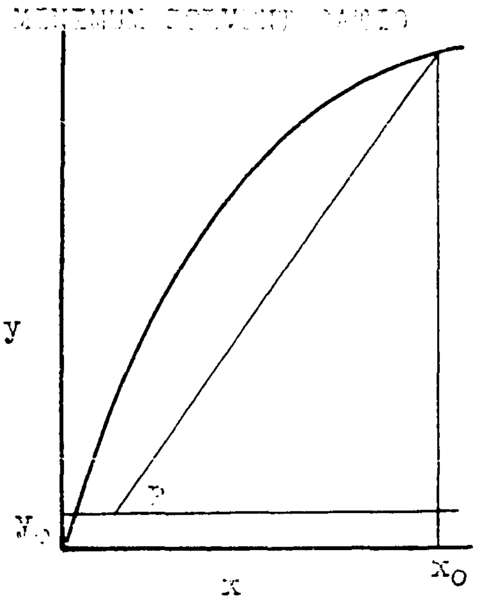


Figure 13

an infinite number of theoretical stages. The minimum solvent ratio is the reciprocal of the slope of the line PQ.

$$a \text{ min.} = (x_0 - x_n)/(y_1 - y_0) \qquad (38)$$

Minimum Concentration. With given values of x_0 and y_0, there is a certain theoretical minimum concentration to which x_n can be reduced with a given solvent ratio. The minimum value will be reached when the number of theoretical stages becomes infinite. To obtain an infinite number of stages, the operating line and equilibrium curve must intersect either at (x_n, y_0) or (x_0, y_1). If the solvent ratio is larger than the reciprocal of the slope AQ as is the case with line AB, the material balance line intersects the equilibrium curve at A; and the minimum concentration corresponds to a solution in equilibrium with the incoming solvent. If the solvent ratio is smaller than the reciprocal of the slope AQ, as would be the case with line PQ, the minimum concentration is given by point P. In this case, the outgoing extract is in equilibrium with the incoming solution.

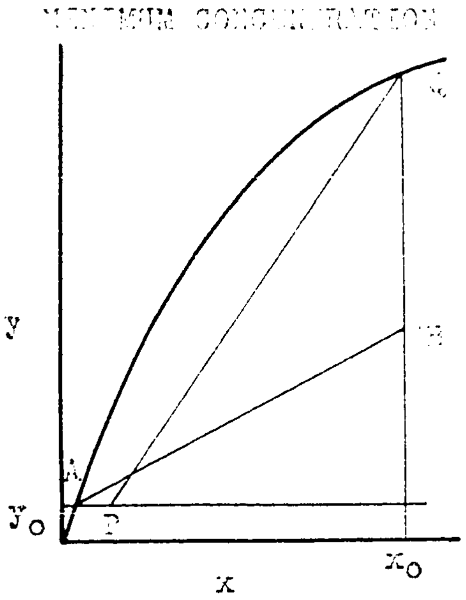


Figure 14

Constant Distribution Coefficient. If the equilibrium curve is straight and k is constant, analytical solutions may be obtained. If the substitution $y = kx$ is made, Equations (33), and (36) and (37) become

$$x_{n+2} - \left[(ak+1)/ak\right] x_{n+1} + (1/ak)x_n = 0 \qquad (39)$$

$$x_{n+1} - (1/ak)\, x_n = (x_1 - x_o/ak) = (ay_o - x_N)ak \qquad (40)$$

$$akx_1 + x_N = ay_o + x_o \qquad (41)$$

The solutions of the second order equation in (39) and the first order equation in (40) must be the same as both are derived from the same physical problem.

To solve (39), first place in standard form

$$\left[E^2 - \frac{ak+1}{ak} E + \frac{1}{ak}\right] x_n = 0 \qquad (42a)$$

Factoring this equation gives

$$(E - 1)(E - 1/ak)x_n = 0 \qquad (42b)$$

This equation has the roots unity and 1/ak, and, hence, the general solution becomes

$$x_n = C_1 + C_2(1/ak)^n \quad ak \neq 1 \qquad (43)$$

In order to obtain C_1 and C_2, the two conditions; $x_n = x_o$ when $n = 0$, and $x_1 = (ay_o + x_o - x_n)/ak$ as obtained from (41) must be employed. Thus

$$x_1 = C_1 + C_2 \qquad (44a)$$

$$x_1 = (ay_0 + x_0 - x_n)/ak = C_1 + C_2/ak \qquad (44b)$$

Solving for C_1 and C_2 gives

$$C_1 = (ay_0 - x_n)/(ak - 1) \qquad (44c)$$

$$C_2 = \left[ay_0 - x_0(ak - 1) - x_n\right]/(1 - ak) \qquad (44d)$$

These values can be substituted in (43) to give the complete answer.

The solution of (40) is given by the sum of the solution of the reduced equation, $c(1/ak)^n$, plus a particular solution of the complete equation, $(ay_0 - x_n)/(ak - 1)$. Thus

$$x_n = C(1/ak)^n + (ay_0 - x_n)/(ak - 1) \qquad ak \neq 1 \qquad (45)$$

The constant C in this equation is identical with C_2.

Equation (45) gives the value of x_n in any nth unit. Of more interest is the number of units, N, necessary to reduce x_0 to x_N. To obtain this information place n = N, and solve for N.

$$N = \frac{1}{\log ak} \log \frac{(ak - 1)x_0 - ay_0 + x_N}{a(kx_N - y_0) + x_N} = \frac{1}{\log ak} \log \frac{kx_0 - y_1}{kx_N - y_0} \qquad (46)$$

The determination of the value of a from (46) may be carried out by successive approximations.

<u>Product ak is Unity</u>. If the quantity ak is unity, Equation (46) reduces to the indeterminate 0/0. While this indeterminate may be evaluated, it is better to return to the original difference Equation (40) which may be placed

in the following form

$$x_{n+1} - x_n = ay_o - x_n \tag{47}$$

The solution of (47) subject to an initial concentration of x_o is

$$x_n = (y_o/k - x_N)n + x_o \tag{48a}$$

Letting n = N and solving for N gives

$$N = (x_o - x_N)/(x_N - y_o/k) \tag{48b}$$

Minimum Concentration. Solving for x_N in (46) gives

$$x_N = \frac{(ak - 1)x_o + (y_o/k)\left[(ak)^{N+1)} - ak\right]}{(ak)^{(N+1)} - 1} \qquad ak \neq 1 \tag{49a}$$

If ak = 1, x_N is obtained from (48b)

$$x_N = (x_o + Ny_o/k)/(N + 1) \tag{49b}$$

It is important to differentiate between x_n and x_N. The variable x_n represents the concentration in any arbitrary stage with a fixed x_N. In Equations (49a) and (49b), the variation of x_N with N and the various parameters is given. It is not possible to use this equation to obtain values of the liquid concentration in intermediate stages.

The minimum concentration x_1 is obtained when N becomes infinite. Two different limits are approached by x_N depending on whether ak is greater or less than unity. If ak < 1 in (49a) the quantity $(ak)^{N+1}$ will approach zero as

N approaches infinity while if $ak > 1$, $(ak)^{N+1}$ approaches infinity. Thus the minimum concentration is given by

$$x_i = y_o/k \qquad ak \geq 1 \qquad (50a)$$

$$x_i = ay_o + (1 - ak)x_o \qquad ak \leq 1 \qquad (50b)$$

Relative Efficiency. The relative efficiency as defined by Equation (28) is the ratio, $(x_o - x_N)/(x_o - x_i)$. As the expression for x_i depends on the value of ak, it may be expected that the expression for the relative efficiency will take on different forms also dependent on ak. Substitution of x_N from (49) in the defining equation for the relative efficiency produces

$$E_N = \frac{(x_o - y_o/k) \left[(ak)^{N+1} - ak \right] / \ (ak^{N+1} - 1}{x_o - x_i} \qquad (51)$$

where x_i is given by (49) or (50). If the quantity $ak = 1$, Equation (51) must be modified to give

$$E_N = \frac{(x_o - y_o/k) \left[N/(N+1) \right]}{x_o - x_i} \qquad (52)$$

Substituting the proper values of x_i in (51) and (52) leads to the following set of equations

$$E_N = \frac{(ak)^{N+1} - ak}{(ak)^{N+1} - 1} \qquad ak > 1 \quad . \qquad (53)$$

$$E_N = N/(N+1) \qquad ak = 1 \qquad (54)$$

$$E_N = \frac{1 - (ak)^N}{1 - (ak)^{N+1}} \qquad ak < 1 \qquad (55)$$

Overall Efficiency. The overall efficiency is defined by Equation (29) and is $(x_0-x_N)/x_0$. The maximum overall efficiency is obtained when an infinite number of stages are employed and is

$$e_i = 1-y_0/kx_0 \qquad ak \geq 1 \qquad (56)$$

$$e_i = ak(1-y_0/kx_0) \qquad ak < 1 \qquad (57)$$

The actual overall efficiency may be obtained from Equation (31) as $e_N = e_iE_N$. In Figure 15, the relative efficiency and maximum overall efficiency are plotted against ak for various values of N and y_0/kx_0. It is desirable to have as high an overall efficiency as is practicable without using too much solvent. In Figure 15, the overall efficiency is obtained by multiplying the relative efficiency times the maximum overall efficiency. For the maximum overall efficiency to be high, it is necessary that ak > 1. When ak is in the region of unity, the relative efficiency approaches a minimum value. Thus it is best to operate at values of ak larger than unity, the actual value depending upon the number of units. Above four units, there is not much improvement gained in relative efficiency by increasing the number of stages. The region in which operation would probably be carried out for reasonable efficiencies is in the shaded area of Figure 15.

Decrease in Concentration per Contact. It is of interest to inquire what decrease in concentration may be

RELATIVE AND OVERALL EFFICIENCY VS. ak

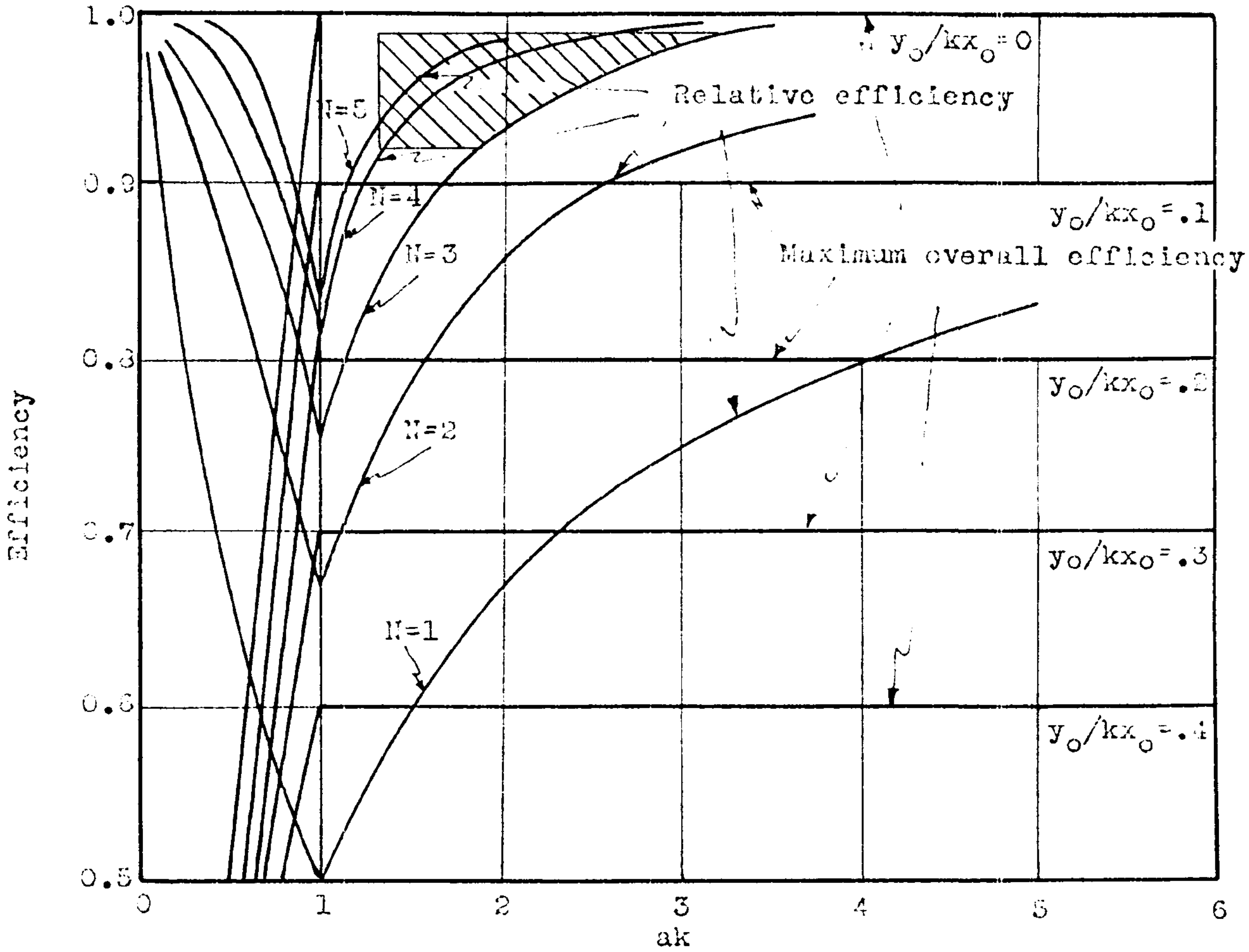


Figure 15

obtained in adding additional contactors, i.e., how will Δx_N vary with N? The decrease per contact, $-\Delta x_N$, may be obtained by differencing equation (49) to obtain

$$\frac{-\Delta x_N}{x_o - y_o/k} = \frac{(ak)^{(N+1)} \quad (ak - 1)^2}{\left[(ak)^{(N+2)} - 1\right]\left[(ak)^{(N+1)} - 1\right]} \tag{58a}$$

and when ak = 1

$$\frac{-\Delta x_N}{x_o - y_o/k} = 1/(N+1)(N+2) \tag{58b}$$

Dilution Ratio. In countercurrent operation, only one extract is taken from the system; and as defined by Equation (32) the dilution ratio simply becomes the extract concentration, y_1. From Equation (37)

$$y_1 = (ay_o + x_o - x_N)/a \tag{59}$$

where x_N is given by Equations (49) as a function of N.

Solvent Efficiency.[35] In the previous discussion of efficiency, emphasis was placed on producing a product free of dissolved material. On the plots of extraction, and overall efficiency, it is easily seen that low recoveries result with low values of ak. However, small solvent ratios possess the advantage of producing strong extracts. Where the solution is to be evaporated and recovery of solute is important, close attention must be paid to the extract concentration.

Solvent efficiency is defined as the ratio of the extract concentration to the maximum concentration it may have. Obviously, the maximum concentration is that concentration which corresponds to an extract in equilibrium with fresh incoming material. The solvent efficiency S_N is

$$S_N = y_1/kx_o = x_1/x_o \qquad (60)$$

In terms of other variables

$$S_N = (ay_o + x_o - x_N)/akx_o \qquad (61)$$

The solution efficiency is related to the overall efficiency by

$$S_N = e_N/ak + y_o/x_o \qquad (62)$$

S_N approaches a maximum as N approaches infinity. The limiting value, S_i, approached by the solution efficiency as N approaches infinity is

$$S_i = (1-y_o/kx_o)/ak + y_o/kx_o \qquad ak \geq 1 \qquad (63)$$

$$S_i = 1 \qquad ak < 1 \qquad (64)$$

<u>Comparison of cocurrent and Countercurrent Operation</u>. While countercurrent operation produces a strong extract, fewer units are required in cocurrent operation. The ratio of the number of units, N, required in countercurrent operation to the number N' in cocurrent operation for producing the same final concentration is

$$\frac{N}{N'} = \frac{\log(ak+1)\log\left[(kx_0-y_1)/(kx_N-y_0)\right]}{\log(ak)\ \log\left[(kx_0 - y_0)/(kx_N-y_0)\right]} \tag{65}$$

It is apparent that for most cases the term log(ak+1)/ log(ak) will be the controlling factor in (65).

Cocurrent and countercurrent processes can best be compared on the basis of the raffinate ratio, $r = (x_n-y_0/k)/(x_0-y_0/k)$, which represents the ratio of the material remaining after N treatments that can be extracted to the total original amount of extractable material. A plot of N vs ak for various values of r is shown in Figure 5 for cocurrent extraction. The raffinate ratio for countercurrent operation can easily be obtained from Equation (49a) by subtracting y_0/k from each side

$$x_N - \frac{y_0}{k} = \frac{(ak-1)x_0 + (y_0/k)\left[(ak)^{N+1} - ak\right]}{(ak)^{N+1} - 1} - \frac{y_0}{k} \tag{66}$$

On simplifying, this yields

$$r = \frac{x_n - y_0/k}{x_0 - y_0/k} = \frac{\left[ak - 1\right]}{(ak)^{N+1} - 1} \tag{67}$$

The raffinate ratio for cocurrent extraction may be obtained from Equation (7) and is

$$r = 1/(ak+1)^N \tag{68}$$

A comparison of the types of operation is shown in Figure 16.

COMPARISON OF COUNTERCURRENT AND COCURRENT OPERATION

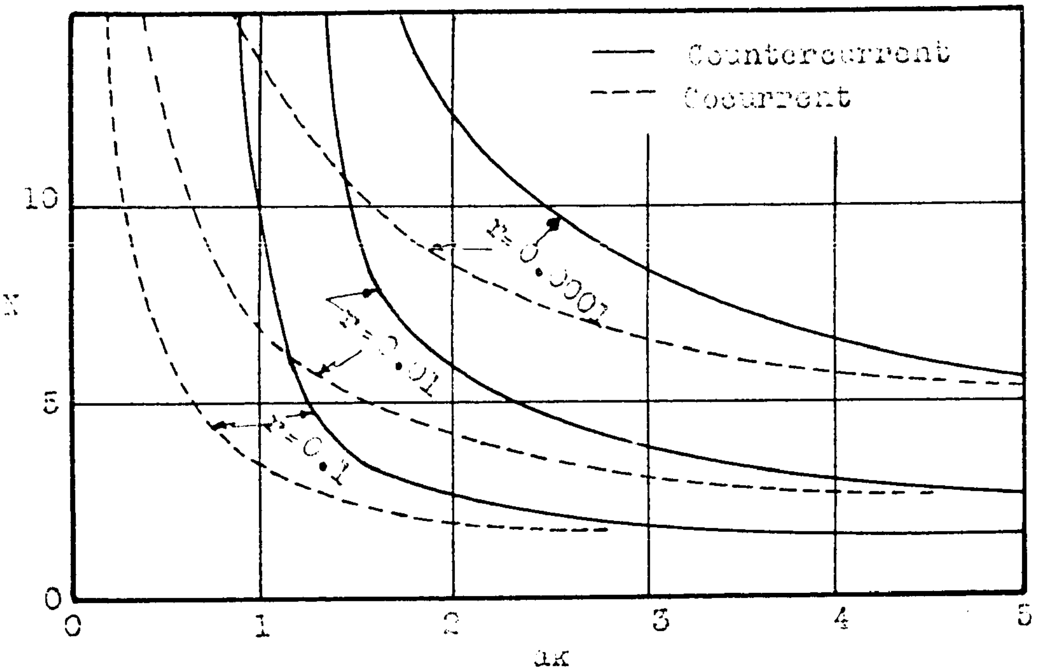


Figure 16

Countercurrent Washing. Continuous countercurrent decantation is an important operation in chemical engineering. It is an effective method for removing solute from the surface of inert solids. If the solvent ratio is constant and a uniform concentration is established in each contactor, the formulas derived in equations (33) through (68) may be used with confidence if k is placed equal to unity. The number of units required for a definite reduction in concentration may be obtained graphically in a manner similar to the method indicated in Figure 12. If the solvent ratio is constant the operating line will be straight with a slope of 1/a. In all cases the equilibrium curve is a 45° line starting at the origin and terminating at a point representing the solubility of the dissolved material. If the liquid retained by the inert varies with the concentration, the operating line will be curved, and this operating line must be obtained before it is possible to carry out graphical calculations. Previous investigators have developed various methods for determining the number of contactings required for systems in which the solvent retained varies with the liquid concentration.

Variable Solvent Ratio.[1] Consider a portion of the countercurrent decantation process which includes the (n+1)st and Nth contactors as indicated in Figure 17. All streams indicated pertain to one pound of inert. A material balance for the solute may be written over this section of the process to obtain the equation of the operating line

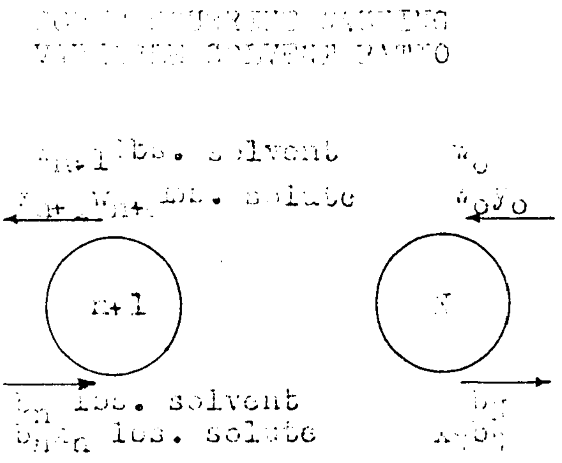


Figure 17

$$b_nx_n + w_oy_o = w_{n+1}y_{n+1} + b_Nx_N \qquad (69)$$

Another material balance for the solvent may also be determined as follows

$$b_n + w_o = b_N + w_{n+1} \qquad (70)$$

Combining equations (69) and (70) gives the equation of the operating line

$$x_{n+1} = \frac{b_n}{b_n + w_o - b_N} x_n - \frac{b_N x_N - w_o y_o}{b_n + w_o - b_N} \qquad (71)$$

As b_n is a function of x_n alone, this solution of this equation falls under case 2 of section A in Part IV of the Appendix. A curved operating line x_{n+1} vs x_n as calculated from Equation (71) is plotted and the usual stepwise procedure for determining the number of stages is carried out.

NOMENCLATURE FOR CHAPTER VI

a = w/b, solvent ratio; for solvent extraction, pounds of solvent (solute free basis) per pound of solution (solute free basis); for washing pounds of solvent (solute free basis) per pound of solvent (solute free basis) retained by inert solids

A = $N\, a$, overall solvent ratio for cocurrent extraction, total pounds of solvent (solute free basis) used in all contactings per pound of solution (solute free basis) or per pound of solvent retained by the inert solids

b = pounds of solution (solute free basis) per hour or per batch; pounds of solvent (solute free basis) retained per pound of inert solid

b_n = variable b referring to nth unit

b_s = value of variable b_n when solution is saturated

C = arbritrary constant

D = dilution ratio, pounds of solute extracted per pound of solvent

E = $1 + \Delta$, operator which increases independent variable by unity

E_N = relative efficiency, ratio of mass of material actually extracted to maximum amount which could be extracted with an infinite number of units

e_N = overall efficiency, ratio of material extracted to total material present

e_i = maximum overall efficiency

k = distribution coefficient (used only where coefficient is constant), concentration in solvent phase divided by concentration in solution phase, concentrations expressed in mass ratio units

k_n = distribution coefficient in nth stage (used where coefficient is variable)

n = variable stage number

N = total number of stages

r = $(x_N-y_o/k)/(x_o-y_o/k)$ raffinate ratio, amount of material remaining in solution that could be extracted divided by total amount originally present that could be extracted with an infinite amount of solvent

S_N = solvent efficiency, ratio of extract concentration to maximum possible concentration

S_1 = maximum solvent efficiency obtained with an infinite number of stages

V = total lbs. of solvent (solute free basis) per hour per stage or per batch

w = pounds of solvent (solute free basis) per hour or per batch; in washing, pounds of solvent per pound of inert (used only where quantity is constant)

w_n = value of w in nth stage (used as a variable)

W = Nw, total pounds of solvent used in cocurrent extraction

W_n = pounds of extract (solute free basis) taken from the nth contactor in cocurrent extraction

x_n = raffinate concentration in nth contactor, pounds of solute per pound of solvent in raffinate; in washing, pounds of soluble material per pound of solvent

x_N = concentration from last stage

x_o = inlet concentration

x_s = concentration of saturated solution

x' = $x + X/b$

X = pounds of undissolved soluble material per pound of inert

X_o = pounds of undissolved soluble material per pound of inert entering process

y_n = extract concentration in nth contactor, pounds of solute per pound of solvent in extract layer; in washing, pounds of soluble material per pound of solvent in overflow

y_1 = concentration of extract leaving process in countercurrent solvent extraction

y_o = inlet concentration of solvent

θ = $\tan^{-1}(-1/a)$

GAS ABSORPTION

Chapter IV

The unit operation of gas absorption[82,96] is concerned with the design and performance[26,54,69,71,84,97] of equipment in which removal of the soluble constituents of a gaseous mixture is accomplished by bringing the gas into intimate contact with a liquid. If the removal is effected by contacting the gas with a solid, the operation is termed adsorption. The absorbable gas may range from a mere fraction of a per cent in the case of undesirable impurities up to nearly 100 per cent as in the absorption of hydrogen chloride. In order for absorption to take place, i.e., for the soluble gas to pass from the gaseous to liquid phase, it is necessary that there be a concentration driving force causing the soluble gas to dissolve. The condiditons necessary for absorption are illustrated on the equilibrium diagram in Figure 1. Suppose P which lies above the equilibrium curve represents the coordinates of a gaseous mixture of concentration y brought into contact with a liquid of concentration x. As p does not lie

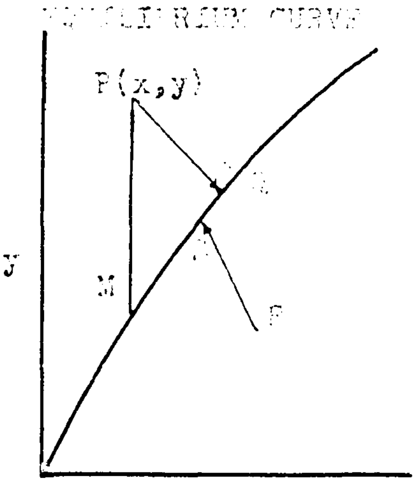


Figure 1

on the equilibrium curve, an interphase material transfer must take place. As P is above M, the point corresponding to a gas mixture in equilibrium with the liquid of concentration x, the gas is richer than this equilibrium mixture at M, and, hence, solute must pass from the gas to liquid phase. During absorption the gas concentration decreases while the liquid concentration increases, and the path followed is along PQ. When Q is reached no further mass transfer takes place as equilibrium is established. The slope of PQ depends upon the relative amounts of gas and liquid.

If R represents the coordinates of the gas and liquid in contact, the solute gas must pass in the reverse direction from the liquid to the gas. This process is termed stripping. Mathematically absorption and stripping can be treated in the same manner. In gas absorption, the material balance line lies above the equilibrium curve while in stripping it lies below the equilibrium curve.

In gas absorption and stripping, there are generally an inert gas and inert liquid which act as carriers for the soluble material. Between the inert components comprising the gas and liquid phases, there is a unidirectional mass transfer of the solute. In this respect, gas absorption differs from fractionation where there is a mass transfer simultaneously in two directions from both vapor to liquid and liquid to vapor. Distillation operations are carried out with substances having volatilities not too far apart while in gas absorption the solute usually has a much greater vapor pressure than the liquid in which it dissolves. There is no distinct borderline between gas absorption and fractionation.

Gas absorption is similar to solvent extraction, particularly for the case involving immiscible solvents. In both extraction and gas absorption, there is a unidirectional transfer of mass from one phase to another, the only difference being in the state of the phases. The mathematical treatments of the two operations are identical. Many of the solutions obtained in the previous chapter can be used for gas absorption with simple changes in notation.

Equilibria. Underlying the concept of theoretical stages in absorption is the basic liquid-gas equilibria. For graphical computations, the analytical representation of the data is unimportant. However, in developing formulas relating the number of plates to the operating variables, the mathematical form of the data determines the functional nature of the solutions. Certain forms lead to cumbersome expressions while others lead to simple formulas. In this dissertation equations for theoretical plates employing Henry's and Raoult's laws and modifications will be used.

In general Henry's law can be represented as

$$\text{(Concentration in gas)} = H \text{ (Concentration in liquid)} \quad (1)$$

where various types of units can be employed for expressing concentrations. In general, those units should be used which most nearly conform to the experimental data for the system when H is treated as a constant. Usually Equation (1) can normally only be employed in the dilute range regardless of what units are used. If molar ratio units are employed (1) takes the form[96]

$$y = H x \qquad (2)$$

where x and y are respectively mols of solute per mol of liquid and mols of solute per mol of gas. If mol fraction units are employed in (1), the equation becomes[21]

$$y/(1+y) = H x/(1+x) \qquad (3)$$

For small values of x and y, (2) and (3) are approximately the same as the denominators approach unity as x and y approach zero. Normally equations of the form of (2) and (3) only hold in dilute ranges, and it makes but little difference what units are used.

The gaseous concentration can be represented in terms of partial pressures and the liquid concentration as mol fraction, X, or mols of solute per cubic foot, c. In the first case, Henry's law becomes

$$p = H X \qquad (4)$$

Dividing through by the total pressure P gives

$$p/P = Y = (H/P)X \qquad (5)$$

where Y is the mol fraction in the gas. This is essentially the same as (3) except that H has been replaced by H/P. If the liquid concentration is expressed as mols/cubic foot,

(1) becomes

$$p = Hc \qquad (6)$$

If p and c are eliminated in terms of x and y, Equation (6) changes to

$$Py/(1+y) = H\rho x/(1+x) \qquad (7)$$

where ρ is the liquid density in mols/cubic foot. If the density is essentially constant (7) is of the same form as Equation (3) except that H is replaced by $H\rho/P$.

If Raoult's law can be used to represent the data, the relationship between gas and liquid concentration is

$$p = P_v X \qquad (8)$$

where P_v is the vapor pressure. This is equivalent to Henry's law in (4) if H is replaced by the vapor pressure.

It is apparent that for the forms presented, only Equations (2) and (3) need be considered as the others require no more than modification of the constants in (2) and (3).

Determination of the Number of Theoretical Plates[55,88]

The functional form of the analytical expressions for the number of theoretical plates depends upon the form in which the equilibrium is expressed. When the equilibrium is expressed as in Equation (2), the resulting formulas are relatively simple; however, the use of Equation (3) for expressing the equilibrium produces a cumbersome expression. Determination of the theoretical plates will be taken up first using Equation (2), second using Equation (3), and last expressing the equilibrium graphically.

Molar Ratio Units in Henry's Law.[91] Consider the tower represented in Figure 2. The gas enters at the bottom at a rate of G pound mols per hour of carrier gas with a concentration of y_o mols of solute gas per mol of carrier gas. The absorbent liquid enters the top at a rate of L pound mols of pure solvent per hour containing x_o mols solute per mol of liquid. If it is assumed that only the solute undergoes an interphase transfer, it is unnecessary to write material balances over the inert components. An overall material balance yields

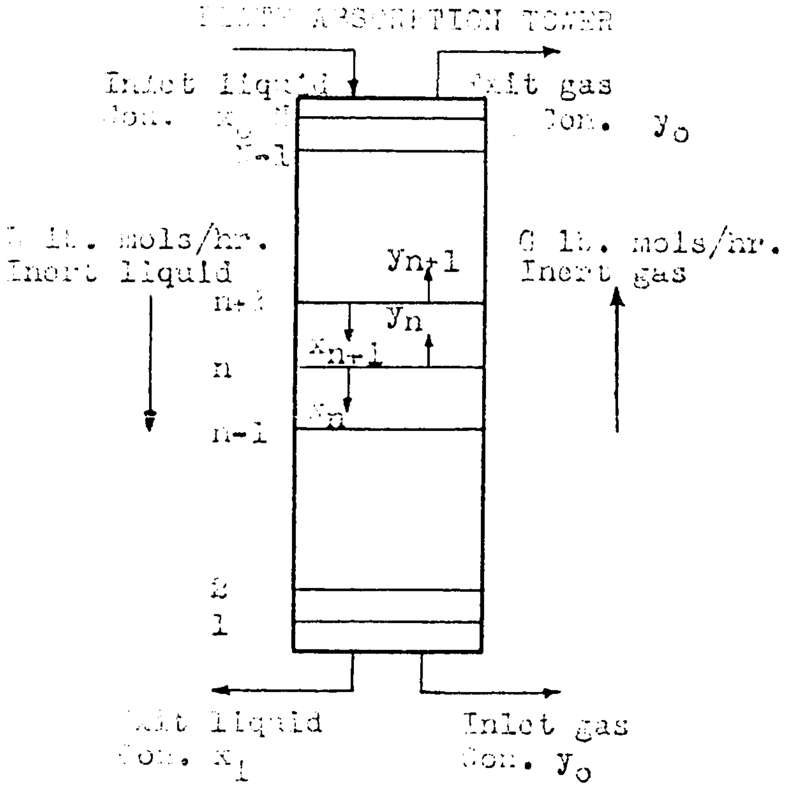


Figure 2

$$L(x_1 - x_o) = G(y_o - y_N) \tag{9}$$

where the symbols are indicated in Figure 1. A second material balance over that portion of the process including the (n+1)st and top or Nth plate produces

$$G(y_n - y_N) = L(x_{n+1} - x_o) \qquad (10)$$

Solving for y_n

$$y_n = (L/G)x_{n+1} + (y_N - (L/G)\ x_o) \qquad (11)$$

By means of Equation (9), it can be seen that the last term in (11) is also equal to $y_o - (L/G)x_1$. If the last term in (11) is replaced by this value, an equation results which is identical with the equation obtained from writing a material balance over the first n stages.

A material balance over the (n+1)st and adjoining stages gives

$$L(x_{n+2} - x_{n+1}) = G(y_{n+1} - y_n) \qquad (12)$$

which can be written in the alternative form

$$L\ \Delta\ x_{n+1} = G\ \Delta\ y_n \qquad (13)$$

Integrating

$$y_n = (L/G)\ x_{n+1} + C \qquad (14)$$

The constant in this equation is necessarily identical with the constant in Equation (11). As pointed out in the previous chapter, a material balance over any nth and adjoining stages produces a second order equation which may be integrated once to give a first order equation identical with the equation obtained from writing a material balance over the first n units. Equation (14) is a first order difference equation involving the three variables, x, y, and n. Before a solution can be obtained, it is necessary to obtain a relationship between x and y and then eliminate one or the other from (14). If it is assumed that the plates are theoretical, i.e., vapor and liquid on any plate are in equilibrium, the necessary relationship can be obtained from the previous section on equilibria. If Henry's law in the form of Equation (2) is assumed, then x_{n+1} can be replaced by y_{n+1}/H

$$y_n = (L/HG)y_{n+1} + (y_N - \frac{L}{G} x_o) \tag{15}$$

This is a first order linear difference equation and can be solved by the methods presented in the Appendix. First, place in standard form

$$y_{n+1} - (HG/L)y_n = Hx_o - (HG/L)y_N \tag{16}$$

Second, consider the reduced equation in E form

$$(E - HG/L)y_n = 0 \tag{17}$$

The general solution of the reduced equation is $C(HG/L)^n$ provided $HG/L \neq 1$. Third, to the solution of the reduced equation must be added a particular solution of the complete equation. This is obtained by letting $y_{n+1} = y_n = K$. Solving for K gives

$$K = \frac{Hx_o - (HG/L)y_N}{1 - HG/L} \tag{18}$$

The desired solution is the sum of (18) and the general solution of (17)

$$y_n = C(HG/L)^n + \frac{Hx_o - (HG/L)y_N}{1 - HG/L} \qquad (19)$$

It remains to determine the value of the arbitrary constant from known conditions. When $n = 0$, $y_n = y_o$, and $(HG/L)^o = 1$, hence from (19)

$$C = \frac{y_o - Hx_o + (HG/L)(y_o - y_N)}{1 - HG/L} \qquad (20)$$

From an overall material balance, it is evident that $y_o - y_N = (L/G)(x_1 - x_o)$. Eliminating $y_o - y_N$ from the numerator of (20) and placing the resulting expression for C in (19) yields the solution

$$y_n = \left[\frac{y_o - Hx_1}{1 - HG/L}\right] (HG/L)^n + \left[Hx_o - (HG/L)\, y_N\right]/(1 - HG/L) \qquad (21)$$

The final object is the determination of the total number, N, of stages necessary to reduce the vapor concentration from y_o to y_N. This may be done by placing $y_n = y_N$ and $n = N$ and then solving for N to obtain

$$N = \frac{1}{\log HG/L} \log(y_N - Hx_o)/(y_o - Hx_1) \qquad (22)$$

If $HG/L = 1$, N becomes indeterminate in (22) and it is necessary either to evaluate the indeterminate form or else return to the original difference equation. If this latter procedure is followed, Equation (16) becomes

$$y_{n+1} - y_n = \Delta y_n = Hx_o - y_N \qquad (23)$$

Integration of this equation produces

$$y_n = (Hx_o - y_N)n + C \qquad (24)$$

To obtain C let n = 0, then

$$y_n = (Hx_o - y_N)n + y_o \qquad (25)$$

Thus for this particular case in which HG/L = 1, y_n is a linear function of n. To obtain the total number of stages let n = N and $y_n = y_N$, then

$$N = \frac{y_o - y_N}{y_N - Hx_o} \qquad HG/L = 1 \qquad (26)$$

When HG/L = 1, the operating line is parallel to the equilibrium curve.

<u>Mol Fraction Units in Henry's Law.</u>[21,91] If Henry's law in the form of Equation (3) is used, the analytical solution for the number of stages becomes more involved. Returning to Equation (11), x_{n+1} must be eliminated by means of Equation (3). Solving for x in (3) gives

$$x = \frac{y}{H + (H - 1)y} \qquad (27)$$

Elimination of x_{n+1} from (11) by means of (27) leads to

$$y_n = \left(\frac{L}{G}\right)\frac{y_{n+1}}{H + (H - 1)y_{n+1}} + \left[y_N - \frac{L}{G}x_o\right] \qquad (28)$$

Multiplying this equation out yields

$$y_n\, y_{n+1} - Ay_{n+1} + By_n - D = 0 \qquad (29)$$

where A, B, and D are defined by

$$A = L/G(H - 1) + y_N - (L/G)x_o$$

$$B = H/(H - 1)$$

$$D = \frac{H}{H-1}\, y_N - \frac{L}{G}\, x_o$$

Equation (29) is a Riccati difference equation which arises frequently in chemical engineering unit operations. Analytical and graphical solutions of Riccati's equation are presented in Parts III and IV of the Appendix. In one of the analytical methods, the constant term D is eliminated by a substitution. Physically, this substitution for the elimination of the constant term amounts to moving the origin of coordinates to the intersection of the material balance and equilibrium curves. To find the intersection, Equations (11) and (27) are solved simultaneously after dropping the subscripts n and (n+1) in (11). The following value, y', is obtained for the y coordinate of the intersection

$$2y' = A - B + \left[(A - B)^2 + 4D\right]^{1/2} \qquad (30)$$

On making the substitution, $u_n = y_n - y'$, the constant term disappears in the new equation, and a form results which can be reduced to a solvable linear equation

$$u_n\, u_{n+1} + (y' - A)u_{n+1} + (y' + B)u_n = 0 \qquad (31$$

Dividing through by $u_n \, u_{n+1}$ gives

$$\frac{y' + B}{u_{n+1}} + \frac{y' - A}{u_n} + 1 = 0 \tag{32}$$

Making the substitution $v_n = 1/u_n$ and placing the resulting equation in standard form gives

$$v_{n+1} + \frac{y' - A}{y' + B} v_n = - \frac{1}{y' + B} \tag{33}$$

This is a first order linear equation whose reduced solution is $C \left[\frac{A - y'}{y' + B}\right]^n$ provided $(A - y')/(B + y') \neq 1$. A particular solution of the complete equation is $1/(A - B - 2y')$. Thus the complete solution is

$$v_n = C \left[\frac{A - y'}{y' + B}\right]^n + 1/(A - B - 2y') \tag{34}$$

Replacing v_n by $1/(y_n - y')$ and solving for the arbitrary constant C which is then substituted in (34) gives

$$1/(y_n - y') = \left[\frac{1}{y_0 - y'} - \frac{1}{A - B - 2y'}\right]\left[\frac{A - y'}{y' + B}\right]^n + 1/(a - B - 2y') \tag{35}$$

where A, B, and y' are as previously defined. In this equation y_n represents mols of solute per mol of inert carrier gas. In order to obtain the total number of stages, let $n = N$ and $y_n = y_N$. Denoting the quantity under the square root sign in (30) by S, and solving for N in (35) gives

$$N = \frac{1}{\log (A-y')/(B+y')} \log \frac{(y_0-y')}{(y_N-y')} \frac{(y'-y_n-S)}{(y'-y_0-S)} \qquad (36)$$

If $A-y' = B+y$ then (36) becomes indeterminate, and it is necessary to return to (32) or (33) to obtain a solution. For this special case, Equation (33) becomes

$$\Delta v_n = - 1/(y'+B) = 1/(y'-A) \qquad (37)$$

Integrating

$$v_n = n/(y' - A) + C \qquad (38)$$

Replacing v_n by $1/(y_n - y')$ and determining C gives

$$1/(y_n - y') = n/(y' - A) + 1/(y_0 - y') \qquad (39)$$

Letting $n = N$ and solving for N to obtain the desired result yields

$$N = (y' - A)/(y_N - y') - (y' - A)/(y_0 - y') \qquad (40)$$

Minimum Concentration. For every set of operating conditions, there is a definite minimum value to which y_N can be reduced. As y_N monotonically decreases with N, the minimum y_N is approached as N approaches infinity. In Figure 3, the method for obtaining the minimum concentration graphically is shown. The minimum concentration for a given slope of the operating line is obtained when N becomes infinite. Three different cases arise in each of which the operating line must intersect the equilibrium

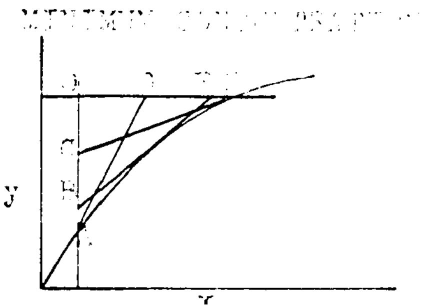


Figure 3

curve for N to be infinite. If the ratio of L/G is large indicating a large rate of flow of liquid as compared to gas, it is mathematically possible for the gas to leave in equilibrium with the liquid. This is shown in Figure 3 for the operating line AD, which has a steep slope and consequently a large L/G. The point of intersection of the line $x = x_0$ with the equilibrium curve is the only point at which an operating line with a slope corresponding to AD can intersect the equilibrium curve. Thus the y coordinate of point A represents the minimum concentration in this case. If the slope of the operating line is somewhat less corresponding to EB, the intersection is obtained when the operating line becomes tangent to the equilibrium curve, and the y coordinate of A corresponds to the minimum obtainable concentration. If L/G is small, the slope of the operating line is small, and the intersection will be at F with the minimum concentration at C. In this case the exit liquid leaves in equilibrium with the incoming gas.

Analytical expressions for the minimum concentration can be obtained from the equations previously developed. From Equation (22) y_N is determined as

$$y_N = \frac{y_0\,(1-HG/L) + Hx_0\left[(L/HG)^n - 1\right]}{(L/HG)^n - 1} \tag{41}$$

This equation gives the variation of the <u>exit gas concentration</u> with changing number of plates. It does not show the plate to plate variation which is obtained from Equation (21) for a fixed value of N. If L/HG = 1, y_N is obtained from (26)

$$y_N = (NHx_0 + y_0)/(N + 1) \tag{42}$$

If L/HG ≥ 1, the minimum value, y_i, obtained from (41) and (42) as N approaches infinity is

$$y_i = Hx_0 \qquad L/HG \geq 1 \tag{43}$$

If L/HG < 1, the minimum concentration is given by

$$y_i = (L/G)\,x_0 - y_0(L/HG - 1) \tag{44}$$

If the first case for L/HG ≥ 1, the gas leaves in equilibrium with the liquid, while in the second case there is insufficient liquid to dissolve all the gas present, and consequently the gas cannot leave in equilibrium with the incoming liquid. However, in the latter case the liquid becomes saturated and leaves the tower in equilibrium with the incoming gas.

In Equation (36), it is not possible to solve for y_N as the variables cannot be separated. However, the minimum concentration can be obtained from a consideration of Figure 4. When the slope of the operating line is greater than or equal to the slope of PQ, the minimum concentration is given by P. When the slope of the operating line is less than PQ, the minimum

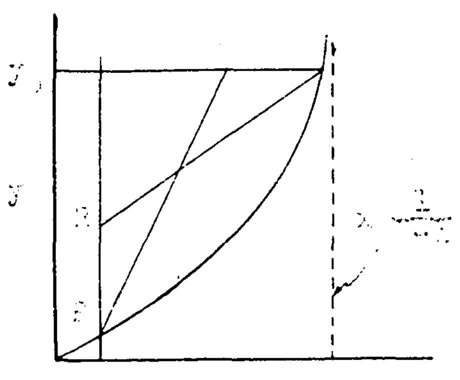


Figure 4

concentration is found at point R. Thus

$$y_i = \frac{Hx_o}{1 - (H-1)x_o} \qquad \frac{L}{G} \geq \frac{H + (H-1)y_o}{1 - (H-1)x_o} \tag{45}$$

$$y_i = (L/G)x_o + y_o - \frac{(L/G)y_o}{H + (H-1)y_o} \qquad \frac{L}{G} < \frac{H + (H-1)y_o}{1 - (H-1)x_o} \tag{46}$$

Efficiencies.[88] The overall efficiency as defined in the previous chapter is given by

$$e_N = \text{solute removed} \;/\; \text{solute originally present} = (y_o - y_N)/y_o \tag{47}$$

For a given L/G, the maximum overall efficiency is obtained when y_N reaches its minimum value, y_i. Thus

$$e_i = (y_o - y_i)/y_o \tag{48}$$

where e_i is the maximum overall efficiency. If y_i is obtained from Equations (43) and (44), e_i becomes

$$e_i = 1 - Hx_o/y_o \qquad L/GH \geq 1 \tag{49}$$

$$e_i = (L/HG)(1 - Hx_o/y_o) \qquad L/HG < 1 \tag{50}$$

If the minimum concentration as given by Equations (45) and (46) is employed, then

$$e_i = 1 - Hx_o/\left[1 - (H-1)x_o\right] y_o \qquad L/G \geq \left[H + (H-1)y_o\right] / \left[1-(H-1)x_o\right] \tag{51}$$

$$e_1 = (L/HG)\left[1/\left[H + (H-1)y_0\right] - x_0/y_0\right] \qquad L/G < \left[H+(H-1)y_0\right] / \left[1-(H-1)x_0\right] \tag{52}$$

The relative efficiency as defined in the previous chapter represents the ratio of the amount of solute that is removed to the maximum amount that could be removed if an infinite number of stages were employed. Thus if E_N is the relative efficiency

$$E_N = G(y_o - y_N)/G(y_o - y_1) = (y_o - y_N)/(y_o - y_1) \tag{53}$$

From the definitions in (47), (48), and (53) it is apparent that

$$e_N = e_1 E_N \tag{54}$$

Substitution of y_N from (41 or (42) and y_1 from (43) or (44) in (53) leads to

$$E_N = \frac{(L/HG)^{N+1} - (L/HG)}{(L/HG)^{N+1} - 1} \qquad L/HG > 1 \tag{55}$$

$$E_N = N/(N+1) \qquad L/HG = 1 \tag{56}$$

$$E_N = \frac{1 - (L/HG)^N}{1 - (L/HG)^{N+1}} \qquad L/HG < 1 \tag{57}$$

The graphical representation of this set of equations is similar to the plot of Figure 15 given for the efficiencies in the chapter on extraction and will not be duplicated here. As it is not possible to solve for y_N in Equation (36), formulas similar to (55), (56), and (57) cannot be obtained for the case in which the Henry's law is used with mol fraction units.

Height Equivalent to a Theoretical Plate.[73] The performance of packed towers can be expressed in terms of the mass transfer coefficient, (lb. mols)/(hr.)(sq. ft.)(unit of concentration driving potential), the height of a transfer unit, H.T.U., or the height equivalent to a theoretical plate, H.E.T.P. The relationships between these quantities is of value in that the relationships indicate that under certain conditions it is possible to obtain the height of a packed tower with the methods developed for stagewise operations. When this can be done, the easier graphical stepwise procedure can be substituted for the lengthier differential graphical integration.

If it is assumed that the equilibrium is expressible as $y = Hx$ and that the rate of mass transfer for gas film controlling is

$$(\text{lb. mols})/(\text{hr.})(\text{cu.ft.}) = K_G a(y-Hx) \qquad (58)$$

a material balance over the differential height in Figure 5 gives[58]

$$G\,dy = K_G aS(y-Hx)\,dh \qquad (59)$$

where S is the cross sectional area and Sdh is the differential volume. A material balance over

PACKED TOWER

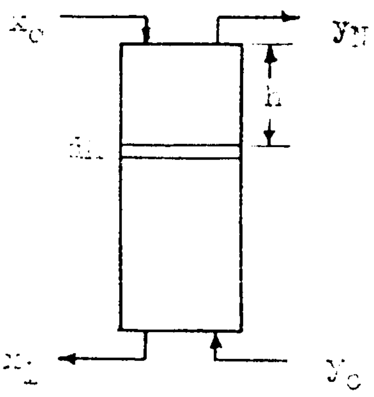


Figure 5

the top h feet yields

$$G(y - y_N) = L(x - x_o) \qquad (60)$$

and over the entire tower

$$G(y_o - y_N) = L(x_1 - x_o) \qquad (61)$$

Eliminating x between (59) and (60) and integrating over the entire tower, and using Equation (61) gives

$$h = \frac{G/S}{K_Ga(HG/L-1)} \ln(y_N - Hx_o)/(y_o - Hx_1) \qquad HG/L \neq 1 \qquad (62)$$

If HG/L = 1, Equation (62) becomes

$$h = \frac{G/S}{K_Ga} (y_N - y_o)/(y_N - Hx_o) \qquad HG/L = 1 \qquad (63)$$

The H.E.T.P. is the height required to produce a given separation divided by the number of theoretical plates required for the same separation, i.e., H.E.T.P. = h/N. Using h from (62) and N from (22) produces

$$H.E.T.P. = \frac{(G/S) \ln(HG/L)}{K_Ga(HG/L-1)} \qquad L/HG \neq 1 \qquad (64)$$

with h from (63) and N from (26)

$$H.E.T.P. = (G/S)/K_Ga \qquad L/GH = 1 \qquad (65)$$

The number of transfer units, $(T.U.)_{OG}$ based on the overall gas film is

$$(T.U.)_{OG} = \int_{y_0}^{y_N} dy/(y - Hx) \tag{66a}$$

$$= \frac{1}{HG/L-1} \ln(y_N - Hx_0)/(y_0 - Hx_1) \tag{66b}$$

$$= (y_N - y_0)/(y_N - Hx_0) \quad L/HG = 1 \tag{66c}$$

The height equivalent to one transfer unit based on the overall gas film is

$$(H.T.U.)_{OG} = (T.U.)_{OG}/h = (G/S)/K_G a \tag{67}$$

In the above expressions only the overall gas film coefficient has been employed. Corresponding equations can be written involving the overall liquid film coefficient, $K_L a$, the gas film coefficient, $k_G a$, and the liquid film coefficient, $k_L a$. The relationship between these quantities is[82]

$$1/K_G a = 1/k_G a + H/k_L a \tag{68}$$

$$1/K_L a = 1/Hk_G a + 1/k_L a \tag{69}$$

$$K_L a = HK_G a \tag{70}$$

If subscripts OG and OL represent overall gas and overall liquid film coefficients, it can be shown that[17]

$$(H.T.U.)_{OG} = (H.T.U.)_G + (HG/L)(H.T.U.)_L \tag{71}$$

$$(H.T.U.)_{OL} = (H.T.U.)_L + (L/HG)(H.T.U.)_G \tag{72}$$

$$(H.T.U.)_{OL} = (L/HG)(H.T.U.)_{OG} \tag{73}$$

From Equations (64) and (65) it is apparent that if the transfer coefficient and H.T.U. are constant the H.E.T.P. will be a constant and independent of gas concentration provided the equilibrium curve is straight. As these equations are of value primarily in dilute regions, it is in this region that the H.E.T.P. could be used with confidence in predicting tower heights. The relationship between H.E/T.P. and H.T.U. is

$$\text{H.E.T.P.} = (\text{H.T.U.})_{OG}\ \ln(HG/L)/(HG/L-1) \qquad HG/L \neq 1 \tag{74}$$

$$\text{H.E.T.P.} = (\text{H.T.U.})_{OG} \qquad HG/L = 1 \tag{75}$$

The H.E.T.P. and $(\text{H.T.U.})_{OG}$ are exactly equal when the operating line is parallel to the equilibrium curve as can be seen by letting HG/L approach 1 in (74). Equations (74) and (75) can also be coupled with (71) and (73) by eliminating $(\text{H.T.U.})_{OG}$.

<u>Efficiencies in Packed Towers</u>. While operations carried out in packed towers are not classified as stagewise processes, the values of minimum concentration and the expressions for efficiencies obtained for packed towers are of interest inasmuch as they are related to similar material previously given for plate towers. The final concentration as a function of tower height can be obtained from Equations (62) and (63). Equation (62) can be rearranged to give

$$\frac{hK_Ga(HG/L - 1)}{G/S} = \frac{h\ \ln(HG/L)}{\text{H.E.T.P.}} = \ln(y_N - Hx_0)/\left[y_0(1-HG/L) - Hx_0 + (HG/L)y_N\right] \tag{76}$$

where $K_G\,a$ is eliminated by Equation (64) and x_1 from an overall material balance. Solving this equation for y_N and noting that h/H.E.T.P. = N leads to an equation which is identical with (41). In order to obtain the minimum value of y_N, h is allowed to approach infinity, and as this is the same as letting N approach infinity, exactly the same equations are obtained for the minimum concentration with packed towers as are obtained with plate towers. The maximum overall efficiency for packed towers is also identical with the expressions for plate towers given in (49) and (50). The equations for relative efficiency are identical with (55), (56), and (57). To place in a more convenient form for packed towers, N may be replaced by

$$N = h/(H.E.T.P.) = h(1-HG/L)/(H.T.U.)\ \ln\ (L/HG) \qquad (77)$$

and as $h/(H.T.U.)_{OG} = (T.U.)_{OG}$

$$N = (T.U.)_{OG}(1-HG/L)/\ln(L/HG) \qquad L/HG \neq 1 \qquad (78)$$

$$N = (T.U.)_{OG} \qquad L/HG = 1 \qquad (79)$$

Using the relationship

$$(L/HG)^{(T.U.)_{OG}(1-HG/L)/\ln(L/HG)} = e^{(T.U.)_{OG}(1-HG/L)} \qquad (80)$$

and substituting in (55), (56), and (57) gives

$$E = \frac{(L/HG)\left[e^{(T.U.)_{OG}(1-HG/L)} - 1\right]}{(L/HG)\ e^{(T.U.)_{OG}(1-HG/L)} - 1} \qquad L/HG > 1 \qquad (81)$$

$$E = (T.U.)_{OG}/\left[(T.U.)_{OG} + 1\right] \qquad L/HG = 1 \qquad (82)$$

$$E = \frac{1 - e^{(T.U.)_{OG}(1-HG/L)}}{1 - (L/HG)e^{(T.U.)_{OG}(1-HG/L)}} \qquad L/HG < 1 \qquad (83)$$

The limit approached by E as L/HG approaches zero is unity regardless of the number of transfer units as can be seen from Equation (83).

The limit of E as L/HG approaches infinity must be obtained from (81). Allowing L/HG to approach infinity leads to an indeterminate form which may be evaluated to give $E = 1 - e^{-(T.U.)_{OG}}$. The graphical representation of the relative and overall efficiencies for packed towers is illustrated in Figure 6. The curves are of exactly the same form as those presented for the relative and overall efficiencies in the section on countercurrent extraction in the previous chapter. These plots and Equations (78) and (79) show the similarity between the number of plates and the number of transfer units and the dependence of the relative efficiencies on these quantities. If it is desirable to absorb as much of a solute material from a gas mixture as is practicable, the overall efficiency should be high and the plots in Figure 6 indicate that L/HG should be greater than unity. In order to have a large relative efficiency when L/HG is greater than unity, there should be at least three transfer units based on the overall gas film concentration driving potential. However, after five transfer units have been reached, there is little improvement in the tower efficiency with the addition of extra transfer units due to greater heights.

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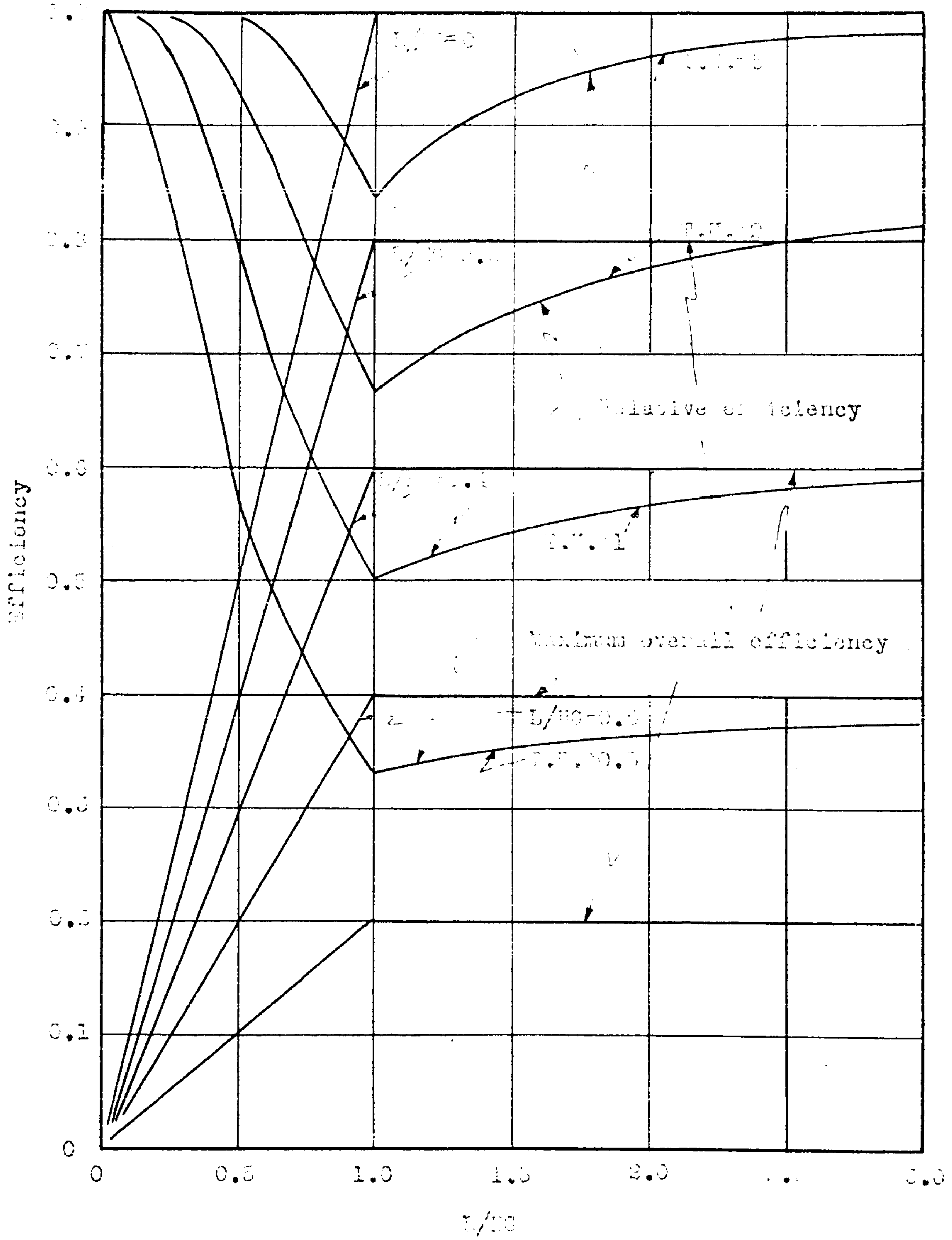

Efficiency
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.5
1.0
1.5
2.0
2.5
3.0
L/HG
L/HG=0.5
T.F.=0.5
T.F.=1
T.F.=2
Relative efficiency
Maximum overall efficiency

Figure 6

NOMENCLATURE FOR CHAPTER VII

a = packing coefficient, square feet of area for mass transfer per cubic foot of tower volume

A = $L/G(H-1) + y_N + (L/G)x_o$

B = $H/(H-1)$

c = liquid concentration, pound mols solute / cubic foot

C = arbitrary constant

D = $\frac{H}{H-1}(y_N - \frac{L}{G}x_o)$

e = overall efficiency for packed tower h feet tall

e_i = maximum overall efficiency, packed or plate tower

e_N = overall efficiency for N stages, mass of solute removed/mass of solute originally present

E = relative efficiency for packed tower h feet tall

E_N = relative efficiency for N stages, mass of solute removed/maximum mass which can be removed with fixed L/HG and an infinite number of plates

G = mols inert gas per hour (pounds may also be used).

h = tower height in feet measuring down from top

H = Henry's constant = concentration in gas/concentration in liquid

k_Ga = gas film mass transfer coefficient, based on concentration driving force across gas film, (pound mols)/(hour)(cubic foot) (unit of gas concentration driving force based on molar ratio units)

K_Ga = overall gas film mass transfer coefficient, based on overall gas film concentration driving force, same units as k_Ga.

k_La = liquid film mass transfer coefficient, based on concentration driving force across liquid film, (pound mols)/(hour)(cubic foot)(unit of liquid concentration driving force based on molar ratio units)

K_La = overall liquid film mass transfer coefficient, based on overall liquid film concentration driving force, same units as k_La.

L = mols of inert liquid per hour (pounds may also be used)

n = plate number counting up from bottom

N = total number of plates

p = partial pressure

P = total pressure

P_v = vapor pressure

ρ = liquid density, mols/cubic foot

s = tower cross-sectional area, sq. ft.

u_n = $y_n - y'$

v_n = $1/u_n$

x = liquid concentration h feet from top of packed tower, mols of solute per mol of inert liquid

x_n = liquid concentration on nth plate, mols of solute per mol of inert liquid

x_o = inlet liquid concentration at top of tower

x_1 = exit liquid concentration from bottom of tower

X = mol fraction in liquid

y = gaseous concentration h feet from top of packed tower, mols of solute per mol of inert gas

y_n = gaseous concentration arising from the nth plate, mols of solute per mol of inert gas

y_o = inlet gas concentration at bottom of tower

y_N = exit gas concentration from top of tower

y' = $A - B + \left[(A - B)^2 + 4D\right]^{1/2}$, y coordinate of intersection equilibrium curve and operating line

y_i = minimum concentration obtainable with an infinite number of plates.

Y = mol fraction in gas

H.E.T.P. = height equivalent to a theoretical plate

H.T.U. = height of a transfer unit

T.U. = number of transfer units defined by Equation (66a)

Subscripts

n = plate number

N = top plate

o = inlet stream

G = individual gas film

OG = overall gas film

L = individual liquid film

OL = overall liquid film

FRACTIONAL DISTILLATION

Chapter V

Fractionation[4,75,96] is that operation in which a simultaneous interphase counterflow of two or more chemical components takes place between intimately contacted liquid and vapor phases as the two phases pass countercurrently through a containing vessel. The particular fractionator governs the manner in which the vapor and liquid phases are contacted and may bring the phases into either differential or stagewise contact.[75] The usual stagewise fractionating column consists of a vertical tower equipped with suitable means for bringing the liquor into intimate contact at intervals throughout the tower. Plates that retain liquid and have various types of vapor risers and liquid downcomers are normally employed, and the term plate tower is used to describe this type of unit. In fractionating columns, the feed is introduced at some intermediate point where it mixes with the liquid already present. Vapor is produced in a boiler at the bottom of the column and rises to the first plate where it gives up its latent heat and produces more vapor which in turn passes to the next plate. At the top of the column the vapor is condensed, part of the condensate being returned to the column to form the liquid phase and part being drawn off as product. Two streams are involved, a liquid phase produced at the top of

SCHEMATIC DIAGRAM OF THE DISTILLATION COLUMN

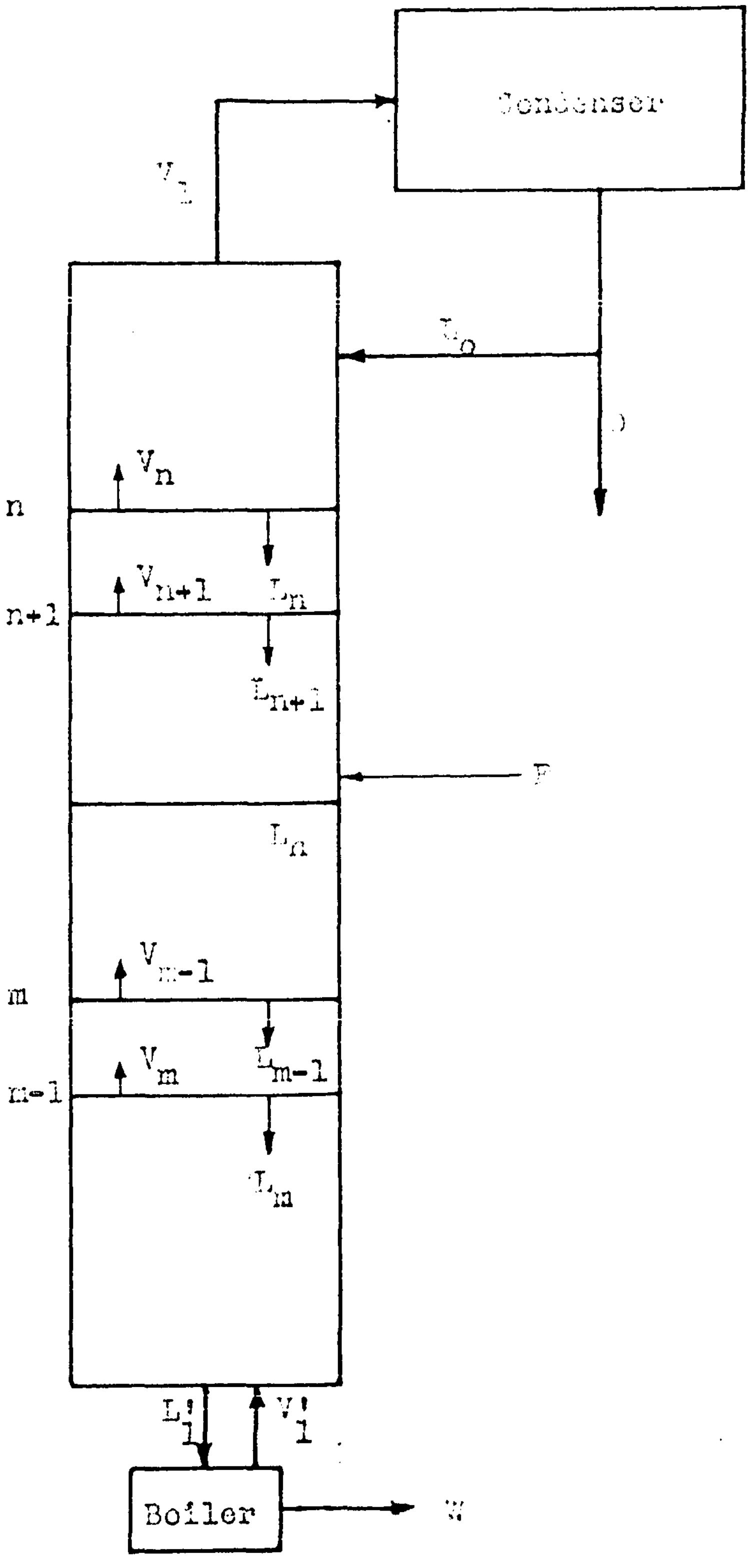


Figure 1

the column and augmented by the feed at an intermediate point and a vapor phase produced at the bottom of the tower in the boiler. In some columns used for separating multicomponent mixtures, side streams are involved in addition to the product and bottoms.

Heat and material balances and phase data are necessary for development of design equations relating the variables. In the following material, binary systems will be treated first followed by multicomponent systems.

Binary Systems

Material Balances. A plate fractionating column is shown schematically in Figure 1. For convenience it is divided into first, the enrichment section which includes the vapor from the feed plate and the remainder of the column above the feed plate and including the condenser; and, second, the exhausting section which includes the boiler, the column below the feed plate, and the liquid on the feed plate. The plates are numbered as indicated in Figure 1. Subscripts m and n are used for plate numbers in the exhausting and enriching sections respectively. The plates are numbered down from the top in the enriching section and up from the bottom in the exhausting section. The resulting difference equations are easier to handle when this numbering method is used in preference to the usual way of numbering plates up from the bottom in both enriching and exhausting sections. A number of different material balances can be written including (1) a balance around the entire process, (2) a balance in the enriching section including the nth plate and the remainder of the column above the nth plate, and (3) a balance over the first m plates in the exhausting section.

(1) Material Balance Around the Entire Process. Designating F, D, and W as mols per hour of feed, distillate, and waste respectively, a material balance over both components gives

$$F = D + W \tag{1}$$

and over the more volatile component

$$x_f F = x_d D + x_w W \tag{2}$$

where x_f, x_d, and x_w are respectively the mol fractions of the F, D, and W streams.

(2) Material Balance in Enriching Section. The only stream entering the section of the tower including and above the nth plate is the vapor from the (n+1)st plate while liquid leaves both as distillate and overflow from the nth plate. Thus

$$V_{n+1} = L_n + D \tag{3}$$

and over the more volatile component

$$y_{n+1} V_{n+1} = x_n L_n + x_d D \tag{4}$$

where x_n and y_n are the molar concentrations of the more volatile component in the liquid and vapor respectively on the nth plate.

(3) Material Balance in Exhausting Section. The only stream entering the mth plate is the liquid from the (m+1)st plate while vapor leaves the mth plate and liquid leaves the boiler. In terms of both components

$$L_{m+1} = V_m + W \tag{5}$$

or for the more volatile component

$$x_{m+1} L_{m+1} = y_m V_m + x_w W \tag{6}$$

Equations (3) and (4) and Equations (5) and (6) can be combined to give the following equations of the operating lines. Eliminating V_{n+1} between (3) and (4)

$$y_{n+1} = \frac{L_n}{L_n+D} x_n + Dx_d/(L_n + D) \tag{7}$$

and for the exhausting section, elimination of V_m gives

$$y_m = \frac{L_{m+1}}{L_{m+1}-W} x_{m+1} - Wx_w/(L_{m+1} - W) \tag{8}$$

Defining the reflux ratio as $R_n = L_n/D$, Equation (7) becomes

$$y_{n+1} = \frac{R_n}{R_n+1} x_n + x_d/(R_n+1) \tag{9}$$

This equation involves the four variables x_n, y_n, R_n, and implicitly n. Before a solution can be obtained for this equation or for Equation (8), it is necessary to eliminate two of the variables. This can be accomplished by a heat balance which will relate R_n to x_n and by assuming that the plates are theoretical, i.e., y_n is related to x_n by equilibrium data. Equation (9) can then be reduced to a form containing only x_n and n.

Heat Balances. The heat effects involved primarily consist of (1) latent heat of vaporization, (2) heat of reaction (if any), (3) heat of dilution, and (4) sensible heat due to the difference in temperature of the streams leaving the various plates. An exact solution requires a knowledge of the thermodynamic properties of the system. Where the complete thermodynamic data are not available, the best assumption is that the major part of the heat transfer is effected by the latent heat of vaporization. If all other heat effects are neglected and h_n represents the average molar latent heat on the nth plate, a heat balance around the nth and (n+1)st trays gives

$$h_n V_n = h_{n+1} V_{n+1} \tag{10}$$

Assuming no heat losses, it is apparent that the total latent heat given up from plate to plate is constant and must equal the total heat removed in the condenser which is $h_1 V_1$. Thus

$$h_n V_n = h_{n+1} V_{n+1} = h_1 V_1 \tag{11}$$

From Equation (3) and the definition of the reflux ratio

$$V_1 = L_o + D = (R_o + 1)D \tag{12}$$

Eliminating V_1 from (11) and solving for V_{n+1} gives

$$V_{n+1} = h_1(R_o + 1)D/h_{n+1} \tag{13}$$

where at a given pressure, h_n is a function of the composition of the liquid on the (n+1)st plate. Equation (13) gives one of the relations necessary for the elimination of either L_n in (7) or R_n in (9). Elimination of V_{n+1} between Equations (3) and (13) yields

$$L_n = h_1(R_o + 1)D/h_{n+1} - D \tag{14}$$

In the exhausting section heat to the tower is supplied from the boiler. An equation similar to (11) can be written as follows

$$h_m V_m = h_{m+1} V_{m+1} = h_1{}' \; V_1{}' \tag{15}$$

where the primes are used on $h_1{}'$ and $V_1{}'$ to differentiate from the corresponding values in the enriching section. From (15) and (5) there results

$$L_{m+1} = h_1{}' \; V_1{}'/h_m + W \tag{16}$$

This equation can be combined with Equation (8).

The thermal condition of the feed determines the relationship between the vapor flows in the enriching and exhausting sections. The thermal properties of the feed may be represented by q which is defined as the ratio of the heat necessary to vaporize one mol of feed to the molar latent heat. The heat produced in the boiler augmented or decreased due to the condition of the feed must be removed in the condenser. Thus

$$h_1' \, V_1' + h_f(1-q)F = h_1 V_1 = h_1(R_o + 1)D \qquad (17)$$

Eliminating $h_1' \, V_1'$ from (16) gives

$$L_{m+1} = \left[h_1(R_o + 1)D - h_f(1-q)F \right] / h_m + W \qquad (18)$$

Graphical Solution of Binary Fractionation Equations. For the enriching section, the value of L_n in (14) can be substituted in Equation (7) to yield

$$y_{n+1} = \frac{R_o + 1 - h_{n+1}/h_1}{(R_o + 1)} x_n + x_d h_{n+1}/h_1(R_o + 1) \qquad (19)$$

Elimination of L_{m+1} between (8) and (18) produces

$$y_m = \frac{(R_o + 1)D - (1-q)fh_f/h_1 + Wh_m/h}{(R_o + 1)D - (1-qF)h_f/h_1} x_{m+1} - \frac{h_m W x_w}{h_1(R_o+1)D - h_f(1-qF)} \qquad (20)$$

If it is assumed that the plates are theoretical, Equations (19) and (20) can be solved graphically to give the relationship between the liquid and vapor concentrations and the plate number. These equations fall under case 3 of Part IV of the Appendix and their

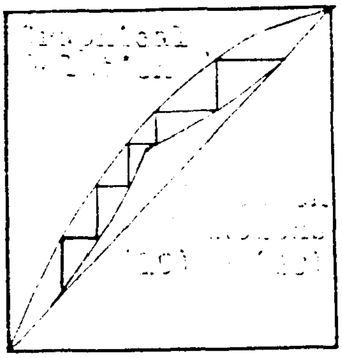


Figure [illegible]

solutions are indicated in Figure 2. In (19) all quantities except x_n, y_{n+1}, and h_{n+1} are known constants. In order to plot the operating line it is necessary to solve (19) for x_n in terms of y_{n+1} and the molar latent heat of vaporization on the (n+1)st plate, h_{n+1}

$$x_n = \left[(R_o + 1)y_{n+1} - x_d\, h_{n+1}/h_1\right]/(R_o + 1 - h_{n+1}/h) \qquad (21)$$

Assuming values of y_{n+1}, x_{n+1} can be obtained from the equilibrium curve. If the latent heat is an additive function of the liquid composition or some other known function, h_{n+1} can be obtained; and then x_n can be computed from (21). In this manner the curved operating line can be constructed, and the usual stepwise procedure gives the liquid and vapor concentrations as a function of the plate number. A similar procedure can be employed in the exhausting section.

Although molar units have been used as a basis for the material and heat balances in the previous discussion, the equations and procedures are equally applicable to pound units. In fact, where latent heats and equilibrium data are available in terms of B.T.U. per pound and mass percentages, pound units are easier to use.

Approximate Graphical Solution.[67] Under certain conditions, the graphical procedure of the previous section can be modified and simplified to give straight operating lines. If the molar latent heats remain constant in distillation where only latent heat is of importance, the terms h_{n+1}/h_1,

h_m/h_1, and h_f/h_1 become unity; and Equations (19) and (20) become

$$y_{n+1} = Rx_n/(R + 1) + x_d/(R + 1) \tag{22}$$

$$y_m = (RD + qF)\, x_{m+1}/(RD + qF - W) - Wx_w/(RD + qF - W) \tag{23}$$

These are the equations of straight lines, and the method of Figure 2 reduces to the well known McCabe-Thiele solution.[67] In general, molar latent heats are not equal, but can be made approximately so by assigning an arbitrary molecular weight to one of the components. Even with such closely related compounds as benzene and toluene, the molecular weight of one should be modified several per cent for best results.

Binary Equilibrium Relationships. Before an analytical solution of the fractionation equations can be obtained, it is necessary to determine a functional relationship between the equilibrium values of the liquid and vapor concentrations. If it is assumed that the relative volatility, α, is constant, a condition rarely met, the following relationship between x and y can be developed

$$y = \frac{\alpha x}{(\alpha - 1)x + 1} \tag{24}$$

A two parameter equation can be generalized from this expression, and for certain regions of concentration the generalized expressed may more accurately represent the data than (24). Thus

$$y = \alpha x/(\beta x + 1) \tag{25}$$

represents a form similar to (24) in which (α - 1) has been replaced by β. Equation (25) will not satisfy the condition that x = 1 when y = 1, and cannot be used in the region close to this point.

When x is very small, Equation (24) reduces to

$$y = \alpha x \tag{26}$$

and when x approaches unity

$$y = \frac{1}{\alpha} x + \frac{\alpha - 1}{\alpha} \tag{27}$$

Analytical Solutions.[86] Subject to the assumption of constant molal overflow, the relationship between the number of theoretical stages and other variables can be determined based on the equilibrium relationships presented in Equations (24) through (27).

If the equilibrium relationship takes the form of (26) for the dilute or stripping region, y_m can be eliminated in (23) to give

$$\alpha x_m = (RD + qF)x_{m+1}/(RD + qF - W) - Wx_w/(RD + qF - W) \tag{28}$$

Rearranging this equation and placing in standard form

$$x_{m+1} - \frac{(RD + qF - W)}{RD + qF} \alpha x_m = Wx_w/(RD+qF) \tag{29}$$

The complete solution of this linear first order difference equation is

$$x_m = C\left[\frac{(RD + qF - W)\alpha}{RD + qF}\right]^m + \frac{Wx_w}{(1-\alpha)(RD + qF) + W} \qquad (30)$$

With most systems under normal operating conditions, Equation (30) could only be used for the lower section of the tower and would not be applicable at the feed plate. Actually this equation would be employed to calculate the number of remaining plates, after having reached a point with a graphical procedure where Equation (26) would accurately represent the data and the graphical solution had become tedious. Assuming that the concentration on the Mth plate from the bottom is x_M, the constant in (30) can be determined. Thus

$$C = (x_M - K')/(r')^M \qquad (31)$$

where K' and r' are defined by

$$K' = wx_w/\left[(1-\alpha)(RD + qF) + W\right] \qquad (32)$$

$$r' = \alpha(RD + qF - W)/(RD + qF) \qquad (33)$$

substituting (31) in (30) gives

$$x_m = (x_M - K')(r')^{m/M} + K' \qquad (34)$$

The concentration on the first plate is given by x_w. Thus to obtain M from (34) let m = 1 and $x_m = x_w$, then

$$M = \frac{1}{\log r'} \log (x_m - K')/(x_w - K')$$

In the concentrated region, Equation (27) can be employed to represent the equilibrium relationship. Combining

(22) and (27) gives

$$\frac{1}{\alpha} x_{n+1} + \frac{\alpha - 1}{\alpha} = \frac{R}{R+1} x_n + x_d/(R + 1) \tag{36}$$

Rearranging into standard form

$$x_{n+1} - \frac{\alpha R}{R+1} x_n = \alpha x_d/(R + 1) - (\alpha - 1) \tag{37}$$

The complete solution is

$$x_n = C \left[\frac{\alpha R}{R+1}\right]^n + \left[\alpha x_d - (\alpha - 1)(R+1)\right] / \left[R(1-\alpha) + 1\right] \tag{38}$$

This equation would be employed in a manner similar to (32) except that it would be applicable only to the concentrated region near the top of the tower. To evaluate C, place $n = 0$ and $x_n = x_d$, then

$$x_n = (x_d - K)\, r^n + K \tag{39}$$

where K and r are defined by

$$K = \left[\alpha x_d - (\alpha - 1)(R+1)\right] / \left[R(1-\alpha) + 1\right] \tag{40}$$

$$r = \alpha R/(R+1) \tag{41}$$

If x_N represents some known concentration on the Nth theoretical plate from the top, the number of plates in the section in which the liquid concentration varies from x_N to x_d may be obtained from (39)

$$N = \frac{1}{\log r} \log (x_N - K)/(x_d - K) \tag{42}$$

Equations (35) and (42) are solutions applicable to only a small concentration range in which the equilibria can be represented by (26) and (27). They possess the advantage of being simple and, consequently, useful where applicable. For small relative volatilities, they can be employed over relatively wide concentration ranges.

The solution of the fractionation equations in connection with the use of Equation (24) is considerably more involved than the solutions just presented. Before taking up the general case, the equations for infinite reflux ratio will be considered. If R is infinite, the material balance equations reduce to

$$y_{n+1} = x_n \tag{43a}$$

$$y_m = x_{m+1} \tag{43b}$$

regardless of whether the molal latent heat in constant or not. Equations (43a) and (43b) are identical, and only the solution of (43a) will be considered. Eliminating y_{n+1} produces

$$\alpha x_{n+1} / \left[(\alpha - 1) x_{n+1} + 1 \right] = x_n \tag{44}$$

Multiplying out and gathering terms

$$(\alpha - 1) x_n x_{n+1} - \alpha x_{n+1} + x_n = 0 \tag{45}$$

(45) is a Riccati difference equation and can be solved by Method 4 presented in Part III of the Appendix. Dividing through by $x_n x_{n+1}$ and rearranging terms

$$\frac{1}{x_{n+1}} - \alpha \frac{1}{x_n} = (1 - \alpha) \tag{46}$$

This equation is linear in $1/x_n$ and its solution is

$$1/x_n = C\alpha^n + 1 \qquad (47)$$

As $x_n = x_d$ when $n = 0$, C may be determined to give

$$1/x_n = (1/x_d - 1)\alpha^n + 1 \qquad (48)$$

At infinite reflux ratio, it is desired to know how many stages are required to reduce x_n to x_w. Thus

$$n = \frac{1}{\log\alpha}\log\left[x_d\,(1 - x_w)/x_w\,(1 - x_d)\right] \qquad (49)$$

For finite reflux ratio,[86] elimination of the vapor concentration from Equations (22) and (23) yields

$$\frac{\alpha x_{n+1}}{(\alpha - 1)x_{n+1} + 1} = \frac{R}{R+1}x_n + x_d/(R+1) \qquad (50)$$

$$\frac{\alpha x_m}{(\alpha - 1)x_m + 1} = \frac{RD + qF}{RD + qF - W}\,x_{m+1} - Wx_w/(RD + qF - W) \qquad (51)$$

Multiplying these equations out and gathering terms produces

$$x_n x_{n+1} + Ax_{n+1} + Bx_n + G = 0 \qquad (52)$$

$$x_m x_{m+1} + A'x_{m+1} + B'x_m + G' = 0 \qquad (53)$$

Where the constants are defined by

$$A = x_d/R - \alpha(R+1)/R(\alpha-1) \tag{54a}$$

$$B = 1/(\alpha-1) \tag{54b}$$

$$G = x_d/R(\alpha - 1) \tag{54c}$$

$$A' = 1/(\alpha - 1) \tag{55a}$$

$$B' = -Wx_w/(RD + qF) - \alpha(RD + qF - W)/(\alpha-1)(RD + QF) \tag{55b}$$

$$G' = - Wx_w/(RD + qF)(\alpha-1) \tag{55c}$$

Equations (52) and (53) are Riccati difference equations with constant coefficients. The solutions are presented in Part III of the Appendix, and the solution of similar equations for gas absorption have been obtained in Chapter IV. The procedure consists in making the substitution $x_n = 1/u_n + k$ where k is a root of the following equation

$$k^2 - (A + B)\,k + R = 0 \tag{56}$$

Then Equation (52) can be reduced to

$$u_{n+1} + \Big[(A - k)/(B - k)\Big]\,u_n = 1/(B - k) \tag{57}$$

The general solution of (57) is

$$u_n = C\,\Big[(k - A)/(B - k)\Big]^n + 1/(A + B - 2k) \tag{58}$$

Replacing u_n by $1/(x_n + k)$ and solving for C subject to $x_o = x_d$ gives

$$1/(x_n-k) = \Big[1/(x_d-k) - 1/(A+B-2k)\Big]\,\Big[(k-A)/(B-k)\Big]^n + 1/(A+B-2k) \tag{59}$$

To obtain the total number, N, of plates in the enriching section x_n is placed equal to x_f and $n = N$, then

$$N = \frac{1}{\log(k-A)/(B-k)} \log \frac{1/(x_f-k) - 1/(A+B-2k)}{1/(x_d-k) - 1/(A+B-2k)} \qquad (60)$$

For the exhausting section the total number of units, M, is given by an expression identical with (60) except that k, A, and B are replaced by k', A', and B' and x_d is replaced by x_w. As the feed plate is counted twice, the total theoretical plates in the column is given by

$$\text{theoretical plates} = N + M - 1 \qquad (61)$$

Graphical Solution with Constant Relative Volatility. Equation (57) serves as the basis of a simple graphical solution of the binary fractionation equations with constant relative volatility. If u_n and u_{n+1} are replaced in terms of x_n, (59) becomes

$$\frac{1}{x_{n+1}-k} + \left[(A-k)/(B+k)\right] \frac{1}{x_n-k} = 1/(B-k) \qquad (62)$$

The graphical solution of this equation falls under case C of Part IV of the Appendix. A plot of $1/(x_{n+1} - k)$ vs $1/(x_n - k)$ gives a straight line with slope (A-k)/(B+k) and intercept 1/(B-k) as indicated in Figure 3. Knowing the initial composition x_d, the point $1/(x_1-k)$ can be located on the operating line. Proceeding from $1/(x_1-k)$ horizontally to the 45° line and then vertically to the operating line

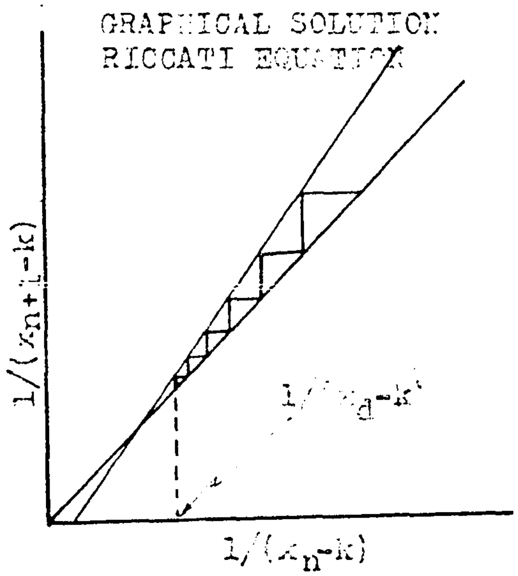


Figure 3

the point $1/(x_2-k)$ is located. This procedure can be continued until the value at the feed plate is located. A similar procedure can be employed to determine the number of theoretical plates in the exhausting section. This method has the particular advantage that only straight lines need be plotted for determining the number of theoretical plates.

Multicomponent Fractionation[19,37,48,56,75,92]

Both rigorous stepwise and approximate analytical and graphical methods are available for determining the number of theoretical plates in the fractionation of multicomponent mixtures. Up to the present time, no exact analytical solutions have been developed except for infinite reflux ratio. In the following sections a discussion of equilibria in multicomponent systems will be followed by graphical and analytical methods for determination of the number of theoretical plates.

Equilibria in Multicomponent Systems.[22,75] If the relative volatilities are constant, it is possible to obtain analytical relationships between the vapor and liquid concentrations. If x_i and y_i are the liquid-vapor concentrations of the ith component of an s component system and α_{ij} is the relative volatility of the ith component with respect to the jth component, then by definition of the relative volatility

$$\alpha_{ij} = y_i (1-x_j)/x_i(1-y_j) \tag{63}$$

From the definition in (63) it is apparent that $\alpha_{ik} = \alpha_{ij} \alpha_{jk}$. If the first component is the most volatile, and the volatility decreases with increasing subscript i, the relative volatility of the ith component with respect to the first component becomes

$$\alpha_{1i} = y_1(1-x_i)/x_1(1-y_i) \tag{64}$$

There are (s-1) equations of the form of (64) forming a set of simultaneous equations involving the variables x_1, x_2,... x_s and y_1, y_2 ...y_s. Solution for y_i in terms of the liquid concentrations from the (s-1) equations involved in (64) gives

$$y_i = \alpha_{is}x_i/\sum_1^s \alpha_{is}x_i \tag{65}$$

where Σ indicates a summation on i between unity and s. For the intermediate component of a three component system, (65) becomes

$$y_2 = \alpha_{23}x_2/(\alpha_{13}\, x_1 + \alpha_{23}x_2 + x_3) \tag{66}$$

Material and Heat Balances in Multicomponent Systems. The material and heat balances which arise in multicomponent fractionation are identical with the equations presented for binary fractionation. Assuming constant molal overflow, a combined material and heat balance for the ith component yields

$$y_{i,n+1} = \frac{R}{R+1} x_{i,n} + x_{i,d}/(R+1) \qquad (67)$$

$$y_{i,m} = \left[\frac{RD + qF}{RD + qF-W}\right] x_{i,m+1} - Wx_w/(RD + qF - W) \qquad (68)$$

where the first subscript refers to the particular component and the second subscript refers to the plate number. There are s equations of the form (67) and also of form (68). These actually constitute a set of simultaneous difference equations. If the vapor concentration is eliminated from (67), a typical equation without the vapor concentrations for the ith component results

$$\alpha_{is}\, x_{i,n+1}/\sum_{1}^{s} \alpha_{is}\, x_{i,n+1} = \frac{R}{R+1} x_{i,n} + x_{i,d}/(R + 1) \qquad (69)$$

Infinite Reflux Ratio.[31] If R is infinite, (69) reduces to

$$\alpha_{is} x_{i,n+1}/\sum_{1}^{s} \alpha_{is}\, x_{i,n+1} = x_{i,n} \qquad (70)$$

and for the jth component

$$\alpha_{js}\, x_{j,n+1}/\sum_{1}^{s} \alpha_{js} x_{n,n+1} = x_{j,n} \qquad (71)$$

Dividing (70) by (71) gives

$$\alpha_{ij} x_{i,n+1}/x_{j,n+1} = x_{i,n}/x_{j,n} \qquad (72)$$

Equation (72) is linear in $x_{i,n}/x_{j,n}$ and can be rearranged into standard form

$$\frac{x_{i,n+1}}{x_{j,n+1}} - \frac{1}{\alpha_{ij}}\frac{x_{i,n}}{x_{j,n}} = 0 \tag{73}$$

The solution of this equation is

$$x_{i,n}/x_{j,n} = (x_{i,d}/x_{j,d})(1/\alpha_{ij})^n \tag{74}$$

Solution for N, subject to $x_{i,N}/x_{j,N}=x_{i,w}/x_{j,w}$ gives

$$N = \frac{1}{\log \alpha_{ij}} \log \frac{x_{i,d}x_{j,w}}{x_{j,d}x_{i,w}} \tag{75}$$

There are (s-1) independent equations of the form of (74). If i is taken with reference to the most volatile component, it is possible to solve for the individual liquid concentrations in terms of the plate number and product compositions. Treating the (s-1) equations of the form of (74) as simultaneous equations in the liquid concentration variables, there results

$$x_{i,n} = x_{i,d}(\alpha_{1i})^n \Big/ \sum_1^s x_{i,d}(\alpha_{1i})^n \tag{76}$$

For a three component system, (76) takes the forms

$$x_{1,n} = x_{1,d}/(x_{1,d} + x_{2,d}\,\alpha_{12}^n + x_{3,d}\alpha_{13}^n) \tag{77a}$$

$$x_{2,n} = x_{2,d}\alpha_{12}^n/(x_{1,d} + x_{2,d}\alpha_{12}^n + x_{3,d}\alpha_{13}^n) \tag{77b}$$

$$x_{3,n} = x_{3,d}\alpha_{13}^{n} / (x_{1,d} + x_{2,d}\alpha_{12}^{n} + x_{3,d}\alpha_{13}^{n}) \qquad (77c)$$

With Equations (75) and (76) it is possible to predict either the total number of plates for infinite reflux ratio or the theoretical plate to plate compositions.

Graphical Solution of Multicomponent Equations.[44] With the help of the equations just developed for infinite reflux ratio, it is possible to develop a graphical procedure for determining the number of plates in multicomponent rectification. If the vapor liquid equilibria for any component is known, the stepwise McCabe - Thiele procedure for obtaining theoretical plates can be used. In the following section, an approximate graphical method for determining the number of plates will be developed.

For binary systems there is but a single equilibrium curve for each pressure. Hence, the vapor concentration is a single valued function of the corresponding liquid concentration. However for multicomponent systems, specifying a value of a liquid concentration x_1 does not in itself uniquely determine the vapor concentration y_1. There must be (s-1) liquid concentrations known at constant pressure in order that the vapor concentrations be definitely fixed. Thus it is possible to have different values of y_1 in equilibrium with liquid having a constant value of x_1.

In the fractionation of multicomponent systems under fixed conditions in plate towers, there are a series of equilibrium curves for the various components, i.e., plots of $y_{i,n}$ vs $x_{i,n}$. Physically these equilibrium "curves" are but a series of points as no values of x_i and y_i can exist for other than integral values of n. However for interpretative purposes, it is of value to draw a smooth curve through the points. The $x_{i,n} - y_{i,n}$ curves are affected by boundary concentrations, relative volatilities, and the reflux ratio. For a given system and a given set of exit concentrations, there are an infinite number of equilibrium paths or curves to be followed on the equilibrium surface depending on the reflux ratio. It is a matter of speculation as to the extent of variation in the equilibrium curves due to the reflux ratio, relative volatilities, and boundary concentrations. One of the objects of this section is the determination of the effect of these parameters on the equilibrium paths taken. It will be shown that for some three component systems the reflux ratio does not appreciably affect the equilibrium paths of certain components while for other systems, the actual equilibrium curve for any reflux ratio may be approximated.

To determine the equilibrium paths, recourse to platewise calculations is possible. If the relative volatilities are constant, considerable simplification in the calculations can be made. Underwood[92] derived expressions with which it is possible to make plate to plate calculations without resort to a trial and error process.

Treating Equation (69) as a set of simultaneous equations in $x_{i,n+1}$, it is possible to derive expressions relating the concentration $x_{i,n+1}$ to the concentrations $x_{1,n}$ $x_{2,n}$, ... For the enriching section

$$x_{i,n+1} = \frac{\alpha_{1i}(Rx_{i,n} + x_{i,d})}{\Sigma\alpha_{1i}(Rx_{i,n} + x_{i,d})} \qquad (78)$$

In the stripping section the equations become

$$x_{i,m+1} = \frac{(R + qF - W)\alpha_{is}x_{i,m}}{(R + qF)\Sigma\alpha_{is}x_{i,m}} + \frac{Wx_{i,W}}{R + qF} \qquad (79)$$

These equations are in a form most convenient for making calculations starting at either the top or the bottom of the tower. With Equations (78) and (79), it is possible to determine the path of the vapor liquid equilibria as affected by the various parameters.

<u>Three Component Systems.</u> For the most volatile component of a three component system, Equations (64) and (78) become

$$y_1 = \frac{\alpha_{13}x_1}{\alpha_{13}x_1 + \alpha_{23}x_2 + x_3} \qquad (80)$$

$$x_{1,n+1} = \frac{Rx_{1,n} + x_{1,d}}{R(x_{1,n} + \alpha_{12}x_{2,n} + \alpha_{13}x_{3,n}) + (x_{1,d} + \alpha_{12}x_{2,d} + \alpha_{13}x_{3,d})} \qquad (81)$$

On the basis of these equations and similar equations for the other components, preliminary calculations were made for a hypothetical system to obtain information as to the variation of the equilibrium curve with reflux ratio. Assuming product concentrations at the top for a system in which all relative volatilities were constant stepwise calculations were made down the tower for various reflux ratios. The computations were continued into the region near minimum concentration for the enriching section only. The first system considered was one in which $\alpha_{12} = 2$, $\alpha_{13} = 4$, $x_{1,d} = 0.90$, $x_{2,d} = x_{3,d} = 0.05$. In Figure 4, a partial summary of the results is indicated in the form of plots of liquid concentration of the most volatile component vs plate number for reflux ratios varying from 0.5 to infinity. Similar curves for the vapor concentration are not shown. While these curves vary widely, the data may be correlated in the form of vapor vs liquid concentration plots. In Figure 5 the x - y plots for the least and most volatile components are shown. The data for these components correlate into apparently smooth curves; but as illustrated in Figure 6, the vapor liquid paths for the intermediate component consist of a series of distinctly different curves. As the variations from the mean curves are slight for the first and third components, these curves may be used as a basis for approximate yet accurate graphical McCabe - Thiele calculations. If the equilibrium data for this system were

MOL FRACTION IN LIQUID OF MOST VOLATILE COMPONENT
VS.
PLATE NUMBER

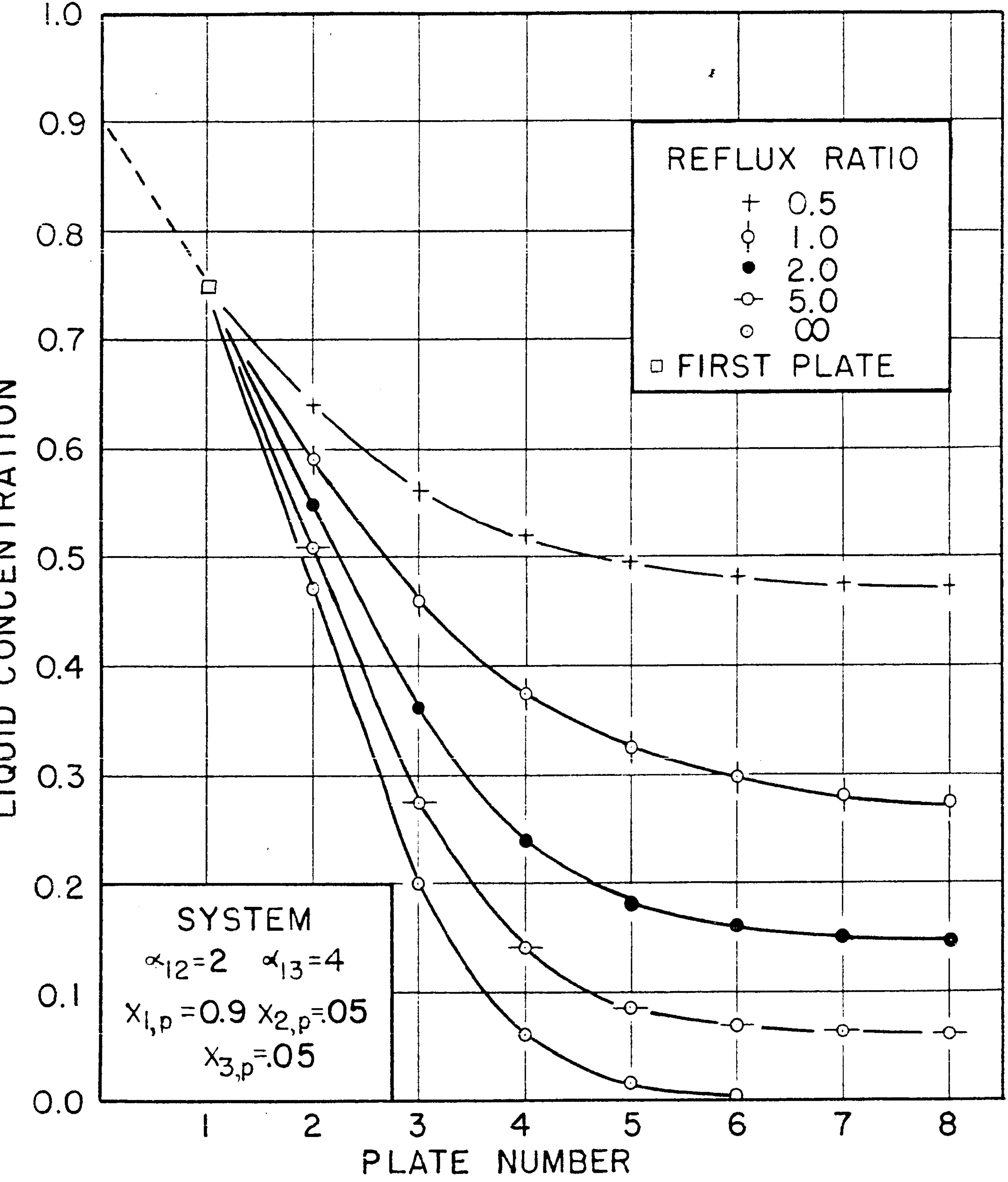


Figure 4

EQUILIBRIUM DIAGRAMS FOR MOST AND LEAST VOLATILE COMPONE

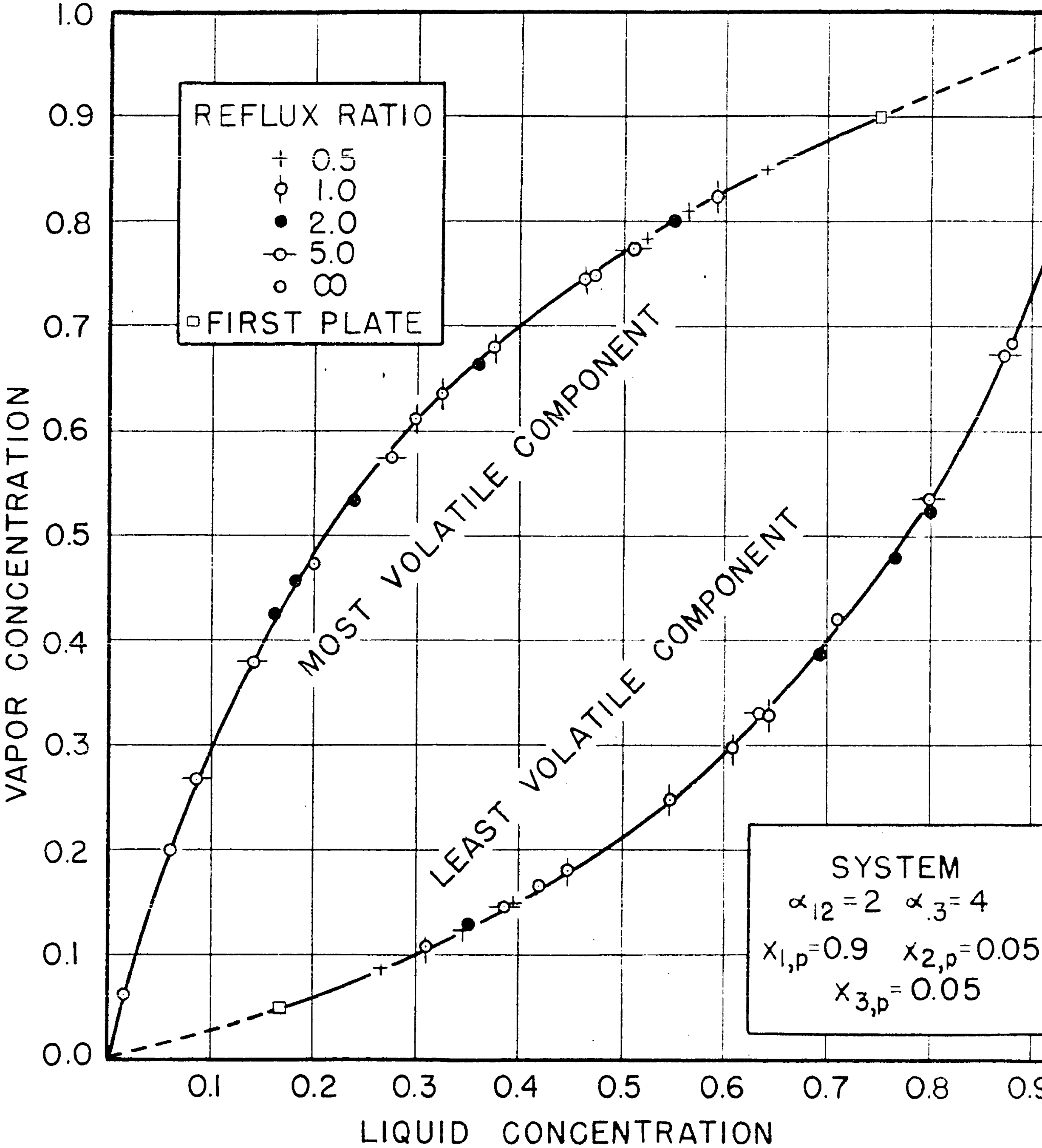


Figure 5

EQUILIBRIUM DIAGRAMS FOR MOST AND LEAST VOLATILE COMPONENTS

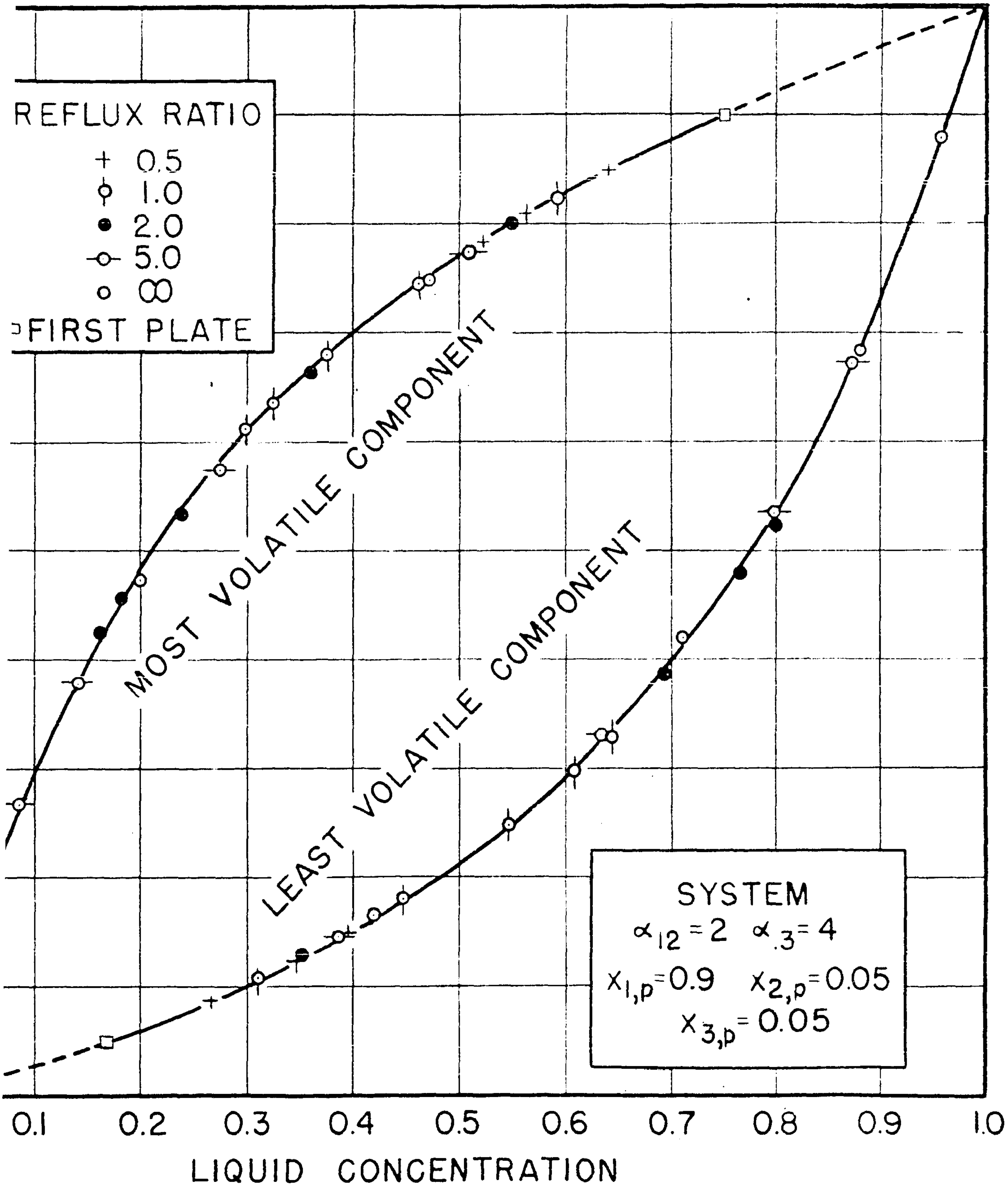


Figure 5

EQUILIBRIUM DIAGRAM FOR INTERMEDIATE COMPONENT

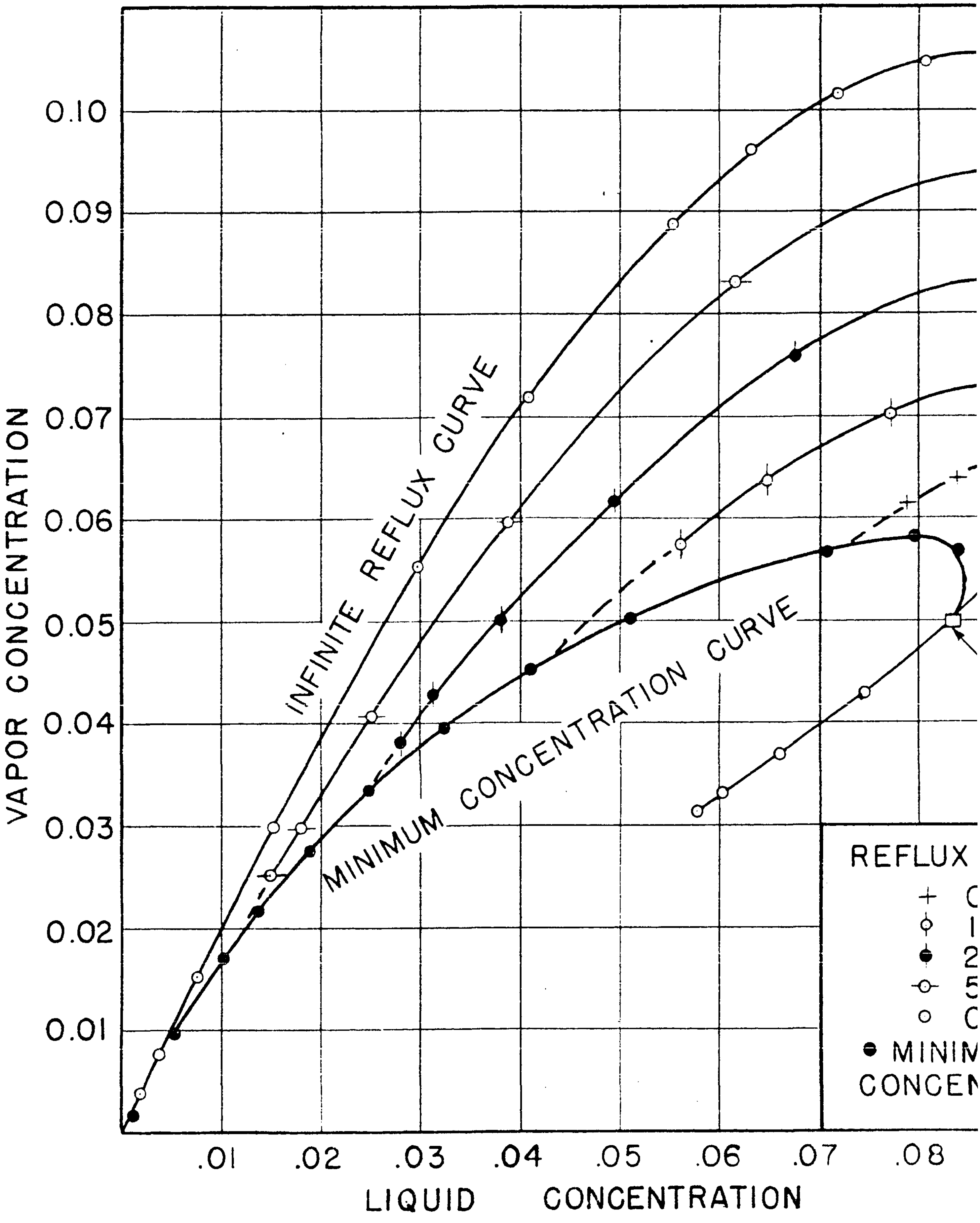


Figure 6

EQUILIBRIUM DIAGRAM FOR INTERMEDIATE COMPONENT

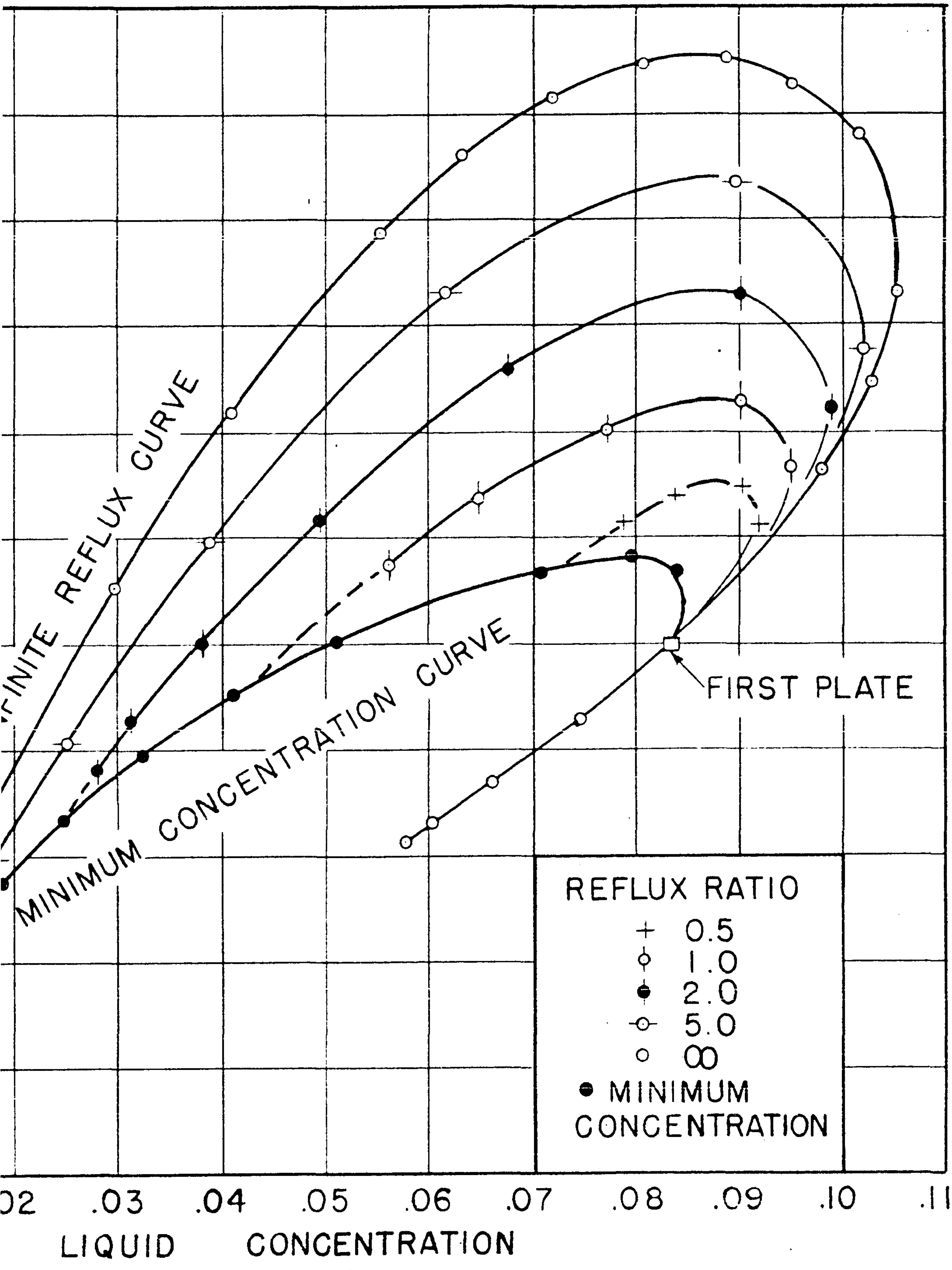


Figure 6

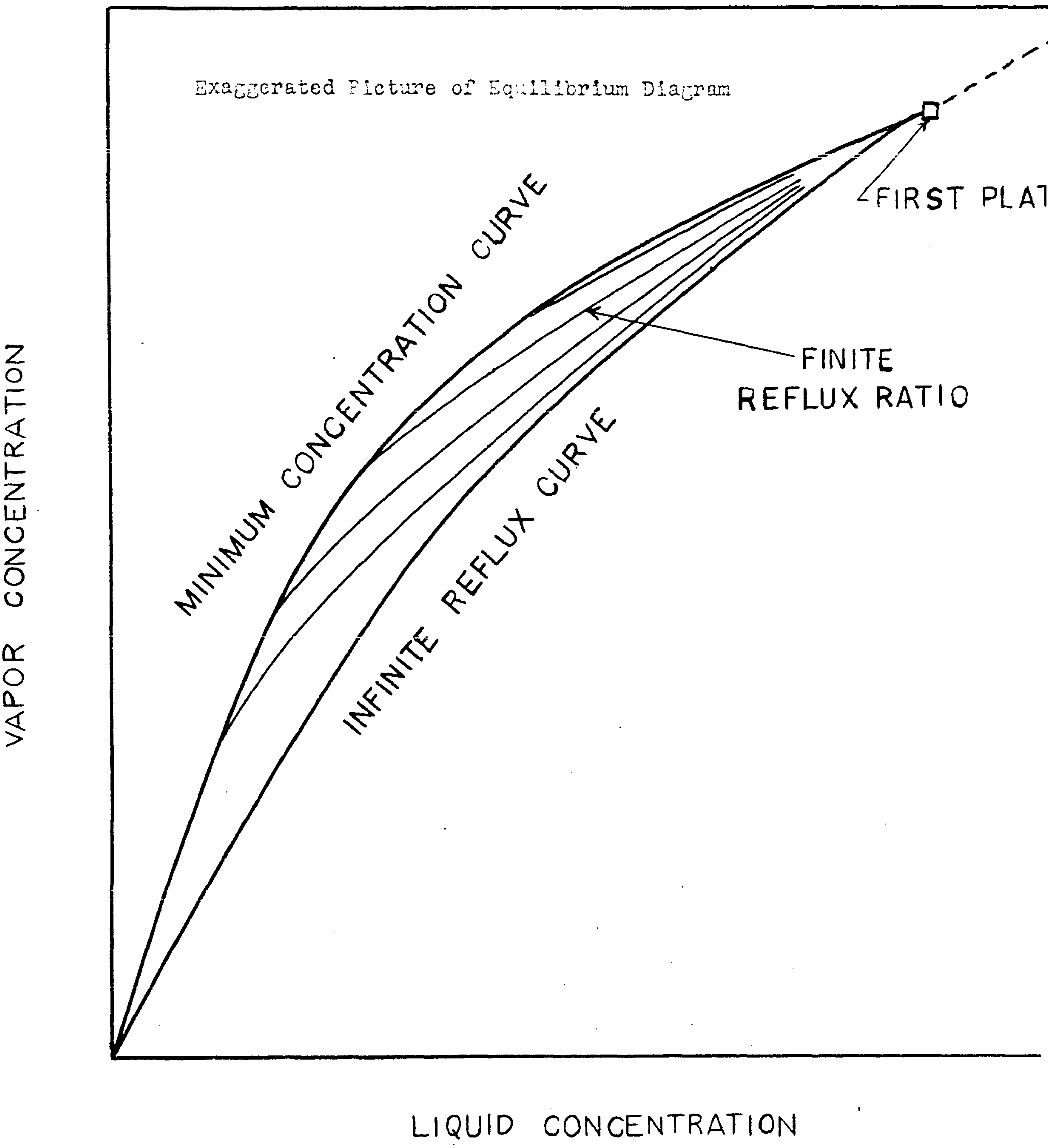
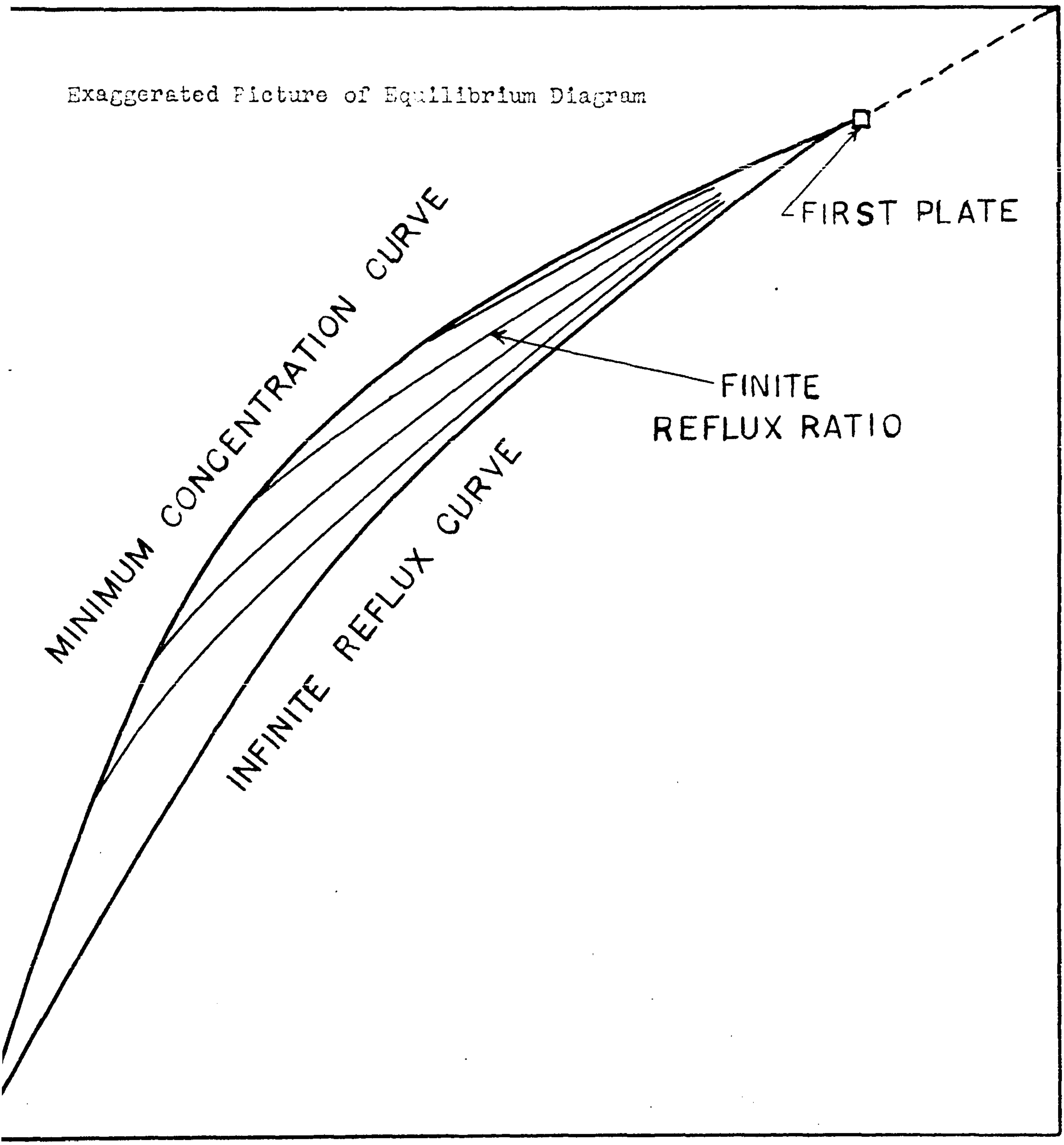

Exaggerated Picture of Equilibrium Diagram
MINIMUM CONCENTRATION CURVE
FIRST PLAT
FINITE REFLUX RATIO
INFINITE REFLUX CURVE
VAPOR CONCENTRATION
LIQUID CONCENTRATION

Figure 7



LIQUID CONCENTRATION

Figure 7

obtained for a single reflux ratio, the resulting x - y plot would be sufficiently close to the true equilibrium curve to permit accurate determination of the number of plates.

For systems that can be treated in this manner, it is desirable to discover an easy method for obtaining the equilibrium curve and to know what the maximum variation is. In Figure 7 an exaggerated picture of the equilibria for the most volatile component is shown. For each reflux ratio, the equilibrium curves approach a limit which represents the minimum concentration obtainable with the given reflux ratio. This point represents the intersection of the operating line and the equilibrium surface. The locus of the points of minimum concentration will be called the "minimum concentration curve." This curve passes through the terminal points of the equilibrium curves for each reflux ratio, and represents the boundary, above which no equilibrium curve will lie. The curve for infinite reflux ratio forms the lower boundary of these same curves. Thus if the equations for these limiting curves are obtained, it is possible to predict the maximum variation in the x - y curves.

In the following paragraphs, equations will be derived for predicting the maximum variation of the equilibrium curves with reflux ratio. The results obtained will apply quantitatively only for systems having constant relative volatilities. However, it should not be construed that the method proposed is more exact for systems in which all relative volatilities are constant than for systems in which the relative volatilities are not constant. Comparison of ideal and non-ideal systems can only be obtained by examining actual calculations. Systems having constant relative volatilities are chosen because analytical expressions may be obtained for the desired curves.

Minimum Concentration Curve. For a given reflux ratio the intersection of the operating line of Equation (81) and the equilibrium surface of Equation (80) represents the point of minimum concentration. To obtain the intersection for a three component system, equate the vapor concentrations in Equations (80) and (81) as follows

$$\frac{\alpha_{13} x_1}{\alpha_{13} x_1 + \alpha_{23} x_2 + x_3} = \frac{Rx_1 + x_{1,d}}{R + 1} \tag{82}$$

$$\frac{\alpha_{23} x_2}{\alpha_{13} x_1 + \alpha_{23} x_2 + x_3} = \frac{Rx_2 + x_{2,d}}{R + 1} \tag{83}$$

$$\frac{x_3}{\alpha_{13} x_1 + \alpha_{23} x_2 + x_3} = \frac{Rx_3 + x_{3,d}}{R + 1} \tag{84}$$

Subscripts representing plate numbers are dropped as unnecessary in the region of minimum concentration, i.e., $x_n = x_{n+1}$ as n approaches infinity. Dividing Equation (82) by Equations (83) and (84) respectively yields

$$\alpha_{12}\frac{x_1}{x_2} = \frac{Rx_1 + x_{1,d}}{Rx_2 + x_{2,d}} \tag{85}$$

$$\alpha_{13}\frac{x_1}{x_3} = \frac{Rx_1 + x_{1,d}}{Rx_3 + x_{3,d}} \tag{86}$$

Elimination of the parameter R between these two equations gives

$$\frac{\alpha_{12}(\alpha_{13} - 1)}{\alpha_{13} - \alpha_{12}}\left[\frac{x_{2,d}}{x_{1,d}}\right]\left[\frac{x_1}{x_2}\right] = \frac{\alpha_{13}(\alpha_{12} - 1)}{\alpha_{13} - \alpha_{12}}\left[\frac{x_{3,d}}{x_{1,d}}\right]\left[\frac{x_1}{x_3}\right] + 1 \tag{87}$$

Defining the coefficients of x_1/x_2 and x_1/x_3 as A and B leads to

$$A\ x_1/x_2 = B\ x_1/x_3 + 1 \tag{88}$$

If x_2 is eliminated by means of $x_1 + x_2 + x_3 = 1$, an expression results in which x_3 can be obtained as a function of x_1 and the various parameters. Rearranging terms after elimination of x_2 leads to the quadratic expression

$$x_3^{\,2} + \left[(1 + A + B)x_1 - 1\right] x_3 - B(x_1 - x_1^{\,2}) = 0 \tag{89}$$

Solving for x_3 yields

$$2x_3 = 1 - (1 + A + B)x_1 - \sqrt{\left[(1 + A + B)x_1 - 1\right]^2 + 4B(x_1 - x_1^{\,2})} \tag{90}$$

The plus sign is chosen because x_3 approaches unity as x_1

approaches zero. An analogous procedure produces a similar expression for x_2

$$2x_2 = 1 - (1 - A - B)x_1 - \sqrt{\left[(1 - A - B)x_1 - 1\right]^2 - 4A(x_1 - x_1^{\,2})} \tag{91}$$

It is easy to demonstrate that the two quantities under the square root signs in Equations (90) and (91) are equal. To obtain y_1 as a function of x_1 alone, the values of x_2 and x_3 from Equations (90) and (91) may be substituted in Equation (82) to give

$$y_1 = \frac{\alpha_{13}\, x_1}{2\left[\alpha_{13}/2 - \alpha_{23} - 1 + (\alpha_{12} - 1)(A + B)\right] x_1 - (\alpha_{23} - 1)C} \tag{92}$$

where

$$A = \frac{(\alpha_{13} - 1)}{(\alpha_{23} - 1)}\left[\frac{x_{2,d}}{x_{1,d}}\right] \qquad B = \frac{\alpha_{13}(\alpha_{12} - 1)}{(\alpha_{13} - \alpha_{23})}\left[\frac{x_{3,d}}{x_{1,d}}\right]$$

$$C^2 = \left[(1 + A + B)x_1 - 1\right]^2 + 4B(x_1 - x_1^2) = \left[(1 - A - B)x_1 - 1\right]^2 - 4A(x_1 - x_1^2)$$

<u>Infinite Reflux Ratio Curve</u>. The x components of the equilibrium curves at infinite reflux ratio can be obtained from Equations (77) as a function of the plate number. When R is infinite the material balance equations become

$$y_{1,n+1} = x_{1,n} \tag{93a}$$

$$y_{2,n+1} = x_{2,n} \tag{93b}$$

$$y_{3,n+1} = x_{3,n} \tag{93c}$$

With these equations or with Equations (65), (66), and (80) the vapor concentrations can be obtained for infinite reflux ratio, and the equilibrium curves can be obtained.

Deviations in Equilibrium Curves. With the equations that have been developed, it is possible to determine the maximum variation in the equilibrium curves. To do this, x - y data for the minimum concentration curve as calculated from Equation (92) will be compared graphically with the corresponding data for the infinite reflux curve as determined from Equations (77) and (93). The decrease in concentration per plate at infinite reflux ratio may be rather large in certain concentration regions, and in such cases the points will be spaced rather far apart. To increase the number of points for plotting the infinite reflux curve, fractional values of n will be used. Use of fractional plates does not imply that concentrations exist for other than integral plate numbers; it is simply a practical expedient for aiding in plotting the infinite reflux curve. In Figure 8 the calculated data for three systems are shown. In each system the exit concentrations are : $x_{1,d} = 0.90$, $x_{2,d} = x_{3,d} = 0.05$. The relative volatilities for the three systems are respectively: for A, $\alpha_{12} = 4$, $\alpha_{13} = 20$; for B, $\alpha_{12} = 2$, $\alpha_{13} = 4$; and for C, $\alpha_{12} = 1.25$, $\alpha_{13} = 1.75$. The curves marked A1, B1, and C1 refer to the most volatile component, and the curves marked A3, B3, and C3 refer to the least volatile component. From these curves it is easy to

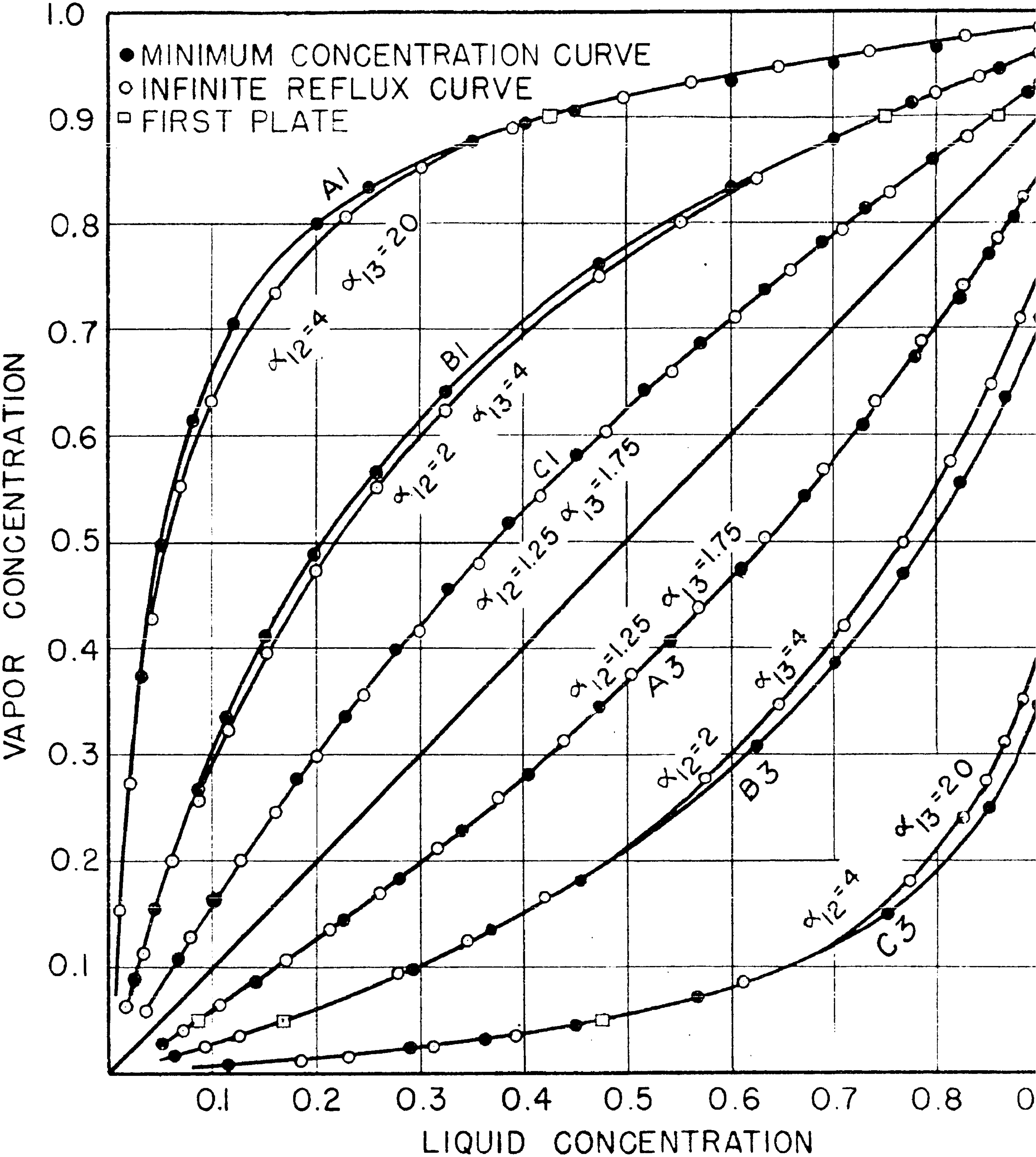

● MINIMUM CONCENTRATION CURVE
○ INFINITE REFLUX CURVE
□ FIRST PLATE
A1
α12=4
α13=20
B1
α12=2
α13=4
C1
α12=1.25
α13=1.75
α12=1.25
α13=1.75
A3
α12=2
α13=4
B3
α12=4
α13=20
C3
VAPOR CONCENTRATION
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
LIQUID CONCENTRATION

Figure 8

EQUILIBRIUM DIAGRAMS

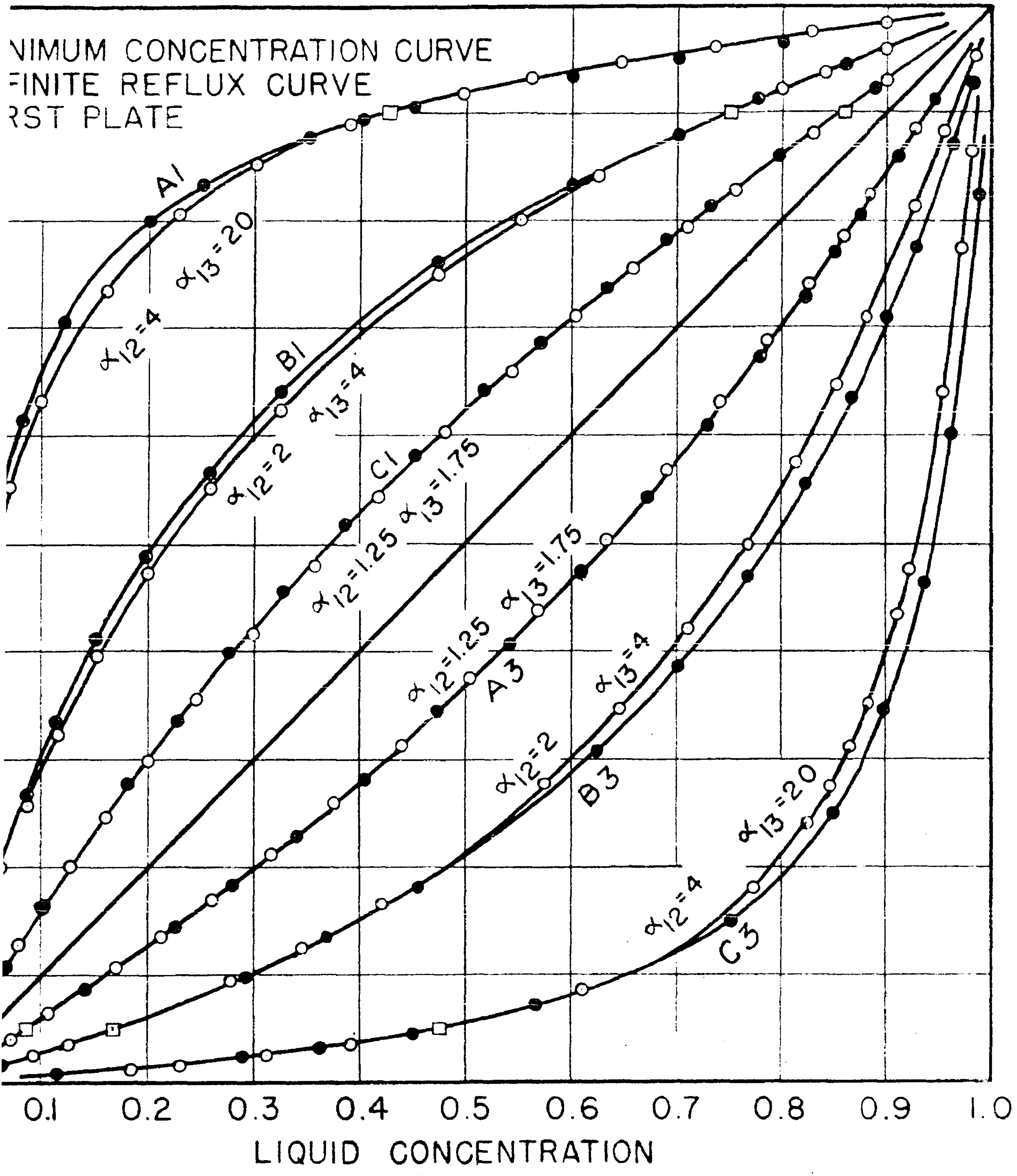


Figure 8

EQUILIBRIUM DIAGRAMS

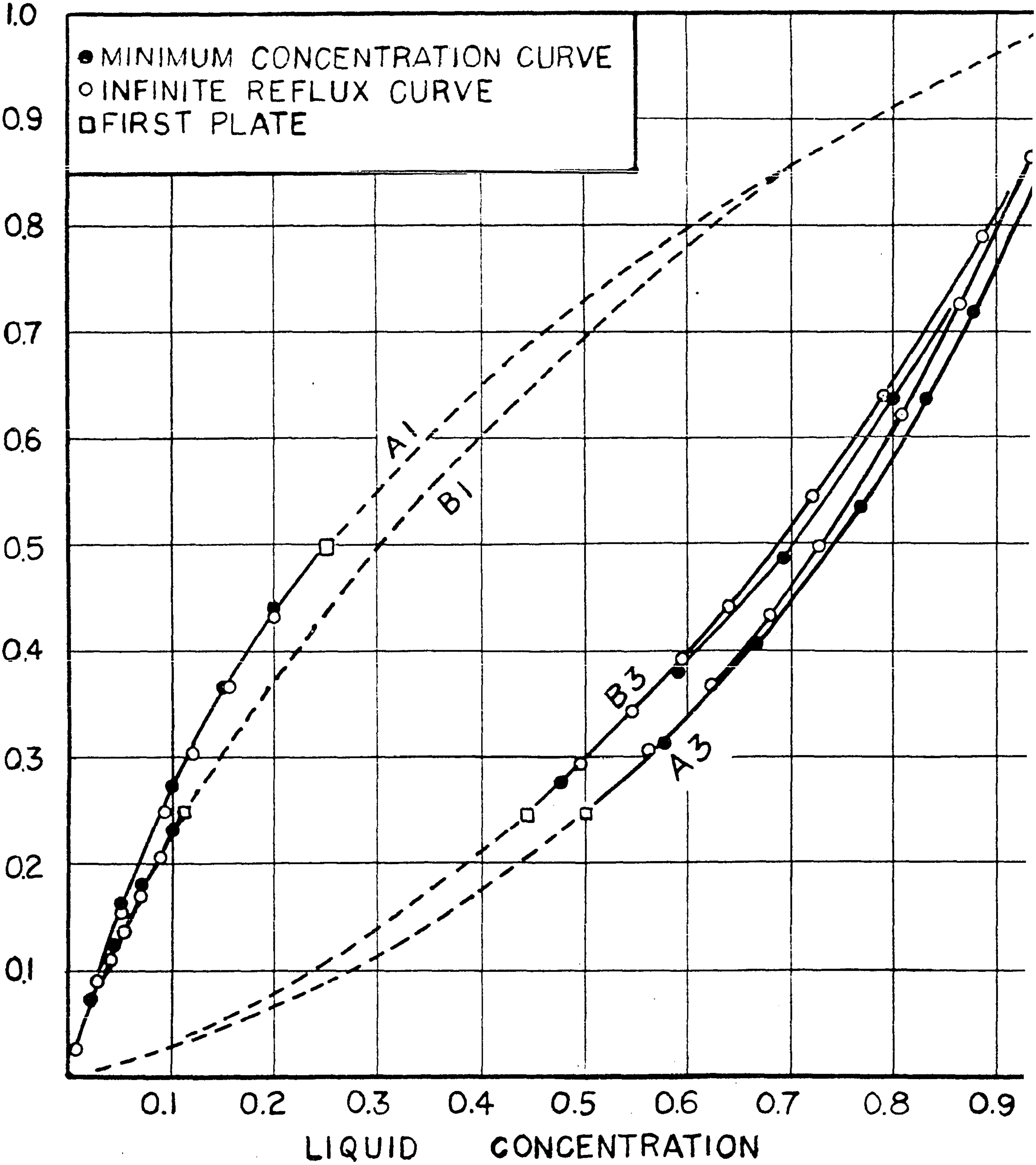


Figure 9

EQUILIBRIUM DIAGRAMS

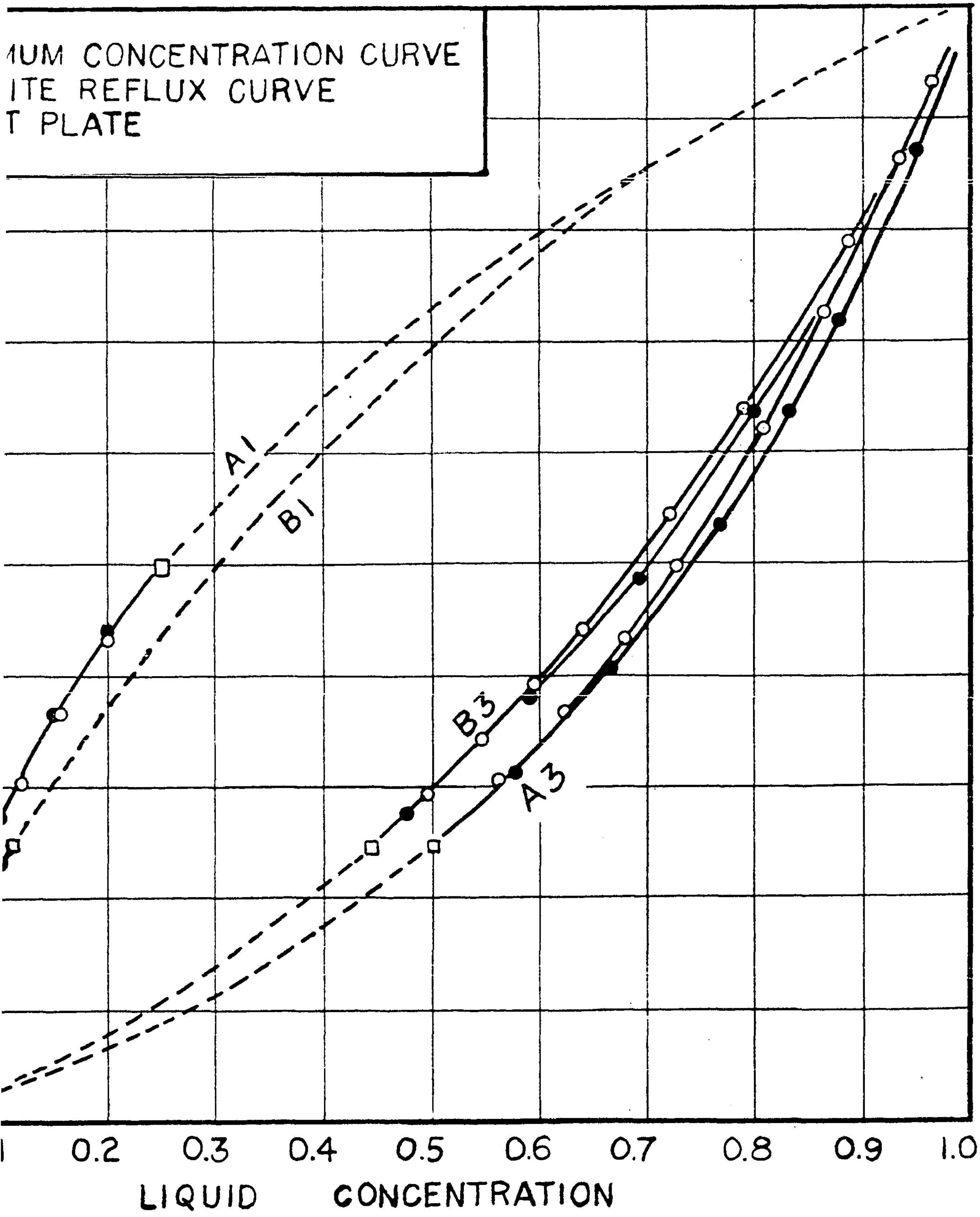


Figure 9

see that there is but little variation in the equilibrium curves. The maximum percentage deviation determined as the difference in y for the two curves divided by the average y is in the neighborhood of 4% for the most volatile component. While the deviations in the dilute region for the least volatile component are not large, the percentage deviation greatly increases in the more concentrated region near the point (1,1). However this region, in which the greatest variation occurs, will usually be in the exhausting section, and a different minimum concentration curve would be in effect. Thus the difference in the two limiting curves for the least volatile component will be less than indicated in Figure 8 in the concentrated region. For these systems it would probably be best to use an equilibrium curve for the most volatile component for approximate McCabe-Thiele calculations.

The effect of the product compositions on the equilibrium curves is shown in Figure 9. The relative volatilities for these systems are $\alpha_{12} = 2$ and $\alpha_{13} = 4$. The product compositions for the two systems are: for A, $x_{1,d} = 0.50$; $x_{2,d} = x_{3,d} = 0.25$; and for B, $x_{1,d} = x_{3,d} = 0.25$, and $x_{2,d} = 0.50$. It is apparent from the curves that there is little variation between the minimum concentration and infinite reflux curves for these systems. In Figure 10, the variation in the equilibrium curves for the system:

EQUILIBRIUM DIAGRAMS

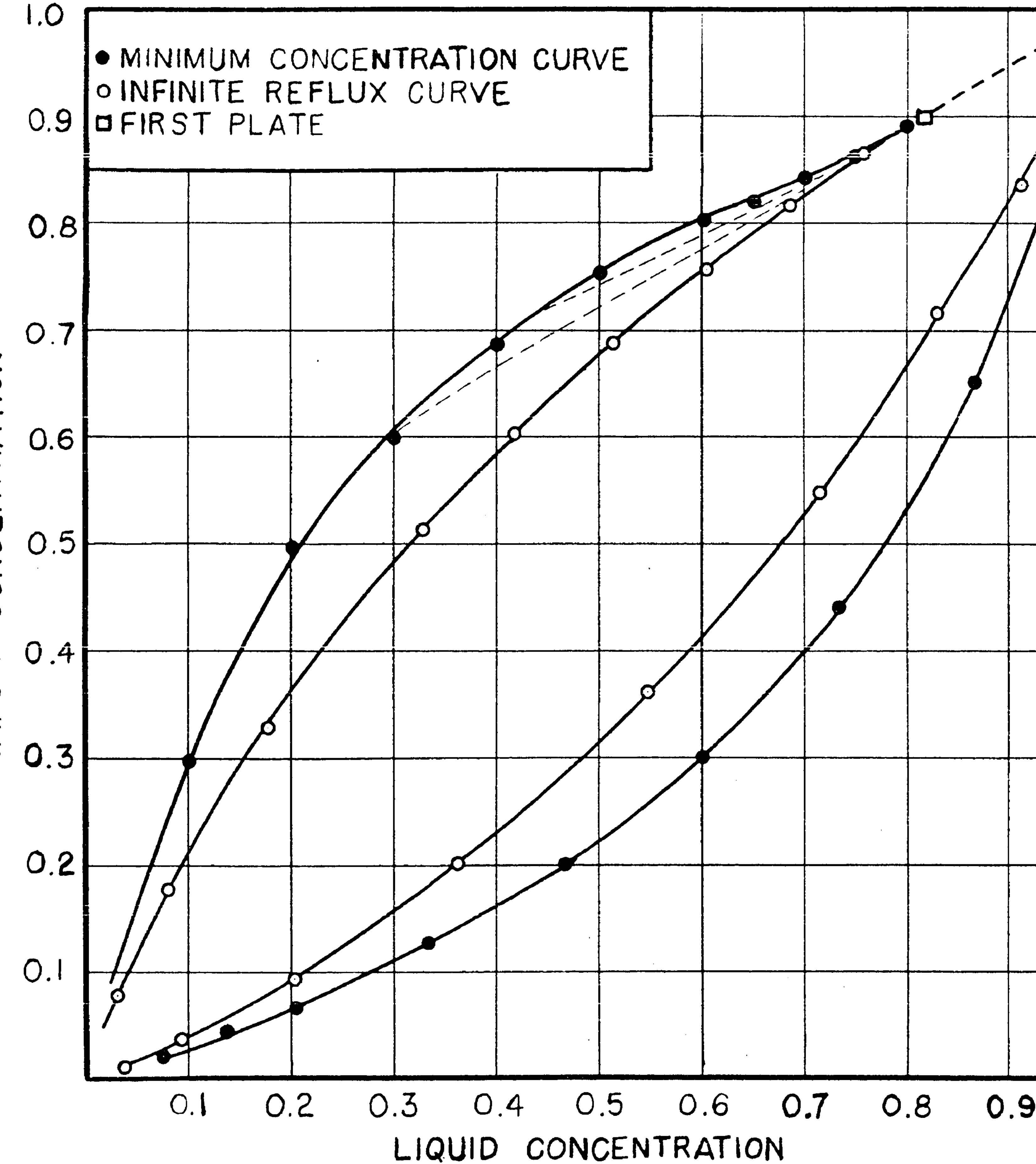


Figure 10

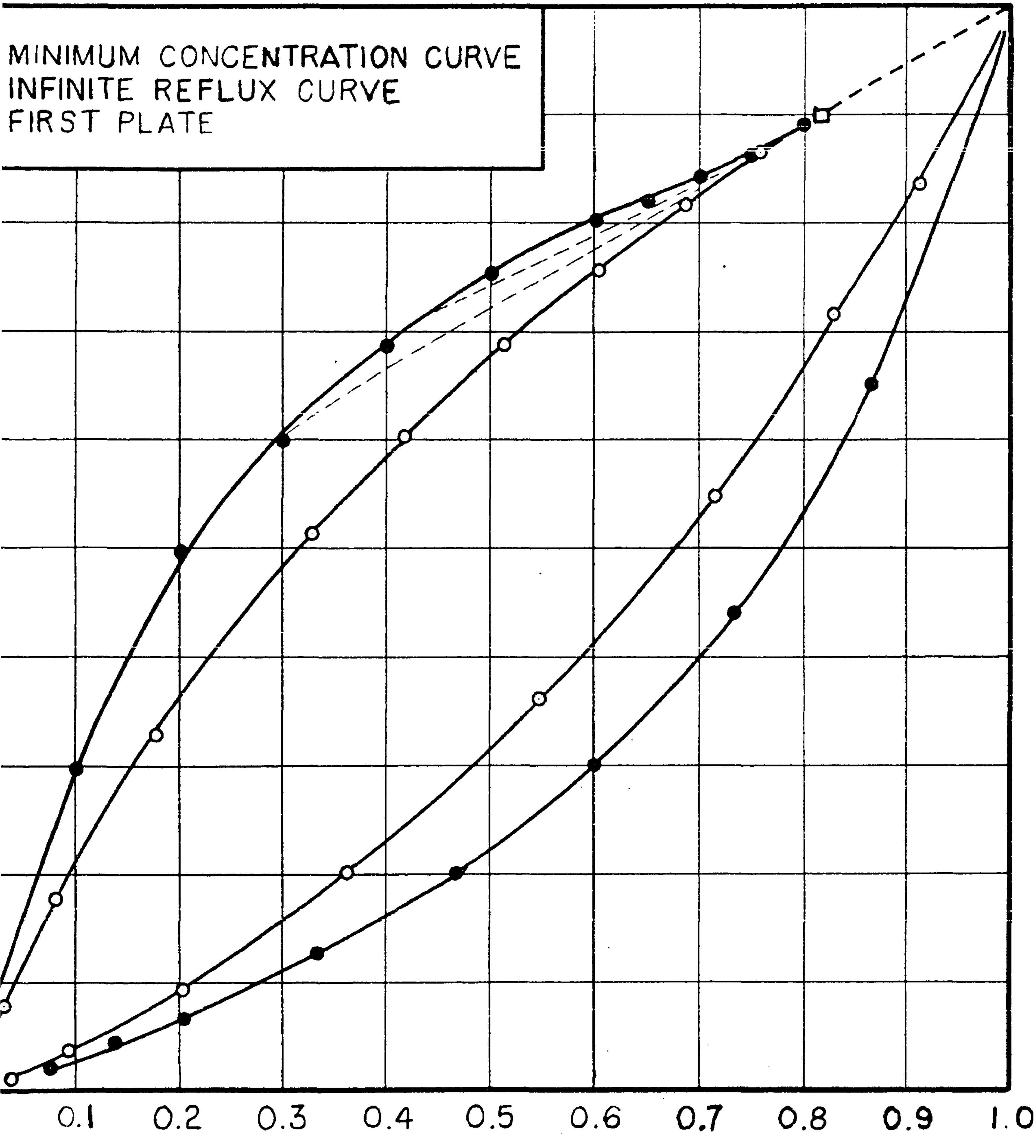

MINIMUM CONCENTRATION CURVE
INFINITE REFLUX CURVE
FIRST PLATE
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
LIQUID CONCENTRATION

Figure 10

$\alpha_{12} = 2$, $\alpha_{13} = 4$, $x_{1,d} = 0.90$, $x_{2,d} = 0.099$, and $x_{3,d} = 0.001$. The deviation in these curves is greater than for the previous systems. In the previous cases, the infinite reflux ratio curve could be used as the equilibrium curve for computation of the number of theoretical plates at any reflux ratio because of the small deviations between the minimum concentration and infinite reflux ratio curves. However, for the system shown in Figure 10, the deviations are too great to use either the minimum concentration or the infinite reflux ratio curve for any arbitrary reflux ratio. However, these limiting curves can be used as guides along with the operating line for drawing approximate equilibrium curves as indicated for two different reflux ratios.

The Stripping Section. The minimum concentration and infinite reflux curves may be determined for the stripping section in a similar manner to that employed in the enriching section. If the vapor concentrations as obtained from the operating line and the equilibrium curve are placed equal to each other for all three components and R + qF is eliminated, the following equation results

$$E\, x_1/x_2 = G\, x_1/x_3 + 1 \qquad (94)$$

where the coefficients E and G are defined as

$$E = \frac{\alpha_{13} - 1}{\alpha_{23} - 1}\left[\frac{x_{2,w}}{x_{1,w}}\right] \qquad G = \frac{\alpha_{13}(\alpha_{12} - 1)}{\alpha_{13} - \alpha_{12}}\left[\frac{x_{3,w}}{x_{1,w}}\right]$$

Thus Equation (94) is of the same form as Equation (14) for the enriching section. If x_2 or x_3 is eliminated from Equation (94), a quadratic expression results and the solution is analogous to those presented in Equations (90) and (91). The constants A and B are replaced by E and G respectively.

The infinite reflux ratio curves are identical for both enriching and exhausting sections.

System Benzene - Toluene - Xylene.[75] The results of the previous sections can be applied to systems in which the relative volatilities are not constant. There the minimum concentration curve is difficult to obtain, the infinite reflux ratio curve may still serve as an approximation of the equilibrium curve. When the relative volatilities are not constant, the infinite reflux ratio curve must be obtained by plate to plate calculations. For systems in which all the components are distributed between distillate and bottom, it makes no difference whether calculations are started at the top or at the bottom. The same infinite reflux curve serves as an approximation in the exhausting section as well as in the enriching section even though the minimum concentration curves differ in the two sections.

Robinson and Gilliland proposed the following problem: A mixture containing 60 mole per cent of xylene is to be fractionated into a product containing not over 0.5 mole per cent of benzene. The xylene is to drop to a negligible value in the overhead distillate, and the product will contain 99.5 mole per cent of benzene. A reflux ratio of 2 is used and the feed enters the column at its boiling point. On the basis of constant molal overflow, Raoult's law, and experimental equilibrium data, Robinson and Gilliland found by stepwise calculations that 16 theoretical plates were required.

For the same system plate to plate calculations similar to those of Robinson and Gilliland were made at infinite reflux ratio in order to obtain an approximate x - y curve. These calculations yielded only four points in the range of x between 0.1 and 0.8 for benzene, the most volatile component. To actually construct a curve through such few points is at best hazardous, and it is advantageous to be able to determine additional points on the curve in the uncertain ranges. Since some data are available, an accurate means of interpolating between the known points is desirable. While many interpolation formulas are available it was found that the following empirical formula is suitable for interpolation purposes

$$y = \frac{M x}{(M - 1)x - 1} \qquad (95)$$

or solving for M

$$M = \frac{y(1 - x)}{x(1 - y)} \qquad (96)$$

BENZENE - TOLUENE - XYLENE

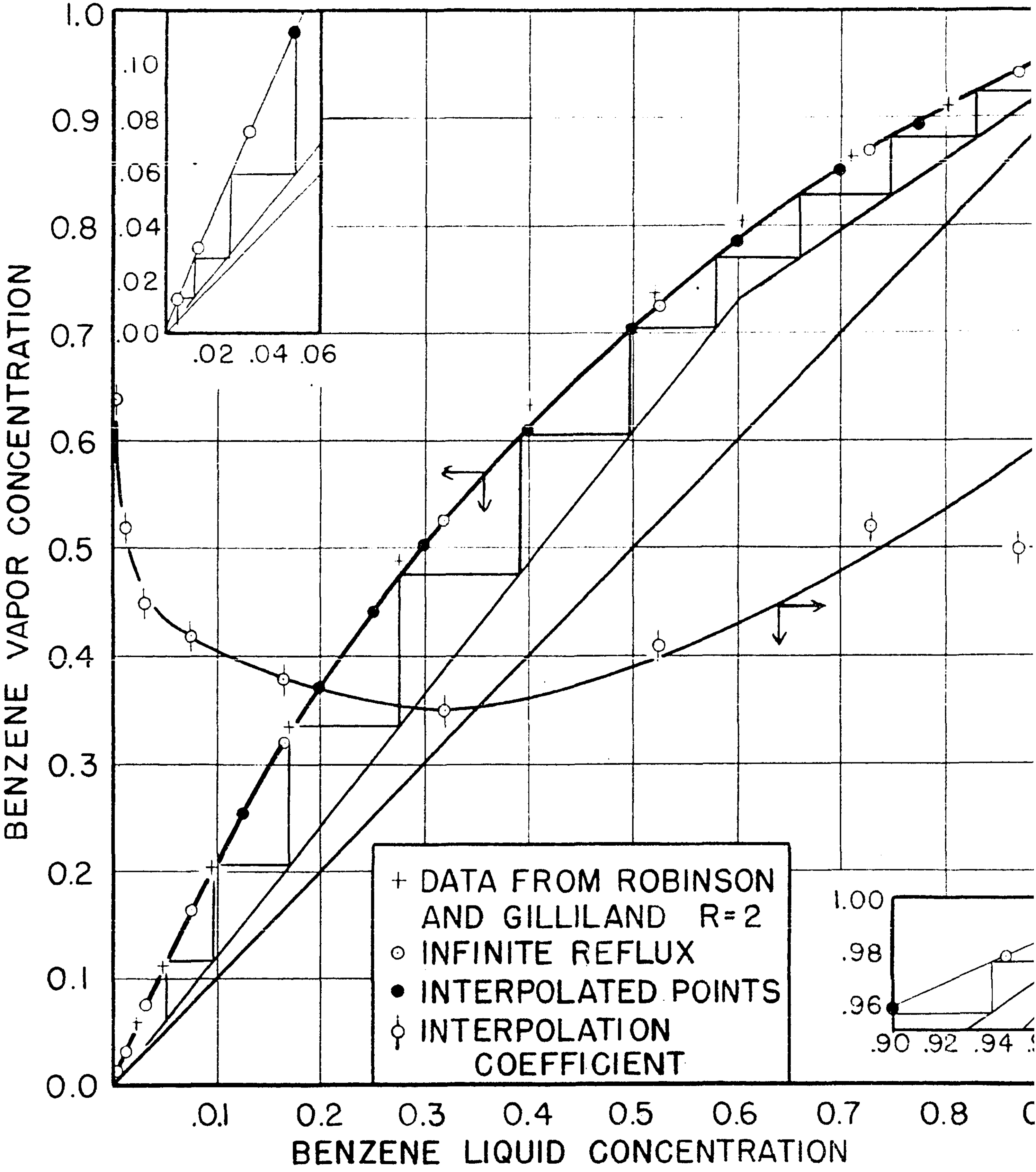


Figure 11

BENZENE - TOLUENE - XYLENE

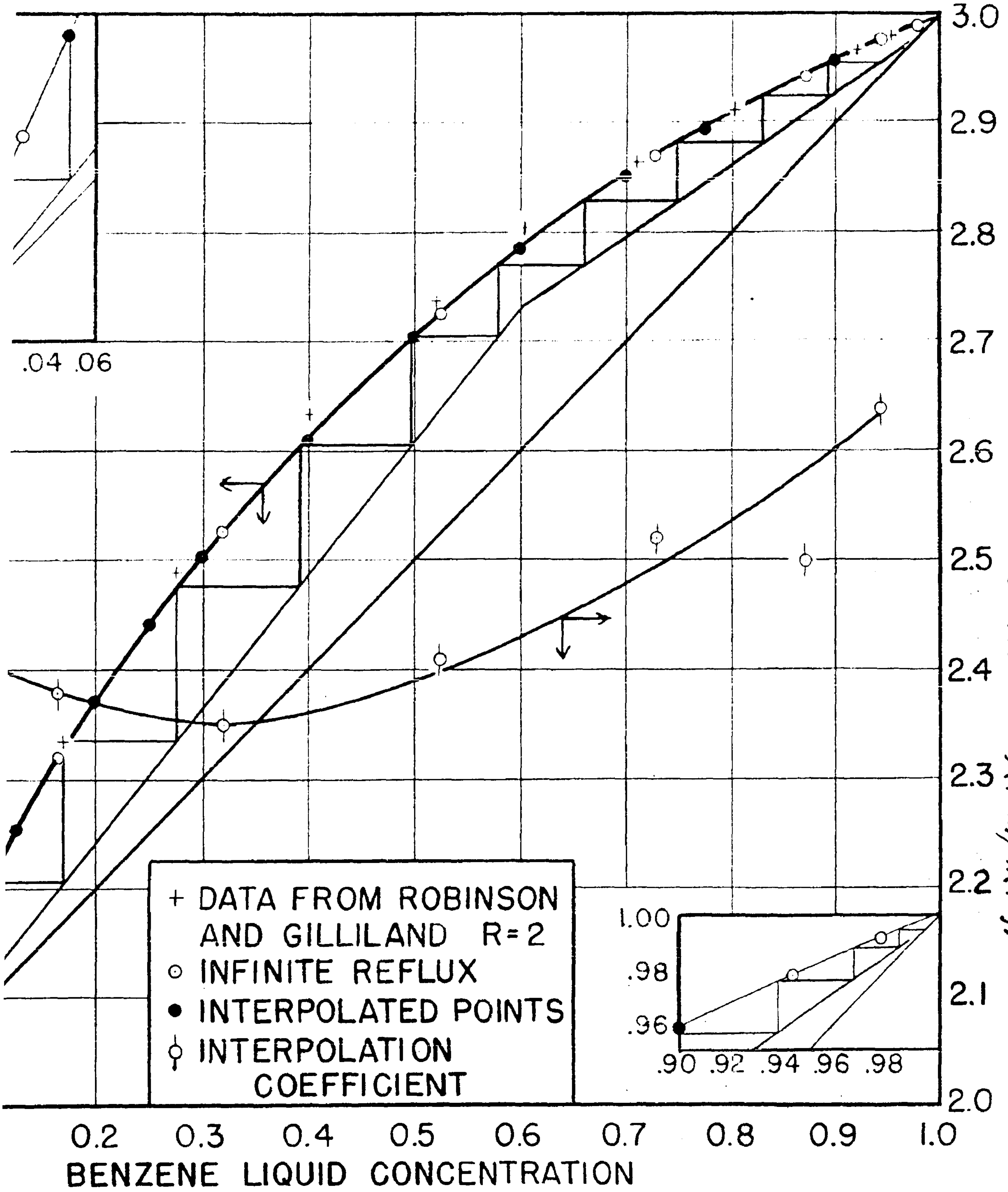


Figure 11

The quantity M is defined as the interpolation coefficient. While M depends upon the liquid concentration, it varies but slightly in this problem.

The method of procedure was to determine M for known values of x and y previously obtained by the stepwise calculations. A plot of M vs x made possible a determination of M for intermediate values of x, and then the corresponding values of y were calculated from Equation (96). It should be noted that this interpolation formula is only valuable when the variation in M is not large over the desired range.

Since no xylene appeared in the distillate, the plate to plate calculations were made from the bottom up. The results of calculations for this system are shown on Figure 8. The variation in M was 10%, and the interpolation coefficient method was used with confidence. The interpolated points are shown, and it is apparent they are very helpful in accurately constructing the curve. Some of the equilibrium data calculated by Robinson and Gilliland for $R = 2$ are shown on the plot, and it is apparent there is not a great variation in the equilibrium curves calculated by the two procedures. If the value of the reflux ratio had been larger this variation would have become less. Using the approximate equilibrium curve, 17 theoretical plates were obtained by the McCabe-Thiele method which compares favorably with the 16 plates as reported by Robinson and Gilliland.

NOMENCLATURE FOR CHAPTER V

α	Relative volatility in two component system
α_{ij}	Relative volatility of ith component with respect to jth component
A, B, C, E, G, K, r, A', B', G', K', r'	Constants defined in text.
D	Mols of distillate per hour
F	Mols of feed per hour
L	Mols of liquid reflux per hour for constant molal overflow
L_m	Mols of liquid reflux per hour leaving mth plate in stripping section
L_n	Same for nth plate in enriching section
L_o	Mols of reflux per hour returned to column from condenser
M	Interpolation coefficient or total plates in stripping section
N	Total plates in enriching section
q	Ratio of heat needed to convert one mol of feed into saturated vapor to molal latent heat
s	Total number of components
R	Reflux ratio for constant molar overflow
R_n	Reflux ratio on nth plate, ratio of L_n to D
R_o	Reflux ratio at condenser
V_m	Mols of vapor per hour in exhausting section leaving mth plate
V_n	Mols of vapor per hour in enriching section leaving nth plate
W	Mols of bottoms per mol of product
x_i	Mol fraction of ith component in liquid

$x_{i,n}$	Mol fraction of ith component in liquid on nth plate
y_i	Mol fraction of ith component in vapor
$y_{i,n}$	Mol fraction of ith component in vapor on nth plate

Subscripts

i	1, 2, ... s Subscript denoting any component
m	Plate number counting up from boiler in stripping section
n	Plate number counting down from top plate in enriching section
d	Product
s	As subscript denotes least volatile component

DIFFERENCE CALCULUS

Appendix Part I

The calculus of finite differences[8,68,89,91] is concerned with the ratio of finite increments $\Delta y/\Delta x$ of mutually dependent variables, while the infinitesimal calculus deals with the limit of this ratio as Δx becomes infinitesimally small. In many practical aspects, the operations of finite calculus are analogous to the operations of differential calculus. The operations of differentiation and integration have close parallels in differencing and summation. The solutions of difference equations are similar in many aspects to the solutions of differential equations. These similarities make possible the rapid mastery of the elements of finite calculus.

The First Difference

The first difference (sometimes termed the difference quotient) of a function, f(x), is defined by

$$\frac{\Delta y}{\Delta x} = \frac{f(x + \Delta x) - f(x)}{\Delta x} \qquad (1)$$

This may be compared with the first derivative which is defined as the limit to which the first difference approaches, provided the limit exists, as Δx approaches zero. Thus

$$\lim_{x \to 0} \frac{\Delta y}{\Delta x} = \frac{dy}{dx}$$

It is apparent that no question of limits is involved in the first difference defined by Equation (1) as both Δ y and Δ x are finite quantities. It should be noted that Δ x represents a constant difference of the independent variable. The quantities Δ y and Δ x are actual algebraic quantities of finite magnitude in contrast to the infinitesimals dy and dx. Thus the first difference is a true fraction while the first derivative is not a true fraction but rather a limit. The quantity, $\Delta/\Delta x$, is analogous to the differential operator d/dx. The value of Δ x may be taken as any constant value.

In stagewise processes, the increment, Δ x, will be unity as it corresponds to the difference between successive stages x and (x+1). If Δx is identically unity and Δ y is the corresponding increment, Equation (1) becomes

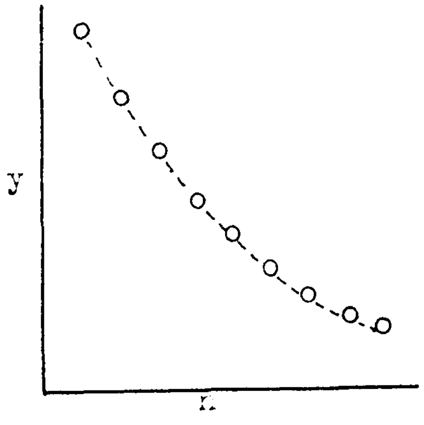
$$\Delta y = f(x+1) - f(x) = y_{x+1} - y_x \tag{2}$$

The notation $y_x = f(x)$ and $y_{x+1} = f(x+1)$ is used for convenience and simplicity. With $\Delta x = 1$, the operator $\Delta/\Delta x$ is replaced by Δ . The operation of obtaining Δ y as in (2) by subtracting y_x from y_{x+1} is termed differencing. The dependent variable, y, need not be a continuous function of x for the difference to exist. It is only necessary that it be defined at the points x, (x+1), (x+2), etc.

Interpretation of the First Difference. If the vapor concentration of the more volatile component in a binary fractionation is plotted against the plate number, a series of isolated points is obtained as indicated in Figure 1. While a smooth curve may be drawn through these points as indicated by the dotted line, no concentrations exist between theoretical plates, and the parts of the curve between integral values of the plate number have no physical significance. The change in vapor concentration from plate to plate is represented by

$$\Delta y_n = y_{n+1} - y_n \tag{3}$$

This is simply the difference or increment in concentration between the nth and (n+1)st plates, and is identical with the first difference $\Delta y_n/\Delta n$ as defined in the difference calculus. In this case $\Delta n = (n+1) - n = 1$ and $\Delta y_n/\Delta n$ becomes Δy_n.



VAPOR CONCENTRATION VS. PLATE NUMBER

Figure 1

The first difference is numerically equal to the tangent of the angle between a line passing through the points (x, y_x) and $(x+1, y_{x+1})$ and the x axis. Whereas the derivative represents the instantaneous rate of change at the point (x, y_x), the difference corresponds to the average rate of change in the interval x and (x+1).

Rule for Obtaining Differences

A simple three step rule for computing differences can be developed from Equation (2):

(a) Compute the function at x+1, i.e., wherever x occurs in f(x), replace it by (x+1).

(b) Compute the function at x, i.e., as it stands.

(c) Subtract (b) from (a).

Higher Differences

The second difference is defined as the difference of the first difference and is represented by $\Delta^2 y_x$. The nth difference is given by $\Delta^n y_x$. Higher differences may be obtained in terms of the dependent variable from Equation (2). Thus

$$\Delta^2 y_x = \Delta(y_{x+1} - y_x) = \Delta y_{x+1} - \Delta y_x \qquad (4a)$$

$$= y_{x+2} - 2y_{x+1} + y_x \qquad (4b)$$

The third difference is given by

$$\Delta^3 y = y_{x+3} - 3y_{x+2} + 3y_{x+1} - y_x \qquad (5)$$

As an example of the differences of an explicit function of x consider the successive differences of $y_x = x^3$

$$\Delta y_x = \Delta x^3 = (x+1)^3 - x^3 = 3x^2 + 3x + 1 \qquad (6a)$$

$$\Delta^2 y_x = 3(x+1)^2 + 3(x+1) + 1 - (3x^2 + 3x + 1) \qquad (6b)$$

$$= 6x + 6 \qquad (6c)$$

$$\Delta^3 y_x = 6 \qquad \Delta^4 y_x = 0 \qquad (6d)$$

All higher differences than the third are zero.

Differences of Elementary Functions

In this section the differences of some of the elementary functions will be obtained.

Constant. The difference of $y_x = c$ is zero

The Linear Function, ax. Differencing ax gives

$$\Delta(ax) = a(x+1) - ax = a \qquad (7)$$

Factorials. The quantity $x^{(n)}$ (read x factorial n power) plays an analogous role in finite calculus to that of the simple power function x^n in the differential calculus. Its definition is given by

$$x^{(n)} = x\,(x-1)(x-2)\,\ldots..\left[x - (n-1)\right] \qquad (8)$$

Factors = 1st,2nd,3rd .... nth

Thus the (n) indicates that there are n factors involved. The last factor in Equation (8) can be written as $(x - n + 1)$. If $x = n$, the quantity in (8) reduces to the simple factorial encountered in elementary algebra, i.e.,

$$n^{(n)} = n(n-1)(n-2)\,\ldots\ldots\,(n - n + 1) = n! \qquad (9)$$

The first difference of $x^{(n)}$ is

$$\Delta\, x^{(n)} = (x+1)^{(n)} - x^{(n)} \qquad (10a)$$

which on factoring yields

$$= \left[(x+1) - (x-n+1)\right](x)(x-1)\,\ldots.\,(x-n+2) \qquad (10b)$$

$$= nx^{(n-1)} \qquad (11)$$

The results of Equation (11) are similar to the derivative of x^n.

Exponential Functions. Exponentials of the form a^x are of considerable importance in the theory of difference equations. The first difference of a^x is

$$\Delta a^x = a^{x+1} - a^x = (a-1)\, a^x \tag{12}$$

The second difference is

$$\Delta^2 a^x = \Delta(a-1)\, a^x = (a-1)^2\, a^x \tag{13}$$

Repetition of this process gives

$$\Delta^n a^x = (a-1)^n\, a^x \tag{14}$$

Trignometric Functions

Sine. The difference of $\sin u_x$ where u_x is an arbitrary function of x is

$$\Delta \sin u_x = \sin u_{x+1} - \sin u_x \tag{15a}$$

$$= \sin (u_x + \Delta u_x) - \sin u_x \tag{15b}$$

$$= \sin \left[(u_x + \frac{\Delta u_x}{2}) + \frac{\Delta u_x}{2}\right] - \sin \left[(u_x + \frac{\Delta u_x}{2}) - \frac{\Delta u_x}{2}\right] \tag{15c}$$

Expanding the sine functions and combining terms

$$\Delta \sin u_x = 2 \sin \frac{\Delta u_x}{2} \cos (u_x + \frac{\Delta u_x}{2}) \tag{15d}$$

Cosine. In a manner similar to that for the sine, it can be shown that

$$\Delta \cos u_x = -2 \sin \frac{\Delta u_x}{2} \sin (u_x + \frac{\Delta u_x}{2}) \tag{16}$$

Tangent. To find the difference of $\tan u_x$

$$\Delta \tan u_x = \tan u_{x+1} - \tan u_x \tag{17}$$

$$= \frac{\sin u_{x+1}}{\cos u_{x+1}} - \frac{\sin u_x}{\cos u_x} \tag{18a}$$

$$= \frac{\sin (u_{x+1} - u_x)}{\cos u_x \cos u_{x+1}} \tag{18b}$$

$$\Delta \tan u_x = \frac{\sin \Delta u_x}{\cos u_x \cos u_{x+1}} \qquad (18c)$$

Inverse Tangent. Differencing $\tan^{-1} u_x$ gives

$$\Delta \tan^{-1} u_x = \tan^{-1} u_{x+1} - \tan^{-1} u_x \qquad (19a)$$

$$\Delta \tan^{-1} u_x = \tan^{-1} \frac{\Delta u_x}{1 + u_x u_{x+1}} \qquad (19b)$$

Summary of Differences. In the following table a list of the more common differences and comparisons with corresponding or similar derivatives is given. The symbol D is used for d/dx

Difference	Derivative
$\Delta c = 0$	$D c = 0$
$\Delta ax = a$	$d\ ax = a$
$\Delta x^{(n)} = n\, x^{(n-1)}$	$D x^n = n\, x^{n-1}$
$\Delta a^x = (a-1)\, a^x$	$D a^x = (\ln a) a^x$
$\Delta 2^x = 2^x$	$D e^x = e^x$
$\Delta \log x = \log \frac{x+1}{x}$	$D \ln x = \frac{1}{x}$
$\Delta \sin u_x = 2 \sin \frac{\Delta u_x}{2} \cos (u_x + \frac{\Delta u_x}{2})$	$D \sin u = \cos u\, D u$
$\Delta \cos u_x = -2 \sin \frac{\Delta u_x}{2} \sin (u_x + \frac{\Delta u_x}{2})$	$D \cos u = -\sin u\, D u$
$\Delta \tan u_x = \frac{\sin \Delta u_x}{\cos u_x \cos u_{x+1}}$	$D \tan u = \sec^2 u\, D u$

Differences of Sums, Products, and Quotients. The difference of a sum of several functions is the sum of the differences of the functions, i.e.,

$$\Delta(u_x + v_x + w_x) = \Delta u_x + \Delta v_x + \Delta w_x \tag{20}$$

The difference of the product of two functions is given by

$$\Delta(u_x v_x) = u_{x+1} v_{x+1} - u_x v_x \tag{21}$$

This equation can be placed in the alternative forms

$$\Delta (u_x v_x) = u_x \Delta v_x + v_{x+1} \Delta u_x \tag{22}$$

$$\Delta (u_x v_x) = v_x \Delta u_x + u_{x+1} \Delta v_x \tag{23}$$

Expansion of the differences in (22) and (23) will show that both are equal to (21). The similarities and dissimilarities between (22) and (23) and the corresponding derivative $\frac{d}{dx}(uv) = u\frac{dv}{dx} + v\frac{du}{dx}$ should be noted.

A similar procedure for u_x/v_x gives

$$\Delta \frac{u_x}{v_x} = \frac{u_{x+1}}{v_{x+1}} - \frac{u_x}{v_x} \tag{24}$$

Combining over a common denominator and adding and subtracting $u_x v_x$ from the numerator yields

$$\Delta \frac{u_x}{v_x} = \frac{v_x \Delta u_x - u_x \Delta v_x}{v_x v_{x+1}} \tag{25}$$

This corresponds to the derivative

$$\frac{d}{dx}\frac{u}{v} = \frac{v\, du/dx - u\, dv/dx}{v^2} \tag{26}$$

Reciprocal of $\Delta y_x/\Delta x$. In the differential calculus, frequent use is made of the fact that dx/dy is the reciprocal of dy/dx. A similar relationship does not hold in the finite calculus. This is due to the way the differences $\Delta y_x/\Delta x$ and $\Delta x_y/\Delta y$ are defined. In either case, the difference, Δx or Δy, of the variable serving as independent variable is taken as constant and equal to unity. Thus in one case $\Delta y = 1$ and in the other Δy_x is a variable quantity depending upon Δx. In general

$$\Delta y_x \neq 1/\Delta x_y \tag{27}$$

Another useful relation of differential calculus, $\frac{d}{dx} f(y) = \frac{d}{dy} f(y) \frac{dy}{dx}$ similarly has no corresponding analog in the finite calculus. If the functions are of such a nature that it is impossible to solve explicitly for the dependent variable, no general method for obtaining the difference similar to the above method for derivatives exists. Thus if

$$x = f\,(y_x) \tag{28}$$

and it is impossible to solve for y_x in terms of simple functions of x, the difference must be obtained as

$$(x+1) - x = f\,(y_{x+1}) - f\,(y_x) \tag{29}$$

whence

$$1 = f\,(y_x + \Delta y_x) - f\,(y_x) \tag{30}$$

It is not possible to say $x = \frac{\Delta}{\Delta y} f\,(y) \frac{\Delta y}{\Delta x}$

Definition of the Operator E. The defining equation for the first difference can be placed in the form

$$y_{x+1} = y_x + \Delta y_x \tag{31}$$

If Δ is treated as a symbol of quantity y_x can be factored in Equation (31) to give

$$y_{x+1} = (1 + \Delta)\, y_x \tag{32}$$

The symbolic quantity $(1 + \Delta)$ is important and is defined as E; thus

$$y_{x+1} = E y_x \tag{33}$$

Equation (33) may be considered as the defining equation for E. In words, E is that operator which increases the independent variable by unity.

Repetition of the operation gives

$$E\,E\,y_x = E^2 y_x = y_{x+2} \tag{34}$$

In general

$$E^n y_x = y_{x+n} \tag{35}$$

and

$$E^{-n} y_x = y_{x-n} \tag{36}$$

The operator E may act on an explicit function of x, thus

$$E\,x = (x+1) \tag{37}$$

and

$$E^{-2}\,x = (x-2) \tag{38}$$

Use of the Operators Δ and E. Solving for Δ in terms of E yields

$$\Delta = E - 1 \tag{39}$$

The operators Δ and E may be treated exactly as algebraic quantities. As an example of the use of (39) the third difference of y_x will be obtained. Since $\Delta = E - 1$

$$\Delta^3 y_x = (E-1)^3 \quad y_x = (E^3 - 3E^2 + 3E - 1)\ y_x$$

$$\Delta^3 y_x = y_{x+3} - 3y_{x+2} + 3y_{x+1} - y_x$$

This is the same result obtained in Equation (5). In general the nth difference of y_x is given by

$$\Delta^n y_x = (E - 1)^n\ y \qquad (40)$$

This equation shows that the coefficients of the various terms in the expansion of $\Delta^n y_x$ are the same as the binomial coefficients from the expansion $(E-1)^n$.

FINITE INTEGRATION AND SUMMATION

Appendix Part II

Introduction. In the previous chapter, the differences of various functions have been found. In this chapter the inverse process of finding a function whose difference is known will be investigated. The inverse process, termed finite integration or summation may be carried out in several manners. While no general method exists for finding the finite integral of a function, many simple forms may be obtained by inspection.

Symbol of Finite Integration. For the finite integration of f(x) the following notation is used:

$$\Sigma f(x)\Delta x \qquad (1)$$

The reasons for using Σ will appear subsequently. The symbols used in Equation (1) are quite similar to the differential integration sign $\int f(x)dx$. For the usual case in which $\Delta x = 1$, Equation (1) becomes

$$\Sigma f(x) \qquad (2)$$

For the present, Equation (2) will be referred to as the finite integral or simply integral of f(x).

Constant of Finite Integration. If F(x) is the integral indicated by (2), then F(x) + C is also an integral if C is such a quantity that $\Delta C = 0$. Any constant satisfies this condition, and, in addition, any function of x that takes on the same value at x, x+1, x+2, etc., will also satisfy the requirement that $\Delta C = 0$. In general, functions with period Δx, i.e., $C(x+\Delta x) - C(x) = 0$ may be treated as constants of integration. If $\Delta x = 1$, then $C_{x+1} - C_x$ must be zero.

Integration of Elementary Functions

Zero. As the difference of a constant is zero, conversely the integral of zero is a constant.

$$\Sigma 0 = C \tag{3}$$

Constant. By inspection it is apparent that the integral of the constant, a, is given by

$$\Sigma a = ax + C \tag{4}$$

Factorial Powers. From Equation (11) of Part I of the Appendix, the difference of $x^{(n)}$ is $nx^{(n-1)}$, thus

$$\Sigma x^{(n)} = \frac{x^{(n+1)}}{n+1} + C \tag{5}$$

Equation (5) holds for all values of n except $n = -1$. The finite integration of $1/x$ has not been carried out in terms of simple functions. The quantity $\Sigma(1/x)$ is termed the psi function snd various tables of numerical values are available.[68]

Exponentials. From Equation (12) of the previous chapter $\Delta\, a^x = (a-1)a^x$ and hence

$$\Sigma a^x = \frac{a^x}{a - 1} + C \tag{6}$$

Sine. To obtain the sum of sin ax, note that Equation (15d) of Part I of the Appendix gives on placing $u_x = ax$

$$\Delta \sin ax = 2 \sin \frac{a}{2} \sin \left(ax + \frac{a + \pi}{2}\right)$$

Integrating this equation as it stands gives

$$\Sigma \Delta \sin ax = \sin ax = 2 \sin(a/2)\ \Sigma \sin\left[ax + (a+\pi)/2\right] + C$$

The preceding equation can be placed in the form

$$\Sigma \sin\left[ax + (a+\pi)/2\right] = \frac{1}{2 \sin (a/2)} \sin ax + C \qquad (7)$$

As it is $\Sigma \sin ax$ that is desired, (7) must be modified to give

$$\Sigma \sin ax = \frac{1}{2 \sin (a/2)} \sin\left[ax - (a+\pi)/2\right] + C \qquad (8)$$

Cosine. A procedure similar to the above produces

$$\Sigma \cos ax = \frac{1}{2 \sin (a/2)} \left[\cos\ ax - (a+\pi)/2\right] + C \qquad (9)$$

In the preceding trignometric functions, it is not necessary that ax be in radian measure.

Summary of Integrals. In the following table a comparison of finite and differential integrals is given.

$\Sigma 0 = C$	$\int 0\, dx = C$
$\Sigma a = ax + C$	$\int a dx = ax + C$
$\Sigma x^{(n)} = x^{(n+1)}/(n+1) + C$	$\int x^n dx = x^{n+1}/(n+1) + C$
$\Sigma a^x = a^x/(a-1) + C$	$\int a^x dx = a^x/\ln a + C$
$\Sigma \sin ax = \frac{1}{2 \sin \frac{a}{2}} \sin \left(ax - \frac{a+\pi}{2}\right)$	$\int \sin ax\, dx = \frac{-1}{a} \cos ax + C$
$\Sigma \cos ax = \frac{1}{2 \sin \frac{a}{2}} \cos \left(ax - \frac{a+\pi}{2}\right)$	$\int \cos ax\, dx = \frac{1}{a} \sin ax + C$

Integrals of Sums and Products. The integration of the sum of several functions is the sum of the integrals of the functions.

$$\Sigma(u_x + v_x + w_x) = \Sigma u_x + \Sigma v_x + \Sigma w_x + C \qquad (10)$$

The integral of a constant times a function is the product of the constant and the integral of the function.

$$\Sigma a\, u_x = a\Sigma u_x + C \qquad (11)$$

Summation

In the first part of this chapter it has been demonstrated that it is sometimes possible to obtain a function whose difference is known by a process that is the inverse of differencing. The method has been termed finite integration. It will now be shown that the desired answer may be obtained as the sum of a series.

To discover a means for finding y_x from the equation $\Delta y_x = u_x$, place the equation in the following form:

$$y_{x+1} - y_x = u_x \qquad (12a)$$

As this equation holds for any value of x, consider the equations

$$y_x - y_{x-1} = u_{x-1} \qquad (12b)$$

$$y_{x-1} - y_{x-2} = u_{x-2} \qquad (12c)$$

....

$$y_{a+2} - y_{a+1} = u_{a+1} \qquad (12d)$$

$$y_{a+1} - y_a = u_a \qquad (12e)$$

If these equations are added, the left hand side telescopes into $y_x - y_a$ and

$$y_x = y_a + u_a + u_{a+1} + \dots + u_{x-2} + u_{x-1} \tag{13a}$$

$$= \sum_a^{x-1} u_x + y_a \tag{13b}$$

to test (13b) to see if it is truly the desired solution, place (13b) in Equation (12a). If $y_a = C$, then

$$y_{x+1} = C + u_a + \dots + u_{x-2} + u_{x-1} + u_x$$

$$y_x = C + u_a + \dots + u_{x-2} + u_{x-1}$$

by subtracting y_x from y_{x+1} there results $\Delta y_x = u_x$; and, thus, it is definitely shown that Equations (13) represent the required solution. In general the constant C is unnecessary and will be omitted leaving

$$y_x = \sum_a^{x-1} u_x \tag{14}$$

Equation (14) states that y_x is given by a sum on u_x starting at some <u>fixed lower limit</u> and ending at the <u>upper limit, x-1</u>. It is impossible for the upper limit to be x instead of x-1. In Equation (14) x and a must both be integral.

From the results of this section, it is apparent that Σ is descriptive of the operation carried out. Symbols suggested by other authors are Δ^{-1}, P^{-1}, and S.

<u>Connection between Summation and Finite Integration</u>. As two different methods have yielded two different solutions

to $\Delta y_x = u_x$, these solutions must be equivalent. Because of this it is possible to obtain values for the sum of a finite number of terms for many different series. If the integral of u_x obtained by the inverse process is F(x), then

$$\sum_{a}^{x-1} u_x = F(x) + C \qquad (15)$$

The constant C is determined by the value of the lower limit a on the sum. If it is desired to include u_x as the last term in the summation instead of u_{x-1} in (4), then x must be replaced by x + 1 giving

$$\sum_{a}^{x} u_x = F(x+1) + C \qquad (16)$$

Summation of Factorials. If the general term of a series is of a form that is directly integrable by the methods presented in Chapter III, the sum may be readily found. Consider the sum of an arithmetic series

$$s_x = 1 + 2 + 3 + \ldots. + x \qquad (17)$$

The general term is x and integration gives

$$\sum_{1}^{x-1} x = \Sigma x + C = \frac{x(x-1)}{2} + C \qquad (18)$$

The right hand member gives the value of the sum of the first x-1 terms if C is properly evaluated. In order to include the x(th) term, it is necessary to change the limit on the sum from x-1 to x as indicated in Equation (16).

This gives

$$s_x = \sum_{1}^{x} x = \frac{(x+1)(x)}{2} + C \qquad (19)$$

To evaluate C, a value of x must be substituted. Let x = 1, then

$$s_1 = 1 = \frac{2(1)}{2} + C$$

and C = 0. If x = 2 is substituted, the equation becomes 3 = 3 + C. Thus

$$s_x = x^{(2)}/2 \qquad (20)$$

Many other series with factorials for the general term can be evaluated in a similar manner.

Summation of Exponentials. Geometric series actually consist of exponential terms in the form a^x. The sum of $2^0 + 2^1 + 2^2 + 2^3 \; . \; . + 2^x$ may be obtained by integrating 2^x, thus

$$1 + 2 + 4 + 8 \ldots 2^{x-1} = \sum_{0}^{x-1} 2^x + C \qquad (21)$$

In order to include the x(th) term, replace x by x + 1, then

$$1 + 2 + 4 + \ldots + 2^x = \sum_{0}^{x} 2^x = 2^{x+1} + C \qquad (22)$$

To evaluate C, let x = 0. Then 1 = 2 + C and C = -1. Thus

$$2^{x+1} - 1 = \sum_{0}^{x} 2^x \qquad (23)$$

Graphical Interpretation of the Sum. A graphical picture of the sum as presented in Equation (14) is of interest in comparison with graphical differential integration. Just as a differential integral can be represented as the area under a continuous curve so can a finite integral be represented as the area under a stepwise curve. In Figure 1, a plot of Δy_x vs x is shown. As indicated by Equation (14), the sum of Δy_x or u_x from 1 to x-1 is a solution for y_x. As each rectangle in Figure 2 has an area equal to the corresponding term in Equation (3), y_x is given by the area under the stepwise curve shown. It should be noted that in order to include u_{x-1}, it is necessary to draw the curve up to x.

GRAPHICAL [illegible]

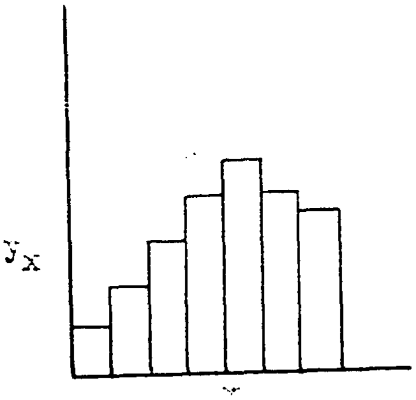


Figure 1

The Definite Sum

The finite integration formulas previously presented have been indefinite integrals in the sense that the value of the constant is arbitrary and the variable is not fixed. If limits of integration or summation are placed upon the function, it becomes possible to dispense with the arbitrary constant. In Equation (14) the limits on the sum correspond to a definite integral with a variable upper limit. The definite sum is defined by the following three equations

$$\sum_{a}^{b} u_x = u_a + \dots\dots + u_b \qquad a < b \tag{24a}$$

$$\sum_{a}^{b} u_x = u_a \qquad a = b \tag{24b}$$

$$\sum_{a}^{b} u = -u_a - \dots\dots - u_b \qquad a > b \tag{24c}$$

<u>Connection between Definite and Indefinite Sums.</u> If the indefinite integration of u_x produces $F(x)$, then

$$\Sigma\, u_x = F(x) + C = \sum_{p}^{x-1} u_x \tag{25}$$

where p is a fixed lower limit. If it is desired that the upper limit equal b, it is necessary to place $x = (b + 1)$ wherever it occurs in (25). Thus

$$F(b+1) + C = \sum_{p}^{b} u_x = u_p + u_{p+1} + \dots\dots + u_{a-1} + u_a + \dots\dots + u_b \tag{26}$$

Now consider the same integral with the upper limit equal to (a-1), then

$$F(a) + C = \sum_{p}^{a-1} u_x = u_p + u_{p+1} + \dots\dots + u_{a-1} \tag{27}$$

Subtracting (27) from (26) gives

$$\sum_{a}^{b} u_x = F(b+1) - F(a) = u_a + \dots\dots + u_b \tag{28}$$

It is of utmost importance to notice that the upper limit to be substituted in the integrated form is <u>b+1 and not b</u>. The following notation will be employed for convenience

$$\sum_{a}^{b} u_x = F(x)\Big]_{a}^{b+1} = F(b+1) - F(a) \qquad b \geq a \qquad (29)$$

Because of the definitions in (24a,b,c), Equation (29) is valid only when $b \geq a$. If $b < a$, then

$$\sum_{a}^{b} ux = -\sum_{b}^{a} ux = - \Big[F(a+1) - F(b)\Big] \qquad (30)$$

Rearranging (30) gives

$$\sum_{a}^{b} u_x = F(b) - F(a+1) \qquad b < a \qquad (31)$$

DIFFERENCE EQUATIONS

Appendix Part III

A difference equation,[8,53,66,68,70,81,89,91] involves a relationship of differences, Δy_x, $\Delta^2 y_x$ and the variables x and y. The order of an equation is equal to the order of the highest difference involved while the degree is the power to which the highest difference is raised. The problem encountered is, given a difference equation of the form (1)

$$f(x, y_x, \Delta y_x \ldots) = 0 \qquad (1)$$

to obtain a complete primitive. It is obvious that (1) can be expressed in another form in which the differences are replaced by successive values of the dependent variable y_x, y_{x+1}, ...

$$f(x, y_x, y_{x+1}, \ldots) = 0 \qquad (2)$$

As an example of the genesis of a difference equation, consider the primitive

$$y = C a^x \qquad (3)$$

where C is an arbitrary constant and a some fixed number. To obtain the difference equation for (3), it is necessary to difference (3) with respect to x

$$\Delta y_x = C (a - 1) a^x \qquad (4)$$

and then eliminate C between (3) and (4) to obtain (5) which is free of the arbitrary constant

$$\Delta y_x = (a - 1) y_x \qquad (5)$$

Where two arbitrary constants are involved, it is necessary to obtain another equation involving the second difference in order that both constants can be eliminated. In general an nth order equation results from the elimination of n arbitrary constants from a complete primitive. It is the objective of this chapter to present methods for solving difference equations similar to (5) in order to obtain the primitives such as (3).

The Linear Difference Equation of First Order. An equation in which the dependent variable and the various differences occur only in the first degree is called linear. The linear equation may be expressed in either the form (1) or (2). While both forms are employed, the latter is generally more useful. The complete linear equation of the first order has the form

$$y_{x+1} - P_x y_x = Q_x \qquad P_x \neq 0 \tag{6}$$

The general solution of this equation is that function of x containing one arbitrary constant which when substituted in (6) produces the identity $Q_x = Q_x$. The general solution[33,89] consists of the sum of the general solution of the reduced equation

$$y_{x+1} - P_x y_x = 0 \tag{7}$$

and any particular solution of the complete Equation (6). To show this, let u_x be the general solution of the reduced equation, i.e., contains an arbitrary constant in addition to satisfying (7), and let c_x be a particular solution of the complete solution.

If it can be shown that $y_x = u_x + c_x$ is a solution of (6), then that is sufficient for it to be the general solution because the general solution is any solution containing an arbitrary constant such as u_x contains. Substituting $y_x = u_x + c_x$ in (6) yields

$$y_{x+1} - P_x y_x = (u_{x+1} - P_x u_x) + (c_{x+1} - P_x c_x)$$

The quantity $(u_{x+1} - P_x u_x)$ equals zero by definition, and $(c_{x+1} - P_x c_x)$ equals Q_x. Hence, $u_x + c_x$ is the general solution of (6).

To obtain the actual form of the solution of (6) first consider the reduced equation

$$y_{x+1} - P_x y_x = 0 \tag{8}$$

and as this equation holds true for all values of x

$$y_x = P_{x-1}\, y_{x-1} \tag{9a}$$

$$y_{x-1} = P_{x-2}\, y_{x-2} \tag{9b}$$

$$\cdots\cdots$$

$$y_2 = P_1 y_1 \tag{9c}$$

$$y_1 = P_o y_o \tag{9d}$$

Multiplying all these equations together and eliminating $y_1, y_2, \ldots y_{x-1}$ gives

$$y_x = \prod_{0}^{x-1} P_x y_o = C \prod_{0}^{x-1} P_x \tag{10}$$

where $\prod_{0}^{x-1} P_x = P_o P_1 \ldots\ldots P_{x-1}$ and $y_o = C$. This may then be viewed as the solution of the reduced equation where y_0 is simply some arbitrary constant. If p_x is constant, the solution is $y_x = C\ P^x$.

The solution of (8) may also be determined by first taking logarithms and placing in the form

$$\log y_{x+1} - \log y_x = \log P_x \tag{11}$$

Letting $u_x = \log y_x$, Equation (11) becomes

$$\Delta u_x = \log P_x \tag{12}$$

and the solution is obtainable when (12) is summable. Equation (12) is equivalent to

$$y_x = C\ a^{\Sigma \log_a P_x} = C \sum_{0}^{x-1} \log P_x \tag{13}$$

which is the same as (10).

To obtain a particular solution of (6), let c become an arbitrary function c_x in (10), then substitution in (6) produces

$$c_{x+1} \prod_{0}^{x} P_x - P_x c_x \prod_{0}^{x-1} P_x = Q_x \tag{14}$$

As $P_x \prod_{0}^{x-1} P_x = \prod_{0}^{x} P_x$

$$c_{x+1} - c_x = \frac{Q_x}{\prod_{0}^{x} P_x} \tag{15}$$

Summation of (62) gives

$$c_x = \sum_{0}^{x-1} \frac{Q_x}{\prod_{0}^{x} P_x} \tag{16}$$

and the particular solution is

$$y_x = \prod_{0}^{x-1} P_x \sum_{0}^{x-1} \frac{Q_x}{\prod_{0}^{x} P_x}$$

The general solution of the first order linear equation becomes

$$y_x = c \prod_{0}^{x-1} P_x + \prod_{0}^{x-1} P_x \sum_{0}^{x-1} \left[Q_x / \prod_{0}^{x} P_x \right] \qquad (17)$$

If P and Q are constants, Equation (17) becomes

$$y_x = c\ P^x + P^x\ \Sigma\ Q\ P^{-x-1} = c\ P^x + Q\ P^{x-1}\ \Sigma\ P^{-x} \qquad (18a)$$

$$= c\ P^x + Q/(1-P) \qquad (18b)$$

The Linear Equation with Constant Coefficients. The general linear equation of nth order has the form

$$\mathop{S}_{i=o}^{i=n} P_i\ y_{x+i} = Q_x \qquad P_n \neq 0 \qquad (19)$$

where S represents a sum on i from 0 to n and is used to avoid confusion with Σ which represents the inverse operation of Δ. The terms P_i are a series of unrelated constants with $P_n = 1$. The general second order equation of the form of (19) is

$$y_{x+2} + P_1 y_{x+1} + P_2 y_x = Q_x \qquad (20)$$

The terms in Equation (19) involving y_{x+i} may be replaced by $E^i y_x$, thus (19) becomes

$$\mathop{S}_{i=o}^{i=n} P_i E^i y_x = Q_x \qquad (21)$$

As y_x is common to all the terms on the left of (21), it can be factored out to give

$$f(E)y_x = Q_x \tag{22}$$

where

$$f(E) = \sum_{i=o}^{i=n} P_i E^i \tag{23}$$

The function f(E) is a rational and integral function of E of degree n and can be factored into n factors of the form $(E-r_i)$ where the constants, r_i, are roots of the auxilliary equation $f(r) = 0$. Thus f(E) can be broken down as follows:

$$f(E) = \prod_{1}^{n} (E-r_i) \tag{24}$$

where all the r_i's are not necessarily real or distinct. Equation (19) becomes

$$\prod_{1}^{n} (E-r_i)\, y_x = Q_x \tag{25}$$

In a manner analogous to that used for the first order linear equation, it can be shown that the general solution of (25) consists of the general solution of the reduced equation plus any particular solution of the complete equation. The general solution of the reduced equation is a linear combination of n linearly independent solutions.[33]

To explicitly solve (25), it is first necessary to obtain the linearly independent solutions of the reduced equation. Consider the case in which the roots of $f(x) = 0$ are all real and unequal, then the reduced form of (25) is

$$(E - r_1)(E - r_2) \ldots (R - r_n)\, y_x = 0 \qquad (26)$$

By first considering the solution of

$$(E - r_i)\, y_x = 0 \qquad (27)$$

it is possible to obtain a set of linearly independent solutions. If the solution to (27) is obtained, it will also be a solution of (26) because further operations of the factors, $(E-r_1)$ $(E-r_2)$ etc. on $(E-r_i)\, y_x = 0$ will still be zero. From Equation (18b) it is seen that the solution of (27) is $y = r_i^x$. As r_i can be any of the n roots, there are obviously n solutions of the form r_i^x. These solutions form a fundamental set since Casorati's determinant vanishes for finite x. Hence the general solution of (26) is

$$y_x = \overset{n}{\underset{1}{S}}\, C_i\, r_i^x \qquad (28)$$

Should any of the roots be repeated, it is necessary to consider

$$(E - r)^m\, y_x = 0 \qquad (29)$$

where r is repeated m times. To solve this it should be noted that

$$(E - r)^m\, y_x = r^{x+m} \Delta^m (r^{-x}\, y_x) = 0 \qquad (30)$$

Hence

$$y_x = (C_0 + C_1 x + \ldots C_{m-1} x^{m-1})\, r^x \qquad (31)$$

Should the roots be complex, the solution given in

Equation (28) is best modified by changing the exponentials to sines and cosines. Consider a pair of roots of the form $(\alpha \pm \beta i)$. If the roots are placed in polar form, then

$$c_1 \, (\alpha + \beta i)^x + c_2 \, (\alpha - \beta i)^x = c_1 \, r^x e^{i\theta x} + c_2 \, r^x e^{-i\theta x}) \tag{32a}$$

where $r^2 = \alpha^2 + \beta^2$ and $\tan \theta = \beta/\alpha$. Expanding (32a) gives

$$c_1 \, r^x e^{i\theta x} + c_2 \, r^x \, e^{-i\theta x} = r^x \quad (A \sin \theta x + B \cos \theta x) \tag{32b}$$

where $A = c_1 + c_2$ and $B = i(c_1 - c_2)$. If the roots are repeated m times, A must be replaced by $(A_0 + A_1 x + A_2 x^2 + \ldots A_{m-1} \, x^{m-1})$ and B by a similar term.

Having obtained the general solution of the reduced equation, it is then necessary to obtain a particular solution of the complete equation. With certain forms of Q, a particular solution is easily obtainable while with others it is not. If Q is constant, it is apparent that

$$y_x = Q/\overset{n}{\underset{0}{S}} P_i = \text{cons't} \qquad \overset{n}{\underset{0}{S}} P_i \neq 0 \tag{33}$$

is a solution for substitution of this value of y_x in (25) produces an identity. Special methods for obtaining particular solutions will be considered after the solutions of several equations have been taken up.

Example 1. $\quad y_{x+2} + 3y_{x-1} + 2y_x = 12$

First step; Place the reduced equation in standard E form

$$(E^2 + 3E + 2) \, y_x = 0$$

Second step; Find the roots of the auxilliary equation

$$r^2 + 3r + 2 = 0$$

These roots are -1, and -2.

Third step; Factor the equation to obtain

$$(E + 1)(E + 2)\ y_x = 0$$

Fourth step; The general solution of the reduced equation is a linear combination of $(-1)^x$ and $(-2)^x$. Thus

$$y_x\ (\text{reduced}) = C_1(-1)^x + C_2\ (-2)^x$$

Fifth step; To find a particular solution of the complete equation, let y_x be a constant. Then $y_x = y_{x+1} = y_{x+2} = K$ and

$$K + 3K + 2K = 12$$

$$K = 6$$

The general solution of the complete equation is

$$y_x = c_1\ (-1)^x + c_2(-2)^x + 6$$

Example 2. Consider a case in which there are repeated real roots.

$$y_{x+3} + 3y_{x+2} + 3y_{x+1} + y_x = 0$$

Placing this equation in standard E form gives

$$(E^3 + 3E^2 + 3E + 1)\ y_x = (E + 1)^3\ y_x = 0$$

The solution is

$$y_x = (c_1 + c_2 + c_3\ x^2)(-1)^x$$

Example 3. Consider an equation having imaginary roots.

$$y_{x+2} + 2y_{x+1} - 2y_x = 0$$

Placing in standard E form gives

$$(E^2 + 2E - 2)\, y_x = (E + 1 - i)(E + 1 + i)\, y_x = 0$$

The modulus of the complex number (1+i) is $\sqrt{2}$ and the argument is $\theta = \tan^{-1} 1 = \pi/4$. Thus the solution is

$$y = 2^{x/2} \left[A \sin(\pi x/4) + B \cos(\pi x/4) \right]$$

Particular Solutions. In the previous section the solution of the reduced linear equation with constant coefficients has been considered in detail. To obtain the complete solution, it is necessary to find a particular solution of the complete equation. Several methods for obtaining particular solutions will now be presented. The methods are analogous to those used in differential equations.

Undetermined Coefficients. This method will work whenever successive differencing of the right hand member of the complete equation eventually causes repetition of the form of the function without regard to the constant multiplier. Examples of functions which are amenable to treatment by this method are

Function	Differences (disregarding constants)		
	1st	2nd	3rd
a^x	a^x		
$x^{(2)}$	x	1	0
$\sin \pi x$	$\cos \pi x$	$\sin \pi x$	

On the other hand log x, 1/x, and x^n where n is not integral cannot be treated by the method of undetermined coefficients.

Two examples will be taken up to show the mechanism of the method. In the first case, no function on the right hand side corresponds to any part of the general solution of the reduced solution. Thus consider the equation

$$y_{x+1} - 2y_x = x^{(2)} + 3^x$$

The reduced solution is $C2^x$. To obtain a particular solution, form a table of the functions on the right hand side and all differences having different function form. Thus

Function	Difference 1st	2nd	3rd
3^x	3^x		
$x^{(2)}$	x	1	0

There are four different functions in the table, and a particular solution of the form

$$y_x = A3^x + Bx^{(2)} + Cx + D(1)$$

will be assumed in which the undetermined coefficients A, B, C, and D must be found. Placing this equation in the original difference equation gives

$$A3^{x+1} + B(x+1)^{(2)} + C(x+1) + D - 2A3^x - 2Bx^{(2)} - 2Cx - 2D = x^{(2)} + 3^x$$

Equating coefficients of like terms gives

3^x: $3A - 2A = 1$

x^2: $B - 2B = 1$

x : $B + C + 2B - 2C = -1$?

constant terms b + $D + C - 2D = 0$?

Solving these equations gives A = 1, B = -1, C = -2, D = -2. The complete solution is

$$y_x = C2^x + 3^x - x^{(2)} - 2x - 2$$

In the second type, a function on the right is of the same form as part of the reduced solution. In this case, all the functions and their differences appearing on the right hand side that are the same as any part of the reduced solution must be multiplied by the least power of x that will make them different. Thus suppose $x^{(2)}$ were a solution and the term $x^{(3)}$ appeared on the right. Then $x^{(3)}$ and the successive differences $x^{(2)}$, x and 1 would have to be multiplied by x^3 in order that no part of the particular solution would be the same as the reduced solution.

Consider

$$y_{x+1} - 2y_x = 2^x$$

The reduced solution is $C2^x$ and the particular solution is $Ax2^x$. To find A, substitute in the difference equation

$$A(x+1)2^{x+1} - 2Ax2^x$$

Dividing out 2^x

$$2A(x+1) - 2Ax = 1$$

$$A = 1/2$$

The complete solution is

$$y_x = C2^x + 1/2$$

Symbolic Methods. Symbolic methods may be employed when Q has the form $r_x a^x$ if r_x is a rational and integral function of x. Consider Equation (22) with $Q_x = xa^x$, then

$$y_x = \frac{1}{f(E)} \; x a^x \tag{34}$$

It can be shown that

$$y_x = a^x \frac{1}{f(aE)} \, x \tag{35}$$

Breaking $f(aE) = \prod_{1}^{n} (aE - r_i)$ into partial fractions gives

$$y_x = a^x \left[\frac{c_1}{aE - r_1} + \frac{c_2}{aE - r_2} + \dots \right] x \tag{36}$$

Consider a typical factor

$$\frac{c_i}{aE - r_i} \, x = \frac{c_i}{a - r_i} \left[\frac{1}{1 + a\Delta/(a - r_i)} \right] x \tag{37}$$

Expanding

$$\frac{c_i}{aE - r_i} \, x = \frac{c_i}{a - r_i} \left[1 - \left(\frac{\Delta a}{a - r_i} \right) + \frac{a^2 \Delta^2}{(a - r_i)^2} - \dots \right] x \tag{38}$$

$$= \frac{c_i x}{a - r_i} \tag{39}$$

Thus the particular solution is

$$y_x = x \, a^x \overset{n}{\underset{1}{S}} c_i/(a - r_i) \tag{40}$$

Riccati Difference Equation. The Riccati difference equation with constant coefficients arises sufficiently often to deserve special attention. It has the general form

$$y_{x+1} \, y_x + A y_{x+1} + B y_x + D = 0 \tag{41}$$

This equation can be reduced to a linear equation of the first order by making the substitution $y_x = \frac{1}{u_x} - k$ and choosing k so that the constant term in the new equation drops out. It can also be solved by making the substitution $y_x = \frac{v_{x+1}}{v_x} - A$ which changes it to a second order linear equation. Making the first substitution gives

$$\left[\frac{1}{u_{x+1}} - k\right]\left[\frac{1}{u_x} - k\right] + A\left[\frac{1}{u_{x+1}} - k\right] + B\left[\frac{1}{u_x} - k\right] + D = 0 \qquad (42)$$

Choose k such that

$$k^2 - (A + B)\,k + D = 0 \qquad (43)$$

Then

$$\frac{1}{u_{x+1}\,u_x} + \frac{A-k}{u_{x+1}} + \frac{B-k}{u_x} = 0 \qquad (44a)$$

and

$$u_{x+1} + \frac{A-k}{B-k}\,u_x = \frac{1}{B-k} \qquad (44b)$$

The general solution of this equation is

$$u_x = C\left[\frac{k-A}{B-k}\right]^x + \frac{1}{A+B-2k} \qquad (45)$$

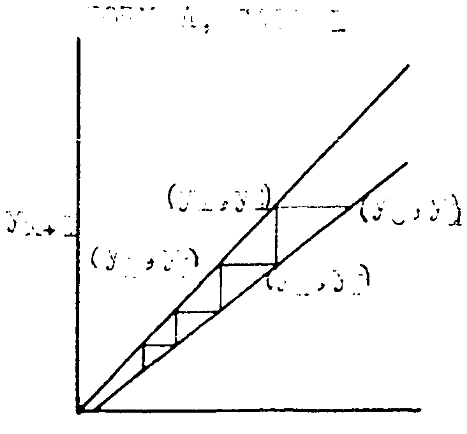
GRAPHICAL SOLUTIONS OF DIFFERENCE EQUATIONS

Appendix Part IV

Those difference equations that cannot be solved analytically require graphical solutions. In some practical cases where involved calculations to a considerable degree of accuracy must be made in analytical formulas, graphical methods may permit of shorter solutions. In general all the difference equations that arise may be solved by graphical methods or by stepwise calculations. Solutions of various types of equations will be considered.

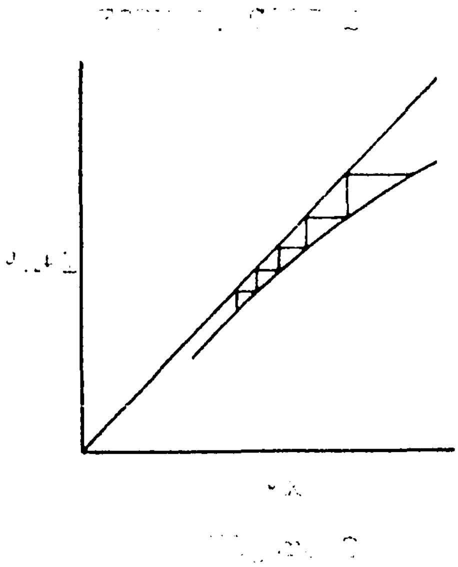
A. Equations of the Form $y_{x+1} - Py_x = Q.$[67]

Case 1, P and Q Constant. Although this equation can be solved analytically, the graphical solution will also be considered. In Figure 1, the straight line $y_{x+1} = Py_x + Q$, termed the operating line, and a 45° line through the origin are constructed. The points lying on the operating line are (y_0, y_1), (y_1, y_2), etc. while the points (y_1, y_1), (y_2, y_2), ... (y_x, y_x) lie on the 45° line. A horizontal line drawn from (y_0, y_1) intersects the 45° line at (y_1, y_1). Then having y_1, it is possible to obtain y_2 from the operating line. This process can be continued



until the desired value of y_x is reached. The value of x is determined by the number of points on the 45° line.

Case 2, P and Q Functions of y_x. The solution[1] of this equation differs from the solution of the previous equation only in that the operating line is no longer straight. It is obtained from the equation



$$y_{x+1} = P(y_x)y_x + Q(y_x) \qquad (1)$$

To find values for plotting the operating line, different values of y_x are chosen and the corresponding values of y_{x+1} are computed from the equation of the operating line.

Case 3, P and Q Functions of y_{x+1}. This case is treated graphically in exactly the same manner as the previous case. In obtaining points for the operating line, it is necessary to solve for y_x to obtain

$$y_x = \left[y_{x+1} - Q(y_{x+1}) \right] / P(y_{x+1}) \qquad (2)$$

Values of y_{x+1} are chosen first and the corresponding values of y_x computed.

Case 4, P and Q Functions of x. To solve this type[36] of equation it is necessary to construct a series of operating lines corresponding to x = 0, 1, 2, 3, etc. In Figure 3, the following operating lines are shown

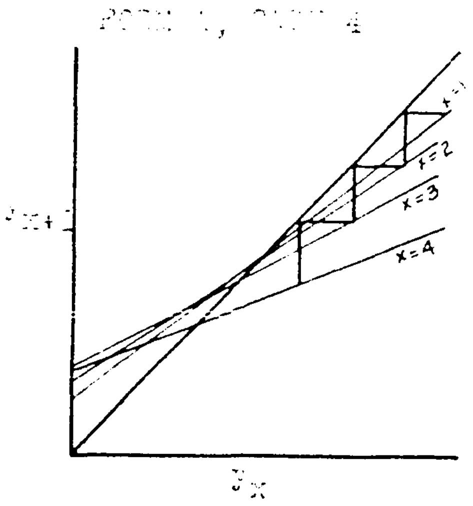


Figure 3

$$y_{x+1} = P_o\, y_x + Q_o \tag{3a}$$

$$y_{x+1} = P_1\, y_x + Q_1 \tag{3b}$$

$$\cdots\cdot$$

$$y_{x+1} = P_n\, y_x + Q_n \tag{3c}$$

where P_o is the value of P computed for x = 0. If y_o is known, y_1 can be found on the x = 0 operating line. Then after obtaining (y_1, y_1) on the 45° line, the value of y_2 is found on the x = 1 operating line and so on until the desired y_x is reached. Sometimes in practice these operating lines all emanate from a single point which makes their construction relatively simple.

Case 5, P and Q Functions of x and y_x. If P and Q are functions of y_x or y_{x+1} in addition to x, the operating lines of the previous case will all be curved and individually treated as the operating lines in Case 2 and 3.

Case 6, P and Q Functions of x, y_x, and y_{x+1}. If it is not possible to reduce this type to one of the previous cases, the only alternative is to solve the equation by trial and error in a stepwise manner. This case is seldom encountered in practice.

B. Summation of Δy_x

Case 1, $\Delta y_x = f(x)$. If it is not possible to integrate the function directly, y_x can be obtained in two ways.

First, Δy_x can be replaced by $y_{x+1} - y_x$ and the equation placed in the form

$$y_{x+1} - y_x = f(x) \tag{4}$$

This equation falls under Case 4 of the previous section with P = 1 and Q = f(x). Second, the methods for summation from Part II of the Appendix may be used, thus

$$y_x = \sum_{0}^{x+1} f(x) \tag{5}$$

This summation can be carried out by actual addition of $f(o) + f(1) + \ldots. + f(x-1)$ to obtain y_x.

Case 2, $\Delta y_x = f(y_x)$. This equation reduces to Case 2 of the previous section

Case 3, $\Delta y_x = f(x, y_x)$. This equation reduces to Case 5 of the precious section if Δy_x is replaced by $y_{x+1} - y_x$.

C. The Riccati Equation

At the close of the last chapter, it was indicated that the Riccati equation

$$y_x\, y_{x+1} + A\, y_{x+1} + B\, y_x + D = 0 \tag{6}$$

where A, B, and D are constants, was of considerable importance and analytical solutions were given. Various ways for solving Equation (6) graphically will be considered.

Method 1. Equation (6) can be placed in the form

$$y_{x+1} + \frac{B}{A+y_x}\, y_x = -\frac{D}{A+y_x} \tag{7}$$

The solution of this equation falls under the classification of Case 2 in Section A.

Method 2. In the previous chapter two different substitutions were employed for reducing the Riccati equation to a linear form. The first substitution, which produced a first order equation, is especially well adapted to graphical calculations. Thus, making the substitution

$$u_x = \frac{1}{y_x - k} \tag{8}$$

where k is given by

$$2k = -(A+B) \pm \sqrt{(A+B)^2 - 4D} \tag{9}$$

This value of k represents the intersection of the operating line from (7) and the 45° line. The substitution of (8) in (6) leads to

$$u_{x+1} + \frac{k+A}{k+B} u_x = -1/(k+B) \tag{10}$$

or

$$\frac{1}{y_{x+1} - k} + \frac{k+A}{k+B} \frac{1}{y_x - k} = -\frac{1}{k+B} \tag{11}$$

Thus if $1/(y_{x+1} - k)$ is plotted against $1/(y_x - k)$, a solution can be obtained according to the method of Case 1 in Section A.

Method 3. Solving for y_{x+1} in (6) gives

$$y_{x+1} = -(By_x + D)/(y_x + A) \tag{12}$$

Dividing the denominator into the numerator yields

$$y_{x+1} = (AB - D)/(y_x + A) - B \tag{13}$$

Adding A to each side

$$y_{x+1} + A = (AB - D)/(y_x + A) + (A - B) \tag{14}$$

In Figure 4A, the graphical solution of this equation is indicated for AB - D $<$ 0. The straight line represents a plot of $(y_{x+1} + A)$ vs $1/(y_x + A)$ while the rectangular hyperbola represents a plot of $(y + A)$ vs $1/(y + A)$.

[illegible]

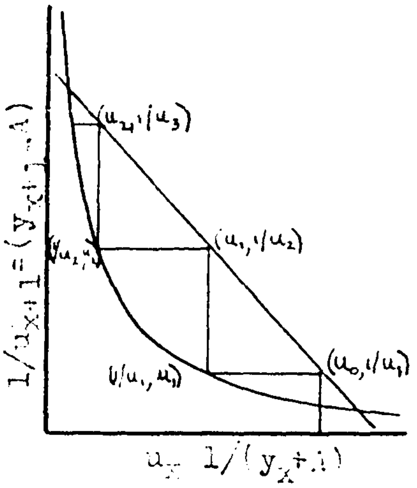


Figure 4A

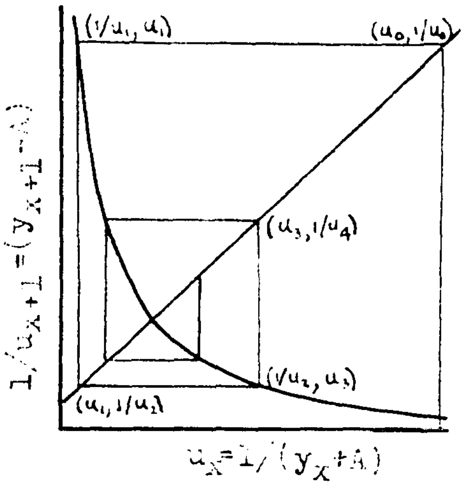


Figure 4B

If y_o is known $1/(y_o + A)$ can be calculated and $y_1 + A$ obtained from the straight line plot at point P. Knowing $y_1 + A$, the reciprocal $1/(y_1 + A)$ can be found on the hyperbola at Q. Proceeding in a stepwise manner, it is possible to obtain the successive values of y_x. In Figure 4B, the solution is shown for the case in which the slope of the operating line is positive. The order of the steps taken are indicated by 1, 2, 3, etc.

Method 4. If D is zero the equation can be placed in a form which falls under Case 1 of Section A. Dividing through (6) by $(By_x \, y_{x+1})$ and assuming $D = 0$ gives

$$\frac{1}{y_{x+1}} + \frac{A}{B}\,\frac{1}{y_x} = -\frac{1}{B} \qquad (15)$$

This equation is linear in $1/y_x$ and can be solved by the methods previously developed.

D. Equations of the Form $u_{x+1} - Pv_x = Q$

Equations of this form involve the three variables, u, v, and x. Before a solution for u and v in terms of x can be obtained, it is necessary to have a relationship between u and v. If u is a function of v as indicated in Figure 5, and the straight line $u - Pv = Q$ is plotted assuming P and Q to be constant, a stepwise solution for u and v in terms of x can be obtained. The points (u_1, v_1), (u_2, v_2) ... (u_x, v_x) lie on the curve $u = f(v)$ while the points (u_1, v_0), (u_2, v_1), ... (u_{x+1}, v_x) lie on the straight operating line. If v_0 is known, the point (u_1, v_0) is obtained from the operating line. Having u_1, v_1 is found on the curve $u = f(v)$. With v_1, u_2 may be found

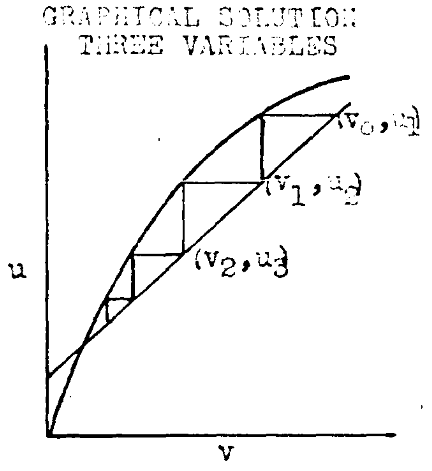


Figure 5

and so on until the desired values of u and v are obtained. The value of x is given by the number of points on the curve u = f(v).

If P and Q are not constant, the operating line is curved and may be obtained by the methods given in Section A.

E. Second Order Equations

Whereas the first order equations generally require one operating line, higher order equations require more than one operating line if solved according to the methods presented in this section. The second order equation to be considered may be placed in the linear form

$$y_{x+2} + P\,y_{x+1} + Q\,y_x = R \tag{16}$$

where P, Q, and R may be constants or functions of x and y_x. In Figure 6, the graphical solution of this equation for constant P, Q, and R is illustrated. In order to solve a second order equation for a particular case, it is necessary to have two known values of y_x such as y_0 and y_1. In Figure 6, the lines, (R - Qy) represented by AC, the 45 degree line, and a third line R - (Q + P)y represented by AB have been constructed. The difference between the lines AB and AC is Py corresponding to the second

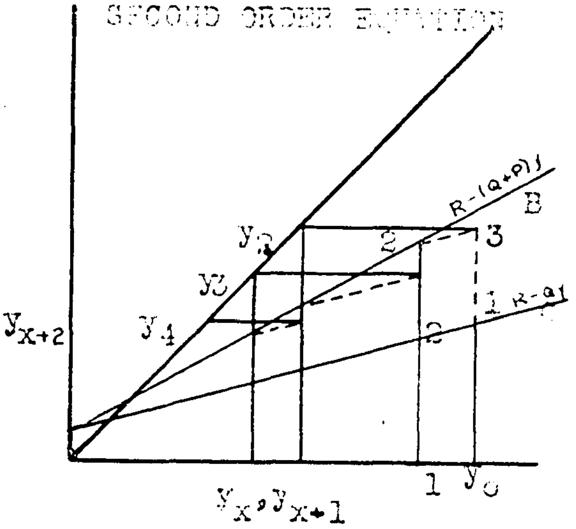


Figure 6

term in Equation (16). With y_o the point $(-Qy_o + R)$ is located on line AC at (1). The line (2-2) corresponding to $(-Py_1)$ is added to $(-Qy_o + R)$ by drawing a line parallel to AC from (2) to (3). The ordinate of point (3) is $(R - Qy_o - Py_1 = y_2)$. With y_2 and y_1, y_3 may be found in a similar manner. Continuing this construction, the relation between y_x and x may be obtained.

If P, Q, and R are not constant the lines AB and AC become curves. A discussion of the various cases which might arise would simply be an extension of the methods presented under Section A.

F. Third Order Equations

The methods developed in Section E can be employed for solving higher order equations of the same general type. Consider the equation

$$y_{x+3} + Py_{x+2} + Qy_{x+1} + Ry_x = S \qquad (17)$$

in which P, Q, R, and S are constants. Suppose that y_o, y_1, and y_2 are known values located as indicated in Figure 7. According to the way in which the lines are drawn Q and R are negative while P and S are positive. To obtain y_{x+3} as given by Equation (17), the distances (1-1) and (2-2) are added to give (1-3) and then (44) is subtracted to

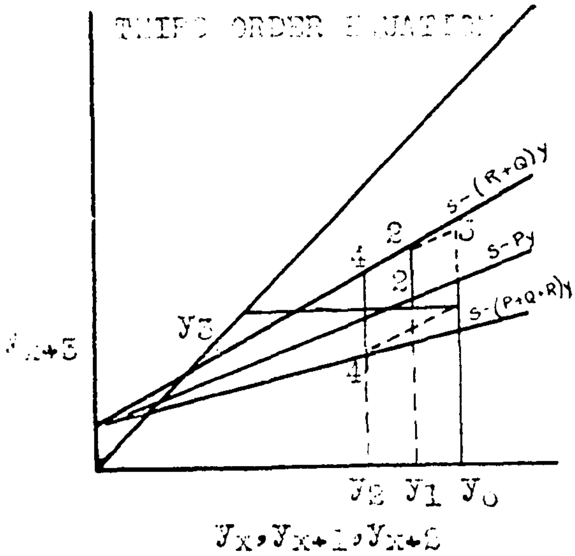


Figure 7

give point 5 whose ordinate is y_3. Continuation of this process will yield successive values of y_x.

NUMERICAL EXAMPLES

Appendix Part V

In order to illustrate the principles that have been presented in this dissertation, representative numerical examples will be presented. The following list contains a description of the problems to be presented with references to the mathematical principles presented:

Prob. No.	Type	Page	Mathematical Type	Page
1	Cocurrent extraction	27	Linear equation, const. coef.	164
2	Countercurrent washing with variable solvent ratio	63	Non-linear equation, graphical solution	175
3	Gas absorption, applications of H.E.T.P.	84	Linear Equation, const. coef.	164
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Problem 1

Statement: A solution containing 0.15 pound of acetic acid per pound of water is to be treated with isopropyl ether which is nearly immiscible with water for removal of the acid at 20°C. If the ether is pure and the acid concentration is to be reduced to 0.05 pound per pound of water, calculate the following:

1. Minimum amount of solvent required per pound of original solution
2. Number of stages required with an amount of solvent 40% greater than the minimum
3. Relative efficiency
4. Overall efficiency

The following phase data are available:[29]

Lbs. acid/lb. water, x	0.0197	0.0398	0.0827	0.1290	0.1790
Lbs. acid/lb. ether, y	0.00493	0.0103	0.0227	0.0379	0.0558

While the problem can be solved graphically, an analytical calculation based upon a constant value of the distribution coefficient is sufficiently accurate. As determined by the above data, k equals 0.289 lbs. acid/lb. water/lbs. acid/lb. ether.

Part 1. The minimum amount of solvent will be used when the final concentration coincides with the minimum concentration given in Equation (24) Chapter III. Solving for the overall solvent ratio, A, with $y_0 = 0$, yields

$$A = (1/H)\ \ln\ (x_0/x_i)$$

$$= (1/0.289)\ \ln\ (o.15/0.005) = 11.78$$

This represents the pounds of ether required per pound of water. The pounds of ether per pound of original solution is given by A'

$$A' = (0.85)(11.78) = 10.0$$

Part 2. As 40% greater than the minimum is to be employed and this solvent is to be divided equally between

N stages

$$A = 16.60 = Na$$

From Equation (8), with $y_o = 0$

$$N = \log (x_o/x_N)/\log (ak + 1)$$
$$= \log (30)/\log (6.289a + 1)$$

Solving these two equations simultaneously for N yields a value between 5 and 6, and as N must be integral, a value of 5 will be used. This requires a readjustment of a, A, and A' which gives 3.37, 16.85, and 14.32, respectively.

The relative efficiency can be calculated or more easily obtained from Figure 10, Chapter III, which yields $E_N = .977$.

The overall efficiency based upon Equation (29), Chapter III, becomes

$$e_N = (x_o - x_N)/x_o = 1 - 0.005/0.15$$
$$= .967$$

Problem 2[80]

Statement: One ton per hour of meal containing 800 pounds of oil and 50 pounds of benzene is to be washed in a countercurrent process with 1310 pounds of benzene containing 20 pounds of oil. The meal is to leave the process containing 120 pounds of oil per ton of meal after the benzene is distilled. The benzene retained by the meal varies with the solvent ratio as follows:[80]

Lbs. oil/lb. benzene, x	0	0.111	0.250	0.427	0.667	1.000
Lbs. benzene/lb.meal, b	0.5	0.505	0.515	0.530	0.550	0.571

Lbs. oil/lb. benzene, x	1.500	2.333
Lbs. benzene/ lb. meal, b	0.595	0.620

Calculate the following:

1. Concentration of extract
2. Concentration of liquid adhering to meal removed from process
3. Number of stages.

A schematic diagram of the process is shown on Figure 1. To obtain answers to parts 1 and 2, it is necessary to write several material balances.

<u>Overall solute balance</u>

Based upon one pound of meal

$$0.40 + 0.01 = 0.06 + w_1 x_1$$

$$w_1 x_1 = 0.35$$

<u>Overall solvent balance</u>

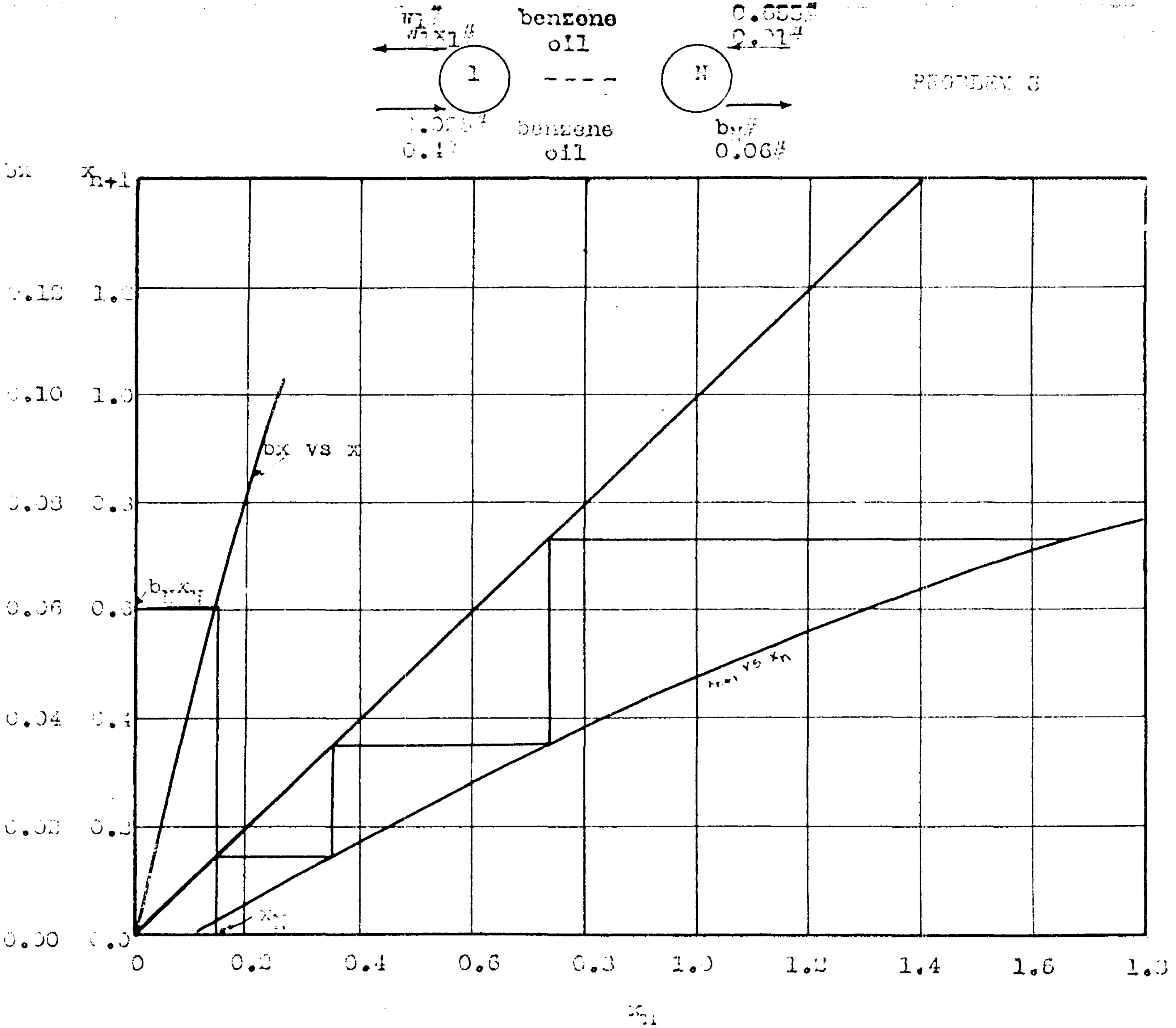
$$0.025 + 0.655 = w_1 + b_N$$

By obtaining b_N, w_1 and x_1 can be found. The quantity, b_N, may be obtained from the plot of bx vs x on Figure 1. As $b_N x_N = 0.06$, $x_N = 0.136$ and $b = 0.443$. This gives $w_1 = 0.237$ and $x_1 = 0.148$. The values of x_1 and x_N are the required values for parts 1 and 2.

To obtain the number of stages, the proper values are substituted for w_o, b_N, x_N, and y_o in Equation (71), Chapter III. This yields

$$x_{n+1} = \frac{b_n}{b_n + 0.212} x_n - \frac{0.05}{b_n + 0.212}$$

PROBLEM 3


w₁#
w_1x_1#
benzene
oil
1
N
0.035#
0.01#
0.026#
0.4#
benzene
oil
b_N#
0.06#
bx
x_{n+1}
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.0
0.2
0.4
0.6
0.8
1.0
1.2
bx vs x
$b_N x_N$
x_{n+1} vs x_n
x_N
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
x_n

This equation coupled with the b-x data is sufficient for construction of the graph of the operating line in Figure 1. Starting the stepping off process at x_1, continuing to x_N, produces three points on the equilibrium curve. Adding one to this for the first stage gives a total of four units required for the separation.

Problem 3

An ammonia-air mixture containing 6% ammonia by weight is to be scrubbed in a packed tower with pure water. The tower handles 2220 lbs./hour of gas and operates isothermally. The following information is available:

1. Water rate = 400 lbs./(hr.)(sq.ft.)
2. Tower diameter = 2 ft.
3. 99.6% of ammonia to be removed
4. Equilibrium data expressed by $y = 0.0047x^4$ where y = lbs. NH_3/lb. air, and x = lbs. NH_3/lb. water
5. H.E.T.P. = 9 ft.

Based on these conditions, calculate the required tower height.

In order to calculate the number of theoretical plates, it is necessary to obtain the quantities x_o, x_1, y_o, y_N, L, and G as defined in Chapter IV.

The inlet concentration y_o is given by

$$y_o = .06/.94 = 0.0638 \text{ lbs. } NH_3\text{/lb. air}$$

The exit concentration is

$$y_N = (1 - 0.996)(0.0638) = 0.000255 \text{ lbs. } NH_3\text{/lb. air}$$

PROBLEM 4

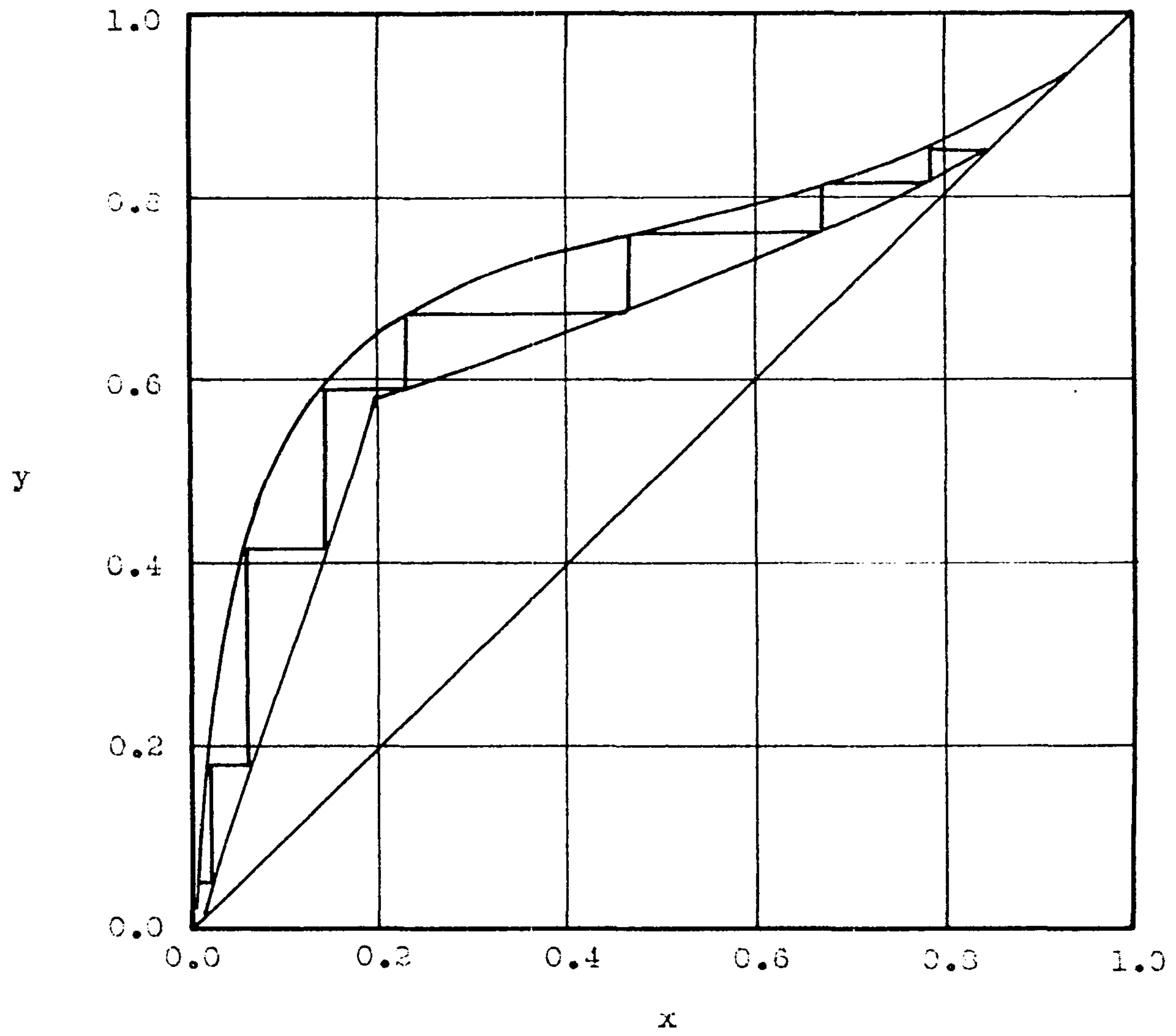


Figure 2

The exit liquid concentration can be obtained from a material balance. Thus

$$x_N = (G/L)(y_o - y_N)$$

$$= (2220/400)(0.996)(0.0639) = 0.111 \text{ lbs. } NH_3/\text{lb. water}$$

From Equation (22), Chapter IV

$$N = \frac{\log 0.000255/\left[0.0638 - (0.0047)(0.111)\right]}{\log (0.0047)(2200)/400}$$

$$= 1.145$$

Therefore the required height is given by

$$h = (1.145)(9) = 10.32 \text{ ft.}$$

Problem 4

An ethanol-water mixture containing 20% by weight of ethanol is to be fractionated into an overhead product and bottoms containing 85% and 1% by weight respectively of ethanol. Assuming that the feed is at its boiling point, the reflux is returned at its boiling point, the vapor rising from the pot is saturated, and that the molar latent heats are not constant, calculate the number of plates required for the separation. The reflux ratio at the top of the column is to be 2 pounds of reflux per pound of product. Neglecting all heat effects except the latent heats, Equations (19) and (20) of Chapter V and the graphical methods presented for the solution of these equations can be used. The equations for the enriching and exhausting sections become

$$x_n = \frac{854y_{n+1} - 0.85h_{n+1}}{854 - h_{n+1}}$$

$$x_{m+1} = \frac{854y_m + 0.0341h_m}{854 + 3.41}$$

In the first equation for the operating line in the enriching section, a value of y_{n+1} is assumed and x_{n+1} is taken from the equilibrium curve. Knowing x_{n+1}, the latent heat, h_{n+1}, can be obtained (assuming it varies linearly with the concentration) and a value of x_n calculated. A similar procedure may be used for the exhausting section. Calculations based on these procedures lead to the following values for the operating lines:

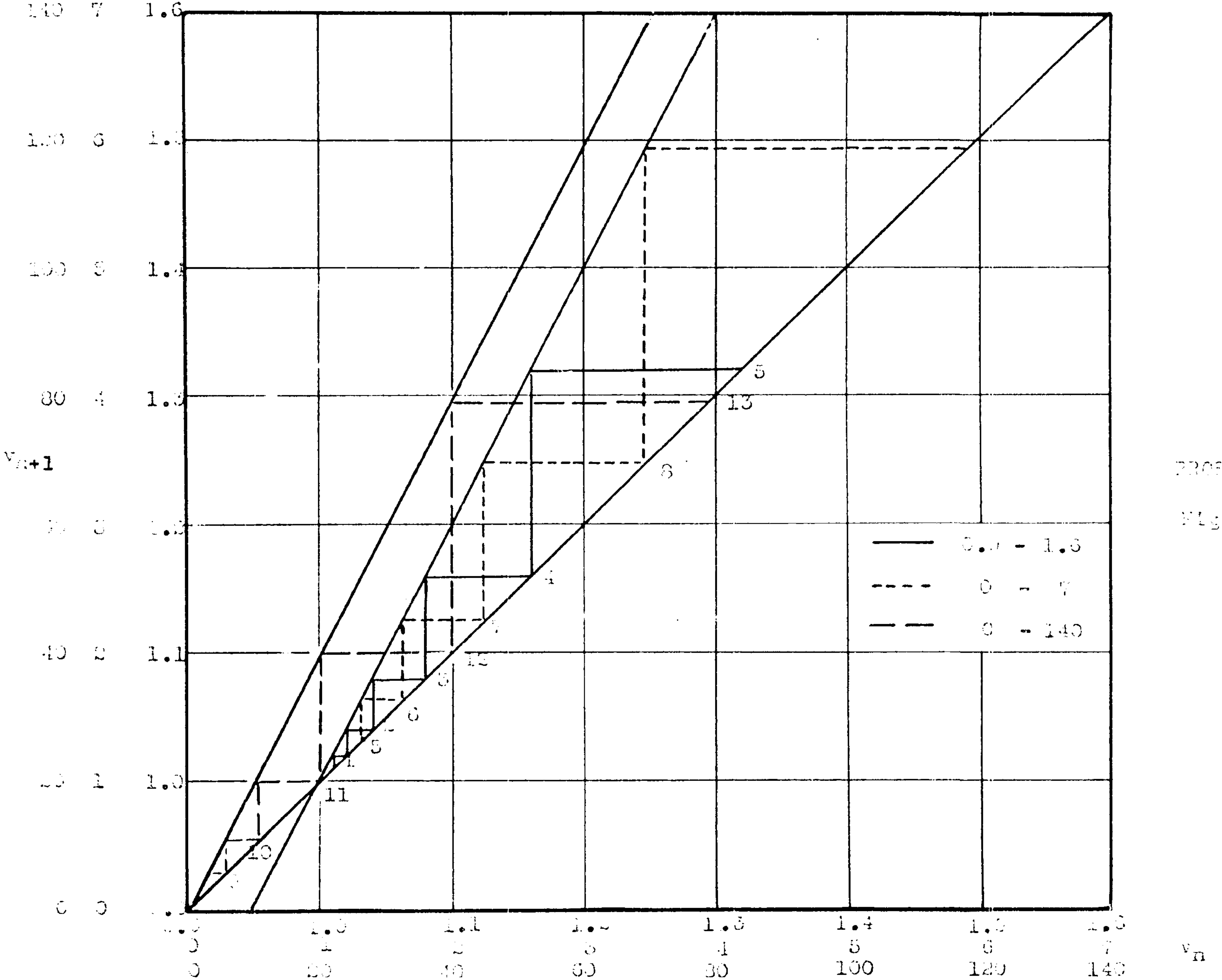
Enriching section

x_n	0.785	0.701	0.671	0.636	0.611	0.578	0.542	0.406	0.352	0.289	0.218	0.133
y_{n+1}	0.809	0.767	0.754	0.740	0.731	0.719	0.705	0.655	0.635	0.612	0.586	0.555

Exhausting section

x_{m+1}	0.034	0.066	0.091	0.107	0.123	0.135	0.158	0.176	0.190
y_m	0.085	0.185	0.263	0.312	0.360	0.398	0.463	0.516	0.555

A plot of these operating lines and the equilibrium curve are shown in Figure 2. Approximately 8 theoretical plates are required.



PROBLEM 3

Figure 3

Problem 5

Consider a hypothetical binary system consisting of A and B in which the relative volatility of A with respect to B is $\alpha = 2$. What is the minimum number of plates necessary to produce a separation in which the top product contains 99 mol per cent of A and the bottom product contains 1 mol per cent of A. Assume that the molal latent heats of A and B are equal.

For infinite reflux ratio, the binary equation for constant relative volatility reduces to

$$x_{n+1} = (\alpha - 1)\, x_n\, x_{n+1} + x_n$$

Placing this in a form equivalent to Equation (11) of Part IV of the appendix gives

$$v_{n+1} - 2v_n = -1$$

where $v_n = 1/x_n$. This equation can be solved either analytically or graphically. The graphical solution is indicated in Figure 3 and is equivalent to the solution presented in Part IV of the Appendix. The operating line is plotted with a slope of 2 and a y-intercept of - 1. The limits on v_n corresponding to x_n = 0.01 and 0.99 are v_n = 100, and 0.0101 respectively. Slightly more than 13 theoretical stages are required in the graphical solution. An analytical solution gives 13.24 utilizing Equation 49 in Chapter V.

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