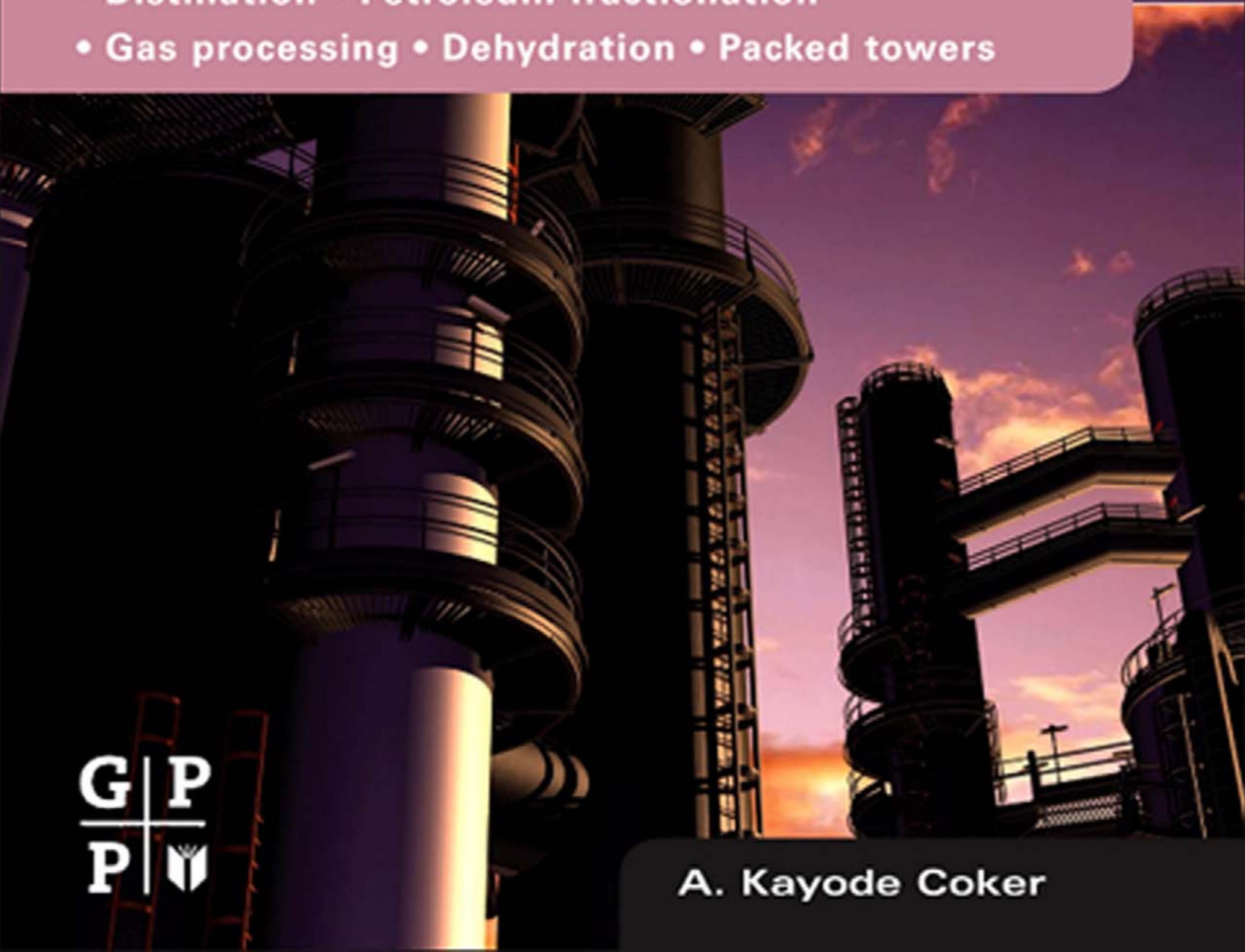
VOLUME 2 | FOURTH EDITION

Ludwig's Applied Process Design for Chemical and Petrochemical Plants

- Distillation • Petroleum fractionation
- Gas processing • Dehydration • Packed towers



A. Kayode Coker

He who bears within himself the firm volition for what is good, and strives to give purity to his thoughts has already found the way to the Highest. All else will then be added unto Him.

Keep the hearth of your thoughts pure, by so doing you will bring peace and be happy.

"In the Light of Truth" by Abd-ru-shin

In memory of Ernest E. Ludwig
(A great chemical engineer)

and

In loving memory of my parents
Mr. Gabriel Shodipo Coker and Mrs. Modupe Ajibike Coker
To my wife, Victoria
Love and thanks

Ludwig's Applied Process Design for Chemical and Petrochemical Plants

Volume 2. Fourth Edition

A. Kayode Coker

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Preface to the Fourth Edition

This complete revision of *Applied Process Design for Chemical and Petrochemical Plants, Volume II*, builds upon the late Ernest E. Ludwig's classic text to enhance its use as a chemical engineering process design manual of methods and proven fundamentals with supplemental mechanical and related data, nomographs and charts (some in the expanded appendices). Significantly expanded and thoroughly updated, this fourth edition contains new topics that will assist the engineer in examining and analyzing problems and finding design methods and mechanical specifications to secure the proper mechanical hardware to accomplish a process objective.

This latest edition includes improved techniques and fundamental design methodologies to guide the engineer in designing process equipment, such as distillation and absorption columns, and applying chemical processes to the properly detailed hardware (equipment). Like its predecessor, this edition continues to present updated information for achieving optimum operational and process conditions and avoiding problems caused by inadequate sizing and lack of internally detailed hardware. The various derived and proven equations have been employed in actual plant equipment design, process control and operator's training, and some of the most reasonable available to inexperienced and experienced engineers.

This book further provides both fundamental theories where applicable and directs application of these theories to applied equations essential in the design effort. This approach at presentation of design information serves well for troubleshooting distillation and absorption equipment/system performance analysis.

Chapter 10 on Distillation incorporates further insights in the theory of chemical engineering thermodynamics, azeotropic mixtures, and simulation of thermodynamic programs. It includes equilibrium flash calculations, Smoker's equations for determining the number of theoretical plates at constant relative volatility, enlarged batch separation fundamentals, the Ponchon–Savarit method of binary mixture with expanded fundamental theory, and additional multicomponent systems. It provides details to distillation operation involving side streams; expanding on the sizing of towers with valve trays, detailing steps in achieving optimum number of trays; troubleshooting predictive maintenance and controls of distillation columns, further illustrations of Gamma scanning and heat integration in distillation columns employing the grand composite curve, distillation sequencing and capital cost considerations of distillation columns.

Chapter 11 is a new chapter that covers fractionation of crude oil, gas processing, dehydration technique, hydrocarbon absorption and sour water stripping. This chapter provides case studies using Honeywell design simulation software (UniSim™) to perform simulation of these processes. It includes a developed computer program for designing dehydrating equipment and a glossary.

Chapter 12 is a new chapter that features enhanced distillation techniques, such as pressure swing distillation, vapor recompression, extractive distillation, reactive distillation and residue curve maps. In reactive distillation, thermodynamic and reaction mechanism involving the production of methyl acetate are provided. Further, the chapter includes a case study using Honeywell UniSim™ design simulation software to simulate the reaction in the production of methyl acetate at specified conditions.

Chapter 13 deals with mechanical hardware and internal specifications of distillation columns, and provides charts and specification forms that can be used to specify details required for manufacturing the hardware. A detailed distillation equipment diagram of a debutanizer unit with its specification can be accessed on the Elsevier website (www.elsevier.com).

Chapter 14 extensively reviews packed columns with various generalized pressured drop charts (GPDC), and provides detailed equations for sizing a packed column with random packings. The chapter includes a developed computer program for specifying the size of a column with different packing types. The chapter also provides new GPDCs for structured type packings, and simulation exercises using Honeywell UniSim™ software.

Software/Programs/Excel Spreadsheets/Charts

New additions to the fourth edition are Excel™ spreadsheet programs as worked examples, and developed computer programs (Absoft Fortran™) that use the Microsoft Runtime Windows Environment (MRWE) in various sections of the chapters. These programs are in executable format and Appendix I provides an illustration of its use.

Incorporated is Honeywell UniSim™ simulation design software to perform case studies and some worked examples in the text. The programs were developed using UniSim R360.1 and UniSim R370 build 13058 version and the text includes the solutions of these examples and case studies. Also, many vapor-liquid equilibrium (VLE) diagrams of binary mixtures have been developed using established literature data and Microsoft Excel spreadsheet program (eighty six figures). These diagrams are in appendix M and are readily available from the website.

A program on Conversion Table developed by Mr. Ahmed Mutawa from SASREF Co., is available. All of the above can be accessed from the Elsevier website (www.elsevier.com).

This volume includes new appendices J, K, L and M, new charts and updated references with corresponding websites for review. Appendix J contains figures of equilibrium K- values, appendix K reviews the description of Honeywell UniSim simulation software, appendix L contains simulation results of chapter 11 using UniSim simulation software and appendix M contains eighty six diagrams of vapor-liquid equilibrium (VLE) of binary mixtures.

The author assumes that the reader is an advanced undergraduate/graduate or equivalent chemical/process or related engineer, having a sound knowledge of the fundamentals of the profession. With this assumption, the author illustrates the techniques of design and mechanical details necessary for construction of processes. The aim of the process engineer is to ensure that results of his or her process calculations for equipment are specified in terms of something that can be economically constructed or selected from special designs or manufacturers. This edition follows the format of previous editions, and the concept is stressed to a reasonable degree in the various chapters.

The techniques of applied chemical plant process design continue to improve as the science of chemical engineering develops new and better interpretations of the fundamentals of chemistry, physics, metallurgy, mechanical engineering, and polymer/plastic science. Accordingly, this fourth edition presents additional reliable design methods based on sound experimental data, proven techniques developed by companies and individuals and groups considered competent in their subjects and who are supported by pertinent data. In many chemical and petrochemical processes, the designer will find design techniques adaptable to 75 to 80 percent of his/her requirements. Thus, an effort has been made to place this book in a position of utilization somewhere between a handbook and an applied teaching text. The present work is considered suitable to provide a practical guide to chemical process design for advanced undergraduate and graduate students in chemical engineering, practicing process engineers, and chemical/process engineers working in process development. The text can readily be used, if a general course in plant design is available to fill in the broader factors associated with overall plant layout and planning.

To access additional material accompanying this book, please visit: http://www.elsevierdirect.com/companions/9780750683661

On this companion website there are many useful Excel spreadsheets, additional appendices, examples and software.

Acknowledgments

This project is a culmination of three years of research, collating relevant and recent materials from organizations, institutions, companies and publishers. Soliciting for proofreaders has also been an important step in the editorial process. Emulating the work of the late E. Ludwig is a formidable task, and without the help of various individuals and organizations, this project would have been impossible to achieve.

I would like to express my deepest gratitude to Dr. Clive J. Mumford for volunteering, once again to review chapter 10. I am grateful for his analyses, criticisms and suggestions. His views on various aspects in the chapter and his attention to intricate details on some diagrams are greatly appreciated. Sincere thanks also to Dr. James Ryan for his analyses and comments and invaluable suggestions. His willingness in helping to review the chapter and provide succinct comments and guidance has indeed helped in enhancing the contents of this edition.

Sincere appreciation and thanks are given to Mr. Amjed El-Zubeir of Honeywell Process Solutions and also to Honeywell Process Solutions Amjed, thanks for your patience and help in reviewing chapter 11 and providing guidance on the simulation exercises. Sincere gratitude goes to Honeywell Process Solutions for granting permission to incorporate the use of UniSim design simulation software in the book. Dr. P. A. Bryant, a professor at Louisiana State University, contributed to updating the Absorption and Stripping section in this chapter.

I would like to record my appreciation and thanks to Lee Partin and Bob Huss of Eastman Co., USA for providing useful comments on chapter 12 and my sincere gratitude also goes to Professor James Fair of the University of Texas at Austin, USA for his expert opinions, comments and invaluable suggestions.

Mr. Joseph Rivera has provided some astonishing diagrams, seeking attention to details, and I am grateful for his professionalism. Thank you to Mr. Ahmed Mutawa for developing the Conversion Table program for this book.

Many organizations, institutions and companies such as Armfield Co. U.K., Gas Processors Suppliers Association (GPSA) USA, Eastman Co. USA, Honeywell Process Solutions, Sulzer ChemTech, Ltd. Switzerland, SASREF Co. Saudi Arabia, Absoft Corporation© USA, American Institute of Chemical Engineers, C*hemical Engineering magazine* by Access Intelligence, USA, and *Hydrocarbon Processing* have readily given permission for the use of materials, and their release for publication. I greatly acknowledge and express my deepest gratitude to these organizations.

I have been privileged to have met with nice people as Tim Calk and Phil Carmical, former editors of Gulf Publishing Company and Elsevier respectively. Phil first suggested Ludwig's classic work several years ago and defended my proposals in the presence of Elsevier's management to revise the three volumes of Ludwig. It's a formidable task, and thanks for your trust and encouragement, and to you Tim, I'm deeply grateful for your assistance since our work together on my second book project several years ago, and for your encouragement and assistance since.

I also wish to express my thanks to the Elsevier team: Jonathan Simpson, Melanie Benson, Naomi Robertson, Pauline Wilkinson, TNQ for typesetting, Calum Ross for copy-editing and Helen Stedman for proofreading. I am truly grateful for your assistance and help in the production of this volume.

Finally,

Without Him, I am nothing
Life is in God alone
In Him alone is the energy that lies in life.

A. Kayode Coker

BIOGRAPHY

A. Kayode Coker, Ph.D., Formerly, Chairman of Chemical & Process Engineering Department at Jubail Industrial College, Saudi Arabia, is a consultant for AKC Technology in England. He is a Chartered Chemical Engineer, a Chartered Scientist and a Fellow of the Institution of Chemical Engineers, U.K., (C.Eng, CSci, FIChemE). He is also a Senior member of the American Institute of Chemical Engineers (AIChE). He holds a B.Sc. honors degree in Chemical Engineering, a Master of Science degree in Process Analysis and Development, and a Ph.D. degree in Chemical Engineering, all from Aston University, Birmingham, U.K., and a Teachers' Certificate in Education at the University of London, U.K. He has directed and conducted short courses in both the U.K. and for SABIC industries in Saudi Arabia. His articles have been published in several international journals, and an author of three books in Chemical Engineering and a contributor to the Encyclopaedia of Chemical Processing and Design, Vol. 61. He was named as one of the International Biographical Centre (Headquarters in Cambridge, U.K.) LEADING ENGINEERS of the World, 2008.

Chapter 10

10

Distillation

Part 1: Distillation Process Performance

An important unit operation in the chemical process industries (CPI) is to separate a mixture into its components. This is termed diffusional or mass transfer. A typical chemical plant, as illustrated in the schematic flow sheet of Figure 10-1 will consist of both reaction and separation units. The raw materials are first purified in a separating unit and then fed to the reactor. A factor representing the efficiency with which raw materials are converted to products is the selectivity. This is given by moles of primary product produced divided by the moles of limiting reactant consumed. It can vary between 0 to 1, depending on the stoichiometry, the molar feed ratio of reactants, reactor temperature(s), reactor configuration, the catalyst if required etc. Any unreacted feed that remains is separated from the reaction products and recycled back to the reactor. The products are further separated and purified, before being marketed or used in subsequent processes. If the products contain "noncondensable" components, such as methane, hydrogen, argon, these must be separated by flash separation or similar process. Before flash separation, the process stream is usually cooled and depressurized. Afterwards, it may be fed to another separator to remove and purify useful components. Any remaining raw materials are recycled to the chemical process. The arrangement of Figure 10-1 is typical of many chemical processes, and is illustrated in Hydrocarbon processing magazine [257] and many textbooks [258-261].

The main techniques used for separations are distillation, absorption, liquid-liquid extraction, drying, leaching, crystallization and gas adsorption. These processes account for 40% to 70% of both the capital and operating costs in the CPI since they significantly affect energy consumption, product costs and manufacturing profits. About 43% of the energy consumed by the U.S. chemical process industries is used for separation processes [244].

The optimum method for a given process depends on the physical state (e.g. liquid, solid or gaseous) of the components such factors as the achievable degree of separation, the required volatility and toxicity of the components and purity criteria. In general, the choice of the key design parameters will need to balance costs incurred due to the raw materials, the reactor system and the separation processes. For example, in some cases, selectivity increases as conversion of the limiting reactant decreases. Increased selectivity means that less raw material is converted to by-product, thereby saving on raw material costs. However, as conversion decreases, more unreacted raw material must be separated from the product stream before being recycled to the reactor. The related costs increase quite steeply as conversion decreases. Conversely, reactor volume and its cost increases very sharply as conversion approaches unity. An optimum value therefore must balance raw material costs, reactor costs and separation costs. The chosen value will determine the stream temperature, pressure and composition as well as the size of both reactor and the separation system [262].

Although the art and science of distillation have been practiced for many years, studies continue to determine the best design procedures for multicomponent, azeotropic, batch, multidraw, multifeed and other designing. Some shortcut procedures are adequate for complex situations many systems, but have limitations in others.

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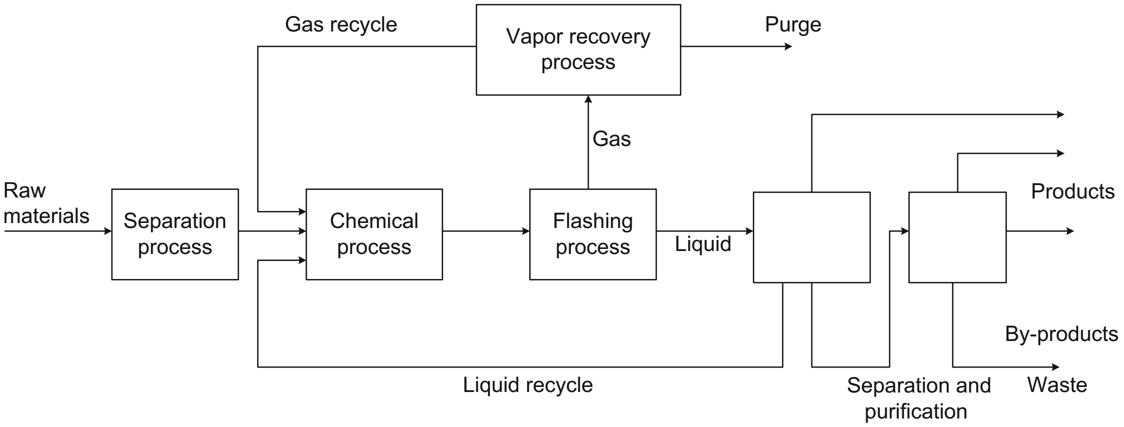


Figure 10-1 Schematic flow diagram of a chemical process.

The methods outlined in this chapter are considered adequate for the stated conditions, but there may be exceptions to these generalizations. The process engineer often "double checks" his or her results by using a second method to verify the "ball-park" results, or to check the findings of shortcut methods that lack fine detail.

Current design techniques using computer programs allow excellent prediction of performance for complicated multicomponent systems, such as azeotropic or high hydrocarbon content process streams as well as those which specify extremely high purity of one or more product streams. Of course, the more straightforward systems can be predicted with excellent accuracy. Such techniques allow examination of an array of variables; invaluable in selecting optimum or preferred conditions of operation.

The high manufacture costs associated with and installation of this equipment warrant the best design and checking techniques. The process diagram of Figure 10-2 will be used as reference for the systems and methods presented in this chapter Figure 10-2a shows fractionating columns in a chemical plant.

The right size of equipment should be chosen for the process. In addition, a choice between a stagewise or continuous, i.e., tray or packed process needs to be made. Trays act as individual stages and produce stepwise changes in concentration, whereas packed towers produce continous differential changes in concentration.

This chapter reviews the vapor-liquid equilibria of some representative mixtures, conditions of bubble of liquid mixtures and dew points of gaseous mixtures, isothermal equilibrium flash calculations, the design of distillation towers with valve trays, packed tower design, Smoker's equation for estimating the number of plates in a binary mixture, petroleum fractionation, gas processing, dehydration, reactive distillation, the computation of multicomponent recovery and minimum trays in distillation columns troubleshooting, distillation sequencing and heat integration of distillation columns. Computer programs and Honeywell UniSim simulation software are used to illustrate various examples in this volume.

10.1 Equilibria Basic Considerations

Distillation design is based on the theoretical premise that heat and mass transfer from stage to stage (theoretical) are in equilibrium [225-229]. Actual columns with actual trays are designed by establishing column tray efficiencies, and applying these to the theoretical trays or stages that have been determined by the calculation methods to be presented in later sections.

Dechman [109] illustrates a modification to the usual McCabe-Thiele diagram that allows for unequal molal overflow. Ryan [272] provides an alternative McCabe-Thiele diagram for relative volatilities below 1.25. The procedure of generating the revised McCabe-Thiele diagram is provided later in this volume.

Distillation, extractive distillation, liquid-liquid extraction and absorption are all techniques used to separate binary and multicomponent mixtures of liquids and vapors. Reference 121 examines approaches to determine optimum process sequences for separating components from a mixture, primarily by distillation. The most important assumption is that vapor and liquid are in equilibrium at each theoretical stage. Heat and mass transfer are complete and at equilibrium, meaning that the temperature of both phases are the same. The composition in each phase is uniform.

Vapor-liquid equilibrium data is therefore essential to adequately perform distillation calculations and so to correlate composition, temperature, and system pressure.

There are two types of systems: ideal and non-ideal. These terms apply to the simpler binary or two component systems as well as to the often more complex multicomponent systems.

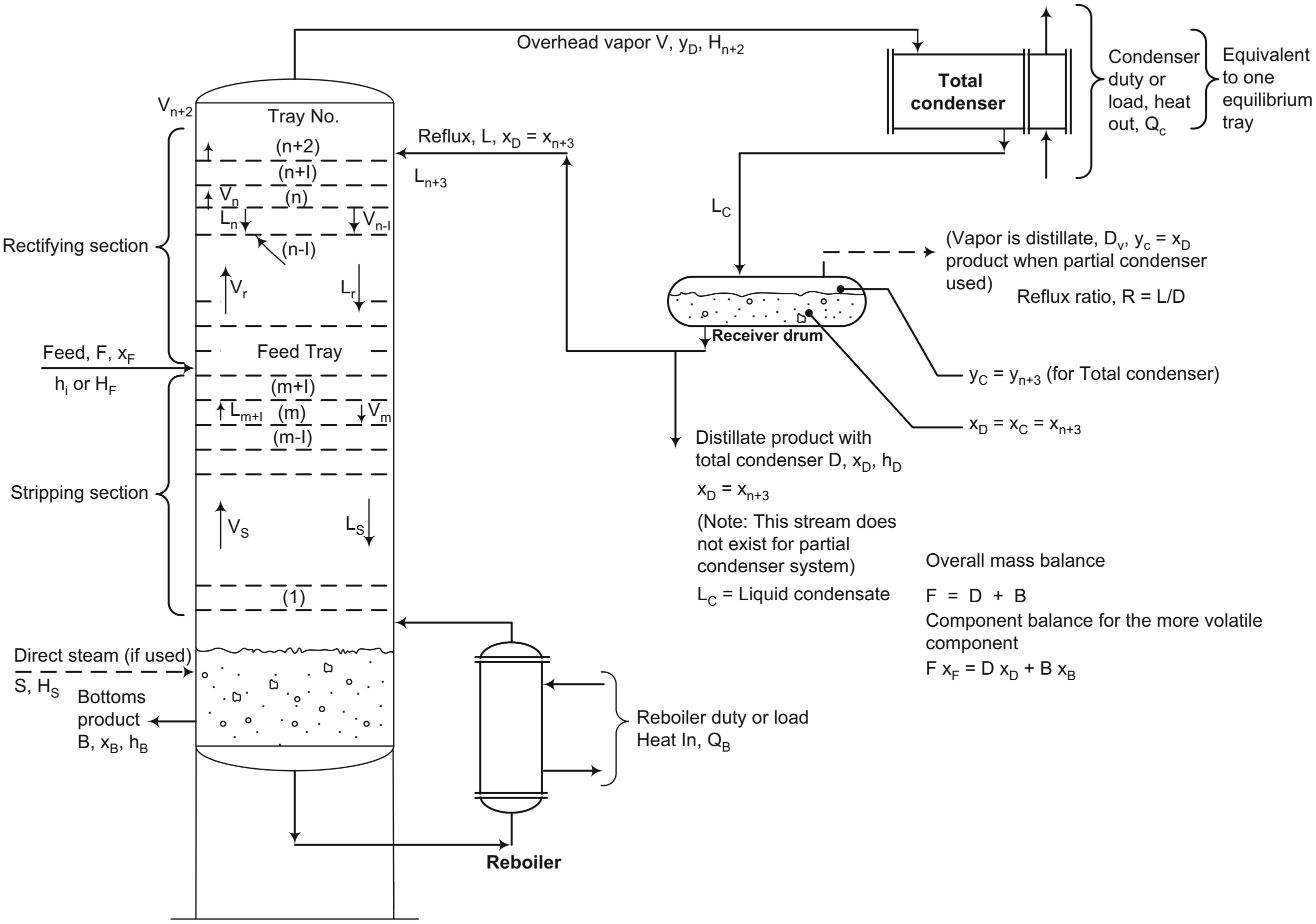


Figure 10-2 Schematic distillation tower/column arrangement with total condenser.

Figure 10-2a A photograph of fractionating columns showing De-methanizer, De-ethanizer, De-propanizer and De-butanizer units. (courtesy of Sulzer Chemtech Ltd.)

Figure 10-3 A photograph of Vapor-Liquid Equilibrium apparatus (courtesy of Saudi Shell-Aramco Refinery Co. (SASREF)).

Figure 10-3 shows a photograph of a typical vapor-liquid equilibrium apparatus with controls. Figures 10-4a and 10-4b show a photograph of a pilot plant distillation column and its schematics respectively; Figures 10-4c and 10-4d show a photograph of the column plates and its schematics with the direction of vapor and liquid flows.

Figure 10-5 illustrates a typical volatility vapor-liquid equilibrium curve for a particular component in a distillation separation. Usually the more volatile component (MVC) of the mixture is the one of interest.

10.2 Vapor-Liquid Equilibria

Vapor-liquid equilibria (VLE) data form the basis for evaluation of distillation operations; the most useful form of this data are boiling point diagrams. An ideal liquid or gas solution is one for which the activity coefficient is unity. There are few liquid systems that behave ideally at any pressure, and the assumption of ideal liquid behavior is generally correct only for members of homologous series that have similar molecular weights. At low pressure, the vapor phase of a mixture approaches ideal behavior and follows the ideal gas law. For these conditions, the fugacity is equated with the partial pressure and the standard state fugacity of the liquid becomes equal to the vapor pressure.

Figure 10-4a Photograph of a pilot plant distillation column (courtesy of Armfield, U.K.)

Figure 10-6a is a phase diagram for a mixture of methanol and water at a constant pressure of one atmosphere (101.3 kPa). The boiling points of pure methanol, the more volatile component (MVC) and pure water are 64.5°C and 100°C respectively. The lower curve represents the locus of the bubble point temperatures for all mixture of methanol and water. This curve is termed the saturated liquid (bubble point liquid); states of subcooled liquid lie below it.

The upper curve represents the locus of the dew-point temperatures; states of superheated vapor lie above it. This curve is termed the saturated vapor (dew-point vapor). Both of these curves originate at the boiling temperature of one constituent (100°C) and terminate at the boiling temperature of the other constituent (64.5°C). The two-phase region lies between these curves.

Assume that a mixture of methanol-water of the composition of point *z* (50 mole %) exists at a temperature of 70°C (represented by point *f* on Figure 10-6a). As this mixture is heated, it will remain liquid until point

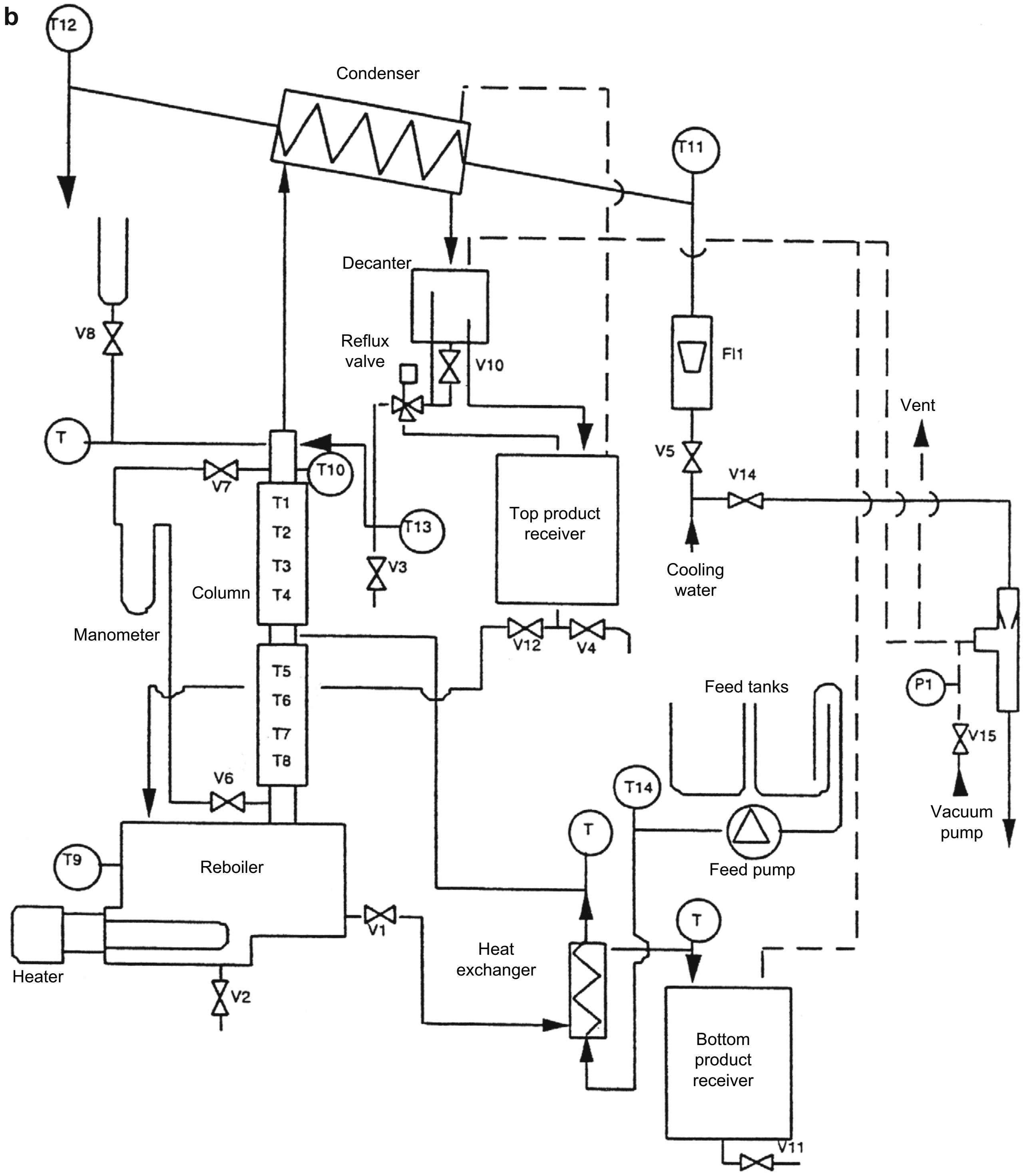


Figure 10-4b Schematics of a pilot plant distillation column (courtesy of Armfield, UK).

d (74°C) is reached, at which the first bubble of vapor is formed. This is the bubble-point temperature for a 50 mole % mixture at the system pressure of 1 atmosphere. The vapor phase composition at the bubble point is 78 mole % of methanol (point *e*). If heating of the mixture is continued, and the vapor generated is maintained in equilibrium with the liquid, the mixture reaches point *c* on the diagram, at which both vapor and liquid exist. The overall composition of the total mixture remains *z*, but the entire liquid portion will have a composition *x* (28 mole %), and the vapor portion will have a composition *y* (66 mole %). However, once a small amount of

Figure 10-4c Photograph of the column plates (courtesy of Armfield, U.K).

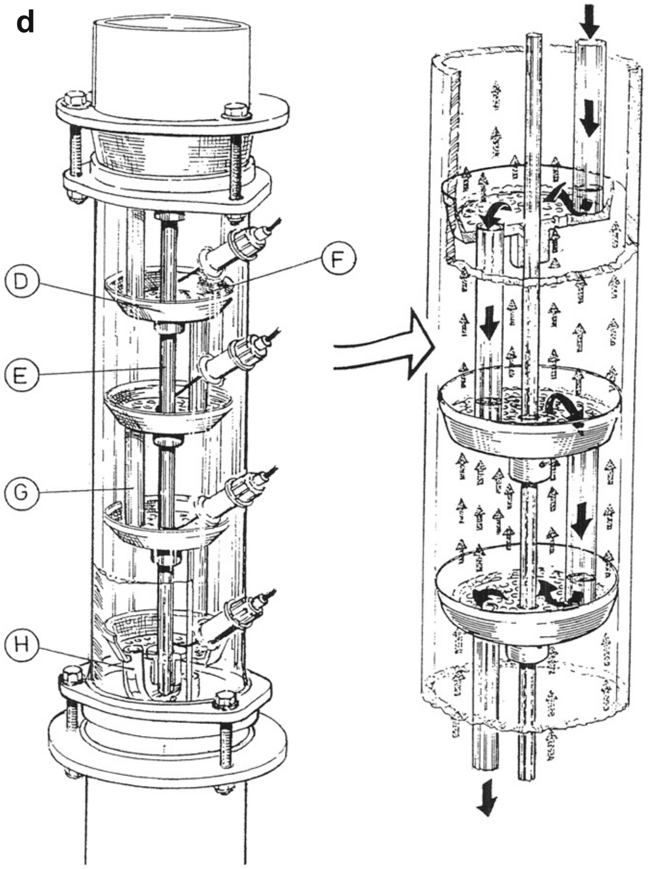


Figure 10-4d Schematics of a pilot plant distillation column plates showing liquid and vapor movements (courtesy of Armfield, UK). D = A plate; E = A Support rod; F = A weir; Liquid Movement ⬇; Vapour Movement ⇧; G = A downcomer; H = U-tube.

liquid has been vaporized, the remainder no longer contains 50 mole % methanol; it contains less, as the vapor produced has a higher concentration of this component. Consequently, the temperature of the system steadily rises as more and more liquid is vaporized, and the compositions of both phases change continuously during the process. The vapor and liquid phase compositions change as indicated by paths *bh* and *ag*, until the dew point is reached at point *g*, at which the last bubble of liquid disappears.

Correspondingly, consider an experiment started with 50 mole % mixture at 90°C (point *i*), where the mixture is 100% vapor. As the temperature is lowered, the dew-point temperature is encountered at 85°C at system pressure (point *g*), and the first drop of liquid is formed – which is about 15 mole % (point *h*). As the temperature of the system steadily decreases, more and more vapor is condensed, and the compositions of both phases change continuously as indicated by paths *ga* and *hb*, until the bubble point is reached at point *d*, where the last bubbles of vapor disappear.

The bubble and dew temperatures are composition-dependent. For example, the bubble temperature of a 28 mole % mixture is 77°C (point *b*) and the bubble temperature of a 10 mole % is 87°C (point *j*). A similar discussion to that given above could be presented for the dew temperatures of these systems. The bubble and dew-point discussions could also be presented on the pressure diagram at constant temperature as shown in Figure 10-6b; however the references are to the bubble and dew pressures. The horizontal dotted lines connecting coexisting compositions are tie lines, and the relative amounts of the vapor and liquid present can be determined by the material balances.

In Figure 10-6a, any point above the saturated vapor curve represents an all vapor mixture (superheated). Correspondingly, all points below the saturated liquid curve represent an all-liquid condition (subcooled), and points between the two curves correspond to a liquid-vapor mixture. Where the boiling points diagram is unavailable for a particular system, equilibrium relationships are obtained from vapor pressure data using Raoult's law and Dalton's law, where ideal behavior may be assumed. Recently, simulation software including Chemcad, Aspen plus, HYSYS, and UniSim (Honeywell)

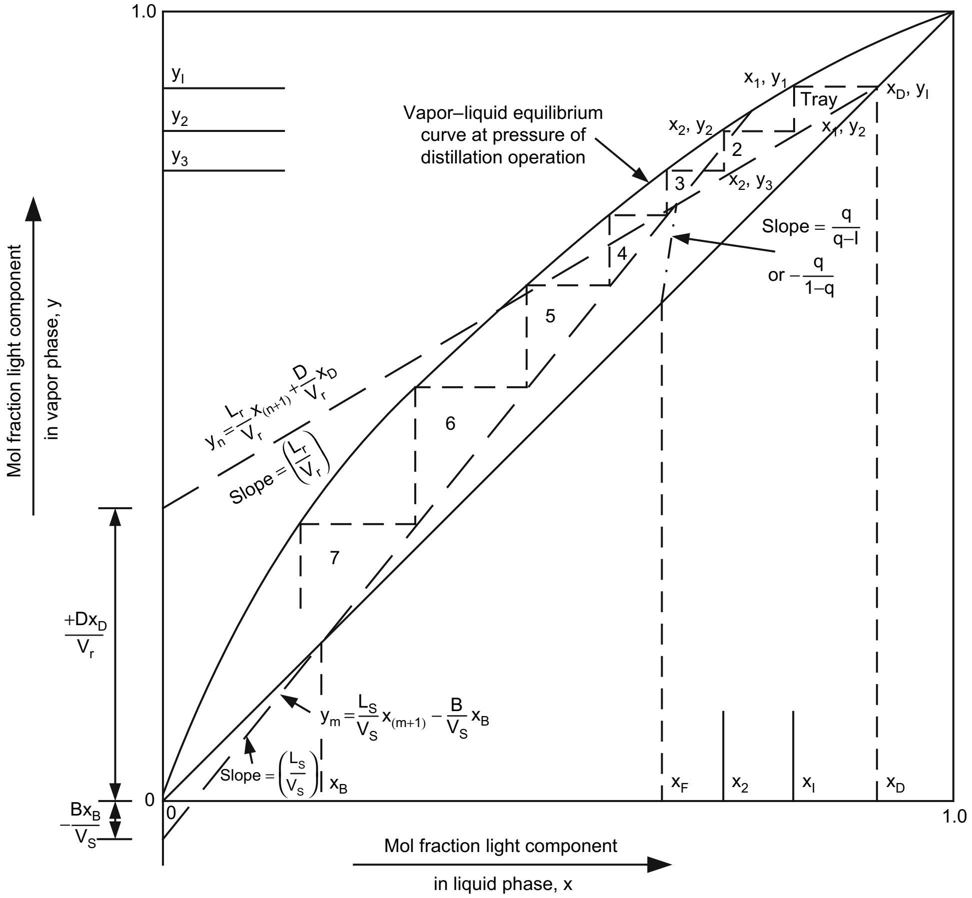


Figure 10-5 Continuous fractionation of binary mixtures; McCabe-Thiele diagram with total condenser.

have incorporated thermodynamic properties in their workbench and thus allowed phase diagrams of mixtures (T-x-y, x-y, etc) to be readily generated. Various VLE diagrams of mixtures have also been constructed using equilibrium data from Perry's Chemical Engineers' handbook [245] and chemical engineering thermodynamic texts [247, 248, 249 and 294]. These phase diagrams can be accessed in this volume, and are available

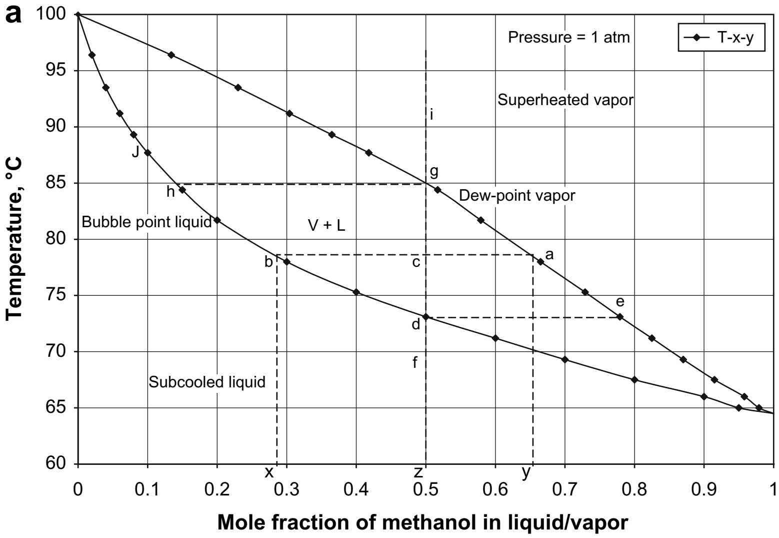


Figure 10-6a Phase diagram for the mixture of methanol and water at 1 atm.

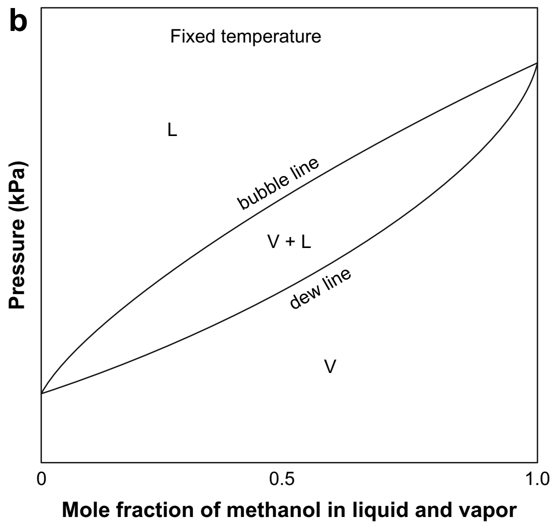


Figure 10-6b Illustration of a P-x-y diagram.

from the Elsevier companion web site. Figure 10-7 shows the VLE (x-y) diagram for methanol and water at one atmosphere, generated from the T-x-y data of Figure 10-6a. Figure 10-8 shows the enthalpy composition diagram for ethanol-water; Figure 10-8a shows the temperature composition diagram of ethanol-water with a minimum boiling azeotrope at 78.2°C, and Figure 10-7 forms the basis of the McCabe-Thiele diagram for calculation of continuous fractionation of binary mixtures; this will be presented in the graphical design of a distillation column.

The distillation process depends on the differences between the compositions of liquid and vapor phases of a mixture at equilibrium. This implies that the temperatures and pressures of the phases must be the same, and no composition change occurs over time. Equilibrium can be achieved after a long period of thorough mixing and contact between the two phases.

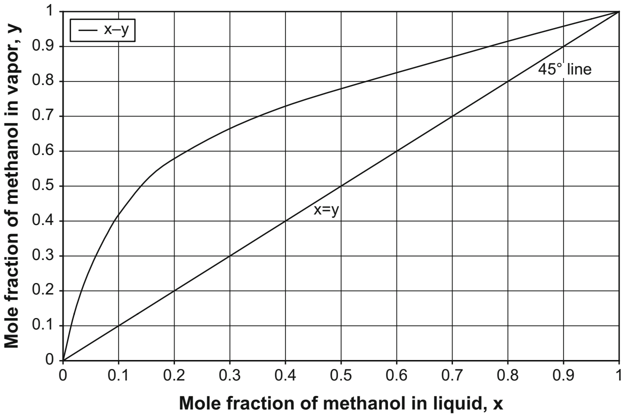


Figure 10-7 VLE diagram for the mixture of methanol and water at 1 atm.

An ideal gas is by definition one that follows the ideal gas laws:

$$PV = nRT \tag{10-1}$$

where

P = absolute pressure
V = total volume
n = number of moles of gas
R = ideal gas constant
T = absolute temperature

The conditions under which a given component or mixture approaches ideal behavior depend on its critical temperature and critical pressure. Other applicable principles of gas behavior are Dalton's law of additive pressures and Amagat's law of additive volumes. These are:

$$\pi = p_A + p_B + \ldots \tag{10-2}$$

and

$$V_T = V_A + V_B + \ldots.. \tag{10-3}$$

where

π = total system pressure
V_A = volume of component A
V_B = volume of component B
V_T = total volume of system
p_A = partial pressure of component A
p_B = partial pressure of component B
A, B = components

These laws are only applicable when conditions are such that each component and the mixture obey the ideal gas law. The equilibrium between two phases can be related to the equality of the chemical potential, and defined in terms of the Gibbs free energy as:

$$\mu_i = \left[\frac{\partial G}{\partial \mu_i}\right]_{T,P,n_i} = \overline{G}_i \tag{10-4}$$

where $\overline{G}_i$ is the partial molar Gibbs free energy. From the fundamental thermodynamic relation:

$$dG = V\,dP - S\,dT \tag{10-5}$$

The effect of pressure is mostly observed at constant temperature, as defined by:

$$dG = VdP(\text{constant T}) \tag{10-6}$$

where G is the molar Gibbs free energy and V is the molar volume. For a pure fluid of component i, substitution of Equation 10-1 into Equation 10-6 yields,

$$dG = RT\frac{dP}{p} = RT\,d(\ln P) \tag{10-7}$$

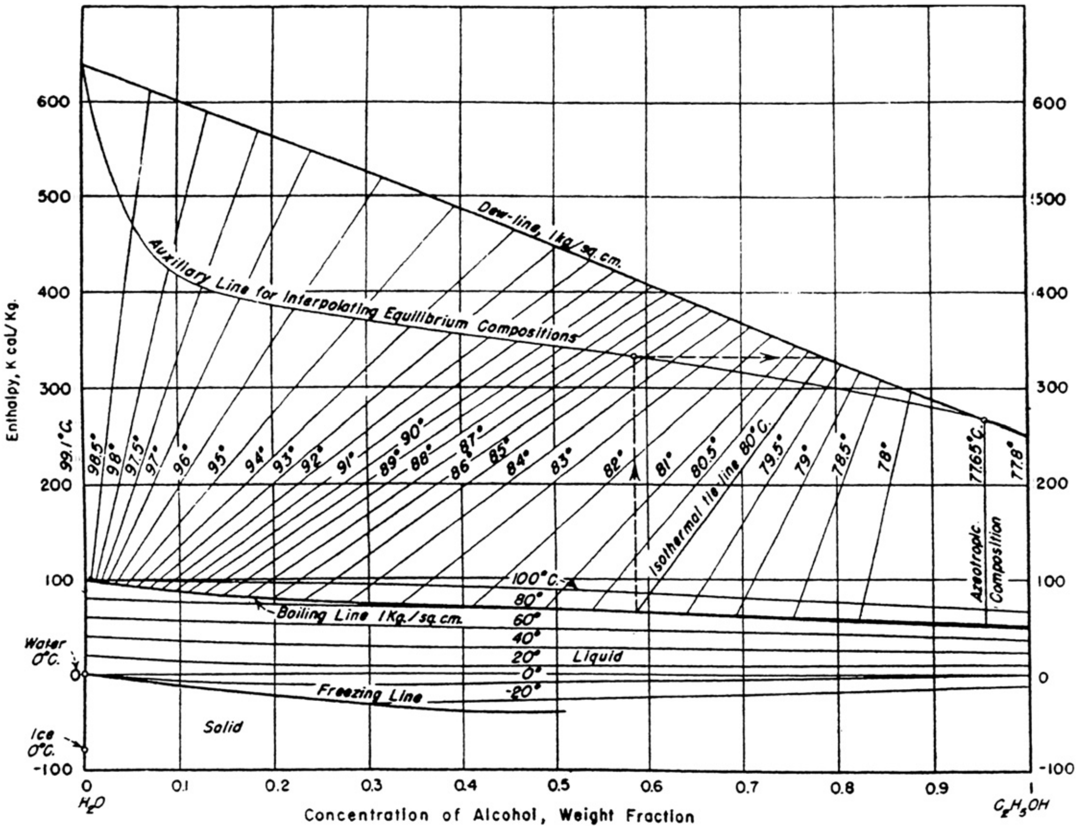


Figure 10-8 Enthalpy-composition diagram for ethanol-water at a pressure of 1 kg/cm^2 (Source: Bosnjakovic, Technishche Thermodynamik, T. Steinkopff, Leipzig, 1935).

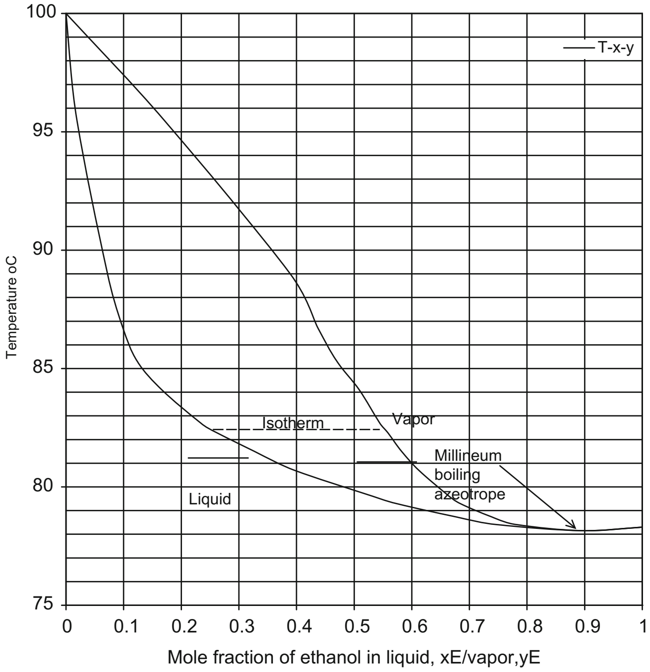


Figure 10-8a Temperature composition diagram for ethanol and water mixture at 1.013 kPa.

The free energy from Equation 10-7 is restricted to ideal gases, but can be modified to cover real fluids by introducing a new function, the fugacity. Equation 10-7 becomes:

$$dG_i = RT\, d(\ln f_i) \tag{10-8}$$

where f_i is the fugacity of pure i with units of pressure. The fugacity becomes equal to the pressure as the pressure approaches zero.

Thus:

$$\lim_{P \to 0} \frac{f_i}{P} = 1.0 \tag{10-9}$$

For a single component in a mixture at constant temperature, the fugacity is defined by:

$$d\overline{G}_i = RT\, d(\ln \overline{f}_i) \tag{10-10}$$

and:

$$\lim_{P \to 0} \frac{\overline{f}_i}{y_i P} = 1.0 \tag{10-11}$$

If a liquid mixture at temperature T and pressure P is in equilibrium with a vapor mixture at the same temperature and pressure, therefore at an equilibrium condition, with the Gibbs free energy minimized, the thermodynamic criterion will be:

$$\hat{f}_i^V = \hat{f}_i^L \quad (i = 1, 2\ldots\ldots\ldots N) \tag{10-12}$$

The vapor fugacity can be regarded as a corrected partial pressure, and given by:

$$\hat{f}_i^V = \phi_i^V (P\, y_i) \tag{10-13}$$

where

$\hat{f}_i^V$ = fugacity of component i in the vapor phase
ϕ_i^V = the vapor fugacity coefficient of species i, based on P, T, y_1, y_2.
N = number of chemical species
y_i = mole fraction of species i in the vapor phase.
P = system total pressure.

The fugacity of a component in a mixture depends on its temperature, pressure and composition. The fugacity $\hat{f}_i^L$, of any component i, in the liquid phase is related to the composition (mole fraction) of the component in that phase by:

$$\hat{f}_i^L = \gamma_i\, x_i\, f_i^{oL} \tag{10-14}$$

Similarly, the liquid fugacity can be regarded as a corrected vapor pressure by:

$$\hat{f}_i^L = \phi_i^L\, \gamma_i\, \Psi_i (x_i\, p_i^o) \tag{10-15}$$

where

ϕ_i^L = the liquid fugacity coefficient of species i based on T and p_i^o for pure liquids
Ψ_i = the Poynting correction factor for component i accounting for the effect of pressure on liquid phase fugacity
γ_i = the liquid phase activity coefficient of species i
x_i = mole fraction of species i in the liquid phase
$\hat{f}_i^L$ = fugacity of species i in the liquid phase
f_i^{oL} = the fugacity of species i in the reference (or standard state)

The fugacity of pure liquid i at temperature T and pressure P is given by:

$$f_i^{oL} = P_{vp,i}(T)\, \phi_i^s(T) \exp\left[\int_{P_{vp,i}}^{P} \frac{V_i^L(T,P)}{RT}\, dP.\right] \tag{10-16}$$

where

$P_{vp,i}$ = the vapor pressure of component i
ϕ_i^s = the vapor phase fugacity coefficient of pure saturated vapor of component i

The exponential term in Equation 10-16 is a correction factor for the effect of pressure on liquid-phase fugacity and is termed the **Poynting correction factor**. In Equation 10-16, V_i^L can be replaced by the partial molar volume of component i in the liquid solution for greater accuracy. For low to moderate pressure, V_i^L is assumed as the saturated liquid molar volume at the specified temperature. Equation 10-16 is simplified to give:

$$f_i^{oL} = P_{vp,i}\, \phi_i^s \exp\left[\frac{V_i^{Ls}(P - P_{vp,i})}{RT}\right] \tag{10-17}$$

Equation 10-17 is used to calculate the reference state fugacity of liquids. Any equation of state can be used to determine ϕ_i^s. For low to moderate pressures, the virial equation is the simplest to use. The fugacities of pure gases and gas mixtures are required for estimation of many thermodynamic properties, e.g. entropy, enthalpy and fluid phase equilibria. For pure gases, the fugacity is:

$$\ln f = \frac{1}{RT}\int_0^P V\, dP \tag{10-18}$$

The fugacity can be calculated from Equation 10-18 once the P-V-T behavior of the fluid is known from an equation of state. The fugacity coefficient is the ratio of the fugacity of a substance to its pressure. For a pure substance:

$$\phi = \frac{f}{P} \tag{10-19}$$

For the vapor phase, the composition is generally expressed by the mole fraction, y_i:

$$\phi_i = \frac{f_i^V}{y_i\, P} \tag{10-20}$$

For a mixture of ideal gases, $\phi_i = 1$. The fugacity coefficient, ϕ_i, depends on temperature and pressure. The fugacity coefficient is normalized, such that as $P \rightarrow 0$, $\phi_i \rightarrow 1$ for all components. At low pressure, ϕ_i is assumed to be unity. When the relationship between volume and pressure is known, either from direct measurement or from an empirical equation of state, changes in fugacity may be found by integration. Thus:

$$\ln \frac{f_2}{f_1} = \frac{1}{RT}\int_{P_1}^{P_2} V dP \tag{10-21}$$

Since $\phi = 1$ when $P = 0$, absolute values of the fugacity coefficient can be determined. Therefore:

$$\ln \phi = \ln \frac{f}{P} = \frac{1}{RT}\int_0^P \left(V - \frac{RT}{P}\right) dP = \int_0^P (Z - 1)\,\frac{dP}{P} \tag{10-22}$$

Methods for estimating fugacities of liquid and vapor phases are given by Reid et al. [246] and by Walas [247] and other thermodynamic texts [248, 249]. These also give detailed derivations of the above equations and their relationships. The various coefficients in these equations are illustrated below [94]:

ϕ_i^V	The vapor fugacity coefficient accounts for the effect of vapor non-ideality on vapor fugacity. It is usually estimated from an equation of state and is based on system temperature, pressure, and vapor mole fraction.
ϕ_i^L	The liquid fugacity coefficient accounts for the effect of vapor non-ideality on liquid fugacity. It is estimated in a similar manner to the vapor fugacity coefficient, but it is based on the system temperature and the pure component vapor pressure.
Ψ_i	The Poynting correction factor accounts for the effect of pressure on liquid fugacity. Since ϕ_i^L is evaluated at the vapor pressure of the pure component, Ψ_i is used to account for the difference between the pure component vapor pressure and the mixture pressure. This effect is small and can be neglected at low pressures, but is important at high pressures.
γ_i	The liquid activity coefficient corrects the liquid fugacity for the effect of composition. Its value depends on how similar the components are. For two similar components, such as an isobutane-normal butane mixture, the liquid activity coefficient is close to unity. If the components are different, activity coefficients deviate from unity.

10.3 Activity Coefficients

Dissimilar molecules repel each other resulting in activity coefficients (γ_i) greater than 1. So, in a mixture of unlike molecules (e.g. polar water molecules are mixed with nonpolar organic molecules) greater partial pressure is exerted, resulting in a positive deviation from ideality. Figures 10-9a and 10-9b show typical plots of activity coefficients γ_1 and γ_2 of the two components of such a mixture.

At $x_1 = 0$; the pure heavy component (component 2) has an activity coefficient (γ_2) of unity. The activity coefficient of the light component (component 1) will be large and is termed the infinite dilution activity coefficient γ_1^∞.

At $x_1 = 1$, the activity coefficient (γ_1) of light component (component 1) is unity. The activity coefficient of heavy component (component 2) is the infinite dilution activity coefficient γ_2^∞.

In the opposite case, where the molecules of the components attract each other, the activity coefficients will be less than 1 as the molecules will exert a lower partial pressure in a mixture than if they were pure. For example, when nitric acid is mixed with water, a lower pressure is exerted. Figures 10-9c and 10-9d show a typical activity coefficient dependence on composition for this case of negative deviation from ideality.

10.4 Excess Gibbs Energy-GE

The excess Gibbs energy $\overline{G}_i^E$ can be expressed by

$$\overline{G}_i^E = RT\ \ln \frac{\hat{f}_i}{x_i\, f_i} \tag{10-23}$$

For an ideal solution, the fugacity of each species is proportional to its mole fraction, i.e.:

$$\hat{f}_i = x_i\, f_i \tag{10-24}$$

where the proportionality constant is the fugacity of pure species i in the same physical state as the solution and at the same temperature, T and pressure, P. Equation (10-24) is known as the ***Lewis/Randall rule*** and it applies to each species in an ideal solution at all conditions of temperature, pressure and composition. The dimensionless ratio $\hat{f}_i/x_i\, f_i$ is the activity coefficient of species i in solution and is represented by γ_i. This is expressed by:

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i\, f_i} \tag{10-25}$$

Substituting Equation (10-25) into Equation (10-23) gives:

$$\overline{G}_i^E = RT\ \ln \gamma_i \tag{10-26}$$

These equations establish a thermodynamic relationship between the excess Gibbs energy and activity coefficient. For a binary system, the excess Gibbs energy is expressed by:

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \tag{10-27}$$

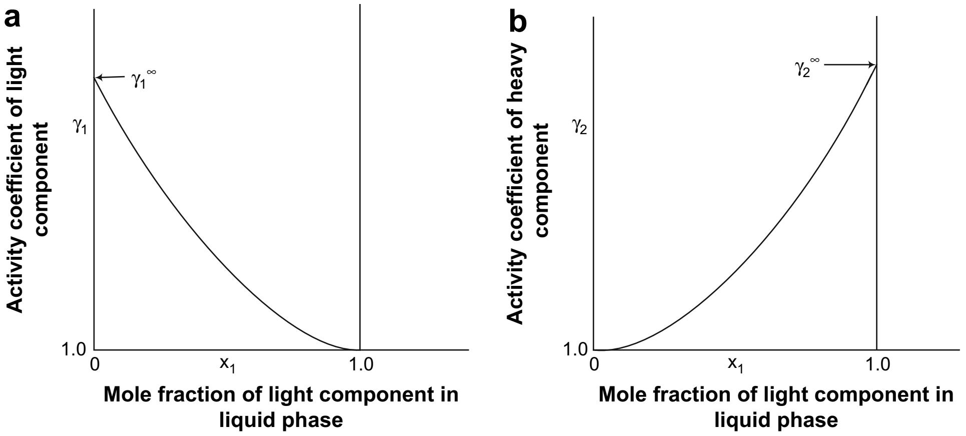


Figure 10-9a–b Composition dependence of activity coefficient showing positive deviation from ideality.

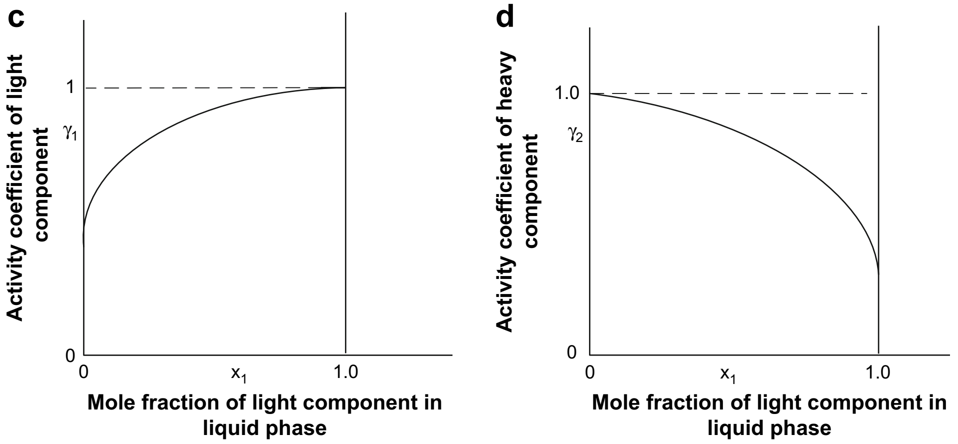


Figure 10-9c–d Composition dependence of activity coefficient showing negative deviation from ideality.

Table 10-1 shows the vapor-liquid equilibrium data for a methyl ethyl ketone (1) and toluene (2) mixture at 50°C, and Figures 10-10a, 10-10b, 10-10c and 10-10d respectively show plots of pressure against compositions of methyl ethyl ketone (1) in liquid and vapor phases, fugacity against the mole fraction of methyl ethyl ketone (1) in liquid phase and the liquid phase properties of methyl ethyl ketone (1) and toluene (2) mixture. These plots use the experimental data of Pena et al. [250] and have been developed using Excel spreadsheet (PhaseEquil.xls). The detailed explanation and derivation of GE and activity coefficient γ_i are given in standard chemical engineering thermodynamic texts [247, 248].

10.5 K- value

The equilibrium constant K can be defined as:

$$K_i = \frac{\text{Mole fraction of component i in vapor phase}}{\text{Mole fraction of component i in liquid phase}} \tag{10-28}$$

where the K-value is a measure of the tendency of component i to vaporize. It is a function of temperature, pressure and composition. At equilibrium, whenever two of these three variables are fixed, the third variable is also fixed. Therefore, the K value can be defined as a function of composition and pressure; composition and temperature or temperature and pressure. If the K-value is above 1.0, the component tends to concentrate in the vapor phase; correspondingly, below 1.0, the component tends to concentrate in the liquid phase. If the K-value is unity, the component concentration is equal in the vapor and liquid phases.

Combining Equations 10-12, 10-14 and 10-15 and 10-28 gives:

$$K_i = \frac{y_i}{x_i} = \frac{p_i^o}{P}\left[\frac{\phi_i^L\,\gamma_i\,\Psi_i}{\phi_i^V}\right] \tag{10-29}$$

At reasonably low pressures,

$$\frac{\phi_i^L}{\phi_i^V} \approx 1, \text{and } [\gamma_i \quad \Psi_i] \approx 1 \tag{10-30}$$

Table 10-1 VLE data for Methyl Ethyl Ketone (1)/Toluene (2) at 50°C.

P/kPa	x_1	y_1	$\hat{f}_1 = y_1 P$	$\hat{f}_2 = y_2 P$	γ_1	γ_2
12.30 (P_2^{sat})	0.0000	0.0000	0.000	12.300		1.000
15.51	0.0895	0.2716	4.212	11.298	1.304	1.099
18.61	0.1981	0.4565	8.496	10.114	1.188	1.026
21.63	0.3193	0.5934	12.835	8.795	1.114	1.050
24.01	0.4232	0.6815	16.363	7.697	1.071	1.078
25.92	0.5119	0.7440	19.284	6.636	1.044	1.105
27.96	0.6096	0.8050	22.508	5.542	1.023	1.135
30.12	0.7135	0.8639	26.021	4.099	1.010	1.163
31.75	0.7934	0.9048	28.727	3.023	1.003	1.189
34.15	0.9102	0.9590	32.750	1.400	0.997	1.268
36.09 (P_1^{sat})	1.0000	1.0000	36.090	0.000	1.000	

Source: M. Diaz, Pena, A. Crespo Colin and A. Compostizo, J. Chem. Thermodyn, vol. 10, pp 337–341, 1978.

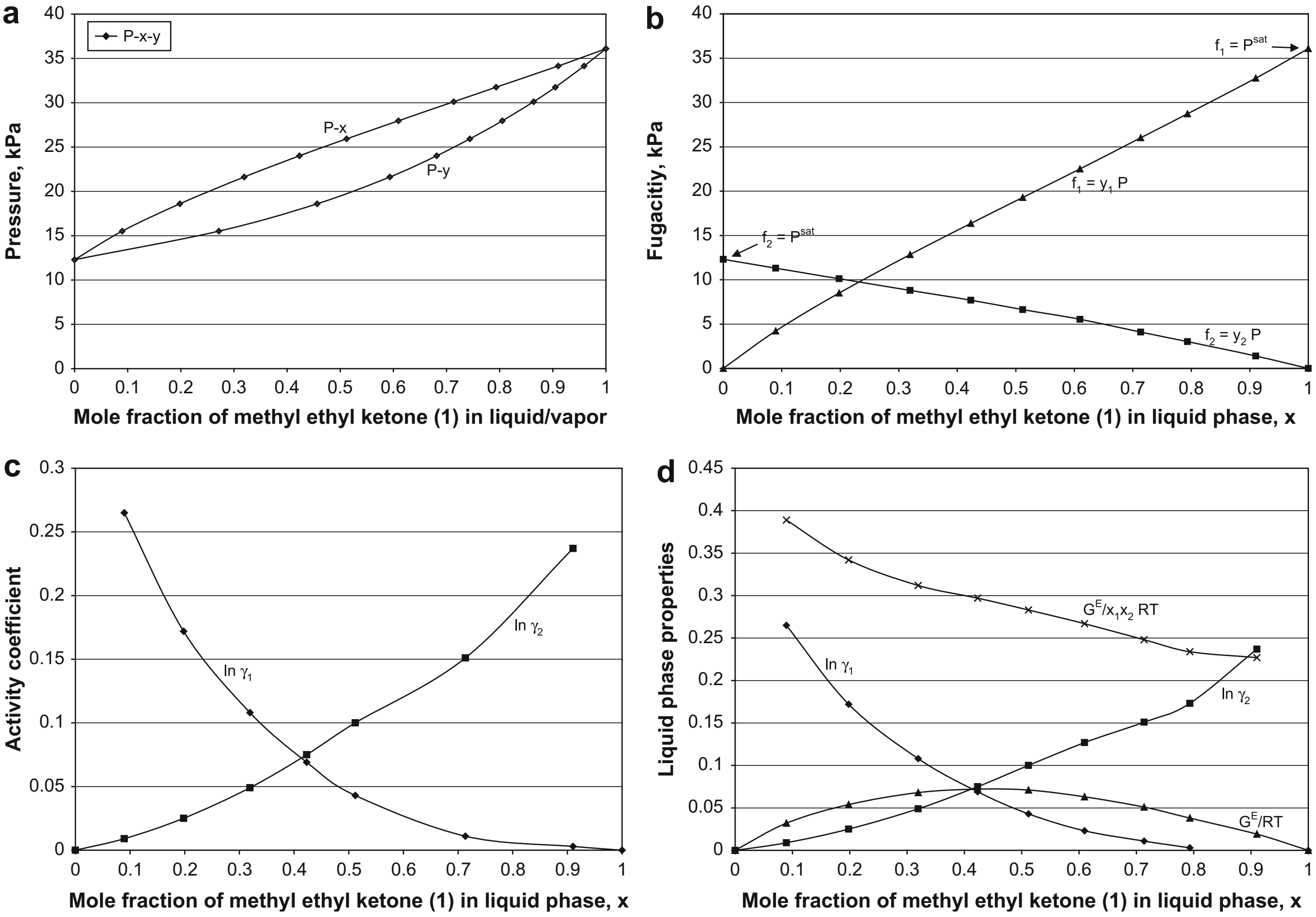


Figure 10-10 a. Phase diagram for methyl ethyl ketone (1) and toluence (2) mixture at 50°C. b. Fugacities of methyl ethyl ketone (1) and toluence (2) mixture at 50°C. c. Logarithms of the activity coefficients for methyl ethyl ketone (1) and toluene (2) at 50°C. d. Liquid phase properties for methyl ethyl ketone (1) and toluene (2) mixture at 50°C.

Equation 10-29 becomes:

$$K_i = \frac{p_i^o}{P} \text{ or } y_i\, P = x_i\, p_i^o \tag{10-31}$$

10.6 Ideal Systems

The separation performance of these systems (generally under conditions of low pressure, not close to critical point, and with similar components) can be predicted by Raoult's Law, applying to vapor and liquid in equilibrium. When one liquid is totally miscible in another, the partial pressure of each is decreased. Raoult's Law states that for any mixture, the partial pressure of any component will equal the vapor pressure of that component in the pure state multiplied by its mole fraction in the liquid mixture.

$$p_i = p_i^* x_i = P_i x_i \tag{10-32}$$

$$p_{ii} = P_{ii}\, x_{ii} \text{(for a second component, ii, in the system)} \tag{10-33}$$

where

p_i = partial pressure, absolute, of one component in the liquid mixture
x_i = mol fraction of component, i, in the liquid mixture
$P_i^\times = P_i$ = vapor pressure of component, i, in its pure state; $P^\times_{ii}$ similar by analogy

Many mixtures of liquids do not follow Raoult's Law, since this represents the performance of ideal mixtures. For systems which do follow the ideal gas law and Raoult's Law for the liquid, for each component,

$$y_i = \frac{P_i}{\pi} = \frac{p_i^* x_i}{\pi} \tag{10-34}$$

(Raoult's Law combined with Dalton's Law)
y_i = mol fraction of component, i, in vapor
π = system total pressure

Raoult's Law is not applicable as conditions approach critical, and for hydrocarbon mixtures accuracy is lost above about 60 psig [81]. Dalton's Law relates composition of the vapor phase to the pressure and temperature well below the critical pressure, i.e., total pressure of a system is the sum of the partial pressures of its components:

$$\pi = p_1 + p_2 + p_3 + \ldots \tag{10-2}$$

where

p_1, p_2, …= partial pressures of components, 1, 2, …

Therefore, for Raoult's and Dalton's Laws to apply, the relationship between the vapor and liquid compositions for a given component of a mixture is only a function of pressure and temperature, and is independent of the other components in the mixture.

For a binary system, Raoult's law states:

$$p_A = x_A\, p_A^o \tag{10-35}$$

where x_A is the mole fraction of component A, and p_A^o is the vapor pressure of component A.

For the vapor phase, Dalton's law can be expressed as:

$$p_A = \pi\, y_A \tag{10-36}$$

where y_A is the mole fraction of component A. Combining Equation 10-35 and Equation 10-36 gives:

$$x_A\, p_A^o = \pi\, y_A \tag{10-37}$$

$$K = \frac{y_A}{x_A} = \frac{p_A^o}{\pi} \tag{10-38}$$

where K is the equilibrium constant.

Few multicomponent systems exist for which completely generalized equilibrium data are available. The most widely available data are those for vapor-liquid systems, frequently referred to as vapor-liquid equilibrium distribution coefficients, or the K value. The K values vary with temperature and pressure, and a selectivity that is equal to the ratio of the K values is used. For vapor-liquid systems, this is referred to as the relative volatility, α. For a binary system:

$$\alpha_{A-B} = \frac{K_A}{K_B} \tag{10-39}$$

where

$$K_A = y_A/x_A \tag{10-40}$$

and

$$K_B = y_B/x_B \tag{10-41}$$

$$\alpha_{A-B} = \frac{y_A \cdot x_B}{x_A \cdot y_B} \tag{10-42}$$

For binary components:

$$x_A + x_B = 1 \tag{10-43}$$

or

$$x_B = 1 - x_A \tag{10-44}$$

and

$$y_A + y_B = 1 \tag{10-45}$$

or

$$y_B = 1 - y_A \tag{10-46}$$

Substituting Equations (10-44) and (10-46) into Equation (10-42) gives:

$$\alpha_{A-B} = \frac{y_A\,(1 - x_A)}{x_A(1 - y_A)} \tag{10-47}$$

Re-arranging Equation (10-47) in terms of y_A gives:

$$y_A = \frac{\alpha_{A-B}\, x_A}{[1 + (\alpha_{A-B} - 1)\, x_A]} \tag{10-48}$$

Equation 10-48 relates equilibrium compositions x_A and y_A in terms of the relative volatility. If it is assumed that α is independent of temperature and composition, Equation 10-48 becomes the equation of the equilibrium line or the x-y curve shown in Figure 10-7. This can be used to determine the compositions of vapor and liquid in equilibrium.

10.7 Henry's Law

Henry's Law applies to the vapor pressure of the solute in dilute solutions, and is a modification or Raoult's Law.

This can be stated as:

$$p_i = kx_i \tag{10-49}$$

where

p_i = partial pressure of the solute
x_i = mol fraction solute in solution
k = experimentally determined Henry's constant

Referring to Figure 10-5, Henry's Law would usually be expected to apply on the vaporization curve for about the first 1 in. of length, starting with zero, i.e. over the dilute end, whereas whereas Raoult's Law applies to the upper end of the curve.

Carroll [82] discusses Henry's Law in detail and explains its limitations. This constant is a function of the solute-solvent pair and temperature, but not the pressure, since strictly it is only valid at infinite dilution.

10.7.1 Strict Henry's Law

It is equal to the reference fugacity only at infinite dilution. From [82]:

$$x_i H_{ij} = y_i P \tag{10-50}$$

for restrictions of: $x_i < 0.01$ and $P < 200$ kPa

10.7.2 Simple Henry's Law

This can be stated as:

$$x_i H_{ij} = P \tag{10-51}$$

for restrictions of: $x_i < 0.01$, $y_i = 0$, and $P < 200$ kPa

$$K = \frac{y_i}{x_i} = \frac{p_i^*}{p} \tag{10-52}$$

where

H_{ij} = Henry's constant
x_i = mol fraction of solute component, i, in liquid
P = pressure, absolute
y_i = mol fraction of solute component, i, in vapor
y_j = mol fraction solvent component, j, in vapor
kPa = metric pressure

Care must be exercised that the appropriate assumptions are made in the evaluation. This requires experience and/or experimentation. Carroll [83] presents evaluation of Henry's Law constant for several multicomponent mixtures; (1) a non-volatile substance (such as a solid) dissolved in a solvent, (2) a gas in a solution of aqueous electrolytes, (3) mixed electrolytes, (4) mixed solvents, i.e., a gas in equilibrium with a solvent composed of two or more components, (5) two or more gaseous solutes in equilibrium with a single solvent, (6) complex, simultaneous phase and chemical equilibrium.

10.8 K-Factor Hydrocarbon Equilibrium Charts

Hydrocarbon systems are amongst those for which most data have been developed. See following paragraph on K-factor charts. For systems of chemical components where such factors are not developed, the basic relation is:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i}{\phi_i}\frac{p_i^*}{P} \tag{10-53}$$

For ideal systems: $\gamma_i = \phi_i$
where

K_i = mol fraction of component, i, in vapor phase in equilibrium divided by mol fraction of component, i, in liquid phase in equilibrium
K_i = equilibrium distribution coefficient for system's component, i
p_i^* = vapor pressure of component, i, at temperature
P = total pressure of system = π
γ = activity coefficient
ϕ = fugacity coefficient

The concept of ideality is usually a good approximation for close boiling components of a system, where the components are all of the same “family” of hydrocarbons or chemicals; for example a mixture of paraffin hydrocarbons. When “odd” or non-family components are present, or if the system has a wide boiling range the probability of deviations from non-ideality becomes greater.

Ideal conditions are often assumed for preliminary calculations, followed by more rigorous design methods. These may be completely satisfactory, particularly when the activities of the individual components approximate to 1.0. Many process components do not however conform to the ideal gas laws, and erroneous results will be obtained if this behavior is assumed to hold. Errors are not serious when the deviation from ideal is not significant. When data are available to confirm the ideality or non-ideality of a system, then the choice of approach is much more straightforward.

K-factors for vapor–liquid equilibrium ratios are usually associated with various hydrocarbons in the presence of some common impurities as nitrogen, carbon dioxide, and hydrogen sulfide [48]. The K-factor is (Equation 10-40) the equilibrium ratio of the mole fraction of a component in the vapor phase divided by the mole fraction of the same component in the liquid phase. K is generally considered a function of the mixture composition, in which a specific component occurs, plus the temperature and pressure of the system at equilibrium.

The Gas Processors Suppliers Association [79] provides a detailed background development of the K-factors and the use of convergence pressure (see Figures 10-11a – 10-11d), i.e. the pressure of system at a temperature when vapor-liquid separation is no longer possible. Convergence pressure alone does not represent a system’s composition effects in hydrocarbon mixtures, but the concept does provide a rather rapid approach for systems calculations and is used for many industrial calculations. These are not well adapted for very low temperature separation systems. Figure 10-11d shows the chart of equilibrium constant for a methane – ethane binary system.

Charts of reference [79] are for binary systems unless noted otherwise. The convergence pressure method can usually predict equilibrium composition with reasonable accuracy for vapor and liquid phases around the convergence pressure and corresponding temperature. The convergence pressure is that pressure where all proportion of vapor and liquid focus to a point (converges). Generally, vapor and liquid cannot coexist at a pressure higher than the convergence pressure. The K values of the components (binary) approach 1.0. Typically, the convergence pressure is higher than the critical pressure of either of the pure components [295].

The convergence pressure is generally a function of the liquid phase, and assumes that the liquid composition is known from a flash calculation using a first estimate for convergence pressure, and is usually the critical pressure of a system at a given temperature. The following procedure is recommended by Reference 79:

Step 1. Assume the liquid phase composition or make an approximation. (If there is no guide, use the total feed composition).

Step 2. Identify the lightest hydrocarbon component that is present in at least 0.1 mole % in the liquid phase.

Step 3. Calculate the weight average critical temperature and critical pressure for the remaining heavier components to form a pseudo binary system. (A shortcut approach suitable for most hydrocarbon systems is to calculate the weight average T_c only).

Step 4. Trace the critical locus of the binary mixture consisting of the light component and pseudo heavy component. When the averaged pseudo heavy component is between two real hydrocarbons, an interpolation of the two critical loci must be made.

Step 5. Read the convergence pressure (ordinate) at the temperature (abscissa) corresponding to that of the desired flash conditions, from Figure 10-11a [79].

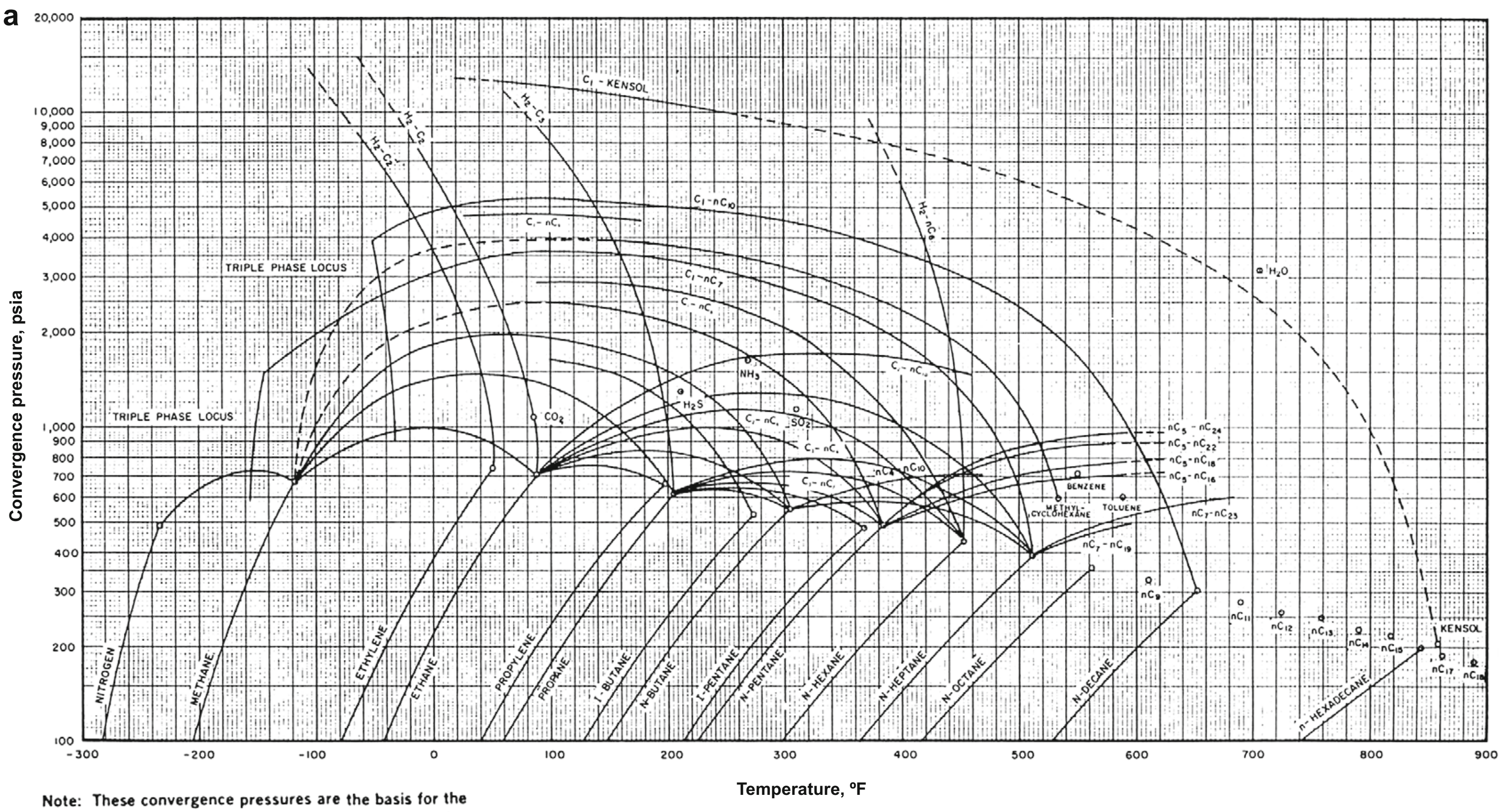
Step 6. Using the convergence pressure determined in Step 5, together with the system temperature and system pressure, obtain K-values for the components from the appropriate convergence-pressure K-charts.

Step 7. Make a flash calculation with the feed composition and the K-values from Step 6.

Step 8. Repeat Steps 2 through 7 until the assumed and calculated convergence pressures agree within an acceptable tolerance.

For n-pentane at convergence pressure of 3,000 psia (nearest chart), the K-value reads 0.99 (see Figure 10-11c) and other K-values are shown in Appendix J. The DePriester charts [80] provide a reasonable check on this (Figures 10-12a, b, c and d). Interpolation between charts of convergence pressure can be calculated, depending on how close the operating pressure is to the convergence pressure. The K-factor charts (or K-values) do not change rapidly with convergence pressure, P_k (psia) [79].

For light hydrocarbons, approximate K values can be determined from the nomographs prepared by DePriester, and as illustrated in Figures 10-12a, b, c and d for different temperature ranges. If temperature



Note: These convergence pressures are the basis for the convergence charts. Later data do not necessarily agree.

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Figure 10-11a Convergence pressures for hydrocarbons (critical locus). Used permission, Gas Processors Suppliers Association Data Book, 12th Ed., V. 1 and 2 (2004), Tulsa, Okla.

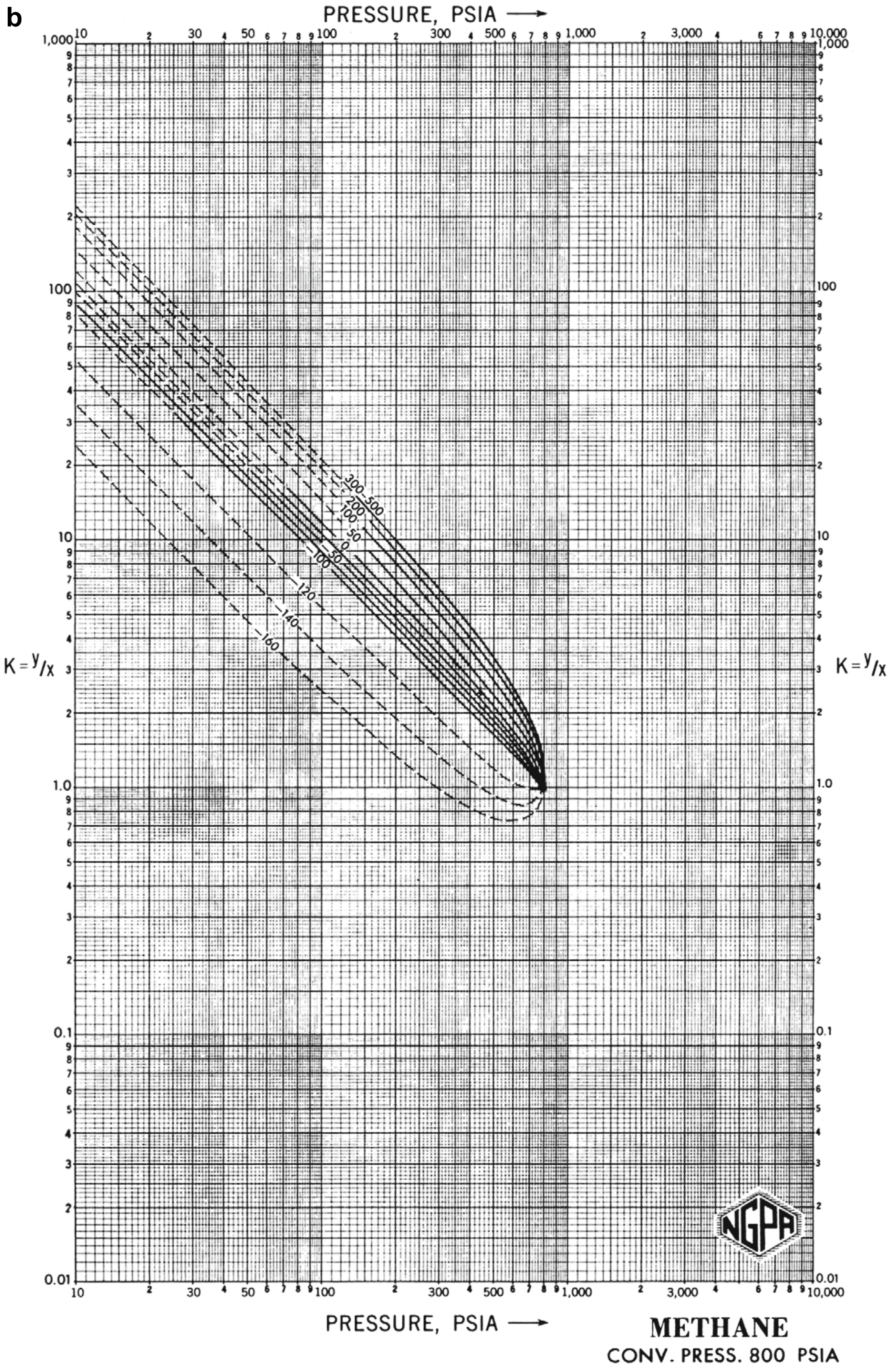

Figure 10-11b Pressure vs. K for methane (CH_4) at convergence pressure of 3000 psia (20,700 kPa). Used by permission, Gas Processors Suppliers Association Data Book, 12th Ed., V. 1 and 2 (2004), Tulsa, Okla.

c

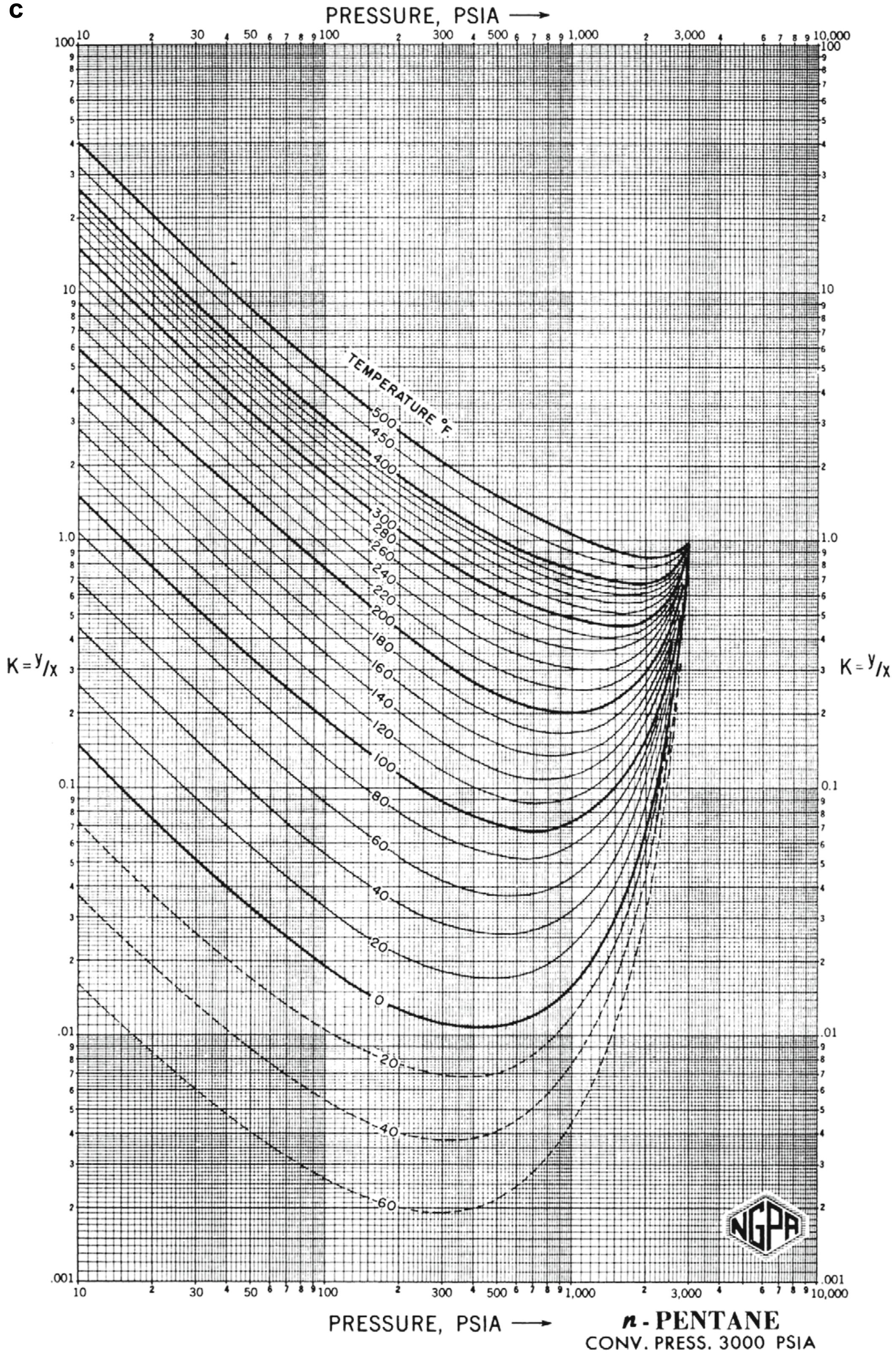

Figure 10-11c Pressure vs. K for n-pentane (n-C_5H_{12}) at convergence pressure of 3000 psia (20,700 kPa). Used by permission, Gas Processors Suppliers Association Data Book, 12th Ed., V. 1 and 2 (2004), Tulsa, Okla.

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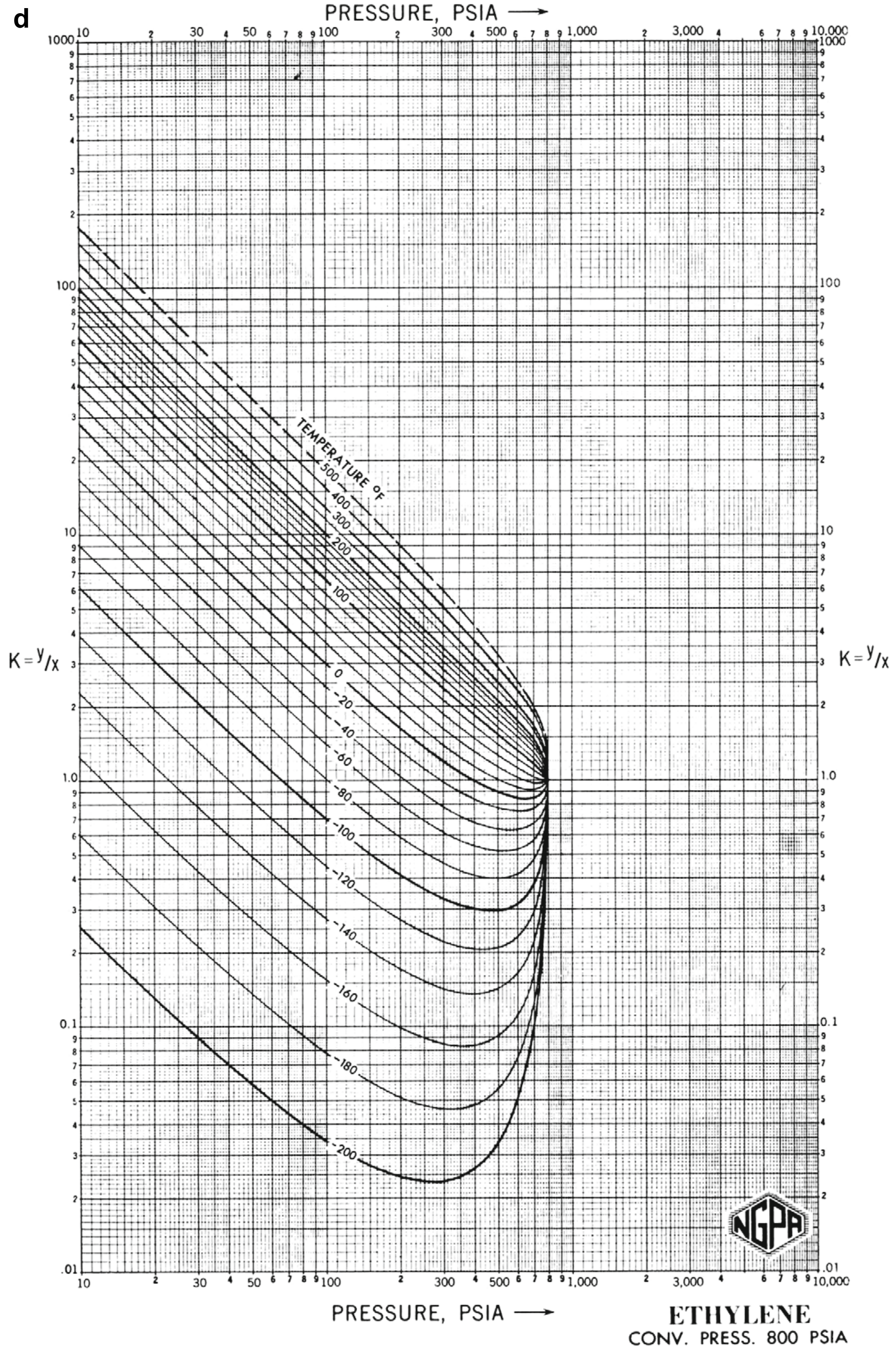
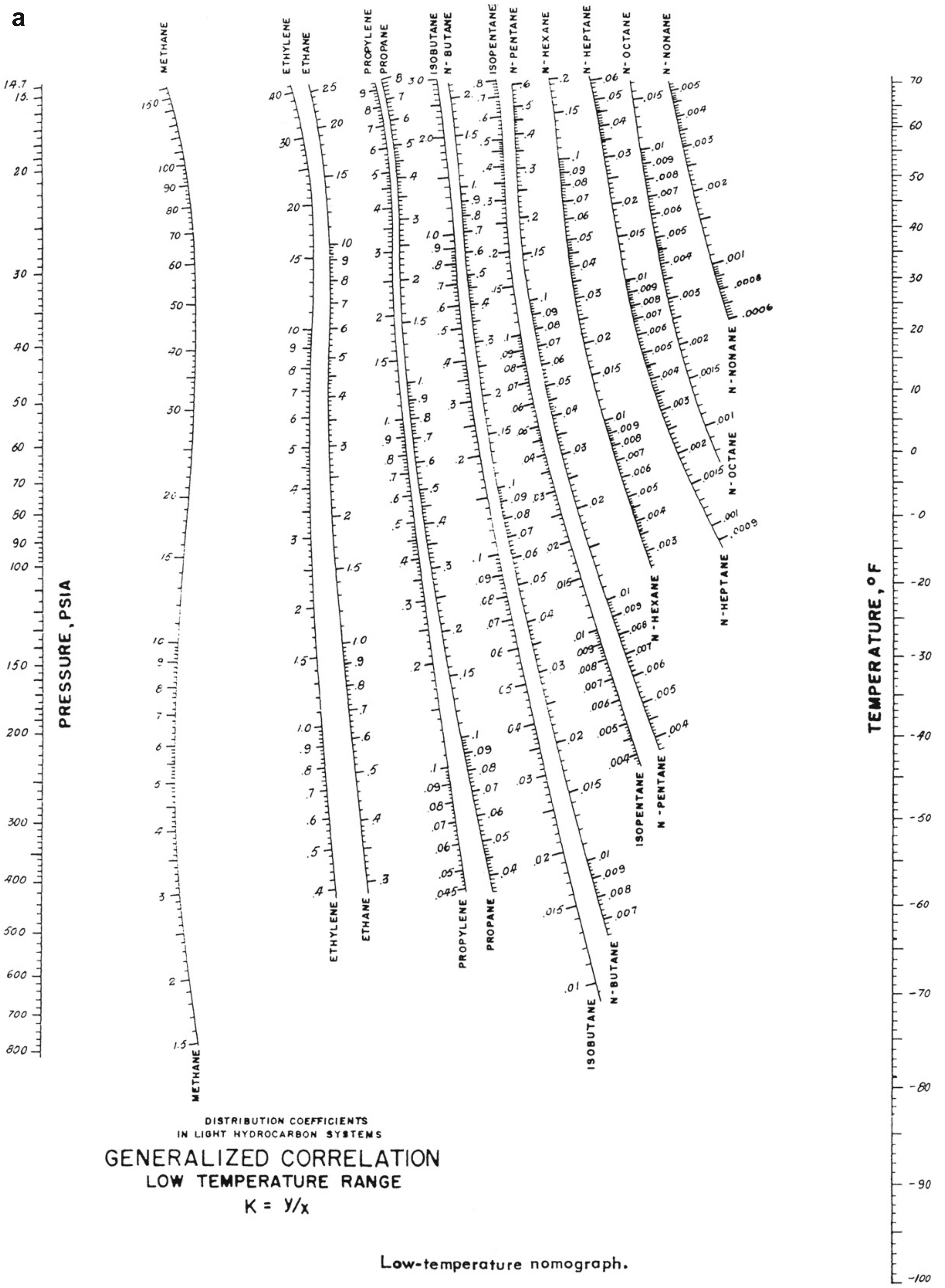


Figure 10-11d Pressure vs. K for methane-ethane binary. Used by permission, Gas Processors Suppliers Association Data Book, 12th Ed., V. 1 and 2 (2004), Tulsa, Okla.



DISTRIBUTION COEFFICIENTS
IN LIGHT HYDROCARBON SYSTEMS

GENERALIZED CORRELATION
LOW TEMPERATURE RANGE
$K = y/x$

Low-temperature nomograph.

Figure 10-12a DePriester Charts; K-Values of light hydrocarbon systems, generalized correlations, low-temperature range. Used by permission, DePriester, C.L., The American Institute of Chemical Engineers, Chemical Eng. Prog. Ser., 49 No. 7 (1953), all rights reserved.

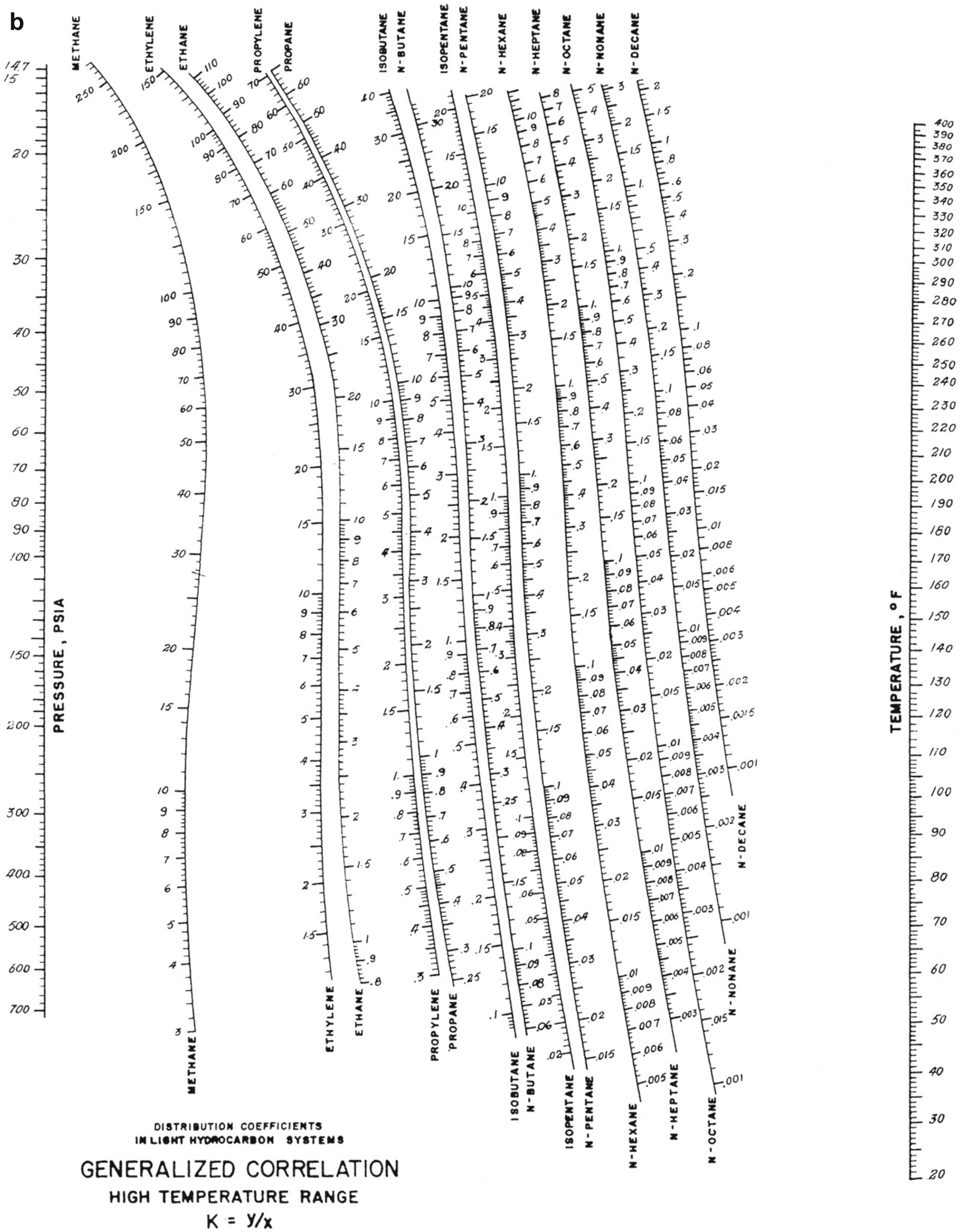


Figure 10-12b DePriester Charts; K-Values of light hydrocarbon systems, generalized correlations, high-temperature range. Used by permission, DePriester, C.L., The American Institute of Chemical Engineers, Chemical Eng. Prog. Ser., 49 No. 7 (1953), all rights reserved.

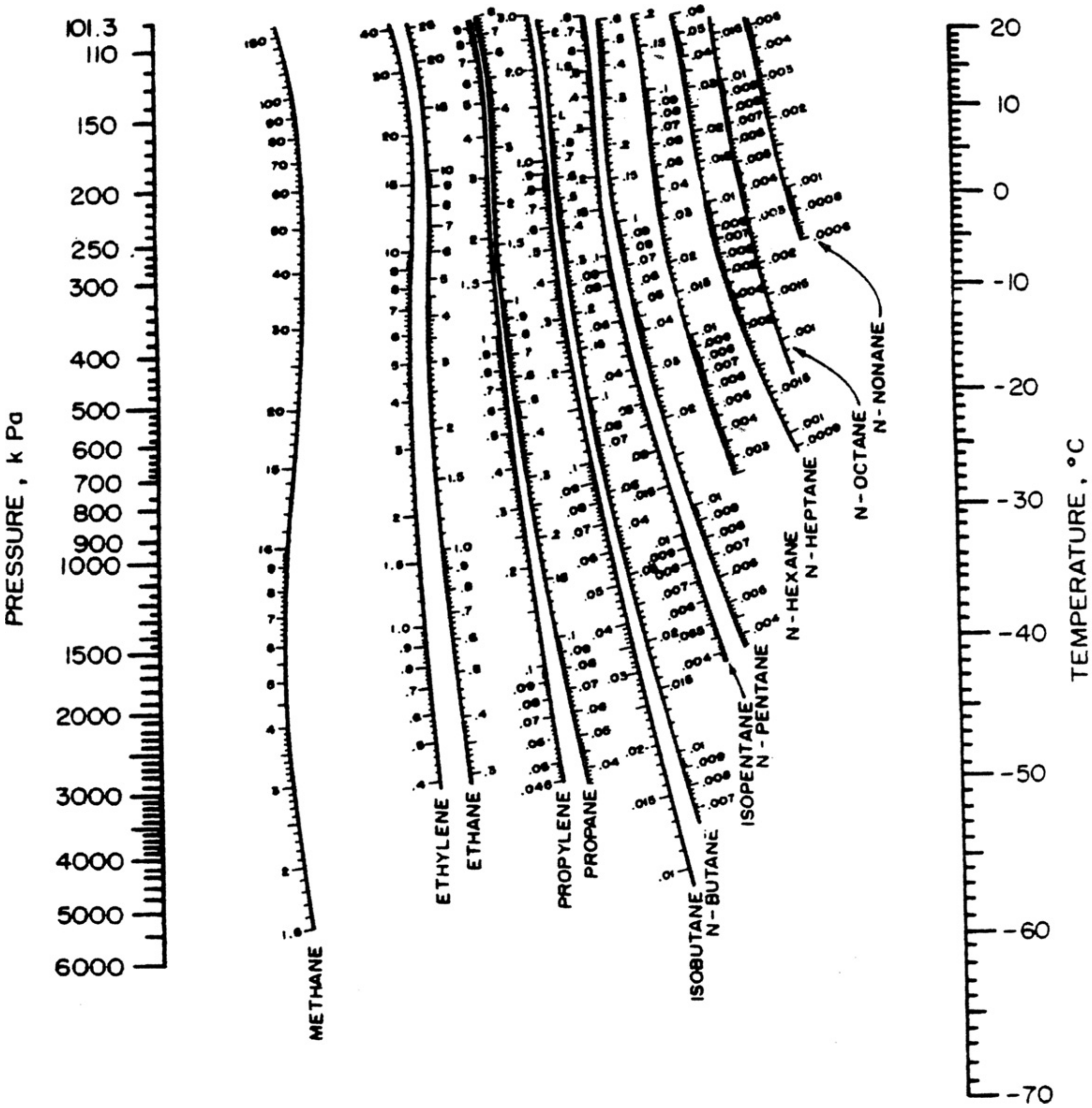


Figure 10-12c Modified DePriester Chart (in S.I. units) at low temperature (D.B. Dadyburjor, Chem. Eng. Prog., 85, April 1978; copyright 1978, AIChE; reproduced by permission of the American Institute of Chemical Engineers).

and/or pressure of the equilibrium mixture are unknown, a trial-and-error method is required. Perry and Green [245], and Smith and Van Ness [248] provide DePriester charts in alternative temperature and pressure units. McWilliams [251] has developed an equation to fit DePriester charts represented by:

$$\ln K = a_{T1}/T^2 + a_{T2}/T + a_{T6} + a_{p1}\ln p + a_{p2}/p^2 + a_{p3}/p \tag{10-54}$$

where

a_{T1}, a_{T2}, a_{T6}, a_{p1}, a_{p2}, a_{p3} = constants
K = equilibrium constant
p = absolute pressure, psia
T = absolute temperature (°R = °F + 460)

Equation 10-54 is valid from 365.7°R (−70°C) to 851.7°R (200°C) and from pressures from 14.69 psia (101.3 kPa) to 870.1 psia (6000 kPa). If K and p are known, Equation 10-54 can be solved for T. The relationship values can be easily incorporated into a computer program and can be determine more accurate than from the charts. Table 10-2 shows the constants for various components, and Equation 10-54 can be simplified for all components, except n-octane and n-decane. This is expressed by:

$$\ln K = a_{T1}/T^2 + a_{T6} + a_{p1}\ln p \tag{10-55}$$

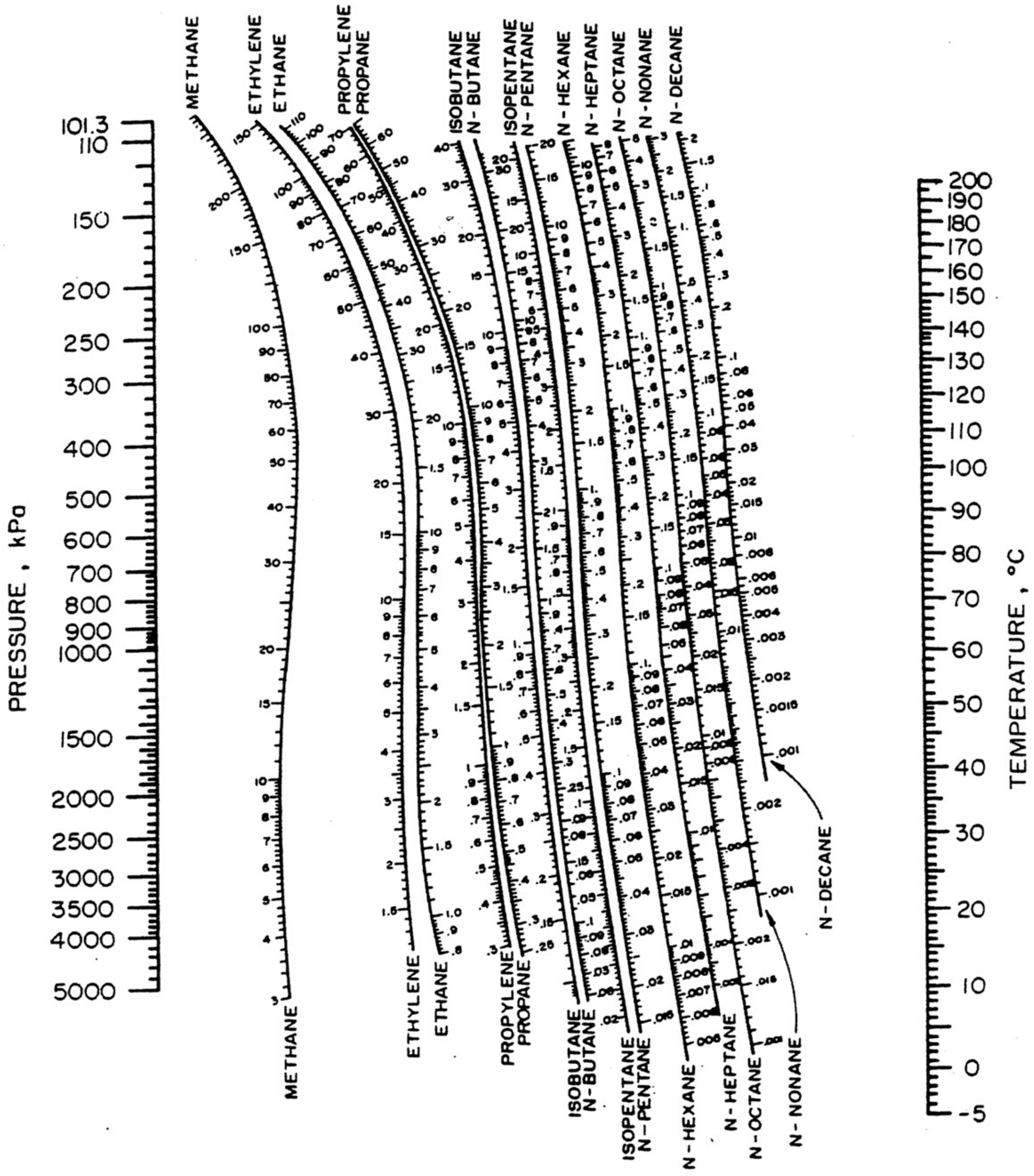


Figure 10-12d Modified DePriester Chart (in S.I. units) at high temperature (D.B. Dadyburjor, Chem. Eng. Prog., 85, April 1978; copyright 1978, AIChE; reproduced by permission of the American Institute of Chemical Engineers).

Solving for T from Equation 10-55 gives:

$$T = \left[\frac{a_{T1}}{\left(\ln K - a_{T6} - a_{p1}\ln p - \dfrac{a_{p2}}{p^2} - \dfrac{a_{p3}}{p}\right)}\right]^{0.5} \tag{10-56}$$

K values are used along with stoichiometric equations which state that the sum of the mole fractions in liquid and vapor phases must equal to unity as defined by Equations 10-43 and 10-45 respectively. For N number of components, Equations 10-43 and 10-45 can be expressed by:

$$\sum_{i=1}^{N} x_i = 1.0, \quad \sum_{i}^{N} y_i = 1.0 \tag{10-57}$$

where

N = number of components

If only one component is present, then x = 1.0 and y = 1.0, which implies that $K_i = y/x = 1.0$. This is a simple way of determining the boiling point of a pure compound

Table 10-2 Constants for fit to K Values Using Equation 10-54.

Compound	a_{T1}	a_{T2}	a_{T6}	a_{p1}	a_{p2}	a_{p3}	Mean Error
Methane	−292,860	0	8.2445	−0.8951	59.8465	0	1.666
Ethylene	−600,076.875	0	7.90595	−0.84677	42.94594	0	2.65
Ethane	−687,248.25	0	7.90694	−0.88600	49.02654	0	1.95
Propylene	−923,484.6875	0	7.71725	−0.87871	47.67624		1.90
Propane	−970,688.5625	0	7.15059	−0.76984	0	6.90224	2.35
Isobutane	−1,166,846	0	7.72668	−0.92213	0	0	2.52
n-Butane	−1,280,557	0	7.94986	−0.96455	0	0	3.61
Isopentane	−1,481,583	0	7.58071	−0.93159	0	0	4.56
n-Pentane	−1,524,891	0	7.33129	−0.89143	0	0	4.30
n-Hexane	−1,778,901	0	6.96783	−0.84634	0	0	4.90
n-Heptane	−2,013,803	0	6.52914	−0.79543	0	0	6.34
n-Octane	0	−7646.81641	12.48547	−0.73152	0	0	7.58
n-Nonane	−2,551,040	0	5.69313	−0.67818	0	0	9.40
n-Decane	0	−9760.45703	13.80354	−0.71470	0	0	5.69

Note: T is in °R, and p is in psia.
Source: McWilliams, M. L., "An Equation to Relate K-factors to Pressure and Temperature", Chem. Eng., 80 (25), 138, Oct 29, 1973.

at any pressure. For example, to determine the boiling point of propane at $p = 200$ psia, place a straightedge on $p = 200$ and $K = 1.0$ on the propane scale on Figure 10-12a. The temperature on the right side of the scale is $T = 100°F$ (560°R), which is the boiling point.

Using Equation 10-54 and values from Table 10-2 gives:

$$\ln K = a_{T1}/T^2 + a_{T2}/T + a_{T6} + a_{p1}\ln p + a_{p2}/p^2 + a_{p3}/p \qquad (10\text{-}54)$$

and

$$a_{T1} = -970,688.5625, a_{T2} = 0, a_{T6} = 7.15059,$$

$$a_{p1} = -0.76984, a_{p2} = 0, a_{p3} = 6.90224$$

$$\ln(1) = \frac{-970,688.5625}{T^2} + 0 + 7.15059 - 0.76984\ln(200) + \frac{0}{200^2} + \frac{6.90224}{200}$$

$$T = 558.98°R\ (98.98°F)$$

This gives a 1.03% deviation from DePriester chart.

The K-factor charts represent pure components and pseudo binary systems of a light hydrocarbon plus a calculated pseudo heavy component in a mixture, when several components are present. For these more complex mixtures it is necessary to determine the average molecular weight of the system on a methane-free basis, and then interpolate the K-value between the two binaries whose heavy component lies on either side of the pseudo-components. If nitrogen is at more than 3–5 mol%, the accuracy becomes poor. Reference 79 provides a more detailed explanation and a more complete set of charts.

10.9 Non-Ideal Systems

A system is non-ideal because the interaction between molecules alters its behavior. The following groups all contribute to non-ideality; hydroxyl groups (-OH), ketone groups (-C=O), aldehyde groups (CHO), halogens (-Cl, -Br) and carboxylic acid groups (-COOH). Systems of two or more hydrocarbon, chemical and water components may be non-ideal for a variety of reasons. Accurate experimental data are necessary to predict the distillation performance of these systems. The use of empirical relationships to predict vapor pressure/concentration relationships at specific temperatures and pressures is inaccurate at best.

Prausnitz [54] presents a thorough analysis of the application of empirical techniques in the absence of experimental data. The basic question is to determine accurately the distribution of the respective system components between liquid and gaseous phases. The concepts of fugacity and activity are fundamental to this. For a pure ideal gas the fugacity is equal to the pressure, and for a component, i, in a mixture of ideal gases it is equal to its partial pressure y_i P, where P is the system pressure. As the system pressure approaches zero, the fugacity approaches ideal. For many systems, the deviations from unity are minor at system pressures less than 25 psig.

The ratio f/fo is termed activity, a. [**Note**: This is not the activity coefficient.] The activity is an indication of how "active" a substance is relative to its standard state (not necessarily zero pressure), fo. The standard state is the reference condition; most references are to constant temperature, with composition and pressure varying as required. Fugacity becomes a corrected pressure, representing a specific component's deviation from ideal. The fugacity coefficient is:

$$\phi_i = \frac{f_i}{y_i P} \tag{10-58}$$

The Virial Equation of State for gases is generally:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots \tag{10-59}$$

where

B, C, D, etc. = Virial coefficients, independent of pressure or density, and for pure components are functions of temperature only

V = molar volume

Z = compressibility factor

Fugacities and activities can be determined using this concept. Other important equations of state, which can be related to fugacity and activity have been developed by Redlich-Kwong [56] with Chueh [10], which develops the original Redlich-Kwong equation, and Palmer's summary of activity coefficient methods [51].

Activity coefficients are equal to 1.0 for an ideal solution when the mole fraction is equal to the activity. The activity (a) of a component, i, at a specific temperature, pressure and composition is defined as the ratio of the fugacity of i at these conditions to the fugacity of i at the standard state [54].

$$a(T, P, x) = \frac{f_i(T, P, x)}{f_i(T^o, P^o, x^o)}, \text{ liquid phase} \tag{10-60}$$

(Zero superscript indicates a specific pressure and composition)

The activity coefficient γ_i is:

$$\gamma_i = \frac{a_i}{x_i} = 1.0$$

for an ideal solution

The ideal solution law, Henry's Law, also enters into the establishment of performance of ideal and non-ideal solutions.

The Redlich-Kister [55, 57] equations provide a good technique for representing liquid phase activity and classifying solutions.

The Gibbs-Duhem equation allows the determination of activity coefficients for one component from data for those of other components.

Wilson's [77] equation has been found to be quite accurate in predicting the vapor-liquid relationships and activity coefficients for miscible liquid systems. The results can be expanded to as many components in a multicomponent system as necessary without additional data requiring. This makes Renon's and Prausnitz's [58] techniques valuable for multicomponent systems when applying computational solutions.

Renon's technique is applicable to partially miscible systems as well as those with complete miscibility. This is described in the reference above and in (54).

Other specific techniques are applicable to particular situations; they should be investigated to make sure that they apply well to the system under consideration. They are often expressed in terms of the effective "K" for the components, i, of a system. Frequently used methods are those of Chao-Seader (CS), Peng-Robinson (PR), Renon, Redlich-Kwong, Soave Redlich-Kwong (SRK/RSK), Wilson. Table 10-3 lists the equations of state that are applied most widely.

The van-der-Waals equation (3) in Table 10-3 was the first successful approach to the formulation of an equation of state for a non-ideal gas. It is seldom used because its range of application is too narrow. The constants a and b are estimated from the critical temperature T_c and pressure P_c. The generalized equation of state (2) given in Table 10-3 defines the compressibility factor Z, which is a function of reduced pressure P_r, ($P_r = P/P_c$) and reduced temperature T_r, ($T_r = T/T_c$). The critical compressibility factor Z_c, or the acentric factor, ω developed by Pitzer et al. [252] is determined from experimental P-V-T data. It accounts for differences in molecular shape, is determined from the vapor pressure curve and defined as:

$$\omega = \left[-\log\left(\frac{P^s}{P_c}\right)_{T_r=0.7} \right] - 1.0 \tag{10-62}$$

Poling et al. [253] give extensive lists of values of ω. The equation, developed by Redlich and Kwong (4), in Table 10-3 is a considerable improvement over the van

Table 10-3 Useful Equations of State.

Name	Equation	Equation constants and functions
(1) ideal gas law	$P = \frac{RT}{V}$	None
(2) Generalized	$P = \frac{ZRT}{V}$	$Z = Z(p_r, T_r, Z_c \text{ or } \omega)$ as derived from data
(3) van-der-Waals	$P = \frac{RT}{(V - b)} - \frac{a}{V^2}$	a and b are species-dependent constants and estimated from the critical temperature and pressure
(4) Redlich-Kwong (R-K)	$P = \frac{RT}{V - b} - \frac{a}{V^2 + bV}$	$b = 0.08664\ RT_c/P_c$ $a = 0.42748\ R^2\ T_c^{2.5}/P_c\ T^{0.5}$
(5) Soave-Redlich-Kwong (S-R-K or R-K-S)	$P = \frac{RT}{V - b} - \frac{a}{V^2 + bV}$	$b = 0.08664\ RT_c/P_c$ $a = 0.42748\ R^2\ T_c^2\ [1 + f_\omega\ (1 - T_r^{0.5})]^2/P_c$ $f_\omega = 0.48 + 1.574\omega - 0.176\omega^2$
(6) Peng-Robinson (P-R)	$P = \frac{RT}{V - b} - \frac{a}{V^2 + 2\ bV - b^2}$	$b = 0.07780R\ T_c/P_c$ $a = 0.45724\ R^2\ T_c^2\ [1 + f_\omega\ (1 - T_r^{0.5})]^2/P_c$ $f_\omega = 0.37464 + 1.54226\omega - 0.26992\omega^2$

der Waals equation. Shah and Thodos [254] showed that a simple R-K equation comparable accuracy with equations containing many more empirical constants. The R-K equation can also approximate the liquid phase region. A cubic equation in V is obtained if the R-K equation is expanded to obtain a common denominator. Alternatively, (3) and (4) in Table 10-3 can be combined to eliminate V, and hence give the compressibility factor Z form of the R-K equation, as expressed by:

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \qquad (10\text{-}63)$$

where

$$A = \frac{aP}{R^2T^2} \qquad (10\text{-}64)$$

$$B = \frac{bP}{RT} \qquad (10\text{-}65)$$

Equation 10-63 can be solved analytically for three roots (e.g. see Appendix-G).

10.10 Thermodynamic Simulation Software Programs

One of the basic tests of a thermodynamic model is to find relevant experimental data to test the predictions of the model. The comparison helps to decide whether the model is good or whether another type would be more suitable. Simulation programs have in-built packages which provide accurate thermodynamic property predictions for hydrocarbons and non-hydrocarbon fluids. Many of these simulation programs have databases of over 1500 components and over 10,000 of fitted binary coefficients. If a component cannot be found within the database, the software programs provide a selection of estimation methods for creating appropriate hypothetical compounds (e.g. pseudo hydrocarbon components of crude oil for determining the true boiling point (TBP) of crude oil). Experimental pure component data can be used as input to the regression package. Alternatively, the designers can supply a set of their own data. The regression package will fit the input data to one of the mathematical expressions, and thus allows the designers to obtain simulation results for specific thermophysical properties which closely match their experimental data.

Selecting the correct thermodynamic models from packages in the simulation programs (e.g. UniSim, Hysys, Aspen, ChemCad, Pro/II, ProSim, etc.) enables the designer to predict properties of mixtures ranging from well-defined light hydrocarbon systems to complex oil mixtures and highly non-ideal (non-electrolytic) chemical systems. To obtain a successful simulation, the input parameters and regression model must be carefully chosen. Changes in temperature and pressure can affect the accuracy of a simulation quite drastically if inappropriate choices are made.

The thermodynamic models used to predict the chemical interaction properties are the NRTL, Wilson, SRK, UNIQUAC, and UNIFAC models. These are incorporated in various simulation packages e.g. Pro II, HYSYS, Aspen Plus, ProSim Plus, ChemCad and UniSim (Honeywell).

The procedure for selection, as illustrated by Seader and Henley [255], is as follows:

RK = Redlich-Kwong
PR = Peng Robinson
SRK/RSK = Soave Redlich Kwong
NTRL = Non-random two-liquid
UNIQUAC = Universal quasichemical
UNIFAC = UNIQUAC Functional group activity

1. Characterize the mixture by the chemical types present: Light gases (LG), Hydrocarbons (HC), Polar organic compounds (PC), and aqueous solutions (A), with or without electrolytes (E).
2. If the mixture is (A) with no (PC), and if electrolytes are present, select the modified NRTL equation. Otherwise, select a special model, such as one for sour water (containing NH_3, H_2S, CO_2, etc.) or aqueous amine solutions.
3. If the mixture contains (HC), with or without (LG), and has a wide boiling range, choose the corresponding states method of Lee-Kesler-Plöcker. If the boiling range of a mixture of (HC) is not larger selection depends on pressure and temperature.
4. For all temperatures and pressures, the Peng-Robinson (PR) equation is suitable.
5. For all pressures and non-cryogenic temperatures, the Soave-Redlich-Kwong (SRK/RSK) equation is recommended.
6. For all temperatures, but not pressures in the critical region, the Benedict-Webb-Rubin-Starling method is suitable.
7. If the mixture contains (PC), the selection depends on whether (LG) are present. If they are, the Predictive Soave-Redlich-Kwong (PSRK) model is recommended. If not, then a suitable liquid-phase activity coefficient method should be chosen.

Table 10-4 Approximate Guides for Selection of K-Values Methods.

Chemical systems		
Low MW alcohol and hydrocarbons	Wilson	
Higher MW alcohol and hydrocarbons	NRTL	
Hydrogen bonding systems	Margules	
Liquid–liquid equilibrium	NRTL/UNIQUAC	
Water as a second liquid phase	NRTL	
Components in a homologous family	UNIQUAC	
Low-pressure systems with associating vapor phase		
Light Hydrocarbon and Oil Systems		
Natural gas systems w/sweet and sour gas	SRK/PR	
Cryogenic systems	SRK/PR	
Refinery mixtures with $p < 5000$ psia	SRK/PR	
Hydrotreaters and reformers	Grayson-Stread	
Simple paraffinic systems	SRK/PR	
Heavy components w/NBP $> 1{,}000°F$	BK10	
Based on polarity and ideality		
Nonpolar – nonpolar	Ideal & non-ideal	any activity coefficient model
Nonpolar – weakly polar	Ideal	any activity coefficient model
Nonpolar – weakly polar	Non-ideal	UNIQUAC
Nonpolar – strongly polar	Ideal	UNIQUAC
Nonpolar – strongly polar	Non-ideal	Wilson
Weakly polar – weakly polar	Ideal	NRTL
Weakly polar – weakly polar	Non-ideal	UNIQUAC
Weakly polar – strongly polar	Ideal	NRTL
Weakly polar – strongly polar	Non-ideal	UNIQUAC
Strongly polar – strongly polar	Ideal	UNIQUAC
Strongly polar – strongly polar	Non-ideal	NO RECOMMENDATION
Aqueous – strongly polar		UNIQUAC

NRTL = non- random two liquid model; SRK = Soave-Redlich-Kwong; PR = Peng-Robinson, BK10 = Braun K10 for petroleum; UNIQUAC = universal quasi-chemical theory.

Source: Wankat, P. C., Separation Process Engineering, 2^{nd}, Prentice Hall, 2007.

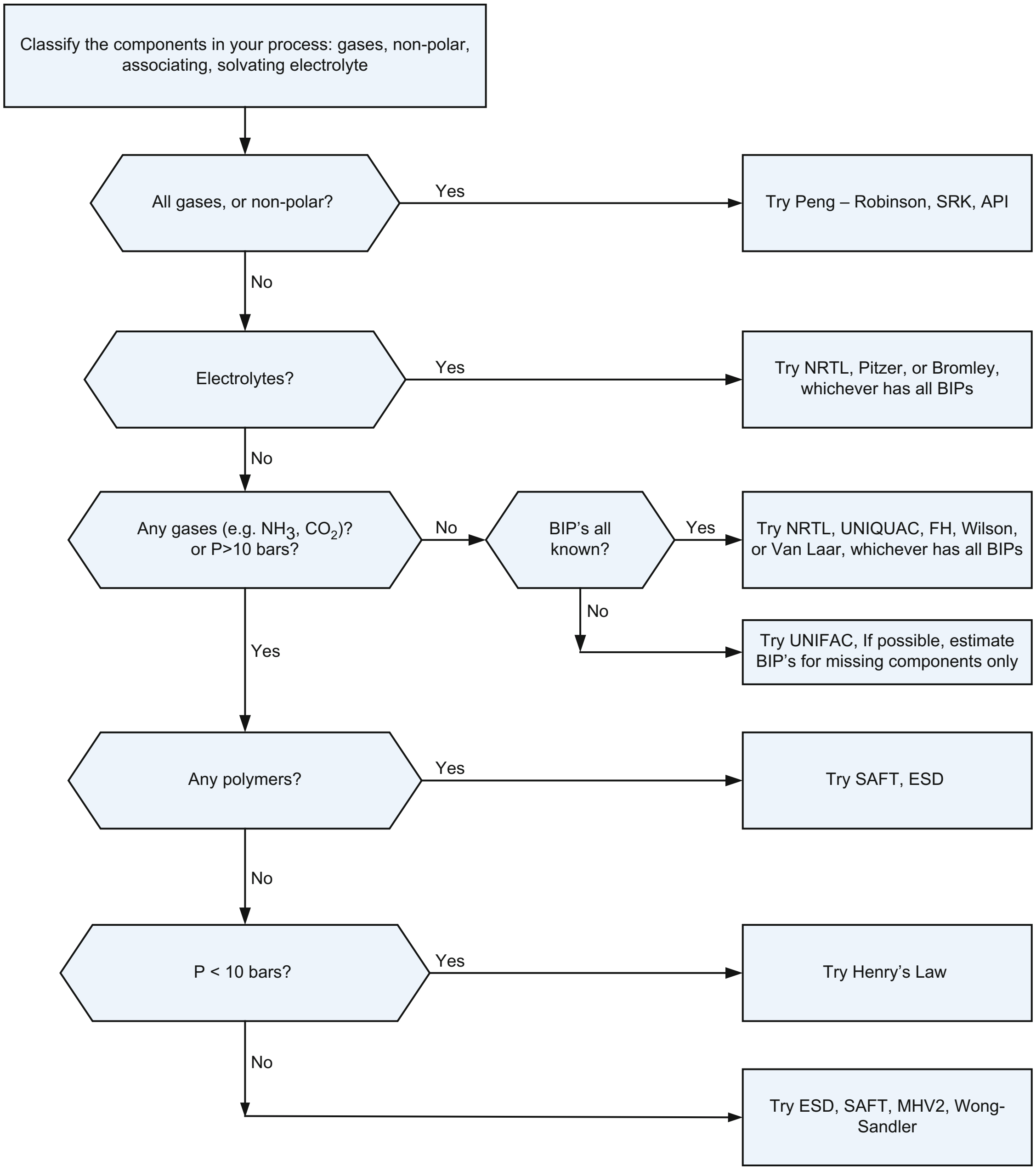


Figure 10-13 Flow chart to select the best thermodynamic model. The abbreviation BIP is used to mean binary interaction parameters (source: Elliot, J. R., and Carl. T. Lira, Introductory Chemical Engineering Thermodynamics, Prentice Hall Int. Series, 1999).

8. If binary interaction coefficients are not available, select the UNIFAC method. Its results should be considered as only a first approximation.

9. If the binary interaction coefficients are available, and splitting into two liquid phases will not occur, select the Wilson or NRTL equation.

10. If phase splitting is likely, select the NRTL or UNIQUAC model.

Table 10-4 shows the conditions of some of these models, and Figure 10-13 [249] gives the selection process in the form of a flow chart. Table 10-5 lists some typical systems and recommended correlations.

10.11 Vapor pressure

If the vapor and liquid of a pure component are in *equilibrium*, then the equilibrium pressure is known as the vapor pressure. Vapor pressure can be defined as the pressure that a pure component exerts at a given temperature, when both liquid and vapor phases are

Table 10-5 Generalized Antoine Constant Functions for the SRK Equation.

$0.6 \le T_r \le 0.7$

$A' = 4.0434 + 2.1456f - 0.43477f^2 + 0.38481\,f^3 - 0.050479\,f^4$

$B' = 4.3755 + 1.2981\,f - 0.53208\,f^2 + 0.44506\,f^3 - 0.074005f^4$

$C' = 0.0708033 - 0.240584\,f + 0.0801510\,f^2 - 0.00990303\,f^3 - 0.000160472\,f^4$

$0.7 \le T_r \le 0.84$

$A' = 4.4401 + 2.2128f - 0.53518\,f^2 + 0.17368\,f^3 - 0.018512\,f^4$

$B' = 5.0075 + 1.2494\,f - 0.78155\,f^2 + 0.32010\,f^3 - 0.047601f^4$

$C' = 0.124652 - 0.273702\,f + 0.0750076\,f^2 - 0.0137818\,f^3 - 0.00145038\,f^4$

$0.84 \le T_r \le 1.0$

$A' = 4.8817 + 2.5164f - 0.53557f^2 + 0.\ 09639\,f^3 - 0.012108\,f^4$

$B' = 5.8938 + 1.6311\,f - 0.91992\,f^2 + 0.24694\,f^3 - 0.034344f^4$

$C' = 0.206497 - 0.281653\,f + 0.0716095\,f^2 - 0.0174537\,f^3 - 0.00236311\,f^4$

Source: DeDoes, A. J, et al., CEP, pp 39–44, Jan. 2007.

Table 10-6 Generalized Antoine constant functions for the SRK equation.

$0.6 \le T_r \le 0.7$

$A' = 4.0434 + 2.1456f - 0.43477f^2 + 0.38481\,f^3 - 0.050479\,f^4$

$B' = 4.3755 + 1.2981\,f - 0.53208\,f^2 + 0.44506\,f^3 - 0.074005f^4$

$C' = 0.0708033 - 0.240584\,f + 0.0801510\,f^2 - 0.00990303\,f^3 - 0.000160472\,f^4$

$0.7 \le T_r \le 0.84$

$A' = 4.4401 + 2.2128f - 0.53518\,f^2 + 0.17368\,f^3 - 0.018512\,f^4$

$B' = 5.0075 + 1.2494\,f - 0.78155\,f^2 + 0.32010\,f^3 - 0.047601f^4$

$C' = 0.124652 - 0.273702\,f + 0.0750076\,f^2 - 0.0137818\,f^3 - 0.00145038\,f^4$

$0.84 \le T_r \le 1.0$

$A' = 4.8817 + 2.5164f - 0.53557f^2 + 0.\ 09639\,f^3 - 0.012108\,f^4$

$B' = 5.8938 + 1.6311\,f - 0.91992\,f^2 + 0.24694\,f^3 - 0.034344f^4$

$C' = 0.206497 - 0.281653\,f + 0.0716095\,f^2 - 0.0174537\,f^3 - 0.00236311\,f^4$

A', B', C' = constants in generalized Antoine equation, f = acentric factor function, T_r = reduced temperature.
Source: DeDoes, A. J, et al., CEP, pp 39–44, Jan. 2007.

present. It is a physical property of a pure chemical component, and depends only on temperature.

Vapor pressure is an essential parameter in the analysis of separation processes, such as flash separation, distillation or absorption. Various approaches such as tables and charts listing vapor pressure or boiling point among their physical properties are used in these analyses. These include steam tables, thermodynamic property tables and phase equilibrium diagrams such as pressure-enthalpy, pressure-volume or detailed some temperature-entropy diagrams.

DeDoes et al. [256] have detailed some drawbacks of these approaches. They have also developed a generalized method, which combines pressure-volume-temperature (PVT) equations of state with thermodynamic criteria that are related to chemical potential or fugacity. The method uses three constants; critical temperature, critical pressure and the acentric factor. Other phase properties, such as molar volume or density, residual enthalpy and residual entropy are also predicted and generate mixture compositions, K-values or relative volatilities when combined with appropriate mixing rules or a liquid solution model. The generalized method uses a three-constant Antoine vapor pressure relationship for any substance for which the critical temperature, critical pressure and acentric factor are known. Vapor pressure predictions have been found to agree to within ±0.1% with those generated by an algorithm-based approach over a range of reduced temperatures between 0.60 to 1.00 for Soave-Redlich-Kwong (SRK) and between 0.7 and 1.00 for Peng-Robinson (PR) as shown in Table 10-6. Figure 10-14 shows Cox chart plots of vapor pressure for various substances, Figure 10-14a and Figure 10-14b show the vapor pressures for light hydrocarbons at a low temperature range and at a high temperature range respectively.

Vapor pressure determination using the Clausius-Clapeyron and the Antoine Equations

Standard chemical engineering texts [246, 247 and 248] provide equations to predict vapor-pressure of compounds, and a commonly given equation for the vapor pressure (Refer to chapter 3, page 109, volume 1 of this series) is:

$$\log_{10} P_v = A + \frac{B}{T} + C\,\log_{10} T + DT + ET^2 \qquad (3\text{-}16)$$

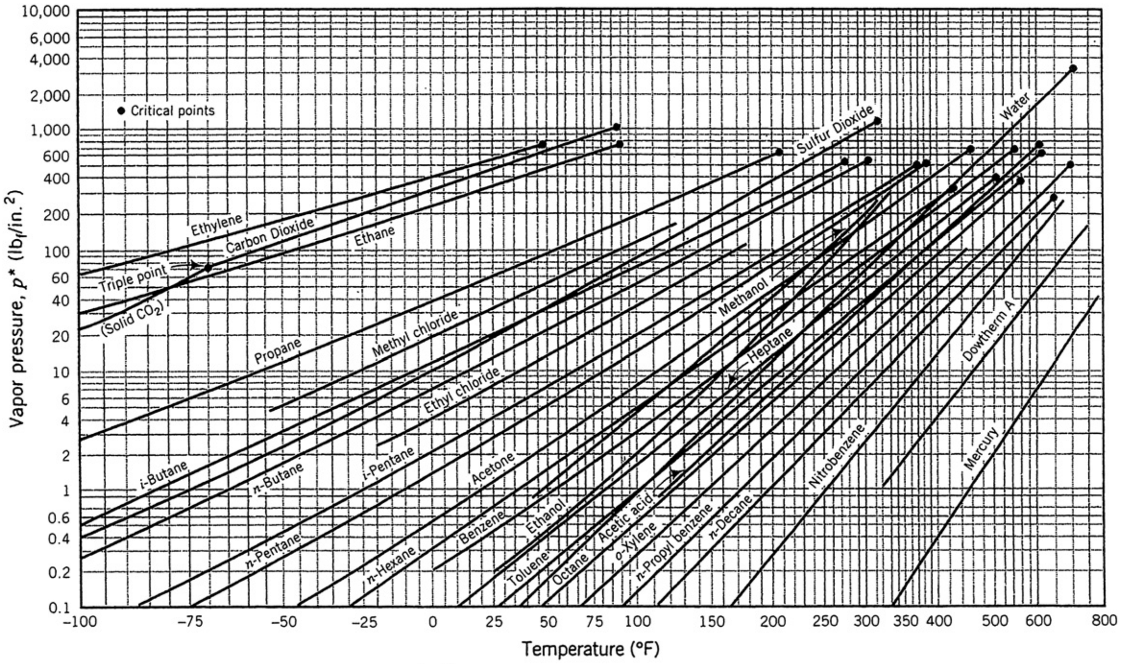
where P is the vapor pressure in mm Hg, and A, B, C, D and E are constants. Sometimes it is useful to estimate the saturated vapor pressure from the Clausius-Clapeyron equation as:

$$\frac{d\,P^{vap}}{dT} = \frac{P^{vap}\Delta H_{vap}}{R\,T^2} \quad \text{or} \quad \frac{d\,\ln P^{vap}}{dT} = \frac{\Delta H_{vap}}{RT^2} \qquad (10\text{-}66)$$

and

$$\ln\left[\frac{P^{vap}(T_2)}{P^{vap}(T_1)}\right] = \int_{T_1}^{T_2} \frac{\Delta H_{vap}}{RT^2}\,dT \qquad (10\text{-}67)$$

where ΔH_{vap} is the molar latent heat of vaporization and T is the absolute temperature. $\Delta H_{vap} = H^V - H^L$ is a



Conversions: $°F = 1.8\,°C + 32$, $1\,lb/in^2 = 0.06895\,bar$

Figure 10-14 Cox chart vapor pressure plots. (Source: A. S. Foust et. al., Principles of Unit Operations, Wiley, New York, p. 550, 1960).

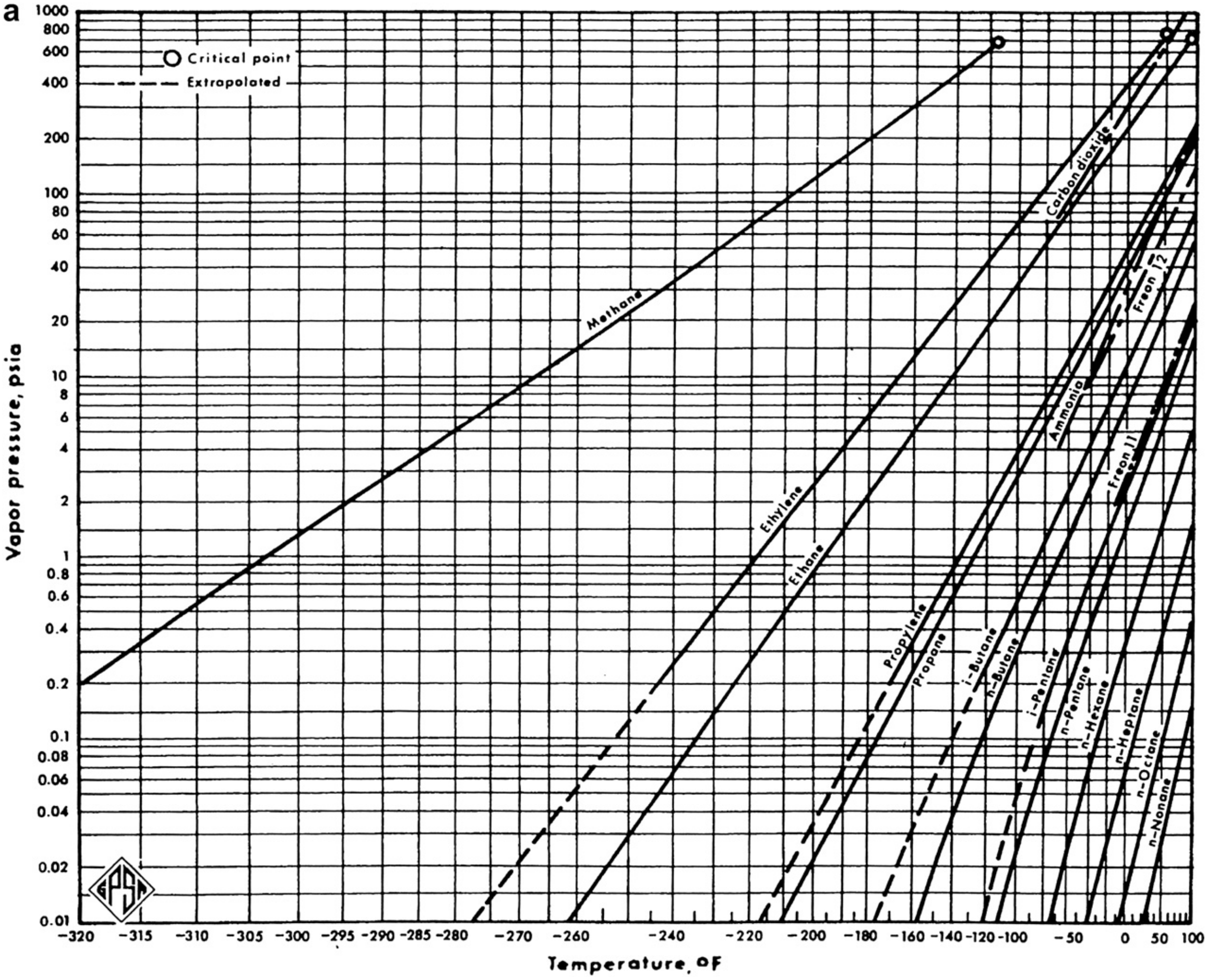


Figure 10-14a Low-Temperature Vapor Pressures for Light Hydrocarbons. Used by permission, Gas Processors Suppliers Association Data Book, 12th Ed., V. 1 and 2 (2004) Tulsa, Okla.

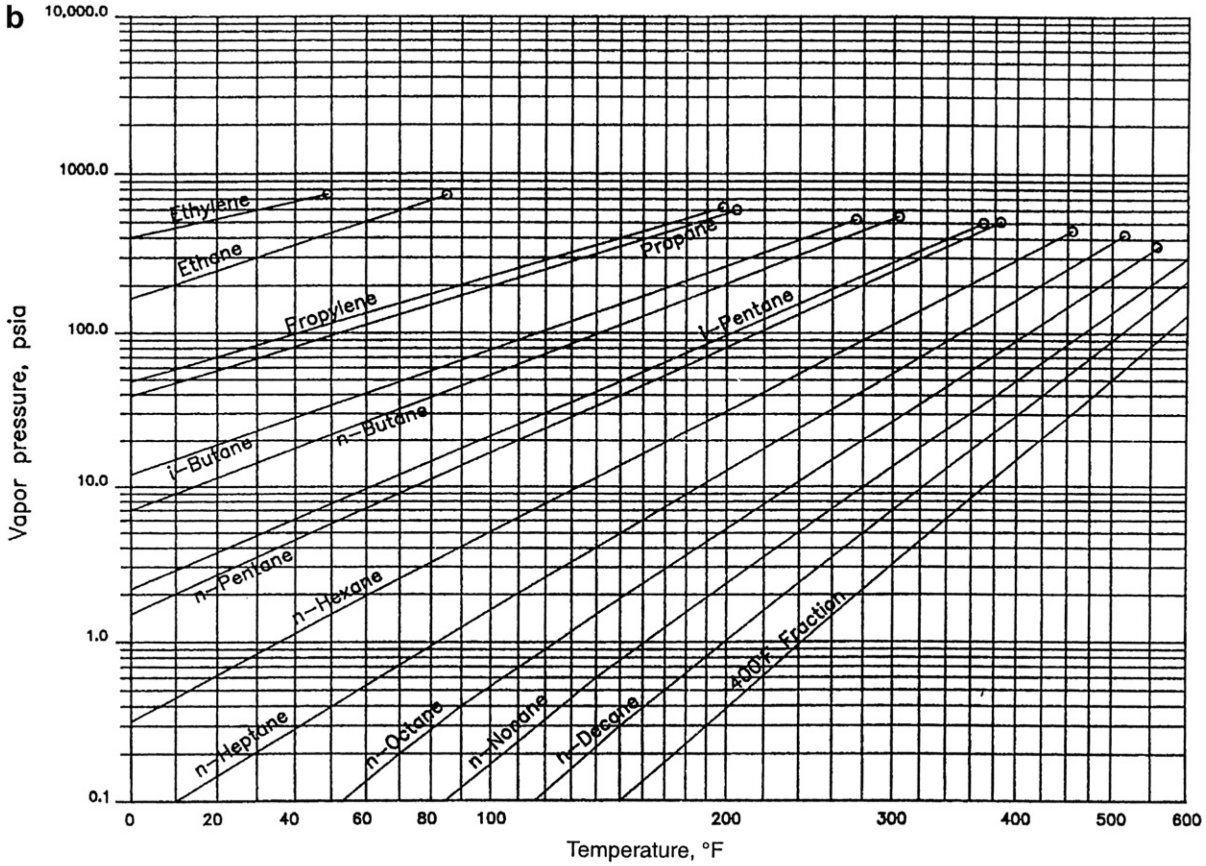


Figure 10-14b High-Temperature Vapor Pressures for Light Hydrocarbons. Used by permission, Gas Processors Suppliers Association Data Book, 12th Ed., V. 1 and 2 (2004) Tulsa, Okla.

function of temperature; but if it assumed to be independent of temperature, Equation 10-67 can be integrated to give:

$$\ln\left[\frac{P^{vap}(T_2)}{P^{vap}(T_1)}\right] = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \qquad (10\text{-}68)$$

Equation 10-68 has been found to be fairly accurate for correlating the temperature dependence of the vapor pressure of liquids over limited temperature ranges.

Note: $\ln P^{vap}$ should be a linear function of $1/T$, where T is the absolute temperature with the lower limit of integration as the normal boiling conditions, i.e. $T_1 = T_{nb}$ at $P^{vap}(T_1) = P_{atm}$ where P_{atm} is the atmospheric pressure, ΔH_{vap} and R are in a consistent set of units. One can obtain an estimate of the temperature variation of the heat of vaporization by noting that the integration of Equation 10-68 can be carried out as an indefinite rather than definite integral, which gives:

$$\ln P^{vap}(T) = -\frac{\Delta H_{vap}}{RT} + C \qquad (10\text{-}69)$$

where C is a constant. A plot of $\ln P^{vap}$ versus $1/T$, should give a straight line with a slope equal to $-\Delta H_{vap}/R$, if the heat of vaporization is independent of temperature, and a curve if $-\Delta H_{vap}/R$ varies with temperature. Equation 10-69 can be re-written as:

$$\ln P^{vap}(T) = A - \frac{B}{T} \qquad (10\text{-}70)$$

with $B = \Delta H_{vap}/R$, and it is reasonably accurate for estimating the temperature dependence of the vapor pressure over small temperature ranges.

Correspondingly, the Antoine equation can be expressed by:

$$\ln P^* = A - \frac{B}{T+C} \qquad (10\text{-}71)$$

or

$$\log P^* = \frac{\ln P^*}{\ln 10} = A - \frac{B}{T+C} \qquad (10\text{-}72)$$

where A, B and C are dimensional constants, P^* is the vapor pressure and T is the temperature. Equation 10-72 is used to correlate vapor pressure accurately over the

Table 10-7 Generalized Antoine Constant Functions for the PR Equation.

$0.7 \leq T_r \leq 0.84$
$A' = 4.8512 + 2.3617f - 0.45894f^2 - 0.070461\,f^3 + 0.10809\,f^4$
$B' = 5.5675 + 1.3213\,f - 0.80186\,f^2 + 0.11081\,f^3 + 0.087503f^4$
$C' = 0.145395 - 0.287367\,f +$
$0.0815004\,f^2 - 0.0253619\,f^3 - 0.00813261\,f^4$

$0.84 \leq T_r \leq 1.0$
$A' = 5.3988 + 3.0095f - 0.68621\,f^2 + 0.10190\,f^3 - 0.0027322\,f^4$
$B' = 6.7141 + 2.3263\,f - 1.3630\,f^2 + 0.35003f^3 - 0.035704f^4$
$C' = 0.243432 - 0.260581\,f +$
$0.0448442\,f^2 - 0.00718139\,f^3 - 0.00122297\,f^4$

A', B', C'= constants in generalized Antoine equation, f = acentric factor function, T_r = reduced temperature.
Source: DeDoes, A. J, et al., CEP, pp 39–44, Jan. 2007.

range from 1 to 200 kPa. The generalized Antoine equation is expressed as:

$$\ln P_r^* = A' - \frac{B'}{T_r + C'} \tag{10-73}$$

where A′, B′ and C′ are constants that depend upon the acentric factor. Tables 10-6 and 10-7 represent the generalized Antoine constants derived from the vapor pressure predictions of the RSK equation and the PR equation respectively. Table 10-8 shows the transformation required to convert values of A′, B′ and C′ to Antoine constants of A, B and C for use with various temperature and pressure units in Equation 10-70. An Excel spreadsheet program (Example 10-1.xls) has been developed to determine the vapor pressure, molar volumes, and fugacity coefficients from the Soave-Redlich-Kwong (SRK) equation of state. The spreadsheet also compares the vapor pressure obtained by using the generalized Antoine equation with the polynomial expressed in Volume 1 (page 109), and the calculated vapor pressure from SRK equation. Another spreadsheet program (Example 10-2.xls) has been developed to compare the vapor pressure of components using the Antoine Equation 10-71 and coefficients in Table 10-9 with the Clausius-Clapeyron Equation 10-68, over a range of temperatures. The saturated vapor pressure curves of acetone that were predicted by Equations 10-68 and 10-71 are shown in Figure 10-15. The parameters are taken from Reid, et al. [246], and have the values $T_{nb} = 329.4$ K, $\Delta H_{vap} = 6960$ cal/gmol, $R = 1.98721$ cal/gmol·K. At pressures <10 atm., the Clausius-Clapeyron equation reproduces the experimental data very closely and would be appropriate for use in vapor-liquid equilibrium (VLE) calculations. At high pressure, the predictions are not so good, and by comparison, the Antoine coefficients can only be obtained by regression of experimental vapor pressure data. If the constant ΔH_{vap} in the Clausius-Clapeyron equation is treated as an adjustable parameter and fitted to the experimental vapor pressure data, a value of 7175 cal/gmol produces a curve that fits the data as accurately as the Antoine equation [262].

Table 10-8 Transforming Antoine Constants A′, B′ and C′ from Table 10-6 to Dimensional Constants A, B and C for use in Equation 10-71.

$A = A' + \ln P_c$	The units of P_c must be absolute pressure Vapor pressure P* in Equation 10-71 will have the same units as P_c
$B = B'\,T_c$	The units of T_c must be absolute temperature in K or °R
$C = C'\,T_c$	Temperature T in Equation 10-71 will have the same as T_c
$C = C'\,T_c + 273.15$	Temperature T in Equation 10-71 in °C and T_c in K
$C = C'\,T_c + 459.56$	Temperature T in Equation 10-71 in °F and Tc in °R

Source: DeDoes, A. J, et al., CEP, pp 39–44, Jan. 2007

Example 10-1: Soave-Redlich-Kwong Prediction of Vapor Pressure

For n-pentane, $T_c = 469.76$K, $P_c = 33.7$ bar, $\omega = 0.252$. Use these data to verify that the SRK equation predicts a vapor pressure of 1.05bar at 309.2K. Also, verify these data with the generalized Antoine equation. R = 83.14 cm^3-bar/mol-K.

Solution

The Excel spreadsheet, Example 10-1.xls, has been developed to calculate the molar volumes of liquid and vapor of any component such as pentane, its fugacity coefficient in liquid and vapor phases, and the vapor pressure of n-pentane using the SRK, the generalized Antoine equation and a polynomial Equation (3-61). The percentage deviation in the value of the vapor pressure between the SRK equation and the generalized Antoine's equation can be calculated. Equation 10-73 depends on the reduced temperature and acentric factor, and Table 10-6 provides the constants A′, B′ and C′ for SRK at a range of reduced temperature, T_r $(0.64 \leq T_r \leq 1.0)$. The spreadsheet calculates the vapor pressure of SRK equation by using a Goal seek/Solver optimization tool in the Excel spreadsheet. The SRK (Equation 5) in Table 10-3 is:

$$P = \frac{RT}{V - b_{SRK}} - \frac{a_{SRK}(T)}{V(V + b_{SRK})} \tag{10-74}$$

Table 10-9 Antoine Coefficients for Selected Substances.

Substance	A	B	C	Temperature range, °C
Acetone	7.63132	1566.69	273.419	57 to 205
Water	8.01767	1715.70	234.268	100 to 265
Benzene	6.87987	1196.76	219.161	8 to 80
Toluene	6.95087	1342.31	219.187	−27 to 111
Ethylene glycol	8.09083	2088.936	203.454	50 to 150
Hexane	6.91058	1189.64	226.280	−30 to 170
p-Xylene	6.99053	1453.430	215.310	27 to 166
Ethanol	8.11220	1592.864	226.184	20 to 93
Acetic acid	8.02100	1936.010	258.451	18 to 118
Acetaldehyde	7.20812	1099.810	233.945	−82 to 20
Methanol	8.08097	1582.271	239.726	15 to 84
Methyl ethyl ketone	7.06356	1261.340	221.969	43 to 88
Chloroform	6.95465	1170.966	226.232	−10 to 60
Ethylenediamine	8.09831	1893.720	245.676	11 to 117
4-Methyl-2-pentanol	8.46706	2174.869	257.780	25 to 133
Dichloromethane	7.08030	1138.910	231.450	−44 to 59
1,3-Butadiene	6.85364	933.586	239.511	−75 to −2
Styrene	7.50233	1819.810	248.662	−7 to 145
Ethyl acetate	7.10179	1244.950	217.881	16 to 76
Vinylacetylene	7.02515	999.110	235.817	−93 to 5
Acetic anhydride	7.69301	1781.29	230.395	2 to 140
Dichlorosilane[§]	7.18600	1224.50	273.16	−45 to 121
Trichlosilane	6.95524	1102.900	238.865	−81 to 32
Silicon tetrachloride	7.02404	1212.890	235.910	−63 to 57
Hydrogen chloride[†]	7.44899	868.358	274.904	−85 to 36

[§] Bawa, M. S., Texas Instruments (1988).

[†] Ohe, S., Computer-Aided Data Book of Vapor Pressure, Data Book Publishing Company, Tokyo, Japan (1976).

Source: Vapor-Liquid Equilibrium Data Collection of the DECHEMA Chemistry Data Series, except where noted. The form of the equation is $\log_{10} P^{vap} = A - B/(T + C)$ with pressure in mmHg and temperature in °C.

where

$$a_{SRK}(T) = 0.42748 R^2 T_c^2 [1 + f_\omega (1 - T_r^{0.5})]^2 \Big/ P_c \tag{10-75}$$

$$b_{SRK} = 0.08664 RT/P_c \tag{10-76}$$

$$f_\omega = 0.48 + 1.574\omega - 0.176\omega^2 \tag{10-77}$$

The constant parameter a_{SRK} in Equation 10-75 is calculated from Equation 10-77, with known and calculated values of the critical temperature, reduced temperature, critical pressure and the Universal gas

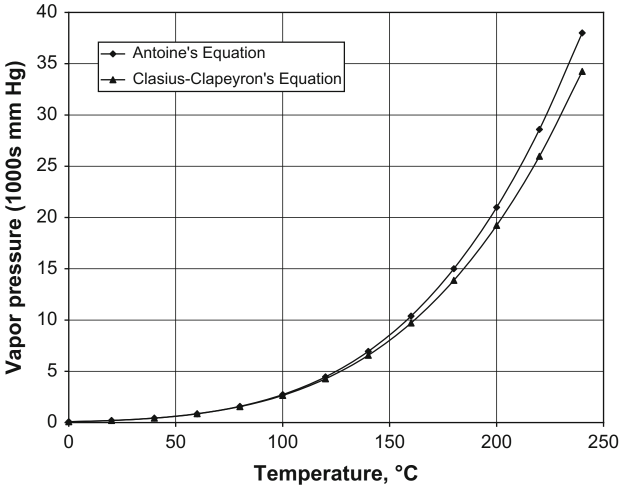


Figure 10-15 Vapor pressure of Acetone vs. temperature

constant; the constant parameter b_{SRK} is calculated from Equation 10-76. Equation 10-74 is rearranged in terms of the molar volume as a cubic equation and is solved for liquid and vapor molar volumes using the developed Excel spreadsheet (Example 10-1.xls). The SRK equation is now expressed in terms of the molar volume as:

$$f(V) = V^3 - \frac{RT}{P}V^2 + \left(\frac{a_{SRK} - b_{SRK} - Pb_{SRK}^2}{P}\right)V - \frac{a_{SRK}\, b_{SRK}}{P} = 0 \tag{10-78}$$

Using the calculated vapor pressure from the generalized Antoine Equation 10-73, the molar volumes (three real roots) are determined. The liquid molar volume and the vapor molar volume (i.e. the lowest and highest values) are then chosen from these three roots, and are used to determine the fugacity of the liquid and vapor phases from the following equations [256]:

$$Z = \frac{PV}{RT} \tag{10-79}$$

$$h = \frac{b_{SRK}}{V} \tag{10-80}$$

$$\ln \phi = Z - 1 - \ln Z - \ln(1 - h) - \frac{a_{SRK}}{b_{SRK}\, RT}\ln(1 + h) \tag{10-81}$$

Equation 10-74 is rearranged in the form

$$f(P) = P - \frac{RT}{V - b_{SRK}} + \frac{a_{SRK}(T)}{V(V + b_{SRK})} = 0 \tag{10-82}$$

Equation 10-82 in the Excel spreadsheet (Example 10-1.xls) is set to zero (cell B44) and is optimized by changing cell G37 using Solver or Go-Seek optimizer in the spreadsheet. This is carried out for known value of the calculated molar volume V, by changing the value of the vapor pressure in the cell. When the final value of Equation 10-82 becomes 0, then the computed value of P (cell G37) gives the required vapor pressure. Since the calculated fugacity coefficients for both liquid and vapor are equal, the vapor pressure as calculated from SRK equation is the estimated known vapor pressure at the specified temperature. In this example, the vapor pressure of n-pentane at 309.2 K is 1.05 bar. Figures 10-16a-d show snap shots of the Excel spreadsheet for calculating the vapor pressure using the SRK model.

Example 10-2: Use of the Clausius-Clapeyron Equation to Predict Heat of Vaporization

The vapor pressure of liquid 2, 2, 4 trimethyl pentane at various temperatures is given below. Estimate the heat of vaporization of this compound at 25°C.

Vapor pressure (kPa)	0.667	1.333	2.666	5.333	8.000	13.33	26.66	53.33	101.32
Temperature (°C)	−15.0	−4.3	7.5	20.7	29.1	40.7	58.1	78.0	99.2

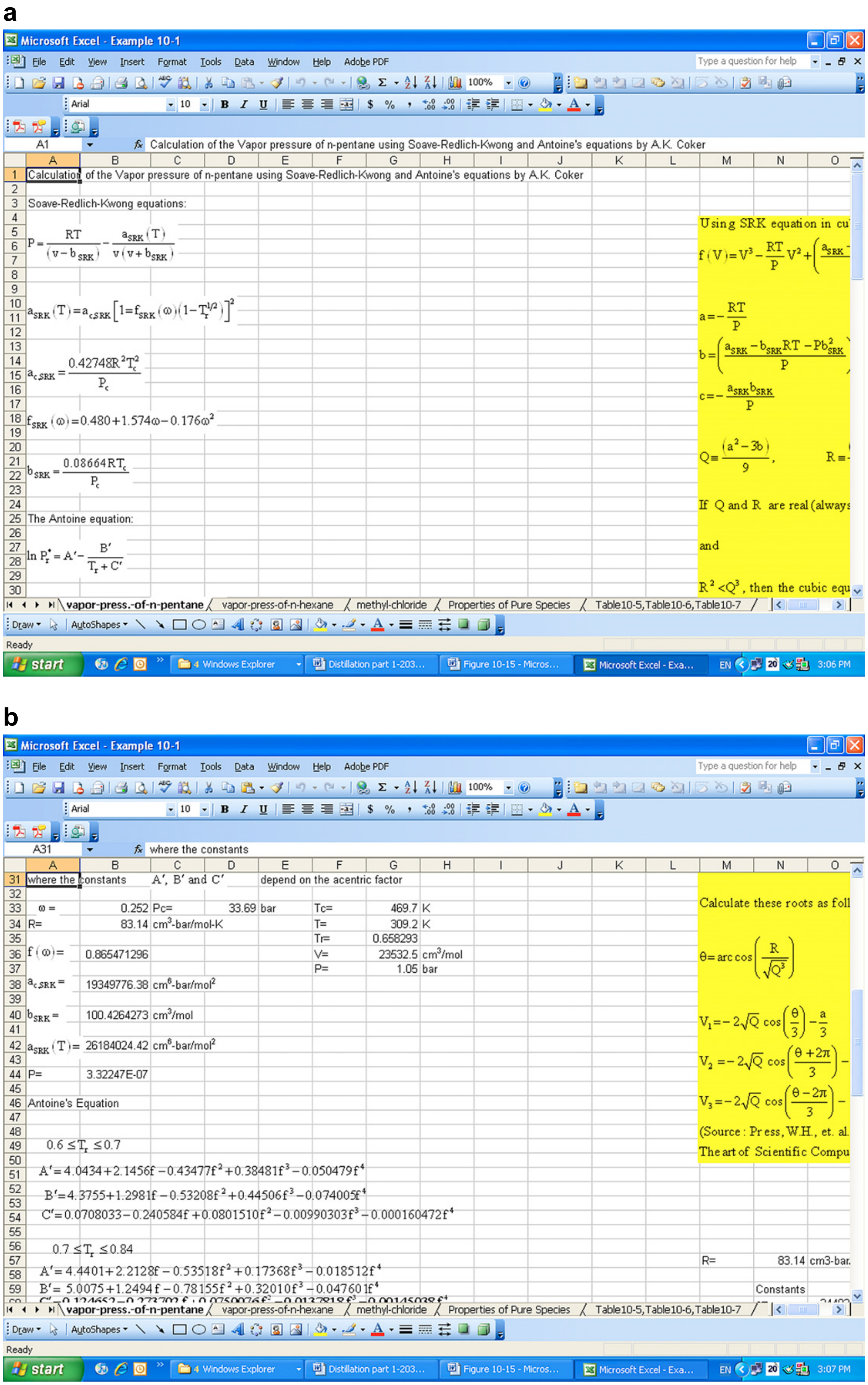
Solution

The Excel spreadsheet Example 10-2.xls (vapor-pressure-calculation-2.xls) has been developed to estimate the heat of vaporization and Figure 10-17 shows the trend line from the spreadsheet indicating that ΔH_{vap} is constant over the whole range of temperature. The value of the slope from the trend line is:

$$\frac{\Delta H_{vap}}{R} = 4.2289 \times 10^3$$

$R = 8.314$ J/mol·K and the estimated $\Delta H_{vap} = 8.314 \times 4.2289 \times 10^3$ J/mol

The calculated heat of vaporization, $\Delta H_{vap} = 35.16$ kJ/mol.



a

Calculation of the Vapor pressure of n-pentane using Soave-Redlich-Kwong and Antoine's equations by A.K. Coker

Soave-Redlich-Kwong equations:

$$P=\frac{RT}{(v-b_{SRK})}-\frac{a_{SRK}(T)}{v(v+b_{SRK})}$$

$$a_{SRK}(T)=a_{c,SRK}\left[1=f_{SRK}(\omega)(1-T_r^{1/2})\right]^2$$

$$a_{c,SRK}=\frac{0.42748R^2T_c^2}{P_c}$$

$$f_{SRK}(\omega)=0.480+1.574\omega-0.176\omega^2$$

$$b_{SRK}=\frac{0.08664RT_c}{P_c}$$

The Antoine equation:

$$\ln P_r^{\bullet}=A'-\frac{B'}{T_r+C'}$$

Using SRK equation in cu

$$f(V)=V^3-\frac{RT}{P}V^2+\left(\frac{a_{SRK}}{}\right.$$

$$a=-\frac{RT}{P}$$

$$b=\left(\frac{a_{SRK}-b_{SRK}RT-Pb_{SRK}^2}{P}\right)$$

$$c=-\frac{a_{SRK}b_{SRK}}{P}$$

$$Q=\frac{(a^2-3b)}{9},\qquad R=$$

If Q and R are real (always

and

$R^2<Q^3$, then the cubic equ

b

where the constants A′, B′ and C′ depend on the acentric factor

ω =	0.252	Pc=	33.69	bar	Tc=	469.7	K
R=	83.14	cm^3-bar/mol-K			T=	309.2	K
					Tr=	0.658293	
$f(\omega)$=	0.865471296				V=	23532.5	cm^3/mol
					P=	1.05	bar
$a_{c,SRK}$ =	19349776.38	cm^6-bar/mol^2					
b_{SRK} =	100.4264273	cm^3/mol					
$a_{SRK}(T)$=	26184024.42	cm^6-bar/mol^2					
P=	3.32247E-07						

Antoine's Equation

$$0.6\le T_r\le 0.7$$

$$A'=4.0434+2.1456f-0.43477f^2+0.38481f^3-0.050479f^4$$

$$B'=4.3755+1.2981f-0.53208f^2+0.44506f^3-0.074005f^4$$

$$C'=0.0708033-0.240584f+0.0801510f^2-0.00990303f^3-0.000160472f^4$$

$$0.7\le T_r\le 0.84$$

$$A'=4.4401+2.2128f-0.53518f^2+0.17368f^3-0.018512f^4$$

$$B'=5.0075+1.2494f-0.78155f^2+0.32010f^3-0.047601f^4$$

Calculate these roots as foll

$$\theta=\arccos\left(\frac{R}{\sqrt{Q^3}}\right)$$

$$V_1=-2\sqrt{Q}\cos\left(\frac{\theta}{3}\right)-\frac{a}{3}$$

$$V_2=-2\sqrt{Q}\cos\left(\frac{\theta+2\pi}{3}\right)-$$

$$V_3=-2\sqrt{Q}\cos\left(\frac{\theta-2\pi}{3}\right)-$$

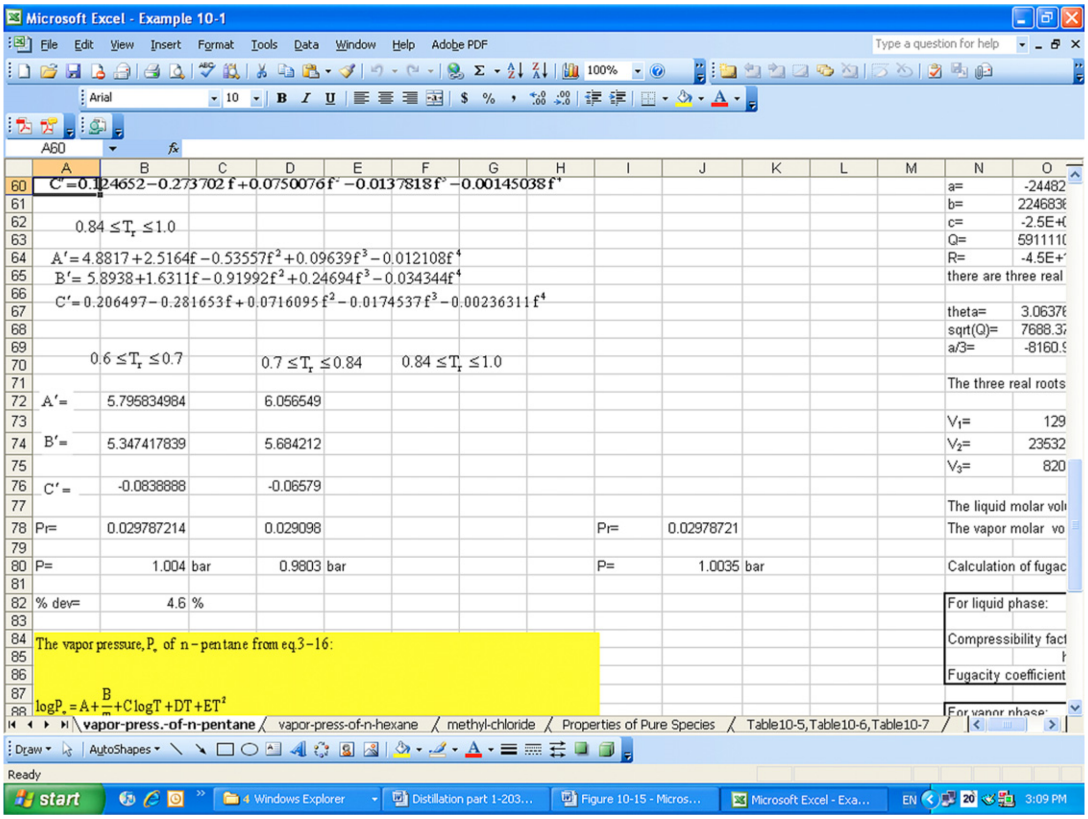
(Source: Press, W.H., et. al.
The art of Scientific Compu

R= 83.14 cm3-bar.

Constants

Figure 10-16a–b Snapshot of the Excel spreadsheet for calculating the vapor-pressure using SRK method and Antoine's Equation (Example 10-1).

c



$C' = 0.124652 - 0.273702f + 0.0750076f^2 - 0.0137818f^3 - 0.00145038f^4$

$0.84 \le T_r \le 1.0$

$A' = 4.8817 + 2.5164f - 0.53557f^2 + 0.09639f^3 - 0.012108f^4$

$B' = 5.8938 + 1.6311f - 0.91992f^2 + 0.24694f^3 - 0.034344f^4$

$C' = 0.206497 - 0.281653f + 0.0716095f^2 - 0.0174537f^3 - 0.00236311f^4$

	$0.6 \le T_r \le 0.7$	$0.7 \le T_r \le 0.84$	$0.84 \le T_r \le 1.0$
A′=	5.795834984	6.056549	
B′=	5.347417839	5.684212	
C′=	-0.0838888	-0.06579	
Pr=	0.029787214	0.029098	Pr= 0.02978721
P=	1.004 bar	0.9803 bar	P= 1.0035 bar
% dev=	4.6 %		

The vapor pressure, P_v of n-pentane from eq.3-16:

$\log P_v = A + \frac{B}{T} + C\log T + DT + ET^2$

a=	-24482
b=	224683
c=	-2.5E+
Q=	591111
R=	-4.5E+

there are three real

theta=	3.0637
sqrt(Q)=	7688.3
a/3=	-8160.

The three real roots

V_1=	129
V_2=	23532
V_3=	820

The liquid molar vol

The vapor molar vo

Calculation of fugac

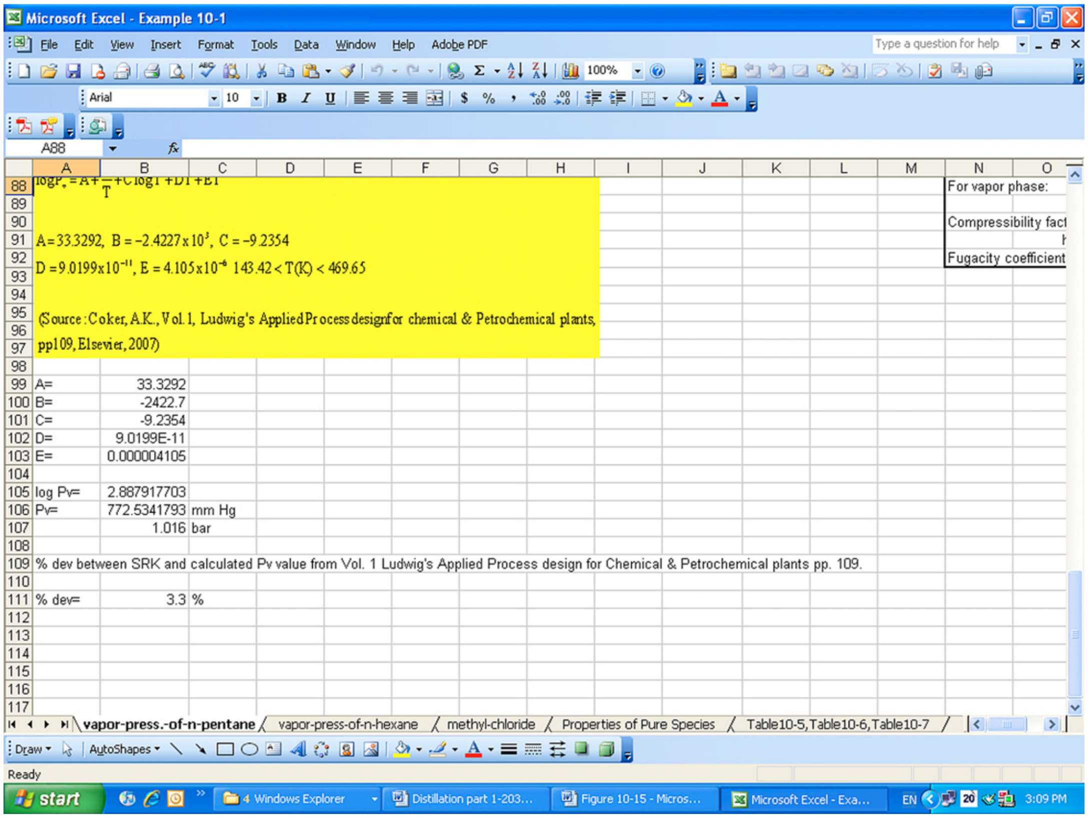
For liquid phase:

Compressibility fact

Fugacity coefficient

For vapor phase:

d



$\log P_v = A + \frac{B}{T} + C\log T + DT + ET^2$

$A = 33.3292,\ B = -2.4227 \times 10^3,\ C = -9.2354$

$D = 9.0199 \times 10^{-11},\ E = 4.105 \times 10^{-6}\quad 143.42 < T(K) < 469.65$

(Source: Coker, A.K., Vol. 1, Ludwig's Applied Process design for chemical & Petrochemical plants, pp109, Elsevier, 2007)

A=	33.3292	
B=	-2422.7	
C=	-9.2354	
D=	9.0199E-11	
E=	0.000004105	
log Pv=	2.887917703	
Pv=	772.5341793	mm Hg
	1.016	bar

% dev between SRK and calculated Pv value from Vol. 1 Ludwig's Applied Process design for Chemical & Petrochemical plants pp. 109.

% dev= 3.3 %

For vapor phase:

Compressibility fact

Fugacity coefficient

Figure 10-16c–d Snapshot of the Excel spreadsheet for calculating the vapor-pressure using SRK method and Antoine's Equation (Example 10-1).

Example 10-3: Construction of Temperature Composition Diagram, Equilibrium Diagram and Plot of Relative Volatility vs Mole Fraction of Phenol in Liquid for Phenol-Orthocresol mixture

The following vapor pressures were obtained for phenol and orthocresol.

Temperature (K)	Vapor pressure (kN/m^2) Orthocresol	Phenol
387.0	7.70	10.0
387.9	7.94	10.4
388.7	8.21	10.8
389.6	8.50	11.2
390.3	8.76	11.6
391.1	9.06	12.0
391.9	9.40	12.4
392.7	9.73	12.9
393.3	10.00	13.3

Assuming Raoult's and Dalton's laws apply; construct the following data for a total pressure of 10 kN/m^2

1. A temperature composition diagram.
2. An x–y diagram.
3. Relative volatility against mole fraction of phenol in liquid.

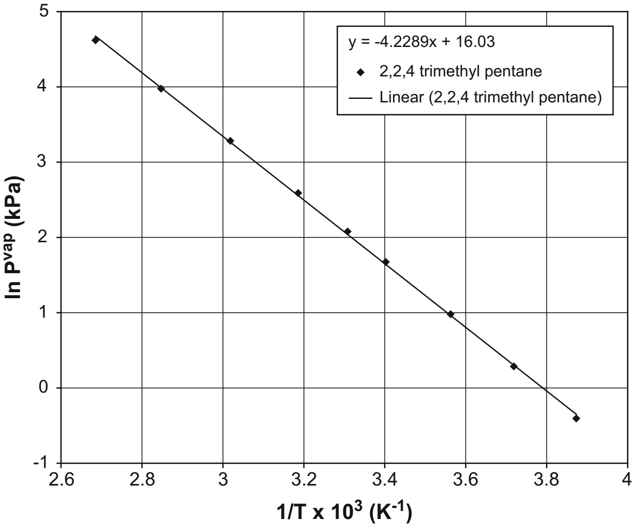


Figure 10-17 A plot of ln P^{vap} versus 1/T of 2,2,4 trimethyl pentane.

Solution

If Raoult's law and Dalton's law apply, the following equations may be used.

$$\pi = p_A + p_B \tag{10-2}$$

$$p_A = y_A \cdot \pi = x_A \cdot p_A^o \tag{10-31}$$

where

π = the total pressure
p_A = the partial pressure of component A
p_B = the partial pressure of component B
p_A^o = the vapor pressure of component A.
p_B^o = the vapor pressure of component B.

Hence from Equations 10-2 and 10-31:

$$x_A = \frac{(\pi - p_B^o)}{(p_A^o - p_B^o)} \tag{10-83}$$

$$y_A = \frac{x_A \cdot p_A^o}{\pi} \tag{10-84}$$

The relative volatility, α_{A-B}, is defined in terms of the more volatile component (eg. phenol) by:

$$\alpha_{A-B} = \frac{p_A^o}{p_B^o} \tag{10-85}$$

Table 10-10 shows the results of the computation.

Figures 10-18 and 10-19 show the temperature composition diagram and the equilibrium diagram respectively. The values obtained for the relative volatility vary between 1.300 and 1.330 and the average value of 1.319 could be used in subsequent computations. The Excel spreadsheet Example 10-3.xls shows the calculations of x_A, y_A and α_{A-B}.

Table 10-10 Mole Fractions x_A, y_A and α_{A-B} in Example 10-2.

Temperature, K	x_A (from Eq. 10-83)	y_A (from Eq. 10-84)	$\alpha_{A-B} = \frac{p_A^o}{p_B^o}$ (from Eq. 10-85)
387.0	1.0	1.0	1.300
387.9	0.837	0.871	1.310
388.7	0.691	0.746	1.315
389.6	0.556	0.622	1.318
390.3	0.437	0.506	1.324
391.1	0.320	0.384	1.325
391.9	0.200	0.248	1.319
392.7	0.085	0.110	1.326
393.3	0	0	1.330

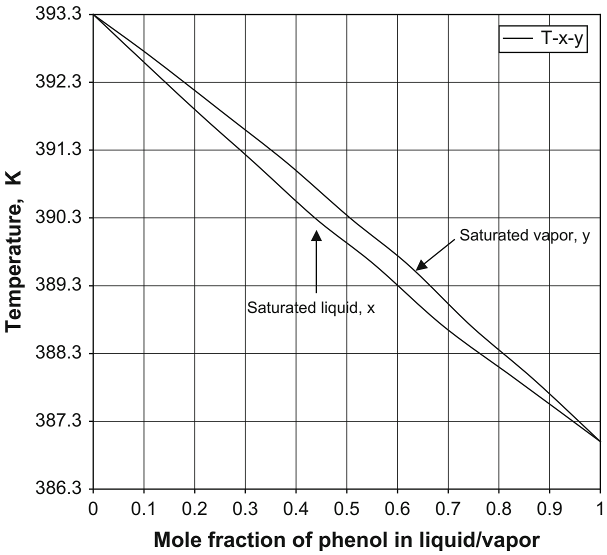


Figure 10-18 Phase diagram for the mixture phenol and orthocresol at 10 kN/m.^{2}

10.12 Azeotropic Mixtures

Azeotrope is derived from the ancient Greek words meaning *"to boil unchanged"*, and is defined as a mixture of composition at which the equilibrium liquid and vapor compositions are equal. Figures 10-5, 10-6a, 10-6b, 10-6c and 10–7 are phase diagrams for normal systems, showing that the concentration of the less volatile component increases with increase in the dew and bubble points. However, if the components exhibit strong physical and chemical interaction, the resulting phase diagrams are significantly different. In such systems, there is a critical composition (i.e. the point of intersection of the equilibrium curve with the 45° line) for which the vapor and liquid compositions are identical. At this point, the components cannot be separated at the given pressure, and such mixtures are termed azeotropes.

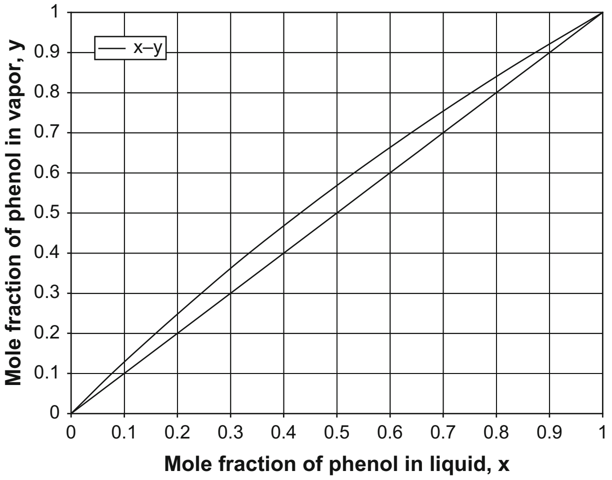


Figure 10-19 VLE data for the mixture phenol and orthocresol at 10 kN/m.^{2}

Azeotropes are common when polar organic compounds, such as alcohols, ketones, ethers and acids are mixed with water, and this complicates their separation by distillation. In practice, there will be no change in liquid and vapor compositions from tray to tray, and hence a simple distillation process will not separate the mixture. To determine methods that will separate such mixtures, it is useful to examine their deviations from Raoult's Law.

Azeotropes occur in various systems as binary, ternary and multicomponent mixtures, and can be "homogeneous" (single liquid phase) or "heterogeneous" (two liquid phases). They can exhibit a minimum-boiling point or maximum- boiling point.

A minimum-boiling azeotrope boils at a temperature lower than either of the pure components. Consequently, when distilling a binary system made up of these components, the top is azeotrope and the bottom is one or the other of pure components depending on the "side" of the azeotrope that the feed was. A maximum-boiling azeotrope boils at a temperature higher than either of the pure components and leaves from the bottom of a column and the top product is the high boiling point component containing the More Volatile Component (MVC) at low concentrations. The top product is the MVC when it is present at high concentrations. When liquid phase separation occurs, the boiling temperature of the mixture as well as the vapor phase composition remains constant until one of the liquid phases disappears. Under such conditions, depending on the composition, a mixture of the two liquids will leave the top of the column and either of the components will leave at the bottom.

Azeotropic mixtures consist of two or more components, and are surprisingly common in distillation systems. It is therefore essential with any new system to determine whether an azeotrope exists. Fortunately, if experimental data are unavailable, reference can be made to excellent lists for known azeotropic systems, with vapor pressure information [20, 28, 43]. Typical forms of representation of azeotropic data are shown in Figures 10-20a and 10-20b, 10-21a and 10-21b respectively. These are homogeneous, with one liquid phase at the azeotrope point. Figures 10-22a and 10-22b illustrate a heterogeneous azeotrope where two liquid phases are in equilibrium with one vapor phase. The system butanol-water is an example of the latter. Chloroform-methanol and acetone-chloroform are examples of binary homogeneous azeotropes with "minimal-boiling point" and "maximum-boiling point" respectively.

A "minimum" boiling binary azeotrope exhibits a constant composition as shown by its crossing of

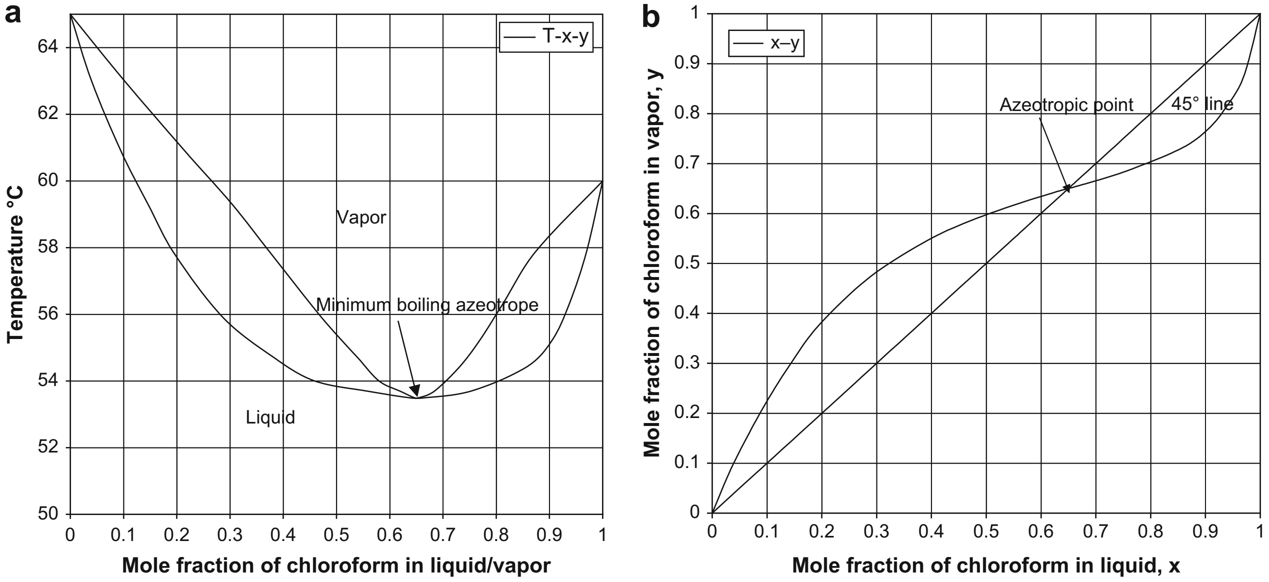


Figure 10-20 a. Phase diagram for the mixture of chloroform and methanol at 1 atm. b. VLE diagram for choloroform and methanol mixture at 1 atm.

the x = y along the 45° line in Figure 10-20b, which boils at a lower temperature than either of its pure components. This class of azeotrope results from positive deviations from Raoult's Law. Likewise, the "maximum" (Figure 10-21b) boiling binary azeotrope represents a negative deviation from Raoult's Law, and exhibits a constant boiling point greater than either of the pure components. At the point where the equilibrium curve crosses x = y, 45° line, the composition is constant and cannot be further purified by normal distillation. Both minimum and maximum boiling point azeotropes can be modified by changing the system pressure, and/or addition of a third component, which should be chosen such that will form a minimum boiling azeotrope with one of the original pair. To be effective the new azeotrope should boil well below or above the original azeotrope. Using this technique, one of the original components can often be recovered as a pure product, while still obtaining the second azeotrope for separate purification.

In a minimum-boiling azeotrope, the molecular species repel each other, whereas in a maximum-boiling azeotrope they attract each other. However, if the azeotrope occurs in the composition range in which the two liquids are immiscible, phase splitting occurs and a heterogeneous azeotrope is formed. Table 10-11 lists some examples of binary mixtures that form azeotropes.

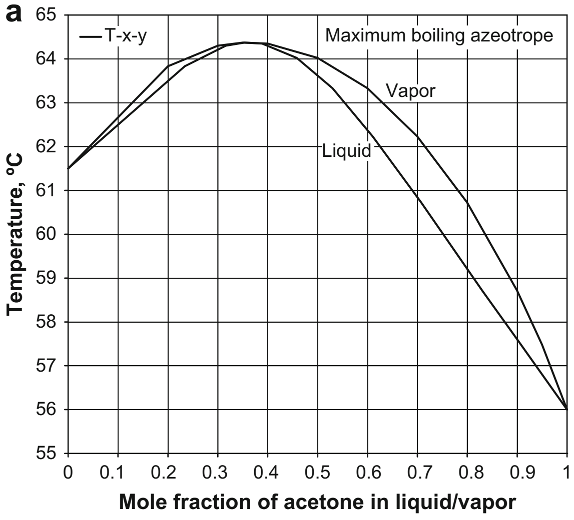


Figure 10-21a Phase diagram for the mixture chloroform and acetone at 1 atm.

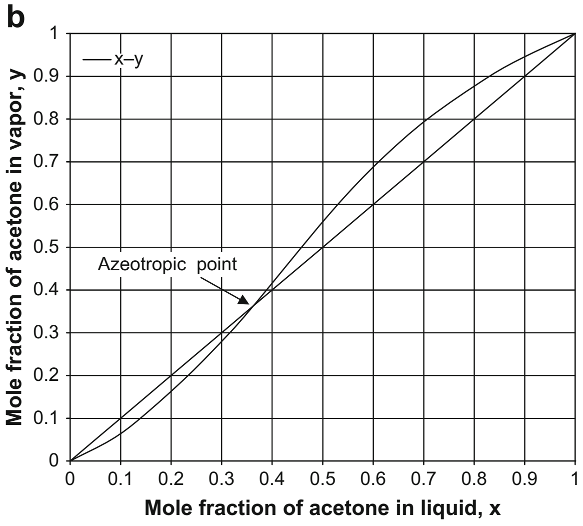


Figure 10-21b Vapore Liquid equilibrium diagram for chloroform acetone mixture at 1 atm.

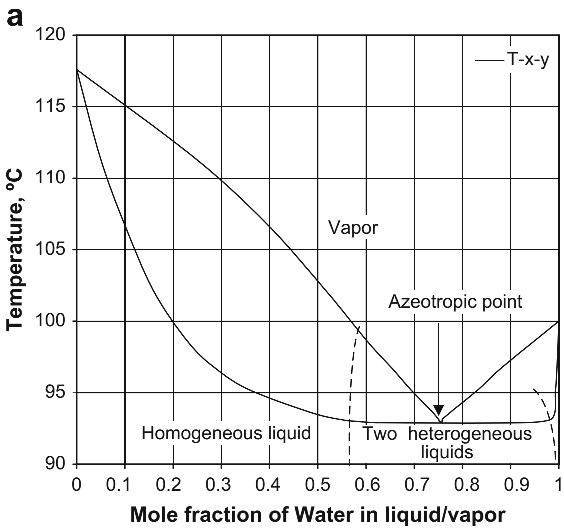


Figure 10-22a Phase diagram for the mixture of water and 1-butanol at 1 atm.

For a "minimum" boiling azeotrope, the partial pressures of the components will be greater than predicted by Raoult's Law, and the activity coefficients will be >1.0.

$$\gamma = (y_i P)/(x_i p_i^*) \tag{10-86}$$

where

p_i^* = vapor pressure of component i, at temperature
$P = \pi$ = total pressure
$\gamma = a_i/x_i$ = activity coefficient of component, i
p_i = partial pressure of component i.
Raoult's Law: $p_i = x_i\, p_i^* = y_1 P$

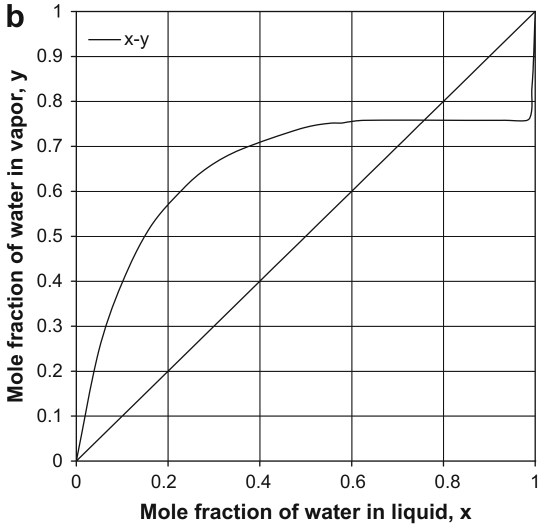


Figure 10-22b VLE diagram for the mixture of water and 1-butanol at 1 atm.

For "maximum" boiling binary azeotropes, the partial pressures will be less than predicted by Raoult's Law and the activity coefficients will be less than 1.0.

In reference to distillation conditions, the azeotrope represents a point in the system where the relative volatilities reverse. This applies to either type of azeotrope but the direction of reversal is opposite. For example in Figure 10-20b the lower portion of the x-y diagram shows that $y_i > x_i$, while at the upper part, the $y_i < x_i$. In any distillation, without addition of an azeotrope "breaker" or solvent to change the system characteristics, if a feed of composition 30% x_i were used, the column could only yield a bottom product, which approaches pure x_2 and an azeotrope composition of about 65% x_i and 35% x_2 at the top. The situation would be changed only to the extent of recognizing that if the feed came in above the azeotropic point, the bottoms product would be the azeotrope composition.

Successful azeotropic distillation is largely dependent on the correct choice of entrainer (i.e. solvent). Entrainers are selected on the basis of making a seperation distillation possible. Stichlmair and Fair [263] have presented the criteria for entrainer selection, which are illustrated in Table 10-12 and Figure 10-23. The entrainer, selected such that the constituents *a* and *b* of the azeotropic mixture to be separated are both origins or termini of distillation lines, and such systems always have distillation borders. The entrainer must also permit the recovery of products *a* and *b* at the top or bottom of distillation columns.

Stichlmair and Fair [263] have presented a generalized process for separating out the higher boiling components, *b*. In this instance, the sequence of the separations differs from that in Figure 10-23. Both modifications of the generalized process are characterized by two separations performed on the convex side and one separation performed on the concave side of the border distillation line. Using the criteria selection of Table 10-12, a minimum azeotrope can be separated by an intermediate boiling or a high boiling entrainer instead of a low boiler, if additional azeotropes are formed. Smith [65] discusses azeotropic distillation in detail; Widalgo and Seider [264] have presented an excellent review of azeotropic distillation. References 153-157, 171, and 172 also describe azeotropic design techniques.

Generally, all activity coefficient models are capable of representing phase diagrams of the type shown in Figures 10-10c and 10-10d, but not always to same level of accuracy. It is essential therefore, to plot the x-y diagram for each binary pair in the (multicomponent) mixture before using the VLE model in design calculations. If the predicted diagrams do not provide satisfactory agreement with experimental data, other models should be considered. Otherwise, a poor design could result.

Table 10-11 Examples of Binary Mixtures with an Azeotrope.

						Azeotropic data		
Formula	**Name**	**B.P., °C**	**Formula**	**Name**	**B.P., °C**	**xa, mol %**	**B.P., °C**	**Type**
H_2O	water	100	HBr	hydrobromic acid (a)	−67	16.7	126	max.
			HCl	hydrochloric acid (a)	−85	11.1	108.6	max.
			HNO_3	nitric acid (a)	86	38.3	121	max.
			$CHCl_3$	chloroform (a)	61.2	83.9	56.12	hetero
			CH_2Cl_2	dichloromethane (a)	40.1	93.3	38.1	hetero
			CH_3NO_2	nitromethane (b)	101.2	51.1	83.6	hetero
			C_2H_6O	ethanol (a)	78.3	90.4	78.2	min.
			$C_3H_6O_2$	methyl acetate (a)	57	87.2	56.4	min.
			C_3H_8O	n-propyl alcohol (a)	97.3	42.2	87.8	min.
			$C_4H_6O_2$	methyl acrylate (a)	80	72.9	71	min.
			C_4H_8O	tetrahydrofurane (a)	66	81.7	64	min.
			C_4H_8O	2-butanone (a)	79.6	66.2	73.4	min.
			$C_4H_8O_2$	butyraldehyde (a)	74	79.6	68	min.
			$C_4H_8O_2$	dioxane (b)	101.3	51.7	87.8	min.
			$C_4H_8O_2$	ethyl acetate (a)	77.1	68.2	70.4	hetero
			$C_4H_{10}O$	butyl alcohol (b)	117.4	75.2	92.7	hetero
			$C_4H_{10}O_2$	2-ethoxyethanol (b)	135.1	92.5	99.4	min.
			C_5H_5N	pyridine (b)	115	76.8	94	min.
			$C_5H_{12}O$	ethyl propyl ether (a)	63.6	83.1	59.5	hetero
			C_6H_6	benzene (a)	80.2	70.4	69.3	hetero
			C_7H_8	toluene (b)	110.7	55.6	84.1	hetero
$CHCl_3$	chloroform	61.2	CH_4O	methanol (b)	64.7	65.0	53.4	min.
			C_2H_6O	ethanol (b)	78.3	83.7	59.4	min.
			C_3H_6O	acetone (a)	56.1	36.7	64.4	max.
CH_4O	methanol	64.7	CH_2Cl_2	dichloromethane (a)	40.1	70.5	37.8	min.
			C_3H_6O	acetone (a)	56.2	80.2	55.5	min.
			C_4H_8O	2-butanone (b)	79.6	84	63.5	min.
			$C_4H_8O_2$	ethyl acetate (b)	77.1	69.9	62.3	min.
			C_6H_6	benzene (b)	80.2	61	57.5	min.
			C_7H_8	toluene (b)	110.7	86.5	63.8	min.
			C_7H_{16}	n-heptane (b)	98.5	76.5	59.1	min.
			C_8H_{18}	n-octane (b)	125.6	90.2	63	min.
C_2H_6O	ethanol	78.3	$C_4H_6O_2$	methylacrylate (b)	80	57.5	73.5	min.

Table 10-11 Examples of Binary Mixtures with an Azeotrope. (*Cont'd*)

						Azeotropic data		
Formula	**Name**	**B.P., °C**	**Formula**	**Name**	**B.P., °C**	**xa, mol %**	**B.P., °C**	**Type**
			C_4H_8O	2-butanone (b)	79.6	50.0	74	min.
			$C_4H_8O_2$	ethylacetate (b)	77	53.8	71.8	min.
			$C_4H_{10}O_2$	Eth.methoxymeth (a)	65.9	77	64	min.
			$C_5H_{12}O$	ethylpropylether (a)	63.6	61	61.2	min.
			C_6H_{14}	n-hexane (a)	68.7	66.5	58.4	min.
			C_7H_{18}	toluene (b)	110.7	81	76.7	min.
C_3H_6O	acetone	56.2	C_6H_{12}	cyclohexane (b)	80.8	74.6	53	min.
			C_6H_{14}	hexane (b)	68.9	68.1	49.8	min.
			C_7H_{16}	heptane (b)	98.4	93.6	55.9	min.
$C_4H_{10}O_2$	2-ethoxyethanol	135.1	C_8H_{10}	ethylbenzene (b)	136.2	56.9	127.1	min.
			C_8H_{18}	octane (a)	125.8	61	116.1	min.
C_5H_5N	pyridine	115	C_7H_8	toluene (b)	110.7	75.3	110.1	min.
			C_8H_8	n-octane (b)	125.8	$<$92.9	128.8	min.
C_6H_6	benzene	80.2	C_3H_8O	2-propanol (b)	82.5	61	71.8	min.
			C_6H_{12}	cyclohexane (b)	80.8	53	77.6	min.

B.P. = boiling point, xa = mol % of component a (low boiler) at the azeotrope, p = 1.013 bar
Source: Stichlmair, J. G., and James R. Fair, Distillation: Principles and Practice, Wiley-VCH, 1998

Commencing with the equality of the fugacities of the species in the vapor and liquid mixtures in Equation 10-12:

$$f_i^V = f_i^L \; i = 1, \ldots\ldots, N \qquad (10\text{-}12)$$

and substituting the expressions for the mixtures fugacities in terms of the mole fractions, activity coefficients, and fugacity coefficients in Equations 10-13 and 10-14:

$$y_i \, \phi_i^V P = x_i \, \gamma_i^L \, f_i^L = 1, \ldots\ldots, \; N, \qquad (10\text{-}87)$$

Consider an ideal binary mixture ($\gamma_i^L = 1$), at low pressure ($\phi_i^V = 1$ and $f_i{}^L = P_i^s$), where P_i^s is the vapor pressure of species i. Substituting in Equation 10-87,

Table 10-12 Criteria for Entrainer Selection for Processes With Distillation Borders, See Process in Figure 10-23.

Entrainer for the separation of a mixture with a minimum azeotrope

- Low boiler (lower than the minimum azeotrope)
- Medium boiler, which forms a new minimum azeotrope with the low boiling constituent of the given mixture.
- High boiler, which forms new minimum azeotropes with both constituents of the given mixture. At least one of them has to boil lower than the azeotrope of the given mixture.

Entrainer for the separation of a mixture with a maximum azeotrope

- High boiler (higher than the maximum azeotrope).
- Medium boiler, which forms a new maximum azeotrope with the high boiling constituent of the given mixture.
- Low boiler, which forms new maximum azeotropes with both constituents of the given mixture. At least one of them has to boil higher than the azeotrope of the given mixture.

Source: Stichlmair, J.G., and J. R. Fair, Distillation: Principles and Practice, Wiley-VCH, 1998.

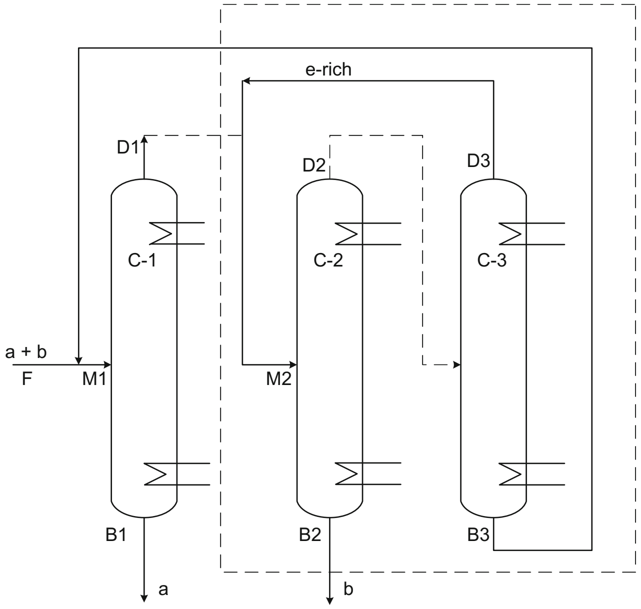


Figure 10-23 Process flow diagram for the separation of a binary mixture with a minimum azeotrope by using a low boiling entrainer. The feed is rich in a. Components a and b are obtained as pure bottoms products from columns C-1 and C-2 respectively.

$$y_1\,P = x_1\,P_1^s \tag{10-88}$$

and

$$y_2\,P = x_2\,P_2^s \tag{10-89}$$

Adding Equations 10-88 and 10-89:

$$P = x_1\,P_1^s + x_2 P_2^s = x_1\,P_1^s + (1 - x_1) P_2^s \tag{10-90}$$

$$= P_2^s + (P_1^s - P_2^s) x_1 \tag{10-91}$$

Equation 10-91 shows the relationship between the total pressure, P and the mole fraction of the more volatile species, which is characteristic of Raoult's law as shown in Figure 10-24 for a benzene-toluene mixture. However, the mixture exhibits a positive deviation from ideality $(\gamma_i^L > 1, i = 1, 2)$ or Raoult's law, so Equation 10-90 becomes:

$$P = x_1\,\gamma_1^L P_1^s + (1 - x_1)\gamma_2^L P_2^s \tag{10-92}$$

Therefore, if γ_1^L and γ_2^L are ≥ 1 for all compositions under isothermal boiling, then it is common for the bubble and dew point curves to reach a maximum at the same composition, that is the azeotropic point. This situation is illustrated in Figures 10-25a and 10-25b for an ethyl acetate-ethanol mixture. Figure 10-25a shows the bubble and dew point curves on a T-x-y diagram at 1 atmosphere pressure (101.3 kPa). Note the minimum boiling azeotrope at 71.8°C, where $x_1 = y_1 = 0.54$. Feed streams having lower mole fractions cannot be purified beyond 0.54 in a distillation column, and streams having higher mole fractions produce distillate mole fractions that are bounded by 0.54 and 1.0. Consequently, the azeotropic composition is commonly referred to as a distillation boundary.

Similarly, when the mixture exhibits a negative deviation from ideality or Raoult's law, γ_1^L and γ_2^L are ≤ 1,

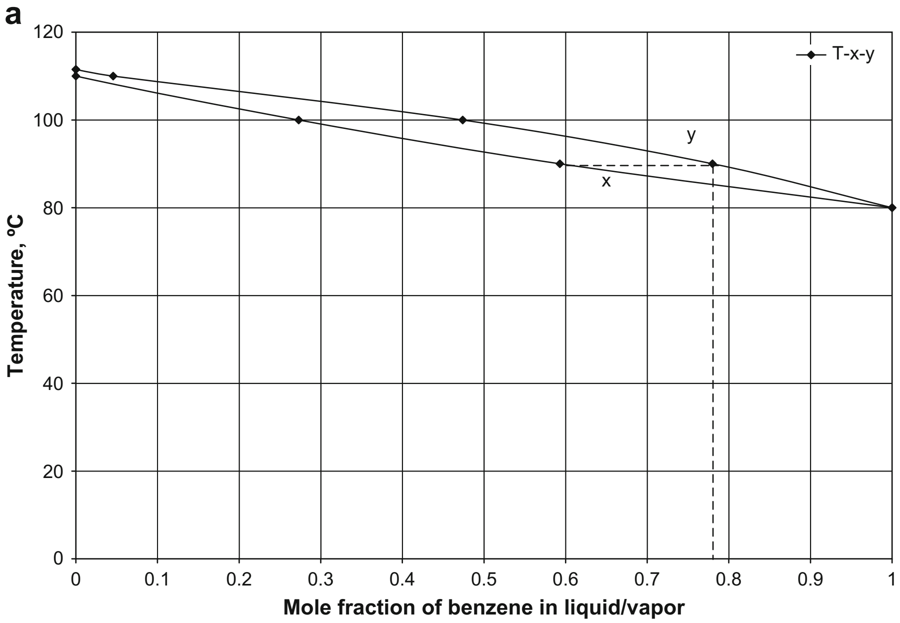


Figure 10-24a Boiling point diagram for benzene-toluene mixture, total pressure = 760 mm Hg.

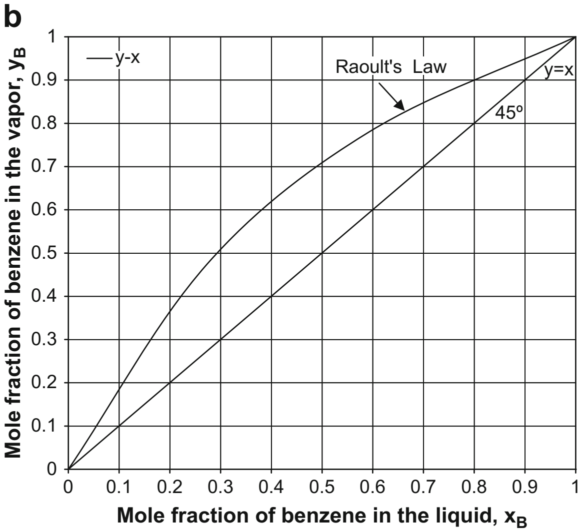


Figure 10-24b VLE diagram for the mixture benzene and toluene at 760 mm Hg total pressure.

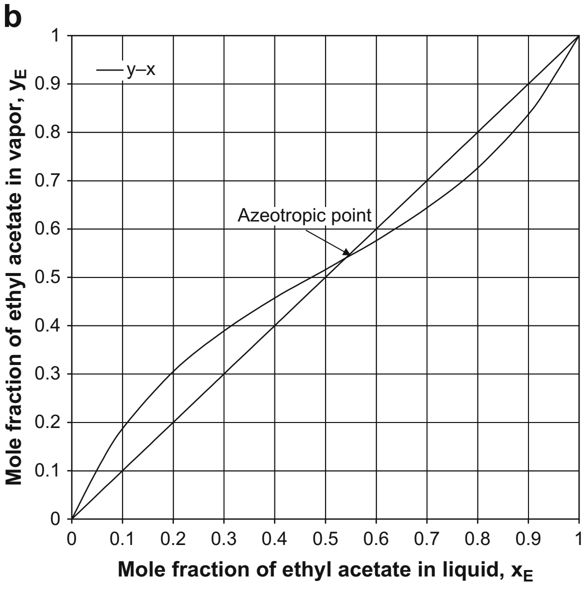


Figure 10-25b VLE diagram for the mixture ethyl acetate and ethanol at 1 atm.

and both the bubble and dew point curves drop below the straight line that represents an ideal mixture. Figures 10-26a and 10-26b respectively show the phase and VLE diagrams of a water-formic acid binary mixture at 1 atmosphere pressure (101.3 kPa). The T-x-y diagram shows the boiling point curving upwards above ideality, and consequently the system is said to have the maximum boiling azeotrope at 107.6°C, where $x_1 = y_1 = 0.41$. In this instance, feed streams having lower mole fractions cannot be purified beyond 0.41 water in the bottoms product of a column, and feed streams having higher mole fractions have a lower bound of 0.41 water in the mole fraction of the bottoms product. The azeotropes in Figure 10-25a and 10-26a occur where $(\partial T/\partial x_1)_P = (\partial T/\partial y_1)_P = 0$, or equivalently, where $x_1 = y_1$. Therefore, azeotropic mixtures produce x-y curves that cross the 45° line at the azeotropic composition. The slope of the curve at the crossing point is <1.0 for minimum-boiling azeotropes and >1.0 for maximum-boiling azeotropes, as shown in Figures 10-25a and 10-26a respectively.

At homogeneous azeotrope, $x_i = y_i$, $i = 1, \ldots.C$, the equilibrium constant, K_i for species becomes unity. The

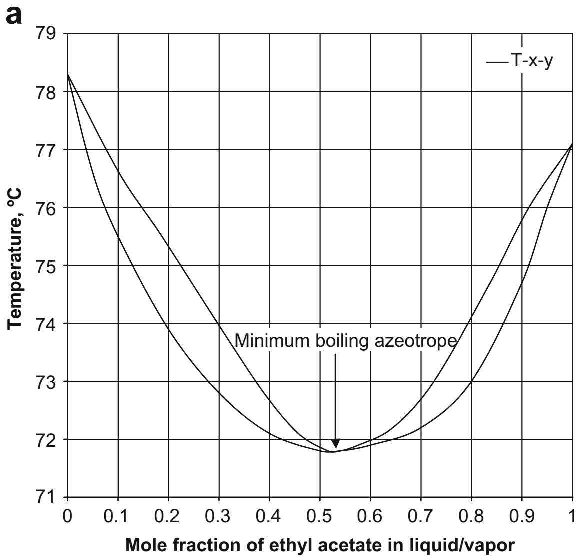


Figure 10-25a Phase diagram for the mixture of ethyl acetate and ethanol at 1 atm.

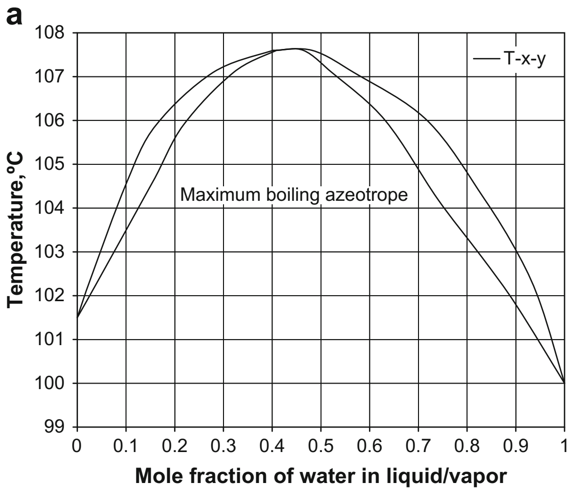


Figure 10-26a Phase diagram for the mixture of water and formic acid at 101.3 kPa.

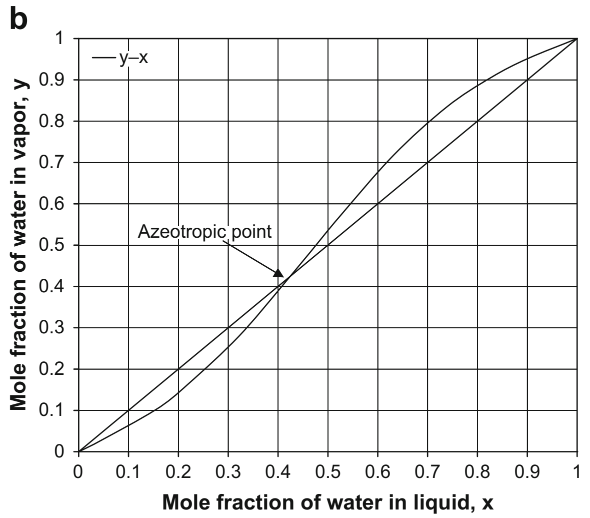


Figure 10-26b VLE diagram for the mixture of water and formic acid at 101.3 kPa.

equilibrium constant for species i in Equation 10-27 becomes:

$$K_i \equiv \frac{y_i}{x_i} = \frac{\gamma_i^L f_i^L}{\phi_i^V P} = 1, i = 1, \ldots\ldots, N \tag{10-93}$$

where the degree of non-ideality is expressed by the deviations from unity of the activity coefficients, γ_i^L, for the liquid phase, and the fugacity coefficients, ϕ_i^V for the vapor phase. At low pressure, $\phi_i^V = 1$ and $f_i^L = P_i^s$ and Equation 10-93 reduces to:

$$K_i \equiv \frac{y_i}{x_i} = \gamma_i^L \frac{f_i^L}{P} = 1,\ i = 1, \ldots..N \tag{10-94}$$

Since the equilibrium constants for all of the species are unity at an azeotrope point, a simple distillation approaches this point, after which no further separation can occur. For this reason, an azeotrope is often referred to as a stationary, or fixed pinched point. For a minimum-boiling azeotrope where the deviations from Raoult's law are sufficiently large ($\gamma_i^L >> 1.0$), phase splitting may occur and a minimum-boiling heterogeneous azeotrope may occur with a vapor phase in equilibrium with two liquid phases. A heterogeneous azeotrope occurs when the vapor-liquid envelope overlaps with the liquid-liquid envelope as shown in Figure 10-14. The author has developed phase diagrams of many binary systems from available literature using Microsoft Excel. These diagrams are shown in Appendix M and can be downloaded from the Elsevier companion website.

Example 10-4: Raoult's Law, Total Pressure Calculations for Multicomponent Mixture

A hydrocarbon liquid is a mixture at 55°F of the following components:

Component	Mole %
Iso-butane ($i-C_4H_{10}$)	41.5
Pentane (C_5H_{12})	46.5
n-Hexane ($n-C_6H_{14}$)	12.0
	100.0

A vaporizer is to heat the mixture to 190°F at 110 psia; determine the total pressure of the hydrocarbon liquid mixture.

Data from vapor pressure charts such as [48]:

Component	Vapor pressure, psia at 190°F
Iso-butane ($i-C_4H_{10}$)	235.0
Pentane (C_5H_{12})	65.0
n-Hexane ($n-C_6H_{14}$)	26.0

Specific gravity of pure liquid at 55°F [79]:

Component	Specific gravity, SpGr.
Iso-butane ($i-C_4H_{10}$)	0.575
Pentane (C_5H_{12})	0.638
n-Hexane ($n-C_6H_{14}$)	0.678

Moles in original liquid. Basis 100 gallons liquid

Assume Raoult's Law:

Component	Mols of component	
Iso-butane ($i-C_4H_{10}$)	$= 41.5(8.33 \times 0.575)/MW$ $= 198.77/58.12$	3.420
Pentane (C_5H_{12})	$= 46.5\ (8.33 \times 0.638)/MW$ $= 247.12/72.146 =$	3.425
n-Hexane ($n-C_6H_{14}$)	$= 12\ (8.33 \times 0.678)/MW$ $= 67.77/86.172 =$	0.786
Total		7.631

Component	Mole fraction in the liquid phase	
iso-butane ($i-C_4H_{10}$)	$x_1 = 3.42/7.631$	0.448
Pentane (C_5H_{12})	$= x_2 = 3.425/7.63$	0.449
n-hexane ($n-C_6H_{14}$)	$= x_3 = 0.786/7.631$	0.103
Total		1.000

Mol fraction in vapor phase at 190°F. Raoult's Law:

$$y_i = p_i/\pi = (p_i^* x_i)/\pi \text{ (for a binary system)} \qquad (10\text{-}36)$$

$$y_1 = (x_1 P_1)/(x_1 P_1 + x_2 P_2 + x_3 P_3) \times \text{(for multicomponent mixtures)} \qquad (10\text{-}95)$$

$$\begin{aligned} y_1 &= 0.448\ (235)/[(0.449)\ (65) + (0.448)\ (235) + (0.103)\ (26)] \\ &= 105.28/[29.185 + 105.28 + 2.678] \\ &= 105.28/[137.143] \\ &= 0.767 \\ y_2 &= 0.449\ (65)/137.143 = 0.212 \\ y_3 &= 0.103\ (26)/137.143 = 0.0195 \\ \Sigma y_i &= 0.998 \text{ (not rounded)} \end{aligned}$$

$P_{Total} = p_{iC_4H_{10}} + p_{C_5H_{12}} + p_{C_6H_{14}}$ (i.e. the total pressure = sum of the partial pressures).

Because, $P_{total} = (0.448)\ (235) + 0.449\ (65) + 0.103\ (26) = 137.14$ psia

This is greater than the selected pressure of 110 psia. Therefore, for a binary mixture the results can be obtained without a trial-and-error solution. But for the case of mixtures of three or more components, the trial-and-error assumption of the temperature for the vapor pressure will require a new temperature, re-determination of the component's vapor pressure, and repetition of the process until a closer match with the pressure is obtained.

Example 10-5: Determination of the Composition At An Azeotropic Temperature

The ethyl acetate (1) –ethyl alcohol (2) azeotrope has a boiling point of 71.8°C at a pressure of 101.325 kN/m^2 and a composition of 53.9 mole % ethyl acetate.

(a) Determine the composition of the azeotrope at 95°C from the table below.

(b) Comment briefly upon the implications of changing the pressure of an azeotropic distillation operation.

	Vapor Pressure	kN/m^2
Temperature °C	**Ethyl Acetate**	**Ethyl Alcohol**
70	79.03	72.55
80	110.75	108.32
90	151.38	158.27
100	195.11	217.49

The van Laar equations are:

$$\ln \gamma_1 = \frac{A}{\left[1 + \left(\frac{Ax_1}{Bx_2}\right)\right]^2} \quad \text{and} \quad \ln\gamma_2 = \frac{B}{\left[1 + \left(\frac{Bx_2}{Ax_1}\right)\right]^2} \qquad (10\text{-}96)$$

or, by rearrangement,

$$A = \ln \gamma_1 \left[1 + \frac{x_2 \ln \gamma_2}{x_1 \ln\gamma_1}\right]^2 \text{ and}$$

$$B = \ln \gamma_2 \left[1 + \frac{x_1 \ln\gamma_1}{x_2 \ln \gamma_2}\right]^2 \qquad (10\text{-}97)$$

Solution

(a) The mole fraction in the liquid phase of ethyl acetate = x_1

The mole fraction in the vapor phase of ethyl acetate = y_1

The mole fraction in the liquid phase of ethyl alcohol = x_2

The mole fraction in the vapor phase of ethyl alcohol = y_2

At equilibrium and azeotropic conditions the following relationships hold:

$$f_i^V = f_i^L \text{ and } x_1 = y_1 \qquad (10\text{-}12)$$

where

f_i^V = fugacity of component i in the vapor phase

f_i^L = fugacity of component i in the liquid phase.

For a perfect gas and non ideal solution

In the vapor phase, the fugacity:

$$f_1^V = y_1 \cdot \pi \qquad (10\text{-}98)$$

where π = the total pressure.

For non-ideal liquid solution:

In the liquid phase, the fugacity:

$$f_1^L = \gamma_1\, x_1\, p_1^o \qquad (10\text{-}99)$$

where

γ_1 = activity coefficient of ethyl acetate. It is a measure of the deviation from Raoult's law. It is greater than unity for positive deviations and less than unity for negative deviation.

p_1^o = vapor pressure of ethyl acetate.

Activity coefficients are defined for each component of a mixture as:

$$y_1\,\pi = \gamma_1\,p_1^o\,x_1 \tag{10-100}$$

and

$$y_2\,\pi = \gamma_2\,p_2^o\,x_2 \tag{10-101}$$

At azeotropic composition the values $x_1 = y_1$ and $x_2 = y_2$; so the activity coefficients become:

$$\gamma_1 = \frac{\pi}{p_1^o} \tag{10-102}$$

and

$$\gamma_2 = \frac{\pi}{p_2^o} \tag{10-103}$$

Dividing Eq. 10-102 by Eq. 10-103 gives:

$$\frac{\gamma_1}{\gamma_2} = \frac{\pi/p_1^o}{\pi/p_2^o} = \frac{p_2^o}{p_1^o} \tag{10-104}$$

At the boiling point of 71.8°C, the vapor pressures of ethyl acetate, $p^o_{1,71.8^\circ C}$ and ethyl alcohol, $p^o_{2,71.8^\circ C}$ are by interpolation:

Ethyl acetate component	**Ethyl alcohol component**
$\frac{71.8-80}{70-80}=\frac{p^o_{1,71.8^\circ C}-110.75}{79.03-110.75}$	$\frac{71.8-80}{70-80}=\frac{p^o_{2,71.8^\circ C}-108.32}{72.55-108.32}$
$p^o_{1,71.8^\circ C} = 84.74\ \text{kN/m}^2$	$p^o_{2,71.8^\circ C} = 78.98\ \text{kN/m}^2$
$= 85\ \text{kN/m}^2$	$= 79\ \text{kN/m}^2$

The activity coefficients at the boiling temperature of 71.8°C are:

$$\gamma_1 = \frac{\pi}{p_1^o} = \frac{101.325}{85} = 1.192$$

$$\text{and } \gamma_2 = \frac{\pi}{p_2^o} = \frac{101.325}{79} = 1.2826$$

The level of ethyl acetate in the mixture is 53.9 mole % and that of ethyl alcohol is 46.1 mole %.

The van Laar coefficients A and B are:

$$A = \ln(1.192)\left[1 + \frac{0.461\ \ln 1.2826}{0.539\ \ln 1.192}\right]^2$$

$$= 0.859$$

$$B = \ln(1.2826)\left[1 + \frac{0.539\ \ln 1.192}{0.461\ \ln 1.2826}\right]^2$$

$$= 0.829$$

Using the values of A and B, the activity coefficients γ_1 and γ_2 are computed for various values of x_1 and x_2 from the equations as shown below. The values of γ_1 and γ_2 are shown in the subsequent table.

$$\ln \gamma_1 = \frac{A}{\left[1 + \left(\frac{Ax_1}{Bx_2}\right)\right]^2} \quad \text{and} \quad \ln \gamma_2 = \frac{B}{\left[1 + \left(\frac{Bx_2}{Ax_1}\right)\right]^2}$$

x_1	x_2	γ_1	γ_2	γ_1/γ_2
0.4	0.6	1.3505	1.1484	1.176
0.6	0.4	1.1407	1.3593	0.839
0.8	0.2	1.0329	1.7127	0.603

At the azeotrope temperature of 95°C, the values of p_1^o and p_2^o are determined by interpolation as follows:

$$\frac{95-100}{90-100} = \frac{p^o_{1,95^\circ C} - 195.11}{151.38 - 195.11} \quad \text{and} \quad \frac{95-100}{90-100} = \frac{p^o_{2,95^\circ C} - 217.49}{158.27 - 217.49}$$

$$p^o_{1,95^\circ C} = 173.245\,\text{kN/m}^2 \text{ and } p^o_{2,95^\circ C} = 187.88\,\text{kN/m}^2$$

$$\frac{\gamma_1}{\gamma_2} = \frac{p_2^o}{p_1^o} = \frac{187.88}{173.245} = 1.0845$$

The corresponding liquid phase mole fraction x_1 is calculated by interpolation as follows:

$$\frac{x_1 - 0.6}{0.4 - 0.6} = \frac{1.0845 - 0.839}{1.176 - 0.839}$$

At 95°C, $x_1 = 0.454$

(b) Changing the pressure infers (by Charles' Law) that the temperature, and therefore the boiling point will change directly. The composition will also change, so that an azeotrope may be avoided.

10.13 Bubble Point of Liquid Mixture

An equilibrium between a liquid and a vapor implies that the liquid is on the point of boiling, is producing bubbles of vapor within it, and the vapor is on the point of condensing or forming a dew. These conditions are referred to as saturated liquid and saturated vapor. At the prevailing total pressure, the liquid is at its bubble point temperature and the vapor at its dew point temperature. The amount of the vapor formed is assumed to be so small as to have no effect on the liquid composition. For a binary system:

$$x_1 = \frac{1 - K_2}{K_1 - K_2} \qquad (10\text{-}105)$$

and

$$x_2 = 1.0 - x_1 \qquad (10\text{-}106)$$

In the majority of cases involving multicomponent mixtures, no direct solution to Equation 10 –105 exists. The basic definition of the equilibrium coefficient is:

$$y_i = K_i\, x_i \qquad (10\text{-}107)$$

For a stable system, the total mole fraction is unity, i.e.

$$\sum y_i = \sum K_i x_i = 1.0 \qquad (10\text{-}108)$$

Equation 10-108 is used to determine the bubble point temperature and pressure. In using it, the temperature or pressure is fixed, while the other parameter is varied until the criterion for a stable system is identified. A combination of temperature and pressure is altered, if the summation of the calculated vapor composition differs from unity. There is no direct method that will allow a reasonable estimation of the amount of change required. However, Dodge [265], Hines and Maddox [266] have provided techniques for reducing the number of trials required.

10.13.1 Dew point calculations

The dew point of a vapor is that combination of temperature and pressure at which the first drop of the liquid condenses. The dew point criterion is:

$$\sum x_i = \sum \frac{y_i}{K} = 1.0 \qquad (10\text{-}109)$$

For binary mixtures of components 1 and 2, then:

$$y_i = \frac{K_1\,(1 - K_2)}{K_1 - K_2} \qquad (10\text{-}110)$$

and

$$y_2 = 1.0 - y_1 \qquad (10\text{-}111)$$

These two equations can be used to calculate the composition of a binary vapor that will begin to condense at a given temperature and pressure.

Example 10-6: Dew-point Temperature Calculations For a Multicomponent Mixture

A multi-component hydrocarbon vapor mixture is of composition:

Component	Mol %	K
Methane (CH_4)	27.52	7.88
Ethane (C_2H_6)	16.34	2.77
Propane (C_3H_8)	29.18	1.18
Isobutane (iC_4H_{10})	5.37	0.61
Normal butane (nC_4H_{10})	17.18	0.48
Isopentane (iC_5H_{12})	1.72	0.264
Normal pentane (nC_5H_{12})	2.18	0.225
Hexane (C_6H_{14})	0.47	0.102
Heptane (C_7H_{16})	0.04	0.048

Operating temperature and pressure are 178°C and 400 psia. Determine the dew point temperature of the mixture.

Solution

The computer program PROG101 calculates the dew and bubble points of any multicomponent hydrocarbon mixture based on user supplied K-values (see Figures 10-12a –10-12d). The program will handle feed streams containing up to 15 components. The feed entries may be expressed in moles, mole fraction or mole %. The dew point ($\sum x = \sum y/K$) should be 1.0 or very close to 1.0, depending on the acceptable tolerance. If the sum obtained is not equal to 1.0 (within the user tolerance), a message is shown instructing the user to assume a new temperature. The iteration is repeated using the K_i's corresponding to the new temperature selected. The temperature supplied does not affect the computation, but is printed and stored as a reminder to the user of which temperature (and corresponding K-values) was used for the last iteration. Program PROG101 can be run from its executable file (PROG101.EXE) generated from the latest Absoft Pro Fortran version 10 compiler using the Microsoft Run time Windows Environment (MRWE) application. The user only needs to supply the data file (e.g. DATA101.DAT) and run the executable PROG101.exe to generate the results. Both the source and executable codes can be downloaded from the Elsevier companion website. Table 10-13 shows the input data and results instructing the user that the dew point temperature should be increased. Appendix I illustrates the steps followed in creating and running the program.

Table 10-13 Input Data and Computer Results for Dew and Bubble Points Calculations.

```
Data name: Data101. Dat
Dew
178.0
400.0
9
27.52     7.88
16.34     2.88
29.18     1.18
5.37      0.61
17.18     0.48
1.72      0.264
2.18      0.225
0.47      0.102
0.04      0.048

Dew and bubble points calculations at 178.0°F and 400.0 psia
Dew point calculation

Temperature °F: 178.00
Number of components in the feed stream: 9
Number of              Feed composition
components             (Mole %)               K-Value

1                      27.5200                7.8800
2                      16.3400                2.7700
3                      29.1800                1.1800
4                       5.3700                0.6100
5                      17.1800                0.4800
6                       1.7200                0.2640
7                       2.1800                0.2250
8                       0.4700                0.1020
9                       0.0400                0.0480

Total composition:     100.0000
Number of
components             Mole fraction          X = Y/K

1                      0.2752                 0.0349
2                      0.1634                 0.0590
3                      0.2918                 0.2473
4                      0.0537                 0.0880
5                      0.1718                 0.3579
6                      0.0172                 0.0652
7                      0.0218                 0.0969
8                      0.0047                 0.0461
9                      0.0004                 0.0083

Total dew point:                              1.0036
Raise the dew-point temperature of: 178.00°F
```

Example 10-7: Bubble-point temperature Calculations For Multicomponent Mixture

At 200 psia, calculate the bubble point temperature of the following:

Component	Mol %	K @ 260°F	K @ 235°F	K @ 237°F
iC_4H_{10}	18.2	1.92	1.62	1.65
nC_4H_{10}	23.8	1.58	1.35	1.35
iC_5H_{12}	33.7	0.93	0.76	0.77
nC_5H_{12}	12.1	0.81	0.64	0.64
C_6H_{14}	12.2	0.42	0.315	0.32

Solution

The computer program PROG101 determines the bubble points of the hydrocarbon mixture. As with the dew point, the bubble point ($\sum y = \sum K x$) is computed until the sum = 1.0, or close to this value, obtained depending on the accuracy required. If the sum is not equal to 1.0 (within tolerance), the iteration is repeated using the K_i's corresponding to the new temperature. Tables 10-14, 10-15, and 10-16 give input data and results for the bubble points of the hydrocarbon mixture at 260°F, 235°F and 237°F respectively. By interpolation, the bubble temperature is 237.3°F at 200 psia pressure.

Table 10-14 Input Data and Computer Results for Dew and Bubble Points Calculations.

```
Data name: Data101. Dat
Bubble
260
200
5
18.2      1.92
23.8      1.58
33.7      0.93
12.1      0.81
12.2      0.42

Dew and bubble points calculations at 260.0°F and 200.0 psia
Bubble point calculation

Temperature of: 260.00
Number of components in the feed stream: 5
Number of                  Feed composition
components                 (mole %)            K-Value

1                          18.2000             1.9200
2                          23.8000             1.5800
3                          33.7000             0.9300
4                          12.1000             0.8100
5                          12.2000             0.4200

Total composition:         100.0000
Number of components       Mole fraction       Y=KX

1                          0.1820              0.3494
2                          0.2380              0.3760
3                          0.3370              0.3134
4                          0.1210              0.0980
5                          0.1220              0.0512

Total bubble point:                            1.1881
Lower the bubble point temperature of: 260.00°F
```

Table 10-15 Input Data and Computer Results for Dew and Bubble Points Calculations.

Data name: Data101. Dat		
Bubble		
235		
200		
5		
18.2	1.62	
23.8	1.35	
33.7	0.76	
12.1	0.64	
12.2	0.315	
Dew and bubble points calculations at 235.0°F and 200.0 psia		
Bubble point calculation		
Temperature of: 235.00		
Number of components in the feed stream: 5		
Number of components	**Feed composition (Mole %)**	**K-Value**
1	18.2000	1.6200
2	23.8000	1.3500
3	33.7000	0.7600
4	12.1000	0.6400
5	12.2000	0.3150
Total composition:	100.0000	
Number of components	Mole fraction	Y=KX
1	0.1820	0.2948
2	0.2380	0.3213
3	0.3370	0.2561
4	0.1210	0.0774
5	0.1220	0.0384
Total bubble point:		0.9881
Raise the bubble point temperature of: 235.00°F		

Table 10-16 Input Data and Computer Results for Dew and Boiling Points Calculations.

Data name: Data101. Dat		
Bubble		
237		
200		
5		
18.2	1.65	
23.8	1.35	
33.7	0.77	
12.1	0.64	
12.2	0.32	
Dew and bubble points calculations at 237.0°F and 200.0 psia		
Bubble point calculation		
Temperature of: 237.00		
Number of components in the feed stream: 5		
Number of components	**Feed composition (Mole %)**	**K-Value**
1	18.2000	1.6500
2	23.8000	1.3500
3	33.7000	0.7700
4	12.1000	0.6400
5	12.2000	0.3200
Total composition:	100.0000	
Number of components	Mole fraction	Y=KX
1	0.1820	0.3003
2	0.2380	0.3213
3	0.3370	0.2595
4	0.1210	0.0774
5	0.1220	0.0390
Total bubble point:		0.9976
Raise the bubble point temperature of: 237.00°F		

10.14 Equilibrium Flash Computations

Flash vaporization calculations involving multicomponent mixtures are necessary for numerous processes, often to determine the condition of the feed to a fractionating column, or to determine the flow of vapor from reboiler or condenser.

Such calculations often involve trial-and-error solutions, which are time-consuming, tedious and subject to error if performed manually. They are better carried out with computer-aided process design and simulation programs, such as UniSim® (Honeywell) Design, Aspen Plus, HYSYS, ChemCad, and Pro II. This author [267] has developed an improved iterative convergence method first suggested by Oliver [268], and later modified by Kostecke [269], for isothermal equilibrium flash computations. Multicomponent flash (isothermal and adiabatic) computations are now incorporated as part of an overall process simulation and equipment design package. However, single-stage flash fractionation processes are also employed to separate light components in a feed, and as a preliminary step before a multicomponent fractionation column, e.g. crude oil distillation. Table 10-17 lists ways of producing two-phase mixtures from a single phase under appropriate conditions. The last process in the table typifies the well-head separation that takes place in an oil field. It is termed a flash process because the vapor forms due to the rapid drop in the pressure.

10.14.1 Fundamentals

To carry out an appropriate flash calculation, the pressure, P and the temperature, T, must be known. If the values of P and T in the separating vessel are fixed, the value of P must not be so high that the two phases cannot exist at any value of T. Nor must T lie outside the bubble point and dew point range corresponding to P. For a valid two-phase equilibrium calculation, the following relationship must be satisfied:

$$T_{bp} < T_s < T_{dp} \tag{10-112}$$

where

T_{bp} = the bubble point temperature
T_s = the specified temperature
T_{dp} = the dew point temperature

The existence of a valid two-phase flash point can be verified with the design equations for the bubble point, dew point, and equilibrium data calculated at the specified pressure and temperature.

10.14.2 Calculation Of Bubble Point And Dew Point

The design equations for the bubble point and dew point are:

Bubble point

$$f_1 = \sum_{i=1}^{n} K_i x_i \tag{10-113}$$

Dew point

$$f_2 = \sum_{i=1}^{n} y_i/K_i \tag{10-114}$$

The calculation method is as follows (at constant pressure):

1. Assume a temperature, T.
2. Calculate K –values.
3. Calculate the sum of the right side of Equation 10–113 for a bubble point calculation. If < 1.0, increase the temperature. If > 1.0, decrease the temperature. Repeat steps 2 and 3 until convergence is attained.
4. For a dew point calculation, obtain the right side of Equation 10-114. If < 1.0, decrease the temperature. If > 1.0, increase the temperature. Repeat steps 2 and 4 until a convergence is reached.

Table 10-18 illustrates the phase condition using the light-vapor data associated with the specified pressure and temperature. From Table 10-18, the conditions for a valid two-phase equilibrium flash are:

$$f_1 = \sum_{i=1}^{n} K_i\, n_i > 1.0 \tag{10-115}$$

and

$$f_2 = \sum_{i=1}^{n} n_i/K_i > 1.0 \tag{10-116}$$

Feed analyses of component concentrations are generally unavailable for complex hydrocarbon mixtures with a final boiling point of >38°C, unless the feed is subdivided into pseudo-components (narrow boiling fractions). This sub-division enables the mole fraction and equilibrium constant, K, to be estimated, and consequently, a flash calculation can be carried out for the mixture. A source of K values for light hydrocarbon systems is the DePriester [80] charts, which are shown in Figures 10-12 to 10-12d. These give the K values over a wide range of temperature and pressure. Because the charts are nomographs, a straight line connecting the temperature and pressure for which K values are required will intersect curves for each compound at its K value. The values have been obtained by calculating fugacities from an equation of state. Use of these charts for exact determination of K values requires a trial-and-error approach. Hadden and Grayson [270] have presented correlations for hydrocarbon vapor-liquid distribution ratios, and the charts from their work are shown in Figures 10-27 and 10-28. These charts can be readily used for determining the vapor-liquid distribution coefficients. Figure 10-29 shows a continuous equilibrium flash fractionation process.

The Equations

The following equations are used for the multicomponent equilibrium flash calculations.

$$f_1 = \sum_{i=1}^{n} n_i K < 1 \text{ all liquid} \tag{10-117}$$

$$f_2 = \sum_{i=1}^{n} n_i/K_i < 1 \text{ all vapor} \tag{10-118}$$

$$C_i = \frac{[M_i\,(K_i - 1)\,(R + 1)]}{(K_i + R)} \tag{10-119}$$

where

R = the liquid-vapor (L/V) ratio. The new L/V ratio for each iterative calculation, R′, is determined from:

$$R' = \frac{[FR - E(R + 1)]}{[F + E(R + 1)]} \tag{10-120}$$

The constants E and F are determined by:

$$E = \sum_{i=1}^{n} C_i \tag{10-121}$$

and

$$F = \sum_{i=1}^{n} (C_i)^2/M_i \tag{10-122}$$

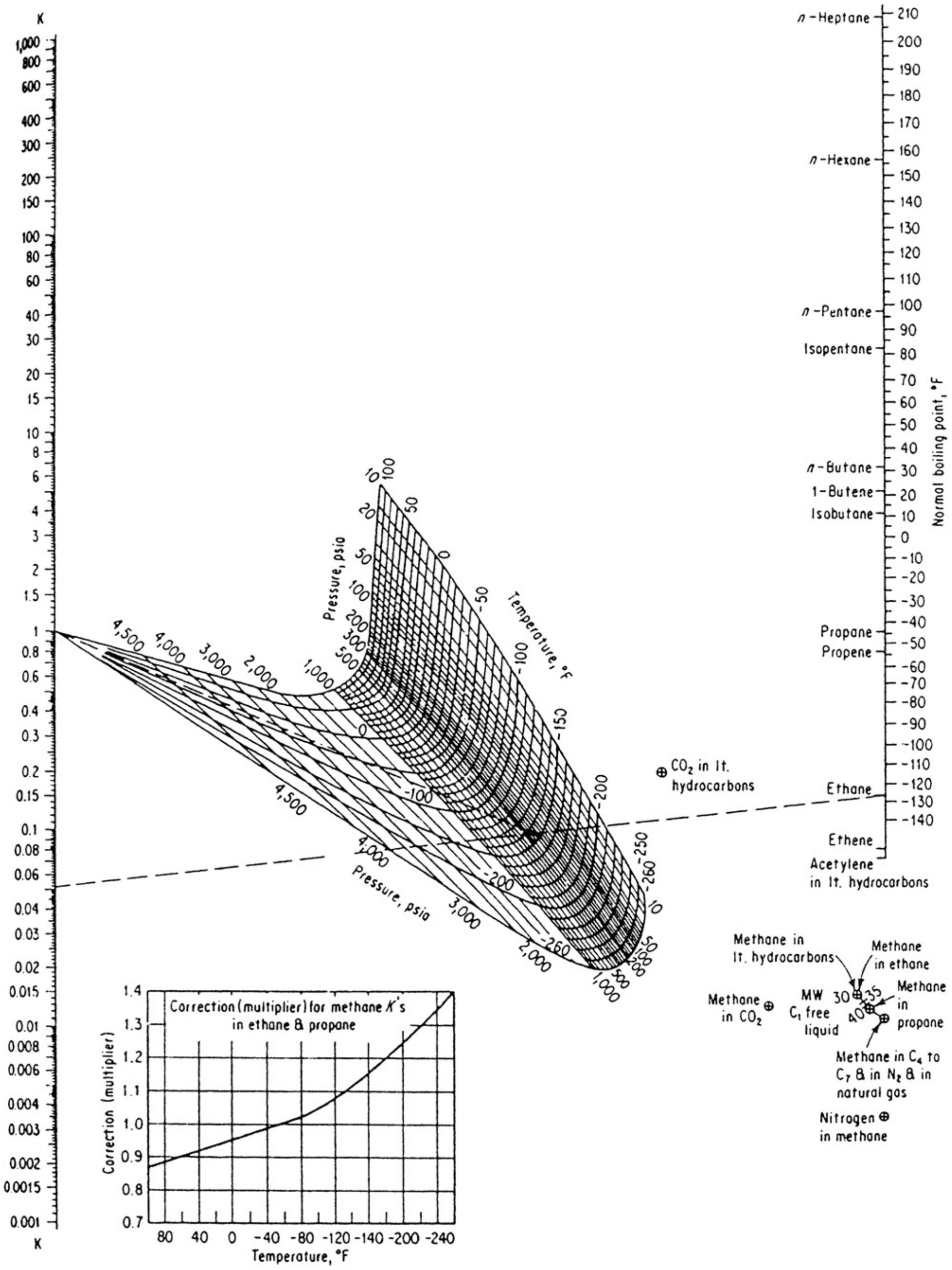


Figure 10-27 Vapor-liquid equilibrium constants, −260 to + 100°F (source: Hadden and Grayson [270]).

The Algorithm

The computation then determines whether $|E| < 0.001$. If $|E|$ is $\not< 0.001$, R is set equal to R′ and the calculations of Equations 10-119 , 10-120, 10-121, and 10-122 are repeated until $|E| < 0.001$.

Once $|E| < 0.001$, the calculation proceeds to find the total moles of component i in both the liquid and vapor phases, that is L_i and V_i. These are given by:

$$L_i = \frac{M_i\ R}{(K_i + R)} \tag{10-123}$$

and

$$V_i = M_i - L_i \tag{10-124}$$

The mole fractions of components in the feed, the liquid and vapor phases are evaluated as follows:

$$n_i = \sum_{i=1}^{n} M_i \tag{10-125}$$

$$x_i = \sum_{i=1}^{n} L_i \tag{10-126}$$

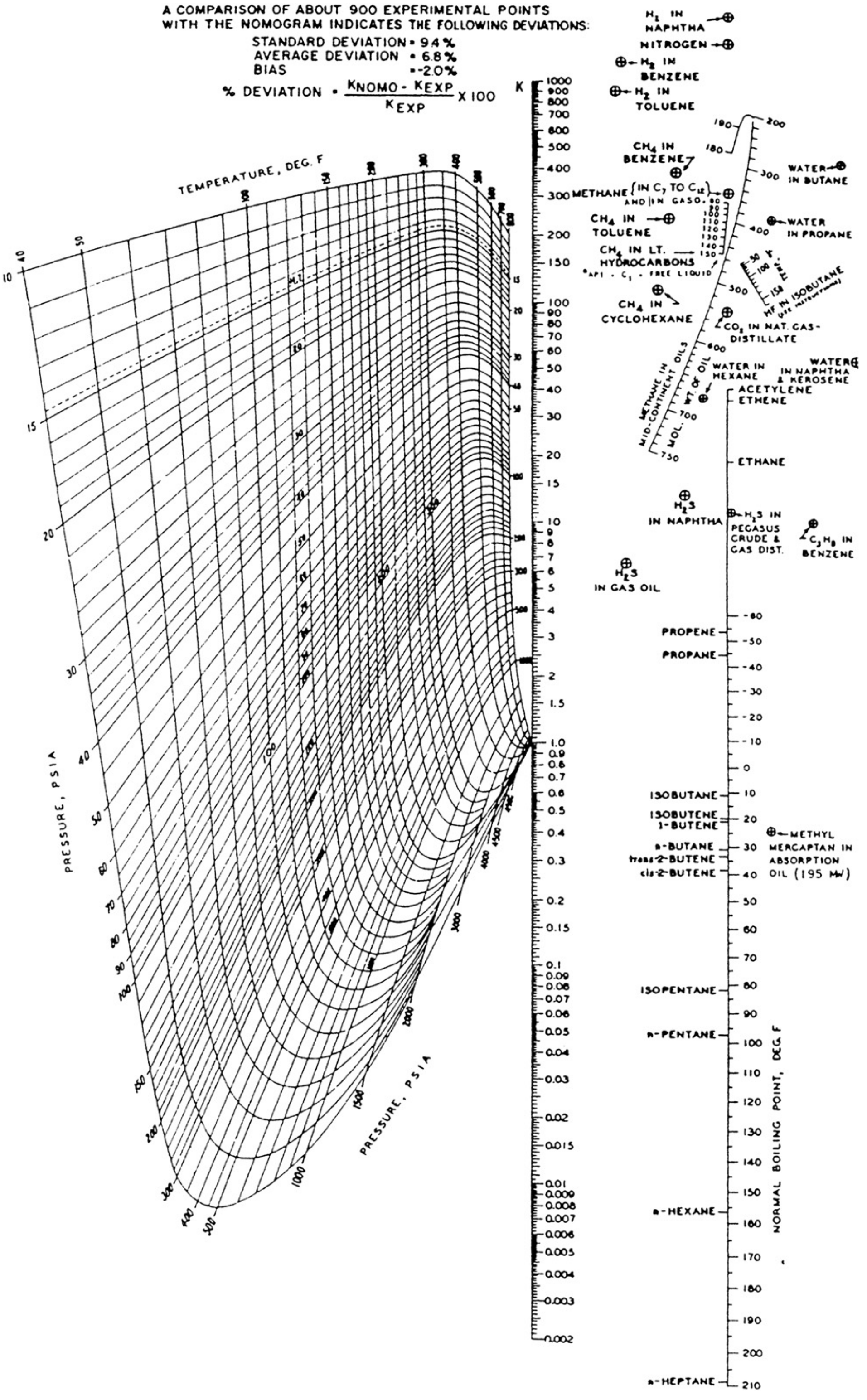


Figure 10-28 Vapor-liquid equilibrium constants, 40 to 800° F (source: Hadden and Grayson [270]).

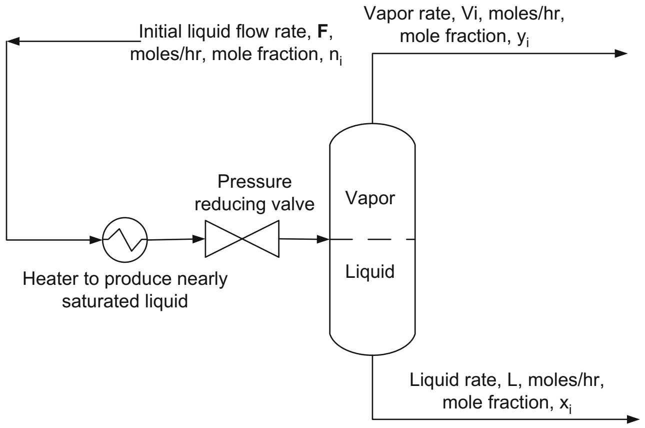


Figure 10-29 Continuous equilibrium flash fractionation.

and

$$y_i = \frac{V_i}{\sum_{i=1}^{n} V_i} \tag{10-127}$$

where

$$\sum_{i=1}^{n} n_i = \sum_{i=1}^{n} x_i = \sum_{i=1}^{n} y_i = 1 \tag{10-128}$$

where

E, F = constants
K_i = equilibrium flash constant for each component in the feed stream
L_i = total moles of component i in the liquid phase
L = total moles of liquid at equilibrium conditions
M_i = total moles of component i the feed stream
n_i = mole fraction of component i in the feed stream
R = liquid-vapor (L/V) ratio
R′ = new L/V ratio for each iteration calculation
V = total moles of vapor at equilibrium conditions
V_i = total moles of component i in the vapor phase
x_i = mole fraction of component i in the liquid phase
y_i = mole fraction of component i in the vapor phase

The method described here is based on the vapor-liquid equilibrium relationships given in Engineering Data books available from the Gas Processors Suppliers Association [79].

The Program

A Fortran program named PROG102 has been developed for flash calculation; it is based upon the vapor-liquid equilibrium relationships given in Engineering Data books available from the Gas Processors Suppliers Association, Tulsa and other literature. It will handle calculations with feed streams containing up to 15 components. In addition, the calculation will check the feed composition at flash conditions for dew and bubble points (i.e. whether the feed is either all vapor or all liquid). These checks are performed before the flash calculations are started. If the feed is above the dew point or below the bubble point, an appropriate message is displayed on the screen. A default value of R (L/V ratio) = 1 is incorporated in the program to start the iterative process. The program is not applicable to an adiabatic flash process, when the feed stream is at pressure higher than the flash pressure, and the heat of vaporization is provided by the enthalpy of the feed. In this situation, the flash temperature will be unknown and must be obtained by trial and error. A temperature must be found at which both the material and energy balances are satisfied.

PROG102 has been developed using the Absoft v.10 Fortran compiler with Microsoft Run time Windows Environment (MRWE) application. The user need only create the data source file (e.g. DATA102.DAT) and run the executable PROG102.exe to generate the results. Both the source and executable codes can be downloaded from the Elsevier companion website.

Example 10-8: Determination of the Amount of Liquid and Vapor in A Multi-Component Mixture

Determine the amount of liquid and vapor in a nine-component still product accumulator stream that is compressed to a pressure of 370 psia and cooled to 90°F.

Process Data

Number	Component	Feed mols/hr	Equilibrium constant, K
1	CH_4	2,752	7.2
2	C_2H_6	1,634	1.65
3	C_3H_8	2,918	0.54
4	iC_4H_{10}	537	0.25
5	nC_4H_{10}	1,718	0.185
6	iC_5H_{12}	172	0.088
7	nC_5H_{12}	218	0.069
8	C_6H_{14}	47	0.028
9	C_7H_{16}	4	0.00078

Table 10-17 Ways to Produce Two-Phase Mixture.

Initial	Action to Produce Two-Phase Mixture
Gas	Cool, possibly after initial compression
Gas	Expand through a valve or an engine
Liquid	Heat to achieve partial vaporization
Liquid	Reduce pressure through a valve, if close to saturation

Table 10-18 Equilibrium Flash Criteria.

	$f_1 = \sum_{i=1}^{n} K_i n_i$	$f_2 = \sum_{i=1}^{n} n_i/K_i$
Subcooled liquid	<1	>1
Bubble point	=1	>1
Two-phase condition	>1	>1
Dew point	>1	=1
Superheated vapor	>1	<1

Solution

The computer program PROG102 calculates the liquid and vapor streams from the equilibrium constants and molar flow rates of the components at the supplied temperature and pressure. Table 10-19 shows the input data and results from PROG102.

Example 10-9: Determination Of The Flow Rates of Liquid and Vapor in a Gas Liquefaction Plant

A feed stream of natural gas is flashed at a pressure of 600 psia and 20°F in a gas liquefaction plant. Determine the flow rates of the liquid and vapor streams of a feed flow rate of 1,000 mols/hr.

Process Data

Number	Component	Feed Moles fraction	Equilibrium constant, K
1	CO_2	0.0112	0.90
2	CH_4	0.8957	2.70
3	C_2H_6	0.0526	0.38
4	C_3H_8	0.0197	0.098
5	iC_4H_{10}	0.0068	0.038
6	nC_4H_{10}	0.0047	0.024
7	C_5H_{12}	0.0038	0.0075
8	nC_6H_{14}	0.0031	0.0019
9	nC_7H_{16} and heavier	0.0024	0.0007

Table 10-19 Data Input and Computer Results of Multicomponent Equilibrium Flash Calculations

```
Data name: Data102.Dat
90
370
9
2752.0              7.2
1634.0              1.65
2918.0              0.54
537.0               0.25
1718.0              0.185
172.0               0.088
218.0               0.069
47.0                0.028
4.0                 0.00078
```

Multicomponent equilibrium flash calculation
Multicomponent equilibrium flash calculation at 90.0°F and 370.0 psia

Component number	K-Value	Feed Mols/h.	Feed Mol. frac.	Liquid Mols/h.	Liquid Mol. frac.	Vapor Mols/h.	Vapor Mol. frac
1	7.200	2752.000	0.275	388.353	0.072	2363.647	0.516
2	1.650	1634.000	0.163	682.316	0.126	951.684	0.208
3	0.540	2918.000	0.292	2003.467	0.370	914.533	0.200
4	0.250	537.000	0.054	443.314	0.082	93.686	0.020
5	0.185	1718.000	0.172	1485.664	0.274	232.336	0.051
6	0.088	172.000	0.017	160.091	0.030	11.909	0.003
7	0.069	218.000	0.022	205.985	0.038	12.015	0.003
8	0.028	47.000	0.005	45.913	0.008	1.087	0.000
9	0.001	4.000	0.000	3.997	0.001	0.003	0.000
TOTAL		10000.000	1.000	5419.101	1.000	4580.899	1.000

Table 10-20 Data Input and Computer Results of Multicomponent Equilibrium Flash Calculations

```
Data name: Data102.Dat
20.0
600.0
9
11.2          0.90
895.7         2.70
52.6          0.38
19.7          0.098
6.8           0.038
4.7           0.024
3.8           0.007
3.1           0.0019
2.4           0.0007
```

Multicomponent equilibrium flash calculation
Multicomponent equilibrium flash calculation at 20.0°F and 600.0 psia

Component number	K-Value	Feed		Liquid		Vapor	
		Mols/h.	Mol. frac.	Mols/h.	Mol. frac.	Mols/h.	Mol. frac
1	0.900	11.200	0.011	0.506	0.012	10.694	0.011
2	2.700	895.700	0.896	13.903	0.340	881.797	0.919
3	0.380	52.700	0.053	5.299	0.130	47.301	0.049
4	0.098	19.700	0.020	5.966	0.146	13.734	0.014
5	0.038	6.800	0.007	3.593	0.088	3.207	0.003
6	0.024	4.700	0.005	3.006	0.074	1.694	0.002
7	0.007	3.800	0.004	3.231	0.079	0.569	0.001
8	0.002	3.100	0.003	2.968	0.073	0.132	0.000
9	0.001	2.400	0.002	2.361	0.085	0.039	0.000
TOTAL		1000.000	1.000	40.831	1.000	959.169	1.000

Solution

Table 10-20 shows the input data and results of an isothermal equilibrium flash calculation at 20°F and 600 psia.

10.15 Degrees of Freedom

The design of separation systems involves many parameters, and the number of variables that can be arbitrarily specified is known as the degrees of freedom. This is determined by subtracting the number of thermodynamic equilibrium equations from the number of variables. For non-reacting systems, the Gibbs phase rule is defined by:

$$F = C - P + 2 \qquad (10\text{-}129)$$

where

F = degrees of freedom (i.e. the number of independent properties that have to be specified to determine all the intensive properties of each phase of the system of interest).

C = number of components in the system. For circumstances that involve chemical reactions, C is not identical to the number of chemical compounds in the system but is equal to the number of chemical compounds less the number of independent-reaction and other equilibrium relationships among these compounds.

P = number of phases that can exist in the system. A phase is a homogeneous quantity of material e.g. gas, pure liquid, a solution, or a homogeneous solid.

Variables of the kind with which the phase rule is concerned are termed phase-rule variables, and they are inherent properties of the system, i.e. properties that do not depend on the quantity of material present.

For example, in a binary system such as methanol-water, having liquid and vapor phases,

$C = 2, P = 2$
and:
$F = 2 - 2 + 2 = 2$

When temperature and pressure are set, all the degrees of freedom are used, and at equilibrium all compositions are determined from experiment. Alternatively, the pressure and components' mole fractions (methanol and water) and determine the temperature and the other mole fractions. The phase rule refers to inherent variables where temperature, pressure, specific (per unit mass) values (i.e. specific volume) or mole fractions do not depend on the total amount of material present. The extensive variables i.e. number of moles, flow rate and volume depend on the amount of material and are not included in the degree of freedom.

Another example is the ideal gas equation $PV = nRT$, where if the phase rule is applied for a single phase and for a pure gas, $P = 1$, $C = 1$, then

$F = 1 - 1 + 2 = 2$ variables to be specified. Since the phase rule is concerned with intensive properties only, the following phase-rule variables in the ideal gas law:

$$\left.\begin{array}{l} P \\ \widehat{V} \ \text{(specific molar volume)} \\ T \end{array}\right\} \text{3 intensive properties}$$

By specifying two intensive variables ($F = 2$), the third variable can be determined.

When a set of independent equations representing the material balances for a problem is prepared, the number of variables whose values are unknown is counted. If more variables whose values are unknown exist than independent equations, then an infinite number of solutions exist for a material balance, and such problems are referred to as *underspecified (underdetermined)*. Either values of additional variables must be found to make up the deficit or the problem must be posed as an optimization problem. Alternatively, if fewer values of the variables whose values are unknown exist than the independent equations, the problem is *over specified (over determined)* and no solution exists to the problem, showing that the equations are inconsistent. In this instance, the problem might be posed as an optimization problem to minimize the sum of the squares of the deviations of the equations from zero (or their right-hand constants).

The difference between the number of variables whose values are unknown and the number of independent equations is termed the number of degrees of freedom. If the degrees of freedom are positive, such as 2, two additional independent equations or specifications of variables must be sought to provide a unique solution to the material balance problem. Conversely, if the degrees of freedom are negative e.g. −1, there are many equations or not enough variables in the problem. *Zero degrees of freedom means that the material balances problem is properly specified*, and the equations can be solved for the variables whose values are unknown. In this instance, the number of degrees of freedom is the number of variables in a set of independent equations to which values must be assigned so that the equations can be solved. This can be expressed by:

$$N_d = N_v - N_r \qquad (10\text{-}130)$$

where

N_d = number of degrees of freedom
N_v = number of variables
N_r = number of equations

10.16 UniSim (Honeywell) Software

UniSim® Design R360.1 simulation software is an intuitive and interactive process modeling package that allows engineers to create steady-state and dynamic models for plant design, performance monitoring, troubleshooting, operational improvement, business planning and asset management. Further, it provides users with Honeywell's domain expertise in process simulation and operator training. Using industry-specific unit operating models and powerful tools to optimize operating parameters for feedstock changes, UniSim Design allows the steady-state simulation of oil and gas, refining, chemical and petrochemical processes.

In this book, UniSim Design simulation software is employed to verify some design calculations. Appendix-K shows the steps in creating a simulation run using UniSim Design R360.1.

Example 10-10: Application of UniSim Design Software for Example 10-8

Example 10-8 is repeated using UniSim Design R360.1 software (Example 10-10.usc) to determine the amount of liquid and vapor in a nine-component still product accumulator stream that is compressed to 370 psia and cooled to 90°F. Figure 10-30 shows a screen shot of UniSim Design 360.1.

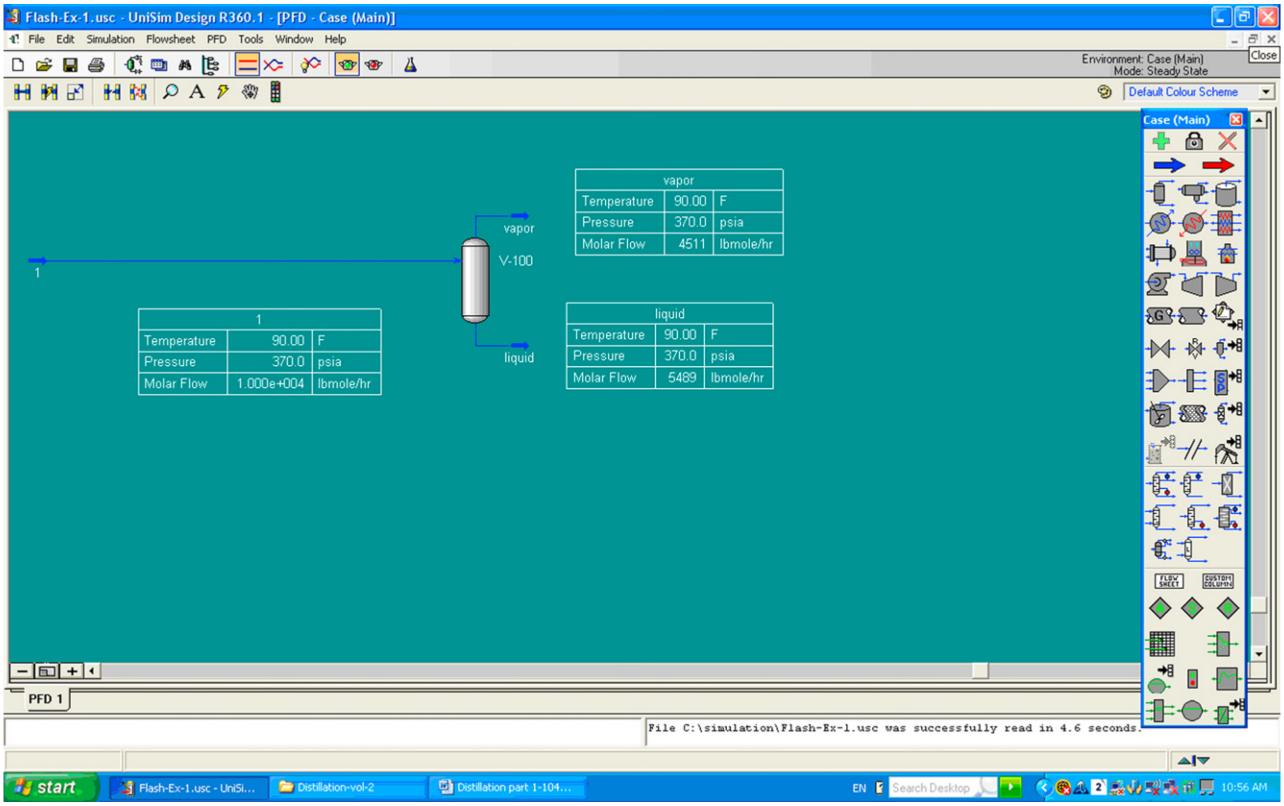
Table 10-21 shows the simulation results from Honeywell UniSim when the Peng Robinson equation for vapor liquid equilibrium (VLE) is used. The results for the total vapor and liquid flow rates give good agreement with the results in Table 10-19.

10.17 Binary System Material Balance: Constant Molal Overflow Tray to Tray

Refer to Figure 10-5. (For an overall review, see Reference 173)

- Rectifying Section:

$$V_r = L_r + D \qquad (10\text{-}131)$$



vapor		
Temperature	90.00	F
Pressure	370.0	psia
Molar Flow	4511	lbmole/hr

1		
Temperature	90.00	F
Pressure	370.0	psia
Molar Flow	1.000e+004	lbmole/hr

liquid		
Temperature	90.00	F
Pressure	370.0	psia
Molar Flow	5489	lbmole/hr

```
File C:\simulation\Flash-Ex-1.usc was successfully read in 4.6 seconds.
```

Figure 10-30 a snap-shot of the Process flow diagram of a flash drum (courtesy of Honeywell UniSim® Design).

For any component in the mixture; using total condenser see Figures 10-5 and 10-33.

$$V_n y_{ni} = L_{n+1}\, x_{(n+1)i} + D x_{Di} \tag{10-132}$$

$$y_{ni} = \frac{L_{n+1}}{V_n} x_{(n+1)i} + \frac{D}{V_n} x_{Di} \tag{10-133}$$

- Operating Line Equation:

$$y_{ni} = \frac{L_r}{V_r} x_{(n+1)i} + \frac{D}{V_r} x_{Di} \tag{10-134}$$

For total condenser: y (top plate) $= x_D$

- Stripping Section:

$$L_s = V_s + B \tag{10-135}$$

$$L_{(m+1)}\, x_{(m+1)i} = V_m\, y_{mi} + B x_{Bi} \tag{10-136}$$

- Operating Line Equation:

$$y_{mi} = \frac{L_s}{V_s} x_{(m+1)i} - \frac{B}{V_s} x_{Bi} \tag{10-137}$$

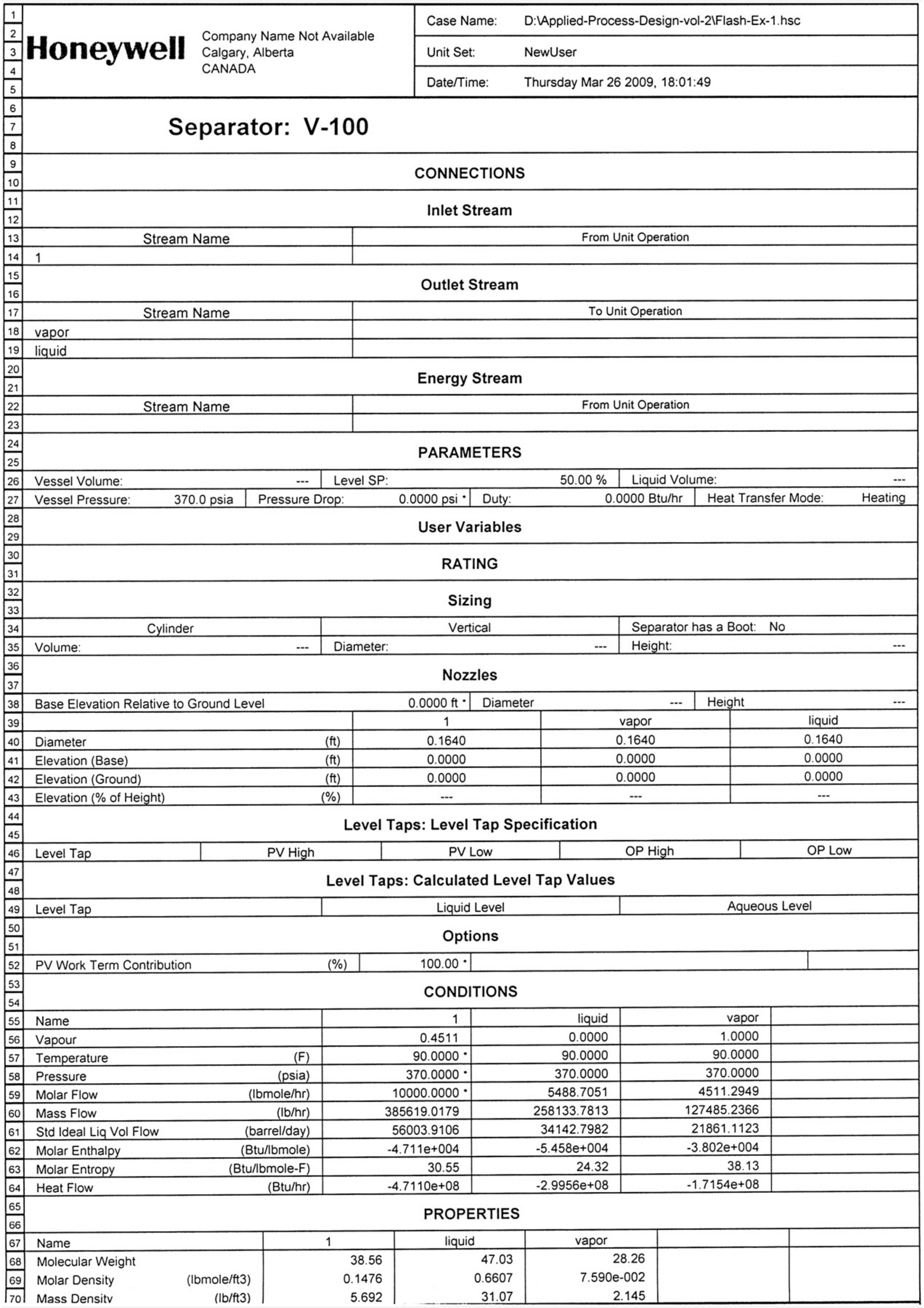
10.17.1 Conditions of Operation (usually fixed)

1. Feed composition, and quantity.
2. Reflux Ratio (this is one of the initial unknowns).
3. Thermal condition of feed (e.g. liquid at boiling point, all vapor, sub-cooled liquid).
4. Degree, type or amount of fractionation or separation, including compositions of overhead or bottoms.
5. Column operating pressure or temperature of condensation of overhead (determined by temperature of cooling medium), including type of condensation, i.e., total or partial.
6. Constant molal overflow from stage to stage (theoretical) for simple ideal systems following Raoult's Law. Techniques that are more complicated apply for non-ideal systems.

10.17.2 Flash Vaporization (see Figure 10-31)

At a total pressure, P, the temperature of flash must be between the dew point and the bubble point of a mixture [144 – 148]. Thus:

Table 10-21 Results of the simulation using UniSim® Design Software for Example 10-8.



Honeywell	Company Name Not Available Calgary, Alberta CANADA	Case Name: D:\Applied-Process-Design-vol-2\Flash-Ex-1.hsc Unit Set: NewUser Date/Time: Thursday Mar 26 2009, 18:01:49

Separator: V-100

CONNECTIONS

Inlet Stream

Stream Name	From Unit Operation
1	

Outlet Stream

Stream Name	To Unit Operation
vapor	
liquid	

Energy Stream

Stream Name	From Unit Operation

PARAMETERS

Vessel Volume:	---	Level SP:	50.00 %	Liquid Volume:	---		
Vessel Pressure:	370.0 psia	Pressure Drop:	0.0000 psi *	Duty:	0.0000 Btu/hr	Heat Transfer Mode:	Heating

User Variables

RATING

Sizing

Cylinder		Vertical		Separator has a Boot:	No
Volume:	---	Diameter:	---	Height:	---

Nozzles

Base Elevation Relative to Ground Level	0.0000 ft *	Diameter	---	Height	---

		1	vapor	liquid
Diameter	(ft)	0.1640	0.1640	0.1640
Elevation (Base)	(ft)	0.0000	0.0000	0.0000
Elevation (Ground)	(ft)	0.0000	0.0000	0.0000
Elevation (% of Height)	(%)	---	---	---

Level Taps: Level Tap Specification

Level Tap	PV High	PV Low	OP High	OP Low

Level Taps: Calculated Level Tap Values

Level Tap	Liquid Level	Aqueous Level

Options

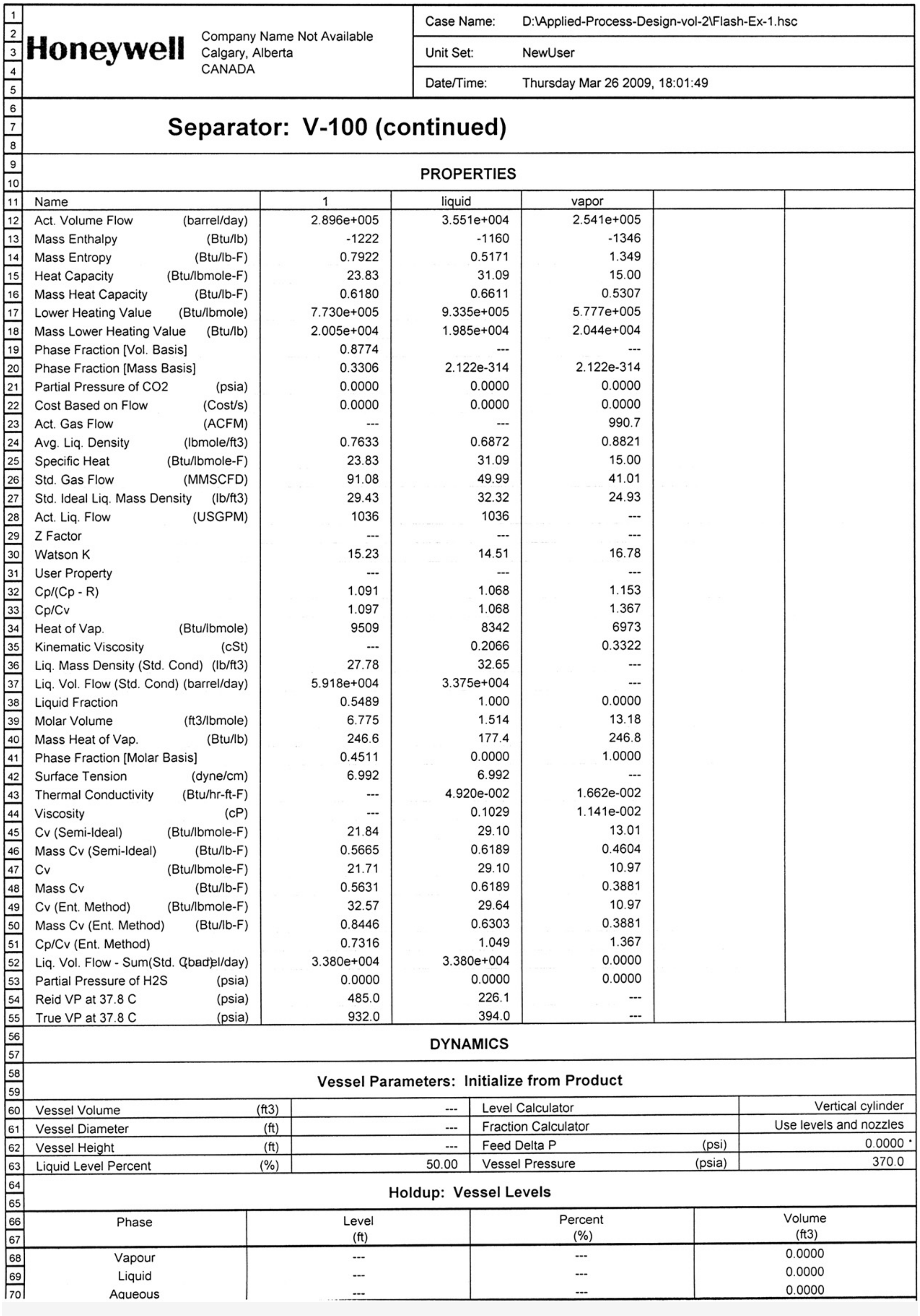
PV Work Term Contribution	(%)	100.00 *	

CONDITIONS

Name		1	liquid	vapor	
Vapour		0.4511	0.0000	1.0000	
Temperature	(F)	90.0000 *	90.0000	90.0000	
Pressure	(psia)	370.0000 *	370.0000	370.0000	
Molar Flow	(lbmole/hr)	10000.0000 *	5488.7051	4511.2949	
Mass Flow	(lb/hr)	385619.0179	258133.7813	127485.2366	
Std Ideal Liq Vol Flow	(barrel/day)	56003.9106	34142.7982	21861.1123	
Molar Enthalpy	(Btu/lbmole)	-4.711e+004	-5.458e+004	-3.802e+004	
Molar Entropy	(Btu/lbmole-F)	30.55	24.32	38.13	
Heat Flow	(Btu/hr)	-4.7110e+08	-2.9956e+08	-1.7154e+08	

PROPERTIES

Name		1	liquid	vapor		
Molecular Weight		38.56	47.03	28.26		
Molar Density	(lbmole/ft3)	0.1476	0.6607	7.590e-002		
Mass Density	(lb/ft3)	5.692	31.07	2.145		



Honeywell	Company Name Not Available Calgary, Alberta CANADA	Case Name:	D:\Applied-Process-Design-vol-2\Flash-Ex-1.hsc
		Unit Set:	NewUser
		Date/Time:	Thursday Mar 26 2009, 18:01:49

Separator: V-100 (continued)

PROPERTIES

Name		1	liquid	vapor		
Act. Volume Flow	(barrel/day)	2.896e+005	3.551e+004	2.541e+005		
Mass Enthalpy	(Btu/lb)	-1222	-1160	-1346		
Mass Entropy	(Btu/lb-F)	0.7922	0.5171	1.349		
Heat Capacity	(Btu/lbmole-F)	23.83	31.09	15.00		
Mass Heat Capacity	(Btu/lb-F)	0.6180	0.6611	0.5307		
Lower Heating Value	(Btu/lbmole)	7.730e+005	9.335e+005	5.777e+005		
Mass Lower Heating Value	(Btu/lb)	2.005e+004	1.985e+004	2.044e+004		
Phase Fraction [Vol. Basis]		0.8774	---	---		
Phase Fraction [Mass Basis]		0.3306	2.122e-314	2.122e-314		
Partial Pressure of CO2	(psia)	0.0000	0.0000	0.0000		
Cost Based on Flow	(Cost/s)	0.0000	0.0000	0.0000		
Act. Gas Flow	(ACFM)	---	---	990.7		
Avg. Liq. Density	(lbmole/ft3)	0.7633	0.6872	0.8821		
Specific Heat	(Btu/lbmole-F)	23.83	31.09	15.00		
Std. Gas Flow	(MMSCFD)	91.08	49.99	41.01		
Std. Ideal Liq. Mass Density	(lb/ft3)	29.43	32.32	24.93		
Act. Liq. Flow	(USGPM)	1036	1036	---		
Z Factor		---	---	---		
Watson K		15.23	14.51	16.78		
User Property		---	---	---		
Cp/(Cp - R)		1.091	1.068	1.153		
Cp/Cv		1.097	1.068	1.367		
Heat of Vap.	(Btu/lbmole)	9509	8342	6973		
Kinematic Viscosity	(cSt)	---	0.2066	0.3322		
Liq. Mass Density (Std. Cond)	(lb/ft3)	27.78	32.65	---		
Liq. Vol. Flow (Std. Cond)	(barrel/day)	5.918e+004	3.375e+004	---		
Liquid Fraction		0.5489	1.000	0.0000		
Molar Volume	(ft3/lbmole)	6.775	1.514	13.18		
Mass Heat of Vap.	(Btu/lb)	246.6	177.4	246.8		
Phase Fraction [Molar Basis]		0.4511	0.0000	1.0000		
Surface Tension	(dyne/cm)	6.992	6.992	---		
Thermal Conductivity	(Btu/hr-ft-F)	---	4.920e-002	1.662e-002		
Viscosity	(cP)	---	0.1029	1.141e-002		
Cv (Semi-Ideal)	(Btu/lbmole-F)	21.84	29.10	13.01		
Mass Cv (Semi-Ideal)	(Btu/lb-F)	0.5665	0.6189	0.4604		
Cv	(Btu/lbmole-F)	21.71	29.10	10.97		
Mass Cv	(Btu/lb-F)	0.5631	0.6189	0.3881		
Cv (Ent. Method)	(Btu/lbmole-F)	32.57	29.64	10.97		
Mass Cv (Ent. Method)	(Btu/lb-F)	0.8446	0.6303	0.3881		
Cp/Cv (Ent. Method)		0.7316	1.049	1.367		
Liq. Vol. Flow - Sum(Std. Cond)	(barrel/day)	3.380e+004	3.380e+004	0.0000		
Partial Pressure of H2S	(psia)	0.0000	0.0000	0.0000		
Reid VP at 37.8 C	(psia)	485.0	226.1	---		
True VP at 37.8 C	(psia)	932.0	394.0	---		

DYNAMICS

Vessel Parameters: Initialize from Product

Vessel Volume	(ft3)	---	Level Calculator		Vertical cylinder
Vessel Diameter	(ft)	---	Fraction Calculator		Use levels and nozzles
Vessel Height	(ft)	---	Feed Delta P	(psi)	0.0000 *
Liquid Level Percent	(%)	50.00	Vessel Pressure	(psia)	370.0

Holdup: Vessel Levels

Phase	Level (ft)	Percent (%)	Volume (ft3)
Vapour	---	---	0.0000
Liquid	---	---	0.0000
Aqueous	---	---	0.0000

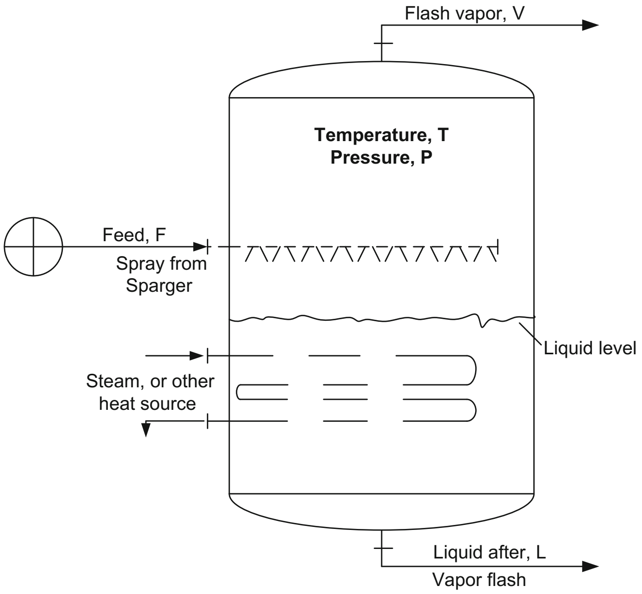


Figure 10-31 Schematic liquid flash tank. Note: Feed can be preheated to vaporize feed partially.

T (Bubble Point) < T (Flash) < T (Dew Point)
For binary mixtures [147]:

1. Set the temperature and pressure of the flash chamber.
2. Perform a material balance on a single component.

$$F_tX_i = V_ty_i + Lx_i \tag{10-138}$$

3. Knowing F, calculate the amounts and compositions of V and L.

   $F_t = F + V_s$ = mols of feed plus mols of non-condensable gases

   From Henry's Law:

$$F_tX_{fi} = V_ty_i + L(yi/Ki) \tag{10-139}$$

$V_t = V + V_s$ = mols of vapor formed plus mols non-condensed gases
$y_i = K_ix_i$

4. $F_t = V_t + L$ (10-140)

$$y_i = \frac{F_tX_{fi}}{V_t + \dfrac{L}{K_i}} = \frac{F_tX_{fi}}{Ft - L + \dfrac{L}{K_i}} \tag{10-141}$$

$$y_i = \frac{X_{fi}}{1 - \dfrac{L}{F_t}\left(1 - \dfrac{1}{K_i}\right)} \tag{10-142}$$

After calculating V, calculate the x_i's and y_i's:

$$y_iV = \frac{FX_i}{1 + \dfrac{L}{K_iV}} \tag{10-143}$$

Then,

$$y_i = \frac{\left(\dfrac{FX_i}{V}\right)}{1 + \dfrac{L}{K_iV}} \tag{10-144}$$

Calculate each y; after calculating the y_i's, calculate x_i's as follows:

$$y_i = K_ix_i \tag{10-38}$$

so, $x_i = y_i/K_i$

$$K_i = P_i/\pi \tag{10-145}$$

Relation for K:

$$y_i = K_ix_i \tag{10-38}$$

$$p_i = P_ix_i \tag{10-146}$$

$$p_i = \pi yi \tag{10-147}$$

$$\pi y_i = P_ix_i \tag{10-148}$$

$$\frac{y_i}{x_i} = \frac{P_i}{\pi} \tag{10-149}$$

where

X_i = mols of a component i in vapor plus mols of same component in liquid, divided by total mols of feed (both liquid and vapor)
= total mol fraction, irrespective of whether component is in liquid or vapor

$$FX_i = Vy_i + Lx_i \tag{10-150}$$

$$x_i = y_i/K_i$$

$$yi = V + L/Ki \tag{10-151}$$

$$y_iV = V\left(1 + \frac{L}{K_iV}\right) \tag{10-152}$$

$$\Sigma y_i = 1.0$$

$$\sum_{i=1}^{c} y_iV = \sum_{i=1}^{c}\left(\frac{FX_i}{1 + \dfrac{L}{K_iV}}\right) \tag{10-153}$$

To calculate, V, L, y_i's, and x_i's:

1. Assume: V
2. Calculate: $L = F - V$
3. Calculate: L/V
4. Look up K_i's at temperature and total pressure of system
5. Substitute in:

$$V = \sum_{i=1}^{c} \frac{FX_i}{1 + \frac{L}{K_i V}} \tag{10-154}$$

6. If an equality is obtained from:
   $V_{calc} = V_{assumed}$ the amount of vapor was satisfactory as assumed.

$$V = \frac{FX_1}{1 + \frac{L}{K_1 V}} + \frac{FX_2}{1 + \frac{L}{K_2 V}} + \frac{FX_3}{1 + \frac{L}{K_3 V}} + \ldots \frac{FX_i}{1 + \frac{L}{K_i V}} \tag{10-155}$$

7. $Vy_i = \dfrac{FX_i}{1 + \frac{L}{K_i V}}$ (10-143)

   and

$$y_i = \frac{FX_i/V}{1 + \frac{L}{K_i V}} \tag{10-144}$$

8. Calculate each y_i as in (7) above, then the x_i's are determined:
   $y_i = K_i x_i$
   or, $x_i = y_i/K_i$
9. $K_i = P_i/\pi_i$ (10-145)

   where
   n = total system pressure absolute.
   P_i = vapor pressure of individual component at temperature, abs.
   $X_i = X$ = mols of a component i, in vapor phase plus mols of same component in liquid divided by the total mols of feed (both liquid and vapor).
   x_f = mol fraction of a component in feed.
   x_f = mol fraction of any component in the feed, F_t where $X_f = Fx_f/F_t$ for all components in F; for the non-condensable gases, $x_f = V_s/F_t$.
   F = mols of feed entering flash zone per unit time contains all components except non-condensable gases.
   $F_t = F + V_s$
   $V_t = V + V_s$ mols of vapor at a specific temperature and pressure, leaving flash zone per unit time.
   V_s = mols of non-condensable gases entering with the feed, F, and leaving with the vapor, V, per unit time.
   V = mols of vapor produced from F per unit time
   $F = V + L$
   L = mols of liquid at a specific temperature and pressure, from F, per unit time
   i = specific individual component in mixture
   K_i = equilibrium K values for a specific component at a specific temperature and pressure, from References 18, 65, 79, 99, 131, 235
   T = temperature, abs
   x_i = mol fraction of a specific component in liquid mixture as may be associated with feed, distillate, or bottoms, respectively
   y_i = mol fraction of a specific component in vapor mixture as may be associated with the feed, distillate or bottoms, respectively
10. For the simplified case of a mixture free of non-condensable gases, see Equation 10-142, where $X_{fi} = x_f$.

Example 10-11: Calculation of Bubble Point and Dew Point

From the hydrocarbon feed stock listed, calculate the bubble point and dew point of the mixture at 165 psia, and using K values as listed, which can be read from a chart in 3rd edition Perry's, Chemical Engineer's Handbook.

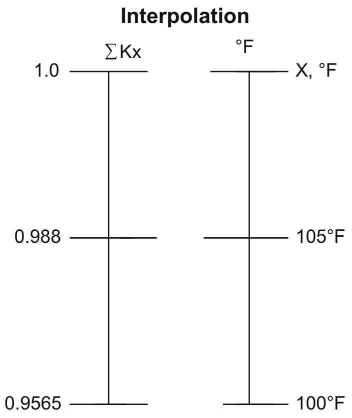
Feed Stock

Composition	**Mol Fraction**
C_2H_6	0.15
C_3H_8	0.15
n-C_4H_{10}	0.30
i-C_4H_{10}	0.25
n-C_4H_{12}	0.15
	1.00

Calculate the Bubble Point (Assume composition is liquid)

Composition	Mol Fraction	Assumed T = 90°F, K	Kx	Assume T = 100°F, K	Kx
C_2H_6	0.15	3.1	0.465	3.4	0.5100
C_3H_8	0.15	1.0	0.150	1.2	0.1800
n-C_4H_{10}	0.30	0.35	0.105	0.39	0.1170
i-C_4H_{10}	0.25	0.46	0.115	0.52	0.1300
n-C_5H_{12}	0.15	0.12	0.018	0.13	0.0195
	1.00		0.853		0.9565
					(Too low)

Assume T = 105°F	K	Kx
	3.45	0.5175
	1.25	0.1875
	0.41	0.1230
	0.55	0.1375
	0.15	0.0225
		0.9880



By interpolation:

$$\frac{105-100}{0.988-0.9565} = \frac{X-100}{1.0-0.9565}$$

X = 106.9°F (107°F)

So, T = 107°F Bubble point at 165 psia.

Calculation of Dew Point:

Composition in vapor	Mol. Frac. in vapor	Assume, T = 160°F, K (from charts)	x = y/K
C_2H_6	0.15	5.1	0.0294
C_3H_8	0.15	1.85	0.0811
n-C_4H_{10}	0.30	0.80	0.3750
i-C_4H_{10}	0.25	1.00	0.2500
n-C_5H_{12}	0.15	0.32	0.4688
	1.00		$1.204 \neq$ $\Sigma y/K = 1$

Composition in vapor	Mol. Frac. in vapor	Assume, T = 180°F, K (from charts)	x = y/K
C_2H_6	0.15	5.95	0.0252
C_3H_8	0.15	2.25	0.0666
n-C_4H_{10}	0.30	0.98	0.3061
i-C_4H_{10}	0.25	1.34	0.1866
n-C_5H_{12}	0.15	0.41	0.3659
	1.00		$0.9504 \neq$ $\Sigma y/K = 1$

Composition in vapor	Mol. Frac. in vapor	Assume, T = 175°F, K (from charts)	x = y/K
C_2H_6	0.15	5.60	0.0268
C_3H_8	0.15	2.20	0.0682
n-C_4H_{10}	0.30	0.91	0.3297
i-C_4H_{10}	0.25	1.20	0.2083
n-C_5H_{12}	0.15	0.39	0.3846
	1.00		1.0176 ≅ $\Sigma y/K = 1$

Dew point is essentially 175°F at 165 psia.

Example 10-12: Calculation of Flashing Composition

If the mixture shown in Example 10-11 is flashed at a temperature midway between the bubble point and dew point, and at a pressure of 75 psia, calculate the amounts and compositions of the gas and liquid phases.

Must Calculate Bubble Point at 75 psia

Composition	Mol Frac.	K @ 50°F	y = Kx	K @ 40°F	y = Kx
C_2H_6	0.15	5.0	0.7500	4.5	0.6750
C_3H_8	0.15	1.2	0.1800	1.07	0.1605
n-C_4H_{10}	0.30	0.325	0.0975	0.28	0.0840
i-C_4H_{10}	0.25	0.48	0.1200	0.415	0.10380
n-C_5H_{12}	0.15	0.089	0.0134	0.074	0.0110
			1.1609		1.0343

Bubble point = 40°F (as close as K curves can be read)
Extrapolating =

$$\left(\frac{1.00 - 1.0343}{1.1609 - 1.0343}\right)(50^\circ - 40^\circ) = 2.7^\circ$$

Therefore, a close value of bubble point would be: $40^\circ - 3^\circ = 37^\circ F$

Calculate Dew Point at 75 psia

Composition	Mol Frac.	K @ 70°F	Σx = y/K	K @ 100°F	Σx = y/K	K @ 130°F	Σx = y/K
C_2H_6	0.15	5.9	0.0254	7.6	0.0197	9.5	0.0158
C_3H_8	0.15	1.55	0.0968	2.18	0.0688	3.0	0.0500
n-C_4H_{10}	0.30	0.45	0.6667	0.70	0.4286	1.06	0.2830
i-C_4H_{10}	0.25	0.58	0.4310	1.0	0.2500	1.45	0.1724
n-C_5H_{12}	0.15	0.13	1.1538	0.225	0.6667	0.37	0.4054
			2.3737		1.4338		0.9266
			(too low temp.)				

Referring to Example 10-11:

Composition	Mol Fraction
C_2H_6	0.15
C_3H_8	0.15
n-C_4H_{10}	0.30
i-C_4H_{10}	0.25
n-C_5H_{12}	0.15
	1.00

Refer to extrapolation curve, Figure 10-32.

At $\Sigma x = y/K = 1.0$, dew point = 124°F

Flash this mixture at temperature midway between bubble point and dew point, or flash temperature = $\frac{37 + 124}{2} = 81^\circ F$

Assume: F (feed) = 100

Pressure: = 75 psia; then tabulating the calculations:

Composition	Feed Mol. Frac., x	FX	L/V	K @ 81°F	$\frac{L}{VK}$	$1+\frac{L}{VK}$	$\sum yV = \frac{FX}{1+\frac{L}{VK}}$
C_2H_6	0.15	15	2.34	6.6	0.3545	1.3545	11.0742
C_3H_8	0.15	15		1.78	1.3146	2.3146	6.4806
n-C_4H_{10}	0.30	30		0.54	4.3333	5.3333	5.6250
i-C_4H_{10}	0.25	25		0.77	3.0390	4.0390	6.1896
n-C_5H_{12}	0.15	15		0.16	14.6250	15.6250	0.9600
							30.33

Vapor phase after flashing at 75 psia and 81°F = 30.3% of original feed.

Liquid phase = 100 − 30 = 70% of original feed
Composition of Vapor

Composition	Mol Fraction y
C_2H_6	11.074/30.33 = 0.3651
C_3H_8	6.481/30.33 = 0.2137
n-C_4H_{10}	5.625/30.33 = 0.1855
i-C_4H_{10}	6.19/30.33 = 0.2041
n-C_5H_{12}	0.96/30.33 = 0.0317
	$\sum y = 1.000$

Composition of Liquid

Feed Composition	K @ 81°F	Mol Fraction x = y/K
C_2H_6	6.6	0.3651/6.6 = 0.0553
C_3H_8	1.78	0.2137/1.78 = 0.1201
n-C_4H_{10}	0.54	0.1855/0.54 = 0.3435
i-C_4H_{10}	0.77	0.2041/0.77 = 0.2651
n-C_5H_{12}	0.16	0.0317/0.16 = 0.1981
		$\sum x = 0.9821$

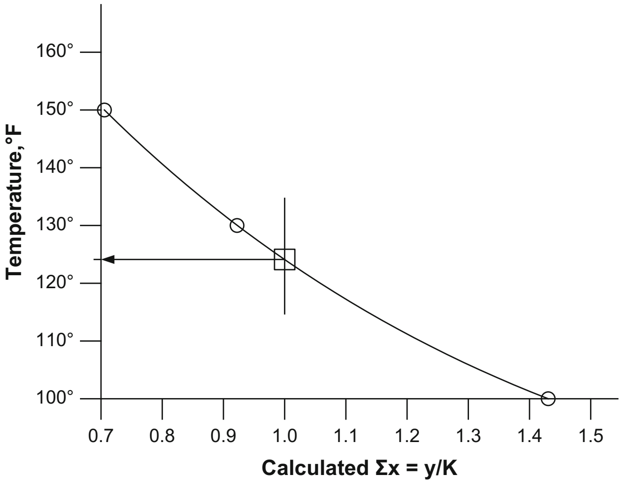


Figure 10-32 Extrapolation curve for dew point for Example 10-12.

This should be = 1.00. Inaccuracy in reading K values probably accounts for most of the difference.

10.18 Determination of Distillation Operating Pressures

Determining the proper operating pressure for a distillation system, whether using trays or packed column, requires examining the conditions by following the pattern of Figure 10-33 [149]. It is essential to establish condensing conditions of the distillation overhead vapors, and any limitations on bottoms temperature at the estimated pressure drop through the system. Preliminary calculations for the number of trays or amount of packing must be performed to develop a reasonable system pressure drop. With this accomplished, the top and bottom column conditions can be established, and more detailed calculations performed. For trays this can be 0.1 psi/actual tray to be installed [149] whether operating at atmospheric or above, or 0.05 psi/tray equivalent for low vacuum (not low absolute pressure).

Because low-pressure operations require larger diameter columns, selected pressures should only be as low as required to accomplish the separation.

For high vacuum distillation, Eckles et al. [150] suggest the use of a thin film, or conventional batch process, for industrial installations. However, many tray and packed columns operate at pressures as low as 4 mm Hg. abs. Eckles [150] suggests that "high vacuum" be taken as 5 mm Hg; molecular distillation as 0.3–0.003 mm Hg pressure, and unobstructed path distillation as 0.5–0.02 mm Hg. These latter two can be classed as evaporation processes. Eckles' [150] rules of thumb can be summarized:

1. Do not use a lower pressure than necessary, because separation efficiency and throughput decrease as pressure decreases.
2. The requirement to select a bottoms temperature to avoid overheating heat sensitive materials may become controlling.

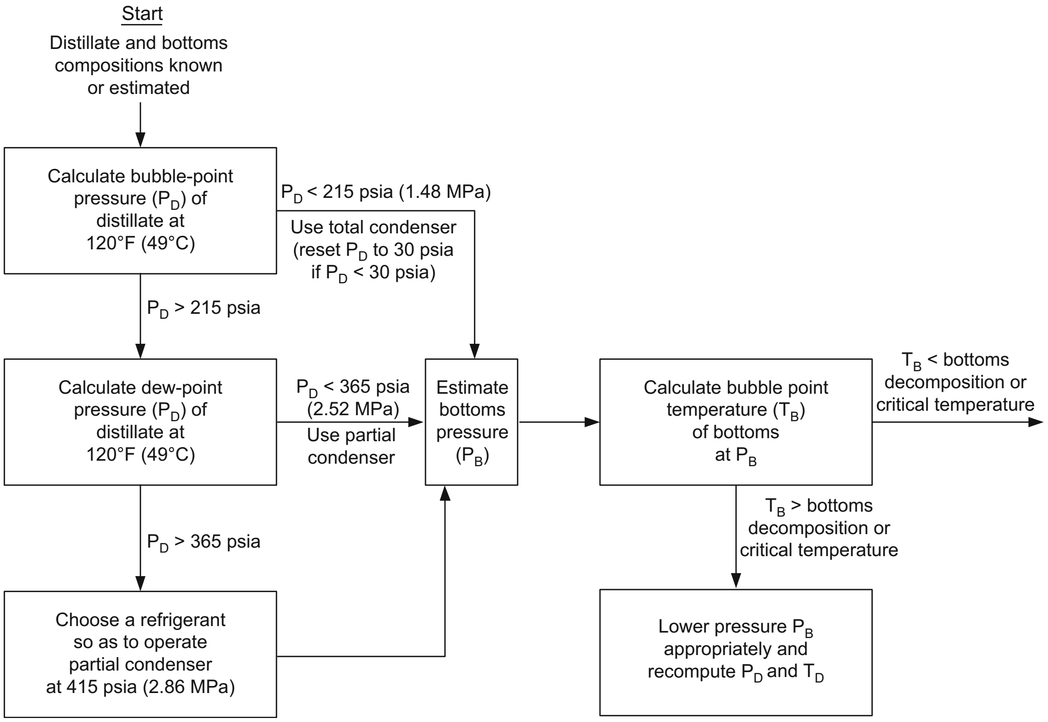


Figure 10-33 Algorithm for establishing distillation column pressure and condenser type. Source: Henley, E. J. and Seader J. D., Separation Process Principles, 2nd Edition, John Wiley © p. 265 (2006)].

3. When separating volatile components such as a single stream from low-volatility bottoms, use a molecular or unobstructed path process of either thin film or batch type.
4. When separating a volatile product from volatile impurities, batch distillation is usually preferable.
5. Do not add a packed column to a thin film evaporator system, because complications may occur.

Note that good vapor-liquid equilibrium data for low-pressure conditions are very scarce and difficult to locate. However, they are essential for proper calculations. This is dealt with in References 151 and 152.

Studies with high-pressure distillation by Brierley [239] provide insight into some FRI studies, the effects of pressure on performance, and the impacts of errors in physical properties, relative volatility, etc. This work makes an important contribution to the understanding and setting of operating pressures.

10.19 Condenser Types from a Distillation Column

10.19.1 Total Condenser

In a total condenser all the overhead vapor is condensed to liquid. The heat load on the condenser is equal to the sum of the sensible heat above the dew point, plus the latent heat of vapor, plus the sensible heat in cooling liquid down to the bubble point. Condensation of liquid will commence at the dew point and end at the bubble point. (Any further removal would proceed due to cooling.) The condenser and accumulator pressure will be the total vapor pressure of the condensate. If an inert gas is present, the system total pressure will be affected accordingly. When using a total condenser, the condensed stream is subsequently split into two streams. One is returned into the column as reflux and the second leaves as distillate product.

10.19.2 Partial Condenser

The effect of a partial condenser is indicated in Figure 10-34, and is represented by the relations given in the rectifying and stripping sections. The product is a vapor that is in equilibrium with the reflux to the column top tray, and hence the partial condenser actually serves as an “external” tray for the system; it should be treated as the top tray when applying the equations for total reflux conditions. This requires care in step-wise calculations of the column performance.

In a partial condenser, there are two general conditions of operation:

1. All condensed liquid is returned to the column as reflux, and all vapor is withdrawn from the

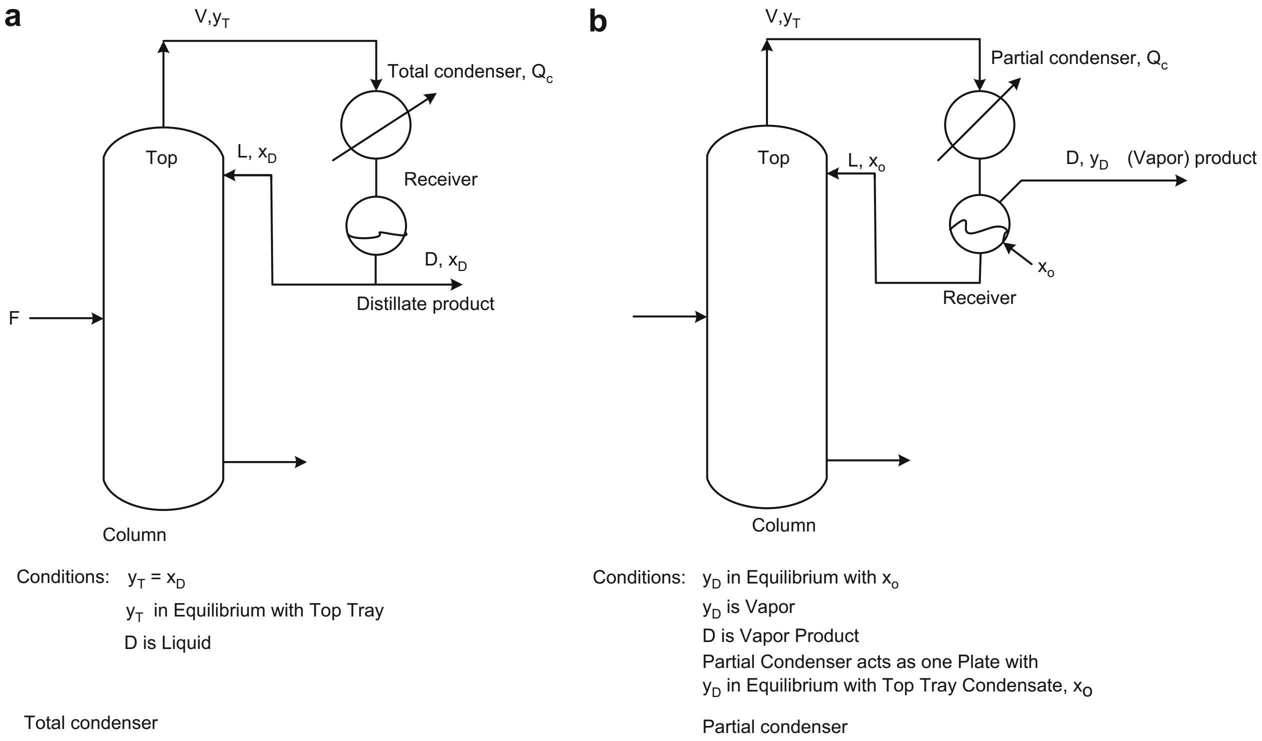


Figure 10-34 Total and partial condenser arrangements.

accumulator as product. In this case the vapor $y_c = x_D$; Figure 10-5 and Figure 10-35.

2. Both liquid and vapor products are withdrawn, with the liquid reflux composition being equal to liquid product composition. On an equilibrium diagram the partial condenser liquid and vapor stream's respective compositions are in equilibrium, but only when combined do they represent the intersection of the operating line with the 45° slope (Figure 10-35).

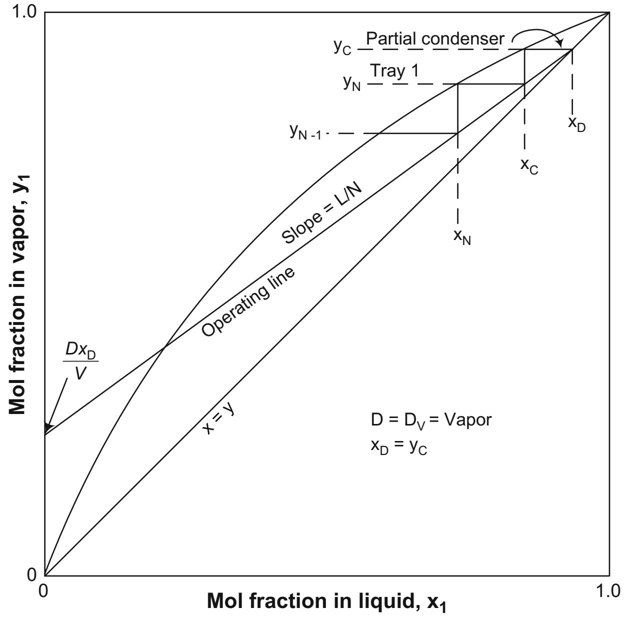


Figure 10-35 Diagram of partial condenser; only a vapor product is withdrawn.

Example 10-13: Calculation of Partial Condensation of a multicomponent feed

A multicomponent vapor feed (F) is partially condensed to produce a vapor (V) and a liquid (L). Mole fractions of components in the vapor feed are designated z, those in the vapor y, and those in the liquid x. The vapor-liquid equilibrium for any component is given by $y = Kx$. Assuming that the vapor and the liquid leave the partial condenser in equilibrium, show that for any component:

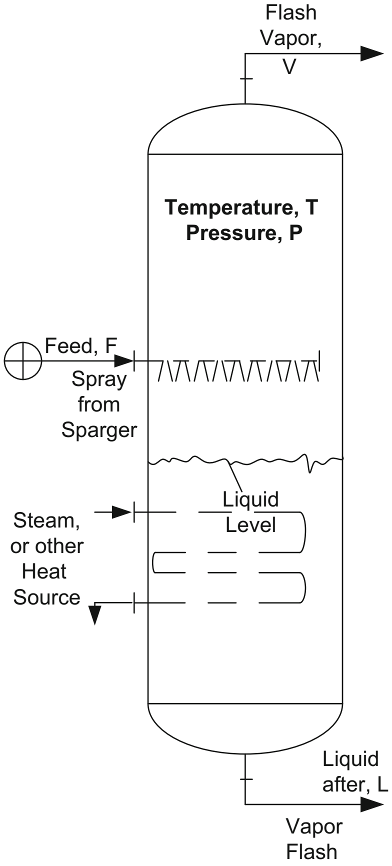
$$y = \frac{z(F/V)}{(1 + L/KV)}$$

It has been calculated that at 18.9 bar and 55°C, one third of the vapor feed will be condensed.

Check this calculation for the feed composition and K values at 18.9 bar and 55°C given as:

Component	C_2H_6	C_3H_8	C_4H_{10}
z	0.0713	0.8978	0.0309
K	2.65	1.0	0.41

Solution



Mass balance at the top of the vessel:

$$F = V + L \tag{10-156}$$

Component balance:

$$F\,z = Vy + L\,x \tag{10-157}$$

Since the vapor phase is in equilibrium with the liquid phase at the top of the vessel:

$$y = K\,x \tag{10-158}$$

$$x = y/K \tag{10-159}$$

Substitution of Eq. (10-159) into Eq. (10-157) gives:

$$Fz = Vy + L\frac{y}{K} \tag{10-160}$$

or

$$Fz = y\left(V + \frac{L}{K}\right) \tag{10-161}$$

$$y = \frac{F\,z}{V + \dfrac{L}{K}} = \frac{z(F/V)}{(1 + L/KV)} \tag{10-162}$$

Let F = 3 kmol/h

Since 1/3 of the vapor feed is condensed, then

L = 1/3 of 3 kmol/h = 1 kmol/h
V = F – L = 2 kmol/h

To check the total mole fraction of the components at the top of the column, determine the mole fractions of individual components from Eq. 10-162, i.e.

Composition	Feed Mol. Frac., z	Fz	Fz/V	K @ 55°F	$\frac{L}{VK}$	$1+\frac{L}{VK}$	$y = \frac{z(F/V)}{\left(1+\frac{L}{VK}\right)}$
C_2H_6	0.07135	0.2139	0.10695	2.65	0.1887	1.1887	0.08997
n-C_3H_8	0.8978	2.6934	1.3467	1.00	0.5000	1.5	0.8978
n-C_4H_{10}	0.0309	0.0927	0.04635	0.41	1.2195	2.219	0.0209
						$\sum y$	1.00867

The condensing temperature range in a total condenser is dependent on the dew and bubble points, cooling water limitations, fouling and the pressure of the distillation column. The reflux temperature is also affected by the pressure control scheme and the presence of excess capacity for cooling. The control aspect example can be referred to when submerged tubes result from some pressure control schemes. The degree of sub cooling can be as much as 50 to 200°F.

10.20 Effect of Thermal Condition of Feed

The condition of the feed as it enters the column has an effect on the number of trays, reflux requirements and energy requirements for a given separation. Figure 10-36 illustrates the possible situations, i.e., sub-cooled liquid feed, feed at the boiling point of the column feed tray, part vapor and part liquid, all vapor, or superheated vapor. The thermal condition of the feed stream is designated as “q”; this is approximately the amount of heat required to vaporize one mol of feed at the feed tray conditions, divided by the latent heat of vaporization of the feed.

For a single feed stream column with a total condenser and a partial reboiler as shown in Figure 10-5, a mass balance on the rectifying section of the more volatile component is:

$$V y = L x + D x_D \tag{10-163}$$

A mass balance on the stripping section is:

$$\overline{V} y = \overline{L} x - B x_B \tag{10-164}$$

Assuming constant molar overflow, at the feed plate the point at which the top operating line intersects the bottom operating line is:

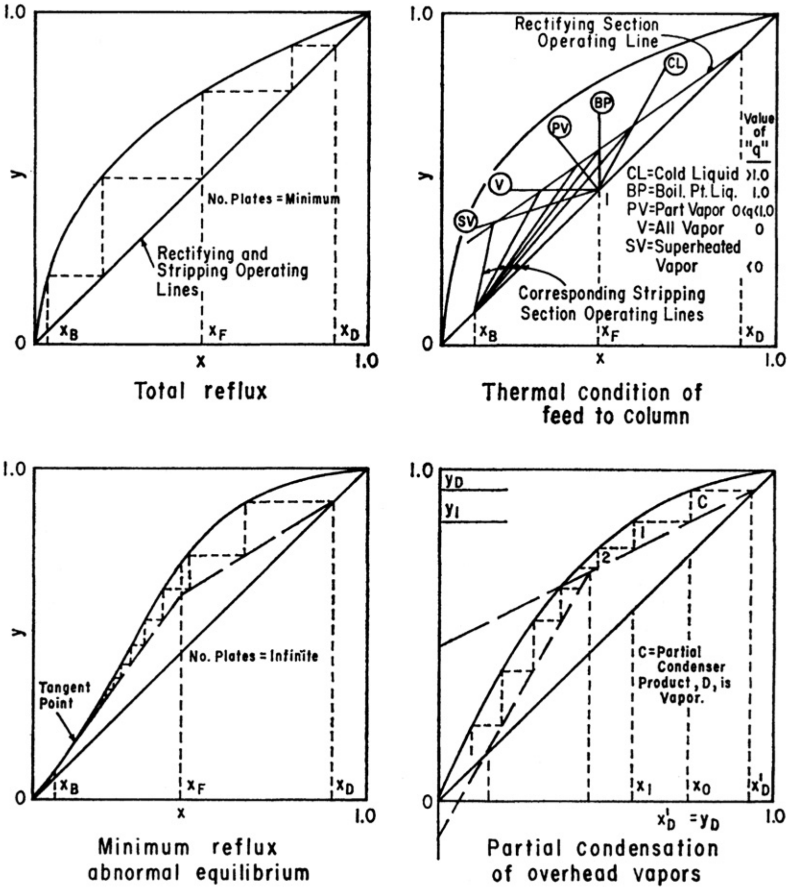
$$x_{top\ op} = x_{bot\ op}, \quad y_{top\ op} = y_{bot\ op} \tag{10-165}$$

Subtracting Eq. 10-163 from Eq. 10-164 gives:

$$y(\overline{V} - V) = (\overline{L} - L)x - (D x_D + B x_B) \tag{10-166}$$

From the overall mass balance around the entire column (see Figure 10-5), where:

$$F x_F = D x_D + B x_B \tag{10-167}$$



Total reflux

Thermal condition of feed to column

Minimum reflux abnormal equilibrium

Partial condensation of overhead vapors

Figure 10-36 Operating characteristics of distillation columns.

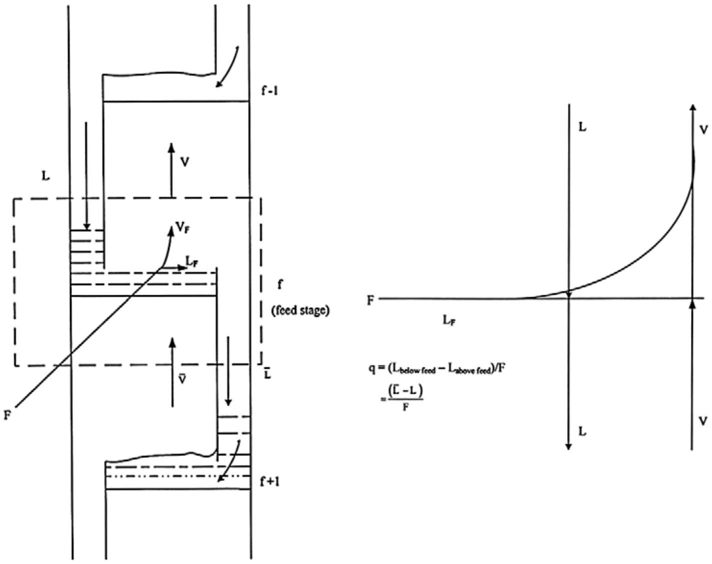


Figure 10-37 Two-phase feed.

$$y = -\left(\frac{\bar{L} - L}{V - \bar{V}}\right) x + \frac{F\,x_F}{V - \bar{V}} \tag{10-168}$$

Equation 10-168 gives a form of the feed equation since L, $\bar{L}$, V, $\bar{V}$, F and x_F are constant. It represents a straight line (the feed line) on a McCabe-Thiele diagram. The case where the feed flashes into the column to form a vapor and a liquid phase is illustrated in Figure 10-37. Part V_F vaporizes while the remainder is liquid, L_F. From Equation 10-168, $(\bar{L} - L)$ is the change in liquid flow rates at the feed stage. That is:

$$L_F = \bar{L} - L \tag{10-169}$$

The change in vapor flow rate is:

$$V_F = V - \bar{V} \tag{10-170}$$

Equation (10-168) becomes:

$$y = -\frac{L_F}{V} x + \frac{F}{V_F} x_F \tag{10-171}$$

Equation (10-171) represents the flashing of the feed into the column, and can be written in terms of the fraction vaporized as:

$$y = -\frac{1 - f}{f} x + \frac{x_F}{f} \tag{10-172}$$

or in terms of the fraction of remaining liquid, $q = L_F/F$

$$y = \frac{q}{q - 1} x + \frac{x_F}{1 - q} \tag{10-173}$$

The slope of a line from the intersection point of the feed composition, x_F, with the 45° line on Figure 10-5 is given by $q/(q - 1) = -q/(1 - q)$. Physically this gives a good approximation of the number of mols of saturated liquid that will form on the feed plate by the introduction of the feed, although under some thermal conditions the feed may vaporize liquid on the feed plate rather than condense any.

Liebert [218] studied feed preheat conditions and the effects on the energy requirements of a column. This is an essential consideration in the efficient design of a distillation system. As an alternative to locating the "q" line, any value of x_i may be substituted in the "q" line equation below, and a corresponding value of y_i determined, which when plotted will allow the "q" line to be drawn in. This is the line for SV – I, V – I, PV – I, BP – I and CL – I of Figure 10-36.

$$y_i = -\frac{q}{1 - q} x_i + \frac{x_F}{1 - q} \tag{10-174}$$

Equation 10-173 or 10-174 is termed the q-line equation. It is located graphically as follows. When $x_i = x_F$, Equation 10-174 gives $y = x_F$. Thus, the q-line passes through the point (x_F, x_F). The slope of the q-line is then calculated on one other convenient point.

A more general definition of q is applied to determine the values of q for subcooled liquid and superheated vapor:

q = enthalpy change to bring the feed to dew-point vapor temperature divided by enthalpy of vaporization of the feed (dew-point minus bubble-point), that is,

$$q = \frac{(H_F)_{\text{Sat'd vapor temperature}} - (h_F)_{\text{feed temperature}}}{(H_F)_{\text{Sat'd vapor temperature}} - (h)_{\text{Sat'd liquid temperature}}} \qquad (10\text{-}175)$$

where

H_F = feed enthalpy at saturated vapor temperature, kcal/kg, Btu/lb mol.

h_F = feed enthalpy (liquid, vapor or two-phase), kcal/kg, Btu/lb mol.

h = liquid enthalpy, kcal/kg, Btu/lb mol

For a subcooled liquid feed, Equation 10-156 becomes

$$q = \frac{(H_{F,\text{Sat'd vapor temp.}} - h_{\text{Sat'd liquid temp.}}) + (h_{\text{Sat'd liquid temp.}} - h_{F,\text{feed temp.}})}{(H_{F,\text{Sat'd vapor temp.}} - h_{\text{Sat'd liquid temp.}})} \qquad (10\text{-}176)$$

where

$$(H_{F,\text{Sat'd vapor temp.}} - h_{\text{Sat'd liquid temp.}}) = \Delta H^{vap} \qquad (10\text{-}177)$$

and

$$(h_{\text{Sat'd liquid temp.}} - h_{F,\text{feed temp.}}) = C_{P_L}(T_b - T_F) \qquad (10\text{-}178)$$

or

$$q = \frac{\Delta H^{vap} + C_{P_L}(T_b - T_F)}{\Delta H^{vap}} \qquad (10\text{-}179)$$

For a superheated vapor, Equation (10-175) becomes:

$$q = \frac{C_{P_V}(T_d - T_F)}{\Delta H^{vap}} \qquad (10\text{-}180)$$

where C_{P_L} and C_{P_V} are the liquid and vapor molar heat capacities respectively, ΔH^{vap} is the molar enthalpy change from the bubble point to the dew point, and T_F, T_d and T_b are the feed, dew-point and bubble-point temperatures, respectively of the feed at the column operating pressure. As q changes from a value greater than 1 (subcooled liquid) to a value less than 0 (superheated vapor), the slope of the q-line, q/(q-1), changes from a positive value to a negative value and then back to a positive value. Figure 10-38 shows the effect of thermal condition of the feed on slope of the q-line. For a saturated liquid feed, the q-line is vertical and for saturated vapor, the q-line is horizontal as shown in Figure 10-38.

The relationship between the various types of feed and the slopes of the feed condition is shown in Table 10-22.

10.21 Effect of Total Reflux, Minimum Number of Plates in a Distillation Column

Total reflux exists in a distillation column, whether a binary or multicomponent system, when all the overhead vapor from the top tray or stage is condensed and returned to it. A column may be brought to equilibrium at total reflux for test purposes or for a temporary plant condition, which requires temporary discontinuation of operation. Rather than shut down, drain, and then re-establish operating conditions later, it is usually more convenient to maintain a total reflux condition with no feed, no overhead and no bottoms products or withdrawals. This approach also requires less energy in the form of reboiler heating and condenser coolant

Conditions of total liquid reflux in a column coincide with the minimum number of plates required for a given separation. Under such conditions the column has zero yield of product, infinite heat requirements, and $L_s/V_s = 1.0$, as shown in Figure 10-36. This is the limiting condition for the number of trays, and is a convenient measure of the complexity or difficulty of separation.

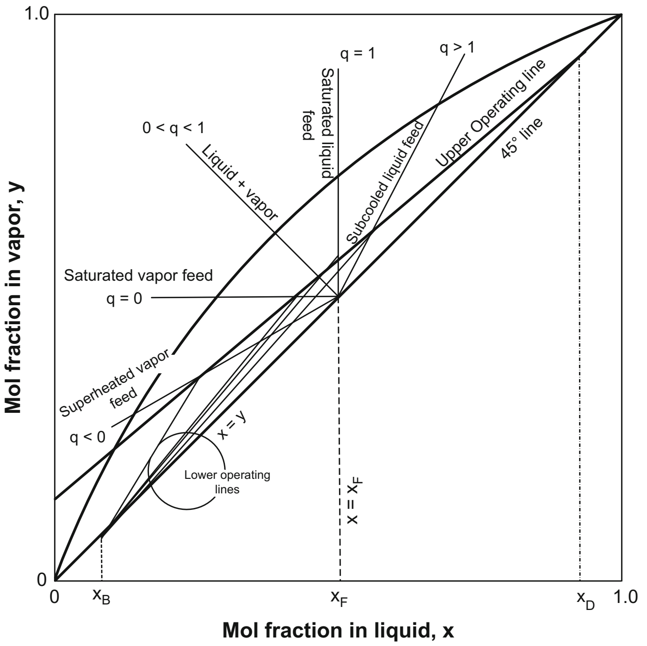


Figure 10-38 Location of q-lines.

Table 10-22 Feed conditions

Type of feed	T	h_F	f	q	Slope of q-line q/(q−1)
Subcooled liquid	$T_F < T_{BP}$	$h_F < h$	$f < 0$	$q > 1.0$	> 1.0
Saturated liquid	$T_F = T_{BP}$	h	0	1.0	∞
Liquid-vapor mixture	$T_{DP} > T_F > T_{BP}$	$H_F > h_F > h$	$0 < f < 1$	$1.0 > q > 0$	Negative
Saturated vapor	$T_F = T_{DP}$	H_F	1	0	0
Superheated vapor	$T_F > T_{DP}$	$h_F > H_F$	$f > 1$	$q < 0$	$1 > \text{slope} > 0$

T_{BP} = bubble point of feed; T_{DP} = dew point of feed.

10.21.1 Fenske Equation: Short-Cut Prediction of Overall Minimum Total Trays In A Column With Total Condenser

$$S_m = (N_{min}+1) = \frac{\log\left(\frac{x_{D_l}}{x_{Dh}}\right)\left(\frac{x_{Bh}}{x_{B1}}\right)}{\log \alpha_{avg}.} \qquad (10\text{-}181)$$

This includes the bottoms reboiler being equivalent to a tray in the system.

Refer to tabulation below.

N_{min} includes only the required trays in the column itself, and not the reboiler.

$\alpha_{avg} = (\alpha_{lk/hk})$ avg.
D refers to overhead distillate; B refers to bottoms

$$S_m = N_{min} = \frac{\log[(x_{lk}/x_{hk})_D(x_{hk}/x_{lk})_B]}{\log(\alpha_{lk/hk})\text{avg.}} \qquad (10\text{-}182)$$

This applies to any pair of components. Ludwig [271] suggested adding +1 theoretical tray for the reboiler, thus making the total number of theoretical trays a conservative estimate. Converting to the actual number of trays requires the calculated tray efficiency:

$$S_m + 1 = N_{min} \qquad (10\text{-}183)$$

For a condition of overall total trays, allowance is to be made for feed tray effect; *add one more theoretical tray to the total*. As demonstrated below, allowance should be made for the reboiler and condenser.

		Total Condenser	Reboiler	Partial Condenser	Total
S_m	N_{min}	+1	0	+0	$N_m + 1$
	N_{min}	+1	+1	+0	$N_m + 2$
	N_{min}	+0	+1	+1	$N_m + 2$

The approach recommended here is not in agreement with Van Winkle [74], who assumes that the reboiler and partial condenser are included in the overall calculation for N_{min}.

Various average values of α for use in these calculations are suggested in the following section on "Relative Volatility". Because the feed tray is essentially non-effective, an additional theoretical tray may be added to allow for this. This can be conveniently solved by the nomographs [21] of Figures 10-39 and 40. The minimum number of trays in the rectifying section can, if necessary, be calculated by the Fenske equation, substituting the limits of x_{Fl} for x_{Bh} and x_{Bl}, and the stripping section can be calculated by difference.

From Fenske's equation, the minimum number of equilibrium stages at total reflux is related to their bottoms (B) and distillate or overhead (D) compositions using the average relative volatility, see Equation 10-161.

To solve for the component split [100] in distillate or bottoms:

$$\left(\frac{x_{LK}}{x_{HK}}\right)_D = \left(\frac{x_{LK}}{x_{HK}}\right)_D (\alpha_{LK})^{S_m} \qquad (10\text{-}184)$$

where

S_m = total number of calculated theoretical trays at total reflux, from Equation 10-181
$x_{lk} = x_{LK}$ = liquid mol fraction of light key
$x_{hk} = x_{HK}$ = liquid mol fraction of heavy key
lk − hk = LK − HK = average relative volatility of column (top to bottom)

Clearly, a column cannot operate at total reflux and produce net product. Hence, a reflux ratio of about *1.1 to 1.5 times the minimum reflux* will usually give practical results. As the reflux ratio is reduced, the number of theoretical trays increases and an economic balance is therefore involved.

10.22 Relative Volatility (α) Separating Factor in a Vapor-Liquid System

The relative volatility is a measure of the ease of separation, and is the volatility separation factor in a vapor-liquid system, i.e., the volatility of one component divided by the volatility of the other and can be defined as:

$$\alpha_{1-2} = \frac{\text{K} - \text{value of component 1}}{\text{K} - \text{value of component 2}} \tag{10-185}$$

It represents the ratio between the tendency to vaporize of the two components. It also quantifies the tendency for one component in a liquid mixture to separate from the other upon distillation. The term can also be expressed as the ratio of vapor pressure of the more volatile to the less volatile component in the

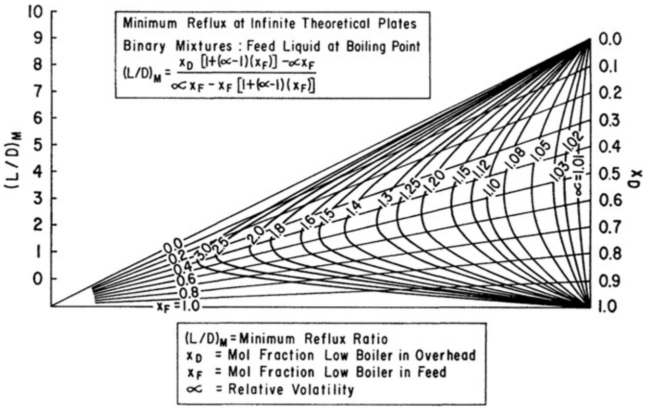


Figure 10-40 Minimum reflux at infinite theoretical plates. Used by permission, The American Chemical Society, Smoker, E. H., Ind. Eng. Chem V. 34 (1942), p. 510, all rights reserved.

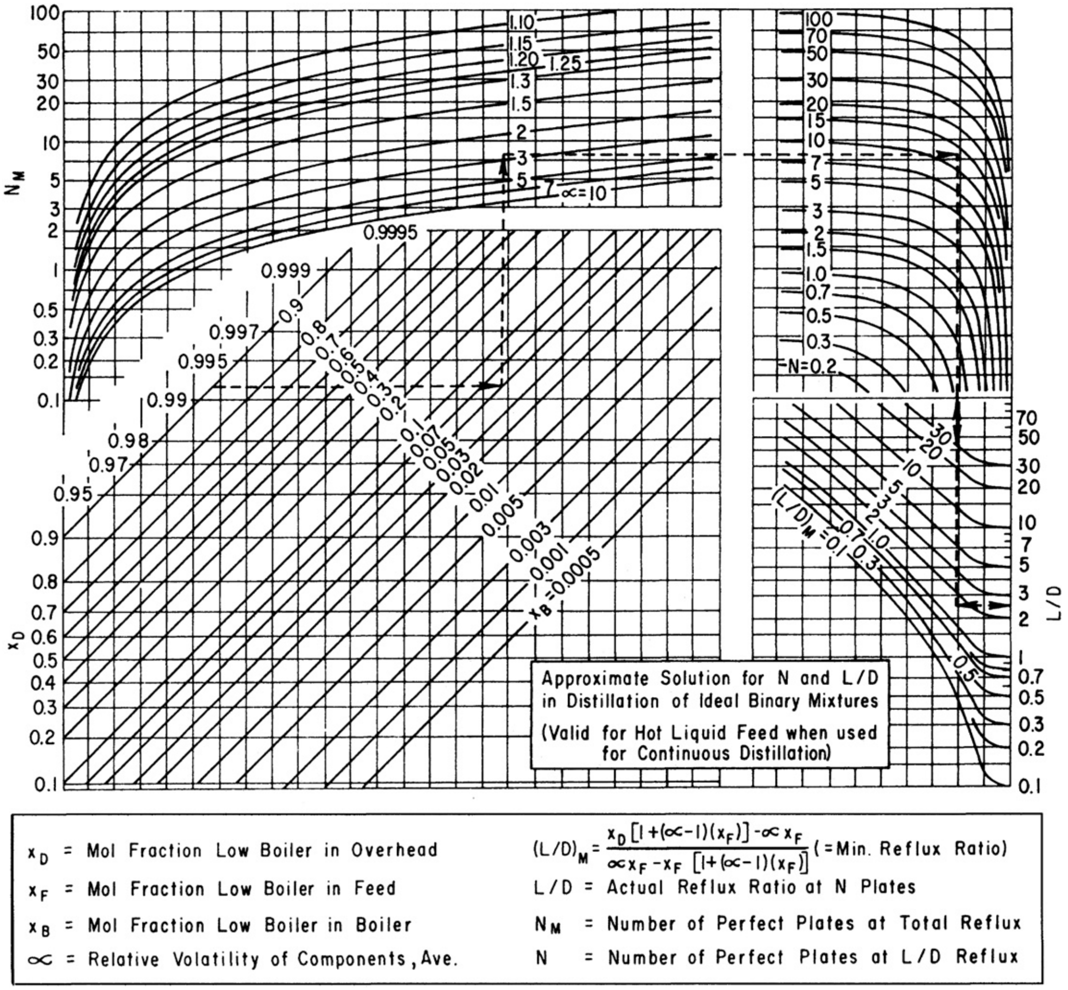


Figure 10-39 Approximate solution for N and L/D in distillation of ideal binary mixtures. Used by permission, Faasen, J.W., Industrial & Eng. Chemistry, V. 36 (1944), p. 248. The American Chemical Society, all rights reserved.

liquid mixture, and therefore $\alpha_{1,2}$ is always ≥ 1.0. If $\alpha_{1,2}$ is high, component 1 has a greater tendency to vaporize (i.e. is more volatile than component 2) and it will be easy to achieve separation by vaporizing one from the other distillation. However, when component 2 has as high a tendency to vaporize as component 1, the relative volatility will approach unity; the components will then be difficult to separate by distillation. If under the specific conditions $\alpha_{1,2} = 1$, the components cannot be separated by distillation. The greater the value of α the easier will be the desired separation.

Relative volatility can be calculated between any two components in a mixture; binary or multicomponent. One of the substances is chosen as the reference to which the other component is compared.

Definition of Relative Volatility: Relative Volatility of Component 1 with respect to component 2:

$$\alpha_{1,2} = (p_1 x_2)/(p_2 x_1) = (y_1 x_2)/(y_2 x_1) \qquad (10\text{-}186)$$

where

1, 2, etc. are component identification
p = vapor pressure of a component
x = liquid mol fraction of a component
y = vapor mol fraction of a component
π = system total pressure, absolute

Partial pressure:

$$p_a = \pi y_a \qquad (10\text{-}36)$$

$$p_b = \pi y_b$$

When temperature is constant and at equilibrium for a homogeneous mixture (such as an azeotrope), the composition of the liquid is identical with the composition of the vapor, thus $x_i = y_i$, and the relative volatility is equal to 1.0.

$$K_i = y_i/x_i, \text{that is, } \frac{\text{mol fraction of i in vapor phase}}{\text{mol fraction of i in liquid phase}} \qquad (10\text{-}38)$$

$$\alpha_{ab} = K_a/K_b$$
$$= \text{relative volatility of components a to b} \qquad (10\text{-}39)$$

where

i = compound identification
r = reference compound

As previously discussed, the charts of K values that are available, apply primarily to hydrocarbon systems. Reference 79 presents other important data on K value relationships. Refer to Figures 10-11a and 10-11b for charts with pressure effects included. (These are not ideal, but practical charts.)

$$\alpha_{1,2} = K_1/K_2 = P_1/\pi \qquad (10\text{-}39)$$

For multicomponent mixtures [79, 59]:

$$y_2 = \frac{x_2}{\alpha_{1/2}x_1 + x_2 + \alpha_{3/2}x_3 + \alpha_{4/2}x_4 + \ldots} = \frac{x_2}{\sum \alpha x} \qquad (10\text{-}187)$$

where

1, 2, 3, 4, … are components in a multicomponent mixture.
$\alpha_{1/2}$ = relative volatility of component 1 with respect to component 2.
$\alpha_{3/2}$ = relative volatility of component 3 with respect to component 2.

$$x_2/y_2 = \alpha_{1/2}(x_1/y_1) \qquad (10\text{-}188)$$

$$y_1 = \alpha_{1/2}x_1 \Big/ \left(\sum \alpha x\right) \qquad (10\text{-}189)$$

$$y_3 = \alpha_{3/2}x_3 \Big/ \left(\sum \alpha x\right), \text{etc.} \qquad (10\text{-}190)$$

$$x_1 = \frac{y_1/\alpha_{1/2}}{\sum (y/\alpha)},\ x_2 = \frac{y_2/\alpha_{2/2}}{\sum (y/\alpha)},\ x_3 = \frac{y_3/\alpha_{3/2}}{\sum (y/\alpha)} \qquad (10\text{-}191)$$

For a binary system with constant relative volatilities:

$$\alpha_{1,2} = \frac{y_1/x_1}{(1-y_1)/(1-x_1)} \qquad (10\text{-}192)$$

or

$$y_1 = \frac{\alpha\, x_1}{[1 + (\alpha - 1)x_1]} \qquad (10\text{-}193)$$

Winn [99] proposes a modification to allow for temperature variation effects on relative volatility. The method does not apply to mixtures forming azeotropes or at conditions near the critical point. Kister [94] proposes:

$$K_1 = \alpha_{1,2}K_2$$

$$N_{min} = \frac{\ln\left[\frac{(x_{lk})_D}{(x_{lk})_B}\left(\frac{(x_{hk})_B}{(x_{hk})_D}\right)\right]^{b_{LK}}}{\ln \beta_{lk/hk}} \qquad (10\text{-}194)$$

α can vary with temperature, so an average α value should be used between top and bottom temperature.

When b_{lk} and $\beta_{lk/hk}$ are constants at a fixed or constant pressure, but evaluated for the light (1) and heavy (h) keys at top and bottom temperatures, their relationship is [94]:

$$\beta_{lk/hk} = K_{lk}/(K_{hk})^{b_{lk}}, \text{at fixed pressure} \tag{10-195}$$

Winn's equation reduced to Fenske's at $b_{lk} = 1.0$ and

$$\beta_{lk/hk} = \alpha_{lk/hk} \tag{10-196}$$

Example 10-14: Determination of Minimum Number of Trays by Winn's Method (used by permission [99])

The minimum number of trays necessary to debutanize the effluent from an alkylation reactor will be calculated. The feed, products, and vapor-liquid equilibrium constants of the key components at conditions of temperature and pressure corresponding to the top tray and reboiler are shown in Table 10-23.

The constants β and b are evaluated using Equation 10-195 as follows:

$0.94 = \beta\,(0.70)^b$
$3.55 = \beta\,(3.00)^b$

Divide to solve for value of b. Then:

$3.78 = (4.29)^b$
$b = 0.913$
$\beta = 1.301$

By use of Winn's Method [99] for product rates:

$$\beta^{n+1} = \left(\frac{L_D}{W}\right)\left(\frac{W'}{L'_D}\right)^b\left(\frac{B}{D}\right)^{1-b}, \tag{10-197}$$

for liquid overhead product

$$\beta^{n+2} = \left(\frac{V_D}{W}\right)\left(\frac{W'}{V'_D}\right)^b\left(\frac{B}{D}\right)^{1-b}, \tag{10-198}$$

for vapor overhead product

where

B = mols of bottoms
b = exponent in Equation 10-195
D = total mols of overhead product
n = minimum number of equilibrium trays in tower
K = y/x = vapor-liquid equilibrium ratio for a component
L = mols of a component in liquid phase
P = vapor pressure, psia
T = absolute temperature, °R
V = mols of a component in vapor phase
W = total mols of bottoms product
x = mol fraction of a component in liquid phase
y = mol fraction of a component in vapor phase
α = relative volatility
β = constant in Equation 10-194
π = total pressure, psia
L = total mols in liquid phase
V = total mols in vapor phase

Table 10-23 Data for Alkylation of Deisobutanizer; Example 10-14, using Winn's Method.

				Equilibrium K's	
Component	**Feed, moles**	**Over-head, moles**	**Bottoms, moles**	**Top tray**	**Reboiler**
Ethylene	1	1			
Ethane	2	2			
Propane	48	48			
Isobutene	863	848	15	0.94	3.55
n-Butane	132	71	61	0.70	3.00
Isopentane	33		33		
n-Pentane	5		5		
Alkylate	277		277		
	1361	970	391		

Used by permission, Winn. F.W., *Pet. Ref.* V. 37, No. 5 (1958). P.216. Gulf Pub. Co.

subscripts or superscripts:

D = distillate
B = bottoms
(′) = heavy key component
1, 2... = tray number

The minimum number of theoretical stages is calculated as follows:

$$(1.301)^{n+1} = (848/15)(61/71)^{0.913}(391/970)^{0.087}$$

$$(1.301)^{n+1} = 45.5$$

$$n + 1 = 14.5$$

This is exactly the number of stages obtained by tray-to-tray calculations with the K correlation of Winn [235]. The minimum number of stages by the Fenske equation, with a geometric average α of 1.261, is 16.8. Hence the Fenske equation gives an answer greater by 2.3 stages, i.e. 16%.

For ideal systems following Raoult's Law; relative volatility $\alpha_{lh} = p_l/p_h$, ratio of partial pressures.

For a binary distillation, α is calculated at top and bottom conditions and a geometric mean used where the differences are relatively small.

$$\alpha_{avg} = \sqrt{\alpha_D(\alpha_B)} \qquad (10\text{-}199)$$

Kister [94] recommends that the determination of α for calculation is:

(1) $\alpha_{avg} = \alpha$ evaluated at $T_{avg} = (T_{top} + T_{Bot})/2$

where $T = o_F$ (10-200)

(2) $\alpha_{avg} = \alpha$ at feed tray temperature

(3) Winn's [99] method previously discussed

For hydrocarbon systems; the following is often used [65]:

$$\alpha_{ir} = \frac{y_i x_r}{y_r x_i} = \frac{K_i}{K_r} \qquad (10\text{-}201)$$

where

i = any component
r = component to which all the relative volatilities are referred
K_i = equilibrium distribution coefficient for component, i
K_r = equilibrium distribution coefficient for component to which relative volatilities are referred

For values of $\alpha \simeq 1.0$, care must be taken in establishing data, as a small change in the value of α_{avg} may double the number of trays.

The exact procedure is to estimate a temperature profile from top to bottom of the column and then calculate α for each theoretical tray or stage by assuming a temperature increment from tray to tray. For many systems this, or some variation, is recommended to perform accurate separation calculations.

$$\alpha_{lh} = \frac{y_l x_h}{x_l y_h} \qquad (10\text{-}202)$$

For non-ideal systems:

$$\alpha_{lh} = \frac{\gamma_l K_l}{\gamma_h K_h} \qquad (10\text{-}203)$$

The vapor–liquid equilibrium relationship may be determined from:

$$y_l = \frac{\alpha_{lh}(x_l)}{1 + (\alpha_{lh} - 1)x_l} \qquad (10\text{-}204)$$

By assuming values of x_l, the corresponding y_l may be calculated.

For hydrocarbon systems, where $K_i = y_i/x_i$, then,

$$y_1/y_2 = (K_1/K_2)(x_l/x_2), \text{and} \qquad (10\text{-}205)$$

$$\alpha i, r = K_i/K_r = \text{relative volatility} \qquad (10\text{-}206)$$

Example 10-15: Construction of Boiling Point Curve and Equilibrium Diagram for Benzene-Toluene Mixture

Using the vapor pressure data for benzene and toluene [59]:

1. Construct a boiling point diagram at a total pressure of 760 mm Hg, Figure 10-41.
2. From the boiling point diagram construct the equilibrium x-y curve for a total pressure of 760 mm Hg, Figure 10-42.

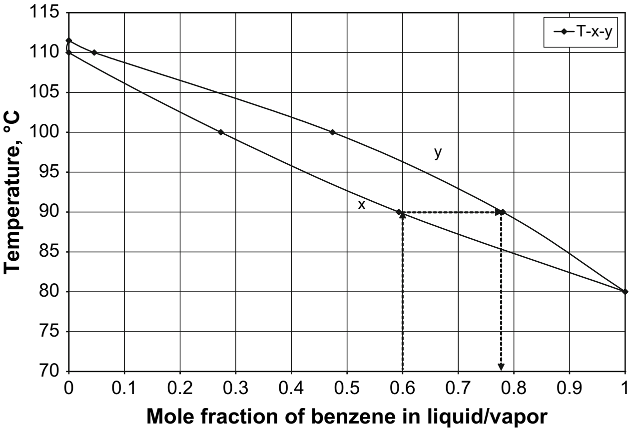


Figure 10-41 Boiling point diagram for Example 10-15. Benzene-toluene mixture, total pressure = 760 mm Hg.

Vapor pressure data as read from tables or graphs;

Temperature°C	Vapor Pressure Benzene, mm Hg	Vapor Pressure Toluene, mm Hg
80	760	280
90	1,000	410
100	1,320	550
110	1,740	740
111.5	1,760	760

Solution

Use Raoult's and Dalton's Laws:

$p_B = P_B x_B$

$p_T = P_T x_T$

Then: $x_B = \dfrac{\pi - P_T}{(P_B - P_T)}$

$x_T = 1 - x_B$

$y_T = 1 - y_B$

$y_B = p_{B/\pi}$

where

P_B = vapor pressure, benzene

P_T = vapor pressure, toluene

π = Total pressure

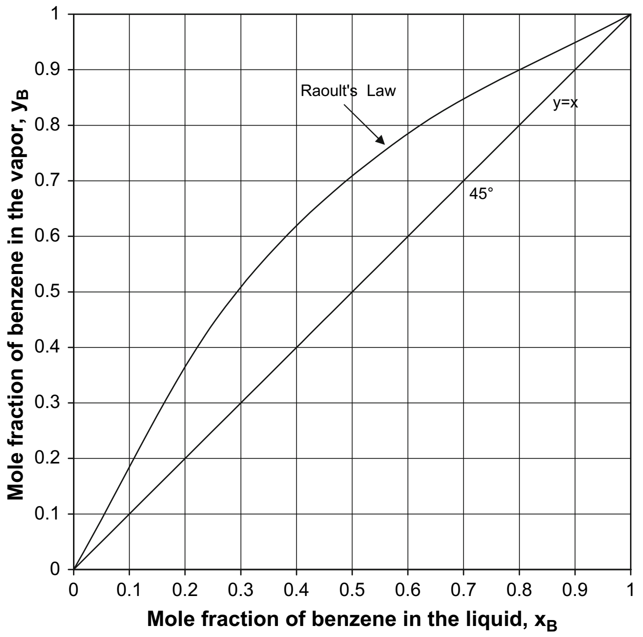


Figure 10-42 VLE diagram for the mixture benzene and toluene at 760 mm Hg total pressure.

Temp, °C	$(P_B - P_T)$	$(\pi - P_T)$	x_B	x_T	$y_B = \dfrac{P_B x_B}{\pi}$	y_T
80	480	480	1.0	0	1.0	0
90	590	350	0.593	0.407	0.780	0.220
100	770	210	0.273	0.727	0.474	0.526

Plot values of x_B, x_T, y_T, and y_B on Figure 10-42.

Example 10-16: Repeat Example 10-15 using K-values. Refer to basis of Example 10-14.

Using the data from Reference 59 (pp. 221, and 233):

Temp. °C	K_T	Relative volatility $\alpha_{B/T}$*	$K_B = \alpha K_T$	$1 - K_T$	$(K_B - K_T)$
80	0.37	2.65	0.981	0.63	0.611
90	0.53	2.48	1.314	0.47	0.784
100	0.73	2.39	1.745	0.27	1.015
110	0.97	2.35	2.28	0.03	1.31
111.5	1.0	2.35	2.35	0.0	1.35

* Read from chart [59]

$X_B = 1 - K_T/(K_B - K_T)$	$x_T = 1 - x_B$	$y_B = K_B x_B$	$y_T = K_T x_T$
*1.031	0.0	*0.981	0.0
0.60	0.40	0.789	0.212
0.266	0.734	0.464	0.535
0.0229	0.977	0.0523	0.946
0.0	1.0	0.0	1.0

* Note: If graphs could be read accurately, these values would equal 1.0.

Procedure

1. Read K value for toluene from tables or charts.
2. Read α values for benzene/toluene from Reference 59.
3. Calculate K (benzene) from: $\alpha_{B/T} = K_B/K_T$

4. Calculate $x_{benzene}$:

$$\begin{aligned} y_B &= K_B\, x_B \\ y_T &= K_T\, x_T \\ \Sigma 1.0 &= K_B\, x_B + K_T\, x_T = K_B\, x_B + K_T\,(1 - x_B) \\ &= x_B\,(K_B - K_T) + K_T \\ x_B &= (1 - K_T)/(K_B - K_T) \end{aligned}$$

5. Calculate $y_{benzene}$: $y_B = K_B\, x_B$
6. Plot boiling point diagram, see Figure 10-43.
7. Plot x–y diagram, see Figure 10-44.

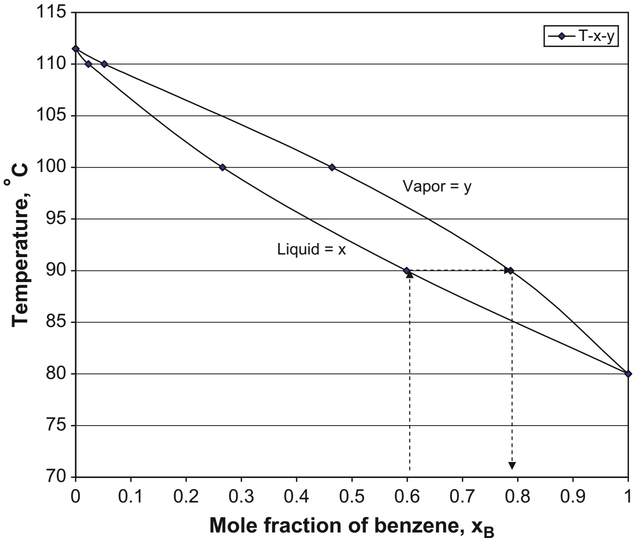


Figure 10-43 Boiling point diagram for benzene-toluene mixture using K values, total pressure 760 mm Hg for Example 10-16.

Example 10-17: Calculation of Flash Vaporization of a Hydrocarbon Liquid Mixture

What fraction of a liquid mixture containing 10 mole % propane, 65% n-butane and 25% n-pentane would be vaporized in a flash vaporization process at a temperature of 40°F and a pressure of 600 mm Hg abs?

The following vapor pressure data for 40°F are available:

Propane	3,800 mm Hg
n-Butane	820 mm Hg
n-Pentane	190 mm Hg

Solution

Assume Raoult's Law is applicable. At a total pressure, π, the temperature of flash must be between the dew point and bubble point.

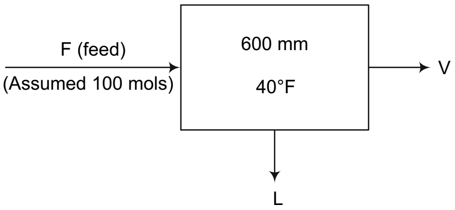
Raoult's Law:

$$\mathbf{p_1 = P_1\, x_1}$$

$$\mathbf{K_1 = y_1/x_l}$$

$$\mathbf{\pi\, y_1 = P_1\, x_1}$$

$$\mathbf{y_1/x_1 = P_1/\pi = K_1}$$



	Mol%	Vapor Press.mm Hg = P_1	$K = \frac{P_1}{600}$	FX	$\frac{L}{V}$	$\frac{L}{KV}$	$1+\frac{L}{KV}$
C_3H_8	10	3,800	6.34	10		0.158	1.158
nC_4H_{10}	65	820	1.37	65	1.0	0.73	1.73
nC_5H_{12}	25	190	0.317	25		3.16	4.16

$$V = \frac{FX_i}{1 + L/(K_i/V)}$$

8.64
37.6
+ 6.0
V = 52.24 NOT a check, reassume

and recalculate. See Figure 10-45 for plot of results and the resultant extrapolation. This type chart serves as a guide to reduce the number of "guesses" to reach an acceptable solution. After several assumptions:

1. Assume feed = 100 mols
2. Assume L = 30
3. Then: V = 100 − 30 = 70 mols

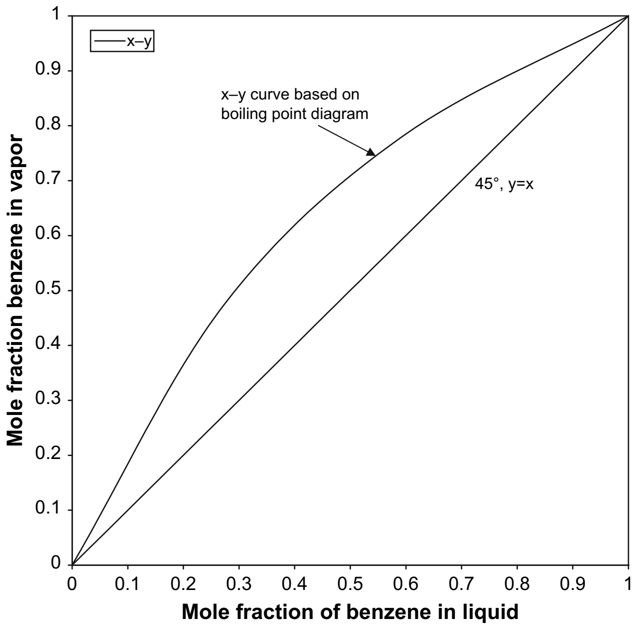


Figure 10-44 x-y diagram for benzene in benzene-toluene mixture, 760 mm Hg pressure, based on K-values, Example 10-16.

X = mols of component i in vapor plus mols of component i in liquid divided by the total mols of feed (liquid + vapor)
F = mols of feed

Following the same headings as in the previous table it continues:

	Mol%	FX	Vapor Press.	$\frac{L}{V}$	$\frac{L}{KV}$	$1+\frac{L}{KV}$
C_3H_8	10	10	3,800	0.429	0.0677	1.067
$n\text{-}C_4H_{10}$	65	65	820	0.429	0.314	1.314
$n\text{-}C_5H_{12}$	25	25	190	0.429	1.352	2.352

$V = \dfrac{FX}{1+\frac{L}{KV}}$	*y ; mol. Frac.
9.38	0.135
49.4	0.711
10.63	0.153
69.41	0.999

These values are sufficiently close for most calculations. Therefore, after several trial-and error calculations the results indicate that after flashing, there would be approximately 70% vapor of the above composition and 30% (mol) liquid.

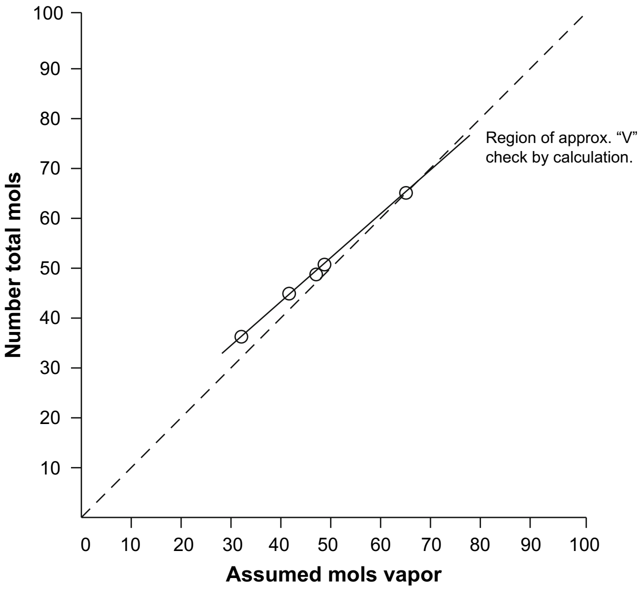


Figure 10-45 Extrapolation curve to determine approximate value of "V" for Example 10-17.

10.23 Rapid Estimation of Relative Volatility

Wagle [92] presents an estimation method for the average relative volatility of two components, related to their normal boiling points and latent heats of vaporization within the temperature range of their individual boiling points:

$$\alpha = \exp\left[0.25164\,(1/T_{bl} - 1/T_{b2})\,(L_1 + L_2)\right] \qquad (10\text{-}207)$$

where

α = relative volatility between the two components in the temperature range T_{bl} to T_{b2}

T_{bl} = normal boiling point of Component l, K
T_{b2} = normal boiling point of Component 2, K
L_l = latent heat of vaporization for Component 1 at T_{bl}, kcal/kmole
L_2 = latent heat of vaporization for Component 2 at T_{b2}, kcal/kmole

If a compound's latent heat is not known, it can be estimated from the normal boiling points and molecular weight.

Example 10-18: Estimation of Relative Volatility by Wagle's Method [92] (used by permission)

The average relative volatility of benzene and toluene can be determined using the following data: $T_{bb} = 353.3$ K, $T_{bt} = 383.8$ K, $L_b = 7{,}352$ kcal/kmole, and $L_t = 7{,}930$ kcal/kmole (where the subscripts b and t denote benzene and toluene, respectively). Substituting these values into Equation 10-207 above gives:

$$\alpha_{bt} = \exp\left[0.25164 \times \left(\frac{1}{353.3} - \frac{1}{383.8}\right) \times (7{,}352 + 7{,}930)\right] = 2.375$$

This compares with a value of 2.421 for α determined using vapor-pressure/temperature charts.

10.24 Estimation of Relative Volatilities under 1.25 (α < 1.25) by Ryan [271]

For key components with relative volatilities <1.25, a McCabe-Thiele diagram is difficult to create, because the stage equilibrium data and the operating line data are very close to the x-y diagonal line, and the graph is indecipherable. Ryan [271] recently developed an alternative diagram in which the transformation spreads out the region close to the diagonal over the whole height of the plot. This approach provides more insight into the separation of iso-butane and n-butane as shown in Table 10-24.

Table 10-24 Components with Relative Volatilities less than 1.25 ($\alpha < 1.25$)

Components	Relative volatility, α
Butane splitters in natural-gas–liquid plants and refineries	about 1.25
De-isobutanizers in butylenes alkylation units in refineries	about 1.25
Argon columns in cryogenic air plants	$1.1 < \alpha < 1.6$
Columns to separate ortho, para- and metaxylene in petrochemical plants	about 1.15
Propane-propylene splitters	about 1.1
Ethylbenzene-xylene superfractionators	about 1.05

The procedure for creating an alternative diagram is as follows:

1. Plot (y – x) vs x instead of y on the y-axis.
2. The operating lines begin on the x-axis at x_B and x_D. Both slopes are [(L/V)-1]. The rectifying line slope will be negative and the stripping line slope positive.
3. The q-line starts on the x-axis at x_F. The value of q is the same as for a conventional McCabe-Thiele calculation. The slope of the q-line in the graph is the McCabe-Thiele slope minus 1. Therefore for a feed at its bubble point, the q-line is vertical (slope = infinity) for the conventional McCabe-Thiele and Ryan calculations. For the dew point feed, the slope is 0 for the conventional McCabe-Thiele and −1 for Ryan.
4. The familiar steps for the determination of theoretical stages on the McCabe-Thiele diagram are modified on the Ryan plot. The vertical portions remain vertical, but the horizontal portions become slanted with a slope of −1. Figures 10-46 and 10-47 show McCabe-Thiele and Ryan's plots respectively.

10.25 Estimation of Minimum Reflux Ratio: Infinite Plates

As the reflux ratio is decreased from infinity for the total reflux condition, more theoretical steps or trays are required for a given separation. When the limiting condition of Figure 10-48 is reached; where the operating line touches the equilibrium line, the number of steps from the rectifying to stripping sections becomes infinite.

If the operating lines of Figure 10-48 intersect at x_c, y_c outside or above the equilibrium line when insufficient reflux is used, the separation is impossible.

This graphical representation is easier to use for nonideal systems than the calculation method. This is another limiting condition for column operation, i.e., below this ratio the specified separation cannot be achieved even with an infinite number of plates. This minimum reflux ratio can be determined graphically from Figure 10-48, as the line with smallest slope from x_D intersecting the equilibrium line at the same point as the "q" line for mixture following Raoult's Law.

External reflux ratio = L/D

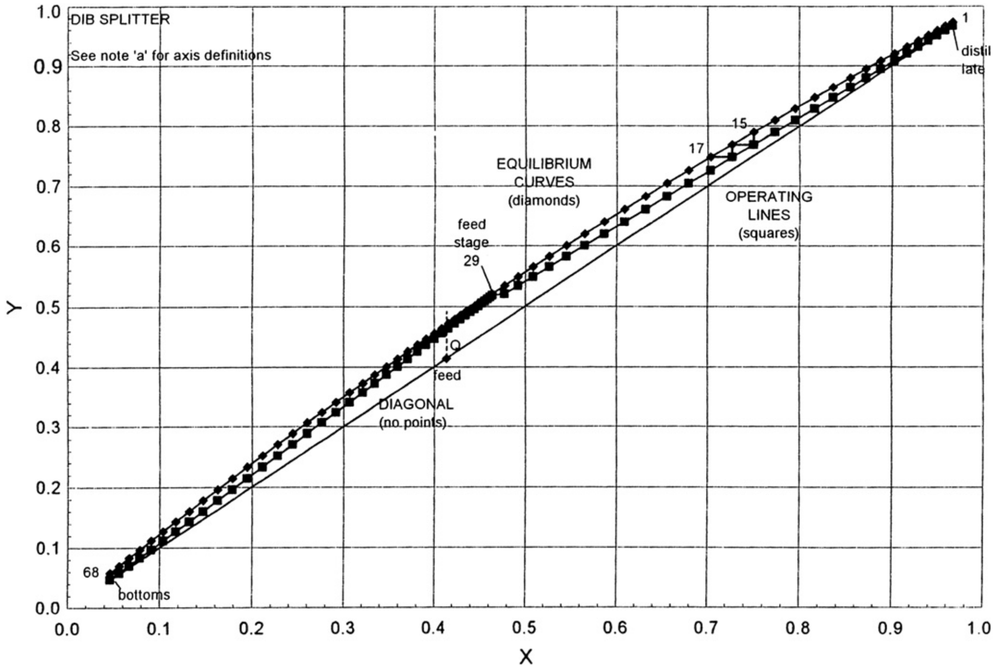


Figure 10-46 McCabe-Thiele diagram.

Slope of line from x_D:

$$\left(\frac{L}{V}\right)_{min} = \frac{(L/D)_{min}}{(L/D)_{min}+1} = \frac{x_D - y_c}{x_D - x_c} \qquad (10\text{-}208)$$

L/V = internal reflux ratio

For non-ideal mixtures the minimum L/V may be as indicated in Figure 10-36 (abnormal equilibrium), and hence not fixed as indicated above.

Figure a 10-40 presents a convenient and acceptably accurate nomogram by Smoker [66].

$$\left(\frac{L}{D}\right)_{min} = \frac{x_D - y_c}{y_c - x_c} \qquad (10\text{-}209)$$

where x_c and y_c are coordinates of intersection of the minimum reflux "operating" line with the equilibrium curve. At boiling point $x_c = x_F$.

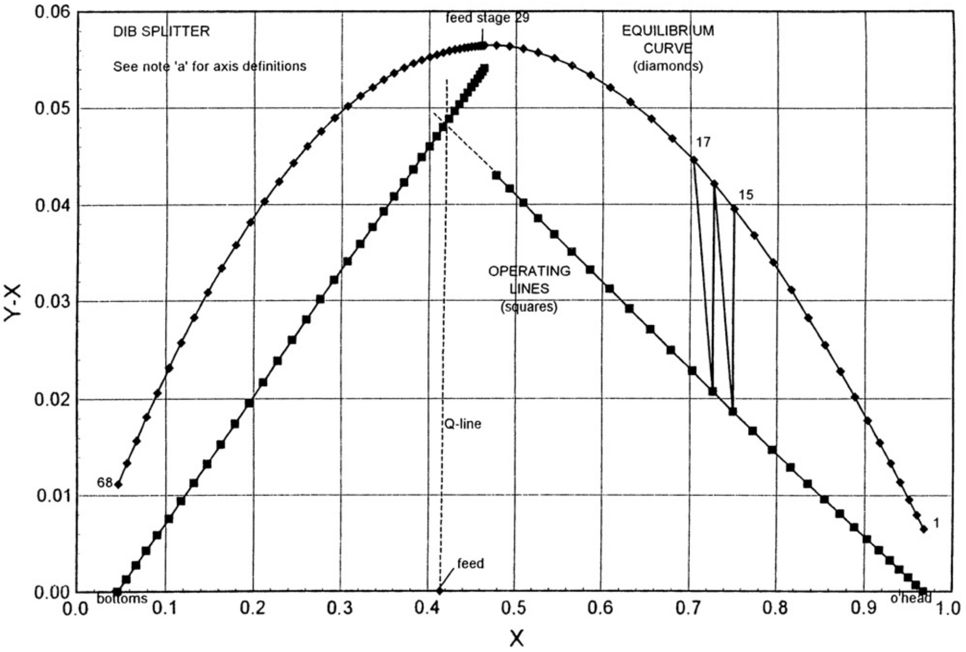


Figure 10-47 Revised McCabe-Thiele diagram.

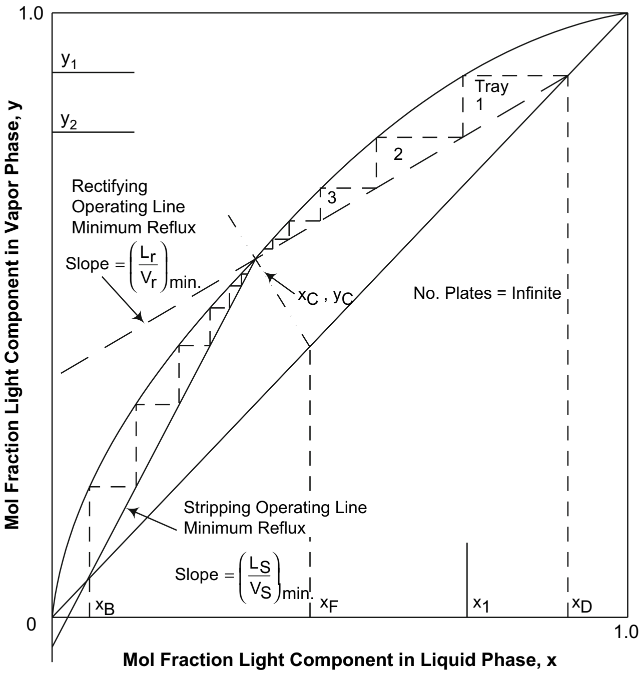


Figure 10-48 Fractionation of binary mixture at minimum reflux condition.

Underwood's algebraic evaluation [73] for minimum reflux ratio is applicable to handling ideal, or near ideal, systems:

For a liquid at its bubble point, q = 1.0

$$\left(\frac{L}{D}\right)_{min} = \frac{1}{\alpha - 1}\left[\frac{x_{lD}}{x_{lF}} - \frac{\alpha(1 - x_{lD})}{(1 - x_{lF})}\right] \qquad (10\text{-}210)$$

For high-purity separations where $x_D \sim 1.0$, with reasonably well balanced columns (where $0.2 < x_F < 0.8$) and moderate values of α,

$$\left(\frac{L}{D}\right)_{min} \approx \frac{1}{(\alpha - 1)x_F} \qquad (10\text{-}210a)$$

For a vapor feed with no superheat, q = 0

$$\left(\frac{L}{D}\right)_{min} = \frac{1}{\alpha - 1}\left[\frac{\alpha x_{lD}}{x_{lF}} - \frac{(1 - x_{lD})}{(1 - x_{lF})}\right] - 1 \qquad (10\text{-}211)$$

For the general case, the relation is more complex in order to solve for $(L/D)_{min}$

$$\frac{(L/D)_{min}(x_{lF}) + q x_{lD}}{(L/D)_{min}(1 - x_{lF}) + q(1 - x_{lD})} = \frac{\alpha[((L/D)_{min} + 1)y_{lF} + (q - 1)x_{lD}]}{[(L/D)_{min} + 1](1 - x_{lF}) + (q - 1)(1 - x_{lD})} \qquad (10\text{-}212)$$

Short et al. [230] discuss minimum reflux ratio estimation for complex fractionators.

10.26 Calculation of Number of Theoretical Trays at Actual Reflux

The Gilliland correlation [23], Figure 10-49a, has proven satisfactory for many binary as well as multicomponent mixtures over a wide range of reflux ratios and number of theoretical plates. Many systems appear to be economically designed for $\frac{(L/D) - (L/D)_{min}}{(L/D) + 1} = 0.1$ to 0.33 and with actual reflux ratios of 1.2 to 1.5 times at minimum. This is inapplicable to systems of greatly varying relative volatility. A Ponchon-Savarit or enthalpy method must then be followed.

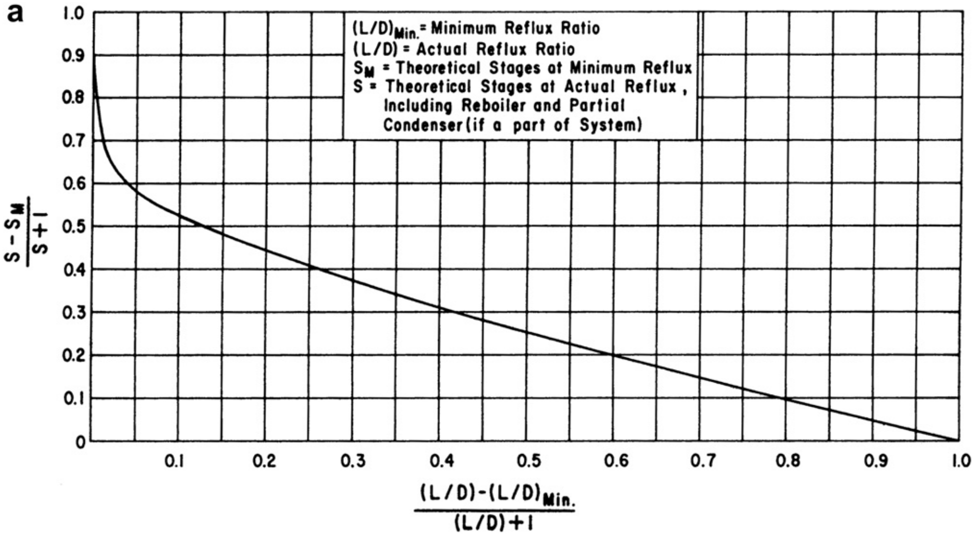


Figure 10-49a Correlation of theoretical plates with reflux ratio.

Eduljee [84] suggests an easier equation to replace the Gilliland plot. The data input is the same. For tray towers:

$$Y_T = 0.75 - 0.75 \times^{0.5668} \tag{10-213}$$

$$Y_T = \frac{S_t - S_{min}}{(S+1)} \tag{10-214}$$

$$X = \frac{(L/D) - (L/D)_{min}}{(L/D)+1} \tag{10-215}$$

where

S_t = theoretical actual trays at actual reflux ratio, L/D, including overhead total condenser and reboiler
Y_T = correlation expression similar to Gilliland's
X = correlation expression similar to Gilliland's
R = reflux ratio, L/D, where L is liquid returned to the column in mols/hr
D = distillate rate in mols/hr
L = liquid returned to column, mols/hr

subscripts:

h = heavy
min = minimum
P = for packed towers
T = for tray column

After calculating X, and solving for Y using Equation 10-213, then solve for the theoretical trays, S_t, at the actual selected reflux ratio (L/D) from the equation for Y. The equation appears to represent several reliable data references. A review of alternative equations to replace the Gilliland plot is provided later in this book.

For packed towers, the corresponding relation for theoretical trays is [84]:

$$Y_p = 0.763 - 0.763 \times^{0.5806} \tag{10-216}$$

and,

$$Y_P = \frac{NTU - NTU_{min}}{NTU + 2\alpha} \tag{10-217}$$

where

NTU = total number of transfer units

$$\alpha = \frac{\ln\alpha}{(\alpha - 1)}, \text{ where } \alpha_h \text{ taken as } 1.0$$

Mapstone [122] and Zankers [123] developed the chart shown in Figure 10-49b to follow Figure 10-49a to allow for a rapid evaluation of Gilliland's equation for the number of theoretical plates at any reflux, minimum number of theoretical plates and minimum reflux ratio. The accuracy appears generally satisfactory for initial industrial design. It can therefore be a useful time-saving device when evaluating a range of values. For another interesting attempt to improve the Gilliland plot by use of equations, refer to Reference 136.

Example 10-19: Using Figure 10-49B to Solve The Gilliland Equation to Determine the Minimum Number of Theoretical Plates for Selecting An Actual Reflux Ratio (used by permission [122])

If the minimum reflux ratio is 2.0 and the minimum number of theoretical plates is 20, how many theoretical plates will be required if a reflux ratio 1.5 times the minimum is used?

Solution

The required reflux ratio, R = 1.5 × 2.0 = 3.0

1. Connect 2.0 on left hand R_{min} scale with 3.0 on left diagonal R scale and extend to cut Tie Line 1.
2. Transfer this value across the central maze to Tie Line 2.
3. Connect this point on Tie Line 2 with 20 on the right hand S_{min} scale to cut the right diagonal S scale at 35 (calc. 34.9).

The number of theoretical plates required will be 35. If any three of the four variables, S, S_{min}, R, and R_{min} are known, this chart can be used by an analogous procedure to give the fourth.

where

S = theoretical plates at any reflux ratio
S_{min} = minimum number of theoretical plates
R = any reflux ratio
R_{min} = minimum reflux ratio

10.27 Identification of "Pinch Conditions" on a x-y Diagram at High Pressure

A column is referred to be "pinching" when the component balance line is too close to the equilibrium curve. This physically represents a situation where several stages in the column are accomplishing very little separation and are thus redundant. This phenomenon not only wastes stages, but could result in an oversized column. Additionally, inaccuracies in relative volatilities and enthalpies may bring the component balance line and the equilibrium curve closer or even cross the equilibrium curve earlier. This could increase the stage requirement, and if the additional stages required are unavailable, the column will not achieve its desired separation.

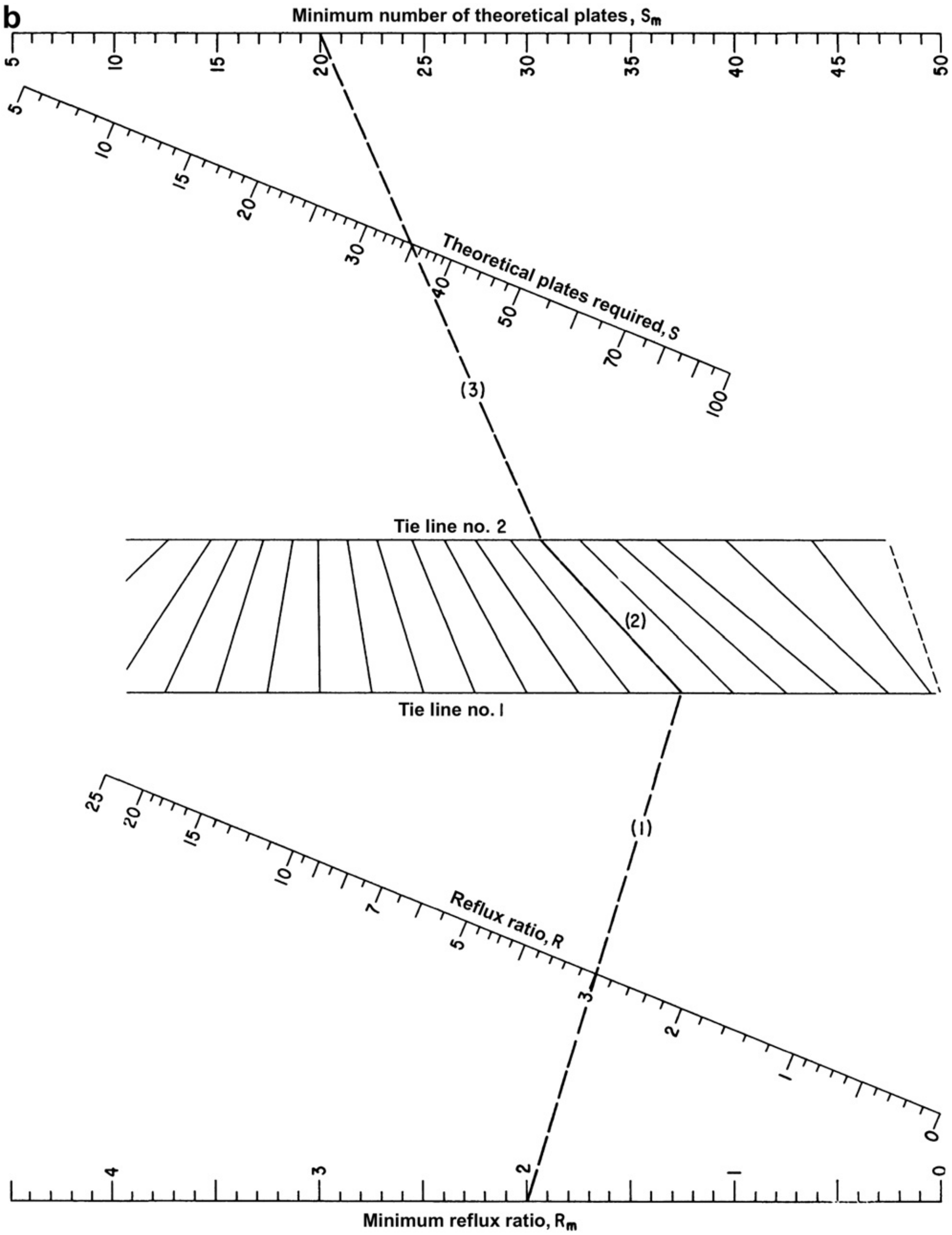


Figure 10-49b Chart for reflux vs. trays. Use this nomogram for Gilliland's calculations for number of theoretical plates/trays. Used by permission, Mapstone, G. E., Hydrocarbon Processing, V/47, No. 5 (1968), p. 169, Gulf Publishing Co., all rights reserved.

Wichterle et al. [91] identify that near the critical pressure point of the more volatile component, all systems exhibit a "pinch" phenomenon at high pressure, as shown in Figure 10-50 [91]. To obtain separation performance, the K-value data used must be accurate in this narrow range of separation. For hydrocarbon systems, as well as systems involving hydrogen, nitrogen, and methane, the data must be accurate and use of a general equation for the particular compound is inadequate. This is crucial for high accuracy in computer performance analysis.

In an existing column, where the feed location is already in position, a pinch can be remedied by increasing the reflux and reboil. This invariably draws the component balance line and the equilibrium curve further apart, enlarging the steps and thereby permitting the required separation to be achieved with the existing feed location. The drawback is lower feed capacity, higher energy consumption, greater vapor and liquid flows through the column, and eventual higher operating costs. Therefore, it is essential to design a column away from the pinched region.

McCormick [97] presents a correlation for Gilliland's chart relating reflux ratio, minimum reflux ratio, number of theoretical stages, and minimum theoretical stages for

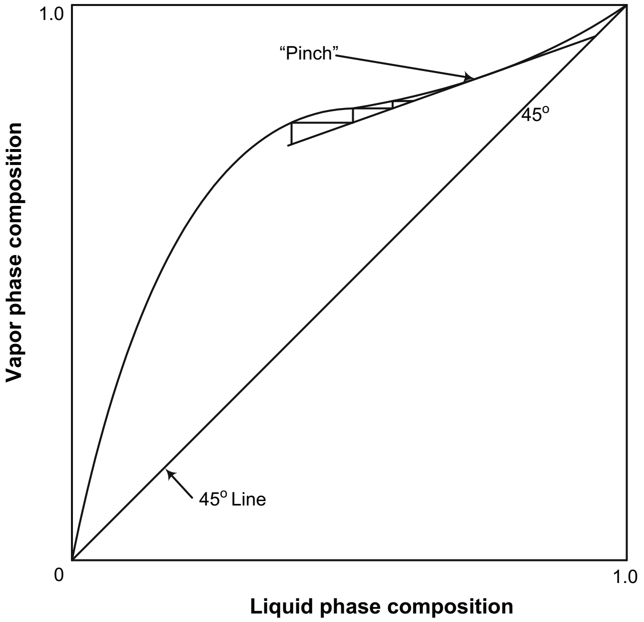


Figure 10-50 Example of typical "pinch point" for critical region for high-pressure distillation. Used by permission, Wichterle, I., Kobayashi, R., and Chappelear, P. S., Hydrocarbon Processing, Nov. (1971) p. 233, Gulf Publishing Co., all rights reserved.

a multicomponent distillation. Selection of a multiplier for actual reflux ratio over minimum reflux ratio is important. Depending on the complexity and analysis of the component's separation by the stages, the actual reflux ratio may vary from 1.2 to 1.5 to 2.0, dependent on economics. The proposed equation agrees satisfactorily with other methods, especially in the extreme ranges of Gilliland's plots [97], as well as the most used region.

$$R = AR_{min} \tag{10-218}$$

$$X = \frac{R - R_{min}}{R + 1} = \frac{(A - 1)(R_{min})}{(AR_{min} + 1)} = \frac{A - 1}{(A + 1/R_{min})} \tag{10-219}$$

Representative values of X calculated from Equation 10-219 are given in the following Table 10-25 for values of R_{min} and multiplier A. Actual reflux ratio values can be assumed, and the system tested for R_{min}.

For actual versus minimum number of stages in a column:

$$Y = (N - N_{min})/(N + 1) \tag{10-220}$$

$$Y = 1 + \left[\frac{(R - R_{min})}{(R + 1)}\right]^{(0.0456 \ln X + 0.44)} \tag{10-221}$$

$$X = (R - R_{min})/(R + 1) \tag{10-222}$$

where

A = parameter in correlating equation or multiplier on R_{min}
B = parameter in correlating equation
ln = natural logarithm
log = logarithm to the base 10
N = actual number of theoretical stages required for a given separation
N_{min} = minimum number of theoretical stages required for a given separation
R = external reflux ratio for a given separation
R_{min} = minimum external ratio for a given separation
X = $(R - R_{min})/(R + 1)$
Y = $(N - N_{min})/(N + 1)$

The following is a short approximation method for minimum reflux ratios for multicomponent mixtures [98]:

$$R_{min} = \frac{1}{[(x_{FLK})_{eff}][(\alpha_{LK})_{avg} - 1]} \tag{10-223}$$

where

$(x_{FLK})_{eff} = x_{FLK}/(x_{FLK} + x_{FHK})$
n = number of components

Table 10-25 Operational Values of X Calculated via Equation 10-219 for a Range of Reflux Ratios*.

R_{min}	Multiplier A										
	0.02	**1.05**	**1.07**	**1.10**	**1.12**	**1.15**	**1.17**	**1.20**	**1.30**	**1.40**	**1.50**
1	0.010	0.024	0.034	0.048	0.063	0.070	0.092	0.091	0.130	0.167	0.200
3	0.015	0.036	0.050	0.070	0.092	0.101	0.132	0.130	0.184	0.231	0.273
5	0.016	0.040	0.055	0.077	0.102	0.111	0.145	0.143	0.200	0.250	0.294
10	0.018	0.043	0.060	0.083	0.110	0.120	0.157	0.154	0.214	0.267	0.313
Total reflux	0.020	0.048	0.065	0.091	0.120	0.130	0.170	0.167	0.231	0.286	0.393

* Used by permission, McCormick, J. E., Chemical Engineering V. 95, No. 13 (1988), all rights reserved.

R_{min} = minimum reflux ratio
x = liquid mol fraction
α_i = relative volatility of component i based on heavy key
α_{LK} = relative volatility of component, i, based on light key

subscripts:

avg = average
eff = effective
F = feed
FHK = heavy key in feed
FLK = light key in feed
i = component
LK = light key
HK = heavy key

Kister [94, 95] examines binary distillation systems with multiple feeds, one or more side products, one or more points of heat removal or addition, and various combinations.

10.28 Distillation Column Design

In designing a distillation column, the chemical/process engineer often is confronted with three basic tasks:

- Choice between tray or packed column
- Design of the column, and its ancillaries, eg. feed preheater, reflux condenser, reflux splitter, reboiler, etc.
- Rating problem

In the design of a plate column, it is a basic requirement to calculate how many plates/trays are required to achieve the desired degree of separation of the components from the specified feed conditions. This aspect relates to size and configuration of the equipment. In the rating, the performance of a column under various conditions with a fixed number of plates/trays after it is specified should be predicted.

10.28.1 Design Method for a Plate Column

The following is a design procedure using graphical solution.

Given:

Feed conditions

(i) Feed flow rate, F
(ii) Feed composition, z
(iii) Feed temperature or enthalpy or thermal condition, q
(iv) Column pressure
(v) Reflux temperature or enthalpy (usually saturated liquid)

Product Conditions

$$\left.\begin{array}{l}\text{(i) Distillate composition } x_D \\ \\ \text{(ii) Bottoms composition } x_B\end{array}\right\} \text{all with respect to light component}$$

Reflux Ratio, R: Relative volatility, α, The vapor liquid equilibrium curve.

Procedure

1. Plot the vapor-liquid equilibrium curve from the data available at the column pressure. In terms of relative volatility:

$$y = \frac{\alpha x}{[1 + (\alpha - 1)x]} \tag{10-48}$$

where α is the geometric average relative volatility of the lighter (more volatile) component with respect to the heavier component (less volatile).

2. Draw the 45° – line, that is, $x = y$ line.
3. Make a material balance over the column to determine the top and bottom compositions, x_B, x_D from the data given.
4. Locate the points x_B, x_D and z on the 45°-line. That is, draw perpendiculars on x-axis at points x_B, x_D and z. Their points of intersection with the 45°-line are the required locations.
5. Calculate the distillate and bottoms flow rates.

Distillate flow rate:

$$D = F\left[\frac{(z - x_B)}{(x_D - x_B)}\right] \tag{10-224}$$

Bottoms flow rate:

$$B = F - D \tag{10-225}$$

6. The point of intersection of the two operating lines depends on the phase condition of the feed. The line on which the intersection occurs is referred to as the q line. The q-line is found as follows:

(i) Calculate the value of the ratio q given by

$$q = \frac{\text{heat to vaporize 1 mol of feed}}{\text{molar latent heat of feed}} \tag{10-226}$$

where the numerator in Equation 10-226 is the heat to make saturated vapor at the feed tray pressure from 1 mol of feed at its thermal condition, as fed.

(ii) Plot the q-line, slope = $q/(q-1)$, intersecting the diagonal at x_F (the feed composition).

7. Select the reflux ratio and determine the point where the top operating line extended cuts the y axis:

$$\phi = \frac{x_D}{1+R} \tag{10-227}$$

8. Draw in the top operating line, from x_D on the diagonal ϕ to the y-axis at the value ϕ.
9. Draw in the bottom operating line; from x_B on the diagonal to the point of intersection of the top operating line and the q-line.
10. Starting at x_D or x_B, step off the number of stages.
11. The design is complete.

Count the number of trays in the rectifying section.

Count the number of trays in the stripping section.

Sum the number of trays in both rectifying and stripping sections.

Note: The feed point should be located on the stage closest to the intersection of the operating lines.

The reboiler and a partial condenser (if used) act as equilibrium stages. Figure 10-5 shows the McCabe-Thiele diagram, and the method can be used for the design of columns with side streams and multiple feeds. The liquid and vapor flows in the sections between the feed and the take-off points are calculated and operating lines drawn for each section.

10.28.2 Continuous Fractionating Column

Rating Method

On completion of the column design, it should be checked to see whether it will perform under different conditions. This rating is an operating problem. Typically, the heat input rate to achieve a specified separation when the feed condition varies will be determined. Another type of rating problem can involve a trial-error iterative solution as follows:

(i) An assumption is made of one or more unknown variables.

(ii) On the basis of these assumed values, the design procedure is carried out.

(iii) The results are compared with the column specifications.

(iv) If they agree, no further assumption is required, and the estimated values of the unknown variables are acceptable; otherwise, another set of values are assumed and the design procedure repeated.

An essential difference between the design and rating methods is that the feed is not introduced on the optimum feed tray, but is obtained through design calculation. In general, the actual feed tray is not the optimum feed tray. Iterative procedures are essential to apply rating methods to the design of a new column. An initial estimate of the number of stages can be made using short-cut methods and programs used to calculate the product compositions. Calculations are repeated with revised estimates until a satisfactory design is achieved.

10.29 Simulation of a Fractionating Column

In a simulation exercise, the objective is to predict how much separation can be achieved with a given feed in a column, which has been commissioned or is in use. The number of stages and feed stage location are already fixed, as are the column diameter and the reboiler size; these fix the maximum vapor flow rate. There are various ways of specifying the remaining parameters. The desired composition of the more volatile component in the distillate and bottoms can be set; the requirement is to determine the external reflux ratio that will produce the separation. A check may also be made that the maximum vapor flow rate will not be exceeded. Alternatively, the distillate or bottoms compositions and reflux ratio are specified, and then the unknown compositions and the vapor flow rate are determine. Another alternative is to specify the heat load, in the reboiler, and the distillate or bottoms compositions thus requiring the reflux ratio and unknown product compositions to be determined and the vapor flow rate checked. In general, all variables that can be controlled are specified, and these are illustrated by Wankat [273].

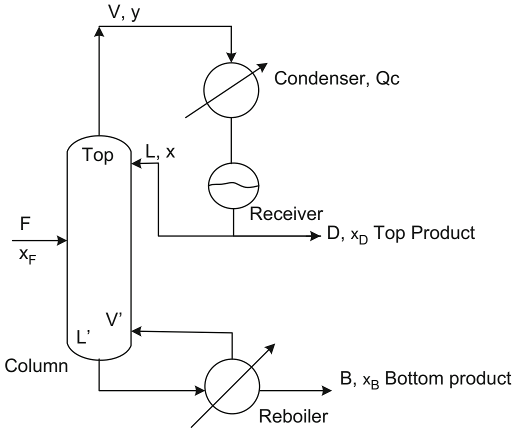
Example 10-20

An equimolar binary mixture with a relative volatility of 2 is fed to a distillation column, which produces a distillate containing 97.5% of the more volatile component, and a residue containing 10% of the more volatile component. The feed is liquid at its boiling point and 80% of the liquid entering the reboiler is vaporized and returned to the column as boil-up.

(i) Estimate the number of theoretical plates provided by this column.

(ii) Check your answer in part (i) by reference to the graph of the Gilliland correlation.

Solution



The overall mass balance on the column.

$$F = D + B \tag{10-228}$$

The component balance on the more volatile component (MVC) is:

$$F\,x_F = D\,x_D + B\,x_B \tag{10-229}$$

Assuming that F = 100 mols/hr.

$x_F = 0.5$, $x_D = 0.975$ and $x_B = 0.1$

Substituting the values of the components in Eq. 10-229 gives:

$$\begin{aligned}100\,(0.5) &= D\,(0.975) + B(0.1)\\ 50 &= 0.975D + 0.1B\end{aligned} \tag{10-230}$$

Rearranging Eq. 10-228 and substituting into Eq. 10-230 gives:

$$50 = 0.975D + 0.1(100 - D) \tag{10-231}$$

$$50 = 0.975D + 10 - 0.1D \tag{10-232}$$

D = 45.71 mols/hr.

B = 54.29 mols/hr.

The overall mass balance on UOL is:

$$V = L + D \tag{10-233}$$

Component balance is:

$$V_n y_n = L_{n+1}\,x_{n+1} + Dx_D \tag{10-234}$$

or

$$y_n = \frac{L_{n+1}}{V_n}x_{n+1} + \frac{D}{V_n}x_D \tag{10-235}$$

$$\text{Reflux ratio}, R = \frac{L}{D} \tag{10-236}$$

Substituting Eq. 10-236 into Eq. 10-233 gives:

$$V_n = RD + D \tag{10-237}$$

Equation Eq. 10-235 (UOL), assuming constant molar overflow, becomes:

$$y_n = \frac{R}{(R+1)}x_{n+1} + \frac{x_D}{R+1} \tag{10-238}$$

The intercept on the UOL, is

$$I = \frac{x_D}{(R+1)} \tag{10-239}$$

Since the feed is liquid at its boiling point (i.e. q = 1) and 80% of the liquid entering the reboiler (L′) is vaporized to give the vapor (V′) leaving the reboiler and returned to the column.

Therefore at the bottom of the column, if $L' = 1.0$ and $V' = 0.8$.

The mass balance at the bottom of the column with the reboiler is:

$$L' = V' + B \tag{10-240}$$

or

$$V' = L' - B \tag{10-241}$$

The component balance at the bottom is:

$$V'y_m = L'\,x_{m+1} - B\,x_B \tag{10-242}$$

or

$$y_m = \frac{L'}{V'}x_{m+1} - \frac{B}{V'}x_B \tag{10-243}$$

Slope is $\frac{L'}{V'} = \frac{1}{0.8} = 1.25$

Using the McCabe-Thiele diagram of Figure 10-48, draw the lower operating line to intercept the "q" line; then draw the upper operating line and extend to the intercept I.

$$I = \frac{x_D}{R+1} = 0.22 \ \left(\text{from McCabe-Theile diagram}\right) \tag{10-244}$$

$$\frac{0.975}{(R+1)} = 0.22, \text{hence}$$

R = 3.43

From McCabe-Thiele diagram:

N +1 = 14 stages, hence

N = 13 stages.

R_{min}: from the points (X_D, X_D), a straight line is drawn that touches the VLE line with the "q" line and extended to the y-axis at a point $I_{min} = \frac{x_D}{(R_m + 1)}$.

$$I_{min} = \frac{x_D}{(R_m + 1)} = 0.34$$

$$\frac{0.975}{(R_m + 1)} = 0.34 \qquad (10\text{-}245)$$

$$R_m = 1.86$$

Applying the Underwood Equation to find the minimum reflux ratio:

$$R_m = \frac{1}{(\alpha - 1)}\left[\frac{x_{LK,D}}{x_{LK,F}} - \frac{\alpha(1 - x_{LK,D})}{(1 - x_{LK,F})}\right]$$

$$= \frac{1}{(2-1)}\left[\frac{0.975}{0.5} - \frac{2(1 - 0.975)}{(1 - 0.5)}\right] \qquad (10\text{-}210)$$

$$R_m = 1.85$$

The Fenske method for the minimum number of theoretical stages at total reflux is:

$$N_m = \frac{\ln[(x_{LK}/x_{HK})_D\ (x_{HK}/x_{LK})_B]}{\ln\ (\alpha_{LK}/\alpha_{HK})_{avg}}$$

$$= \frac{\ln\left[\left(\frac{0.975}{0.025}\right)\left(\frac{0.9}{0.1}\right)\right]}{\ln 2} \qquad (10\text{-}246)$$

$$N_m = 8.45$$

From the Gilliland correlation, (Figure 10-49), the abscissa axis is:

$$\frac{R - R_m}{R + 1} = \frac{3.66 - 1.85}{(3.66 + 1)} = 0.388 \qquad (10\text{-}247)$$

The corresponding point on the ordinate axis of the Gilliland correlation is 0.31.

Therefore the number of theoretical stages can be determined from the ordinate by:

$$\frac{N - N_m}{N + 1} = 0.31$$

$$\frac{N - 8.45}{N + 1} = 0.31, \text{hence}$$

$$N = 12.69 \text{ stages (13 stages)}$$

Example 10-21: Graphical Design of a Fractionation Column for Binary Systems [59]

The benzene–toluene example of Robinson and Gilliland [59] has been elaborated on and expanded after the advanced distillation course of Holland [25], Figure 10-51.

It is desired to separate an equimolal mixture of benzene and toluene into a top product containing 95 mol % benzene and a bottom product containing 95 mol % toluene. The distillation is to be carried out at atmospheric pressure. Use a total condenser.

A. Calculate the minimum reflux ratio if the feed is liquid at its boiling point.

B. Calculate the theoretical plates required if a reflux ratio (L/D) of 1.5 times the minimum is employed.

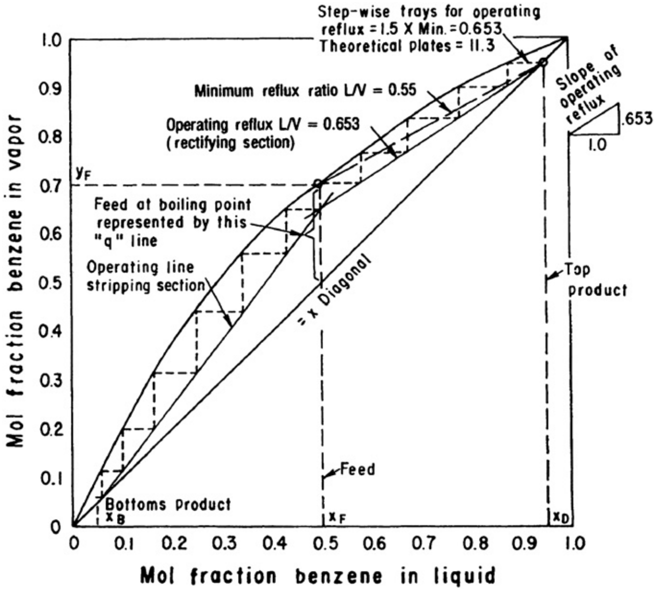


Figure 10-51 Equilibrium curve; benzene-toluene for Example 10-21 (curve data only). Used by permission, Robinson, C. S. R. and Gilliland, E. R., Elements of Fractional Distillation, 4th Ed., McGraw-Hill Book Co. (1950), all rights reserved.

Feed = 50 mols benzene + 50 mols toluene
Overhead = 95% benzene
Bottoms = 95% toluene

Solution

Basis: Feed 100 mols/hr.

Material balance with respect to benzene (more volatile component, MVC):

$F = D + B$

Component balance on the MVC.

$Fx_F = D\,x_D + B\,x_B$

$0.50\ (100) = (0.95)\ (D) + 0.05B$

$45 = 0.90D$

$D = 45/0.90 = 50$ mols/hr overhead product

D = overhead product, mols/hr.

B = bottoms, mols/hr.

A. For a Feed at its Boiling Point:

$$\frac{L_n}{V_n} = \frac{L/D}{L/D+1} \text{ or } \frac{L}{V} = \frac{x_D - y_F}{x_D - x_F}, y_F = 0.70 \text{ (from curve)}$$

$$= \frac{0.95 - 0.70}{0.95 - 0.50}$$

Minimum $L/V = 0.55$ mol reflux/mol vapor up

Substituting: $0.55 = \dfrac{L/D}{L/D+1}$

$0.55\ L/D + 0.55 = L/D$

$0.45\ L/D = 0.55$

Reflux/Product $= L/D = 0.55/0.45 = 1.22$

The value of L/D minimum should be equal to:

$$\frac{L_{12}}{D} = \frac{x_D - y_c}{y_c - x_c} = \frac{0.95 - 0.70}{0.70 - 0.50} = 1.25$$

The slight difference is probably due to inaccuracy in reading $y_c = 0.70$ from the equilibrium curve.

B. Number of Theoretical Plates at $L/D = 1.5$ times minimum:

Operating Reflux Ratio $= (1.5)\ (1.25) = 1.878 = L/D$

Slope of operating line at this reflux ratio:

$$\frac{L}{V} = \frac{L/D}{L/D+1}$$

$$\frac{L}{V} = \frac{1.878}{1.878+1} = 0.653$$

From Graph, $L/V = 0.653$ was plotted based on feed at its boiling point, number of theoretical plates (stepwise graph) = 11.3

Now, to calculate the number of theoretical plates:

Rectifying section:

$$y_n = \frac{L_{n+1}}{V_n}x_{n+1} + \frac{D}{V_n}x_D \text{ operating line}$$

At: $L/D = 1.878$, $D = 50$ mols/hr. overhead

$L = (1.878)\ (50) = 93.9$ mols/hr. reflux to column

$V = L + D$

$= 93.9 + 50 = 143.9$ mols/hr. to vapor overhead

$$y_n = \frac{93.9}{143.9}x_{n+1} + \frac{50}{143.9}(0.95) = 0.652x_{n+1} + 0.331$$

For a total condenser: $y_{top} = x_D = x_R = 0.95$

From the equilibrium curve at $y_t = 0.95$

then:

$x_t = 0.88$

$y_{(t-l)} = 0.651\ (x_t) + 0.331$

$y_{(t-l)} = 0.651(0.88) + 0.331 = 0.903$

$y_{t-1} = 0.903$, then x_{t-1} from equilibrium curve = 0.788

Now calculate y_{t-2}

$y_{t-2} = 0.651\ (0.788) + 0.331 = 0.844$

At $y_{t-2} = 0.844$, curve reads: $x_{t-2} = 0.69$

Then: $y_{t-2} = 0.651\ (0.69) + 0.331 = 0.780$

At y_{t-3}, curve reads: $x_{t-3} = 0.60$

Then: $y_{t-4} = 0.651\ (0.60) + 0.331 = 0.722$

At y_{t-4}, curve reads: $x_{t-4} = 0.52$ (Feed Tray)

Then: $y_{t-5} = 0.651\ (0.52) + 0.331 = 0.669$ (too far below feed)

Now go to stripping section curve:

$$y_m = \frac{L_{m+1}x_{m+1}}{V_m} - \frac{W}{V_m}x_B$$

The feed was at its boiling point:

$V_n = V_m = 143.9$

$B = F - D$

$= 100 - 50$

B = Bottoms = 50 mols/hr.

$L_m = B + V = 50 + 143.9 = 193.9$

$$y_m = \left(\frac{193.9}{143.9}\right)x_{m+1} - \frac{50}{143.9}(0.50)$$

Starting at $t - 4$ = feed tray:

$x_{t-4} = 0.52$

$y_{(feed-1)} = 1.35\ x_f - 0.0176\ (f-1)$

$y_{(f-1)} = 1.35\ (0.52) - 0.01736 + 0.685$

At $y_{t-1} = 0.685$, $x_{f-1} = 0.475$

Note: This is not too accurate due to switched operating line equations before the feed compositions were reached, yet, one more calculation on the stripping line would have placed us below the feed plate composition. Hence a change in reflux ratio is necessary in order to split right at the feed composition [271].

Continuing:

$y_{f-2} = 1.35\ (0.475) - 0.01736 = 0.624$
From curve at $y_{f-2} = 0.624$
$x_{f-2} = 0.405$
$y_{f-3} = 1.35\ (0.405) - 0.01736 = 0.531$
From curve, $x_{f-3} = 0.32$
$y_{f-4} = 1.35\ (0.32) - 0.01736 = 0.416$
$x_{f-4} = 0.23$
$y_{f-5} = 1.35\ (0.23) - 0.01736 = 0.294$
$x_{f-5} = 0.15$
$y_{f-6} = 1.35\ (0.15) - 0.01736 = 0.186$
$x_{f-6} = 0.092$
$y_{f-7} = 1.35\ (0.092) - 0.01736 = 0.107$
$x_{f-7} = 0.05$ (The desired bottoms composition)
Total number of theoretical trays:
rectifying section = 4
feed tray = 1
stripping section = 7
total = 12 Trays

Example: 10-22 Variation of Theoretical Plates in a Column with Thermal Condition of Feed

Using the same operating reflux ratio as in Example 10-21, calculate the number of theoretical plates required for feed of the following thermal conditions: Use Figure 10-52.

(a) $q = 1.5$

(b) $q = 0$

(c) $q = -1.5$

A. For $q = 1.5$
Slope of "q" line $= -q/(1 - q)$

$$\text{Substituting, slope} = \frac{-1.5}{1-1.5} = \frac{-1.5}{-0.5} = +3$$

Referring to calculations of Example 10-21, for an equimolal mixture of benzene and toluene in feed:

overhead product, D = 50 mols/l00 mols feed

$$\text{calculate} \left(\frac{L_R}{D}\right)\text{min} = \frac{x_D - y_c}{y_c - x_c},$$

where $x_D = 0.95$
$y_c = 0.774^*$
$x_c = 0.59^*$

$$= \frac{0.95 - 0.774}{0.774 - 0.59} = \frac{0.176}{0.184}$$

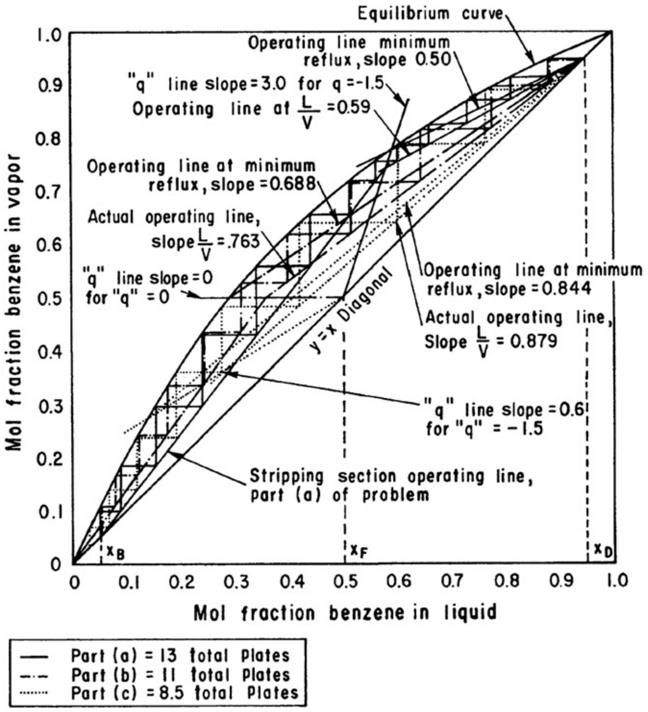


Figure 10-52 Equilibrium curve; benzene–toluene for Example 10-22 (curve data only). Used by permission, Robinson, C. S. R. and Gilliland, E. R., Elements of Fractional Distillation, 4th Ed., McGraw-Hill Book Co. (1950), all rights reserved.

$(L/D)_{min} = (L_R/D)_{min} = 0.956$ min. reflux ratio, reflux/ product

*Read from graph at intersection of "q" line for 1.5 and minimum reflux operating line.

Slope of Operating Line at Minimum Reflux:

$$\left(\frac{L}{V}\right) = \left(\frac{L_R}{V}\right)_{min} = \frac{L/D}{L/D+1} = \frac{0.956}{0.956+1} = 0.49$$

(Graph reads 0.59 but this depends upon accuracy of plot.)

Calculating

$$\left(\frac{L}{V}\right)_{min} = \frac{x_D - y_c}{x_D - x_c} = \frac{0.95 - 0.774}{0.95 - 0.59} = 0.49$$

Actual Operating Line

Operating reflux ratio = (1.5) (L/D) = 1.5 (0.956) = 1.432 reflux/product

Slope of actual operating line:

$$\left(\frac{L}{V}\right) = \frac{L/D}{L/D+1} = \frac{1.432}{1.432+1} = 0.59$$

Graphically, read 13 steps or theoretical plates from the top plate through bottom reboiler (assuming a total condenser).

rectifying section = 5
feed plate = 1
stripping section = 7 (includes reboiler)
13 Plates including reboiler

To calculate this stepwise:

Operating line of rectifying section:

$$y_{n+1} = \frac{L_r}{V_r}x_n + \frac{D}{V_r}x_D$$

$L/V = 0.59$
$L/D = 1.432$, $D = 50$ mols product
$L = (50)\ 1.432 = 71.6$ mols liquid reflux
$V_r = L_r + D = 71.6 + 50 = 121.6$ mols
then:
$y_{n+1} = 0.59\ x_n + 50\ (0.95)/121.6$
$y_{n+1} = 0.59\ x_n + 0.39$, operating line equation
At top: $y_{n+1} = x_D = 0.95$

So: From equilibrium curve at $y_{n+1} = 0.95$, read the liquid in equilibrium, which is x_n (or top plate in this case) $x_n = x_{top} = 0.88$.

Now substitute this value $x = 0.88$ into the equation and calculate the vapor coming up from the first plate below the top $(t - 1)$. Thus, if x_n = top plate, y_{n+1} = vapor from plate below top. Now, read equilibrium curve at $y_{(t-1)}$ and get $x_{(n+1)}$ or x_{t-1} which is liquid on plate below top. Then using x_{t-1}, calculate y_{t-2} (second plate below top, etc.). Then, read equilibrium curve to get corresponding liquid x_{t-2}. Continue until feed plate composition is reached, then switch to equation of stripping section and continue similarly until the desired bottoms composition is reached.

Operating line of stripping section:

$$y_m = \frac{L_s x_{m+1}}{V_s} - \frac{B}{V_s}x_B$$

Because the feed is a super-cooled liquid, $L_s/V_s \neq L_r/V_r$. From definition of "q":

$L_s = L_r + qF$
$L_s = 71.6 + (1.5)\ (100)$
$L_s = 221.6$

Also: $\frac{V_r - V_s}{F} = 1 - q$, so $\frac{121.6 - V_s}{100} = 1 - 1.5$

$121.6 - V_s = -50$
$V_s = 171.6$
Therefore, $\frac{L_s}{V_s} = \frac{221.6}{171.6} = 1.29$

$$\frac{B}{V_s} = \frac{50}{171.6} = 0.291$$

Stripping section operating line:

$y_m = 1.29\ x_{m+1} - 0.291\ x_B$
$x_B = 0.05$
$y_m = 1.29\ x_{m+1} - 0.01455$

Use this equation as described above proceeding down from the feed plate cross-over from the rectifying equation to the stripping equation.

B. For $q = 0$

This represents feed as all vapor (not superheated).

Slope of "q" line:

$$= \frac{-q}{1-q} = \frac{-0}{1-0} = 0$$

This represents no change in overflow from the feed plate, and the increase in vapor flow is equal to the mols of feed.

Minimum reflux: $\left(\frac{L}{D}\right)_{min} = \frac{x_D - y_c}{y_c - x_c}$,

where:

$x_D = 0.95$
$\left.\begin{array}{l} y_c = 0.50 \\ x_c = 0.29 \end{array}\right\}$ read from graph

$$= \frac{0.95 - 0.50}{0.50 - 0.29} = 2.14 \text{ min. reflux ratio, reflux/product}$$

Slope of operating line at minimum reflux:

$$\left(\frac{L}{D}\right)_{min} = \frac{L/D}{L/D + 1} = \frac{2.14}{2.14 + 1} = 0.682$$

Slope from graph = 0.688

Operating reflux ratio = (1.5) (2.14) = 3.21, reflux/product, $(L/D)_{op}$

Slope of operating line = $(L/V)_{op} = 3.21/\ (3.21 + 1) = 0.763$

No. of theoretical plates from graph = 11
No. plates rectifying section = 5
Feed plate = 1
Stripping section = 5 (includes reboiler)
Total = 11 (includes reboiler)

Rectifying Section Equation for Operating Line

$$y_{n+1} = \frac{L_r}{V_r}x_n + \frac{D}{V_r}x_D$$

$L/V = 0.763$
$L/D = 3.21$
$L = (3.21)$ (50 mol product. D) = 160.6 mols (reflux liquid)

$V_r = L_r + D = 160.6 + 50$

$V_r = 210.6$ mols vapor up column

then: $y_{n+1} = 0.763x_n + \frac{50}{210.6}(0.95)$

$y_{n+1} = 0.763\ x_n + 0.225$

Liquid Down Stripping Section

$L_s = L_r + qF$

$L_s = 160.6 + (0)$ (100 mols feed)

$Ls = 160.6 = L_r$

Vapor Up Stripping Section

$$\frac{V_r - V_s}{F} = 1 - q$$

$$\frac{210.6 - V_s}{100} = 1 - 0$$

$210.6 - V_s = 100$

$V_s = 110.6$ mols

Stripping Section Equation for Operating Line

$$y_m = \frac{L_s}{V_s}x_{m+1} - \frac{B}{V_s}x_B$$

$$y_m = \frac{160.6}{110.6}x_{m+1} - \frac{50}{110.6}(0.05)$$

$y_m = 1.452\ x_{m+1} - 0.0226$

Use these equations as described for the (a) part of problem in solving for number of theoretical plates stepwise.

C. For $q = -1.5$

This represents feed as a superheated vapor, and there is a decrease in liquid overflow from feed plate.

$$\text{Slope of ``q'' line} = \frac{-q}{1-q} = \frac{-(-1.5)}{1-(-1.5)} = 0.60$$

$$\text{Minimum reflux}: \ (L/D)_{min} = \frac{x_D - y_c}{y_c - x_c}$$

where

$$x_D = 0.95$$
$$\left.\begin{array}{l} y_c = 0.277 \\ x_c = 0.138 \end{array}\right\}\text{read from graph}$$

$$= \frac{0.95 - 0.277}{0.277 - 0.138}$$

$(L/D)_{min} = 4.84$ reflux/product

Slope of operating line at minimum reflux:

$$\left(\frac{L}{V}\right)_{min} = \frac{L/D}{L/D + 1} = \frac{4.84}{4.84 + 1}$$
$$= 0.830 (\text{graph reads } 0.844)$$

Actual Operating Line

Operating reflux ratio = (1.5) (4.84) = 7.26 reflux/product

Slope of actual operating line = (L/D) = $\frac{7.26}{7.25+1} = 0.879$

Graphically we read 8.5 total plates through to the bottom reboiler

Rectifying section = 5
Feed plate = 1
Stripping section = 2.5 (includes reboiler)

Total = 8.5 (includes reboiler)

Equations for Stepwise Tray to Tray Calculations Rectifying Section operating Line

$$y_{n+1} = \frac{L_r}{V_r}x_n + \frac{D}{V_r}x_D$$

$L_r/V_r = 0.879$

$L/D = 7.26$

$L_r = (7.26)\ (50) = 363$ mols liquid reflux

$V_r = L_r + D = 363 + 50 = 413$

$$y_{n+1} = 0.879x_n + \frac{50}{413}(0.95)$$

$$y_{n+1} = 0.879x_n + 0.115$$

Liquid Down Stripping Section

$L_s = L_r + qF$

$L_s = 363 + (-1.5)\ (100) = 213$ mols liquid

Vapor up Stripping Section

$$\frac{V_r - V_s}{F} = 1 - q$$

$$\frac{413 - V_s}{100} = 1 - (-1.5) = 2.5$$

$$-V_s = 250 - 413$$

$$V_s = 163 \text{ mo1s vapor}$$

Stripping Section Operating Line

$$y_m = \frac{L_s}{V_s} x_{m+1} - \frac{B}{V_s} x_B$$

$$y_m = \frac{213}{163} x_{m+1} - \frac{50}{163}(0.05)$$

$$y_m = 1.307 x_{m+1} - 0.01535$$

Use these equations as described for Part (a) in solving for theoretical plates.

10.30 Determination of Number of Theoretical Plates in a Fractionating Column by the Smoker Equations at constant relative volatility (α = constant)

Smoker [274] developed an analytical equation to determine the number of stages when the relative volatility is constant. This method can be used in preference to the McCabe-Thiele [225] graphical method because the accuracy of the latter depends on the care given to the construction of the plots. The graphical construction for the number of stages also becomes difficult at very low concentrations. Further, if the relative volatility $\simeq$ 1.0, the number of stages required will be very large, and the diagram will be difficult to construct.

The Equations

Smoker's equations consider Raoult's law for a binary mixture, where α is a constant, and represent the vapor–liquid equilibrium relationship. From Equation 10-48:

$$y = \frac{\alpha x}{1 + (\alpha - 1) x} \tag{10-48}$$

Any operating line that is either above or below the feed plate can be represented by the general equation of a straight line:

$$y = mx + b \tag{10-248}$$

Eliminating y from Equation 10-48 and 10-248 gives a quadratic equation in x:

$$m(\alpha - 1)x^2 + [m + (\alpha - 1)b - \alpha]x + b = 0 \tag{10-249}$$

For any particular distillation problem, Equation 10-249 will have only one real root k, between 0 and 1. Representing this root k, and substituting in Equation 10-249 gives:

$$m(\alpha - 1)k^2 + [m + (\alpha - 1)b - \alpha]k + b = 0 \tag{10-250}$$

k is the value of the x-ordinate at the point where the extended operating lines intersect the vapor–liquid equilibrium curve.

Smoker shows that the number of stages required is given by:

$$N = \log\left[\frac{x_o^*(1 - \beta x_n^*)}{x_n^*(1 - \beta\, x_o^*)}\right] \Big/ \log\left(\frac{\alpha}{mc^2}\right) \tag{10-251}$$

where

$$\beta = \frac{mc(\alpha - 1)}{\alpha - mc^2} \tag{10-252}$$

N = number of stages required effecting the separation represented by the concentration change from

x_n^* to x_o^*; $x^* = (x - k)$ and $x_o^* > x_n^*$;

$$c = 1 + (\alpha - 1)k \tag{10-253}$$

k = composition of the liquid where the operating line intersects the equilibrium line

m = slope of the operating line between x_n^* and x_o^*

α = average relative volatility, assumed constant over x_n^* to $x_o^* = (\alpha_{top} + \alpha_{bottom})/2$

10.30.1 Application of Smoker's Method to a Binary Distillation Column

Applying Smoker's equation to actual distillation conditions with a single feed and no side streams.

Rectifying Section

For a rectifying column, the number of plates required to enrich from the feed composition, x_F to the distillate (product) composition, x_D at a fixed reflux ratio, R is obtained from:

$$m = \frac{R}{R + 1} \tag{10-254}$$

and

$$b = \frac{x_D}{R + 1} \tag{10-255}$$

also

$$m(\alpha-1)k^2 + [m + (\alpha-1)b - \alpha]\,k + b = 0 \tag{10-256}$$

where k is the root between 0 and 1

$$x_o = x_D \tag{10-257}$$

$$x_o^* = x_D - k \tag{10-258}$$

$$x_n = x_F \tag{10-259}$$

$$x_n^* = x_F - k \tag{10-260}$$

Stripping Section

For the stripping section, the bottoms composition, x_B, the feed, x_F, the overhead composition, x_D, and the reflux ratio, R all fix the operating line. The values of m and b are:

$$m = \frac{R\,x_F + x_D - (R+1)x_B}{(R+1)\,(x_F - x_B)} \tag{10-261}$$

and

$$b = \frac{(x_F - x_D)x_B}{(R+1)(x_F - x_B)} \tag{10-262}$$

$$x_o^* = x_F - k \tag{10-263}$$

$$x_n^* = x_B - k \tag{10-264}$$

If the feed stream is not introduced at its bubble point, x_F is replaced by the value of x at the intersection of operating lines given by:

$$x_F^* = \frac{b + x_F/(q-1)}{q/(q-1) - m} \tag{10-265}$$

For distillation at total reflux $R = \infty$, $m = 1$, $b = 0$, $k = 0$, $c = 1$ and Equation 10-251 becomes:

$$N = \log\left\{\frac{x_o(1-x_n)}{x_n(1-x_o)n}\right\} \Big/ \log\alpha \tag{10-266}$$

Equation 10-251 simplifies to the equation derived by Underwood [73]. Smoker's equation is not limited to the range of low concentrations, but can be used for stage calculation over the entire range. In such instances, the equation is written twice, one for each section of the column. The average relative volatilities for the rectifying section and for the stripping section are determined.

Example 10-23 Use of Smoker's Equation to Determine the Number of Theoretical Stages and The Optimum Feed Stage for Binary Distillation

A column is to be designed to separate 1000 moles/hr of a binary mixture of benzene (C_6H_6) and toluene (C_7H_8). The feed contains 40% benzene and 60% toluene. A distillate that is 99% benzene and a bottoms that is 1% benzene are desired at a reflux ratio of 3 to 1. For this mixture, the average value of relative volatility (α) is 2.50. Estimate the number of equilibrium stages at this reflux ratio and the optimum feed stage location.

Solution

$$x_F = 0.4, x_D = 0.99, x_B = 0.01, R = 3.0, \alpha = 2.5$$

Rectifying Section

$$m = \frac{R}{R+1} = \frac{3}{3+1} = 0.75$$

$$b = \frac{x_D}{R+1} = \frac{0.99}{3+1} = 0.2475$$

$$m(\alpha-1)k^2 + [m + (\alpha-1)b - \alpha]\,k + b = 0 \tag{10-256}$$

$$0.75(2.5-1)k^2 + [0.75 + 0.2475(2.5-1) - 2.5]$$
$$k + 0.2475 = 0$$

Solving $1.125k^2 - 1.37875k + 0.2475 = 0$

$$k = \frac{-(-1.37875) \pm \sqrt{(-1.37875)^2 - 4(1.125)(0.2475)}}{2 \times 1.125}$$

$$k = 1.0071 \text{ or } 0.21847$$

Since $0 < k < 1$, Use $k = 0.21847$

$$x_o^* = x_D - k = 0.99 - 0.2185 = 0.7715$$

$$x_n^* = x_F - k = 0.4 - 0.2185 = 0.1815$$

$$c = 1 + (\alpha-1)k = 1 + (2.5-1)\,0.2185 = 1.328$$

$$\beta = \frac{mc(\alpha-1)}{\alpha - mc^2} = \frac{0.75 \times 1.328\,(2.5-1)}{2.5 - 0.75 \times 1.328^2} = 1.268$$

$$N = \log\left[\frac{x_o^*(1-\beta x_n^*)}{x_n^*(1-\beta\,x_o^*)}\right] \Big/ \log\left(\frac{\alpha}{mc^2}\right) \tag{10-251}$$

$$= \log\left[\frac{0.7715(1-1.268\times 0.1815)}{0.1815\,(1-1.268\times 0.7715)}\right]\bigg/\log\left(\frac{2.5}{0.75\times 1.328^2}\right)$$

$= 7.88$ stages.

Stripping Section

Feed is taken at its bubble point.

$$m = \frac{R\,x_F + x_D - (R+1)x_B}{(R+1)\,(x_F - x_B)} \qquad (10\text{-}261)$$

$$= \frac{3\times 0.4 + 0.99 - (3+1)0.01}{(3+1)\,(0.4-0.01)} = 1.3782$$

$$b = \frac{(x_F - x_D)x_B}{(R+1)(x_F - x_B)} = \frac{(0.4-0.99)\,0.01}{(3+1)\,(0.4-0.01)}$$

$$= -0.00378$$

$$m(\alpha-1)k^2 + [m + (\alpha-1)b - \alpha]\,k + b = 0 \qquad (10\text{-}256)$$

$$1.3782\,(2.5-1)k^2 + [1.3782 + (2.5-1)(-0.00378) - 2.5]\,k - 0.00378 = 0$$

Solving $2.0673\,k^2 - 1.12747k - 0.00378 = 0$

$$k = \frac{-(-1.12747)\pm\sqrt{(-1.12747)^2 - 4(2.0673)(-0.00378)}}{2\times 2.0673}$$

$= 0.5487$ or -0.00333

Since $0 < k < 1$, use $k = 0.5487$

$$x_o^* = x_F - k = 0.4 - 0.5487 = -0.1487$$

$$x_n^* = x_B - k = 0.01 - 0.5487 = -0.5387$$

$$c = 1 + (\alpha-1)\,k = 1 + (2.5-1)\,0.5487$$

$$c = 1.823$$

$$\beta = \frac{mc(\alpha-1)}{\alpha - mc^2} = \frac{1.3782\times 1.823\,(2.5-1)}{2.5 - 1.3782\times 1.823^2}$$

$$= -1.81168$$

$$N = \log\left[\frac{x_o^*(1-\beta x_n^*)}{x_n^*(1-\beta\, x_o^*)}\right]\bigg/\log\left(\frac{\alpha}{mc^2}\right)$$

$$= \log\left[\frac{-0.1487\,\{1-(-1.81168)(-0.5387)\}}{-0.5387\,\{1-(-1.81168)\,(-0.1487)\}}\right]\bigg/\log\left[\frac{2.5}{1.3782\times 1.823^2}\right] = 7.79$$

Table 10-26 Data Input and Computer Results for Calculating Equilibrium Number of Stages Using Smoker's Equation

Data name:	Data103.Dat	
2.5	2.5	
0.4	0.99	0.01
3		
Equilibrium number of stages by smoker's equation		
The relative volatility of component 1. :		2.500
The relative volatility of component 2. :		2.500
The mole fraction of the feed:		0.4000
The mole fraction of the distillate:		0.9900
The mole fraction of the bottoms:		0.0100
The reflux ratio:		3.00
The number of stages in the rectifying section:		7.87
The number of stages in the stripping section:		7.76
Total number of stages:		15.63
Feed stage location:		7.8

Total number of stages is therefore:

$$N_s = 7.88 + 7.79 = 15.67, \text{ say } 16$$

A Fortran program PROG103.for has been developed, which uses a quadratic equation to determine the number of stages in the rectifying and stripping sections of a distillate column. The program uses Smoker's equations involving two components to calculate the required number of stages. PROG103 was developed using Absoft v.10 Fortran compiler in the Microsoft run time Windows Environment (MRWE) application. The user need only create the data source file (e.g. DATA103.DAT) and run the executable PROG103.exe to generate the results. Both the source and executable codes can be downloaded from the Elsevier companion website. Table 10-26 shows typical input data and results. The required number of stages between benzene and toluene mixture is 16 and the optimum feed location is 8. Constructing the McCabe-Thiele diagram using Figure 10-42a for the more volatile component (i.e. benzene) with the feed at its bubble point (q = 1), gives the number of stages as 18.

10.31 The Jafarey, Douglas and McAvoy Equation: Design and Control [275, 276]

Operability and control are important considerations for any column. For example, it is common practice for operators to increase the reflux rate above its design value and thereby increase the purity of the overhead stream (assuming that the desired product arises from the overhead). Using this approach, the disturbances in the feed composition seldom cause the top product to fall below its quality specification. However, this advantage must be balanced by the excess steam supply needed to over-reflux the column. To solve problems of this type, and to develop better control systems for columns, Shinskey [277] developed an empirical correlation between the boilup ratio and the separation factor for a column, and Smoker [274] developed an exact analytical solution for binary distillation columns for the case of constant relative volatility.

Jafarey et al. [275, 276] derived an approximate equation for binary distillation by simplifying the solution of Smoker's equation. This equation can be used to predict the effect of disturbances on column performance, and is thus useful in computer and microprocessor control, where it can be applied to estimate the effect of disturbances and the control action required to compensate for them. The equation is:

$$N = \frac{\ln S}{\ln\left[\alpha\sqrt{1 - \frac{R+q}{(R+1)(Rz+q)}}\right]} \tag{10-267}$$

where

N = Number of stages.

$$S = (x_{LK}/x_{HK})_D\ (x_{HK}/x_{LK})_B \tag{10-267}$$

R = Reflux ratio.

q = Number of pound-moles of liquid formed on the feed stage when introducing 1 lb-mole of feed.

z = Mole fraction in the feed.

α = Relative volatility.

Example 10-24 Design and Control of a distillation column using The Jafarey, Douglas and McAvoy Algorithm

A benzene-toluene column normally operates as described in Example 10-23 with 30% vaporized. The algorithm manipulates boilup flow to control toluene purity. If the toluene purity is to be temporarily, increased from 90 to 95% and the benzene purity is to remain unaffected, to what the boilup flow rate to set? Assume that any boilup changes will be compensated for by reflux and distillate rate changes, such that the benzene purity remains unaffected. The relative volatility is 2.5.

Solution

The overall mass balance:

$$F = D + B$$

$$1000 = D + B$$

Component balance on the MVC (benzene)

$$F\,x_F = D\,x_D + Bx_B$$

$$\begin{aligned}1000\,(0.4) &= D \times 0.99 + B \times 0.1\\ 400 &= 0.99\,D + 0.1\,B\\ 400 &= 0.99\,(1000 - B) + 0.1B\\ B &= 663 \text{ lb mole/h}\\ D &= 1000 - 663\\ &= 337 \text{ lb mole/h}\end{aligned}$$

In the rectifying section of the column

$V = L + D$

But the reflux ratio, R is:

$R = L/D$

$$\begin{aligned}L &= R\,D = 3 \times 337\\ &= 1011 \text{ lb mole/h}\end{aligned}$$

Mass balance in the rectifying section:

$$\begin{aligned}V &= L + D\\ &= 1011 + 337\\ &= 1348 \text{ lb-mole/h}\end{aligned}$$

Component balance in the rectifying section of the column

$$V\,y_n = L_{n+1}x_{n+1} + D\,x_D$$

$$y_n = \frac{L_{n+1}}{V_n}x_{n+1} + \frac{D}{V_n}x_D$$

$$= \frac{1011}{1348}x_{n+1} + \frac{337}{1348}x_D$$

$$y_n = 0.75x_{n+1} + 0.25\,x_D \text{ passes through } (0.99,\ 0.99)$$

At the feed stage, since 30 percent of the feed is vaporized, q = 0.7. L′ from the definition is:

$$\begin{aligned}L' &= L + qF\\ &= 1011 + 0.7(1000)\\ L' &= 1711\ \text{ lb} - \text{mole/h}\end{aligned}$$

In the stripping section of the column:

$$\begin{aligned}V' &= L' - B\\ &= 1711 - 663\\ &= 1048 \text{ lb} - \text{mole/h}\end{aligned}$$

The component balance in the stripping section of the column

$$V'_m\,y_m = L'_{m-1}\,x_{m-1} - Bx_B$$

$$y_m = \frac{L'_{m-1}}{V'_m}x_{m-1} - \frac{B}{V'_m}x_B$$

$$= \frac{1711}{1048}x_{m-1} - \frac{663}{1048}x_B$$

$$y_m = 1.6323\,x_{m-1} - 0.6322x_B \text{ passes through}(0.1,0.1)$$

Slope of the q – line is:

$$\frac{q}{(q-1)} = \frac{0.7}{(1-0.7)} = -2.33$$

From Equation 10 – 267 is:

$$N = \frac{\ln S}{\ln\left[\alpha\sqrt{1 - \frac{R+q}{(R+1)(Rz+q)}}\right]}$$

where

$$S = \left(\frac{x_{LK}}{x_{HK}}\right)_D \left(\frac{x_{HK}}{x_{LK}}\right)_B$$

$$\ln S = \ln\left[\left(\frac{0.99}{0.01}\right)\left(\frac{0.90}{0.10}\right)\right]$$

$$= 6.79$$

$$N = \frac{6.79}{\ln\left[2.5\sqrt{1 - \frac{3 + 0.7}{(3 + 1)(3 \times 0.4 + 0.7)}}\right]}$$

$$= 11.65 \text{trays}$$

$$= 12 \text{trays}$$

Solve the material and component balances for the new conditions

$$1000 = D + B$$

$$1000 \times 0.4 = D \times 0.99 + 0.05B$$

$$400 = 0.99D + 0.05B$$

Solving these simultaneously gives B = 628 lb-mole/h and D = 372 lb-mole/h.

Recalculate S for the new conditions:

$$\ln S = \ln\left[\left(\frac{0.99}{0.01}\right)\left(\frac{0.95}{0.05}\right)\right]$$

$$= 7.54$$

$$N = \frac{\ln S}{\ln\left[\alpha\sqrt{1 - \frac{R+q}{(R+1)(Rz+q)}}\right]}$$

$$\frac{\ln S}{N} = \ln\left[\alpha\sqrt{1 - \frac{R+q}{(R+1)(Rz+q)}}\right]$$

$$\frac{\ln S}{N} = \frac{7.54}{12} = 0.628$$

$$e^{0.628} = \left[\alpha\sqrt{1 - \frac{R+q}{(R+1)(Rz+q)}}\right]$$

$$\left(\frac{1.8744}{2.5}\right)^2 = \sqrt{1 - \frac{R+q}{(R+1)(Rz+q)}}$$

$$0.562 = 1 - \frac{R+1}{(R+1)(Rz+q)}$$

or

$$\frac{R+q}{(R+1)(Rz+q)} = 1 - 0.562 = 0.438$$

$$\frac{R+0.7}{(R+1)(0.4R+0.7)} = 1 - 0.562 = 0.438$$

$$R + 0.7 = 0.438\left[(R+1)(0.4R+0.7)\right]$$

This gives the quadratic equation:

$$0.175R^2 - 0.5184R - 0.3935 = 0$$

Solving for R gives:

$$R = \frac{0.5184 \pm \sqrt{0.5184^2 + 4 \times 0.175 \times 0.3935}}{2 \times 0.175}$$

$$= 3.58$$

Since D = 372 lb-mole/h, L = 3 × 372 = 1332 lb – mole/h

$$L' = L + qF$$

$$= 1332 + 0.7 \times 1000 = 2032 \text{ lb-mole/h.}$$

$$V' = L' - B$$

$$= 2032 - 628 = 1404 \text{ lb-mole/h}$$

Therefore the computer control will therefore require increasing the boil-up rate from 1048 lb-mole/h to 1404 lb-mole/h.

Summary

Variable	This variable gives a measure of	lb-mole/h
L	Rectifying section liquid load	1011
V	Rectifying section vapor load Condenser duty	1348
L′	Stripping section liquid load	2033
V′	Stripping section vapor load Reboiler duty	1406

Example 10-25: Calculation of Minimum Number of Theoretical Trays/Plates/Stages at Total Reflux for a Binary System

A finishing column is required to produce trichlorethylene at 99.9% (vol.) purity from 10,000 lb/hour of a feed of 40% (wt.) trichlorethylene and 60% (wt.) perchlorethylene. Only 1 % (vol.) of the trichlorethylene can be accepted in the bottoms.

Because the process system that will receive vents from this condensing system is operating at 5 psig, allow

5 psi pressure drop to ensure positive venting and set top of tower pressure at 10 psig.

Feed (158°F)	(1) Wt %	(2) Mol Wt	(1) (2) Mols	Mol Fraction
Trichlorethylene	40	131.4	0.00304	0.456
Perchlorethylene	60	165.9	0.00362	0.544
Total	100		0.00666	1.000

Avg mol wt 1.00/0.00666 = 150.0

Overhead

Overhead temperature for essentially pure products at 10 psig = 223°F from vapor pressure curve.

Bottoms

Allow 10 psi tower pressure drop, this makes bottom pressure = 20 psig = 1,800 mm Hg.

Material balance:
$F = D + B$
Feed rate: $\text{mols/ hr} = \frac{10,000 \text{ lb/hr}}{(150.0)} = 66.7$
$66.7 = D + B$
or
$B = 66.7 - D$
Component balance:
$F\ x_1 = D\ x_1 + B\ x_1$
$(66.7)\ (0.456) = D\ (0.999) + B\ (0.01)$
$30.4 = 0.999\ D + 0.01\ (66.7 - D)$
$D = 30.05$ mols/hr
bottoms: $B = F - D$
$B = 66.7 - 30.05 = 36.65$ mols/hr

Bottoms compositions	Mol fraction	Mols/hr	V.P. (316°F) mm Hg	V.P. mm Hg.
Trichloroethylene	0.01	0.3665	4,200	42
Perchlorethylene	0.99	36.2835	1,780	1,762
	1.00	36.65		1,804 mm

The 1,804 mm compares to the balance value of 1,800 mm ≅ 20 psig.

Overhead Composition	Mol Fraction	Mols/hr
Trichlorethylene	0.999	30.02
Perchloroethylene	0.001	0.03
	1.000	

Relative Volatility: overhead conditions

$$\alpha \text{ tri/per } (223°\text{F}) = \frac{\text{v.p.(tri)}}{\text{v.p.(per)}} = \frac{1,280 \text{ mm}}{385} = 3.32$$

Bottom conditions:

$$\alpha \text{ tri/per}(316°\text{F}) = \frac{\text{v.p.(tri)}}{\text{v.p.(per)}} = \frac{4,200 \text{ mm}}{1,780} = 2.36$$

Thermal Condition of the Feed at 158°F

At conditions of feed tray, assume pressure is 15 psig ≅ 1,533 mm Hg. Determine bubble point:

Component	x_{iF}	Assume t = 266°F V.P mm Hg	Partial Press. = VP. × x_{iF} mm Hg
Trichlorethylene	0.456	2,350	1,072
Perchlorethylene	0.544	880	478
			1,550

This is sufficiently close to 1,533 mm for practical purposes; the actual temperature might be 265°F, although plotted data are probably not that accurate. Because the feed enters at 158°F and its bubble point is 266°F, the feed is sub-cooled.

Heat to vaporize one mol of feed.

Component	x_{iF}	Latent Ht. @ 266°F Btu/mol	$(x_{iF})(L_v)$ Btu/mol	(°F) cP @ 158°F Btu/mol	(x_{iF})(cP)(266°F − 158°F) Btu/mol
Trichlorethylene	0.456	12,280	5,600	30.9	1,523
Perchlorethylene	0.544	14,600	7,950	36.4	2,180
			13,550		3,703

$$q = \frac{\text{heat required to vaporize one mol of feed}}{\text{latent heat of one mol of feed}}$$

$$q = \frac{13,550 + 3,703}{13,550} = \frac{17,253}{13,550} = 1.272$$

Minimum Number of Trays at Total Reflux

$x_{D1} = 0.999$
$x_{Dh} = 0.001$
$x_{B1} = 0.01$
$x_{BH} = 0.99$
$\alpha_{avg} = 2.8$

For a total condenser system:

$$(N_{min} + 1) = \frac{\log(x_{D1}/x_{Dh})(x_{Bh}/x_{B1})}{\log \alpha_{avg}}$$

$$= \frac{\log(0.999/0.001)(0.99/0.01)}{\log 2.8} = 11.17$$

$N_{min} + 1 = 11.17$
$N_{min} = 10.17$ trays, not including reboiler

Summary

Minimum total physical trays in the column	= 10.17
Reboiler	1.0
For conservative design, add feed tray	1.0
Minimum number of total theoretical stages	12.17, say 12

Minimum Reflux Ratio

Because this is not feed at its boiling point, but subcooled liquid, the convenient charts cannot be used with accuracy. Using Underwood's general case:

$$\frac{(L/D)(x_{1F}) + qx_{1D}}{(L/D)(1 - x_{1F}) + q(1 - x_{1D})} = \frac{\alpha\left\{[(L/D) + 1]y_{1F} + (q - 1)(x_{1D})\right\}}{\left[(L/D) + 1\right](1 - x_{1F}) + (q - 1)(1 - x_{1D})} \tag{10-269}$$

Solve first for y_{1F}, assuming that the system follows the ideal (as it does closely in this instance).

$$y_{1F} = \frac{x_{1F}(\alpha_F)}{1 + (\alpha_F - 1)x_{1F}} \tag{10-48}$$

This replaces drawing the equilibrium curve and solving graphically, and is only necessary since the "q" is not 1.0 or zero.

The α should be for the feed tray. However, the value of $\alpha = 2.8$ should be accepted for feed tray conditions (not 158°F). It would not be if this were predominantly a rectifying or a stripping operation.

$$y_{1F} = \frac{0.456(2.8)}{1 + (2.8 - 1)(0.456)} = 0.70$$

Now, substituting to solve for $(L/D)_{min}$

$$\frac{(L/D)(0.456)+1.272(0.999)}{(L/D)(1-0.456)+1.272(1-0.999)} = \frac{2.8\left\{\left[(L/D)+1\right]0.70+(1.272-1)(0.999)\right\}}{\left[\left((L/D)+1)(1-0.456)+(1.272-1)(1-0.999\right)\right]}$$

$$\frac{(L/D)(0.456) + 1.272}{(L/D)(0.544) + 0.00127} = \frac{2.8\left\{(L/D)(0.70) + 0.70 + 0.27188\right\}}{\left[(L/D)(0.544) + 0.544 + 0.000272\right]}$$

Solving this quadratic:

$(L/D)_{min} = 0.644$

Reading Figure 10-40 for $(L/D)_{min}$ assuming a liquid feed at the boiling point, $(L/D)_{min} = 1.2$. This demonstrates the value of taking the thermal condition of the feed into account.

Actually, any point on one of the curves represents a condition of reflux and number of trays that will perform the required separation.

10.32 Number of Theoretical Trays at Actual Reflux

Assume actual reflux ratios of 1.2, 1.8, 2.25, 3.0 times the minimum and plot the effect on the number of theoretical plates using Gilliland plot.

Actual Reflux Ratio	$\frac{(L/D)-(L/D)_{min}}{(L/D)+1}$	(From Fig. 10-49a) $N-N_{min}$	N (Theo.)	Conservative Add 1 for Feed, Total N
0.772	0.0722	0.552	26.2	27
1.16	0.239	0.416	19.8	21
1.45	0.329	0.356	17.9	19
1.93	0.439	0.288	16.1	17

$$\frac{(L/D)-(L/D)_{min}}{(L/D)+1} = \frac{0.772-0.644}{0.772+1} = 0.0722$$

Read value from curve Figure 10-49a.

$$\frac{N-N_{min}}{N+1} = 0.552,\ \text{so}\ \frac{N-11.18}{N+1} = 0.552$$

$$N = 26.2$$

Note that these values are for theoretical trays and, as in earlier calculations, require conversion into actual number of trays. Efficiencies are generally in the range of 50–60% for systems of this type. This indicates a column of actual number of trays almost twice the theoretical number at the operating reflux.

Figure 10-53 presents the usual determination of optimum or near optimum theoretical trays at actual reflux based on performance. It is not necessarily the point of least cost for all operating costs, fabrication costs or types of trays. A cost study should be made to determine the merits of moving to one side or other of the so-called optimum point. From the Figure 10-53:

First choice actual reflux ratio, L/D = 1.33

Corresponding theoretical trays or stages, N = 18.6

Note that the 18.6 includes the reboiler, so physical trays in column = 17.6. Do not round-off decimal or fractions of trays until after efficiency has been included.

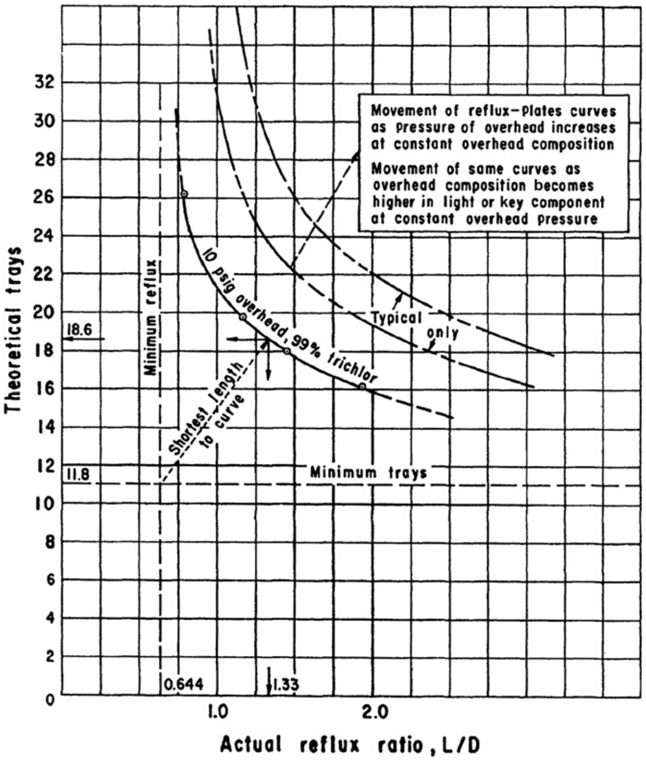


Figure 10-53 Relationship of reflux ratio and theoretical trays, for Example 10-25.

Tray Efficiency

Base at average column temperature of (158 + 266)/2 = 212°F.

Component	x_{iF}	Viscosity, cP	$(\mu)\ (x_{iF})$, cP
Trichlorethylene	0.456	0.27	0.123
Perchlorethylene	0.544	0.36	0.196
			0.319

From Figure 10-54:

Efficiency = 47.5%

Actual Trays at Actual Reflux

Actual L/D = 1.33

Actual trays = 18.6/0.475 = 39.2 (including reboiler)

Physical trays: 39.2 − 1 (reboiler) + 1 (conservative, feed) = 39.2

Round-off to: 40 trays plus reboiler plus total condenser.

Note: If there is any reason to know that the efficiency of this system is usually lower (or in same chemical family), then either the efficiency should be reduced to account for this or extra trays should be added. In practice, the installed column might contain 40 trays to 50 trays [271].

Types of Tray

Tray details will be considered in a later example.

10.33 Estimating Tray Efficiency in a Distillation Column

Several empirical efficiency correlations have been developed from commercial equipment and some laboratory

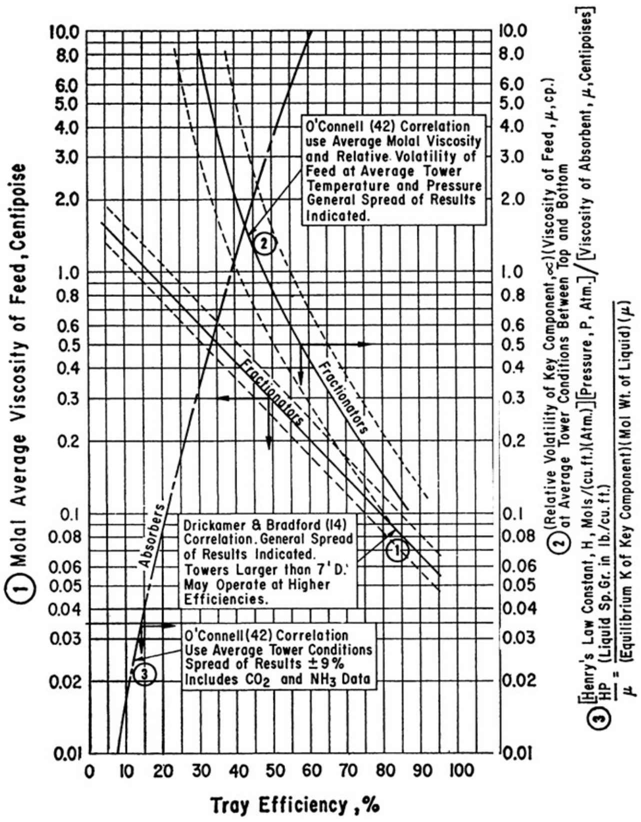


Figure 10-54 Empirical correlations of overall efficiencies for fractionation and absorption.

data, and serve most design problems for the average hydrocarbon and chemical system. They are empirical correlations, and hence application in new systems is unpredictable. For this reason, results for efficiencies should be evaluated by several methods to obtain some idea of the possible spread. In light of the American Institute of Chemical Engineers (AIChE) study discussed below, some of these methods can be off the range by 15−50%. Comparisons indicate these deviations are usually on the safe or low side. The relation of Drickamer and Bradford [16], in Figure 10-54, has been found to give good agreement for hydrocarbons, chlorinated hydrocarbons, glycols, glycerine and related compounds, and some rich hydrocarbon absorbers and strippers.

The relation of O'Connell [49] (Figure 10-54) has generally also given good results for the same systems, but generally the values are high. The absorber correlation of O'Connell (Figure 10-54) can be used as long as it generally gives lower values than the other two relations. It can be used for stripping of gases from rich oils provided great caution is exercised.

The area of absorption and stripping is difficult to correlate for the wide range of peculiarities encountered in such systems. The correlation of Gautreaux and O'Connell [22] allows a qualitative handling of tray mixing to be considered with overall and local efficiencies. In general, it agrees with the Drickamer correlation–at least for towers upto seven feet in diameter. Although the effect of liquid path must be apparently considered, the wide variety of tray and cap designs makes this generally possible, and the overall correlations appear to serve adequately.

The American Institute of Chemical Engineer's Distillation Tray Efficiency Research [2] program has produced a more detailed method than the short-cut methods, and correspondingly is believed to produce reliable results. This method produces information on tray efficiencies of new systems without experimental data. At present, there is not enough experience with using this method and its results to evaluate its complete range of application.

Murphree [85] developed "point" and "overall" distillation tray efficiencies, which are examined in detail in Reference 2. The expressions are [59]:

$$\text{Plate/Tray Efficiency}: \; E_{MV}{}^{o} = \frac{y_i - y_o}{y_i - y_e^*} \qquad (10\text{-}270)$$

The plate/tray efficiency is the integrated effect of all the point efficiencies.

$$\text{Point Efficiency}: \; E_{MV}{}^{o} = \frac{y_i' - y_o'}{y_i' - y_e} \qquad (10\text{-}271)$$

$$\text{Overall tray efficiency, } E_o = \frac{\text{Number of Theoretical Trays}}{\text{Number of Acutal Trays}} \qquad (10\text{-}272)$$

where

y_i = average composition of vapor entering tray
y_o = average composition of vapor leaving tray
y_e^* = composition of vapor in equilibrium with liquid flowing to plate below
y_i' = vapor composition entering local region
y_o' = vapor composition leaving local region
y_e = vapor composition in equilibrium with the liquid in the local region

The proposal for calculating column vapor plate efficiencies by MacFarland, Sigmund, and Van Winkle [86] correlates with the Murphree vapor plate efficiencies in percent:

$$E_M = \frac{y_n - y_{n+1}}{y^* - y_{n+1}} \qquad (10\text{-}273)$$

where

y_n = average light key mol fraction of vapor leaving plate n

y_{n+1} = average light key mol fraction of vapor entering plate n

y_e = light key mol fraction of vapor in perfect equilibrium with liquid leaving plate n

Data from bubble cap and perforated tray columns for the Murphree vapor plate efficiencies are correlated [86]:

$$E_M = 7.0(N_{DG})^{0.14}(N_{SC})^{0.25}(N_{Re})^{0.08} \qquad (10\text{-}274a)$$

or,

$$E_M = 6.8(N_{Re}N_{SC})^{0.10}(N_{DG}N_{SC})^{0.115} \qquad (10\text{-}274b)$$

Referenced to 806 data points for binary systems, Equation 10-274a gives absolute deviation of 13.2%, which is about as accurate, or perhaps more so, than other efficiency equations. Equation 10-274b uses the same data and has an absolute average deviation of 10.6%. See Example 10-26 for identification of dimensionless groups.

Example 10-26: Estimating Distillation Tray Efficiency by Equations 10-274a and 10-274b (used by permission of McFarland et al. [86])

Solving the problem defined in the following table will show the equations for estimating system physical properties and their relation to the calculation of Murphree vapor plate efficiencies:

System properties*	**Acetone**	**Benzene**
Molecular weight, M, lb/lb mole	58.08	78.11
Viscosity, μ lb/hr-ft	0.5082	0.8155
Parachor, [P]	162.1	207.1
API specific gravity coefficient [240]		
A	0.8726	0.9485
B	0.00053	0.00053
C	21.6	18.0
E	536.0	620.6
Operating data		
Acetone mole fraction, x_1	=	0.637
Benzene mole fraction, x_2	=	0.363
Temperature, T, °F	=	166
Superficial vapor mass velocity, G, lb/hr-sq ft	=	3,820
Vapor velocity, U_v, ft/hr	=	24,096
Weir height, h_w, ft	=	0.2082
Fraction free area, FA	=	0.063

---

* Used by permission of McFarland et al. [86].

Liquid densities for pure hydrocarbon are calculated [240] as a function of temperature using the following equation for specific gravity:

$$s_{gL} = A - BT - C/(E - T) \qquad (10\text{-}275)$$

The liquid density is then:

$\rho_L = (62.32)\ (s_{gL})$

For acetone,

$\rho_{L,1} = (62.32)\ [0.8726 - 0.00053\ (166) - 21.6/(536.0 - 166)] = 45.3\ \text{lb/ft}^3$

For benzene,

$\rho_{L,2} = (62.32)\ [0.9485 - 0.00053\ (166) - 18.0/(620.6 - 166)] = 51.2\ \text{lb/ft}^3$

Vapor densities are calculated from the ideal gas relation:

$\rho_V = MP_t/555(T + 460)$

where total pressure P_t is given in millimeters of mercury.

Mixture densities of the binary mixtures require knowledge of volume fraction for each component. The component molar volume is:

$$V_i = M_i/\rho_i \qquad (10\text{-}277)$$

For acetone and benzene, respectively:

$V_{L,1} = (58.08)/45.3 = 1.282\ \text{ft}^3/\text{lb mole}$
$V_{L,2} = (78.11)/1.51.2 = 1.526\ \text{ft}^3/\text{lb mole}$

For the liquid mixture:

$M_{L,MIX} = x_l V_{L,1} + x_2 V_{L,2} = (0.637)\ (1.282) + (0.363)\ (1.526) = 1.371\ \text{ft}^3/\text{lb mole}$

Then the volume fraction of a component is calculated assuming an ideal mixture.

$$\upsilon_i = V_i/V_{mix} \qquad (10\text{-}278)$$

For acetone and benzene, respectively:

$\upsilon_{L,1} = 0.817/1.371 = 0.596$
$\upsilon_{L,2} = 0.554/1.371 = 0.404$

The *liquid density* of the binary mixture is then:

$$\rho_{L,MIX} = \upsilon_{L,1}\rho_{L,1} + \upsilon_{L,2}\rho_{L,2} \qquad (10\text{-}279)$$

$= (0.596)\ (45.3) + (0.404)\ (51.2)$
$= 47.6\ \text{lb/ft}^3$

The *vapor density* can be found in an analogous manner.

$$\rho_{V,MIX} = \upsilon_{V,1}\rho_{L,1} + \upsilon_{V,2}\rho_{L,2} \qquad (10\text{-}280)$$

However, the example problem does not require a calculation for vapor density. Instead, the superficial vapor mass velocity G can be substituted into Equation 10-288 because:

$$G = U_V \rho_V \tag{10-281}$$

Liquid viscosity of the binary mixture, when not reported with the experimental efficiency results, is estimated using:

$$\mu_{L,MIX} = \left(\sum x_i \mu_i^{1/3}\right)^3 \tag{10-282}$$

The pure component viscosities are given in the literature [240, 241] as a function of temperature.

For example,

$\mu_{L,MIX} = [(0.637)\ (0.5082)1/3 + (0.363)\ (0.8155)^{1/3}]^3$
$= 0.609$ lb/hr-ft

Liquid surface tension is calculated using the Sugden Parachor method [242]. Neglecting vapor density, surface tension for the liquid mixture is:

$$\sigma_{L,MIX} = \left[(\rho_{mix}/M_{mix})[P]_{mix}\right]^4 \tag{10-283}$$

where σ is in dynes/cm, ρ is in gm/cm^3 and the parachor,

$$[P]_{mix} = \sum x_i [P]_i \tag{10-284}$$

Values of the parachor are given in the literature [240].

Then the example gives:

$M_{mix} = (0.637)\ (58.08) + (0.363)\ (78.11)$
$= 65.35$ lb/lb mole
$[P]_{min} = (0.637)\ (162.1) + (0.363)\ (207.1)$
$= 1\ 78.4$
$\rho_{min} = 47.6/62.32 = 0.7638$ gm/cu cm
$\sigma_{min} = [(0.7638/65.35)\ (178.4)]^4$
$= 18.96$ dynes/cm

Diffusivity of the liquid light key component is calculated by the dilute solution equation of Wilke-Chang [243].

$$D_{LK} = (3.24 \times 10 - 8)(\Psi M_{mix})^{1/2}\ (T + 460)/\mu_{mix}(V_{LK})^{0.6} \tag{10-285}$$

Wilke-Chang reported the recommended values for Ψ as follows: water, 2.6; benzene, heptane and ether, 1.0; methanol, 1.9; ethanol, 1.5; unassociated solvents, 1.0. The mixture parameter for the example problem is considered unity.

Then,

$D_{LK} = (3.24 \times 10^{-8})\ (65.35)^{1/2}\ (166 + 460)/(0.609)\ (1.282)^{0.6}$
$= 2.32 \times 10^{-0.4}$ ft^2/hr

Dimensionless groups for the example problem are:

$$N_{Dg} = \sigma_L/\mu_L U_V$$
$$= (5.417 \times 10^5)/(0.609)(2.4092 \times 10^4) = 37 \tag{10-286}$$

$$N_{Sc} = \mu L/\rho_L D_{LK}$$
$$= (0.609)/(47.6)(2.32 \times 10^{-4}) = 55 \tag{10-287}$$

$$N_{Re} = h_w G/\mu_L(FA)$$
$$= (0.2082)(3.82 \times 10^3)/(0.609)(0.063) = 2.07 \times 10^4 \tag{10-288}$$

Murphree vapor plate efficiency is calculated two ways:

$$E_M = 7.0(N_{Dg})^{0.14}(N_{Sc})^{0.25}(N_{Re})^{0.08}$$
$$= 7.0(37)^{0.14}(55)^{0.25}(2.07 \times 104)^{0.08}$$
$$= 7.0(1.66)(2.72)(2.26) = 71\% \tag{10-274a}$$

$$E_M = 6.8(N_{Re}N_{Sc})^{0.1}(N_{Dg}N_{Sc})^{0.115}$$
$$= 6.8\left[\left(2.07 \times 10^4\right)\left(55\right)\right]^{0.1}[(37)(55)]^{0.115}$$
$$= 608\left(4.04\right)\left(2040\right) = 66\% \tag{10-274b}$$

In this example, Equation 10-274b gives a more conservative design basis, where

A, B, C, E = constants in equation
D = molecular diffusion coefficient, sq ft/hr
E_M = Murphree vapor plate efficiency, %
FA = fractional free area
h_w = weir height, inches
G = superficial mass vapor velocity based on the cross-sectional area of the column, lb/hr-sq ft
M = molecular weight, lb/lb mole
N = dimensionless number
P = pressure, consistent units
[P] = Sugden parachor
sg = specific gravity
T = temperature, °F
U = superficial velocity, ft/hr
V = molar volume, ft^3/lb mole
υ = volume fraction
x = mole fraction in the liquid
y = mole fraction in the, vapor
μ = liquid viscosity, lb/hr-ft
ρ = density, lb/ft^3
σ = surface tension, dynes/cm
Ψ = mixture parameter

Subscripts

i = component
L = liquid
LK = liquid light key
mix = binary mixture
n = plate number
t = total
V = vapor

Biddulph [90] emphasizes the importance of using point efficiencies rather than tray or overall column efficiencies, due to the wide fluctuations that often exist.

Kessler and Wankat [101] have examined several column performance parameters, and for O'Connell's [49] data presented in Figure 10–54, they propose equations that reportedly fit the data within about ±10%:

A. Distillation Trays

$$E_o = 0.54159 - 0.28531 \log_{10} a\mu \tag{10-289}$$

B. Plate Absorbers (data fit ±5%)

$$E_o = 0.37237 + 0.19339 \log_{10}(HP/\mu) + 0.024816(\log_{10}(HP/\mu))^2 \tag{10-290}$$

where

E_o = overall efficiency
H' = Henry's law constant, lb mole/ (atm) (ft^3)
P = pressure, atmospheres
α = relative volatility
μ = viscosity, centipoise, cP

Gerster [176] presents the results of studies on the tray efficiencies of both tray and packing contacting devices. Note that Gerster compares his work to the AIChE Manual [2].

In terms of the change in gas composition [2]:

$$E_G = E_{OG} = \frac{y - y_{n+1}}{y^* - y_{n+1}} \tag{10-291}$$

where

E_G = overall column efficiency
E_{OG} = overall point efficiency in vapor terms (see Ref. 2)
y_{n+1} = component mol fraction in the gas to the point considered
y = component mol fraction in the gas from the point considered
y^* = composition the leaving gas would have if it left the point in equilibrium with the liquid

In Table 10-27 Proctor [178] compares efficiencies of sieve and bubble cap trays (plates). He concludes that the sieve design provides a 15% improvement in plate efficiency. To fully evaluate actual efficiencies in any particular system, the physical properties, mechanical details of the trays, and flow rates must all be considered. See also Reference 2.

Table 10-27 Comparative Effectiveness of Sieve and Bubble-Cap Trays/Plates [178]

Plate type	Vapor throughput, lb Mole/hr of dry H_2S	Over-all plate efficiency, %	
		Cold tower	Hot tower
Sieve	18,200	69 ± 5	75 ± (8)*
Bubble-cap	16,200	60 ± 5	69 ± 5

* See the discussion of accuracy of the plate efficiency results in the text. Used by permission of the American Institute of Chemical Engineers; all rights reserved.

Strand [179] proposes a better agreement between experimental and predicted efficiencies when recognizing a liquid by-passing factor to correct predicted values determined by the AIChE method. The results suggest that, for the representative systems studied, recognition of a liquid by-passing factor for a tray can increase the agreement of the AIChE method results by as much as 5 or 10%. A vapor by-passing effect was not required to correlate the data. Because the Murphree vapor efficiencies vary considerably for various systems, the data in Reference 179 can only be a guide for systems not studied.

This suggests that caution must be exercised when establishing a tray efficiency for any type of contacting device by: (1) using actual test data if available for some similar system; (2) comparing several methods of predicting efficiency; and (3) possibly using a more conservative efficiency than calculated to avoid the possibility of ending up with a complete column with too few actual trays–a disastrous situation if not discovered prior to start-up.

Sakato [180] evaluates the degree of mixing of the liquid as it flows across a tray and its effect on the tray efficiency, Figure 10-55. For plug flow the liquid flows across the tray with no mixing, while for partial or "spot" mixing as it flows over the tray, improved tray efficiency can be expected. For a completely mixed tray liquid, the point efficiency for a small element of the tray, E_{OG}, and tray efficiency, E_{MV}, are equal.

From Figure 10-56 the effect of mixed and unmixed "pools" of liquid can be noted. For a completely mixed tray, there is no concentration gradient from inlet to outlet, and therefore the entire tray has a uniform composition. The degree of mixing across the tray, as determined by the number of discrete mixing pools on it,

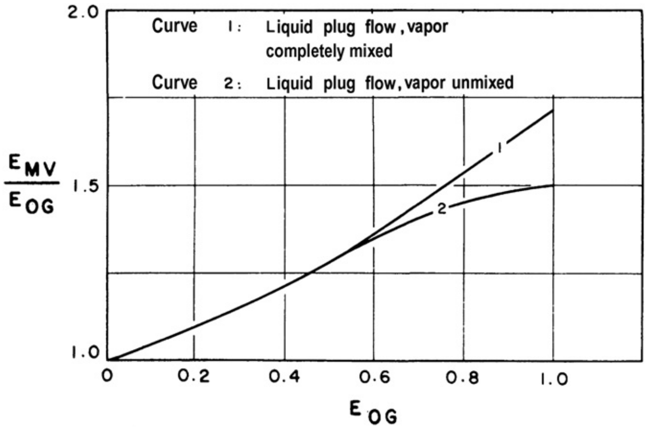


Figure 10-55 Effect of vapor mixing on tray efficiency. Reprinted by permission, Sakato, M., The American Institute of Chemical Engineers, Chem. Eng. Prog., V.62, No. 11 (1966), p. 98, all rights reserved; reprinted by permission from Lewis, W. K., Jr., Ind. & Eng., Chem. V. 28 (1936), and by special permission from Fractionation Research, Inc.

has an effect on the relationship between E_{OG} and E_{MV} as a function of λ, where:

$\lambda = mV/L$
m = slope of vapor-liquid equilibrium curve
V = vapor rate, lb mols/hr
L = liquid rate, lb mols/hr

Hughmark [181] has proposed empirical correlations for better fit of experimental data to transfer units and thus tray efficiency comparison with the AIChE method [2].

10.34 Batch Distillation

Specialty chemicals represent some 15% of worldwide chemical production, and is worth approximately $15 billion annually. Batch distillation is the most suitable unit operation for the separation such material [278]. This is because of its flexibility and versatility in separating small amounts of mixtures, in order to obtain products which are expensive, and to recover compounds or solvents that could adversely affect ecosystems if lost. This flexibility also allows uncertainties in feed stock or product specification to be dealt with, once several mixtures can be handled by switching column operating conditions. Batch distillation is therefore preferable to continuous distillation when small quantities of high technology/high value added chemicals and biochemicals need to be separated.

Previously, calculations for batch processes were based on trial and error; however, such design may not result in an economic optimum. Studies have been conducted with a view of understanding and developing improved design methods for batch processing [278, 279, 280, 281].

In batch distillation, an initial quantity of materials is fed to the still, and during the separation, one or more component is collected in a receiver. The process results in a change of composition in the still over time. Two modes of operation are possible:

1. Maintain a constant top product specification, the reflux ratio and hence increase continuously.
2. If the reflux ratio remains constant throughout the operation, the quality of the top product will decrease with time. To obtain a product specification of composition x_D, the initial product removed will have a composition x greater than x_D and the process will stop when x is less than x_D such that the average composition over the whole operation is equal to x_D.

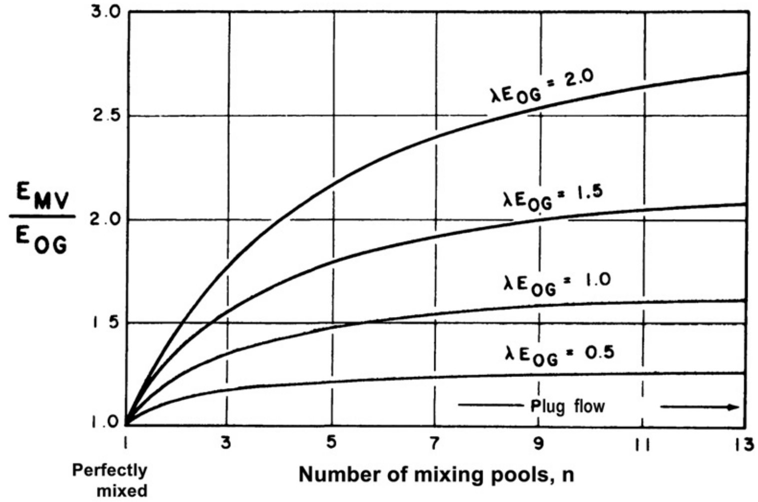


Figure 10-56 Typical effect of liquid mixing on tray efficiency. Reprinted by permission, Sakato, M., The American Institute of Chemical Engineers, Chem. Eng. Prog., V. 62, No. 11 (1966), p. 98, all rights reserved; reprinted by permission from Lewis, W. K., Jr., Ind. & Eng., Chem. V. 28 (1936), and by special permission from Fractionation Research, Inc.

In these modes of operation, the McCabe-Thiele construction may be used for calculations–as illustrated for continuous distillation process.

Batch distillation [129, 130, 131, 133, 138, 140, 142, 170] may be preferred to continuous distillation for process requirements in which: (1) feed composition may change from batch to batch; (2) batches are relatively small fixed volumes of a mixture wherein certain components are to be separated into relatively pure components, leaving a heavier residue; (3) the process improvement requirement is on an irregular cycle; and (4) there is negligible holdup in any column used and condenser relative to that in the receiver and kettle. The system operates on a fixed feed quantity, thereby yielding a fixed distillate and residue (see Figures 10-57 and 10-57a). In batch operation, the kettle is charged with a fixed amount of liquid, and the vapors; the rise either through a trayed or packed column contacting section above the “pot.” This then condenses the vapors, and collects the components, separated according to their boiling points. Thus, the separation can be developed by the boilup to collect only, or nearly only, the light boilers, then the next boiling fraction, etc., until the light ends and the heavies or residues are at the collection and concentration levels desired.

Batch distillation is versatile, since the same unit may be used to process different feeds and generate multiple products. A typical run may be from a few hours to several days depending on the process. The approach is used for purifying materials of high value that are generally handled in relatively small quantities. The techniques are used extensively in the Fine Chemical and Pharmaceutical industries to achieve a variety of processing objectives, such as:

- Removal of impurities/unwanted components from a reaction mixture.
- Solvent change between reaction stages on multistage syntheses.
- Solvent recovery.
- Water removal and drying.
- Heat removal control for reactions at reflux.
- Concentration prior to crystallization.

The simplest form of batch distillation involves a single separation stage (represented by the act of evaporation), where a large difference in volatility exists between the components to be separated. In such a case, there is no need for a fractionating column. Simple batch distillation (sometimes referred to as still or pot distillation) provides only one theoretical plate (Figure 10-58). When the difference in volatility between the components to be separated is relatively small, or when operating over narrow composition ranges, a rectification section is added. Overhead facilities are also required to provide control of reflux ratio and layer of reflux when handling heterogeneous azeotropes. An alternative to a simple batch process is constant level batch distillation, where solvent is fed continually to the still batch to keep the liquid level constant. Figure 10-4a shows a typical multistage batch distillation, where a stage column is placed above the reboiler. Here, the reflux is returned to the column. There are instances where the distillate is withdrawn continually until the column is shut down and drained. Alternatively, where no distillate is withdrawn, the composition of liquid in the accumulator changes. When the distillate in the accumulator reaches the desired composition, both the accumulator and the reboiler are drained. Economic design and operation of batch distillation systems must consider for many time dependent factors. The complex mathematics of the process often involves using computer simulation tools such as BATHFRAC (Aspen Technology, 2000) and Chemcad-BATCH (Chemstations, Inc. 2000) and academic MultiBatch DS to solve batch problems.

10.34.1 Simple or Differential Distillation

In this process, a mixture of initially soluble liquids of different volatilities is heated to the bubble point to evolve vapor that is richer in the more volatile components. This vapor is removed as it is generated, so that the less volatile components accumulate in the liquid. Thus, while the vapor formed at any instant is in equilibrium with the liquid in the still, the total amount of vapor collected over the entire distillation operation will not be in equilibrium with the final residual liquid remaining in the still. Figure 10-59 shows a schematic diagram of a simple batch distillation system. Here, the vapors are withdrawn from contact with the liquid and condensed as fast as they are formed.

In a typical batch distillation, the still pot will be charged with feed F. For stills which must accommodate larger quantities of feed, the bottom portion of the still, is usually cylindrical or spherical in shape, and is larger than the column. After charging, the still bottom is heated until the desired reflux rate is established. Then, distillate is withdrawn from the overhead accumulator until the desired end point is reached.

In the cases where reflux is employed, either of two general types of control may be used. These are:

1. Constant reflux ratio ($R = L/D$) with varying distillate composition.
2. Constant overhead purity with variable reflux ratio.

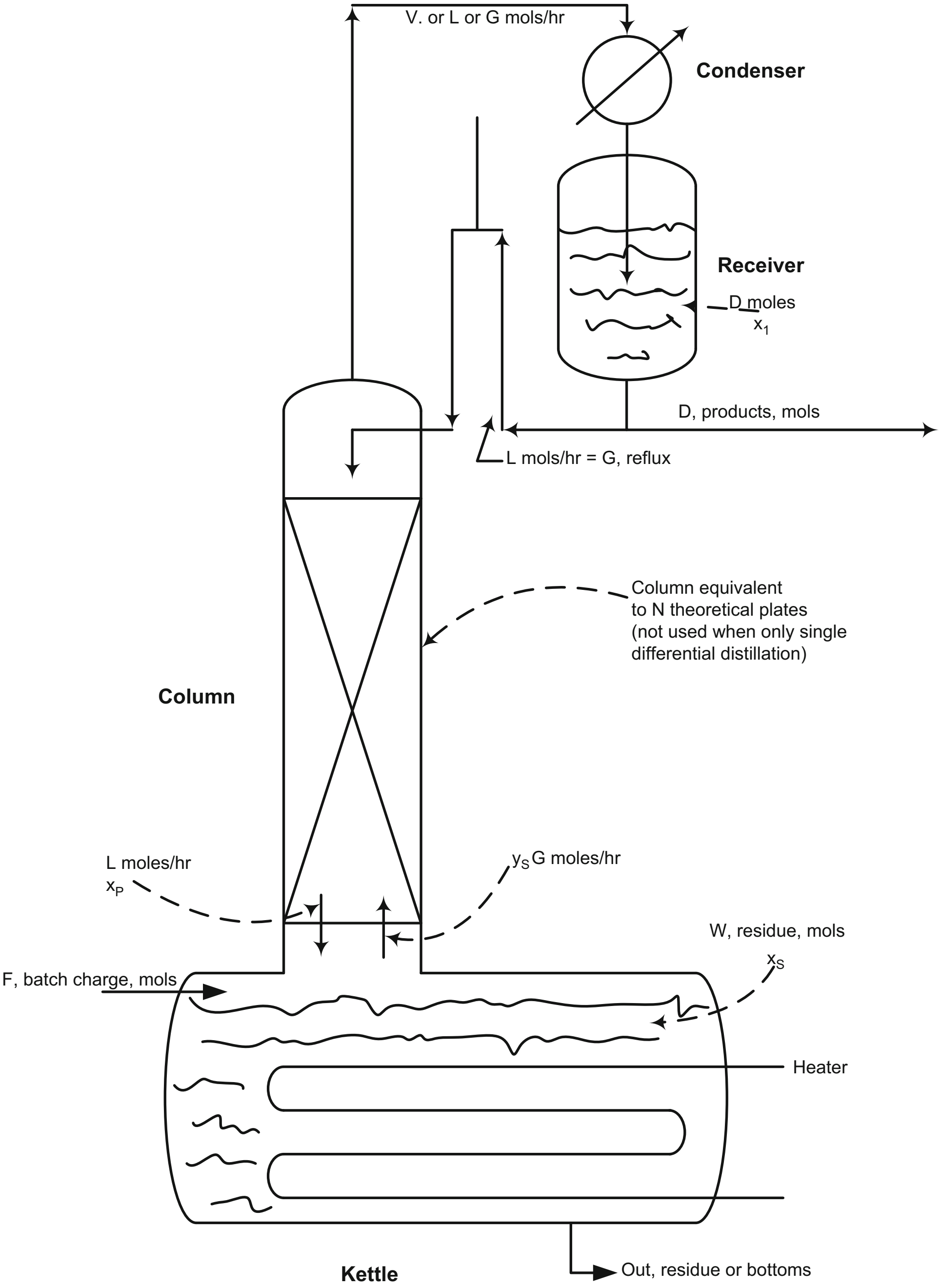


Figure 10-57 Batch operations: constant reflux ratio and variable overhead composition for fixed number of theoretical stages/trays. Used by permission, Treyball, R. E., Chem. Eng. Oct. 5(1970), p. 95.

Control type 1 can be accomplished with various types of stream splitting devices, and type 2 can be performed by placing reflux flow rate in a control loop to maintain constant column top temperature. In either case, one or more distillate cuts may be produced after startup by collecting the distillate in one or more receivers as the process of distillation is carried out. At the end of the process, the heat supply is turned off and the remaining residue can be removed from the pot as a bottom product.

The following assumptions are made for all cases:

1. Hold-up of liquid and vapor in all parts of the still except the bottom (residue) is negligible.
2. Reflux, if any, is at its bubble point.
3. The still or bottom of the still constitutes one equilibrium stage.
4. The residue is completely mixed at all times during the distillation process.
5. The system is a binary one with constant relative volatility.

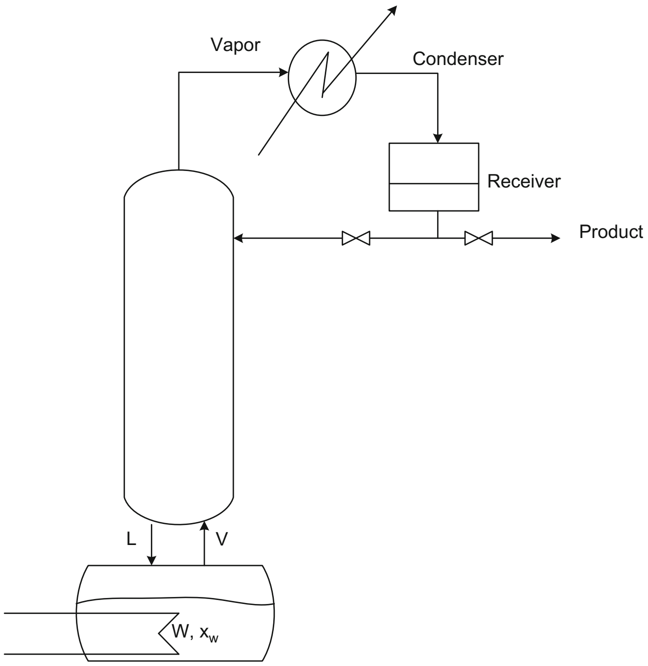


Figure 10-58 Schematic diagram of a simple batch distillation.

6. Heat loss from the column is negligible.
7. Equilibrium stages are numbered from the bottom to the top of the distillation column, starting with the first stage after the still bottom or pot.
8. Where the reflux is used, the liquid downflow rate (L mol/s) does not vary from tray to tray (i.e. constant molal overflow).

Equations

Consider a binary batch of W moles of liquid charged to a batch still. It contains a mixture of two liquid components A and B with A being more volatile (see Figure 10-59).

After a certain time t, a differential amount of liquid dW is vaporized.

Therefore, the amount of liquid left in the still pot is

$$= W - dW, \text{moles} \tag{10-292}$$

The amount of A present in the initial charge

$$= xW, \text{moles} \tag{10-293}$$

The amount of A in the vapor

$$= y\, dW, \text{moles} \tag{10-294}$$

Because of evaporation, the liquid composition will decrease from x to (x – dx) with respect to component A.

Therefore, the amount of A left in the still pot is:

for any component in the mixture,

$$= (x - dx)(W - dW), \text{moles} \tag{10-295}$$

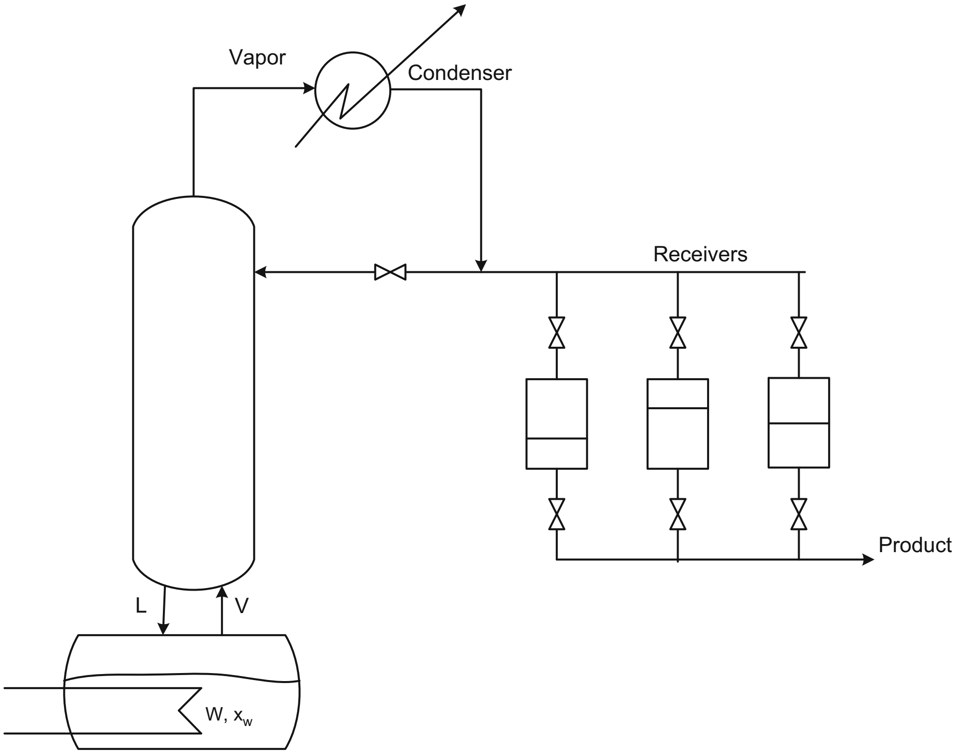


Figure 10-59 Schematic diagram of a multistage batch distillation.

Applying the material balance on component A

Amount of A initially present in the still pot = Amount of A left in the still pot Amount of A + vaporized

$$xW = (x - dx)(W - dW) + y\,dW \qquad (10\text{-}296)$$

$$xW = xW - x\,dW - W\,dx + dx\,dW + y\,dW \qquad (10\text{-}297)$$

Neglecting the higher order (dx dW), Equation 10-297 becomes:

$$x\,dW = -W\,dx + y\,dW \qquad (10\text{-}298)$$

Rearranging Equation 10-298 gives:

$$(y - x)\,dW = W\,dx \qquad (10\text{-}299)$$

Rearranging Equation (10-299) and integrating from the initial charge condition of W_o and x_{wo} to W and x_w after distillation gives:

$$\int_{Wo}^{W} \frac{dW}{W} = \int_{x_{wo}}^{x_w} \frac{dx}{y - x} \qquad (10\text{-}300)$$

$$\ln\left(\frac{W}{Wo}\right) = \int_{x_{wo}}^{x_w} \frac{dx}{y - x} \qquad (10\text{-}301)$$

or

$$\ln\left(\frac{W}{Wo}\right) = -\int_{x_w}^{x_{wo}} \frac{dx}{y - x} \qquad (10\text{-}301a)$$

where

x = composition of A in the binary liquid mixture, mole fraction

x_{wo} = initial composition of liquid in the still, mole fraction

x_w = final composition of liquid in the still, mole fraction

y = composition of vapor of A, mole fraction

W_o = moles of component A in the still pot before distillation

W = moles of component A after distillation

Equations 10-301 and 10-301a are called the Rayleigh equations. Although the time, t does not appear explicitly in the derivation of Equation 10-301 or 10-301a, it is present implicitly since, W, w_x and x_{wo} are all time-dependent.

In a total condenser, where x and y are now in equilibrium, the equilibrium expression of Equation 10-301a can be integrated graphically, analytically or numerically by:

$$\ln\left(\frac{W}{W_o}\right) = -\int_{x_w}^{x_{wo}} \frac{dx}{y-x} = -\int_{x_w}^{x_{wo}} \frac{dx}{[f(x)-x]} \qquad (10\text{-}302)$$

An alternative form of Equation 10-301 is as follows.

At any time during the course of batch distillation, there are L moles of liquid of composition x with respect to A in the still pot. If in time δt, an amount of dD moles of distillate of mole fraction y* in equilibrium with the liquid is vaporized, then the following material balances apply:

Operation	Total material	Component A
Moles in	0	0
Moles out	dD	$y^*\,dD$
Moles accumulated	dL	d (L x)
Accumulation = In - Out	$0 - dD = dL$	$0 - y^*\,dD = d(L\,x)$
	i.e. $- dD = dL$	i.e. $-y^*\,dD = L\,dx + x\,dL$

Substituting –dD = dL in the material balance for component A gives:

$$y^*\,dL = L\,dx + x\,dL \qquad (10\text{-}303)$$

Rearranging Equation 10-303 gives:

$$\frac{dL}{L} = \frac{dx}{y^* - x} \qquad (10\text{-}304)$$

Integrating Equation 10-304 between F, x_F, moles of feed and composition charge initially in the still respectively, and W moles of residual liquid of composition x_w after distillation is carried out for a certain period.

Equation 10-304 becomes:

$$\int_{W}^{F} \frac{dL}{L} = \int_{x_w}^{x_F} \frac{dx}{y^* - x} \qquad (10\text{-}305)$$

or

$$\ln\left(\frac{F}{W}\right) = \int_{x_w}^{x_F} \frac{dx}{y^* - x} \qquad (10\text{-}306)$$

The integrating procedure for Equation 10–302 or Equation 10–306 is:

1. Plot x–y equilibrium curve.
2. At a series of x values, find y – x.

3. Plot $1/(y-x)$ .vs. x or fit it to an equation.
4. Graphically or numerically integrate from x_{wo} to w_x as shown in Figure 10–60
5. From Equation 10-301, find the final charge of material in the still pot.

$$W = W_o \exp\left[\int_{x_{wo}}^{x_w} \frac{dx}{(y-x)}\right] \tag{10-307}$$

$$= W_o e^{Area} \tag{10-308}$$

6. The average distillate concentration of component A can be determined from the mass balances as follows:

   For a binary batch distillation, the mass balance around the entire system for the total batch operation is:

$$F = W + D \tag{10-309}$$

Component balance on A is:

$$F\, x_F = W\, x_w + D\, x_{D,avg} \tag{10-310}$$

Combining Equations (10-309) and (10-310), the average distillate concentration of component A is:

$$x_{D,avg} = \frac{F\, x_F - W\, x_w}{(F-W)} \tag{10-311}$$

$$D = F - W \tag{10-312}$$

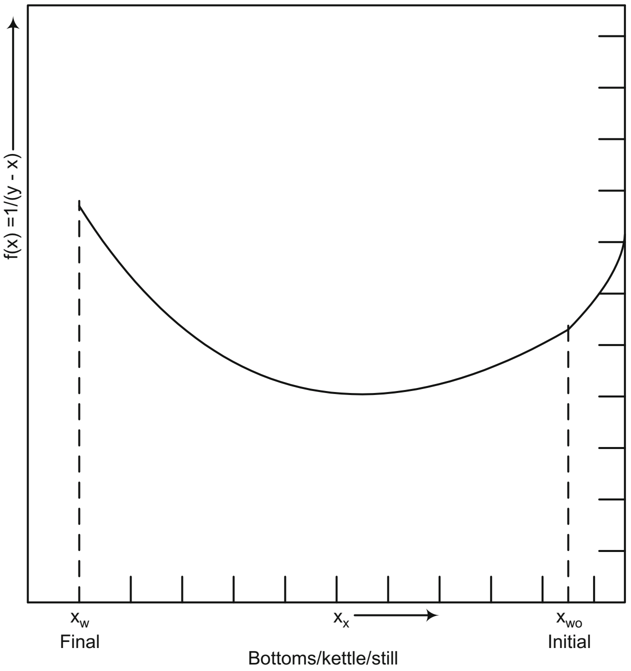


Figure 10-60 Graphical integration of Rayleigh's equation.

The area under the curve of $1/(y-x)$ vs. x can be integrated numerically by Simpson's rule (see Appendix H). If the ordinate in Figure 10–60 is called f(x), then the form of Simpson's 1/3 rule is:

$$A_{curve} = \frac{h}{3}\Big[f_o + 4(f_1 + f_3 + f_5 + f_7 + f_9 + f_{n-1}) + 2(f_2 + f_4 + f_6 + f_8 + f_{n-2}) + f_n\Big] \tag{10-313}$$

where

h = step size

x_{in} = initial component, mole fraction

$x_{fin.}$ = final component, mole fraction

$$f(x_o) = 1/(y^* - x_{in.})$$

$$f(x_n) = 1/(y^* - x_{fin.})$$

y^* = mole fraction in equilibrium with the liquid being vaporized.

Equation (10-301) is easily integrated only when pressure is constant, temperature change in the still is relatively small (close-boiling mixture) and K-values are composition dependent. Then $y = Kx$, where K is approximately constant, Equation (10-300) becomes:

$$\ln\left(\frac{W}{W_o}\right) = \frac{1}{K-1}\ln\left(\frac{x}{x_o}\right) \tag{10-314}$$

For a binary mixture, where the relative volatility α is assumed constant over the concentration range $x_F - x_w$ then.

$$y = \frac{\alpha\, x}{1 + (\alpha - 1)x} \tag{10-48}$$

Substituting Equation (10-48) into Equation (10-300) gives:

$$\int_F^W \frac{dW}{W} = \int_{x_F}^{x_w} \frac{dx}{\left[\dfrac{\alpha x}{(1-\alpha)\,x + 1} - x\right]} \tag{10-315}$$

$$\ln\left(\frac{W}{F}\right) = \frac{1}{\alpha - 1}\ln\left[\frac{x_w(1-x_F)}{x_F\,(1-x_w)}\right] + \ln\left(\frac{1-x_F}{1-x_w}\right) \tag{10-316}$$

where

D = instantaneous distillate rate, mol/h

F = moles of feed

W = moles of liquid left in still.

x_F = composition of liquid in the feed, mole fraction.
$x = x_W$ = composition of liquid left in still, mole fraction
$y = y_D = x_D$ = instantaneous distillate composition, mole fraction.

Example 10-27

A binary mixture of ethanol and water at 101.3 kPa (1 atm) is charged to a batch still. The initial charge is 100 kmol of ethanol-water mixture at 18 mole per cent and the mixture is to be reduced to a minimum ethanol concentration of 6 mol per cent. Determine the following:

1. The amount of ethanol in the leftover after distillation.
2. The amount of ethanol in the distillate.
3. The distillate composition.

Solution

From the vapor–liquid equilibrium data (VLE) (see Figure K-1b in appendix-K). Table 10-28 shows the equilibrium data of ethanol-water system shown. Plotting $1/(y^* - x)$ versus x and integrating between the limits of 0.06 and 0.18 for x, the area under the curve (Figure 10-61) is found, using the Excel spreadsheet (Example 10-27.xls), to be 0.358. Then, ln (F/W) = 0.358, from which W = 100/1.43 = 69.91 kmol. The liquid remaining in the still consists of (69.91)(0.06) = 4.19 kmol of ethanol and 65.72 kmol of water. By material balance, the total distillate must contain (18.0 – 4.19) = 13.81 kmol of ethanol and (82 – 65.72) = 16.28 kmol of water. The total distillate is 30 kmol, and the distillate composition is 13.81/30 = 0.459 mole fraction of ethanol.

An Excel spreadsheet (Example 10-27.xls) has been developed for Example 10-27, and snap-shots of the calculation are shown in Figures 10-61a–d.

A summary of the Excel spreadsheet calculations is shown in the Table 10-29.

Table 10-28 Vapor–Liquid Equilibrium Data of Ethanol-Water Mixture.

x	y^*	$y^* - x$	$f = 1/(y^* - x)$	No. of ordinate (n)
$0.18 = x_{in}$	0.5169	0.3369	2.968	0
0.16	0.5022	0.3422	2.922	1
0.14	0.4853	0.3453	2.896	2
0.12	0.4642	0.3442	2.905	3
0.10	0.4379	0.3379	2.959	4
0.08	0.4052	0.3252	3.075	5
$0.06 = x_{fin}$	0.3529	0.2929	3.414	6

10.34.2 Differential Distillation; Simple Batch, No Trays or Packing; Binary Mixtures, No Reflux

For systems of high (above approximately 3.0) constant relative volatility the Raleigh equation can be expressed:

$$\ln\left(\frac{B_{T1}}{B_{T0}}\right) = \frac{1}{\alpha - 1}\ln\left[\frac{(1 - x_0)\,x_1}{(1 - x_1)\,x_0}\right] + \ln\left[\frac{(1 - x_0)}{(1 - x_1)}\right] \tag{10-317}$$

or

$$\ln\left(\frac{B_{T1}}{B_{T0}}\right) = \int_{x_0}^{x_1} \frac{dx}{y^* - x_1} \tag{10-318}$$

The above Equation 10-318 requires graphical integration or numerical using Simpson's rule, where

B_{T0} = total moles of liquid in bottom of still at start, T_0
B_{T1} = total moles of liquid in bottom of still at time, T_1
x_0 = mol fraction of component, i, in bottoms B_{T0} at start, time T_0
x_l = mol fraction of component, i, bottoms B_T, at time T
α = relative volatility of light to heavy components
y^* = equilibrium value of x_i

The condensed vapor is removed as fast as it is formed.

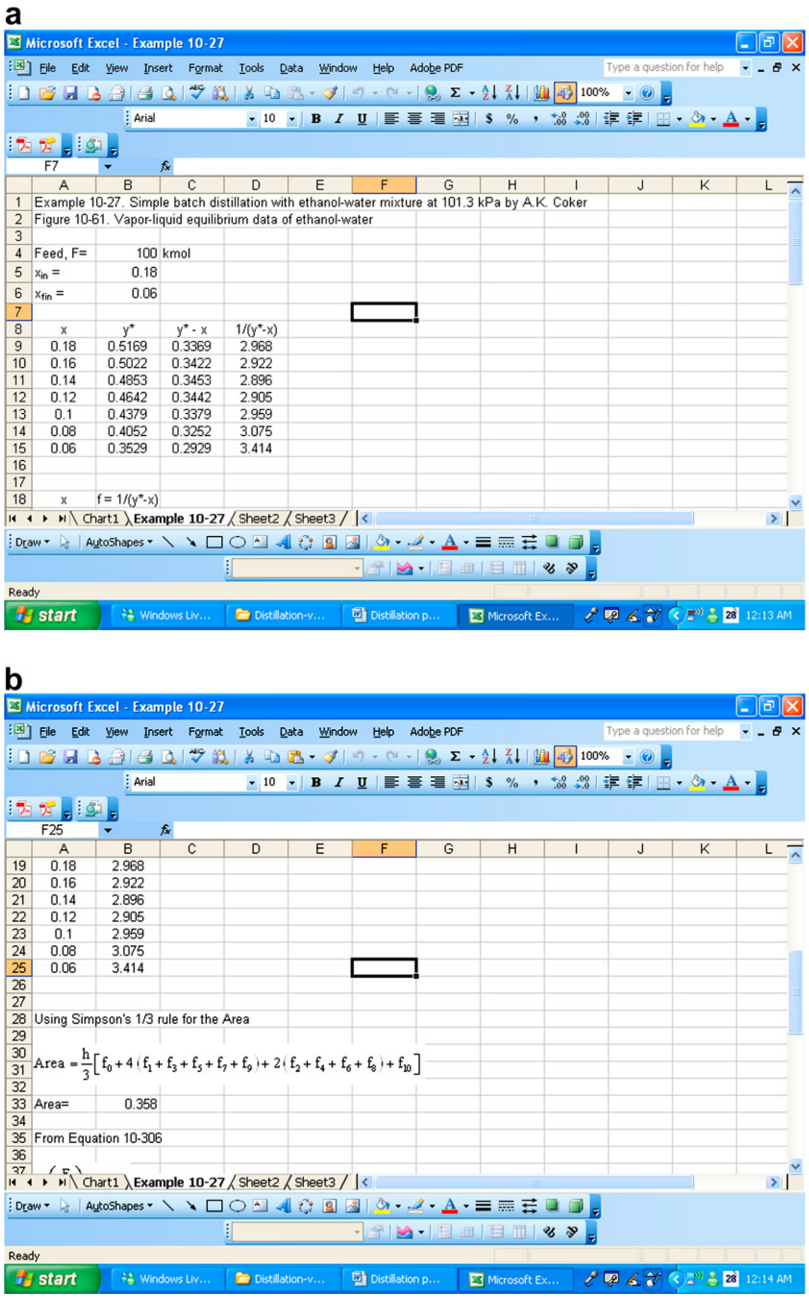
The results of either relation allow the plotting of an instantaneous vapor composition for given percentages of material taken overhead.

The outline of Teller [70, 133] suggests using the differential form above. The vapor is assumed to be in equilibrium with the liquid.

1. Calculate or obtain an x-y equilibrium diagram for the light component.
2. Select values of x_i and read equilibrium values of y_i from Step 1 above.
3. Calculate values of $1/(y_i - x_i)$ and tabulate.
4. Plot curve of $1/(y_i - x_i)$ versus x_i; see Figure 10-60, graphical integration by Simpson's rule.
5. From the plot of Step 4, determine the area under the curve from initial bottoms concentration of x_{i0} mol fraction at beginning of distillation down to the final lower concentration of x_{i1} in bottoms.
6. The area from Step 5 represents

$$\ln(W/W_i) \text{ or } \ln(W_{i1}/W_{i0}) \text{ or } (B_{T0}/B_T)$$

where
W_{i1} = the final kettle/still pot content, mols
W_{i0} = the initial kettle/still pot content, mols



	A	B	C	D
1	Example 10-27. Simple batch distillation with ethanol-water mixture at 101.3 kPa by A.K. Coker			
2	Figure 10-61. Vapor-liquid equilibrium data of ethanol-water			
3				
4	Feed, F=	100	kmol	
5	x_{in} =	0.18		
6	x_{fin} =	0.06		
7				
8	x	y*	y* - x	1/(y*-x)
9	0.18	0.5169	0.3369	2.968
10	0.16	0.5022	0.3422	2.922
11	0.14	0.4853	0.3453	2.896
12	0.12	0.4642	0.3442	2.905
13	0.1	0.4379	0.3379	2.959
14	0.08	0.4052	0.3252	3.075
15	0.06	0.3529	0.2929	3.414
16				
17				
18	x	f = 1/(y*-x)		

	A	B
19	0.18	2.968
20	0.16	2.922
21	0.14	2.896
22	0.12	2.905
23	0.1	2.959
24	0.08	3.075
25	0.06	3.414
26		
27		
28	Using Simpson's 1/3 rule for the Area	
29		
30–31	$\text{Area} = \frac{h}{3}\left[f_0 + 4(f_1 + f_3 + f_5 + f_7 + f_9) + 2(f_2 + f_4 + f_6 + f_8) + f_{10}\right]$	
32		
33	Area=	0.358
34		
35	From Equation 10-306	
36		

Figure 10-61a–b Snap-shot of a batch distillation calculation for a binary ethanol-water system.

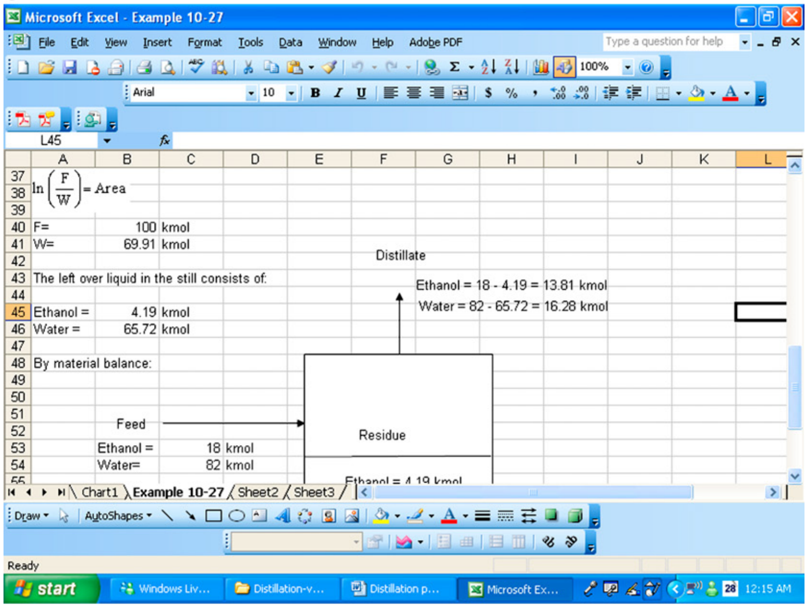
or, for constant relative volatility for a binary mixture for a simple still/kettle/bottoms pot with no internal packing or trays, a direct analytical solution is [133]:

$$\ln\left(\frac{W_1}{W_{io}}\right) = \frac{1}{\alpha - 1}\ln\left[\frac{x_W(1 - x_i)}{x_i(1 - x_W)}\right] + \ln\left[\frac{(1 - x_i)}{(1 - x_W)}\right] \tag{10-319}$$

where

W_1 = content of kettle at any time, mols
W_{io} = initial content of kettle, mols
W_o = mols liquid initially in still or kettle
α = relative volatility
D = distillate rate, mols/h
L = liquid rate, mols/h
V = vapor rate, mols/h
x = mol fraction of a specific component in liquid
y = mol fraction of a specific component in vapor
θ = time, hours

c



$\ln\left(\frac{F}{W}\right) = \text{Area}$

F= 100 kmol
W= 69.91 kmol

The left over liquid in the still consists of:

Ethanol = 4.19 kmol
Water = 65.72 kmol

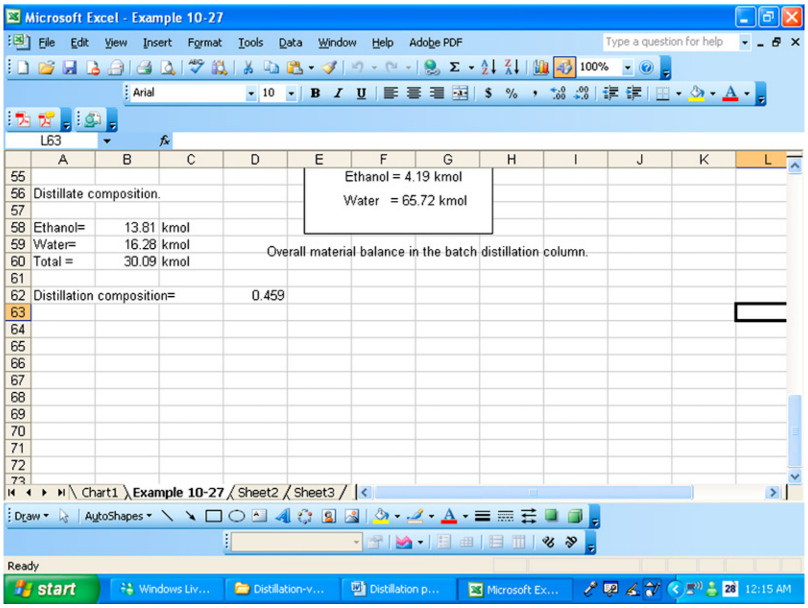
By material balance:

Distillate
Ethanol = 18 - 4.19 = 13.81 kmol
Water = 82 - 65.72 = 16.28 kmol

Feed
Ethanol = 18 kmol
Water= 82 kmol

Residue
Ethanol = 4.19 kmol

d



Ethanol = 4.19 kmol
Water = 65.72 kmol

Distillate composition.

Ethanol= 13.81 kmol
Water= 16.28 kmol
Total = 30.09 kmol

Overall material balance in the batch distillation column.

Distillation composition= 0.459

Figure 10-61c-d Snap-shot of a batch distillation calculation for a binary ethanol-water system.

Table 10-29 A Summary of the Results of Example 10-27.

Composition	Feed, kmol	Residue, kmol	Distillate, kmol
Ethanol	18	4.19	13.81
Water	82	65.72	16.28
Total	100	69.91	30.09

Subscripts:

D = distillate related
i, or o = initial
l = final or later
w = relating to bottoms (kettle/still pot)

7. For each value of x, and the values of (B_{To}/B_{TI}) found above, calculate $\frac{B_{T0} - B_{T1}}{B_{T0}}(100)$, the percent of material taken overhead.

8. A plot of the distillate composition, y versus percent distilled (from Step 7) will show the value of the instantaneous vapor composition.

The usual form of the Raleigh equation [130] is for the conditions of a binary simple differential distillation (no trays or packing), no reflux, but with constant boilup.

$$\ln\left(\frac{W_0}{W_1}\right)=\int_{x_1}^{x_0}\frac{dx}{(y-x)} \tag{10-320}$$

For a binary mixture, the values of x and y can be obtained from the equilibrium curve. Select values of x_l and read the corresponding value of y from the equilibrium curve. Tabulate values of $1/(y-x)$, and plot versus x_l, resulting in a graphical integration of the function $dx/(y-x)$ [130] between x_o and x_l. This system would have no column internals and no reflux.

10.34.3 Simple Batch Distillation: Constant α, with Trays or Packing, Constant Boilup, and with Reflux [129] Using x-y Diagram

The system material balance, from Treybal [129], using a heated kettle and distillation column following a McCabe-Thiele diagram, using reflux, but having only a batch (kettle) charge:

$$F = D + W \tag{10-321}$$

$$Fx_F = Dx_D + Wx_W \tag{10-322}$$

$$D = F(x_F - x_W)/(x_D - x_W) \tag{10-323}$$

G = boilup overhead, mol/hr

L = mols reflux in the column

D = overhead receiver contents, mols

Starting with an empty overhead receiver, the time θ_1 to condense D mols of vapor to fill the receiver, when the vapor boilup rate is G mols/hr.

$\theta_l = D/G$ during which time the receiver is filling and there is no reflux and the kettle mixture follows a Raleigh distillation [129]. Under this condition, when the distillate receiver just becomes full, let the composition of the kettle contents be x_{Si}, then

$$\log\left(\frac{Fx_F}{Wx_{Si}}\right)=\alpha\log\left[\frac{F(1-x_F)}{W(1-x_{Si})}\right] \tag{10-324a}$$

or

$$\frac{(1-x_{Si})^{\alpha}}{x_{Si}}=\left(\frac{F}{W}\right)^{\alpha-1}\frac{(1-x_F)^{\alpha}}{x_F} \tag{10-324b}$$

Equation (10-324b) may be solved for x_{Si} by trial and error.

After this reflux runs down the column the desired lighter components leave, and a desired residual composition is left, following the Raleigh equation to express the material balance.

Most batch distillations/separations are assumed to follow the constant relative volatility vapor–liquid equilibrium curve of:

$$y=\frac{\alpha x}{1+x(\alpha-1)} \tag{10-48}$$

After filling the receiver, reflux runs down the column at the same molar rate as the vapor back up (L = G). The operating line has a slope of 1.0. Then there are "n" plates/trays between composition x_p and x_l (the mol fraction in distillate). As the distillation continues, the operating line moves closer to the 45° line of the diagram, and x_l and x_p (and x_S) become richer and leaner, respectively, until at the end x_l becomes x_D and x_S becomes x_W. The required time is θ_2 hours.

During a batch distillation at constant pressure, the temperature rises to accomplish the separation as the more volatile component's concentration is reduced in the bottoms (kettle) or residue.

For a batch differential distillation where no reflux is used, there is only boilup of a mixture of the desired lighter component, which leaves the kettle, and a desired residual bottoms composition is left in the kettle. This type of distillation follows the Raleigh equation for expression of the material balance. However, while simple, not having tower packing or trays or reflux is not useful in many industrial applications due to the low purities and low yields involved. Repeated charges of the distillate back to the kettle and redistilling will improve overhead purity.

The minimum number of plates required will occur when the operating line coincides with the 45° diagonal [129]. But this corresponds for an infinite time for separation:

$$N_{min}+1=\frac{\log\left(\frac{x_D}{1-x_D}\right)\left(\frac{1-x_W}{x_W}\right)}{\log\alpha} \tag{10-325}$$

For an operating line with a slope of unity, from Smoker's equation:

$$N=\frac{\log\left\{x_1'\left[1-\frac{c(\alpha-1)x_p'}{\alpha-c^2}\right]\Big/x_p'\left[1-\frac{c(\alpha-1)x_1'}{\alpha-c^2}\right]\right\}}{\log(\alpha/c^2)} \tag{10-326}$$

Equilibrium curve:

$$y=\frac{\alpha x}{1+(\alpha-1)x} \tag{10-48}$$

Operating line: $y = x + b$ (see Reference 129 for diagram). They intersect at $x = k$.

Then,

$$y = \frac{\alpha k}{1+(\alpha-1)k} = k + b, \text{when } x = k \tag{10-327}$$

where

$b = (\alpha k/c) - k$
$c = 1 + (\alpha - 1)k$

Then,

$$x_p + b = \frac{\alpha\, x_S}{\left[1+(\alpha-1)x_S\right]} \tag{10-328}$$

Coordinates:

$x_1' = x_1 - k$
$y' = y - (b + k)$
$x_p' = x_p - k$

For the more volatile component at any time:

$$x_1 = (Fx_F - Wx_S)/D \tag{10-329}$$

$b = y_S - x_p$

$$\theta_2 = (W/G)\int_{x_W}^{x_{Si}} (dx_S/b), \text{ time, hrs for refluxed distillation} \tag{10-330}$$

10.34.4 Fixed Number Theoretical Trays: Constant Reflux Ratio and Variable Overhead Compositions

Raleigh equation from [130]:

$$\ln(W_1/W_o) = \int_{x_{W_o}}^{x_W} dx_W/(x_D - x_W) \tag{10-331}$$

where

W_o = mols liquid mixture originally charged to still
W_1 = mols final content in still
x_{W_o} = initial mol fraction of more volatile component in mixture
x_W = composition of liquid in still, mol fraction
x_i = mol fraction of component in liquid phase
x = mol fraction of more volatile component in liquid
x_D = instantaneous mol fraction of the component in the distillate that is leaving the condenser at time θ.
x_{Di} = initial distillate composition, mol fraction
x_i = mol fraction component of i in liquid phase
y_i = mol fraction of component of i in the vapor phase
D = mols of distillate per unit time, or mols of distillate at time θ, or distillate drawoff
K_A, K_B = equilibrium vaporization constants for A and B, respectively
L = mols of liquid per unit time, or liquid return to column
P = distillate drawoff percentage = $100/(R + 1)$
P_i = pure component vapor pressure, mm Hg
R = reflux ratio (liquid returned to column)/(distillate drawoff); subscripts indicate number of plates, R_{min}
V = vapor rate up column, mols per unit time
θ = time

10.34.5 Batch Distillation with Constant Reflux Ratio, Fixed Number of Theoretical Plates in Column, Overhead Composition Varies

In this mode of operation, the column has a fixed number of theoretical trays that operates at constant reflux ratio. The reflux is set to a predetermined value, maintained throughout the run. As long as the still composition is changing in the batch, so the composition of the overhead product (i.e. distillate) continuously changes. The column holdup is assumed to be negligible, and progress is illustrated in Figure 10-62. The figure shows the profiles of the compositions in the distillate and reboiler with respect to total mols distilled. The mole fraction of the lighter component in the reboiler (still-pot) falls off steadily and continuously with the increase of total mols distilled (i.e. as long as the distillation process continues). The profiles of the curves are strongly influenced by factors such as the degree of relative volatility, the predetermined value of the reflux ratio and the number of theoretical plates. Distillation is continued until the average distillate composition attains the desired value. The overhead product is then diverted to another receiver and an intermediate cut is withdrawn until the leftover liquor in the still-pot meets the required specification. This intermediate cut is normally added to the next batch.

At any time θ [131]:

$$\ln(W_1/W_o) = \ln\left(\frac{S}{S_o}\right) = \int_{x_{S_o}}^{x_S} \frac{dx_S}{(x_D - x_S)} = \int_{x_{W_o}}^{x_W} \frac{dx_W}{(x_D - x_W)} \tag{10-332}$$

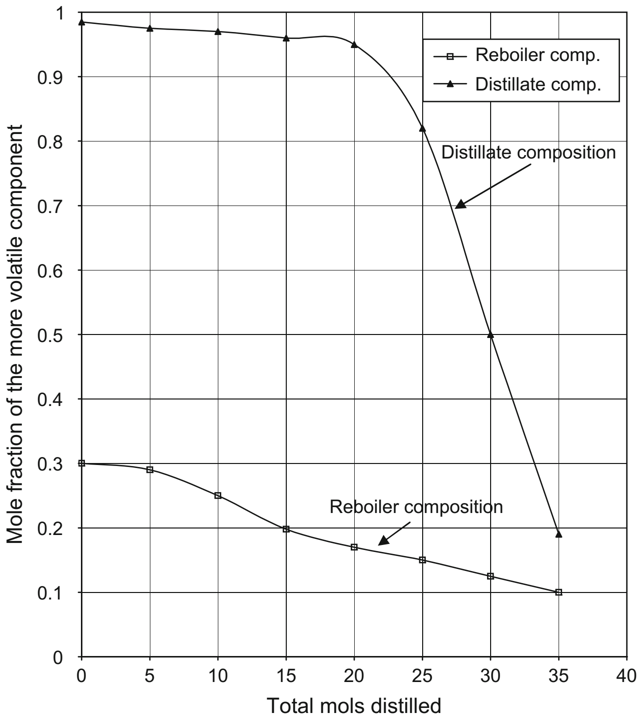


Figure 10-62 A typical example in a binary batch distillation at a constant reflux ratio showing the variation in distillate and reboiler compositions with the amount distilled.

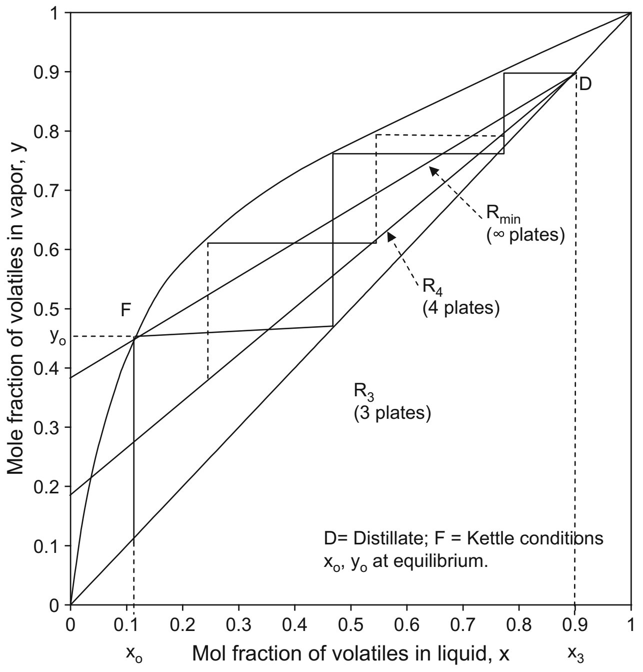


Figure 10-63 Variable reflux ratio at various theoretical plates to achieve a specified separation from x_0 kettle to x_3 distillate overhead. Note, all reflux ratios shown yield same separation, but require different numbers of theoretical places. D = Distillate; F = Kettle conditions x_0, y_0 at equilibrium.

where

S_o = mols initially charged to still
S = mols in mixture in still at time θ
x_D = instantaneous mol fraction of a more volatile component in the distillate entering the receiver at time θ
x_{so} = mol fraction of a more volatile component in the initial still charge
x_s = mol fraction of a more volatile component in the still after time θ
D = mols of distillate at time θ

To solve the right side of the Raleigh-like equation, integrate graphically by plotting or numerically:

$$1/(x_D - x_S) \text{ vs. } x_S$$

The area under the curve between x_{so} and x_s is the value of the integral. Plot the equilibrium curve for the more volatile component on $x-y$ diagram as shown in Figure 10-63. Then, select values of x_D from the operating line having the constant slope, L/V. From equation

$[L_{n+1} = L_n + D$

are drawn from the intersection of x_D and the diagonal. Then from these L/V lines, draw steps to the equilibrium curve, the same for a binary McCabe-Thiele diagram [130]. The proper operating line is the one that requires the specified number of theoretical plates (stages) in moving stepwise down from the initial desired distillate composition to the composition of the mixture initially charged to the kettle (or pot or still). The kettle acts like and is counted as one theoretical stage or plate. The intersection of the last horizontal step (going down the column) from x_D with the equilibrium curve is the still or kettle bottoms composition, x_W, at the completion of this batch distillation. Using the system material balance and the constant reflux ratio used (L/V), calculate the total vapor generated by the kettle. The heat duty of the kettle can be calculated using the appropriate latent and sensible heat of the mixture components.

For a constant reflux ratio, the value can be almost any ratio; however, this ratio affects the number of theoretical plates and, consequently, actual trays installed in the rectification section to achieve the desired separation. Control of batch distillation is examined in Reference 134.

The internal reflux ratio is L/V, and is the slope of the operating line. The external reflux is [133]:

$R = L/D$
and
$V = L + D$
$V/L = L/L + D/L = 1 + 1/R = (R + 1)/R$

Then
L/V = R/(R + 1)
and
R = (L/V)/[l − (L/V)], see Figure 10-63.

10.34.6 Minimum Reflux Ratio

Point F on Figure 10-63 represents conditions in the kettle or still with x_i, y_i, or x_o, y_o. Line DF represents slope of the operating line at the minimum reflux ratio. The step-wise development from point D cannot cross the intersection, F, where the slope intersects the equilibrium line, and leads to an infinite condition, as point F is approached. Thus, an infinite number of theoretical trays/stages is required, and thus a minimum reflux requirement. Minimum reflux is calculated [133]:

$$(L/V_{min}) = (y_D - y_i)/(x_D - x_i);\ (\text{see Figure } 10\text{–}63) \tag{10-333}$$

Note that $y_D = x_D$ on the diagonal of the equilibrium plot, and y_i and x_i are points of intersection with the equilibrium curve. For an abnormal equilibrium curve (as compared to regular or normal shape) see Figure 10-64.

Once the minimum reflux ratio has been established (which is not an operating condition), then a practical reflux ratio from 1.5 – 10 times the minimum can be selected. The larger the reflux value down the column, the more vapor has to be boiled up, and the greater will be the required column diameter; the column height will however be less. An economic balance must therefore be established.

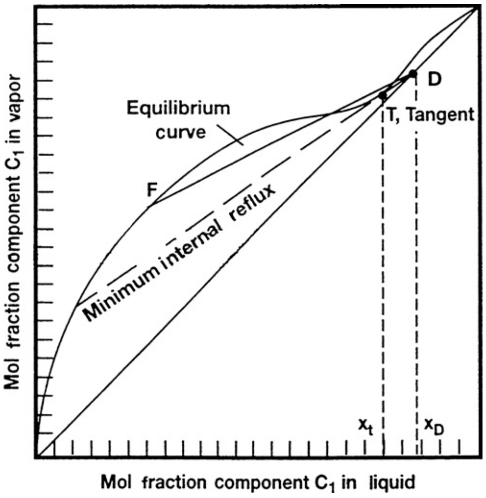


Figure 10-64 Minimum reflux for abnormal equilibrium curve for batch operation, constant reflux ratio.

Solving the typical Raleigh equation:

$$\ln\left(\frac{W_i}{W}\right) = \int_{x_i}^{x_W} \frac{dx_W}{(x_D - x_W)} \tag{10-334}$$

Calculating W from Equation 10-334, an overall component balance gives the average distillate composition.

$$W_i x_i - W x_w = D x_{Davg} = (W_i - W) x_{Davg} \tag{10-335}$$

The average distillate composition will be:

$$x_{Davg} = \frac{W_i x_i - W x_W}{(W_i - W)} \tag{10-335a}$$

A trial-and-error calculation is necessary to solve for W until a value is found from the ln (W_i/W) equation above that matches the x_{Davg} which represents the required overhead distillate composition. By material balance:

$$V = L + D, \text{ and } R = L/D$$
$$V/D = L/D + 1 = R + 1$$
$$D = V/(R+1)$$

$$W = W_i - D\theta = W_i - \frac{V\theta}{R+1} \tag{10-336}$$

$$\text{Let } Q = \int_{x_{W_i}}^{x_W} \frac{dx_W}{(x_D - x_W)} \tag{10-337}$$

Then from Equations 10-334 and 10-336:

$$e^Q = \frac{W_i}{W_i - \dfrac{V\theta}{(R+1)}} \tag{10-338}$$

$$\theta = (R+1)\left[\frac{W_i}{V}\left(\frac{e^Q - 1}{e^Q}\right)\right] \tag{10-339}$$

An alternative equation in determining the time (hours) for distillation is:

$$\theta = \frac{(W_i - W)}{D} = \frac{(R+1)}{V}(W_i - W) \tag{10-340}$$

Referring to Figure 10-65, the constant internal reflux ratio, L/V is shown for several selected values of reflux ratios [131]. Only one can be used at a time for actual operation. Starting at the intersection of the diagonal line (distillate composition), step off the theoretical plates. For example, from Figure 10-65 at constant reflux, using operating line No.1, starting at $x_D = 0.95$, for one theoretical plate, the bottoms composition in component A would be approximately $x_w = 0.885$; then going down one more plate at the same L/V,

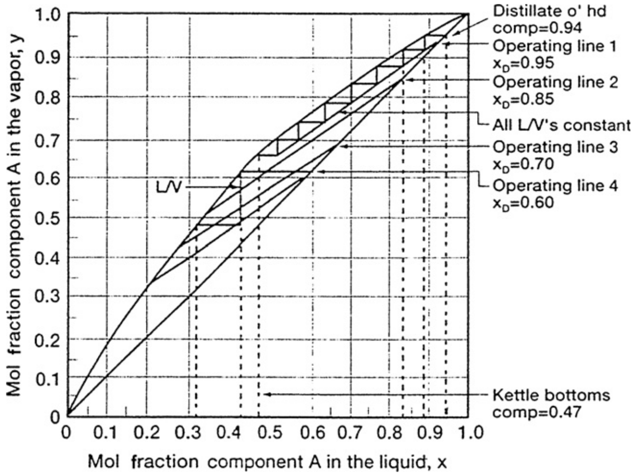


Figure 10-65 Batch distillation: constant reflux ratio after McCabe-Thiele diagram. Revised/adapted and used by permission, Schweitzer, P. A., Handbook of Separation Techniques for Chemical Engineers, McGraw-Hill Book Co. (1979); also reprinted by special permission, Chem. Eng. Jan. 23 (1961), p. 134, © 1961, by McGraw-Hill, Inc. New York.

a second theoretical plate yields a bottoms of x_B or $x_w = 0.83$, still yielding $x_D = 0.95$. If the L/V for the operating line No.4 is used (same slope as line No.1), then the expected performance would be $x_D = 0.60$, and after one theoretical plate, the bottoms would be 0.41 at the same reflux ratio as the first case; and for $x_D = 0.60$ and two theoretical plates, $x_w = 0.31$, where

D = Distillate rate, moles/hr.
L = Liquid flow rate, moles/hr.
V = Vapor flow rate, moles/hr.
x = Mole fraction of substance in liquid.
y = Mole fraction of substance in vapor
W = Bottom or pot liquors
θ = Time, hrs.

Subscript

D = Distillate
i = Initial condition
w = Pot liquors.

Calculation Procedure

1. Plot the vapor–liquid equilibrium (VLE) diagram of the lighter component of the mixture on the x–y coordinate.
2. Draw the 45° line (x = y line).
3. Select several values of x_D and draw operating lines having the same slope (L/V = constant) through the point of intersection of x_D and the 45° line (Figure 10-65).
4. Draw the steps between the operating line and equilibrium curve, as in the McCabe-Thiele method. This technique simultaneously solves the operating line and equilibrium equations.
5. Select the correct line. It is the line that requires the specified number of theoretical stages in going from the initial distillation composition to the composition of the mixture initially charged to the still.
6. Count the still-pot as one theoretical stage.
7. The intersection of the last horizontal step (i.e. moving down from x_D) with the vapor-liquid equilibrium curve is the composition x_w of the liquid in the still.

If the internal reflux ratio (L/V) is specified, the initial distillate composition, x_D represents the composition of the first drop of distillate. In such cases, the usual procedure for determining the initial distillate composition is trial and error. Once x_D is determined, successively lower distillate compositions are arbitrarily chosen and tabulated beside the corresponding composition of the liquid mix in the still. When the still concentration is reduced to the desired value, the distillation is stopped.

Example 10-28

A batch containing 500 kmol of an ethanol-water mixture containing 50 mol % ethanol is to be distilled at 1.013 bara. The rate of vaporization is 80 kmol/h and the product specification is 80 mol % ethanol having a liquid vapor ratio (L/V) of 0.78. If the reflux ratio is 3.0, and the system has 6 theoretical plates including the pot. Calculate the following:

1. The kmol of product that will be obtained.
2. The average or accumulated distillate composition.
3. The time for distillation process.

Solution

Figure 10-66 is a schematic diagram of a multistage batch distillation.

Example 10-28 is solved by trial and error, i.e.

1. Select several arbitrary values of x_D .
2. Locate them on the 45° line.
3. From each point, draw an operating line at a slope of 0.78
4. Step off 6-steps on each such line.
5. At the end of the 6th step, find the equilibrium value of the bottoms.

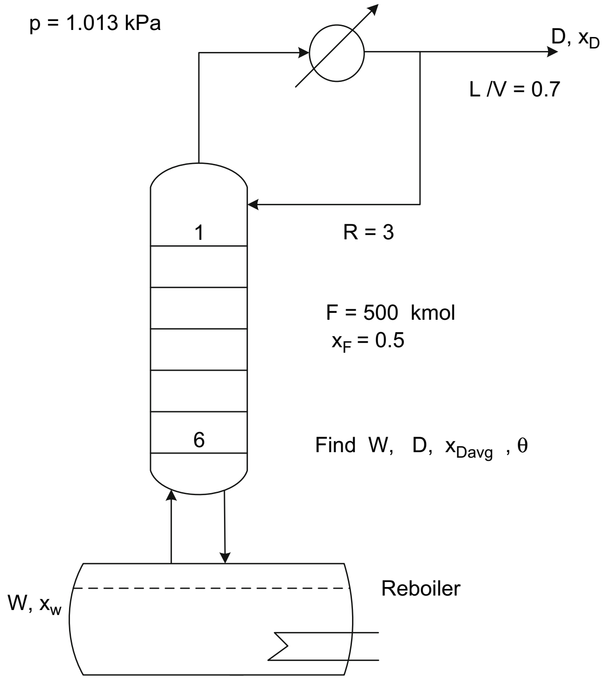


Figure 10-66 Multistage batch distillation.

6. Integrate

$$\int_{x_i}^{x_W} \frac{dx_W}{(x_D - x_W)}$$

between $x_i = 0.5$ and various lower limits of x_W (bottoms).

7. Determine W from:

$$\ln\left(\frac{W_i}{W}\right) = \int_{x_i}^{x_W} \frac{dx_W}{(x_D - x_W)}$$

8. Calculate the average distillation composition.

$$x_{Davg} = \frac{W_i\, x_i - W\, x_W}{(W_i - W)} \tag{10-335}$$

9. Check whether the calculated value of x_{Davg} is the same as (or approximates to) the required product specification.

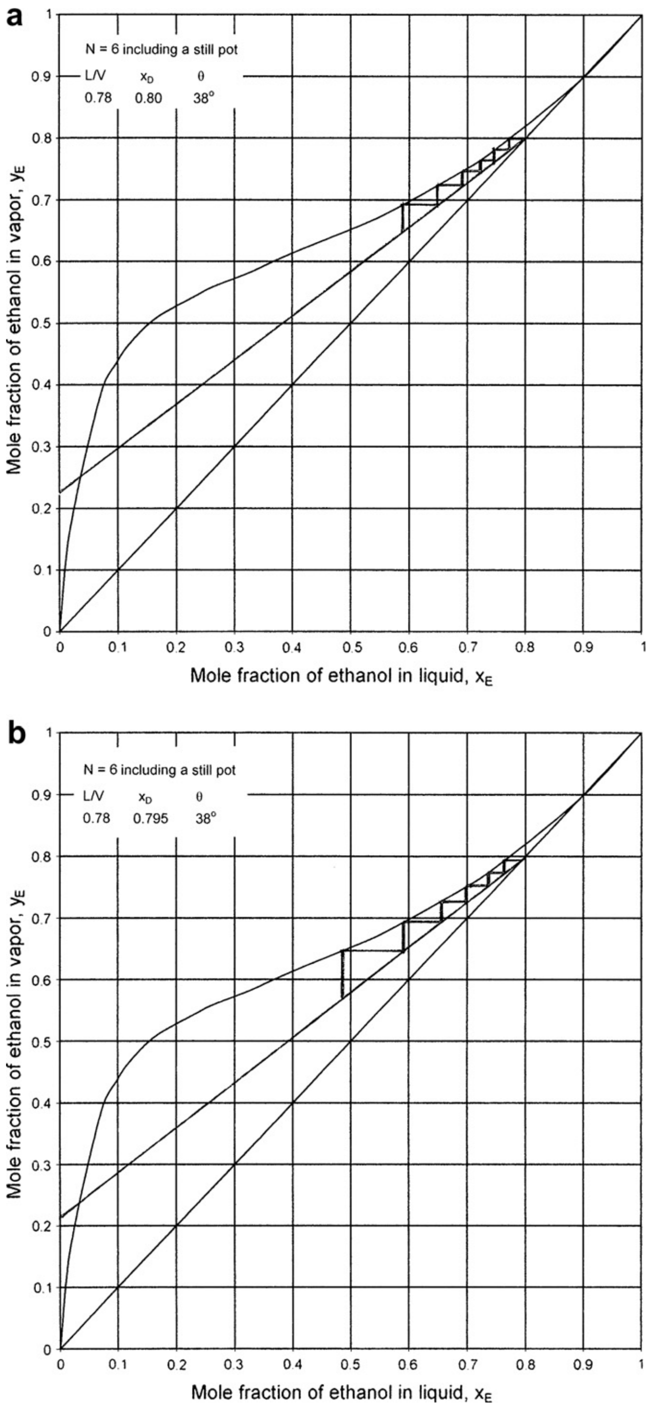


Figure 10-66 (a). Graphical estimation of liquid composition at $x_D = 0.80$ and $L/V = 0.78$ in Example 10-28. (b). Graphical estimation of liquid composition at $x_D = 0.795$ and $L/V = 0.78$ in Example 10-28.

Using the vapor–liquid equilibrium diagram of the ethanol-water system, plot an x-y diagram, and draw a number of operating lines at varying x_D values on the 45°– line with a slope (L/V) of 0.78. Step-off six plates on each to find the equilibrium value of the bottoms product. Figures 10-66a–66f show McCabe-Thiele plots at varying x_D with slope $L/V = 0.78$, and Table 10-30 shows the results of these plots.

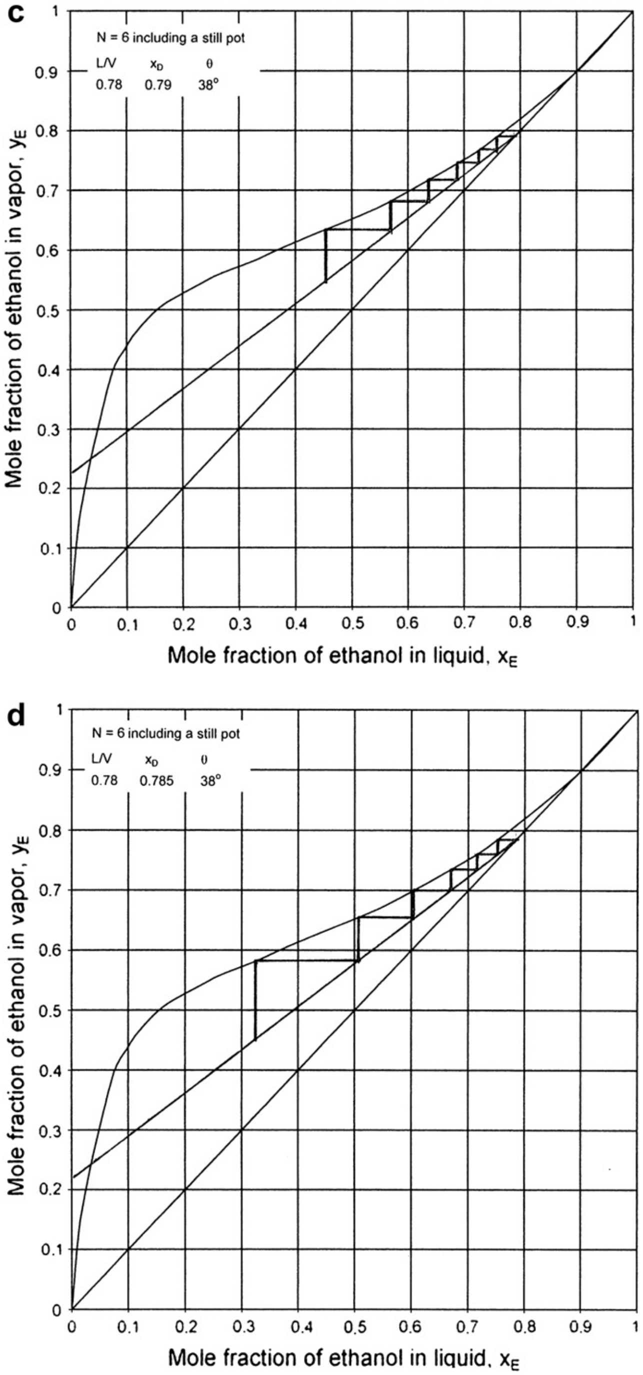


Figure 10-66 (c). Graphical estimation of liquid composition at $x_D = 0.79$ and L/V = 0.78 in Example 10-28. (d). Graphical estimation of liquid composition at $x_D = 0.785$ and L/V = 0.78 in Example 10-28.

Determine the values of the integral $\int_{x_i}^{x_W} \frac{dx_W}{(x_D - x_W)}$ between $x_i = 0.5$ and various lower limits of x_w bottom composition. The area under the curve is:

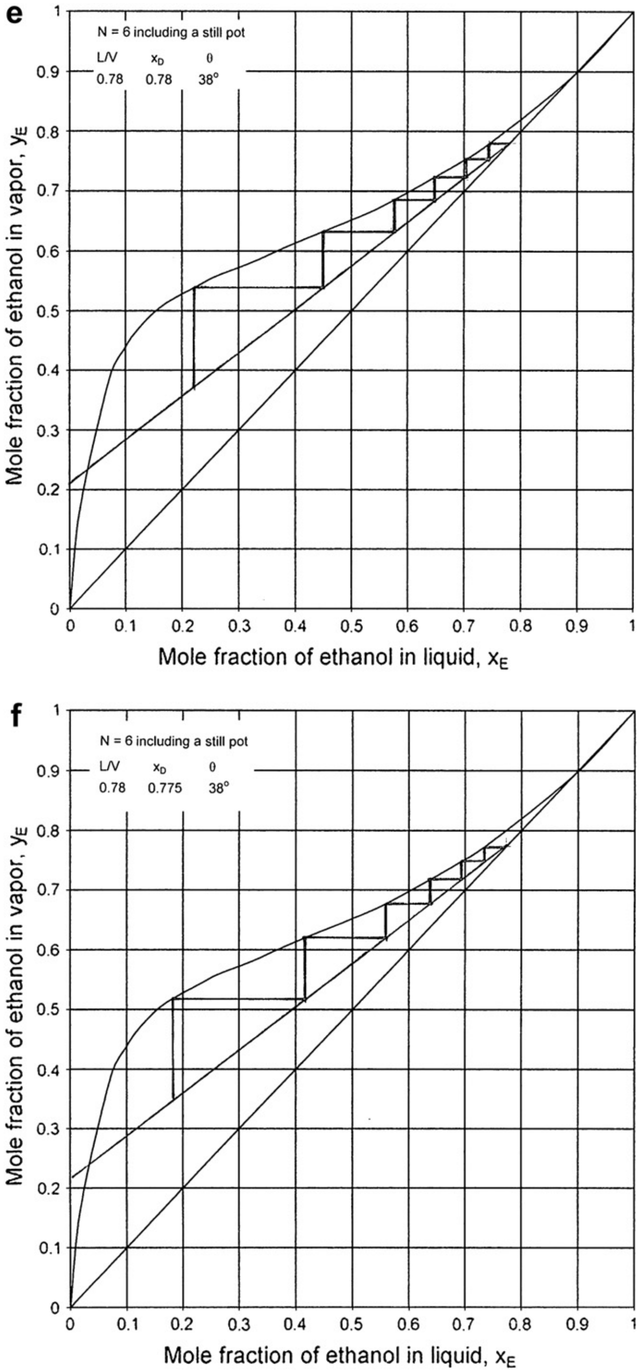


Figure 10-66 (e). Graphical estimation of liquid composition at $x_D = 0.78$ and L/V = 0.78 in Example 10-28. (f). Graphical estimation of liquid composition at $x_D = 0.775$ and L/V = 0.78 in Example 10-28.

$$\text{Area} = \frac{x_i - x_f}{n}\left[\frac{f(x)_0 + f(x)_f}{2} + \sum_{1}^{n-1} f(x)\right]$$

where n = number of ordinates.

Table 10-30 Results of Example 10-28.

x_D	L/V	x_W	$(x_D - x_W)$	$1/(x_D - x_W)$	Number of ordinates
0.800	0.78	0.575	0.225	4.444	
0.795	0.78	0.445	0.350	2.857	0
0.790	0.78	0.350	0.440	2.273	1
0.785	0.78	0.255	0.530	1.886	2
0.780	0.78	0.100	0.680	1.471	3
0.775	0.78	0.080	0.695	1.439	4

x_i	x_W	$\text{Area} = \int_{x_i}^{x_W} dx/(x_D - x_W)$ [Area under the $\frac{1}{x_D - x_W}$ vs. x_W curve]
0.5	0.35	$\text{Area} = (0.5 - 0.35)\,[(2.857 + 2.273)/2] = 0.385$
0.5	0.255	$\text{Area} = (0.5 - 0.255)/2\,[(2.857 + 1.886)/2 + 2.273] = 0.5689$
0.5	0.10	$\text{Area} = (0.5 - 0.10)/3\,[(2.857 + 1.471)/2 + 2.273 + 1.886] = 0.84306$
0.5	0.08	$\text{Area} = (0.5 - 0.08)/4\,[(2.857 + 1.439)/2 + 2.273 + 1.886 + 1.471] = 0.81669$

For a first attempt of $x_W = 0.35$, the area $= 0.385$. W is:

$$W = \frac{W_i}{e^{\text{Area}}} = \frac{500}{e^{0.385}} = 340.23\ \text{kmol}$$

$$D = W_i - W = 500 - 340.23$$
$$= 159.77\ \text{kmol.}$$

The average distillate composition, x_{Davg} is:

$$x_{Davg} = \frac{W_i\,x_i - W\,x_W}{(W_i - W)}$$

$$= \frac{(500)(0.5) - (340.23)\,(0.35)}{(500 - 340.23)}$$

$$= 0.82$$

For a second attempt of $x_W = 0.255$, the area $= 0.5689$ and W is:

$$W = \frac{W_i}{e^{\text{Area}}} = \frac{500}{e^{0.5689}} = 283.1\ \text{kmol}$$

$$D = W_i - W = 500 - 283.1$$
$$= 216.9\ \text{kmol.}$$

The average distillate composition, x_{Davg} is:

$$x_{Davg} = \frac{W_i\,x_i - W\,x_W}{(W_i - W)}$$

$$= \frac{(500)(0.5) - (283.1)(0.255)}{(500 - 283.1)}$$

$$= 0.82$$

For a third attempt of $x_W = 0.10$, the area $= 0.\ 84306$ and W is:

$$W = \frac{W_i}{e^{\text{Area}}} = \frac{500}{e^{0.84306}} = 215.2\ \text{kmol}$$

$$D = W_i - W = 500 - 251.2$$
$$= 284.8\ \text{kmol.}$$

The average distillate composition, x_{Davg} is:

$$x_{Davg} = \frac{W_i\,x_i - W\,x_W}{(W_i - W)}$$

$$= \frac{(500)(0.5) - (251.2)(0.10)}{(500 - 251.2)}$$

$$= 0.79$$

From the above calculations, $x_w = 0.10$ corresponds to the specification of the distillate of 0.8.

The time θ, for the batch distillation is determined from:

$$\theta = (R + 1)\left[\frac{W_i}{V}\left(\frac{e^Q - 1}{e^Q}\right)\right], \text{h} \qquad (10\text{-}339)$$

$W_i = 500.0$ kmol, $R = 3.0$, $V = 80$ kmol/h, $e^Q = 2.323$, $Q = $ Area of $1/(x_D - x_W)$

Substituting these values in Equation (10-339) gives:

$$\theta = (3 + 1)\left[\frac{500}{80}\left(\frac{2.323 - 1}{2.323}\right)\right], \text{h.}$$

$$= 14.2\ \text{h.}$$

An alternative equation in determining the time (hours) for distillation is:

$$\theta = (W_i - W)/D = \frac{(R + 1)}{V}(W_i - W) \qquad (10\text{-}340)$$

$$= \frac{(3 + 1)}{80}(500 - 215.2)$$

= 14.2 h (This time excludes charging, emptying cleaning, etc).

10.34.7 Batch Rectification with Variable Reflux Rate, a Fixed Number of Theoretical Plates in Column and Constant Overhead Composition

This mode of batch rectification requires the continuous adjustment of the reflux to the column to achieve a steady overhead distillate composition. Commencing with a liquid in the kettle that is rich in the more volatile component, a relatively low reflux ratio will be required to achieve the specified overhead distillate composition. This ratio must be continuously increased over time to maintain a fixed overhead composition. Ultimately, a practical maximum reflux is reached and the operation normally would be stopped to avoid distillate contamination.

Overall material balance at time θ [130, 131]:

$$S = S_o\left(\frac{x_D - x_{S_o}}{x_D - x_S}\right) \tag{10-341}$$

$$W = W_o\left(\frac{x_D - x_{W_o}}{x_D - x_W}\right) \tag{10-342}$$

where:

W = mols in still/bottoms at any time

W_o = mols in still/bottoms at initial charge time

Differentiating Equation (10-342) with respect to θ for varying W and x_W,

$$\frac{dW}{d\theta} = W_o\frac{(x_D - x_{W_o})}{(x_D - x_W)^2}\frac{dx_W}{d\theta} \tag{10-343}$$

For constant molar overflow, the rate of distillation is given by the rate of loss of charge:

$$-\frac{dW}{d\theta} = (V - L) = \frac{dD}{d\theta} \tag{10-344}$$

where D is now the amount of distillate, and not the distillation rate. Substituting Equation (10-344) into Equation (10-343) and integrating between the limits x_{W_o} and x_W, the time required for the distillation only is:

$$\theta = \left[W_o(x_D - x_{W_o})/V\right]\int_{x_W}^{x_{W_o}}\frac{dx_W}{\left(1-\frac{L}{V}\right)(x_D - x_W)^2} \tag{10-345}$$

θ does not include the time for charging the kettle, raising the still temperature to the bubble point, shutdown, cleaning, drainage of the product receiver, etc.

For fixed values of W_o, x_{W_o}, x_D, V and the number of equilibrium stages, the McCabe-Thiele diagram is used to determine the values of L/V for a series of values of still composition between x_{W_o} and the final value of x_W. These values are then used with Equation 10-345 to determine, by graphical or numerical integration, the time for rectification, or the time to reach any intermediate value of still composition. The required number of theoretical stages can be estimated by assuming total reflux conditions for the final value of x_W. During distillation, while rectification is proceeding, the instantaneous distillate rate will vary accordingly, and Equation 10-344 can be expressed in terms of L/V as:

$$\frac{dD}{d\theta} = V\left(1 - \frac{L}{V}\right) \tag{10-346}$$

To determine the column diameter (with trays), an approach [130] is to (1) assume θ hours; (2) solve for V, lb/h vapor up the column at selected, calculated, or assumed temperature and pressure; (3) calculate column diameter assuming a reasonable vapor velocity for the type of column internals (refer to "Mechanical Designs for Tray Performance" in this volume).

Solve for the value of θ graphically or numerically.

$1/[1 - (L/V)]\,(x_D - x_w)^2$ versus x_w, and determining the area under the curve between x_{wo} and x_w. Then substitute this value for the integral in the Equation 10-345 and solve for θ.

Figure 10-67 illustrates a distillation with variable reflux ratio; batch operating lines with different L/V slopes all passing through x_{Di} (distillate desired overhead composition for i). Establish the McCabe-Thiele-like steps down each operating line until the last horizontal step or stage intersecting the equilibrium line indicates the required bottoms composition, x_{wi}.

From Figure 10-63 the separation from x_o, initial kettle volatile material to x_3 as the distillate of more volatile overhead requires three theoretical plates/stages at total reflux ratio. Using a finite reflux ratio R_4, four theoretical plates are required. The values of reflux ratio, R, can be determined from the graph with the operating line equation as,

y (intercept) = $x_D/(R + 1)$

where

x_D = concentration of volatiles in the overhead distillate, mol fraction

R = reflux ratio (L/D), where L is the liquid returned as reflux

D = quantity of liquid distillate withdrawn (Figure 10-57)

The distillate percentage draw-off, P,

$P = 100/(R + 1)$, %

$P = 100\,(y/D_D)$, %

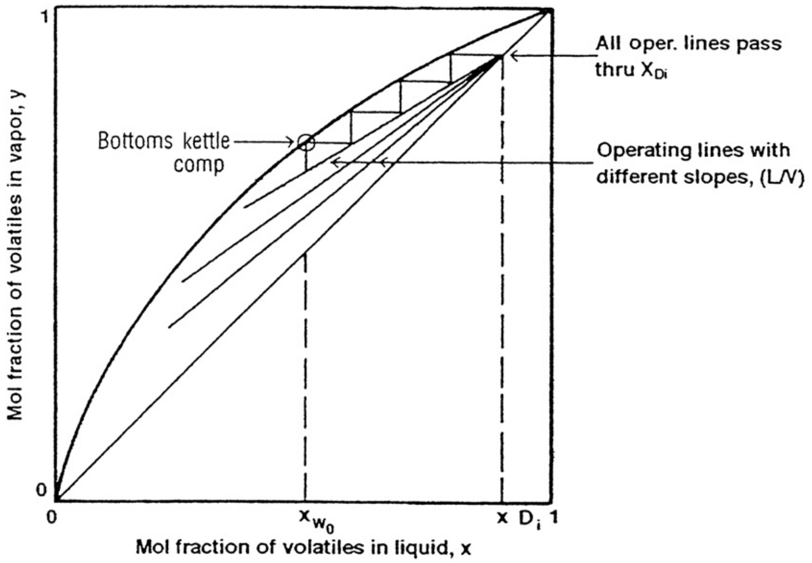


Figure 10-67 Variable-reflux batch process solution. Modified and used by permission, Ellerbe, R. W., Chem. Eng., May 28 (1973), p. 110.

The values of overhead composition can be varied from x_3 of Figure 10-63 to other values as the draw-off percentage changes. As the draw-off percentage decreases, the distillate specification can be better maintained as the distillation operation continues with a fixed number of plates. For further discussion refer to References 129, 130, 131, 133.

In order to determine the time θ of distillation or the vapor load, the following procedure is as follows:

1. Draw the vapor–liquid equilibrium (VLE) diagram for the more volatile component (MVC) on the x–y plot.
2. Draw the 45°-line.
3. Locate the point corresponding to the value of x_D on the 45° line.
4. From this point draw several operating lines with varied slope (L/V) (Figure 10-67).
5. Draw the steps between the operating line and equilibrium curve, similar to that followed in the McCabe-Thiele method (One step is equivalent to one theoretical stage).
6. Select an operating line such that the intersection of the last horizontal step with the VLE curve gives x_W – the desired final value.
7. Plot x_W against

$$\frac{1}{\left(1-\frac{L}{V}\right)(x_D - x_W)^2}.$$

Determine the area under the curve between x_{W_0} and x_W. This area represents the value of the integral of the RHS of Equation 10-345.

Example 10-29 Time of Distillation at Varying Reflux Ratio and Constant Product Specification

A batch containing 500 kmols of ethanol and water mixture is to be distilled at 101.32 kPa. The initial charge contains 50 mol % ethanol, it is reduced to a residual liquor of ethanol at a concentration of 4.5 mol % using a batch distillation column with four theoretical plates including the still pot. The rate of vaporization is 80 kmol/h and the product specification is 70 mol % ethanol. Determine:

1. The time required for the distillation to achieve the desired product specification.
2. The quantity of the product obtained.

Solution

The procedure is analogous to Example 10-28 but using a variable instead of a fixed reflux ratio.

1. Select several arbitrary values of L/V ratio.
2. Draw several operating lines at L/V ratios from the 45° line for MVC (i.e. ethanol).
3. Locate the point 0.7 (x_D) on the 45° line.
4. Draw several operating lines (OL) from this point with slopes equal to the various values of L/V selected.
5. Step-off four steps along each operating line.
6. At the end of the fourth-step, determine the equilibrium value of the bottoms product.

7. Integrate:

$$\int_{x_W}^{x_{W_o}} \frac{dx_W}{(1 - L/V)(x_D - x_W)^2}$$

between the limits $x_{W_o} = 50$ mol % and $x_W = 4.5$ mol % graphically or numerically.

8. Determine the time θ from,

$$\theta = \left[W_o(x_D - x_W)/V\right] \int_{x_W}^{x_{W_o}} \frac{dx_W}{\left(1 - \frac{L}{V}\right)(x_D - x_W)^2}$$

9. Calculate the product quantity from,

$$W_o - W = W_o\left(\frac{x_{W_o} - x_W}{x_D - x_W}\right)$$

Using the vapor–liquid equilibrium data of ethanol and values of L/V, locate the point $x_D = 0.7$ on the 45°- line in Figure 10-67a.

Draw the operating lines at varying values of L/V from this point and step off four plates on each operating line to find the equilibrium value of the bottoms. The results are tabulated below.

L/V	$\mathbf{x_D}$	$\mathbf{x_W}$	$(\mathbf{x_D - x_W})$	$\mathbf{f(x) = \frac{1}{\left(1-\frac{L}{V}\right)(x_D - x_W)^2}}$	**Number of ordinates**
0.60	0.7	0.15	0.55	8.264	0
0.65	0.7	0.09	0.61	7.678	1
0.70	0.7	0.075	0.625	8.533	2
0.75	0.7	0.055	0.645	9.615	3
0.80	0.7	0.045	0.655	11.654	4
0.85	0.7	0.04	0.66	15.305	5

The area under the curve can be determined by:

$$\text{Area} = \frac{x_i - x_f}{n}\left[\frac{f(x)_0 + f(x)_f}{2} + \sum_{1}^{n-1} f(x)\right]$$

where n = number of ordinates (starting from 0).

The area under the curve by the formula given above is:

$$= \frac{(0.15 - 0.045)}{4}\left[\frac{(8.264 + 11.654)}{2} + 7.678 + 8.533 + 9.615\right]$$

$$= 0.939$$

$W_o = 500$ kmols, $V = 80$ kmol/h, $x_D = 0.7$, $x_W = 0.5$,

The time θ for the distillation to achieve the desired product specification of 70 mol % is:

$$\theta = \left[W_o(x_D - x_W)/V\right] \int_{x_W}^{x_{W_o}} \frac{dx_W}{\left(1 - \frac{L}{V}\right)(x_D - x_W)^2}$$

$$= (500/80)\ (0.70 - 0.50)\ (0.939)$$
$$= 1.2 \text{ h } (72 \text{ mins}).$$

The quantity distilled is:

$$W_o - W = W_o\left(\frac{x_{W_o} - x_W}{x_D - x_W}\right)$$
$$= 500\left(\frac{0.50 - 0.045}{0.70 - 0.045}\right)$$
$$= 347.3 \text{ kmols.}$$

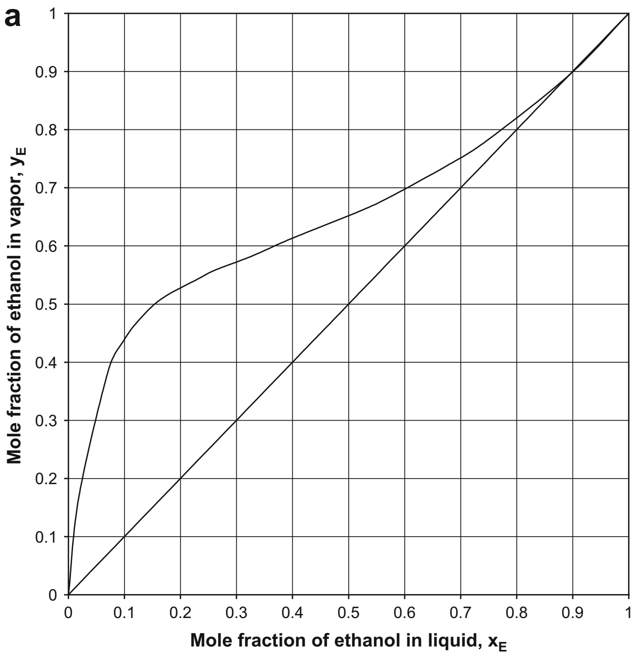
An Excel spreadsheet Example 10-29.xls has been developed to determine the time required for distillation and the amount distilled. Figure 10-68 shows the plot of x_W against:

$$\frac{1}{\left(1 - \frac{L}{V}\right)(x_D - x_W)^2}$$

with an area of 0.95. Figure 10-69 shows typical McCabe-Thiele plots at varying L/V ratio and constant distillate composition at $x_D = 0.7$ using four theoretical stages (including the still pot).

Example 10-30 Minimum Reflux: Ratio Estimation and Associated Distillate Composition

A mixture of ethanol-water is subjected to batch distillation. Determine: (i) the minimum reflux ratio, (ii) the distillate composition; (iii) the still composition at the



N = 4 including a still pot

L/V	x_D	x_W	θ
0.6	0.7	0.15	31°
0.65	0.7	0.09	33°
0.70	0.7	0.075	35°
0.75	0.7	0.055	37°
0.80	0.7	0.045	39°
0.85	0.7	0.040	40°

Figure 10-67a VLE diagram for the mixture ethanol and water at 1 atm. : Example 10-29

end of distillation. Inflection point to the VLE diagram of ethanol occurs at the point (0.7, 0.75).

Solution

From the vapor–liquid equilibrium data of ethanol, the inflection point P (0.7, 0.75) is located in Figure 10–70, and the tangent to the VLE curve is drawn through this point and extended to meet the 45°- line at D, which corresponds to the distillate composition, x_D with the coordinates (0.82, 0.82). The tangent line DP cuts the VLE-curve at point F corresponding to the bottom composition x_W with co-ordinates (0.08, 0.39).

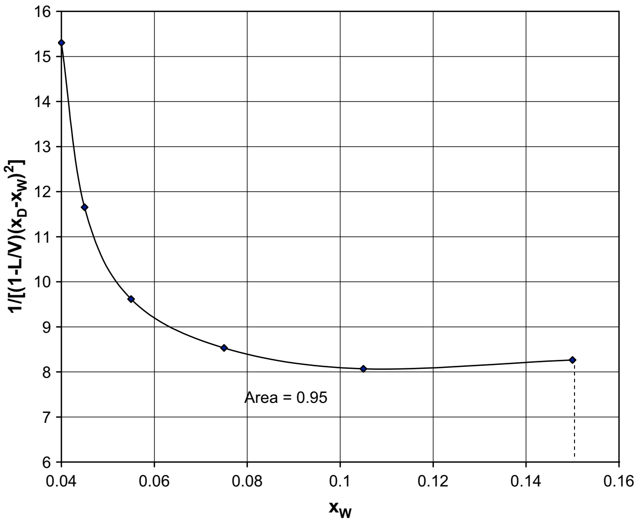


Figure 10-68 Batch distillation of ethanol–water mixture at variable reflux and constant distillate composition.

(i) The VLE-curve in Figure 10-70 has an inflection and the operating line for the minimum reflux is the line that passes through the point of inflection P, and is tangent to the VLE curve at this point. In Figure 10-70, the operating line for the minimum reflux ratio passes through DPF where

P = inflection point
D = Distillate composition
F = Bottom composition

The minimum reflux ratio in Figure 10-70 is:

$$R_m = \frac{y_D - y_P}{x_D - x_p}$$

$$= \frac{0.82 - 0.75}{0.82 - 0.7}$$

$$= 0.583$$

$$R_{min} = (L/V)_{min} = 0.583$$

(ii) The distillate composition is: $(x_D, y_D) = (0.82, 0.82)$ The still composition is determined from point F on the VLE diagram, and the coordinates at these point correspond to the bottom composition at the end of the distillation.

(iii) The still composition is: $(x_W, y_W) = (0.08, 0.39)$

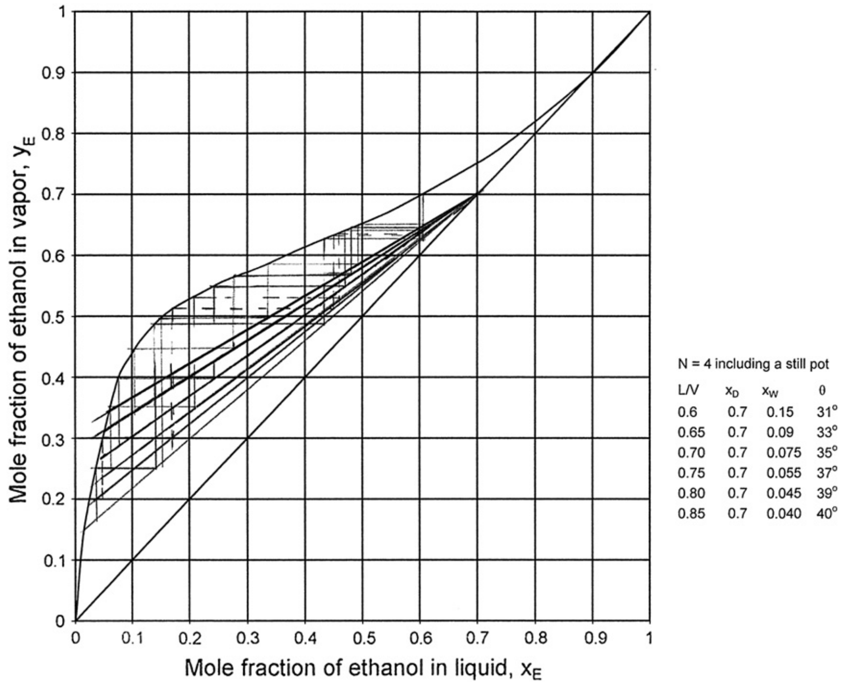


Figure 10-69 Example 10-29: Graphical estimation of liquid composition on 4th place using variable reflux ratio.

Example 10-31: Batch Distillation, Constant Reflux Ratio; Following the Procedure of Block [133]

Purify a mixture of ethanol and water; 11,500 lb.

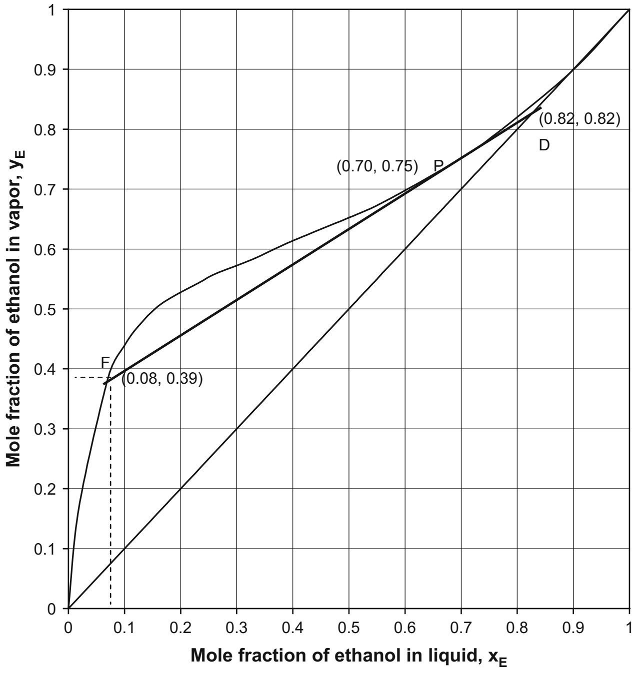


Figure 10-70 Determination of minimum reflux ratio in Example 10-30.

Feed to kettle	Wt Per cent	lb	MW	Mols	Mole fraction
Ethanol	35	4,025	46	87.5	0.174
Water	65	7,475	18	415.27	0.826
Total	100	11,500		502.77	1.000

Overhead distillate product desired: 91.5 wt% ethanol.

Kettle bottoms residue: Not specified, as results from separation.

Vaporization rate: Assume 72 mols/h.

Average mol. weight of feed: = 11,500/502.77 = 22.87.

Solution

Overhead Product

Feed to kettle	Wt Per cent	Lb	MW	Mols	Mole fraction
Ethanol	91.5	91.5	46	1.989	0.808
Water	8.5	8.5	18	0.472	0.192
Total	100	100		2.461	1.000

Select L/V (internal reflux) = 0.75

Then: L/V = R/(R + 1) = 0.7875 = R/(R + 1), see below;

R = 3.705 (external reflux, L/D)

Because V = L + D

72 mols/h = (0.7875 V) + D

Use the ethanol–water curve similar to Figure 10-71, or refer to the data of Reference 133; the point of tangency of the line from the distillate composition of the diagonal is $x_D = 0.80$ and $y_v = 0.80$. Thus the minimum internal reflux is set by this tangent line:

$$L/V = \frac{y_D - y_T}{x_D - x_T} = \frac{0.80 - 0.695}{0.80 - 0.60} = 0.525$$

For practical design, select L/V = (1.5) (0.525) = 0.7875.

Select L/V internal reflux lines and add to the equilibrium plot, similar to that shown for a "normal" curve of Figure 10-65.

Tabulate:

Select x_D	x_W	$(x_D - x_W)$	$1/(x_D - x_W)$
0.808			
0.770			
0.750	read, 0.085	0.665	1.5037

For a plot of $x_D = 0.750$, slope = 0.7875, read x_W at the equilibrium line for each theoretical tray and plot similar to Figure 10-72. Then determine the area under the curve between the selected x_w and the product x_D. Then:

$$\ln (W_i/W) = \int_{x_i}^{x_w} \frac{dx_w}{(x_D - x_w)} = \text{area under curve} \tag{10-345a}$$

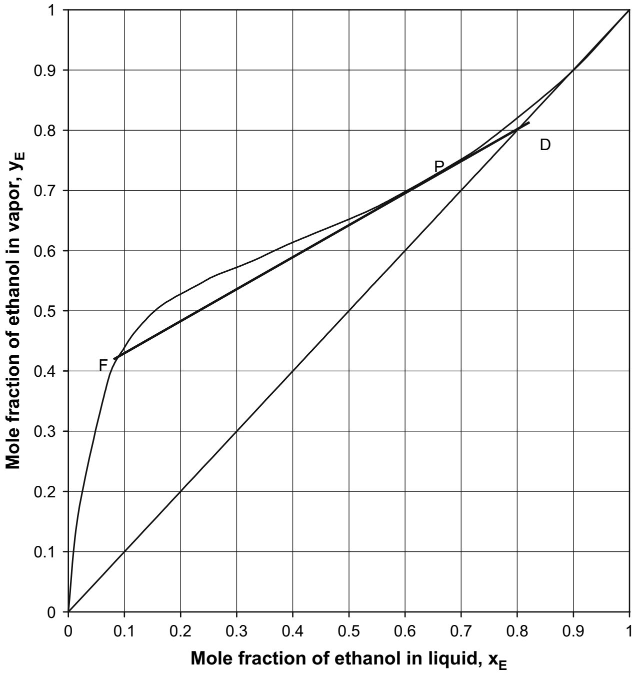


Figure 10-71 x–y diagram for ethanol–water mixture, showing minimum reflux ratio.

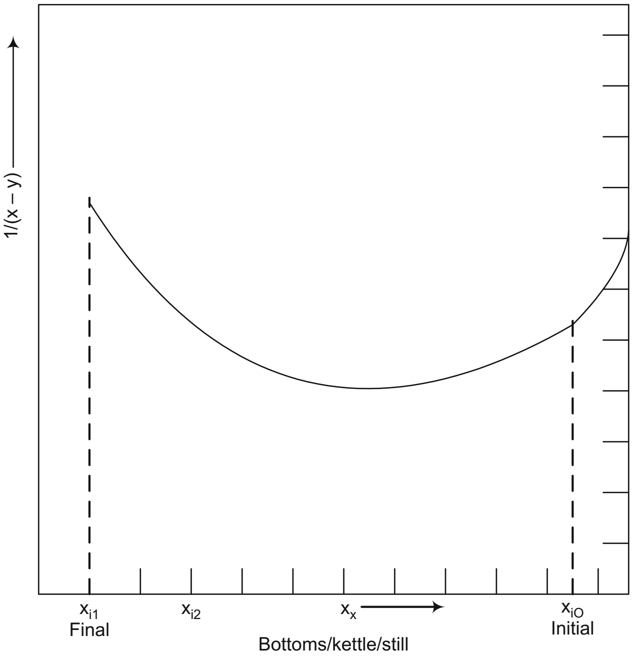


Figure 10-72 Graphical integration of Rayleigh, or similar, equation by Simpson's Rule for Example 10-31.

Here, ln (W_i/W) = approximately 0.210. so, W_i/W = 1.2336

$$W = \frac{502.77}{1.2336} = 407.54 \text{ mols bottoms for } x_w = 0.085$$

Average overhead composition,

$$x_{D\ avg} = \frac{W_i x_i - W x_W}{W_i - W}$$

$$= \frac{\left[(502.77)(0.187) - (407.54)(0.085)\right]}{(502.77 - 407.54)} = 0.6235$$

Time required for distillation only (excluding charging, heating-up, draining, cleaning, etc.):

$$\theta = (R + 1)[W_i/V]\left[(e^Q - 1)/e^Q\right]$$

$$Q = \int_{x_i}^{x_w} \frac{dx_w}{x_D - x_w} = \ln\left(\frac{W_i}{W}\right)$$ (see right side of Equation 10-345a)

$$\theta = (3.705 + 1)\frac{(502.77)(e^{0.210} - 1)}{[72(e^{0.210})]} = 6.22 \text{ h}$$

Distillation rate

$$= \frac{W_i - W}{\theta} = \frac{502.77 - 407.54}{6.22} = 15.31 \text{ mols/h}$$

Checking:

$\theta = (R + l)\ (W_i - W)/V$
$\theta = (3.705 + 1)\ (502.77 - 407.54)/72$
$\theta = 6.22$ h
where:

D = distillate rate, moles/h
L = liquid flow, moles/h
V = vapor rate, mo1es/h
$\overline{V}$ = quantity of vapor, moles
W = contents of still pot, moles
x = mole fraction of substance in liquid
y = mole fraction of substance in vapor
a = relative volatility
θ = time, h

Subscripts:

D = relating to distillate
i = initial
w = relating to pot liquors

Example 10-32: Batch Distillation Calculation of Vapor Boil-up Rate for Fixed Trays (used by permission of Treybal [129]; clarification added by Ludwig [271])

Distill a small quantity each day to obtain relatively pure ortho-xylene from a mixture of ortho and para-xylene, having boiling points of 142.7°C and 138°C, respectively. The feed is 15 lb-mols (about 225 gallons) per batch, at 0.20 mol fraction para-xylene. The desired residue product is 0.020 in the kettle, while the distillate is to be 0.400 mol fraction para-xylene. A distillation column equivalent to 50 theoretical plates is to be used.

The time requirement is to complete the distillation/recovery in six hours, allowing an extra two hours for charging, emptying, and cleaning. What is the constant rate at which the distillation must be carried out?

F = 15 lb-mols/h
$x_F = 0.20;\ x_D = 0.400;\ x_w = 0.02$
The material balance:
$D = F\ (x_F - x_w)/(x_D - x_w)$
$D = 15\ (0.2 - 0.02)/(0.400 - 0.020) = 7.105$ mols
Then, $F = D + W$
$W = 15 - 7.105 = 7.895$ mols
$\theta_1 = D/G$
and, $\theta = 7.105/G$
Using Equation 10-324b,

$$\frac{(1 - x_{Si})^{\alpha}}{x_{Si}} = \left(\frac{F}{W}\right)^{\alpha - 1} \frac{(1 - x_F)^{\alpha}}{x_F} \qquad \text{(10-324b)}$$

Solve for x_{Si} by trial and error.

$$\frac{(1 - 0.18530)^{1.152}}{0.18530} = \left(\frac{15}{7.895}\right)^{1.152-1} \frac{(1 - 0.2)^{1.152}}{0.2}$$

$$= 4.26$$

At 138.4°C, the vapor pressures of ortho- and para-xylene are 660 and 760 mm Hg, respectively.

Because Raoult's law applies:

$\alpha = 760/660 = 1.152$

Solving the equation by trial and error shows that $x_{Si} = 0.18530$. Solving for the minimum number of plates required:

$$N_{min} + 1 = \frac{\log\left(\frac{x_D}{1 - x_D}\right)\left(\frac{1 - x_W}{x_W}\right)}{\log \alpha}$$

$$N_{min} + 1 = \frac{\log\left(\frac{0.40}{1 - 0.40}\right)\left(\frac{1 - 0.02}{0.02}\right)}{\log 1.152}$$

$$N_{min} + 1 = \frac{1.514}{0.06145} = 24.6$$

N_{min} (in column) + 1 (kettle) = 24.6

The results indicate that 25 theoretical plates are the minimum required. Assuming an efficiency of 50%, 50 total actual trays should be adequate. Choose values of k (see nomenclature) and solve for b and x_S by:

$$b = (\alpha k/c) - k$$

$$c = 1 + (\alpha - l)k$$

$$Ax_S^2 + Bx_S + C = 0$$

The tabulated results are:

k	b	x_S
0.0200	0.00297	0.01899
0.0500	0.00716	0.04842
0.0750	0.01043	0.07301
0.1000	0.01347	0.09728
0.1250	0.01631	0.12109
0.1500	0.01895	0.14470
0.1750	0.02137	0.17145
0.2000	0.02360	0.18133

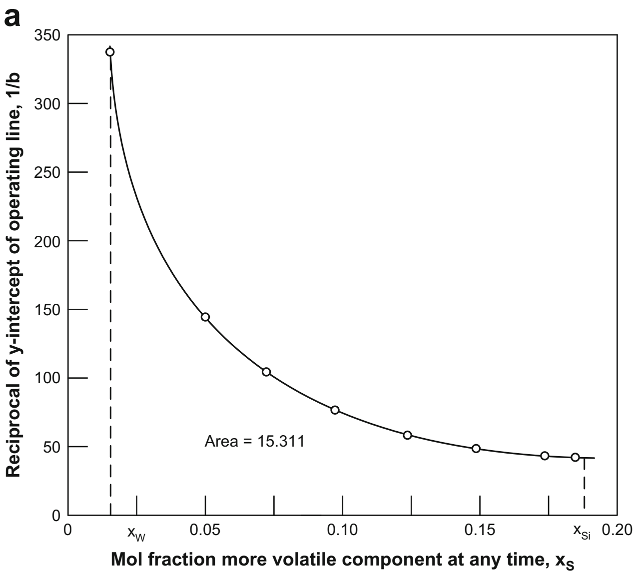


Figure 10-72a Graphical integration for boil-up rate of batch distillation for Example 10-32. Used by permission, Treybal, R. E., Chem. Eng. Oct. 5 (1970), p. 95.

Graphical integration shows the area under the curve, Figure 10-72a to be 15.311. Applying this to:

$$\theta_2 = (W/G)\int_{x_W}^{x_{Si}} (dx_S/b)$$

Then, $\theta_2 = 7.895\ (15.311)/G = 120.88/G$

$\theta_1 + \theta_2 = 6\ h = 7.105/G + 120.88/G$

$G = 21.33$ 1b-mols vapor/h

This is the boilup rate, which is approximately 3.3 ft^3 vapor/sec. An approximately 1 ft. diameter column can handle this rate, where

A, B, C, E, H, J, K = constants developed in article [129]
b = y-intercept of operating line
c = constant
D = distillate, lb-moles
F = charge to batch distillation, lb-moles
G = vapor boilup rate, lb-moles/h
k = value of x at intersection of operating line and equilibrium curve
L = liquid reflux rate, lb-moles/h
N = number of ideal plates in column
N_{min} = minimum value of N
W = residue, lb-moles
x = mole fraction more volatile component in liquid
x_D = mole fraction more volatile component in final distillate
x_F = mole fraction more volatile component in feed
x_p = mole fraction more volatile component in liquid leaving column at any time
x_S = mole fraction more volatile component in kettle at any time
x_{si} = value of x_S when distillate receiver is first filled
x_w = mole fraction more volatile component in final residue
x_1 = mole fraction more volatile component in distillate at any time
y = mole fraction more volatile component in vapor
y_S = mole fraction more volatile component in vapor entering column at any time
α = relative volatility
θ_1 = time for filling distillate receiver, h
θ_2 = time for refluxed distillation, hr

Example 10-33: Batch Differential Distillation of a Binary Mixture

Dimethyl ether is to be separated from a mixture with methanol. A batch operation is to be tested to evaluate whether an existing coil-in-tank can be used as a still. The pressure of the system will be about 55 psia. How many total mols will remain in the bottoms when the bottoms liquid composition contains 0.5 mol percent dimethyl ether? What is the composition of the total overhead collected?

π = system (total) pressure, psia.
p_i^o = vapor pressure of component i.

	Initial Charge				
Component	**Mols**	**Mol Fraction**	**At 104°F Vap. Press. psia**	**$K = p_i^o/\pi$**	**$y^* = Kx$**
Dimethyl ether	61	0.427	125.0	2.27	0.97
Methanol	82	0.573	5.1	0.093	0.05
Total	143	1.000			$\Sigma = 1.02$

Initial boiling point of mixture = 104°F.

$$\ln\left(\frac{B_{T1}}{B_{To}}\right) = \frac{1}{\alpha - 1}\ln\left[\frac{(1 - x_o)x_1}{(1 - x_1)(x_o)}\right] + \ln\left[\frac{(1 - x_o)}{(1 - x_1)}\right] \quad (10\text{-}347)$$

$B_{To} = 143$ mols
$x_o = 0.427$
$x_l = 0.005$
$\alpha = 125/5.1 = 24.5$

$$\ln\left(\frac{B_{T1}}{143}\right) = \frac{1}{24.5 - 1}\ln\left[\frac{(1 - 0.427)(0.005)}{(1 - 0.005)(0.427)}\right] + \ln\left[\frac{(1 - 0.427)}{(1 - 0.005)}\right]$$

$$= 0.0426 \ln\frac{0.00286}{0.425} + \ln\frac{0.573}{0.995}$$

$$\ln\left(\frac{B_{T1}}{143}\right) = -0.765$$

$$\ln\left(\frac{143}{B_{T1}}\right) = 0.765$$

$B_{T1} = 143/2.15 = 67$ mols remaining in bottom when dimethyl ether is 0.5 mol %.

Total vapor collected overhead = 143 − 67 = 76 mols
Mols dimethyl ether in bottoms = 0.005 (67) = 0.335
Mols dimethyl ether overhead = 76 − 0.335 = 75.665
Composition of total overhead collected:

$$\text{Dimethyl ether} = \frac{75.665}{76.0}(100) = 99.6\%$$

Methanol = 100.0 − 99.6 = 0.4%

10.34.8 Differential Distillation-Simple Batch of a Multicomponent Mixture Without a Rectification Column

For multicomponent systems, the relation of the system can be expressed using the relative volatility:

$$B_i = B_{io}\left(\frac{B_b}{B_{bo}}\right)^{\alpha i} \tag{10-348}$$

where

B_i = mols of component, i, after a given time.
B_{io} = mols of component i, at start.
B_b = mols of component, b, used as reference for volatility after a given time.
B_{bo} = mols of component, b, used as reference for volatility.

Knowing the amount of components present at the beginning, the quantity remaining after the end can be calculated.

Example 10-34: Multicomponent Batch Distillation Calculation

A mixture of C_2 to C_4 hydrocarbons is to be differentially distilled at 80 psia until the concentration of propane is reduced to 10 mols per 100 mols of bottom feed material. A kettle with bottom coil is to be used, and no trays.

Material in kettle at start of distillation:

Component	Mol fraction
C_2H_6	0.1
C_3H_8	0.25
n-C_4H_{10}	0.35
i-C_4H_{10}	0.30
	1.00

Solution

Basis: 100 mols of bottoms feed.

Bubble Point of Initial Charge

Component	x_i Mol. Fract.	@ 50°F, K_i	$y = Kx$	Assumed 105°F, K_i	α_i @ 50°F K_i/K_p	α_i @ 105°F K_i/k_p	α_{avg}
C_2H_6	0.10	4.5	0.45	7.2	3.81	3.28	3.54
C_3H_8	0.25	1.18	0.295	2.2	1.0	1.0	1.0
n-C_4H_{10}	0.35	0.33	0.115	0.75	0.28	0.341	0.310
i-C_4H_{10}	0.30	0.48	0.144	1.0	0.407	0.454	0.430
Total	1.00		1.004 O.K.				

Propane is reference material.

$$\alpha_{i,50^\circ F} = \frac{K_i}{K_{propane}} = \frac{4.5}{1.18} = 3.81$$

$$\alpha_{i,105^\circ F} = \frac{K_i}{K_{propane}} = \frac{7.2}{2.2} = 3.28$$

$$B(\text{Total}) = \sum B_i = \sum Bi_o \left(\frac{B_b}{B_{bo}}\right)^{\alpha_i}$$

$$B(\text{ethane}) = (10)\left(\frac{10}{25}\right)^{3.54} = \frac{10}{25.6} = 0.39 \text{ mols in bottoms}$$

Component	B_i	Final Bottoms x_i	Vapor Press. At 105°F, p_i^o psia	$p_i = p_i^o\, x_i$ psia
C_2H_6	0.39	0.00686	840	5.75
C_3H_8	10.00	0.176	200	35.2
n-C_4H_{10}	26.30	0.463	57	26.4
i-C_4H_{10}	20.20	0.355	78	27.6
	56.89	1.000		94.95
				(Too high, assume lower temperature and re-calculate)

$x_i = 0.39/56.89 = 0.00686$
Vapor pressure from N.K. Rector chart in Reference 48.
Second Attempt

Component	Initial x_i	α_i 50°F	Assume 95°F, K_i	α_i @ 95°F K_i/K_p	α_{avg}
C_2H_6	0.10	3.81	6.7	3.35	3.58
C_3H_8	0.25	1.0	2.0	1.0	1.0
n-C_4H_{10}	0.35	0.28	0.67	0.335	0.307
i-C_4H_{10}	0.30	0.407	0.92	0.46	0.432

Component	Final B_i	Vapor Press.@ 95°F, p_i^o psia	Final x_i	$p_i = p_i^o\, x_i$ psia
C_2H_6	0.378	750	0.0066	4.8
C_3H_8	10.0	174	0.175	30.4
n-C_4H_{10}	26.4	47	0.464	21.8
i-C_4H_{10}	20.2	67	0.354	23.7
Total	56.978			80.7 psia

Therefore the final temperature should be close to 95°F, because 80.7 psia is close to the operating pressure of 80 psia.

Total mols of bottoms remaining at end: 57 mols liquid

Total mols vaporized = 100 − 57 = 43

Liquid composition mol fraction is given in column "Final x_i," and corresponds to the actual mols B_i, noting that there are the required 10 mols of propane in the bottoms under these conditions.

10.34.9 Batch Distillation with a Fractionation Column-Constant Overhead Product Composition. Multicomponent or Binary Mixture

The method of Bogart [4] is useful in this case. The basic relation is:

$$\theta = \frac{B_{To}(x_{iD} - x_{iB})}{V} \int_{x_B}^{x_F} \frac{dx}{(1 - L/V)(x_{iD} - x_{iB})^2} \tag{10-349}$$

Application may be (1) to determine a column diameter and number of plates or (2) with an existing column and an assumed operating reflux, determine the time to separate a desired cut or product, where:

θ = time from start when given L/V will produce constant overhead composition, x_{iD}

B_{To} = mols total batch charge to still

V = total mols per hour vapor overhead

x_{iD} = mol fraction light key component in overhead product

x_{iB} = mol fraction light key component in original charge

Procedure for situation (2) above, using an existing column:

1. Calculate the minimum number of plates and minimum reflux ratio:
   - **a.** For multicomponent mixture, select key components, light and heavy.
   - **b.** Calculate relative volatility, α_i, referenced to heavy key component, at top and bottom temperatures, and determine geometric average α.
   - **c.** Calculate minimum theoretical plates at total reflux by Fenske's equation (10-182).

d. Use Gilliland correlation to determine actual reflux ratio, using an estimated number of actual plates, and a minimum reflux ratio from:

$$(L/D)_{min} = \left(\frac{1}{\alpha - 1}\right)\left[\left(\frac{x_{1D}}{x_{1B}}\right) - \alpha\left(\frac{x_{hD}}{x_{hB}}\right)\right]$$

e. Calculate:

$$\text{Internal } (L/V) = \frac{L/D}{L/D + 1}$$

2. Set up table: Keep x_{lD} values constant.

*Assumed "x_1" values	(L/V)	(1 − L/V)	(x_{1D}-x_1^*)	A B
x (bottoms)	•	•	•	• •
x_2	•	•	•	• •
x_3		•	•	• •
:	•	•	•	• •
x (feed)	•	•	•	• •

$A = (1 - L/V)\ (x_{1D} - x_1^*)2$

$$B = \frac{1}{(1 - L/V)(x_{1D} - x_1{}^*)^2}$$

*Assume "x_l" values of bottoms compositions of light key for approximate equal increments from final bottoms to initial feed charge. Calculate L/V values corresponding to the assumed "x_l" values by inserting the various "x_l" values in the Fenske equation for minimum reflux ratio of l-(d). The "x_l" values replace the x_{lB} of this relation as the various assumptions are calculated. The actual (L/D) are calculated as in l-(d) keeping the number of trays constant. Complete the table values.

3. Plot:

$$\frac{1}{(1 - L/V)(x_{1D} - x_1{}^*)^2} \text{ vs } (x_1)^*$$

The total area under the curve ΣA, may be obtained in several ways; the rectangular or trapezoidal rules are generally satisfactory. The area is that between the original feed and the final bottoms composition for the particular component.

4. Time required for a batch:

$$\theta = B_{To}\frac{(x_{iD} - x_{iB})}{V}\left(\sum A\right) \qquad (10\text{-}350)$$

V is an assumed or known value, based on reboiler capacity.

5. Plot of reflux ratio quantity versus time.

From the L/D values of l-(e), knowing the L/V, using V assumed as constant, calculate the necessity reflux fluid, L. Figure 10-73 indicates a plot of time to produce a constant product composition and the necessary external reflux returned to the tower.

The batch distillation calculation of a binary is simpler, as L/V values can be assumed, and because there is only enrichment of the overhead involved only one operating line is used per operating condition. The number of theoretical trays can be stepped-off and x_{iB} values read to correspond. The plots involved are the same as previously described. Table 10-31 provides rules of thumb for batch distillation

Rigorous Methods

The rigorous methods for calculation of batch distillation operations are rather more complex than for continuous steady-state distillation, because of their transient operation. The basic assumption of steady state operation in the continuous column model is not applicable in these instances. The only operation for steady state in batch distillation is at total reflux, which is used as the initial condition for the dynamic solution of the column.

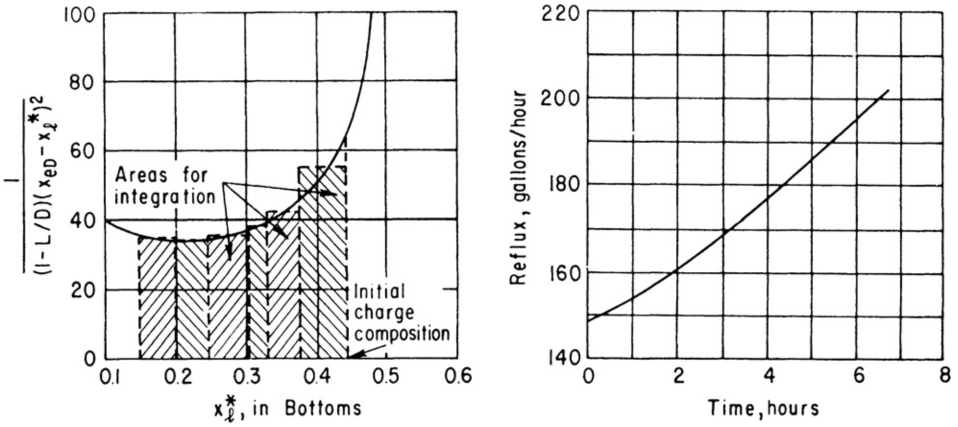


Figure 10-73 Batch distillation with trays: constant overhead product.

Table 10-31 Heuristics on Batch Distillation.

- Too low a reflux ratio cannot produce the required product specification no matter how many trays are installed. Conversely, even infinite reflux will not be sufficient if an inadequate number of equilibrium stages has been provided.
- For optimum separation efficiency, reflux holdup should be minimized by eliminating surge drums and using flow splitters that retain little or no liquid.
- Too little or too much holdup in the column is detrimental to separation efficiency. A reasonable amount provides a flywheel effect that dampens the effects of equilibrium-condition fluctuations; too much, especially at higher reflux ratios, makes it difficult to achieve good purity levels. A hold-up equivalent to 10–15% of the initial batch charge is recommended.
- Since the column consists solely of a rectifying section, there is a limit to how much trays can be profitably installed. The system will “pinch” regardless of stages once the low boiler concentration in the reboiler approaches the intersection of the operating line with the equilibrium curve.
- Once a workable column has been installed, capacity to produce at a given rate and product specification is only minimally affected by changes in reflux ratio or length of a cut.
- As the more-volatile component is being removed from the reboiler, separation becomes progressively more difficult.
- It is impossible to recover in a single operation, at high purity, a low boiling component that represents only a small fraction of the initial charge.

Source: Chemical Engineering magazine, SRI Consulting: A division of Access intelligence, LLC.

The rigorous solution involves coupling both the heat and material balance and phase equilibrium equations. Hold-up terms must also be considered. Distefano [281] assumed a constant volume of liquid holdup, negligible vapor holdup, and negligible fluid dynamic lag. He describes a computational procedure to solve the equations one at a time. Boston et al. [282] describe a more flexible and efficient method that can handle a variety of specifications and column configurations, including side draws, side heaters and multiple feeds. Their method uses advanced numerical procedures to handle non-linearity and stability problems. Khoury [283] has outlined Distefano’s method in order to illustrate some of the potential numerical computational difficulties that are encountered. Further details of these methods are provided by Distefano and Boston et al.

10.35 Steam Distillation

Live steam in steam distillation, is fluids being distilled, either batch or continuous.

Ellerbe [127, 128] provides an excellent summary of the basics of steam distillation. The theory of direct steam distillation evolves around the partial pressures of the immiscible organics/petroleum/petroleum components and the presence of direct open steam in the system. The system may consist of the organic immiscible plus steam (vapor and/or liquid). Each liquid exerts its own vapor pressure independent of the other. The total pressure of the system is hence the sum of the individual vapor pressures of the two liquids (assuming the liquids are immiscible). An important use of this approach is to separate a volatile organic from non-organic impurities.

At constant temperature, the partial pressure for each component, and the composition of the vapor phase, are independent of the mols of liquid water or organic compound present. For example, for a system held at 800 mm Hg, the mixture could boil at, 250°F, and both liquids present would boil over together. Should one component evaporate (boil away) before the other, the system’ vapor pressure would then fall to the temperature corresponding to the boiling point of the residual material.

For a system such as discussed here, the Gibb’s Phase Rule [59] applies and establishes the “degrees of freedom” for control and operation of the system at equilibrium. The number of independent variables that can be defined for a system is expressed as:

$$\phi + F = C + 2 \tag{10-351}$$

where

ϕ = number of phases present
F = degrees of freedom
C = number of components present

For example, for steam (saturated vapor, no liquid) distillation with one organic compound (liquid), there are two phases, two components, and hence no degrees of freedom. The degrees of freedom that could be set for the system could be: (1) temperature and (2) pressure; or (1) temperature and/or (2) concentration of the system components; or either (1) pressure and (2) concentration. In steam distillation, steam may be produced from the water present, so both liquid and vapor phase water (steam) are present. For such a case, the degrees of freedom are $F = 2 + 2 - 3 = 1$.

The basic calculations involve the partial pressures of the components as discussed earlier.

For batch steam distillation: stripping [127, 128]

$$y_s = P_s/\pi \tag{10-352}$$

π = total system pressure (also see Equation 10-3)

$$y_{im} = p_{im}/\pi$$

The steam required for the distillation is:

$$\pi = P_s + p_{im} \tag{10-353}$$

(also see Equation 10-2)

$$y_s = \frac{\pi - p_{im}}{\pi}$$

The steam required per mol of immiscible liquid vaporized is:

$$\frac{y_s}{y_{im}} = \frac{\pi - p_{im}}{p_{im}} = \frac{p_s}{p_{im}} \tag{10-354}$$

$$N_s = N_{im}(\pi - p_{im})/P_i \tag{10-355}$$

When the sum of the partial pressures of the steam and the material distilled reach the system pressure, boiling begins and both components are vaporized in the mol ratio of their partial pressures. Upon condensation of the overhead mixture, the condensate receiver will contain two layers separated by gravity.

The weight ratio of steam to the immiscible liquid in the vapor is:

$$\frac{W_s}{W_{im}} = (p_s M_s)/(p_{im} M_{im}) \tag{10-356}$$

Any non-volatile material in the mixture will remain in the still bottoms. The Hausbrand's vapor-pressure diagram [127, 128] in Figure 10-74 is a useful approach for the steam distillation calculation. This diagram was prepared for six organic compounds and the corresponding water vapor pressure as $(\pi - P_s)$ for three system pressures of 760, 300, and 70 mm Hg versus temperature, where

M = molecular weight of material
p = partial pressure, mm Hg
W = weight of material in vapor
N = number of mols
N_o = number of mols of non-volatile material present
y = mol fraction of material in vapor
π = system pressure, mm Hg
p_{im} = pure component vapor pressure of the immiscible liquid being distilled

Subscripts:

im = immiscible liquid
s = steam
1 = initial
2 = remaining

The water curve intersects the particular organic compound, and at that point the temperature is that at which the steam distillation can take place, because the partial pressures are additive at this point. For example, for 300 mm Hg total pressure system, reading the intersection point for benzene, and steam at 46°C, gives 220 mm Hg for benzene and (300 – 220) or 80 mm Hg. Then the mol ratio of benzene to water vapor is therefore 220/80 = 2.75; or 2.75 parts of benzene to 1 part of water.

When the composition of the compounds in the still or bottoms changes significantly as the batch distillation progresses, an unsteady state condition will exist as for differential distillation.

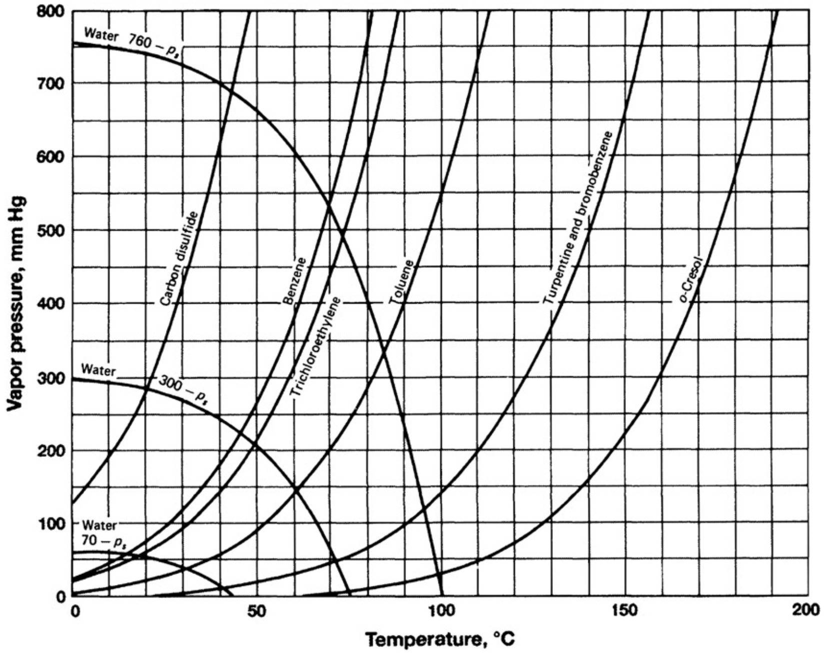


Figure 10-74 Hausbrand vapor-pressure diagram for various liquids and at three system steam pressures. A similar diagram can be constructed for other organic/hydrocarbon systems. Used by permission, Ellerbe, R. W., Chem. Eng. Mar. 4 (1974), p. 108.

When non-volatile material in the bottoms is significant, and no liquid water exists there – that is, p_s is below the saturation of the steam pressure at the still temperature – then the Raoult's Law steam efficiency is [127]: Values of E are found to range from 60% to 70% for many organics, but values of 90% to 95% are reported [127] for good sparger design for steam injection, and molecular weight of organics <100, and 50% for many lubricating oils.

$$E = \frac{p_{im}}{p_{im}\left(\frac{N_{im}}{N_{im} + N_o}\right)} \tag{10-357}$$

where

E = vaporization efficiency of steam distillation

Note that for this discussion now, P_{im} just above and in equations to follow, refers to the pure component vapor pressure of the immiscible liquid being distilled [127].

When steam is added to the still [127]:

$$\frac{p_s}{p_{im}} = \frac{\pi - p_{im}}{p_{im}} = \frac{\pi}{p_{im}} - 1 \tag{10-358}$$

and, for a constant distillation temperature, p_{im} is constant. Then for constant pressure:

$$N_S = \left(\frac{\pi}{E\,p_{im}} - 1\right)(N_{im1} - N_{im2}) + \frac{\pi N_o}{E p_{im}} \ln\left(\frac{N_{im1}}{N_{im2}}\right) \tag{10-359}$$

As the volatile material is reduced over the batch distillation process, the steam pressure rises during the progress of the operation, due to the decrease of p_{im}. When the volatile material is stripped down to a low residual concentration, p_s approaches the total system pressure, π. When the steam saturation pressure with temperature is $>\pi$, no steam condensation will occur during the operation.

When the non-volatile concentration is low to insignificant in the still feed, then N_o is small relative to N_{im}. Then p_{im} is considered constant [127]:

$$p_{im} = E\,p_{im} \tag{10-360}$$

$$N_s = (p_s/p_{im})(N_{im1} - N_{im2}) \tag{10-361}$$

Then, the distillate:

$$\frac{W_s}{W_{im}} = \frac{(\pi - p_{im})M_s}{p_{im}M_{im}} \tag{10-362}$$

Operation of the open still with only a steam injection sparger to bring steam below the liquid level in the still may not be efficient as operating the unit with internal trays to act as a stripping column. This should be examined for each situation, as the installation of trays can be expensive, particularly if they do not aid significantly in achieving the desired separation. Generally, when no liquid water is present, the best operation of an open still (with condenser) may be at the highest working temperature achievable without adverse effects on the fluids (i.e., no polymer formation, no breakdown, etc.). Often, direct steam injection can be reduced for any operation by careful heating of the still by an internal reboiler coil, or possibly a steam jacket. The heat sensitivity of the compounds involved must be recognized.

10.35.1 Steam Distillation-Continuous Flash Operation, Multicomponent or Binary Mixture

This system requires direct steam injection into the still with the liquid; all the steam leaves overhead with the boiled-up vapors (no internal condensation) in a steady-state operation, and system at its dew point. Steam is assumed to be immiscible with the organics. Steam distillation is usually applied in systems containing high boiling organics, or heat sensitive materials which otherwise require separation under vacuum conditions.

$$\frac{M_s}{B_{To}} = \frac{\pi}{P_b\,B_{To}}\left[\sum \frac{B_{io}}{\alpha_i}\right]_{i \neq s} - 1 \tag{10-363}$$

b is more volatile reference component

$i \neq s$ = components, i, are not to include steam, s

M_s = total mols steam required

B_{To} = total mols hydrocarbons at start (not including the steam)

B_{Tl} = mols liquid in bottoms of still at time, T

B_{io} = mols of component, i, at start

α_i = relative volatility of more volatile to each of other components

P_b = vapor pressure of reference more volatile component, b

π = total system pressure, absolute

B_b = mols of component, b, used as reference for volatility, after a given time of distillation

B_o = mols of component, b, used as reference for volatility, at start of distillation

Example 10-35: Multicomponent Steam Flash Calculations

A mixture of bottoms material of composition B_{io} below has accumulated in the run-down tank. It is necessary to separate the volatile organic heavies from the tarry polymerized residue (heavy liquid). Steam is to be injected into the insulated tank containing heating coils. The system is to operate at 200 mm Hg absolute pressure and

250°F with no condensation of the steam. The organic volatile heavies contain:

Component	Vapor pressure @ 250°F, mm Hg	$\alpha = p_i/P_A$	Mols B_{io}	B_{io}/α_i
A		1.0	45	45
B	20	0.57	40	70
C	6	0.171	26	152
Total			111	267

$$\frac{M_s}{B_{To}} = \frac{\pi}{P_b\, B_{To}}\left[\sum \frac{B_{io}}{\alpha_i}\right] - 1$$

$$\frac{M_s}{111} = \frac{200}{35(111)}[267] - 1$$

$$= 13.75 - 1 = 12.75$$

M_s = 1,415 total mols steam required for 111 mols mixture

Mols steam/mol of mixture organic volatiles = 1,415/111 = 12.8

10.35.2 Steam Distillation-Continuous Differential, Multicomponent or Binary Mixture

The results of the differential distillation are the same as the flash distillation, although the mechanism is somewhat different. This is a batch type operation distilling differentially. All sensible and latent heats are supplied separately from the steam or by superheat in the steam. Steam acts as an inert in the vapor phase, and the quantity will vary as the distillation proceeds, whilst temperature and pressure are maintained.

$$\frac{M_s}{B_{T1} - B_{To}} = 1 - \frac{\pi}{P_b(B_{T1} - B_{To})}\left[\sum \frac{B_{io}}{\alpha_i}\left[\left(\frac{B_b}{B_{bo}}\right)^{\alpha i} - 1\right]\right] \tag{10-364}$$

If all the volatile materials are distilled: $\left(\frac{B_b}{B_{bo}}\right) = 0$ and $B_{T1} = 0$

This relation is handled in a similar manner to that in flash steam separation.

If all of the material is not to be removed as overhead vapors from the still, leave a percentage of a particular compound in the bottoms, then select the particular compound as the reference material "b" for α determinations.

B_b = (Fraction retained) (B_{bo}) and $\left(\frac{B_b}{B_{bo}}\right)$ = (Fraction retained)

Substitute and solve for B_{T1}.

$$B_{T1} = \sum_{i \neq S} B_{io}\left(\frac{B_b}{B_{bo}}\right)^{\alpha i} \tag{10-365}$$

Knowing B_{T1}, the relation for M_s can be solved to determine mols of steam to reduce initial material to percentage of a compound in the remaining bottoms. If steam condenses, the requirement for steam increases by this amount.

10.35.3 Steam Distillation-Continuous Flash, Two Liquid Phases, Multicomponent and Binary Mixture

Because water will be present in this system, and is assumed immiscible with the other components, it will exert its own vapor pressure. This situation is similar to that with many systems where the liquid to be flashed enters below its dew point, and hence requires the use of steam for heating (sensible + latent) as well as for the partial pressure effect.

Mols steam in vapor phase only:

M_s (vapor) $= P_s \sum \frac{B_{io}}{P_i}$ (at assumed flash temperature)

where

P_s = vapor pressure of steam

P_i = vapor pressure of each component at the flash temperature

Mols steam to heat is sum of sensible plus latent

Total mols steam is sum of M_s (vapor) plus heating steam

System total pressure:

$$\pi = \frac{M_s + B_{To}}{\sum\limits_{i \neq S} \frac{B_{io}}{P_i}}, \text{ absolute} \tag{10-366}$$

B_{To} = mols (total) volatile material at start

10.35.4 Open Live Steam Distillation-With Fractionation Trays, Binary Mixture

Open or direct injection of steam into a distillation system at the bottom of the column or still may be used to heat the mixture, as well as to reduce the effective partial pressure of the other materials. In general, if steam is used to replace a reboiler, one tray is added to replace the reboiler stage, and from 0.3 – 1.0 more trays may be needed to offset the dilution of the system with water in the lower portion. If steam is acceptable, it replaces the cost of a reboiler and any cleaning associated with this equipment. For most columns, extra trays can be purchased to offset this cost. When one of the components of the binary is water, and steam is used, the equation used for the operating stripping line (there is no rectifying section) is:

For component not including water:

$V_s\, y_{i\,(m)} = L_s\, x_{i\,(m+1)} - B\, x_{iB}$

Slope of operating line $(L/V)_m = B/S$
Operating line intersects the x-axis at x_{iB}
The step-off of trays starts at x_{iB} on the x-axis, $y = 0$.

Open steam is used for stripping of dissolved or absorbed gases from an absorption oil, with all of the steam going overhead, and the stripped oil leaving at the bottom. The absorption coefficient of the oil for the component must be known to be able to construct the equilibrium curve. The operating curve is constructed from several point material balances around the desired component, omitting the oil provided; its volatility is very low. The trays can be stepped-off from a plot of y vs. x as in other binary distillations, but using only the stripping section.

Example 10-36: Continuous Steam Flash Separation Process: Separation of Non-Volatile Component from Organic Components

It is desired to separate a non-volatile material from an equimolal mixture of benzene, toluene, and xylene at 80°C. Vapor pressure data for these compounds are available from several physical property sources. The following approximate values for the specific heats and latent heats of vaporization may be used:

Benzene: $C_p = 0.419$ cal/gm-°C
$\Delta H_v = 97.47$ cal/gm

Toluene: $C_p = 0.44$ cal/gm-°C
$\Delta H_v = 86.53$ cal/gm

Xylene: $C_p = 0.40$ cal/gm-°C
$\Delta H_v = 82.87$ cal/gm

If the mixture is separated by a continuous flash process, the components are considered insoluble in water (check references) and the feed enters at the flash chamber at 20°C, calculate the mols of steam condensed, the total mols steam required per 100 mols of feed, and the total pressure. Use steam at 212°F and atmospheric pressure.

In summary, this involves a continuous flash process:

- All the feed is to be flashed.
- Steam does the heating.
- Some steam condenses.
- Water is immiscible with the materials.

Solution

Feed:

Benzene:	33.33 + mols
Toluene:	33.33 + mols
Xylene:	33.33 + mols
Total	100.00 mols feed

Because water will be present in liquid phase, it will only exert its vapor pressure. Temperature of flash = 80°C.

$$N_2 = P_s \sum L_i^o / P_i$$

where

N_2 = mols steam in vapor only
P_s = vapor pressure of steam
L_i^o = mols of each component at start
P_i = vapor pressure of each component at temperature

Component	Mols at start L_i^o	P_i at 80°C, mm Hg	L_i^o/P_i	Mol Wt
Benzene	33.33	760	0.043	78
Toluene	33.33	280	0.1190	92
Xylene	33.33	120	0.277	106
			0.4397	

P_s at 80°C (176°F) = 6.868 lb/sq in. abs (from steam tables)

$$= \frac{760}{14.7}(6.868) = 354 \text{ mm Hg abs}$$

$$N_2 = P_s \sum L_i^o / P_i$$

= 354 (0.4397) = 155.7 mols steam in vapor per 100 mols of feed (volatile) material

Steam required to heat feed to 80°C:

	Btu
Benzene: Sensible heat	
(78) (33.33) [(0.419 cal/gm-°C) (1.8)](80°−20°)	= 117,800
Latent heat	
(78) (33.33) (97.46 × 1.8)	= 454,000
Toluene: Sensible heat	
(92) (33.33) [0.44 × 1.8] (80°−20°)	= 145,600
Latent heat	
(92) (33.33) (86.53 × 1.8)	= 477,000
Xylene: Sensible heat	
(106) (33.33) [0.40 × 1.8] (80°−20°)	= 153,000
Latent heat	
(106) (33.33) (82.87 × 1.8)	= 525,000
Total heat load:	= 1,872,400

lbs steam required for heat load = $\left[\dfrac{1,872,400 \text{ Btu/100mols}}{970 \text{ Btu/lb at } 212^\circ\text{F}}\right]$

= 1,932 lbs steam/100 mols volatile

Mols steam required for heat load $= \dfrac{1,932}{18} = 107.2$ mols steam/100 mols volatile material

Total mols steam/100 mols volatile feed = 155.7 + 107.2 = 262.9

Total pressure of system:

$$\pi = \frac{N_2 + L_T^o}{\sum\limits_{i \neq S} L_i/P_i}$$

L_T = Total mols volatile material at start = 100

$$\pi = \frac{155.7 + 100}{0.4397} = 580 \text{ mm Hg abs}$$

Neglect pressure drops through the system.

Determine: How much water is removed from the overhead accumulator and the intermediate dehydrator or water removal tray? No water is removed from the bottoms due to the use of superheated steam.

Solution

From steam tables (saturated) at:

Top of tower, 175°F, vapor pressure water, psia	= 6.8
Mol fraction water vapor at top of tower: 6.8/48 psia	= 0.1416
Mol fraction hydrocarbon at top of tower: 1 − 0.1416	= 0.8584
Total mols mix HC vapor and water vapor at tower overhead: $\frac{775 + 850}{0.8584} = 1,893.0$	
Mols of water vapor in tower overhead: 1,893 − (775 + 850)	= 268
Accumulator @ 48 psia & 135°F, water vapor pressure:	= 2.6 psia
Mol fraction water in accumulator vapor: = 2.6/48	= 0.0541
Mol fraction HC in accumulator vapor: = 1 − 0.0541	= 0.9459
Total mols vapor leaving accumulator: = $\left[\frac{(775)(0.55)}{0.8584}\right]$	= 450.6
Mols water vapor leaving accumulator: = 450.6 − (775) (0.55)	= 24.35
Mols liquid water withdrawn from accumulator: = 268 − 24.35	= 243.65
Mols liquid water collected on dehydrator tray and removed at that point up tower above	= 777. 7 − 268
where reflux returns below this tray: (water vapor in tower overhead)	= 509.7 mols/h
Mols steam entering tower: = 14,000/18	= 777.7 mols/hr

Example 10-37: Open Steam Stripping of Heavy Absorber Rich Oil of Light Hydrocarbon Content (used by permission following the method of R. W. Ellerbe, Chemical Engineering [127])

A gas processing plant selectively extracts ethylene and ethane from an incoming natural gas mixture stream. These two light hydrocarbons are absorbed in heavy gasoline type absorber "oil," and then stripped with open steam in an open tower. The system data are (see Figure 10-75):

Rich oil rate to tower:	8,500 mol/h
Overhead product of ethylene and ethane:	775 mol/h
Overhead product from accumulator:	55% vapor and 45% liquid
Accumulator conditions:	48 psia and 135°F
Reflux hydrocarbon in top vapor @ 175°F:	850 mol/h
Steam (superheated) enters bottoms below tray:	14,000 lb/h
Water partial pressure in the mixed vapor at bottoms:	20 psi
Hydrocarbons mix partial pressure:	50 psi − 20 psi = 30 psi

10.36 Distillation with Heat Balance of Component Mixture

This type of evaluation of a distillation system involves a material and heat balance around each tray. This is extremely tedious by conventional means, but is now handled with computers using simulation software (e.g. Hysys, Chemcad, Prosim, UniSim, Aspen). However, the volume of calculations is large and requires a relatively long time. Only those special systems that defy a reasonable and apparently economical solution by other approaches are even considered for this type of approach. The detailed method involves trial and error assumptions of both material and heat balance.

10.36.1 Unequal Molal Overflow

This is another way of expressing that the heat load from tray to tray is varying in the column to such an extent as to make the usual simplifying assumption of equal molal overflow invalid. The relations to follow do not include heats of mixing. In general they apply to most hydrocarbon systems.

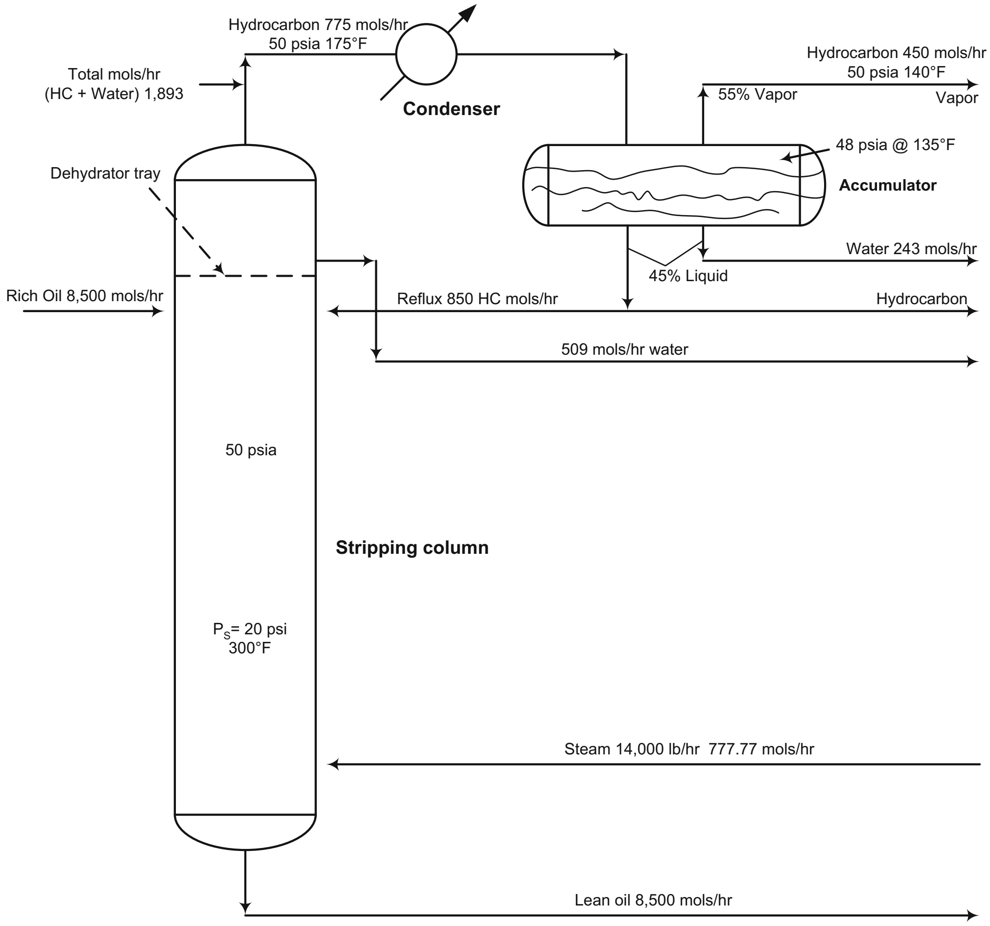


Figure 10-75 Open steam stripping light hydrocarbons from rich oil. Modified for Example 10-37 and used by permission, Ellerbe, R. W., Chem. Eng. Mar. 4 (1974), p. 108.

1. Equation of operating line in rectifying section, light component [59]:

$$L_{n+1} = Vn - D$$

$$y_n = \left(\frac{M_D - H_n}{M_D - h_{n+1}}\right)x_{n+1} + \left(\frac{H_n - h_{n+1}}{M_D - h_{n+1}}\right)x_D$$

$$\frac{L_{n+1}}{V_n} = \frac{M_D - H_n}{M_D - h_{n+1}} = 1 - \frac{H_n - h_{n+1}}{M_D - h_{n+1}} \qquad (10\text{-}367)$$

2. Equation of operating line in stripping section, light component:

$$L_{m+1} = V_m + B$$

$$y_m = \left(\frac{M_B - H_m}{M_B - h_{m+1}}\right)x_{m+1} + \left(\frac{H_m - h_{m+1}}{M_B - h_{m+1}}\right)x_B$$

$$\frac{L_{m+1}}{V_m} = 1 - \frac{H_m - h_{m+1}}{M_B - h_{m+1}} \qquad (10\text{-}368)$$

$$\frac{D}{V_m} = \frac{H_m - h_{m+1}}{M_m - h_{n+1}}$$

where

$M_B = h_B - Q_B/B$

$M_D = Q_c/D + h_D$

$M_B = h_w - \dfrac{Q_s}{W}$

H_n = total molal enthalpy of vapor at conditions of plate n, $H_n = \Sigma H_{ni} (y_{ni})$

h_n = total molal enthalpy of liquid at conditions of plate n, $h_n = \Sigma h_{ni} (x_{ni})$

s = lb (or mols) steam per lb (or mol) bottoms

H_m = total molal enthalpy of vapor at plate m (below feed)

N = mols residue or bottoms per unit time

Q_B = heat added in still or bottoms

10.36.2 Ponchon-Savarit Method-Binary Mixtures

For a binary fractionating tower, illustrated in Figure 10-76, the conditions of the feed, F, x_F, H_F are known and the composition of the distillate product, x_D and the

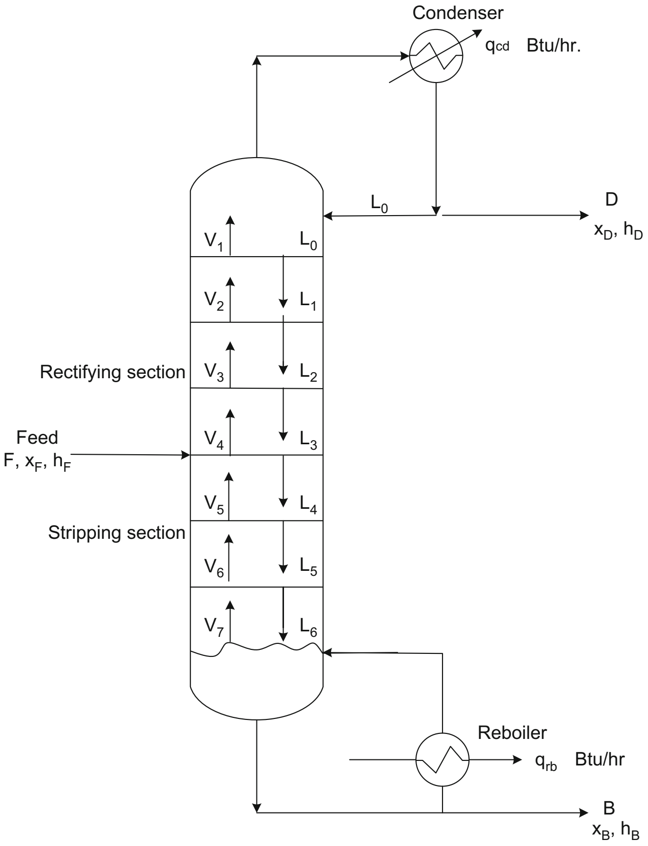


Figure 10-76 Fractionating tower with reboiler and condenser units.

composition of the bottoms product, x_B are specified. If the column is operated at a constant reflux ratio, the number of equilibrium stages required to achieve a desired separation can be estimated. The simplest method of achieving this task is based upon an assumption of constant molal overflow (CMO). This only occurs if:

1. The molal heats of vaporization of the components are identical.
2. Sensible heat distributions are negligible.
3. Heats of mixing are negligible.

With these criteria, the internal energy balances around each plate in the tower are straightforward, as the molal flow rate of liquid and vapor are constant throughout each section. The McCabe-Thiele diagram can be employed to calculate the number of equilibrium stages. However, the above criteria are not met for numerous systems. The use of McCabe-Thiele analysis in these circumstances may lead to under specification of distillation equipment.

Where constant molal overflow is not applicable, enthalpy-composition diagrams can be combined with vapor-liquid equilibrium data and the graphical Ponchon-Savarit method employed. A Ponchon-Savarit analysis does not assume the liquid and vapor flow rates are constant in each section of the tower. The only assumption of this approach is that there are no significant heat losses through the column walls.

This graphical method allows solution of many distillation problems which would require considerable work if attempted by rigorous methods. Robinson and Gilliland have published technical and descriptive details substantiating this method [8, 59]. Figure 10-77 presents a summary of the use of this method and appropriate interpretations. Scheiman [104] uses the Ponchon-Savarit diagrams to determine minimum reflux by heat balances. Campagne [216, 217] suggests a detailed technique for using the Ponchon-Savarit method in a computer simulation, which leads to designs not previously possible.

The basic method allows the non-ideal heat effects of the system to be considered as they affect the plate-to-plate performance. The systems, as represented in the diagrams, are usually at constant pressure, but this is not necessarily the case in reality. The equilibrium tie lines connect points fixed by the x-y values to corresponding saturated liquid and saturated vapor conditions at a constant temperature, such as "a" °F or "b" °F. The mol fractions are obtained from the usual x-y diagram for the system, and the enthalpy values are relative to a fixed datum point for the available heat data of the particular components. For such systems as ammonia-water, methanol-water and ethanol-water the data are readily available (see Figures 10-78a, 79, and 80). The saturated liquid line represents the enthalpies of liquid mixtures at the various compositions, all at a constant pressure. This is the bubble point curve. The dew point curve is produced by plotting the enthalpies of the various vapor mixtures at the saturation temperature at a constant pressure. Figure 10-78b shows the corresponding vapor-liquid equilibrium diagram for ammonia-water system at 1.10325 kPa, and Figure 10-81 illustrates the combined enthalpy-concentration diagrams for ethanol-water system at 1.01325 kPa.

An effort has been made to present the basic understanding of the method as it applies to systems involving unequal molal overflow, open steam distillation and single flash vaporization in Figures 10-77 and 10-82.

To obtain high or even necessary levels of accuracy for some design conditions, the end portions of the graphical representation may require enlargement from the usual size for graphical plotting. In most cases, a size of 11 × 17 inches is suggested. In general, the nonequimolal overflow (NEMO) model of the column is more rigorous, and should be used in those columns where there are:

1. Large temperature differences from the top of the column to the bottom (i.e. where sensible heat effects are important).
2. Large heats of mixing.
3. Significant differences in the molal heats of vaporization of the components.

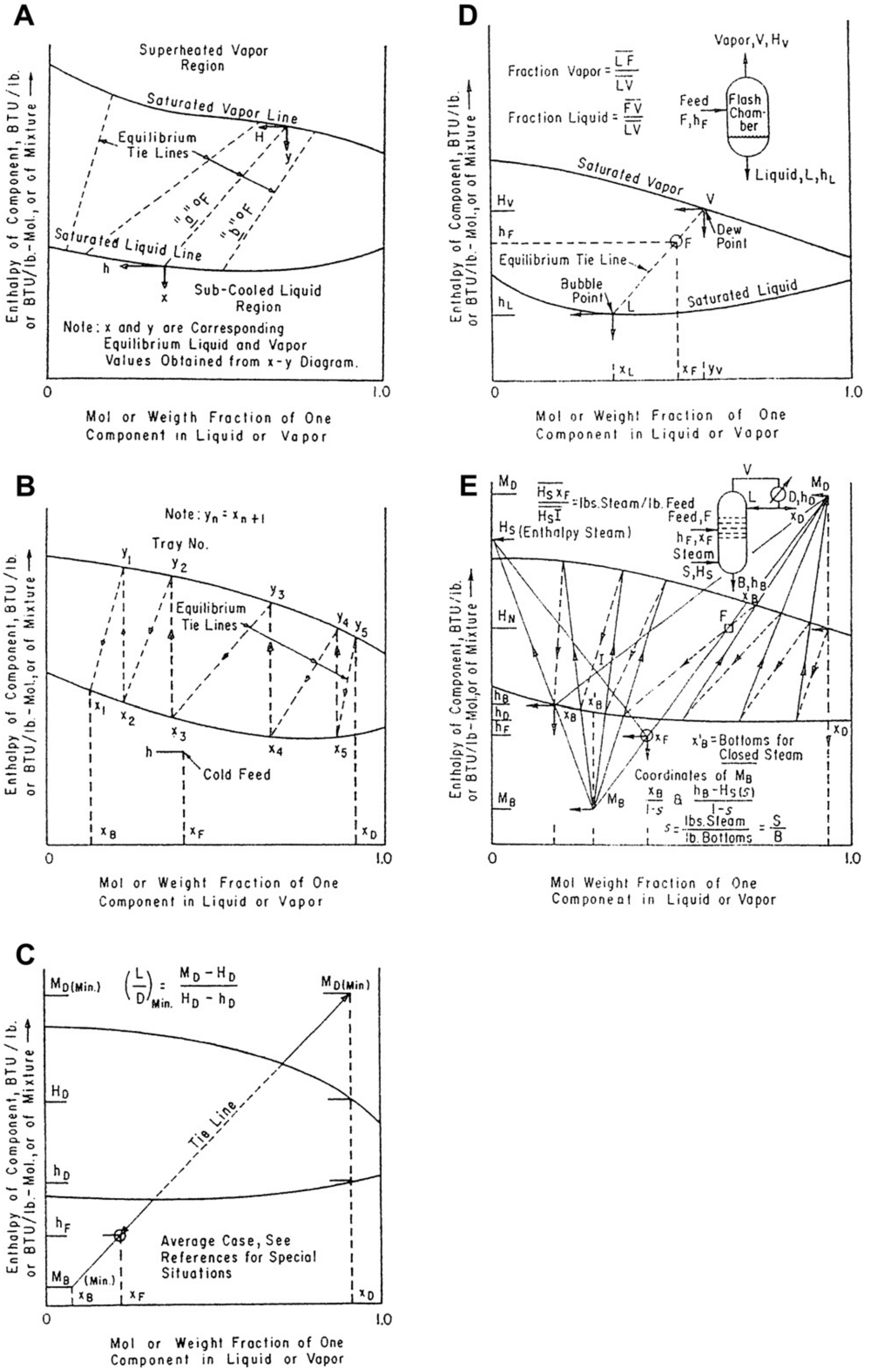


Figure 10-77A–E Performance analysis of unequal molal overflow for binary system using Ponchon-Savarit method.

The Equations

Consider the energy balance around the column, assuming no heat loss through the column wall:

$$Fh_F + q_{rb} = Dh_D + Bh_B + q_{cd} \tag{10-369}$$

where q_{rb} and q_{cd} are the duties of the reboiler and condenser respectively, Btu/h. Since the column reflux ratio R is set, R is defined by:

$$R = L/D \tag{10-370}$$

or

$$L = RD \tag{10-371}$$

with L = the molal flow rate of reflux returned to the column, the condenser duty is:

$$q_{cd} = (L + D)\,\lambda \tag{10-372}$$

Substituting Equation (10-371) into Equation (10-372) gives:

$$\begin{aligned} q_{cd} &= (RD + D)\,\lambda \\ &= D(R + 1)\lambda \end{aligned} \tag{10-373}$$

where

λ is the latent heat of vaporization of the distillate product.

The distillate product flow rate, D and the bottoms product flow rate B can be determined from an overall mass balance and a mass balance on the more volatile component as follows:

$$F = D + B \tag{10-374}$$

$$F\,x_F = D\,x_D + B\,x_B \tag{10-375}$$

Since the feed stream and the composition of distillate and bottoms product have been specified, the two unknown quantities, D and B in Equations 10-374 and 10-375 can be found.

Combining Equations 10-374 and 10-375 gives:

$$(D + B)x_F = Dx_D + Bx_B \tag{10-376}$$

Rearranging Equation 10-376 gives:

$$B(x_F - x_B) = D\,(x_D - x_F) \tag{10-377}$$

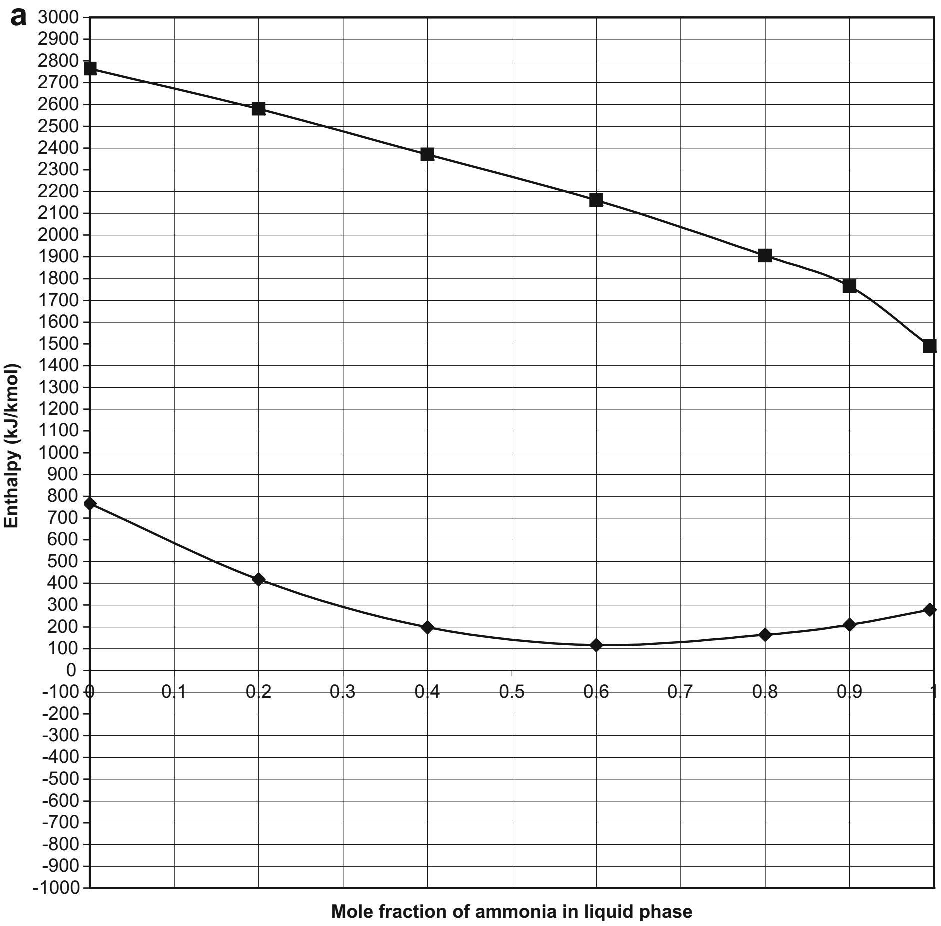


Figure 10-78a Enthaply vs composition of ammonia–water system.

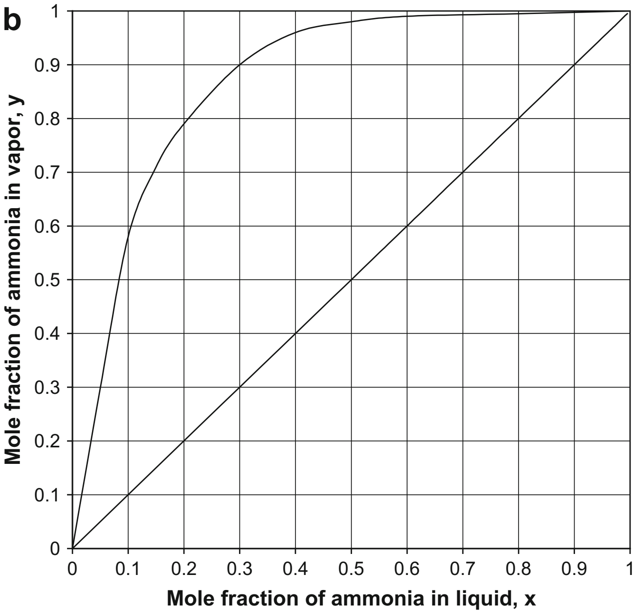


Figure 10-78b VLE data of ammonia-water system at 1atm.

From the heat balance of Equation 10-369,

$$Fh_F + q_{rb} = Dh_D + Bh_B + q_{cd} \tag{10-369}$$

Rearranging Equation 10-369 gives

$$Fh_F = \left(h_B - \frac{q_{rb}}{B}\right) B + \left(h_D + \frac{q_{cd}}{D}\right) D \tag{10-378}$$

Equation 10-377 in the ratio of B/D gives

$$\frac{B}{D} = \frac{x_D - x_F}{x_F - x_B} \tag{10-379}$$

Substituting Equation 10-374 into Equation 10-378 gives

$$(D + B)\, h_F = \left(h_B - \frac{q_{rb}}{B}\right) B + \left(h_D + \frac{q_{cd}}{D}\right) D \tag{10-380}$$

or

$$\left(1 + \frac{B}{D}\right) h_F = \left(h_B - \frac{q_{rb}}{B}\right) \frac{B}{D} + \left(h_D + \frac{q_{cd}}{D}\right) \tag{10-381}$$

Substituting Equation 10-379 into Equation 10-381 gives:

$$\left[1 + \left(\frac{x_D - x_F}{x_F - x_B}\right)\right] h_F = \left[h_B - \frac{q_{rb}}{B}\right] \left(\frac{x_D - x_F}{x_F - x_B}\right) + \left(h_D + \frac{q_{cd}}{D}\right) \tag{10-382}$$

$$h_F + \left(\frac{x_D - x_F}{x_F - x_B}\right) h_F = \left(h_B - \frac{q_{rb}}{B}\right) \left(\frac{x_D - x_F}{x_F - x_B}\right) + \left(h_D + \frac{q_{cd}}{D}\right) \tag{10-383}$$

Rearranging Equation 10-383 gives

$$\left(\frac{x_D - x_F}{x_F - x_B}\right) \left[h_F - \left(h_B - \frac{q_{rb}}{B}\right)\right] = \left(h_D + \frac{q_{cd}}{D}\right) - h_F \tag{10-384}$$

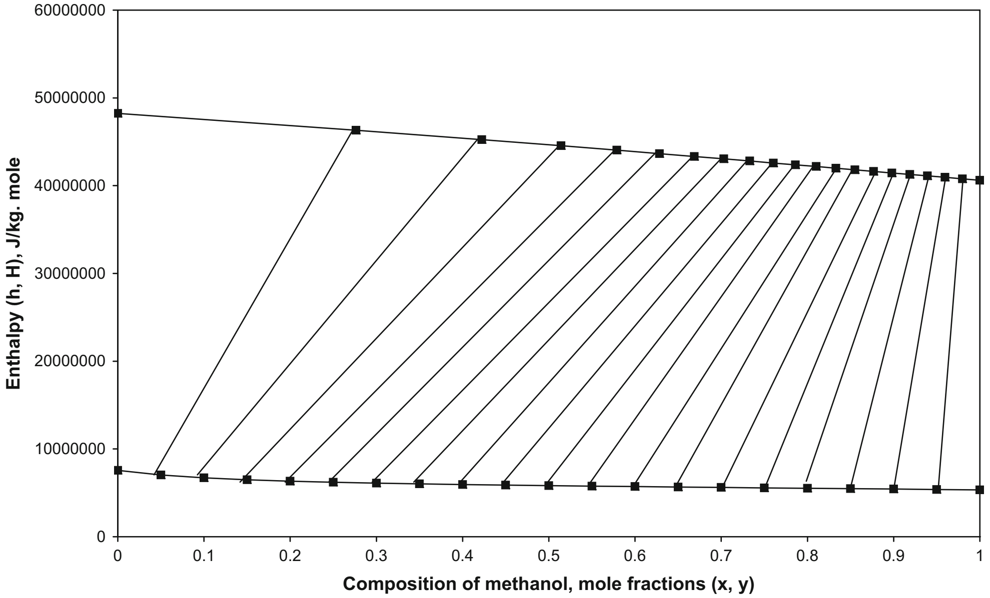


Figure 10-79 Enthalpy composition diagram for methanol–water mixture at a pressure of 101.235 kPa.

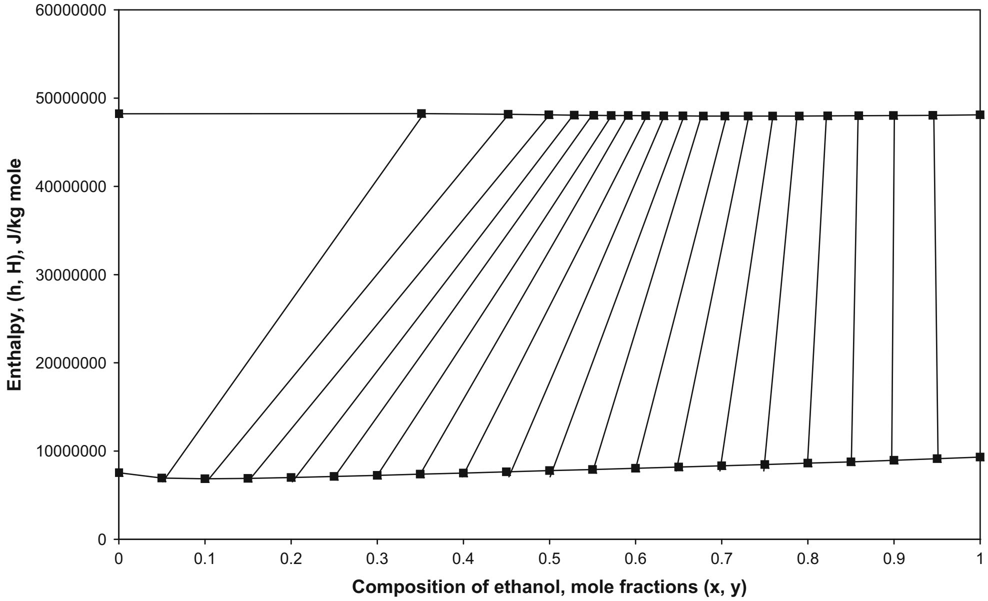


Figure 10-80 Enthalpy composition diagram for ethanol–water mixture at a pressure of 101.235 kPa.

and

$$\frac{x_F - x_B}{\left[h_F - \left(h_B - \frac{q_{rb}}{B}\right)\right]} = \frac{x_D - x_F}{\left[\left(h_D + \frac{q_{cd}}{D}\right) - h_F\right]} \tag{10-385}$$

Equation 10-385 indicates that the points $(h_B - q_{rb}/B), x_B; h_F, x_F$; and $(h_D + q_{cd}/D), x_D$ must all lie on a single straight line on an enthalpy-composition diagram. Since we know the condenser duty, q_{cd}, the point $x_D, (h_D + q_{cd}/D)$ can be positioned on the enthalpy-composition diagram as point d in Figure 10-83a-c. Place the feed point f at h_F, x_F and extend a line through points d and f to a vertical line placed at $x = x_B$ to point b. This point must have the coordinates $x_B, (h_B - q_{rb}/B)$.

Note: the feed is taken as saturated liquid.

Proceed to calculate the number of equilibrium stages in the rectifying section as follows: First, draw a vertical line at $x = x_D$ extending from point d to the saturated line at point l_0. Both the distillate product and reflux are saturated liquid with composition x_D and hence must be represented by point l_0 (Figure 10-83b).

The mass balance, component balance and the energy balance around the condenser are:

$$V_1 = L_1 + D \tag{10-386}$$

$$V_1 y_1 = L_1 x_1 + D x_D \tag{10-387}$$

$$V_1 h_v = L_1 h_L + D\left(h_D + \frac{q_{cd}}{D}\right) \tag{10-388}$$

Around the top plate of the column and the condenser, an energy balance yields:

$$V_2 h_{v2} = L_1 h_{L1} + D\left(h_D + \frac{q_{cd}}{D}\right) \tag{10-389}$$

where

h_v = enthalpy of saturated vapor
h_L = enthalpy of saturated liquid

The total and component mass balances are:

$$V_2 = L_1 + D \tag{10-390}$$

$$V_2 y_2 = L_1 x_1 + D x_D \tag{10-391}$$

Substituting V_2 in Equation 10-390 into Equations 10-389 and 10-391 respectively gives:

$$(L_1 + D) y_2 = L_1 x_1 + D x_D \tag{10-392}$$

$$(L_1 + D) h_{v2} = L_1 h_{L1} + D\left(h_D + \frac{q_{cd}}{D}\right) \tag{10-393}$$

Rearranging Equation 10-393 gives:

$$\left(\frac{L_1}{D} + 1\right) h_{v2} = \frac{L_1}{D} h_{L1} + \left(h_D + \frac{q_{cd}}{D}\right) \tag{10-394}$$

Rearranging Equation 10-392 gives:

$$L_1 y_2 - L_1 x_1 = D x_D - D y_2 \tag{10-395}$$

or

$$L_1 (y_2 - x_1) = D(x_D - y_2) \tag{10-396}$$

$$\frac{L_1}{D} = \frac{x_D - y_2}{y_2 - x_1} \tag{10-397}$$

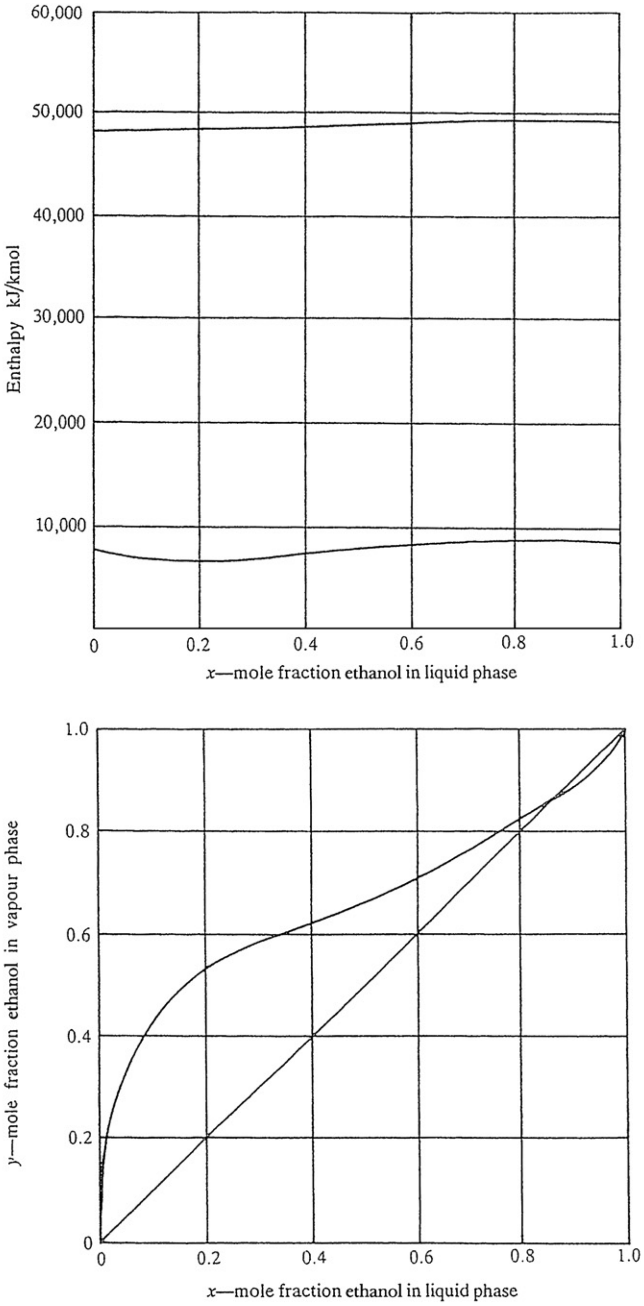


Figure 10-81 Combined enthalpy–concentration diagrams for ethanol–water system at 1.0 bar.

Substituting Equation 10-397 into the energy balance Equation 10-394 gives

$$\left(\frac{x_D - y_2}{y_2 - x_1} + 1\right) h_{v2} = \left(\frac{x_D - y_2}{y_2 - x_1}\right) h_{L1} + \left(h_D + \frac{q_{cd}}{D}\right) \tag{10-398}$$

or

$$(h_{v2} - h_{L1})\left(\frac{x_D - y_2}{y_2 - x_1}\right) = \left(h_D + \frac{q_{cd}}{D}\right) - h_{v2} \tag{10-399}$$

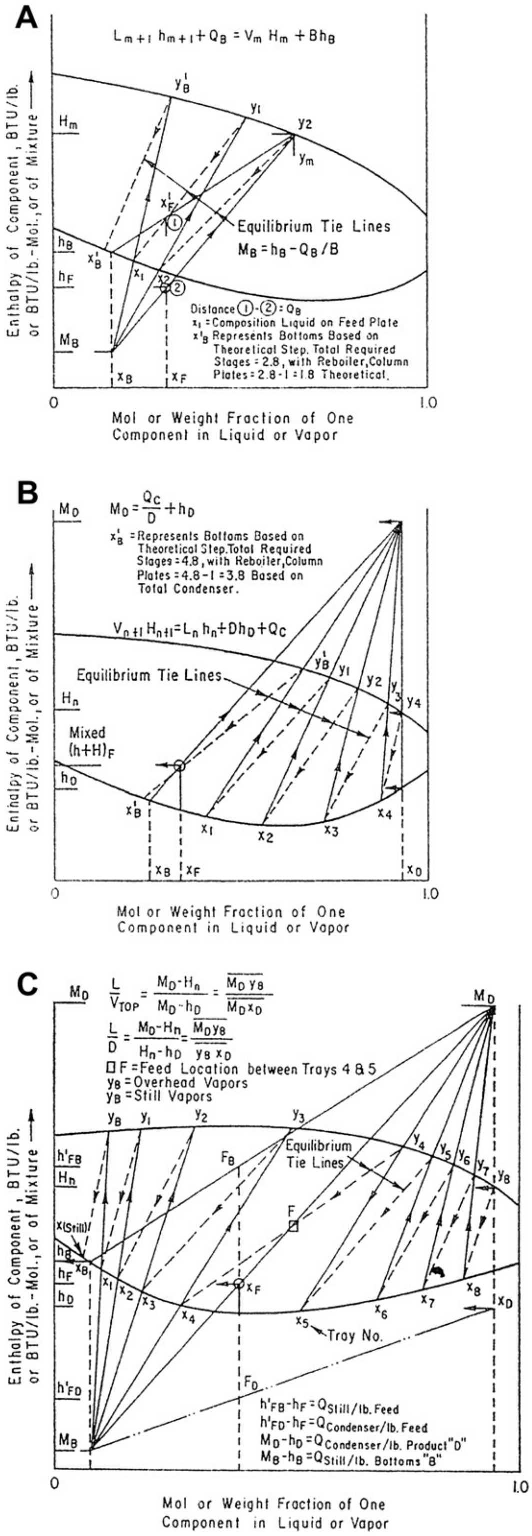


Figure 10-82A–C Graphical solution of unequal molal overflow, binary systems.

$$\frac{L_1}{D} = \frac{x_D - y_2}{\left(h_D + \dfrac{q_{cd}}{D} - h_{v2}\right)} = \frac{y_2 - x_1}{(h_{v2} - h_{L1})} \tag{10-400}$$

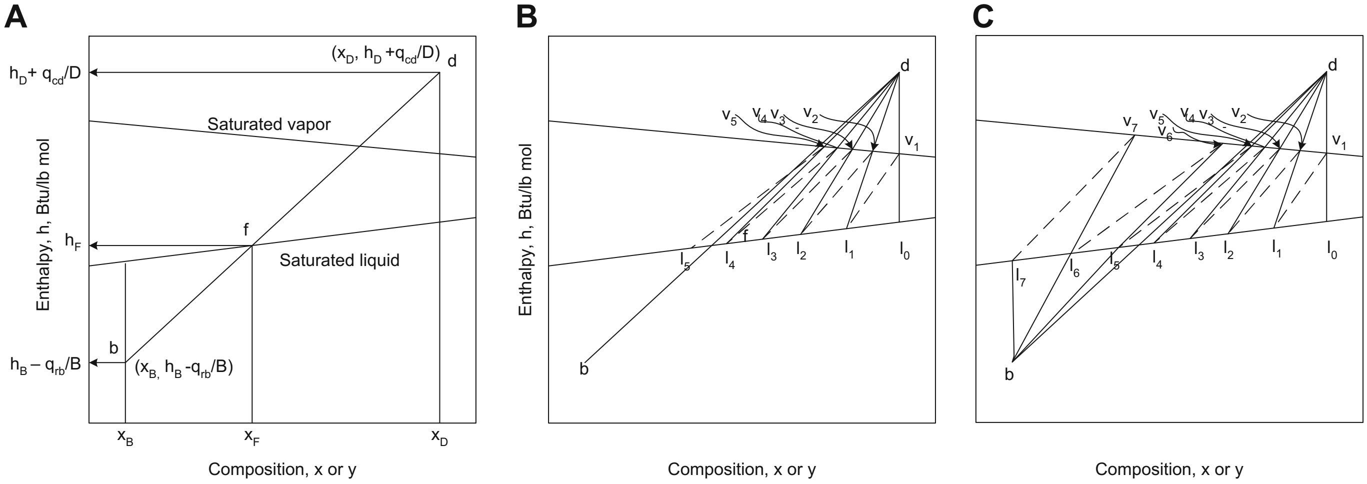


Figure 10-83A–C Ponchon analysis of a fractionating column.

The familiar form of Equation 10-400 indicates that points d and l_1 in Figure 10-83b must be on the same straight line as the point y_2, h_{v2}. Since the location of points d and l_1, is known a line can be drawn connecting these points. Stream V_2 is saturated vapor, and the intersection of line d–l_1 with the saturated vapor line at point V_2 must represent the enthalpy and the composition of stream V_2 on Figure 10-83b. The process is repeated to calculate the enthalpy and composition of streams L_2 and V_3. A tie line is drawn from V_2 to the saturated liquid line. Point l_2 thus determined, specifies stream L_2. From point l_2 a line is constructed to point d. By reasoning analogous to that following Equation 10-400, stream V_3 is represented by the intersection of line l_2d with the saturated vapor line at point V_3. The process is continued for each plate in the rectifying section of the column and the number of plates determined by the number of tie lines which were constructed.

When a tie line crosses line *bfd* (Figure 10-83), the feed point is determined. A new set of material and energy balances is then used to find the number of plates in the stripping section. This corresponds to using different operating lines in the stripping and rectifying sections of a column in a McCabe-Thiele analysis. It is not essential that the feed plate is chosen whose tie line crosses line *bfd* as the feed plate. However, with this criterion for locating the feed plate, the maximum separation per plate is achieved.

Stripping Section (see Figure 10-76):

The number of plates in the stripping section of the column (i.e. plates below the feed point) is determined in the same manner as in the rectifying section and the procedure is as follows.

An energy balance is written around the second plate in the stripping section and the reboiler:

$$L_4\, h_{L4} = V_5\, h_{v5} + B\left(h_B - \frac{q_{rb}}{B}\right) \tag{10-401}$$

The mass and component balances are:

$$L_4 = V_5 + B \tag{10-402}$$

$$L_4\, x_4 = V_5\, y_5 + Bx_B \tag{10-403}$$

Combining Equations 10-402 and 10-403 gives:

$$(V_5 + B)\, x_4 = V_5\, y_5 + Bx_B \tag{10-404}$$

Rearranging Equation 10-404 gives:

$$V_5\,(y_5 - x_4) = B\,(x_5 - x_B) \tag{10-405}$$

Therefore

$$\frac{B}{V_5} = \frac{y_5 - x_4}{x_5 - x_B} \tag{10-406}$$

From the heat balance:

$$(V_5 + B)h_{L4} = V_5\, h_{v5} + B\left(h_B - \frac{q_{rb}}{B}\right) \tag{10-407}$$

or

$$\left(1 + \frac{B}{V_5}\right) h_{L4} = h_{v5} + \frac{B}{V_5}\left(h_B - \frac{q_{rb}}{B}\right) \tag{10-408}$$

Substituting Equation 10-406 into Equation 10-408 gives:

$$\left(1+\frac{y_5-x_4}{x_4-x_B}\right)h_{L4}=h_{v5}+\left(\frac{y_5-x_4}{x_4-x_B}\right)\left(h_B-\frac{q_{rb}}{B}\right) \tag{10-409}$$

Rearranging Equation 10-409 gives:

$$\left(\frac{y_5-x_4}{x_4-x_B}\right)\left[h_{L4}-\left(h_B-\frac{q_{rb}}{B}\right)\right]=h_{v5}-h_{L4} \tag{10-410}$$

or

$$\frac{y_5-x_4}{h_{V5}-h_{L4}}=\frac{x_4-x_B}{\left[h_{L4}-\left(h_B-\frac{q_{rb}}{B}\right)\right]} \tag{10-411}$$

Rearranging Equation 10-411 for the stripping section of the column finally gives:

$$\frac{B}{V_5}=\frac{y_5-x_4}{x_4-x_B}=\frac{h_{V5}-h_{L4}}{\left[h_{L4}-\left(h_B-\frac{q_{rb}}{B}\right)\right]} \tag{10-412}$$

In the stripping section, from Equation 10-412, points b and l_4 must lie on a straight line with points H_{V5} and y_5. Since the location of points b and l_4 is known, a line is extended through these points to the saturated vapor line to determine points V_5 and the enthalpy and composition of a stream V_5 as shown in Figure 10-83c.

Streams V_5 and L_5 are in equilibrium, and a tie line from point v_5 to the saturated liquid line set point l_5 and the conditions of stream L_5. This process is continued by drawing a line through points b and l_5 to find point v_6 on the saturated vapor line. By repeating this process until a tie line intersects the saturated liquid line at or below x_B, we complete the Ponchon-Savarit analysis. The number of equilibrium stages in the fractionating column is determined by counting the number of tie lines that were constructed. In Figure 10-83c, a total of 7 equilibrium stages, three plates in the rectifying section, one feed plate and three plates in the stripping section corresponds to the column reboiler. Points d and b in Figures 10-83a-c are referred to as difference points and lines drawn to d and b are referred to as difference lines.

Minimum Reflux

The condition of minimum reflux is when any equilibrium tie line coincides with any operating line, as shown in Figure 10-84. Usually this coincidence takes place on the operating line through the feed condition, and the location of d for the condition of minimum reflux is found by extending the equilibrium tie line through the feed condition to intersect the composition through x_D or y_D.

Total Reflux

The condition of total reflux is shown in Figure 10-85. In this instance, the operating lines are parallel and vertical, converging at infinity. This results from the condition of $V = L$ since $D = 0$, $B = 0$, $Q_D = q_{cd}/D = \infty$, and $Q_B = q_{rb}/B = \infty$. Thus, the enthalpy coordinates are $h_D - Q_D = h_D - (-\infty)$ and $h_B - Q_B = h_B - \infty$. The minimum number of plates is encountered at the condition of total reflux.

Side streams and multiple feeds

The Ponchon-Savarit method is very versatile and can be applied with columns having multiple feeds or side stream withdrawals. There are situations where feeds of different composition are involved, and it is possible to introduce each at its proper location in the column, and thereby reduce the total number of plates by one or two compared when the feeds are premixed. Alternatively, process requirements may require two or more distillate products of different composition, and these may be removed from the column as distillate and side streams. The Ponchon-Savarit method can be employed in these cases by writing the difference-point equations for each section of the column between streams added or removed. The number of difference points will always be

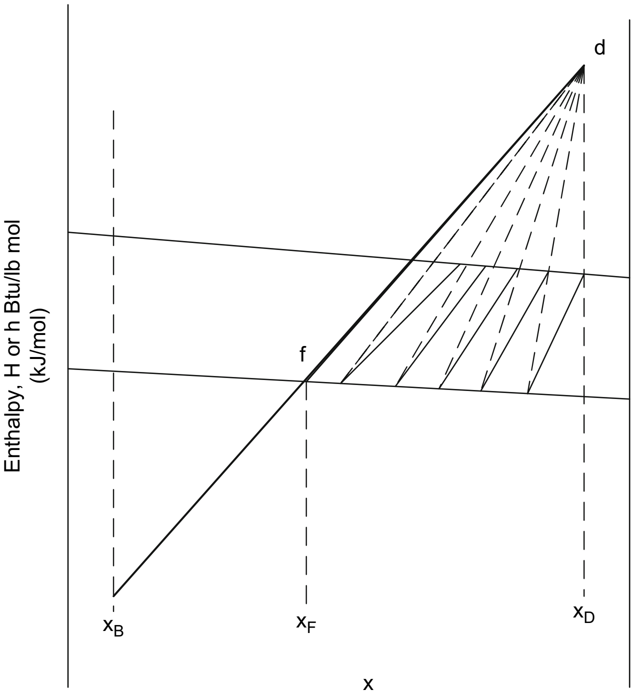


Figure 10-84 Minimum reflux ratio on an enthalpy–concentration diagram.

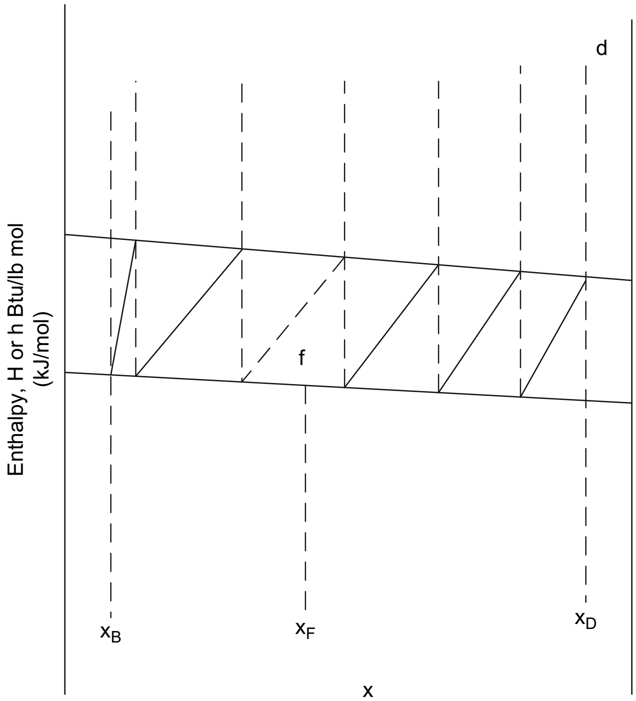


Figure 10-85 Total reflux construction on an enthalpy–concentration diagram.

equal to the number of streams N (including the distillate and bottoms) minus 1 as shown in Figures 10-86 and 10-87.

Columns with side streams may be handled in much the same way as a single feed stream. Here, three difference points are needed to represent the three sections of the column in Figure 10-86. Point d_1 and f′ are located as shown, with f′ representing a hypothetical stream in which a side stream of saturated liquid has been physically subtracted from the saturated liquid feed. Using the lever-arm principle, point f′ must lie on a line extended through points s and f such that $F/S = \overline{f's}/\overline{f'f}$. Similarly, in the case of multiple feeds, the difference point b is found by the intersection of the line d_1 f′ and a vertical line at x_B. The difference point for the intermediate section d_2, is determined by the intersection of lines sb and fd_1. The number of equilibrium stages may be stepped off as usual.

The advantage of the H-x-y chart lies in the fact that the heat quantities required for the distillation are clearly indicated. Therefore, the higher the reflux ratio, the more heat must be removed per mole of product. This immediately shows that both q_c and Q_B are increased. The Ponchon-Savarit method is applicable to a wide range of binary flash and distillation problems. The method is more rigorous and may be used for a larger class of binary systems than the McCabe-Thiele method. However, the final choice between the Ponchon-Savarit and McCabe-Thiele methods must be based on the desired accuracy of results and the availability of data.

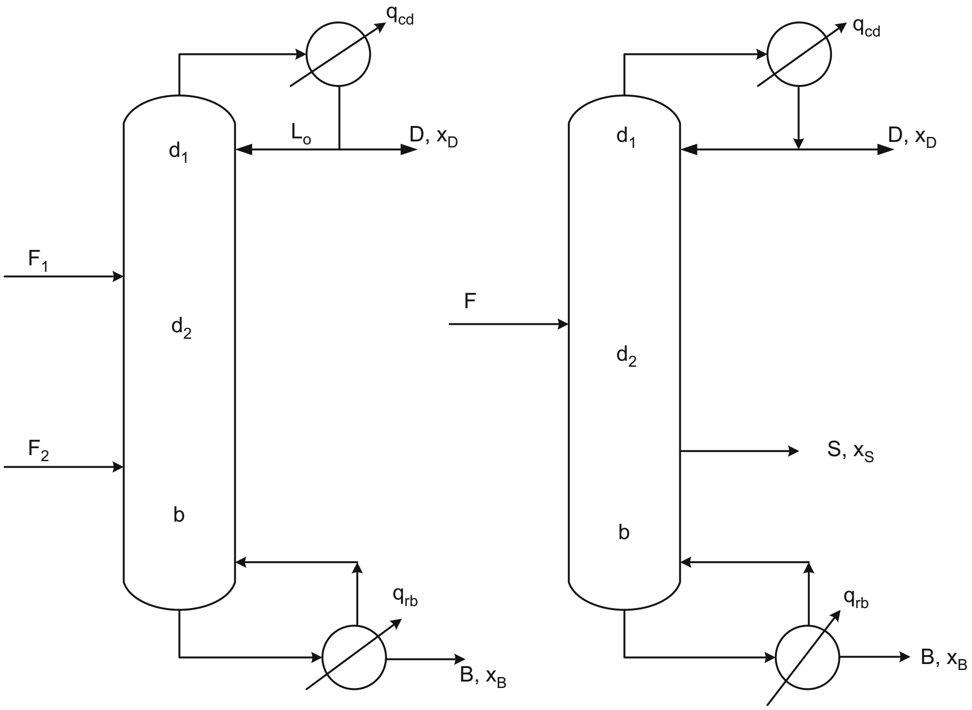


Figure 10-86 Ponchon analysis of a column with Multi feed and with side stream.

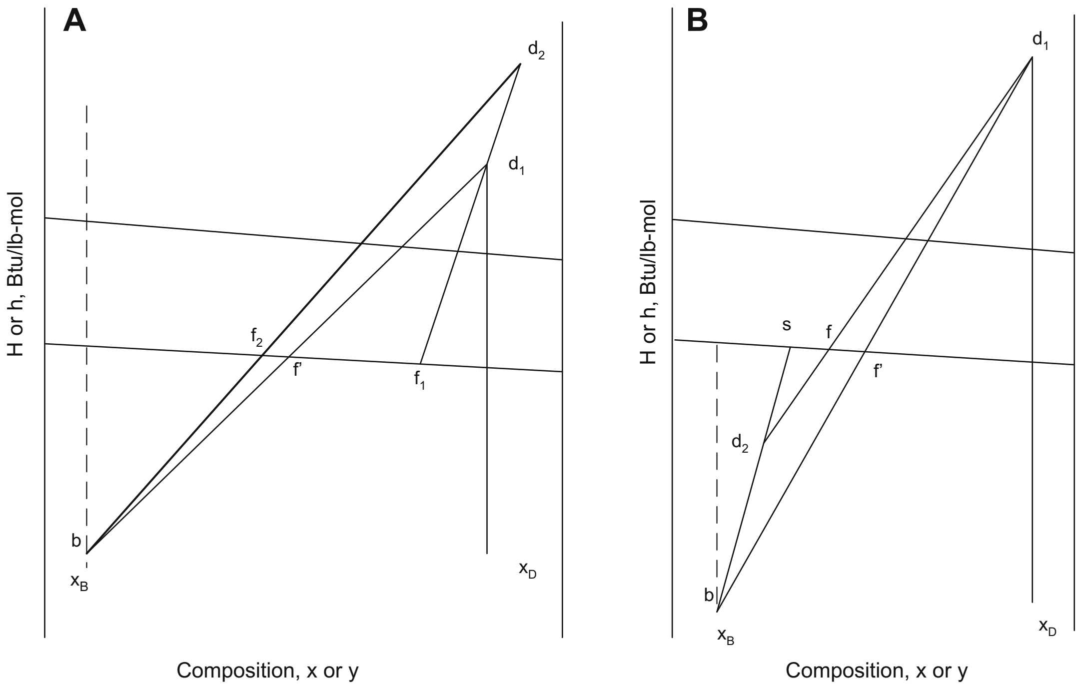


Figure 10-87 Ponchon analysis of a column with two feed streams

Example 10-38: Ponchon-Savarit Unequal Molal Overflow in Ammonia–Water System

An ammonia–water recirculating solution of 62 wt % is to be stripped of the ammonia, for recovery by condensation at 260 psia with river water cooling. The overhead ammonia product is to be at least 99.5 wt % and the bottoms should approach 0.05 wt % ammonia. The feed enters as a liquid at its boiling point, with an enthalpy of 42 Btu/lb.

Enthalpy Diagram

Prepared by reading the h and H values from the Jennings and Shannon Aqua-Ammonia Tables [35] at 260 psia and various wt %'s of ammonia in the liquid. The tie lines connect the vapor compositions with the equilibrium liquid values, Figure 10-88.

Vapor–Liquid Equilibrium Diagram

Prepared from corresponding x and y values in Reference 35 at 260 psia, Figure 10-89.

Number of Trays

$x_F = 0.62$ weight fraction ammonia
$x_D = 0.995$ weight fraction ammonia
$x_B = 0.0005$ weight fraction ammonia

1. Minimum Reflux

$$\left(\frac{L}{D}\right)_{min} = \frac{(M_D)_{min} - H_D}{H_D - h_D} \tag{10-413}$$

From enthalpy-composition diagram:

$H_D = 590$ Btu/lb
$h_D = 92$ Btu/lb (assuming no subcooling)
$(M_D)_{min} = 596$ Btu/lb

$(M_D)_{min}$ is determined by reading the equilibrium y value corresponding to the feed composition 0.62 from the x-y diagram, noting it on the enthalpy diagram on the saturated vapor curve, and connecting the tie line, then extending it on to intersect with the x_D ordinate 0.995, reading $(M_D)_{min} = 596$ Btu/lb

$$\left(\frac{L}{D}\right)_{min} = \frac{596 - 590}{590 - 92} = 0.012$$

2. Operating reflux ratio, L/D

Select $(L/D)_{actual} = 10\,(L/D)min = 10\,(0.012) = 0.12$ This is not unusual to select an operating reflux ratio ten, or even fifty times such a low minimum. Selection of a higher reflux ratio will result in a reduction in the number of trays required. As a consequence this becomes a balance of the reduction in trays versus operating and capital expense in handling the increased liquid both external to the column and internally.

3. Operating M_D

$$\left(\frac{L}{D}\right)_{act} = 0.12 = \frac{M_D - 590}{590 - 92}$$

$M_D = 649.8$ Btu/lb

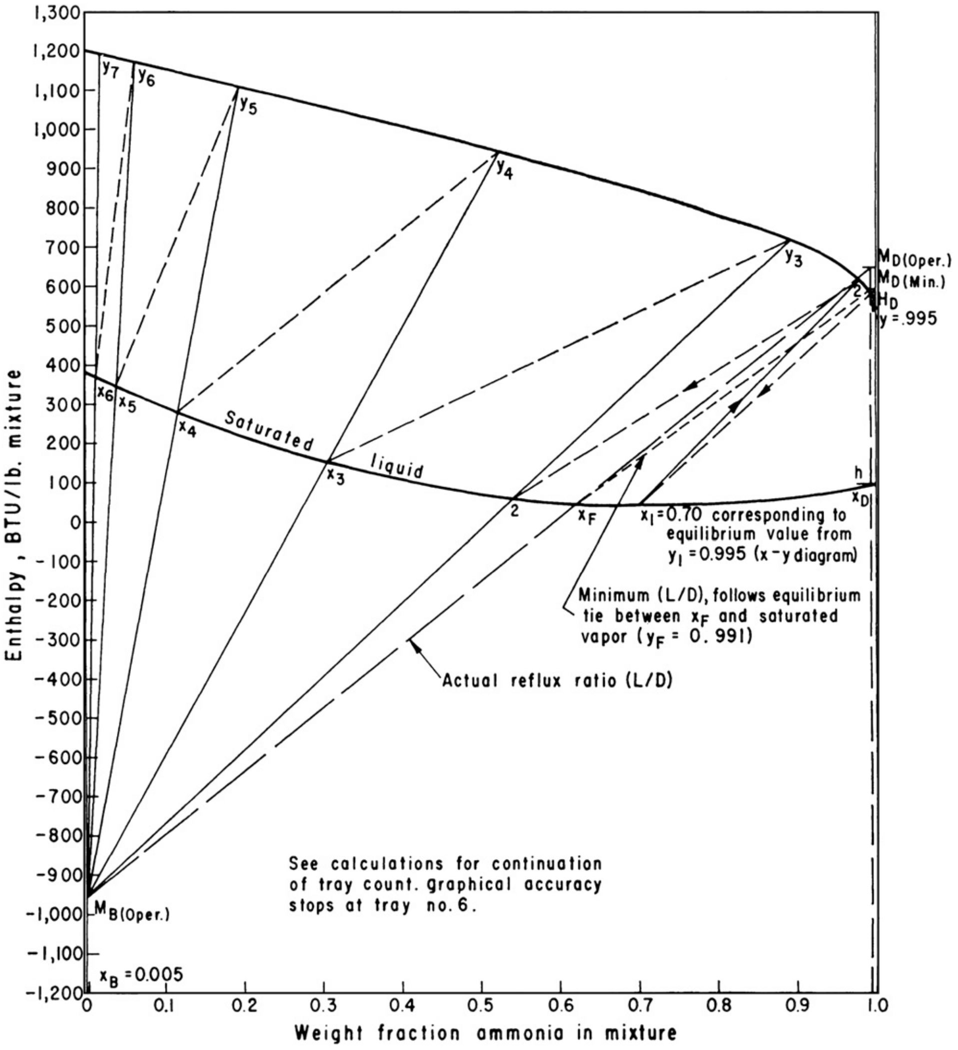


Figure 10-88 Ponchon type diagram for ammonia–water distillation.

Locate this value on the diagram and connect it to the feed point, x_F. Extend this line to intersect the bottoms condition ordinate (extended), x_B. In this case, it is impossible to represent the value, $x = 0.005$, accurately, but construct it as close as possible to the required condition. M_B is now located. The accuracy of this point will be improved later in the problem.

Following the procedures shown in Figures 10-82, 10-88, and 10-89, the trays are constructed from the top or overhead down toward the bottom. The x values are read to correspond to the y values constructed. This establishes the tie line. When the x value tie line points (representing the trays) cross the feed ordinate, the construction is shifted from using the point M_D to the point M_B. Note that only 1½ theoretical trays are required above the feed, since this is predominantly a stripping operation. The number of theoretical trays or stages which can be easily plotted is six to seven counting down from the top. The sixth tray is too inaccurate to use graphically. Instead of calculating the balance of the trays assuming a straight line equilibrium equation from tray seven to the end, the plot could be enlarged in this area and the trays stepped off. By reference to the x–y diagram it can be seen that the equilibrium line from $x = 0.02$ to $x = 0$ is straight.

For the condition of straight operating and equilibrium curves, the number of plates can be calculated including the "reference" plate (number seven in this case) [59].

$$N_B = \frac{\ln\left[\dfrac{[(VK/L) - 1][(x_m/x_{1B}) - 1]}{(V/L)(K - 1)} + 1\right]}{\ln\,(VK/L)} \qquad (10\text{-}414)$$

where

N_B = number of trays from tray m to bottom tray, but not including the still or reboiler

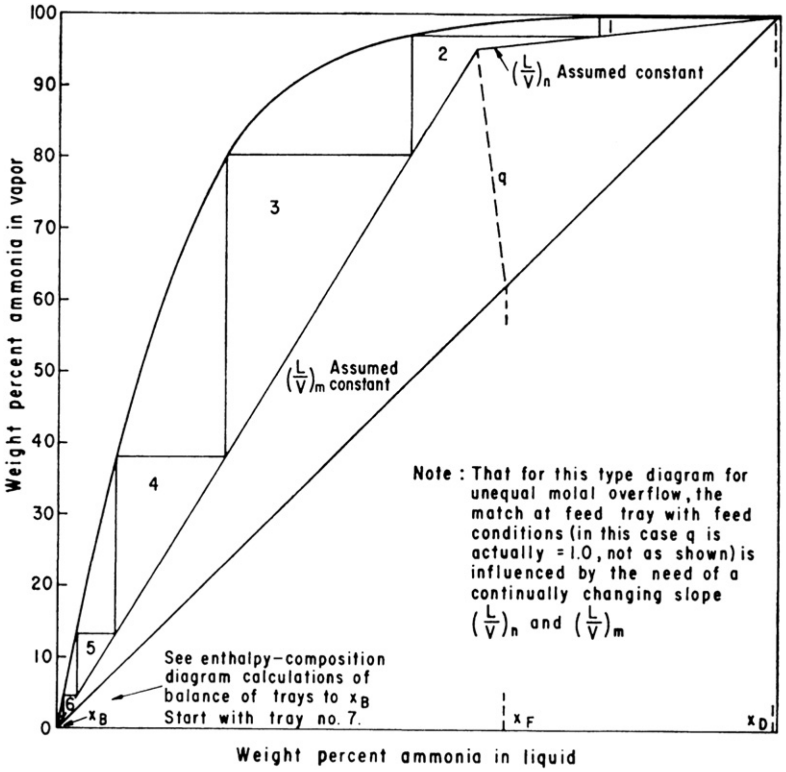


Figure 10-89 McCabe-Thiele diagram for ammonia water system.

x_m = tray liquid mol fraction for start of calculations (most volatile component)

x_{1B} = mol fraction most volatile component in bottoms

For the lower end of the equilibrium curve,

$y_m = 5.0\ x_m$ (by slope calculation of x–y diagram)

For the stripping section: consider top seven trays, vapor entering tray No.6, $y_7 = 0.02$, m = tray 7, m + 1 = tray 6, reading from diagram,

$$(L/V)_m = 1 - \frac{H_m - h_{m+1}}{M_B - h_{m+1}} = 1 - \frac{(1,190 - 369)}{-960 - 369}$$
$$= 1.618$$

use $H_m = 1{,}190$

$h_{m+1} = 369$

$M_B = -960$

$$x_7 = \frac{y_7}{5.0} = \frac{0.02\ \text{(from graph)}}{5.0} = 0.004$$

$$N_B = \frac{\ln\left[\frac{[(5.0/1.618) - 1][(0.004/0.0005) - 1]}{(1/1.618)(5.0 - 1)} + 1\right]}{\ln\ (5/1.618)}$$

$N_B = 1.71$ trays (theoretical) not including reboiler, but including tray number 7, the one used as reference.

Total trays = 7 (from diagram plus (1.71 − 1) = 7.7 theoretical, plus a reboiler or 8.7 including a reboiler.

Tray efficiency is calculated as previously described, but stripping tray efficiencies are normally lower than rectification efficiencies. For ammonia–water stripping, most overall efficiencies are 50–60%.

Note that if the problem of accurate graphical representation occurs in the rectification end of the diagram, the corresponding relationship to use in order to calculate the balance of the trays, (assuming straight line operating and equilibrium lines in the region) is [59]:

Rectifying section:

$$N_n = \frac{\ln\left[\frac{(1 - L/V) + x'_n/y'_D(L/V - K')}{1 - K'}\right]}{\ln\ (L/K'V)} - 1 \tag{10-415}$$

where

K' = equilibrium constant for the least volatile component, K' = y/x

N_n = number of plates above (but not including) reference plate n

y′, x′ = mol fractions least volatile component

Example 10-39 Ponchon-Savarit Unequal Molal Overflow in heptane-ethyl benzene System

A saturated liquid feed mixture composed of 45 mole % heptane and 55 mole % ethyl benzene is to be fractionated at 760 mm Hg to produce a distillate containing 98 mole % heptane and a residue containing 99 mole % ethyl benzene. Using the enthalpy-concentration diagram based on molal enthalpy and mole fraction as shown in the table below, determine the following:

1. The minimum reflux ratio L_o/D
2. The number of theoretical stages for an operating reflux ratio of 2.5 R_{min}.
3. The condenser duty kcal/kg mole.
4. The reboiler duty, kcal/kg mole.

Solution

Temperature °C	x_H	y_H	H_L, kcal/kg mole	H_V, kcal/kg mole
136.2	0	0	5.92	14.52
129.5	0.08	0.233	5.697	14.203
122.9	0.185	0.428	5.52	13.92
119.7	0.251	0.514	5.44	13.87
116.0	0.335	0.608	5.36	13.61
110.8	0.487	0.729	5.26	13.45
106.2	0.651	0.834	5.17	13.11
103.0	0.788	0.904	5.16	12.94
100.2	0.914	0.963	5.124	12.784
98.5	1.0	1.0	5.1	12.675

Figures 10-90a and 10-90b show the VLE and enthalpy composition diagrams of heptane respectively from the above data.

On the enthalpy–composition diagram, vertical lines are constructed at $x_B = 0.01$, $x_F = 0.45$ and $x_D = 0.98$. The point F is the intersection of the feed composition line and the liquid enthalpy curve. The point N is located by producing the line FD to the vertical through x_D. The point D on the vapor enthalpy curve corresponds to the value of y in equilibrium with $x_F = 0.45$ and is obtained from the equilibrium curve at $y = 0.699$.

1. The point N enables the minimum reflux ratio to be determined from:

$$R_{min} = \frac{\text{Length of NA}}{\text{Length of AB}}$$

And the length NB represents the heat removed in the condenser per unit mass of liquid at its boiling point. Points vertically above N correspond to actual reflux ratios (such as P_1), and thus the greater the value of R, the greater is the distance P_1N and fewer number of plates are required for the separation. However, as P_1B represents the condenser duty, this also rises so that an economic selection of the reflux ratio must be made.

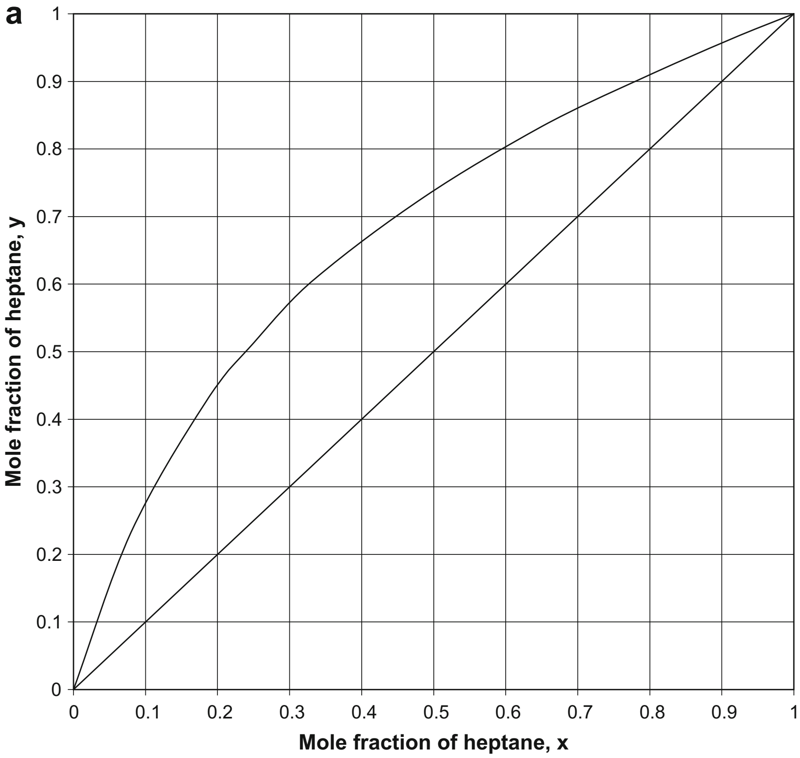


Figure 10-90a VLE diagram of heptane-ethylbenzene mixture at 760 mm Hg.

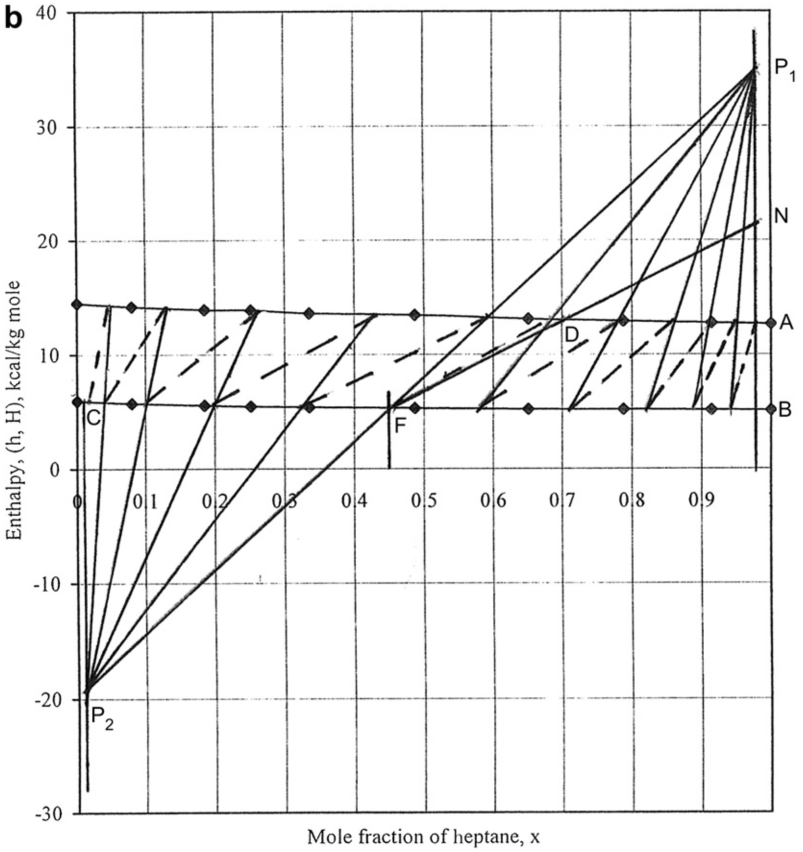


Figure 10-90b Enthalpy composition diagram of heptane-ethyl benzene mixture at 760 mm Hg.

$$R_{min} = \frac{\text{Length of NA}}{\text{Length of AB}}$$
$$= (21.5 - 12.7)/(12.7 - 5.1)$$
$$= 1.158$$

2. The number of theoretical stages for an operating reflux ratio of 2.5 R_{min} is determined as follows:
   $R = 2.5 \times 1.158$
   $= 2.895$
   At the reflux ratio of 2.895, the point P_1 on Figure 10-90b is determined by:

   $$\frac{L}{D} = 2.895 = \frac{P_1A}{AB} = \frac{(P_1 - 12.7)}{(12.7 - 5.1)}$$

   $P_1 = 34.70$ kcal/kg mole.
   Hence P_1 has coordinates (0.98, 34.70).
   The point P_2 is located by producing the line P_1F to its intersection with the vertical through x_B. The length P_2C represents the heat input to the reboiler per unit mass of bottom product. The coordinate of P_2 is -19 kcal/kgmole having the coordinate (0.01, -19). Points P_1 and P_2 are known as the difference points on the rectifying and stripping sections of the column. The construction of the tie lines may start from either side of Figure 10-90b, indicating either the conditions at the top or the bottom of the column and proceed as indicated for the rectifying and stripping sections of the column. In either case, when an equilibrium tie line crosses the line connecting the difference points (P_1P_2) through the feed condition, the other difference point is used to complete the construction. The number of tie lines indicates the theoretical number of stages.
   From Figure 10-90b, the number of theoretical stages is 11.
3. The heat removed in the condenser per unit mass of product (condenser duty) in kcal/kg mole is determined from Figure 10-90b by length P_1B.
   $P_1B = 34.7 - 5.1 = 29.6$ kcal/kg mole.
4. Heat required in the reboiler per unit mass of product is (reboiler duty) in kcal/kg mole is length P_2C in Figure 10-90b.
   $P_2C = 5.9 - (-19) = 24.9$ kcal/kg mole.

Example 10-40 Ponchon-Savarit Unequal Molal Overflow in A–B System

A feed stream of A and B consisting of boiling liquid and saturated vapor whose enthalpy is 1200 kJ/mol contains

40 mol % of A, and is to be separated to produce a distillate of 99% of A and a bottom product containing not more than 2% of A. Calculate:

1. The minimum number of theoretical plates in the column to effect the separation.
2. The minimum reflux ratio, R_{min}.
3. The number of actual plates required if the column efficiency is 60 % and the reflux ratio $1.2R_{min}$.
4. The optimum feed plate for this condition.

Solution

Equilibrium and Enthalpy data

Vapor liquid equilibrium data

x_A	0	0.05	0.10	0.15	0.20	0.30	0.40	0.50	0.60	0.80	1.0
y_A	0	0.30	0.58	0.71	0.79	0.90	0.96	0.98	0.99	0.995	1

Enthalpy data (kJ/kmol)

x_A	0	0.20	0.40	0.60	0.80	0.9	0.99
$H_{L,}$ kJ/kmol	767	418	198	116	163	209	279
$H_{V,}$ kJ/kmol	2765	2580	2370	2160	1905	1765	1490

1. Figure 10-91 shows the enthalpy composition diagram of A, and the minimum theoretical plates occurs at total reflux when the point P_1 on $x = x_D$ is at infinity. The operating lines are therefore vertical. Further, the condition of the feed is located between the liquid and vapor enthalpy lines for a partly vaporized feed. For a feed at its boiling point, or as a saturated vapor, F lies on the liquid and vapor enthalpy lines respectively. Similarly, for a liquid below its boiling point or as superheated vapor, the point F lies below or above the respective curves. With the composition and percent vapor specified, the point F may be located.

   For the minimum number of theoretical plates, starting at the top plate, the vapor leaving the plate has composition $y_T = 0.99$. The corresponding value of x_T from the equilibrium data is $x_T = 0.6$. From these points, the equilibrium tie line $x_T y_T$ is drawn. At total reflux, the operating line is vertical and $y_{T\text{-}1} = 0.6$ and $x_{T\text{-}1} = 0.11$. $y_{T\text{-}2}$ is located at $y_{T\text{-}2} = 0.11$ and $x_{T\text{-}2}$ is found to equal $x_{T\text{-}2} = 0.02$. Therefore, two theoretical plates are required at total reflux.

2. The minimum reflux ratio is located by producing the tie line which passes through F to the line $x = x_D$ at N.

   Then

   R_{min} = length NA/length AB

   $= (2880 - 1500)/(1500 - 290)$

   $= 1.14$

3. $R = 1.2\ R_{min} = 1.368$. Hence the difference points P_1 and P_2 are

   $P_1 = 3155$ kJ/mol, $P_2 = -80$ kJ/mol. The theoretical stages are stepped-off as shown in Figure 10-91, and it is found that five ideal plates are required. For the column efficiency = 60%, the number of actual plates is 5/0.60 = 8 plates.

4. The feed tray is located on the diagram by the tie line which passes through the line P_1FP_2. The optimum feed plate is between the 2nd and 3rd stage.

10.37 Multicomponent Distillation

The basic background and understanding of binary distillation applies to a large measure in multicomponent problems. Reference should be made to Figure 10-1 for the symbols.

Multicomponent distillations are more complicated than binary systems due primarily to the actual or potential interaction of one or more components of the multicomponent system on the others. These interactions may be in the form of vapor-liquid equilibria, such as azeotrope formation, chemical reaction, etc., which may affect the activity relations, and hence cause deviations from ideal behavior. For example, some systems are known to have two azeotrope combinations in the distillation column. Sometimes these can be “broken” by addition of a third chemical or hydrocarbon.

To properly handle the changing composition relationships, it is almost essential to use computational techniques if good accuracy is to be achieved. Even

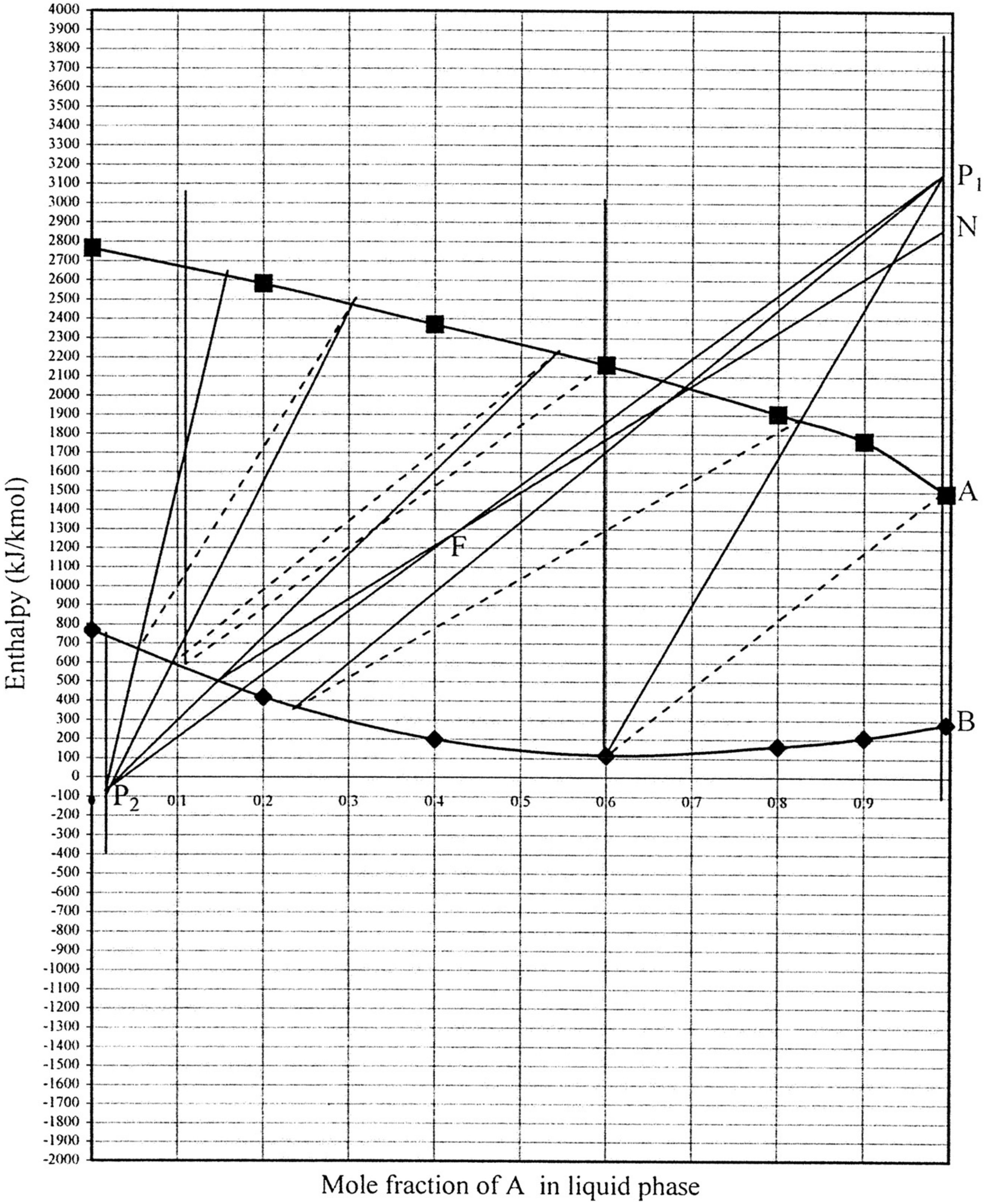


Figure 10-91 Enthalpy vs composition of A–B system.

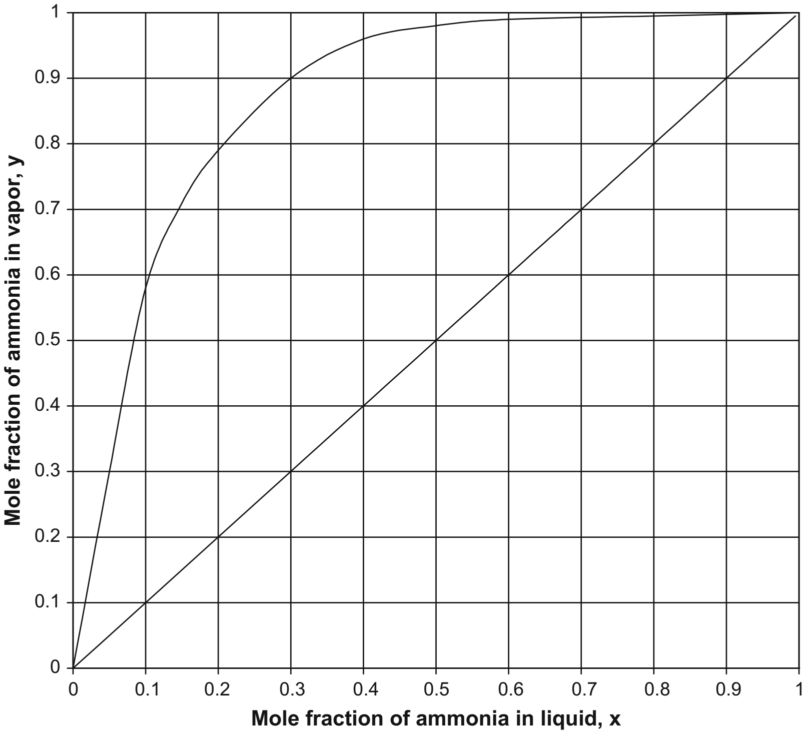


Figure 10-91a VLE data of ammonia–water system at 1 atm.

calculations three component systems become tedious using calculators without significant internal memory. Computers can be for programmed to easily handle the complexities of calculations involving techniques of trial and checking for convergence to a preset acceptable limit.

Digitally programmable algorithms for determining convergence are often the heart of an efficient multicomponent calculation. There are several techniques incorporated into many programs [27, 76, 112, 135, 139, 168]. Several process simulators on the market can be readily employed to size multicomponent distillation/fractionation columns and Table 10-32 shows the most commonly used commercial process simulators. Most of these programs can be licensed by colleges/universities for educational purpose at nominal cost.

Note: Contact the companion website to check the full features of the most recent versions of the programs.

Key Components

The two components in a feed mixture whose separations will be specified.

1. Adjacent keys: key components that are adjacent with respect to their volatilities.
2. Split keys: key components that are separated in volatilities by a non-key component, i.e., the system of components contains one or more whose volatilities fall between the volatilities of the designated keys.
3. Light key: the designation of the key component with the highest volatility of the two key components.
4. Heavy key: the designation of the key component with the lowest volatility of the two key components.
5. Example: component designations.

Component	Relative Volatility $\alpha_{l/h}$ — 7°F. and 550 psia	Designation
Hydrogen	11.7	Lighter than Key
Methane	3.7, α_l	*Light Key, 1*
Ethylene	1.0, α_h	*Heavy Key, h*
Ethane	0.72	Heavier than Key
Propylene	0.23	Heavier than Key
Propane	0.19	Heavier than Key

Hengstebeck [137] presents a simplified procedure for reducing a multicomponent system to an equivalent binary using "key" components. From this, the number of stages or theoretical plates and reflux can be determined using conventional binary procedures and the McCabe-Thiele method.

Table 10-32 Simulation Packages.

Name	Type	Source	Internet address (http//www.)
HYSY	Steady-state and dynamic	Aspen Technology Inc. Ten Canal Park Cambridge, MA 02141-2201, USA	Aspentech.com
Aspen Plus	Steady-state	Aspen Technology Inc. Ten Canal Park Cambridge, MA 012141-2201, USA	Aspentech.com
CHEMCAD	Steady-state	Chemstations, Inc. 2901 Wilcrest Suite 305 Houston, TX 77042	Chemstation.net
PRO/11 and DYNSIM	Steady-state and dynamic	SimSci-Esscor 5760 Fleet Street Suite 100 Carlsbad, CA	Simsci.com
DESIGN II	Steady-state	WinSim Inc. P.O. Box 1885	Winsim.com
UniSim Design	Steady-state and dynamic	Honeywell 300-250 York Stree London, Ontario N6A 6K2, Canada	Honeywell.com
ProSim	Steady-state and dynamic	ProSim SA Stratege Batiment A BP 27210 F-31672 Labege Cedex, France	prosim.net

Liddle [136] presents a shortcut technique for multicomponent calculations based on improving the Fenske and Gilliland correlations.

10.37.1 Minimum Reflux Ratio-Infinite Plates

This is the smallest value of external reflux ratio (L/D) which can be used to obtain a specified separation. This is not an operable condition. Knowledge of this minimum reflux ratio helps to establish an economical and practical operating ratio. Ratios of 1.2 to 2.0 times the minimum are often the economical range for hydrocarbon systems. However, as already discussed, high reflux rates increase column size (but reduce number of trays required), reboiler size, steam rate, condenser size and coolant rate.

For adjacent key systems, all components lighter than the light key appear only in the overhead, and all components heavier than the heavy key appear only in the bottoms, and the keys each appear in the overhead and bottoms at levels in accordance with specifications.

For a split key system in the lights and heavies distribute the same way as adjacent key systems. However, the component(s) between the keys also distribute to overhead and bottoms.

At minimum reflux, the regions in which the number of trays approaches infinity (called the pinch zones and region of constant compositions) are:

1. Binary system: pinch zone adjacent to feed plate.
2. Multicomponent:
    a. Three components with no component lighter than light key: pinch zone in stripping section adjacent to feed plate
    b. Three components with no component heavier than heavy key: pinch zone in rectifying section adjacent to feed plate
    c. Three components mixture: pinch zones may be above and below feed plate
    d. Greater than four components: pinch zones appear in rectifying and stripping sections

For systems with one sidestream drawoff, either above or below the feed, Tsuo et al. [102] propose a method for recognizing that the minimum reflux ratio is greater for a column with sidestream drawoff. At the sidestream the operating line has an inflection. For multifeed distillation systems, the minimum reflux is determined by factoring together the separate effect of each feed [103].

Lesi [105] proposes a detailed graphical procedure for figuring multicomponent minimum reflux by a graphical extension of a McCabe-Thiele diagram, assuming infinite plates or equilibrium stages. In this traditional model, the concentration in the distillate of the components heavier than the heavy key are assumed to be zero, and the heavy key component reaches its maximum concentration at the upper pinch point (see Figures 10-48 and 10-50). Therefore, the assumption is that only the heavy and light keys are present at the upper pinch point, similar in concept to the handling of a binary mixture [106]. The method assumes (a) only the key components are distributed, (b) no split key components exist, (c) total molal overflow rates and relative volatilities are constant.

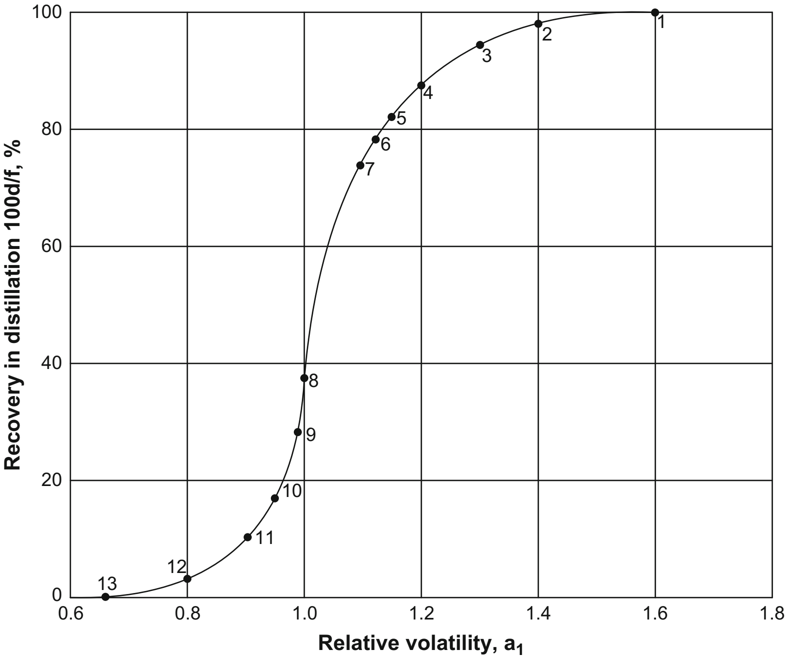


Figure 10-92 Yaws short-cut method compared to plate-to-plate calculations. Used by permission, Yaws, C. L. et al. Hydrocarbon Processing, V. 58, No. 2 (1979) p. 99. Gulf Publishing Co., all rights reserved.

This method provides good agreement with the detailed method of Underwood.

Yaws et al. [124] provide an estimation technique for recovery of each component in the distillate and bottoms, from multicomponent distillation, using short-cut equations and involving specification of the recovery of each component in the distillate, recovery of the heavy key component in the bottoms, and the relative volatility of the light key component. The results compare very well with plate-to-plate calculations. Figure 10-92, for a wide range of recoveries of 0.05 to 99.93% in the distillate.

Equations Surveyed

The availability of desktop computers and simulation software packages has permitted optimization of the number of equilibrium stages in multipurpose fractionating towers and absorbers. Vigorous iterative plate-to-plate computation is still used to study a wide range of process conditions. However, preliminary design with graphical correlations often helps to arrive at an approximate optimum number of stages before reverting to established design methods. Figure 10-1 shows a schematic of a fractionating column with two or more multicomponent and associated equipment items. Alternatives to the preliminary design approach are the short-cut-methods that estimate a realistic optimum number of theoretical stages. Generally, short-cut methods were developed to establish the minimum number of stages at total reflux, and also the minimum reflux at an infinite number of theoretical stages. Many authors have correlated the minimum reflux and minimum stages with operating reflux and corresponding theoretical equilibrium stages required. These methods have enabled the reflux ratio and number of plates to be chosen to achieve an optimum relationship based on investment and operating costs.

Mathematical Modeling

The distribution of components between the distillate and bottoms is given by the Hengstebeck-Geddes equation [124, 125, 126]:

$$\log\left[\frac{d_i}{b_i}\right] = A + B\log\alpha_i \tag{10-416}$$

where

d_i = moles of component i in the distillate
b_i = moles of component i in the bottoms.
α = relative volatility of component i
A, B = correlation constants.

A material balance for the ith component in the feed is

$$f_i = d_i + b_i \tag{10-417}$$

The quantity of component i in the distillate can be expressed as mole fraction recovered, or d_i/f_i. Alternatively, in the bottoms, the mole fraction of component i recovered is b_i/f_i.

If Equation 10-416 is expressed with respect to the heavy key component, then

$$\log\left[\frac{d_{HK}}{b_{HK}}\right] = A + B\log\alpha_{HK} \qquad (10\text{-}418)$$

The relative volatility of the heavy key component (i.e. $\alpha_{HK} = 1.0$).

Therefore,

$$A = \log\left[\frac{d_{HK}}{b_{HK}}\right] \qquad (10\text{-}419)$$

but

$$f_{HK} = d_{HK} + b_{HK} \qquad (10\text{-}420)$$

and

$$f_{LK} = d_{LK} + b_{LK} \qquad (10\text{-}421)$$

Therefore

$$A = \log\left[\frac{f_{HK} - b_{HK}}{b_{HK}}\right] \qquad (10\text{-}422)$$

Equation 10-422 can be expressed in terms of mole fraction recovered as:

$$A = \log\left[\frac{(1.0 - b_{HK}/f_{HK})}{(b_{HK}/f_{HK})}\right] \qquad (10\text{-}423)$$

Substituting Equation 10-419 into Equation 10-416 and expressing in terms of the light key component.

$$\log\left[\frac{d_{LK}}{b_{LK}}\right] = \log\left[\frac{d_{HK}}{b_{HK}}\right] + B\log\alpha_{LK} \qquad (10\text{-}424)$$

Therefore:

$$B = \frac{\log\left[\left(\frac{d_{LK}}{b_{LK}}\right)/\left(\frac{d_{HK}}{b_{HK}}\right)\right]}{\alpha_{LK}}$$

$$= \frac{\log\left[\left(\frac{d_{LK}/f_{LK}}{b_{LK}/f_{LK}}\right)\left(\frac{b_{HK}}{d_{HK}}\right)\right]}{\log\alpha_{LK}} \qquad (10\text{-}425)$$

Expressing Equation 10-425 in terms of fractional recoveries:

$$B = \frac{\log\left[\left(\frac{d_{LK}/f_{LK}}{\frac{f_{LK}-d_{LK}}{f_{LK}}}\right)\left(\frac{b_{HK}/f_{HK}}{\frac{f_{HK}-b_{HK}}{f_{HK}}}\right)\right]}{\log\alpha_{LK}} \qquad (10\text{-}426)$$

$$B = \frac{\log\left[\left(\frac{d_{LK}/f_{LK}}{1-(d_{LK}/f_{LK})}\right)\left(\frac{b_{HK}/f_{HK}}{1-(b_{HK}/f_{HK})}\right)\right]}{\log\alpha_{LK}} \qquad (10\text{-}427)$$

The recoveries of the ith component in the distillate and bottoms:

Equation 10-416 and Equation 10-417 are:

$$\log\left[\frac{d_i}{b_i}\right] = A + B\log\alpha_i \qquad (10\text{-}416)$$

$$f_i = d_i + b_i \qquad (10\text{-}417)$$

Expressing Equations 10-416 and 10-417 in terms of the recoveries of the ith component.

That is:

$$\log\left[\frac{d_i/f_i}{1 - d_i/f_i}\right] = A + B\log\alpha_i \qquad (10\text{-}428)$$

Hence:

$$\left[\frac{d_i/f_i}{1 - d_i/f_i}\right] = 10^A \cdot 10^{\left(\log_{10}\alpha_i^B\right)} \qquad (10\text{-}429)$$

$$= 10^A \cdot \alpha_i^B$$

$$\frac{d_i}{f_i} = 10^A \cdot \alpha_i^B\left(1 - \frac{d_i}{f_i}\right) \qquad (10\text{-}430)$$

The recovery of the ith component in the distillate is given by:

$$\frac{d_i}{f_i} = \frac{\left(10^A \cdot \alpha_i^B\right)}{\left(1 + 10^A \cdot \alpha_i^B\right)} \qquad (10\text{-}431)$$

and the recovery of the ith component in the bottoms is:

$$\frac{b_i}{f_i} = 1 - \frac{d_i}{f_i} \qquad (10\text{-}432)$$

$$= 1 - \frac{\left(10^A \cdot \alpha_i^B\right)}{\left(1 + 10^A \cdot \alpha_i^B\right)} \qquad (10\text{-}433)$$

$$\frac{b_i}{f_i} = \frac{1}{\left(1 + 10^A \cdot \alpha_i^B\right)} \qquad (10\text{-}434)$$

The correlation constants required for Equations 10-431 and 10-434 are obtained by specifying a desired recovery of the light key component (LK) in the distillate, and the recovery of the heavy key component (HK) in the bottoms. The constants are then calculated as follows:

$$A = -\log\left[\frac{(b_{HK}/f_{HK})}{1 - (b_{HK}/f_{HK})}\right] \qquad (10\text{-}435)$$

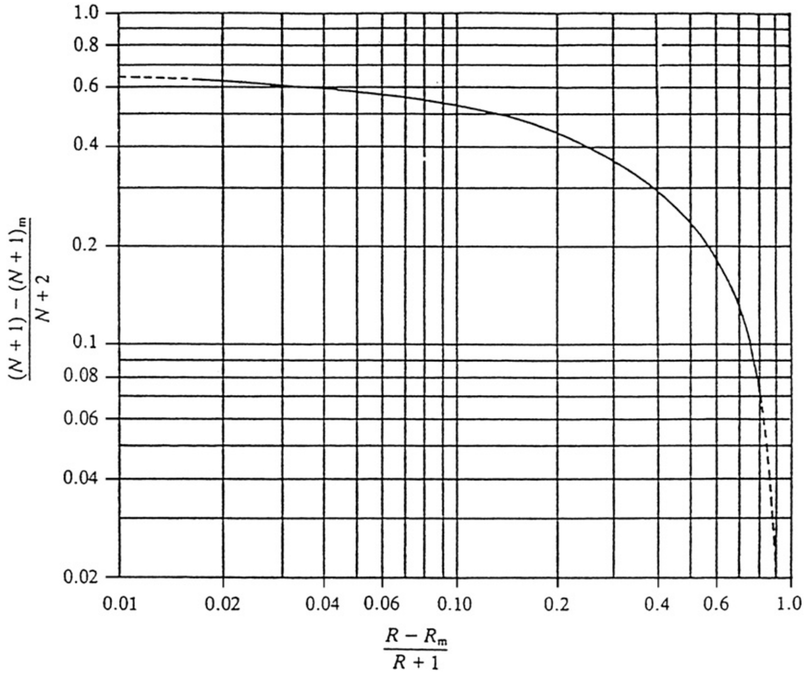
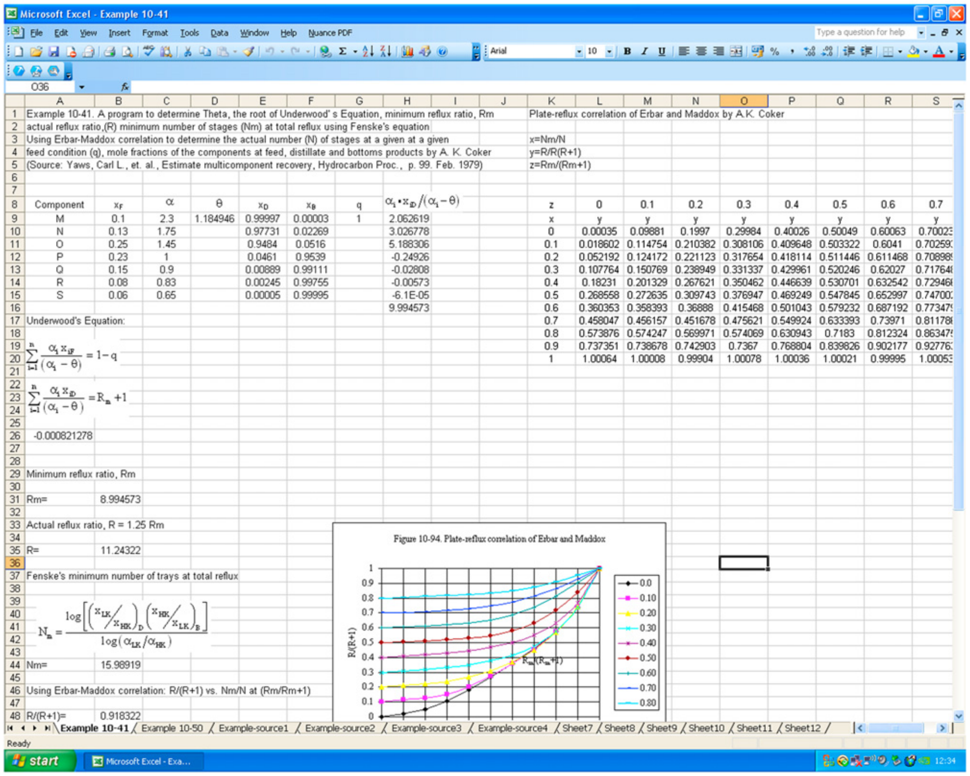


Figure 10-93 Gilliland correlation of reflux ratio, theoretical stages, minimum reflux ratio and minimum number of stages [source: Gilliland, Ind. Eng. Chem., 32: 1101 (1940)]. $(N + 1)_m$ = The number of theoretical stages at total reflux; R_m = The minimum reflux ratio; R = Reflux ratio; N = Number of theoretical stages.

a



1 Example 10-41. A program to determine Theta, the root of Underwood' s Equation, minimum reflux ratio, Rm
2 actual reflux ratio,(R) minimum number of stages (Nm) at total reflux using Fenske's equation
3 Using Erbar-Maddox correlation to determine the actual number (N) of stages at a given at a given
4 feed condition (q), mole fractions of the components at feed, distillate and bottoms products by A. K. Coker
5 (Source: Yaws, Carl L., et. al., Estimate multicomponent recovery, Hydrocarbon Proc., p. 99. Feb. 1979)

Component	x_F	α	θ	x_D	x_B	q	$\alpha_i \cdot x_{iD}/(\alpha_i-\theta)$
M	0.1	2.3	1.184946	0.99997	0.00003	1	2.062619
N	0.13	1.75		0.97731	0.02269		3.026778
O	0.25	1.45		0.9484	0.0516		5.188306
P	0.23	1		0.0461	0.9539		-0.24926
Q	0.15	0.9		0.00889	0.99111		-0.02808
R	0.08	0.83		0.00245	0.99755		-0.00573
S	0.06	0.65		0.00005	0.99995		-6.1E-05
							9.994573

17 Underwood's Equation:

$$\sum_{i=1}^{n}\frac{\alpha_i x_{iF}}{(\alpha_i-\theta)}=1-q$$

$$\sum_{i=1}^{n}\frac{\alpha_i x_{iD}}{(\alpha_i-\theta)}=R_m+1$$

26 -0.000821278

29 Minimum reflux ratio, Rm

31 Rm= 8.994573

33 Actual reflux ratio, R = 1.25 Rm

35 R= 11.24322

37 Fenske's minimum number of trays at total reflux

$$N_m=\frac{\log\left[\left({}^{x_{LK}}/_{x_{HK}}\right)_D\left({}^{x_{HK}}/_{x_{LK}}\right)_B\right]}{\log(\alpha_{LK}/\alpha_{HK})}$$

44 Nm= 15.98919

46 Using Erbar-Maddox correlation: R/(R+1) vs. Nm/N at (Rm/Rm+1)

48 R/(R+1)= 0.918322

Plate-reflux correlation of Erbar and Maddox by A.K. Coker

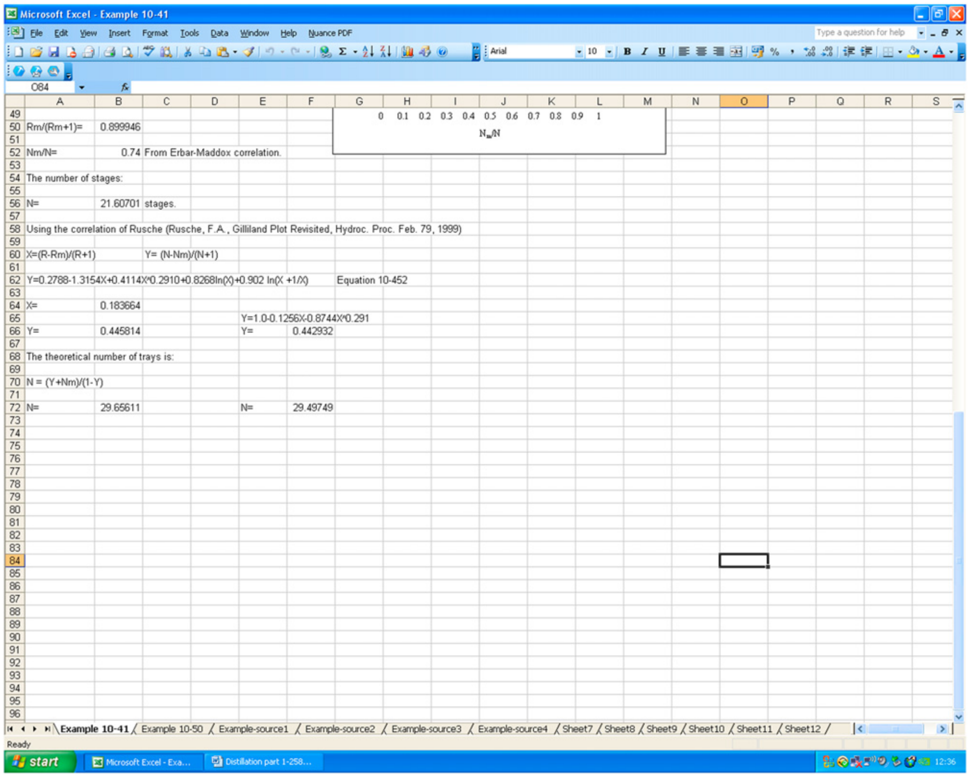
x=Nm/N
y=R/R(R+1)
z=Rm/(Rm+1)

z	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
x	y	y	y	y	y	y	y	y
0	0.00035	0.09881	0.1997	0.29984	0.40026	0.50049	0.60063	0.7002
0.1	0.018602	0.114754	0.210382	0.308106	0.409648	0.503322	0.6041	0.70259
0.2	0.052192	0.124172	0.221123	0.317654	0.418114	0.511446	0.611468	0.70898
0.3	0.107764	0.150769	0.238949	0.331337	0.429961	0.520246	0.62027	0.71764
0.4	0.18231	0.201329	0.267621	0.350462	0.446639	0.530701	0.632542	0.72946
0.5	0.268558	0.272635	0.309743	0.376947	0.469249	0.547845	0.652997	0.74700
0.6	0.360353	0.358393	0.36888	0.415468	0.501043	0.579232	0.687192	0.77347
0.7	0.458047	0.456157	0.451678	0.475621	0.549924	0.633393	0.73971	0.81178
0.8	0.573876	0.574247	0.569971	0.574069	0.630943	0.7183	0.812324	0.86347
0.9	0.737351	0.738678	0.742903	0.7367	0.768804	0.839826	0.902177	0.92776
1	1.00064	1.00008	0.99904	1.00078	1.00036	1.00021	0.99995	1.0005

Figure 10-94. Plate-reflux correlation of Erbar and Maddox

Figure 10-93a Excel program snap-shot for Example 10-41.

b



	A	B	C	D	E	F	G
49							
50	Rm/(Rm+1)=	0.899946					
51							
52	Nm/N=	0.74	From Erbar-Maddox correlation.				
53							
54	The number of stages:						
55							
56	N=	21.60701	stages.				
57							
58	Using the correlation of Rusche (Rusche, F.A., Gilliland Plot Revisited, Hydroc. Proc. Feb. 79, 1999)						
59							
60	X=(R-Rm)/(R+1)		Y= (N-Nm)/(N+1)				
61							
62	Y=0.2788-1.3154X+0.4114X^0.2910+0.8268ln(X)+0.902 ln(X +1/X)						Equation 10-452
63							
64	X=	0.183664					
65					Y=1.0-0.1256X-0.8744X^0.291		
66	Y=	0.445814			Y=	0.442932	
67							
68	The theoretical number of trays is:						
69							
70	N = (Y+Nm)/(1-Y)						
71							
72	N=	29.65611			N=	29.49749	

Figure 10-93b Excel program snap-shot for Example 10-41.

or

$$A = \log\left[\frac{(1.0 - b_{HK}/f_{HK})}{(b_{HK}/f_{HK})}\right] \qquad (10\text{-}435a)$$

$$B = \frac{\log\left[\left(\frac{(d_{LK}/f_{LK})}{1-(d_{LK}/f_{LK})}\right)\left(\frac{(b_{HK}/f_{HK})}{1-(b_{HK}/f_{HK})}\right)\right]}{\log \alpha_{LK}} \qquad (10\text{-}436)$$

10.37.2 The Fenske's Method for Total Reflux [285]

Fenske's [285] equation for determining the minimum equilibrium stages at total reflux was based on an ideal mixture. This suggests that the ratio of vapor pressures or the ratio of equilibrium vaporization of the key components is constant over the range of temperatures (that is, the relative volatilities are constant). Fenske expressed the minimum number of equilibrium stages as:

$$N_{min} = \frac{\log\left[\left(\frac{x_{LK}}{x_{HK}}\right)_D \left(\frac{x_{HK}}{x_{LK}}\right)_B\right]}{\log\left[\frac{\alpha_{LK}}{\alpha_{HK}}\right]} \qquad (10\text{-}182)$$

10.37.3 The Gilliland Method for Number of equilibrium Stages [23]

The number of theoretical equilibrium stages required for a given separation at a given reflux ratio is often determined by empirical correlations [23, 286]. The abscissa X represents a reflux function as:

$$X = \frac{R - R_m}{R + 1} \qquad (10\text{-}219)$$

Correspondingly, the ordinate Y represents a stage function as given by

$$Y = \frac{(N - N_m)}{(N + 1)} \qquad (10\text{-}220)$$

The ratios used for the axes of abscissa and ordinate were chosen because they provide fixed end points for the curve (X = 0.0, Y = 1.0 and at X = 1.0, Y = 0.0). The two functions were found to give good correlations. These correlations are shown in Figures 10-49a and 10-93. Gilliland's correlation has produced relevant results that offer the advantages that:

- They represent an optimum solution concerning the location of the feed plate.

- The splitting for the two key components is verified.
- The maximum deviation using Gilliland's correlation in terms of tray number is within the 7% range [23].

The Gilliland correlation tends to be conservative for feeds with low values of the thermal condition of the feed (q). It can give inaccurate results when there is a large difference in tray requirements above and below the feed. The correlation is adequate for use in preliminary designs before a detailed analysis is carried out, but great caution should be exercised if it is used for final designs. Hines and Maddox [266] have described an improved correlation for determining the number of theoretical stages.

10.37.4 Underwood's Method [72, 73]

If an infinite or nearly infinite number of equilibrium stages is involved, a zone of constant composition must exist in the fractionating column. In this instance, there is no measurable change in the composition of liquid or vapor from stage or stage. Under these conditions, the reflux ratio can be defined as the minimum reflux ratio, R_{min}, with respect to a given separation of two key components (that is, the light key and heavy key) [72].

Therefore, for component i in the distillate:

$$R_{min} + 1 = \sum_{i=1}^{n} \frac{(\alpha_i - x_{i,D})}{(\alpha_i - \theta)} \qquad (10\text{-}437)$$

where θ is Underwood's constant (or root of the equation), and must lie between the relative volatilities of the light and heavy keys (α_{LK} and α_{HK}). The number of components is n.

Correspondingly, for the feed:

$$1 - q = \sum_{i=1}^{n} \frac{(\alpha_i \cdot x_{i,F})}{(\alpha_i - \theta)} \qquad (10\text{-}438)$$

Equation 10-438 shows the relationship for the feed, where q is the fraction of feed that is liquid at the feed tray temperature and pressure. For a bubble point feed, q = 1, and for a dew point feed, q = 0. The minimum reflux ratio is determined from Equation 10-438 by substituting into Equation 10-437. This author [287] has developed a numerical method for computing θ and R_{min} respectively. However, other methods should be tried, if R_{min} gives a negative value. Also, it may be that the separation between the feed and the overhead can be accomplished in less than one equilibrium stage.

10.37.5 Equations for Describing Gilliland's Graph

Many equations have been proposed to describe Gilliland's curve for multicomponent distillation. However, the difficulty with some of these equations has been in meeting the end conditions of $X = 0$, $Y = 1$ and $X = 1$, $Y = 0$. A review of the many equations proposed by these authors is as follows.

Proposed Equations

1. Hengstebeck [106] (1961).

$$\log Y = A + B(\log X) + C(\log X)^2 + D(\log X)^3 + E(\log X)^4 \qquad (10\text{-}439)$$

where

$A = -1.3640187$
$B = -3.0920489$
$C = -3.407344729$
$D = -1.74673876$
$E = -0.33268897$

2. Liddle [136] (1968)

$$\text{For } 0.0 \le X \le 0.01, Y = 1.0 - 18.5715X \qquad (10\text{-}440)$$

$$\text{For } 0.01 \le X \le 0.9, Y = 0.545827 - 0.591422X + 0.002743/X \qquad (10\text{-}441)$$

$$\text{For } 0.09 \le X \le 1.0, Y = 0.16595 - 0.16595X \qquad (10\text{-}442)$$

3. Van-Winkle and Todd [139] (1971)

$$\text{For } 0.0078 < X < 0.125, Y = 0.5039 - 0.5968X - 0.0908(\log X) \qquad (10\text{-}443)$$

$$\text{For } 0.125 < X = 1.0, Y = 0.6257 - 0.9868X + 0.516X^2 - 0.1738X^3 \qquad (10\text{-}444)$$

4. Molokanov [288] (1972)

$$0 \le (X, Y) \le 1.0$$

$$Y = 1 - \exp\left[\left(\frac{1 + 54.4\,X}{11 + 117.2X}\right)\left(\frac{X - 1}{X^{0.5}}\right)\right] \qquad (10\text{-}445)$$

5. Hohman and Lockhart [289] (1972)

$$X = 0, Y = 0.65$$

$$X = 1.0, Y = 0.067$$

$$Y = \frac{0.65 - 0.50X}{1.0 + 1.25X} \tag{10-446}$$

6. Eduljee [84] (1975)

$$X = 0, Y = 1.0$$

$$X = 1.0, Y = 0$$

$$Y = 0.75 - 0.75X^{0.5668} \tag{10-447}$$

7. Huan-Yang Chang [290] (1981)

For $X = 0, Y = 1.0$

$$X = 1.0, Y = 0$$

$$Y = 1 - \exp\left(1.49 + 0.315X - \frac{1.805}{X^{0.1}}\right) \tag{10-448}$$

8. Harg [291] (1985)

For $X = 0, Y = 1.0$

$$X = 1.0, Y = 0$$

$$Y = 1 - X^{1/3} \tag{10-449}$$

9. McCormick [97] (1988)

$$X = 0, Y = 1.0$$

$$X = 1.0, Y = 0$$

$$Y = 1 - X^{B}$$

where

$$B = 0.105\ (\log X) + 0.44 \tag{10-450}$$

10. Rusche [292] (1999)

$$Y = 0.2788 - 1.3154X + 0.4114X^{0.291} + 0.8268 \ln X + 0.9020 \ln\left(X + \frac{1}{X}\right) \tag{10-451}$$

where

$$X = \frac{R - R_{min}}{R + 1},\ Y = \frac{N - N_m}{N + 1} \tag{10-452}$$

from which the number of theoretical trays is:

$$N = \frac{N_m + Y}{1 - Y} \tag{10-453}$$

The Gilliland correlation is conservative for feeds with low values of q (thermal condition of the feed), and can result in erroneous results when there is large difference in tray requirements above and below the feed. The various correlations illustrated are for preliminary exploration of design variables, which should be further refined using simulation packages (Aspen, Chemcad, UniSim® etc.). These correlations should be employed with caution, if applied to final design.

From the equations listed, those of McCormick give good agreement in the normal operating range of real towers. The reflux ratio, R is calculated as a multiple of the minimum reflux ratio, R_{min}.

That is:

$$R = \text{FACTOR} \cdot R_{min} \tag{10-454}$$

10.37.6 Operating reflux ratio, R

As the reflux ratio increases above the minimum, the number of trays required for a given separation decreases, hence the capital cost of the column decreases. However, increasing the reflux ratio will increase the vapor rate in the tower, and this will impact the cost of the reboilers and condensers, as well as increasing cooling water and steam costs. Hence there is an optimum reflux ratio for any specified separation as illustrated later in this volume. Experience has shown that the value of this optimum normally falls in the range $1.03 < R/R_{min} < 1.3$. For the first estimate, the multiplier "FACTOR" generally varies from 1.2 to about 1.5 for conventional columns, but because of economics, the range is now between 1.05 and 1.20.

Rule of thumb:

The operating reflux ratio is chosen so that $R/R_{min} = 1.2$

10.37.7 Feed Tray Location

The approximate location can be determined by the ratio of the total number of theoretical stages above and below the feed plate from the Fenske total reflux relation:

$$\frac{S_r}{S_s} = \frac{n+1}{m+1} = \frac{\log(x_l/x_h)_D(x_h/x_l)_F}{\log(x_l/x_h)_F(x_h/x_l)_B} \tag{10-455}$$

The relation is solved for S_r/S_s. The results are not exact, because the feed tray composition is very seldom the same as the feed; which is the assumption in this relation. Actually, the feed point or correct location for the feed may be wrong by two or three theoretical trays. This will vary with the system. It does mean, however, that when this approach is used for feed plate location, alternative feed nozzles should be installed on the column to allow for location of the best feed point to be determined by experiment. These extra nozzles are usually placed on alternate trays (or more) both above and below the calculated location. A minimum of three alternative nozzles should be available.

When the feed point is located by tray-by-tray calculation, the correct point can be established with greater confidence, but still alternative nozzles are suggested, since even these detailed calculations can be in accurate.

The actual number of trays in the rectifying section $(N_{act})_r$ can be determined by:

$$S_M = S_r + S_s \tag{10-456}$$

$$S_M = S_s(S_r/S_s) + S_s \tag{10-457}$$

Solve for S_s, because S_M and S_r/S_s are known.
Obtain S_r by difference.

$(N_{act})_r = S_r/E_o$ (for total condenser; if partial condenser use

$$(S_r - 1)/E_o) \tag{10-458}$$

$$(N_{act})s = (S_s - 1)/E_o(\text{for columns with reboilers}) \tag{10-459}$$

For systems with wide variation in relative volatility, the suggestion of Cicalese et al. [9] is often used to evaluate the theoretical total equilibrium stages in the rectifying and stripping sections:

$$S_r = \frac{\log\dfrac{(x_l/x_h)_D}{(x_l/h_h)_F}}{\log \alpha(\text{average above feed})} \tag{10-460}$$

$$S_s = \frac{\log\dfrac{(x_l/x_h)_F}{(x_l/h_h)_B}}{\log \alpha(\text{average above feed})} \tag{10-461}$$

where

S_r = number theoretical trays/plates in rectifying section
S_s = number theoretical trays/plates in stripping section

Maas [108] presents a useful analysis for selecting the feed tray in a multicomponent column. For accuracy it involves the use of a tray-by-tray computer calculation.

10.37.8 Kirkbride's Feed Plate Location [174]

After the minimum number of stages and the minimum reflux ratio have been determined, the number of theoretical stages is then calculated. The ratio of the number of plates above the feed stage (including the partial condenser) to the number below the feed stage (including the reboiler) can be obtained using Kirkbride's empirical equation [174]. The equation was developed on the basis that the ratio of rectifying trays to stripping trays depends on:

- The fraction of the heavy key component (in the feed) removed in the overhead.
- The fraction of the light key component removed in the bottoms.
- The concentration of the heavy key component in the overhead.
- The concentration of the light key component in the bottoms.

Kirkbride's feed plate equation is expressed as:

$$\log\left[\frac{m}{p}\right] = 0.206 \log\left\{\left(\frac{B}{D}\right)\left(\frac{x_{HK}}{x_{LK}}\right)_F\left[\frac{(x_{LK})_B}{(x_{HK})_D}\right]^2\right\} \tag{10-462}$$

or

$$\frac{m}{p} = \left\{\left(\frac{B}{D}\right)\left(\frac{x_{HK}}{x_{LK}}\right)_F\left[\frac{(x_{LK})_B}{(x_{HK})_D}\right]^2\right\}^{0.206} \tag{10-462a}$$

Akashah et al. [311] presented a modified version of Equation 10-462 or 10-462a, which gives:

$$m = p[\text{calculated from Eq.}10 - 462a] - 0.5 \log N \tag{10-462b}$$

$$m + p = N \tag{10-462c}$$

where

B = molar flow of bottoms product
D = molar flow of top product
N = total number of theoretical stages
m = number of theoretical stages above the feed plate, including any partial condenser
p = number of theoretical stages below the feed plate, including the reboiler
$(x_{LK})_F$ = concentration of the light key in the feed.
$(x_{HK})_F$ = concentration of the heavy key in the feed.
$(x_{LK})_B$ = concentration of the light key in the bottoms product.
$(x_{HK})_D$ = concentration of the heavy key in the distillate product.

Example 10-41: Multicomponent Distillation by Yaw's Method [124] (used by permission)

Assume a multicomponent distillation operation has a feed whose component concentration and component relative volatilities (at the average column conditions) are as shown in Table 10-33. The desired recovery of the light key component O in the distillate is 94.84%. The

Table 10-33 **Yaw's Method for Selected Distillation Recovery from a Specific Feed for Example 10-41.**

Component	f_i	α_i
M	0.10	2.30
N	0.13	1.75
O (LK)	0.25	1.45
P (HK)	0.23	1.00
Q	0.15	0.90
R	0.08	0.83
S	0.06	0.65

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recovery of the heavy key component P in the bottoms is 95.39%.

The recoveries of the non-key components are estimated by first calculating the correlation constants:

$b_{HK}/f_{HK} = 0.9539$, given

$$A = -\log\left(\frac{0.9539}{1 - 0.9539}\right) = -\log 20.69 = 1.3158$$

$d_{LK}/f_{LK} = 0.9484$, given

$\alpha_{LK} = 1.45$, from Table 10-33.

$$B = \frac{\log\left[\left(\frac{0.9484}{1 - 0.9484}\right)\left(\frac{0.9539}{1 - 0.9539}\right)\right]}{\log 1.45}$$

$$= (\log 380.3)/(\log 1.45) = 15.988$$

The recovery of component M in the distillate is then $d_M/f_M = (10^{-1.3158} 2.30^{15.988})/(1 + 10^{-1.3158}\, 2.30^{15.988}) = 0.99997$, from Equation 10-431.

The recovery of component M in the bottoms is $b_M/f_M = 1/(1 + 10^{-1.3158} 2.30^{15.988}) = 0.00003$, from Equation 10-434.

Repeating Equations 10-431 and 10-434 for each of the other non-key components in the feed mixture gives the results shown in Table 10-34. Good agreement was demonstrated.

Computer Program

The author [287] has developed a program for shortcut multicomponent distillation calculations based on a series of equations developed by Hengstebeck-Geddes [124, 125, 126, 137], while the minimum tray calculations (at total reflux) use the equations developed by Fenske [285]. The number of theoretical equilibrium stages is determined using Gilliland's [23] empirical correlations. The program has an option of entering either the equilibrium constant or the relative volatility with the feed-stream key components.

Table 10-34 Results for Example 10-41 for Multicomponent Distillation.

	Percent recovery	
Component	**In dist. (100 di/fi)**	**In btms. (100 di/fi)**
M	99.997	0.003
N	97.731	2.269
O (LK)	94.840	5.160
P (HK)	4.610	95.390
Q	0.889	99.111
R	0.245	99.755
S	0.005	99.995

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It also arranges the relative volatilities in order of decreasing magnitude before proceeding to compute the correlation constants. The following assumptions are used in the program.

- There is only one feed stream with 12 or fewer key components.
- There is only one heavy key component.
- Feed components may be arranged in order of decreasing relative volatility, but the light key (LK) and heavy key (HK) components must be adjacent to each other.
- The feed enters the column at the optimum stage.
- The column produces two products (distillate and bottoms) with overhead condenser and bottom reboiler.

The program uses the bisection method to determine Underwood's constant θ, or the root of Underwood's equation, and then proceeds to evaluate the minimum reflux ratio. From a given multiplier (FACTOR), the actual reflux ratio is calculated.

From the various equations that have been proposed to describe Gilliland's curve for multicomponent distillation, this author uses that of McCormick (Equation 10-450) because it gives a good agreement in the normal operating range of real towers. The program then proceeds to determine the actual reflux ratio from the minimum reflux ratio using Equation 10-454. Using these equations with Equation 10-462, the program calculates the number of theoretical plates and the optimum location of the feed plate in a distillation column.

NB: This program is best used in preliminary design before a detailed design by a process simulator package is explored.

Table 10-35 Input Data and Computer Results for Multicomponent Fractionation

Data Name: Data104.Dat
Rel
7

0.1	2.3
0.13	1.75
0.25	1.45
0.23	1.0
0.15	0.90
0.08	0.83
0.06	0.65
0.9484	0.9539
41	1.20

Multicomponent System Fractionation

Component Number	Feed Moles	Rel Volatility Alpha	Distilattle %	Moles	Bottoms %	Moles
1	0.1000	2.3000	99.9966	0.1000	0.0034	0.0000
2	0.1300	1.7500	99.7317	0.1297	0.2683	0.0003
3	0.2500	1.4500	94.8400	0.2371	5.1600	0.0129
4	0.2300	1.0000	4.6100	0.0106	95.3900	0.2194
5	0.1500	0.9000	0.8886	0.0013	99.1114	0.1487
6	0.0800	0.8300	0.2451	0.0002	99.7549	0.0798
7	0.0600	0.6500	0.0049	0.0000	99.9951	0.0600

Component Number	Feed Moles	Mol Fract.XF	Distilattle Moles	Mol Fract. XD	Bottoms Moles	Mol.XB
1	0.1000	0.1000	0.1000	0.2088	0.0000	0.0000
2	0.1300	0.1300	0.1297	0.2707	0.0003	0.0007
3	0.2500	0.2500	0.2371	0.4951	0.0129	0.0248
4	0.2300	0.2300	0.0106	0.0221	0.2194	0.4210
5	0.1500	0.1500	0.0013	0.0028	0.1487	0.2853
6	0.0800	0.0800	0.0002	0.0004	0.0798	0.1531
7	0.0600	0.0600	0.0000	0.0000	0.0600	0.1151

The EED condition, Q:	1.0
The heavy key component number is:	4
Percentage recovey of the light key component	94.84
In the distillate is (%):	95.39
Percentage recovery of the heavy key compnent	
In the bottoms is (%) :	0.4789
Total moles in the distillate:	0.5211
Total moles in the bottoms:	1.0000
Total moles in the feed:	1.1850
Underwood constant:	
Factor for the reflux ratio:	1.2000
Minimum reflux ratio:	2.8490
Actual reflux ratio:	3.4188
Minimum number of stages is:	16.0
Number of theoretical plates in the column:	33.6
The position of the feed plate is:	17.2

Table 10-35 shows the input data and results of Example 10-41 using PROG104 is the Absoft Microsoft Runtime Windows Environment (MRWE) Fortran Compiler. An Excel spreadsheet (Example 10-41.xls) has been developed to determine θ, the root of Underwood's equation and the minimum reflux ratio, R_{min} for multicomponent distillation. The program uses Microsoft Excel optimization technique such as Go-Seek or Solver to determine the Underwood constant θ for a given feed condition (q), and then proceeds to calculate the minimum reflux ratio for various values of the distillate composition. The actual reflux ratio is determined by multiplying the minimum reflux ratio by a factor (FACTOR) of 1.15 to 1.3. The program uses the Fenske equation to determine the minimum number of plates at total reflux, using the developed correlation of Erbar-Maddox (Figure 10-94 or 10-94a). The program further calculates the number of theoretical plates and compares

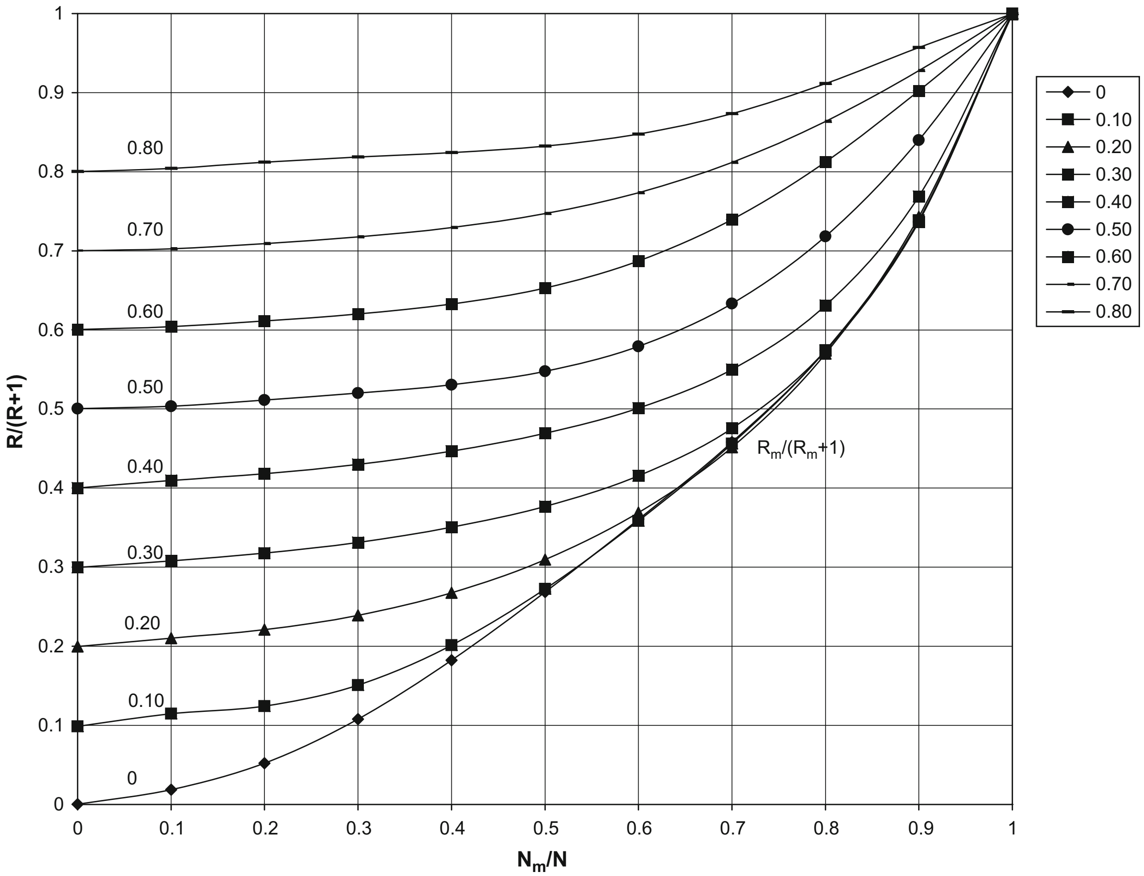


Figure 10-94 Plate-reflux correlation of Erbar and Maddox.

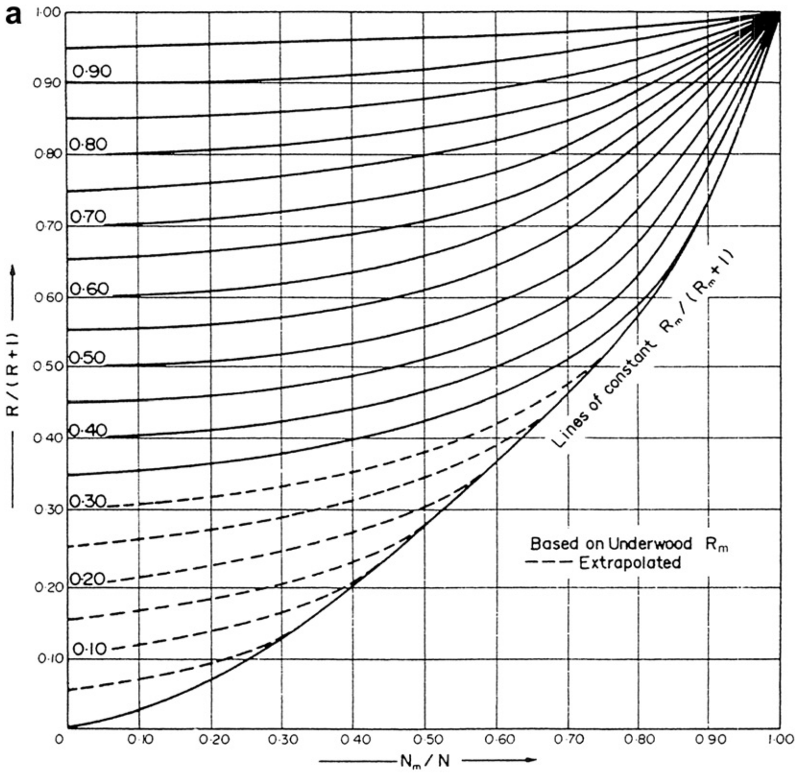


Figure 10-94a Erbar-Gray–Maddox correlation. Dashed Lines: extrapolated (source: Erbar and Maddox, Hydrocarbon Process. Petrol Refiner, 4, No. 5, 183, 1961).

the value with the Rusche correlation (Equation 10-451). Figures 10-93a and 10-93b show snap-shots of the calculations. The results in Table 10-34 by Yaws et al [124] and in Table 10-35 from the developed computer program PROG104 are in good agreement.

10.37.9 Algebraic Plate-to-Plate Method

Like any plate-to-plate calculation, this is tedious and in most instances does not justify the time spent, because shorter methods give reasonably acceptable results. Van Winkle [75] outlines the steps necessary for such calculations.

With current computer technology there are several commercial programs available (as well as personal and private ones) that perform tray-to-tray stepwise calculations up or down a column, using the latest vapor pressure, K-values, and heat data for the components. This then provides an accurate analysis at each tray (liquid and vapor analysis) and also the heat duty of the bottoms reboiler and overhead total or partial condenser.

Torres-Marchal ([110] and [111]) present a detailed graphical solution for multicomponent ternary systems that can be useful to establish the important parameters prior to undertaking a more rigorous solution with a computer program. This technique can be used for azeotropic mixtures, close-boiling mixtures and similar situations.

An alternative improved solution for Underwood's method is given by Erbar, Joyner, and Maddox [113] with an example.

10.37.10 Erbar-Maddox Method [115]

This method is used to determine the actual number of theoretical stages at a practical reflux ratio. It uses a plot of $R/(R+1)$ against N_{min}/N with $R_{min}/(R_{min}+1)$ as the parameter. When $R = R_{min}$, the axis becomes zero. Therefore, the y-axis of the diagram represents minimum reflux conditions. When $N = N_{min}$, both x and y coordinates become unity. Branan [284] has developed a polynomial expression that represents the Erbar-Maddox curves. He represents the equation by the following:

$$y = A + Bx + Cx^2 + Dx^3 + Ex^4 + Fx^5 \qquad (10\text{-}463)$$

where

A, B, C, D, E, F = constants for varying values of z.

$$x = N_m/N \qquad (10\text{-}464)$$

$$y = R/(R+1) \qquad (10\text{-}465)$$

$$z = R_m/(R_m+1) \qquad (10\text{-}466)$$

Table 10-36 shows the constant values at varying z. The author has used the values in Table 10-36 and developed an Excel spreadsheet to create the Erbar-Maddox correlation. Figure 10-94 shows the plates-reflux correlation of Erbar-Maddox and is based on a bubble-point feed. The correlations from Figure 10-94 are in good agreement with the Erbar-Maddox correlation of Figure 10-94a. For other types of feed, the following correlation is used [112]:

$$V_u = V_k + \frac{(1 - D/F)\,(H_{F,u} - H_{F,k})}{Q_c/L_o} \qquad (10\text{-}467)$$

Table 10-36 Constants for the Erbar-Maddox correlation.

z	A	B	C	D	E	F
0	0.00035	0.16287	−0.23193	5.09032	−8.50815	4.48718
0.1	0.09881	0.32725	−2.57575	10.20104	−12.8205	5.76923
0.2	0.19970	0.14236	−0.58646	2.60561	−3.12499	1.76282
0.3	0.29984	0.09393	−0.23913	1.49008	−2.4388	1.79486
0.4	0.40026	0.12494	−0.49585	2.15836	−3.27068	2.08333
0.5	0.50049	−0.03058	0.81585	−2.61655	3.61305	−1.28205
0.6	0.60063	−0.00792	0.60063	−2.06912	3.39816	−1.52243
0.7	0.70023	−0.01109	0.45388	−1.25263	1.94348	−0.83334
0.8	0.80013	−0.01248	0.76154	−2.72399	3.85707	−1.68269
0.9	0.89947	0.00420	0.38713	−1.14962	1.40297	−0.54487
1.0	1.0	0	0	0	0	0

Source: Branan, C.R., Rules of Thumb for Chemical Engineers: A manual of quick, accurate solutions to everyday engineering problems, 4th Ed., Elsevier, 2005.

where

D = Distillate flow rate, lb-mole/h.
F = Feed flow rate, lb-mole/h
H = Enthalpy, Btu/h
L_o = Liquid condensed at the condenser, lb-mole/h.
Q_c = Condenser duty, Btu/h
V = Vapor flow rate in the rectifying section, lb-mole/h.

Subscripts

F = feed.
k = at the bubble point.
u = at the conditions differing from bubble point.

In the Erbar-Maddox correlation, minimum stages are calculated by the Winn method, and minimum reflux by the Underwood method-but the Fenske minimum stages method can also be used.

10.37.11 Underwood Algebraic Method: Adjacent Key Systems [72]

This system for evaluating multicomponent adjacent key systems, assuming constant relative volatility and constant molal overflow, has proven generally satisfactory for many chemical and hydrocarbon applications. It gives a rigorous solution for constant molal overflow and volatility, and acceptable results for most cases which deviate from these limitations.

Overall Column–Constant α

$$(L/D)_{min} + 1 = \frac{(\alpha_a x_a)_D}{\alpha_a - \theta} + \frac{(\alpha_b x_b)_D}{\alpha_b - \theta} + \ldots \frac{(\alpha_i x_i)_D}{\alpha_i - \theta} \qquad (10\text{-}468)$$

In arriving at $(L/D)_{min}$ the correct value of θ is obtained from:

$$1 - q = \frac{(\alpha_a x_a)_F}{\alpha_a - \theta} + \frac{(\alpha_b x_b)_F}{\alpha_b - \theta} + \ldots \frac{(\alpha_i x_i)_F}{\alpha_i - \theta} = \sum \frac{x_{Fi}}{1 - \theta/\alpha_i} \qquad (10\text{-}469)$$

The "q" value that is previously described for the thermal condition of the feed.

Rectifying section only:

$$V_r = \sum_{i=l,h,H} \frac{Dx_{Di}}{1 - \theta/\alpha_i} \qquad (10\text{-}470)$$

Stripping section only:

$$V_s = \sum_{i=l,h,H} \frac{Bx_{Bi}}{1 - \theta/\alpha_i} \qquad (10\text{-}471)$$

At the minimum reflux condition all the θ values are equal, and generally related:

$\alpha_h < \theta < \alpha_l$

Suggested Procedure

1. From Equation 10-468 expressing θ and q evaluate θ by trial and error, noting that θ will have a value between the α of the heavy key and the α of the light key evaluated at or near pinch temperatures, or at α_{avg}. Suggested tabulation, starting with an assumed θ value, θ_a:

Component	x_{Fi}	$\alpha_i\ x_{Fi}$	$\alpha_i - \theta$	$\alpha_i\ x_{Fi}/(\alpha_i - \theta)$	$\alpha_i\ x_{Fi}/(\alpha_i - \theta)^2$
a	x_{Fa}	$\alpha_a\ x_{Fa}$	$\alpha_a - \theta_a$	$\alpha_a\ x_{Fa}/(\alpha_a - \theta_a)$	$\alpha_a\ x_{Fa}/(\alpha_a - \theta_a)^2$
b	x_{Fb}	$\alpha_b\ x_{Fb}$	$\alpha_b - \theta_a$	$\alpha_b\ x_{Fb}/(\alpha_b - \theta_a)$	$\alpha_b\ x_{Fb}/(\alpha_b - \theta_a)^2$
•	•	•	•	•	•
•	•	•	•	•	•
				$\sum \Psi(\theta_a)$	$\sum \Psi'(\theta_a)$

Corrected θ by Newton's approximation method:

$$\theta_c = \theta(\text{assumed}) - \frac{\Psi(\theta_a)}{\Psi'(\theta_a)} \qquad (10\text{-}472)$$

Repeat the same type of tabular computation, substituting the corrected θ_c for the θ_a. If the second, corrected θ'_c checks closely with the θ_c, the right value of θ has been obtained, if not, a third recalculation should be made using the θ'_c value as the new assumed value.

Note that average α values should be used (constant) for each component, unless the values vary considerably through the column. In this latter case follow the discussion given elsewhere in this section.

2. Calculate $(L/D)_{min}$ by substituting the final θ value in Equation 10-468. Note that this requires evaluating the functions associated with θ at the composition of the distillate product. The α values are the constant values previously used above.

10.37.12 Underwood Algebraic Method: Adjacent Key Systems; Variable α

For varying α systems, the following procedure is suggested:

1. Assume $(L/D)_{min}$ and determine the pinch temperature by Colburn's method.
2. At this temperature, evaluate α at pinch and α at overhead temperature, obtaining a geometric average α. As an alternative, Shiras et al. [63] indicate a t_{avg} value which gives acceptable results when compared to pinch and stepwise calculations. This suggestion calculates:

$$t_{avg} = (D_{t_\circ} + B_{t_B})/F$$

3. Determine Underwood's θ value as previously described, using the average α value.
4. Calculate $(L/D)_{min}$ and compare with the assumed value of (1) above. If check is satisfactory, $(L/D)_{min}$ is complete; if not, reassume new $(L/D)_{min}$ using calculated value as basis, and repeat (1) through (4) until satisfactory check is obtained.

where

t_o = overhead temp °F
t_B = bottoms temp °F
t_{avg} = avg temp, °F

To aid in solving the tedious Underwood equation to ultimately arrive at $(L/D)_{min}$, Frank [100] has developed Figure 10-95, which applies for liquid feed at its bubble point and to binary or multicomponent systems, but does require that the key components are adjacent. Otherwise, the system must be solved for two values of θ [74]. To obtain the necessary parameters for Figure 10-95, Frank recommends using the same overhead concentrations that were used in, or calculated by, the Fenske equation for the Underwood solution. (θ = Underwood constant.)

Example 10-42

An equimolar binary mixture with a relative volatility of 2 is fed to a distillation column which produces

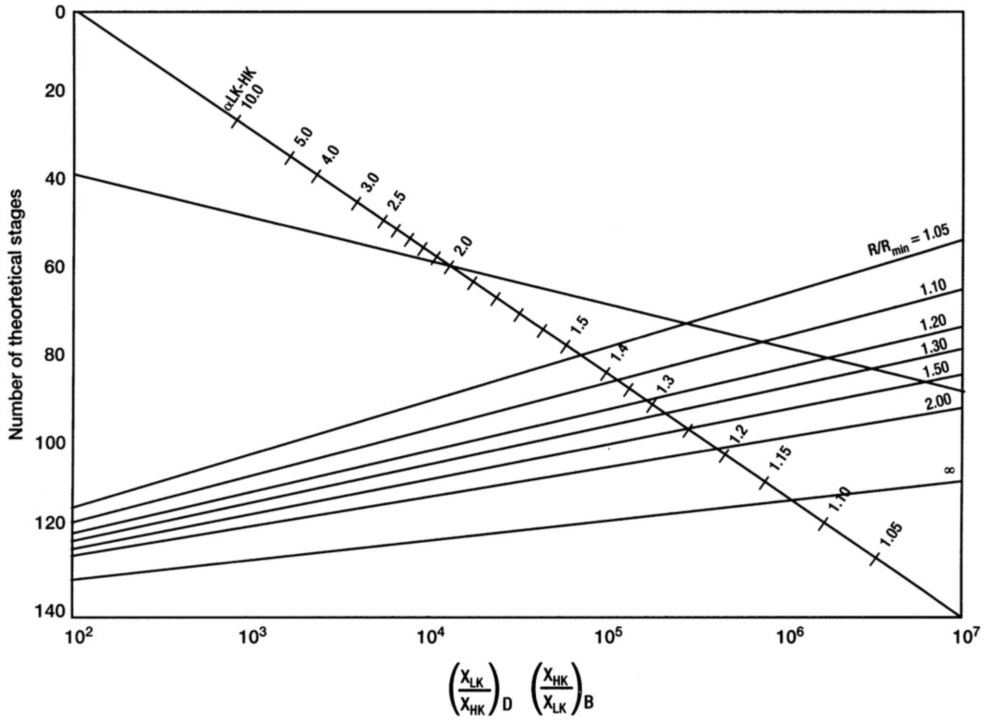


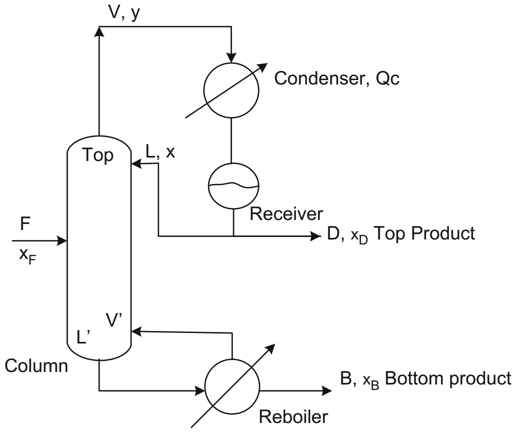
Figure 10-95 Short-cut solution of Fenske-Underwood-Gilliland theoretical trays for multicomponent distillation. Used by permission, Frank, O., Chem. Eng., Mar. 14, p. 109 (1977).

a distillate containing 97.5% of the more volatile component and a residue containing 10% of the more volatile component. The feed is liquid at its boiling point and 80% of the liquid entering the reboiler is vaporized and returned to the column as boil-up.

(i) Estimate the number of theoretical plates provided by this column.

(ii) Check your answer in part (i) by reference to the graph of the Gilliland correlation and Erbar and Maddox correlation.

Solution



The overall mass balance on the column.

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

The component balance on the more volatile component (MVC) is:

$$F\,x_F = D\,x_D + B\,x_B \tag{2}$$

Assuming that F = 100 mols/h.
$x_F = 0.5$, $x_D = 0.975$ and $x_B = 0.1$
Substituting the values of the components in Eq. 2 gives:

$$100\,(0.5) = D\,(0.975) + B(0.1)$$

$$50 = 0.975D + 0.1B \tag{3}$$

Rearranging Eq. 1 and substituting into Eq. 3 gives:

$$50 = 0.975D + 0.1(100 - D) \tag{4}$$

$$50 = 0.975D + 10 - 0.1D \tag{5}$$

D = 45.71 mols/h.
B = 54.29 mols/h.
The upper operating line (UOL) at the top of the column is:

The overall mass balance on UOL is:

$$V = L + D \tag{6}$$

Component balance is:

$$V_n y_n = L_{n+1}\,x_{n+1} + Dx_D \tag{7}$$

or

$$y_n = \frac{L_{n+1}}{V_n}x_{n+1} + \frac{D}{V_n}x_D \tag{8}$$

$$\text{Reflux ratio, } R = \frac{L}{D} \tag{9}$$

Substituting Eq. 9 into Eq. 6 gives:

$$V_n = RD + D \tag{10}$$

And Equation 8 (UOL), assuming constant molar overflow, becomes:

$$y_n = \frac{R}{(R+1)}x_{n+1} + \frac{x_D}{R+1} \tag{11}$$

The intercept on the UOL, is:

$$I = \frac{x_D}{(R+1)} \tag{12}$$

Since the feed is liquid at its boiling point (i.e. q = 1) and 80% of the liquid entering the reboiler (L′) is vaporized to give the vapor (V′), which leaves the reboiler and returns to the column.

Therefore at the bottom of the column, if L′ = 1.0 and V′ = 0.8.

The mass balance at the bottom of the column with the reboiler is:

$$L' = V' + B \tag{6}$$

or

$$V' = L' - B \tag{7}$$

The component balance at the bottom is:

$$V' y_m = L'\,x_{m+1} - B\,x_B$$

or

$$y_m = \frac{L'}{V'}x_{m+1} - \frac{B}{V'}x_B$$

$$\text{Slope is } \frac{L'}{V'} = \frac{1}{0.8} = 1.25$$

where L′/V′ = gradient of lower operating line (LOL). If $\alpha = 2$, using the Excel spreadsheet (Example 10-42.xls)

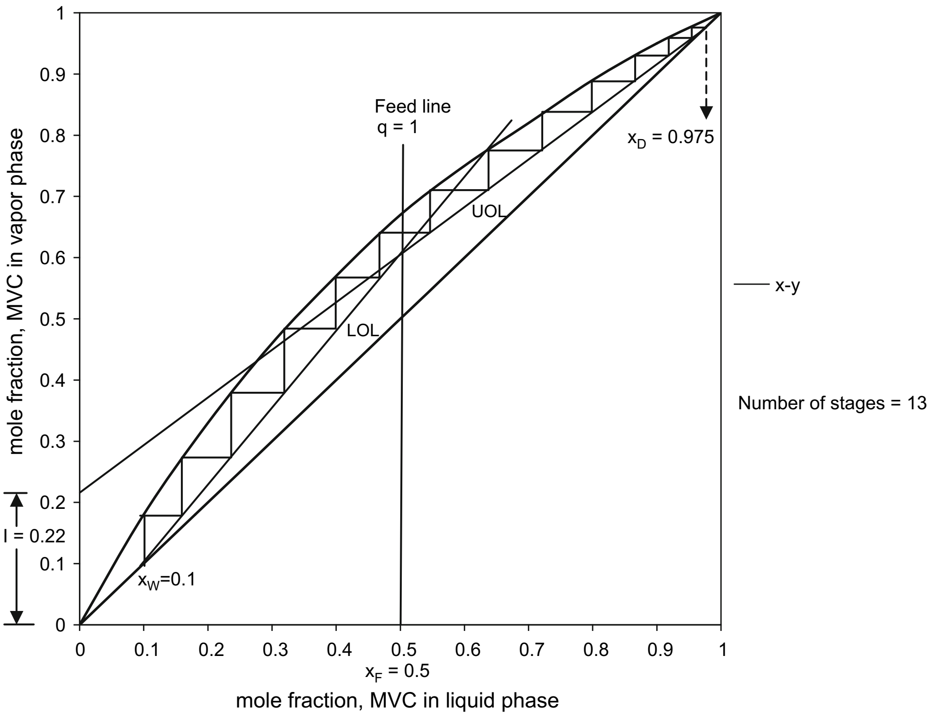


Figure 10-96 The McCabe-Thiele diagram for Example 10-42.

to plot the VLE diagram, The McCabe-Thiele diagram of Figure 10-96 is drawn as follows:

At the co-ordinates $(x_w, x_w) = 0.1$ on the 45° line, draw the Lower operating line (LOL) with the slope of 1.25, to intercept the "q" (i.e. q = 1 @ boiling point) line at $x_F = 0.5$.

At co-ordinates $(x_D , x_D) = 0.975$ on the 45° line, draw the upper operating line to intersect the lower operating line (LOL) at q = 1 and extend to the intercept I on the y-ordinate of the VLE diagram.

Step-off the line between the UOL, LOL and the 45° line from $x_D = 0.975$ to $x_W = 0.1$ to determine the number of equilibrium stages.

$$I = \frac{x_D}{R+1} = 0.22 \text{ (from McCabe-Theile diagram)}$$

$$\frac{0.975}{(R+1)} = 0.22$$

$R = 3.43$

From McCabe-Thiele diagram (Figure 10-96):

$N + 1 = 14$ stages

$N = 13$ stages

(b) R_{min}: from the points (x_D, x_D), a straight line is drawn that touches the VLE line with the "q" line and extended to the y-axis at a point $I_{min} = \frac{x_D}{(R_m+1)}$.

$$I_{min} = \frac{x_D}{(R_m+1)} = 0.34$$

$$\frac{0.975}{(R_m+1)} = 0.34$$

$$R_m = 1.86$$

Using the Underwood Equation for the minimum reflux ratio:

$$R_m = \frac{1}{(\alpha-1)}\left[\frac{x_{LK,D}}{x_{LK,F}} - \frac{\alpha(1-x_{LK,D})}{(1-x_{LK,F})}\right] \quad (10\text{-}210)$$

$$= \frac{1}{(2-1)}\left[\frac{0.975}{0.5} - \frac{2(1-0.975)}{(1-0.5)}\right]$$

$R_m = 1.85$

The Fenske method for the minimum number of theoretical stages at total reflux is:

$$N_m = \frac{\ln\left[(x_{LK}/x_{HK})_D\,(x_{HK}/x_{LK})_B\right]}{\ln\,(\alpha_{LK}/\alpha_{HK})_{avg}} \quad (10\text{-}182)$$

$$= \frac{\ln\left[\left(\frac{0.975}{0.025}\right)\left(\frac{0.9}{0.1}\right)\right]}{\ln 2}$$

$N_m = 8.5$

From the Gilliland correlation (Figure 10-93), the abscissa axis is:

$$\frac{R-R_m}{R+1} = \frac{3.66-1.85}{(3.66+1)} = 0.388 \quad (10\text{-}219)$$

The corresponding point on the ordinate axis of the Gilliland correlation is 0.31

Therefore the number of theoretical stages can be determined from the ordinate by:

$$\frac{N - N_m}{N + 1} = 0.31 \tag{10-220}$$

$$\frac{N - 8.45}{N + 1} = 0.31$$

N = 12.69 stages (13 stages)

Using the Erbar and Maddox correlation (Figure 10-94 or 10-94a).

The lines of constant $\frac{R_m}{R_m + 1}$ is

1.85/2.85 = 0.649 (0.65)

The ordinate axis of Erbar and Maddox correlation is:

$$\frac{R}{(R + 1)} = \frac{3.66}{(3.66 + 1)} = 0.79$$

A line is drawn at point 0.79 on the ordinate of the correlation and intercepts the lines of constant $\frac{R}{R_m + 1}$ at 0.65. The corresponding point on the abscissa is 0.74

The number of theoretical stages is:

$$\frac{N_m}{N} = 0.74$$

N = 8.45/0.74 = 11.4 stages.

Example 10-43. Using Data from Example 10-20 (Erbar-Maddox correlation Figure 10-94a)

Using the Erbar and Maddox correlation.

The lines of constant $\frac{R_m}{R_m + 1}$ is

1.85/2.85 = 0.649 (0.65)

The ordinate axis of Erbar and Maddox correlation is:

$$\frac{R}{(R + 1)} = \frac{3.66}{(3.66 + 1)} = 0.79$$

A line is drawn at point 0.79 on the ordinate of the correlation and intercepts the lines of constant $\frac{R_m}{R_m + 1}$ at 0.65. The corresponding point on the abscissa is 0.74.

The number of theoretical stages is:

$$\frac{N_m}{N} = 0.74$$

N = 8.45/0.74 = 11.4 stages.

10.37.13 Underwood Algebraic Method: Split Key Systems: Constant Volatility [72]

This method appears tedious, but it is not so unwieldy as to be impractical, but it does require close attention to detail. However, a value of $(L/D)_{min}$ can be obtained with one trial that may be satisfactory for "order of magnitude" use, which is often all that is needed before proceeding with detailed column design and establishment of an operational L/D ratio.

1. Assume θ_f values and check by:

$$\sum \frac{\alpha_i x_{Fi}}{\alpha_i - \theta_{fi}} = 1 - q \tag{10-473}$$

There are total solutions of θ_{fi} equal to one more than the number of split components between the keys. The θ_f values will be spaced:

$$\alpha_{l3} \quad \theta_{f3} \quad \alpha_4 \quad \theta_{f4} \quad \alpha_5 \quad \theta_{f5} \quad \alpha_{h6}$$

where α_l is the light key and component number 3, and correspondingly for the heavy key, component number 6. Determine θ values as for constant volatility case of adjacent keys.

For some systems, the θ values can be assumed without further solution of the above relation, but using these assumed values as below.

2. Calculate:

$$v = \frac{\underset{i=h-1}{\overset{1}{(P)}}(\theta_{fi})}{\underset{i=h-1}{\overset{1+1}{(P)}}(\alpha_i)} \tag{10-474}$$

which represents (for the hypothetical system set up in (1)) the product (θ_{f5}) (θ_{f4}) (θ_{f3}) divided by the product of (α_5) (α_4), based upon the lightest component being numbered one, the next two, etc., the heaviest components having the higher numbered subscripts. P means product, and 1, i = h − 1, i = 1 + 1 are limits for evaluation referring to components between the keys, and the light and heavy keys.

3. Calculate:

$$\omega_j = \frac{\underset{i=h-1}{\overset{1+1}{(P)}}\left(1 - \frac{\alpha_i}{\alpha_j}\right)}{\underset{i=h-1}{\overset{1}{(P)}}\left(1 - \frac{\theta_{fi}}{\theta_j}\right)} \tag{10-475}$$

For the θ example shown in (1) above:

$$\omega_3(\text{light key}) = \frac{(1 - \alpha_5/\alpha_3)(1 - \alpha_4/\alpha_3)}{(1 - \theta_{f5}/\alpha_3)(1 - \theta_{f4}/\alpha_3)(1 - \theta_{f3}/\alpha_3)}$$

Also calculate ω for all components lighter than light key.

$$\omega_6(\text{heavy key}) = \frac{(1 - \alpha_5/\alpha_6)(1 - \alpha_4/\alpha_6)}{(1 - \theta_{f5}/\alpha_6)(1 - \theta_{f4}/\alpha_6)(1 - \theta_{f3}/\alpha_6)}$$

Component, j	ω_j	α_j	$\frac{\omega_j}{\alpha_j}$	x_{D_j}	$\omega_j x_{Dj}$	$\frac{\omega_j}{\alpha_j} x_{D_j}$
L (light key)	●	●	●	●	●	●
H (heavy key)	●	●	●	●	●	●
L_{l+1} light						
L_{l+2} than light	●	●	●	●	●	●
L_{l+3} key, etc.					$\sum \omega_j x_{Dj}$	$\sum \frac{\omega_j}{\alpha_j}(x_{Dj})$

4. Calculate $(L/V)_{min}$: (internal)

$$(L/V)_{min} = (v)\frac{\sum\limits_{j=h,l,L} D\left(\frac{\omega_j}{\alpha_j}\right)\left(x_{D_j}\right)}{\sum\limits_{j=h,l,L} D(\omega_j)\left(x_{D_j}\right)} \tag{10-476}$$

5. Calculate External $(L/D)_{min}$:

$$(L/D)_{min} = \frac{1}{(V/L)_{min} - 1} \tag{10-477}$$

For variable α conditions, the pinch temperature can be used for α determinations as previously described.

Example 10-44: Minimum Reflux Ratio Using Underwood Equation: Calculate the Minimum Reflux Ratio

Use $\phi_{fl} = 0.584$ to begin, (assumed).

Expanding to determine more exact value of ϕ_{fl}:

$$\Omega\phi = \Omega\phi_a + \phi - \phi_a\Omega'\phi_a$$

$$\Omega\phi = \sum \frac{\alpha_i x_f}{(\alpha_i - \phi)} - (1 - q)$$

$$\phi_{fl} = \frac{\phi_a - \Omega\phi_a}{\Omega'\phi_a}$$

$$\Omega'\phi = \sum \frac{\alpha_i x_f}{(\alpha_i - \phi)^2}$$

$\Phi_{fl\text{-corrected}} = 0.584 - (-0.016)/(18.948) = 0.584 + 0.00084 = 0.58484$

Now use this new value of Φ_{fl} in Underwood's equations;

$$\sum_{i=h,l,L} \frac{Dx_{Di}}{1 - \frac{\phi_r}{\alpha_i}} - V_r = 0$$

For minimum reflux: $\Phi_{fl} = \Phi_r = \Phi_s$

From calculations of related problem* the value of Dx_{Di} has been calculated:

$Dx_{Di} = 0.01072$ for heavy key

$Dx_{Di} = 0.428$ for light key

$Dx_{Di} = 0.225$ for lighter than light key

$$\left[\frac{0.01072}{1 - \frac{0.5848}{0.50}} + \frac{0.428}{1 - \frac{0.5848}{1.0}} + \frac{0.225}{1 - \frac{0.5848}{2.0}}\right] - V_r = 0$$

$[-0.638 + 1.03 + 0.318] - V_r = 0$

From related problem, D has been determined to be = 0.67 mols/mol feed.

$-V_r = -1.285$

$V_r = 1.285$

$(V_r)_{min} = (L_r)_{min} + D$

$(L_r)_{min} = 1.285 - 0.6637 = 0.622$

$\left(\frac{L_r}{D}\right)_{min} = \frac{0.6622}{0.6637} = 0.94$, Minimum Reflux Ratio

10.37.14 Minimum Reflux Colburn Method: Pinch Temperatures [12]

This method has also found wide usage and might be considered less tedious by some designers. It also yields an approximation of the rectifying and stripping section pinch temperatures. For adjacent keys,

Rectifying:

$$\left(\frac{L}{D}\right)_{min} = \frac{1}{\alpha - 1}\left(\frac{x_D}{x_n} - \alpha\frac{x_{hD}}{x_{hn}}\right) \tag{10-478}$$

Component	x_{fi}	$\alpha_i x_{fi}$	$\alpha_i - \phi_a$	$\left[\frac{\alpha_i x_{fi}}{\alpha_i - \phi_a}\right]$	$\left[\frac{\alpha_i x_{fi}}{(\alpha_i - \phi_a)^2}\right]$
1	0.10	0.025	−0.334	−0.0749	+0.224
2	0.225	0.1125	−0.084	−1.34	+15.9
3	0.450	0.450	+0.416	+1.08	+2.6
4	0.225	0.450	+1.416	+0.318	+0.224
				$\sum = -0.016$	$+18.948 = \Omega'\phi_a$
			$\Omega\phi_a = -0.016 - (1 - q)$ $\phi_a = -0.016 - (1 - 1)$ $\phi_a = -0.016$		

where

α = relative volatility of any component referenced to the heavy key component

x_{hD} = overhead composition of heavy key component, mol frac

x_{hn} = pinch composition of heavy key component, mol frac

x_D = overhead composition of any light component, mol frac

x_n = pinch composition of any light component, mol frac

1. Calculate D, B, Dx_{Di} and Bx_{Bi} from problem specification.

2. Assume or set the operating pressure and overhead temperature (may be calculated).

3. Calculate the liquid and vapor quantities and their respective compositions in the feed to the column.

4. Calculate estimated ratio of key components on feed plate based on the liquid portion of the feed.

$$r_f = \frac{\text{Mol fraction light key}}{\text{Mol fraction heavy key}}$$

a. For all liquid feed at feed tray temperature (boiling point)
r_f = mol fraction ratios in feed.

b. For a part or all vapor feed just at its dew point, r_f = ratio of key components in the equilibrium liquid phase of feed.

c. For all liquid feed below feed plate temperature r_f = ratio of key components at intersection point of operating line (from a McCabe-Thiele diagram).

5. Determine approximate pinch zone liquid composition for light key component

$$x_{ln} = \frac{r_f}{(1 + r_f)(1 + \sum \alpha_i x_{Fi})_H} \qquad (10\text{-}479)$$

$\sum \alpha_i x_{fi}$ = sum of $\alpha_h x_{Fh+1} + \alpha_{h+2} x_{Fh+2} + \ldots$ for all components in liquid portion of feed heavier than heavy key. Note that x_{Fi} values are the mol fractions of the component in the liquid portion of feed only and the $\sum x_{Fi}$ equal to 1.0.

6. Calculate approximate value for $(L/D)_{min}$.

$$(L/D)_{min} = \frac{1}{\alpha_i - 1}\left(\frac{x_{lD}}{x_{ln}} - \alpha\frac{x_{hD}}{x_{hn}}\right)$$

The second term in the right hand parentheses can be omitted unless the mol fraction of the heavy key in the distillate, x_{hD} is 0.1 or greater. Use $x_{hn} = x_{ln}/r_f$.

7. Estimate stripping and rectifying pinch temperatures at values one-third and two-thirds of the interval between the column bottoms and overhead, respectively.

8. Calculate internal vapor and liquid flows.

$(L_r/D)_{min}$ = assumed
Solve for $(L_r/V_r)_{min}$

$$(L_r/V_r)_{min} = \frac{1}{1 + (D/L_r)_{min}} \qquad (10\text{-}480)$$

$L_r = (\text{number})\,(V_r) = (L_r/D)_{min}(D)$
D is known
Calculate V_r and L_r from above.

In stripping section:
Solve directly for L_s
$L_s = L_r + qF$

Solve for V_s:

$$\frac{V_r - V_s}{F} = 1 - q \qquad (10\text{-}481)$$

Calculate L_s/B

9. Evaluate pinch compositions at the assumed temperatures of Step 7. If this temperature does not give a balance, other temperatures should be assumed and a balance sought as indicated below. Either of the following balances can be used, for convenience:
Rectifying:

$$\sum x_{Dri} = \sum x_n = \sum_{i=h,l,L'} \left(\frac{Dx_{Di}/V_r}{\alpha_i K_h - L_r/V_r}\right) = 1 \qquad (10\text{-}482)$$

$$\text{or} \sum x_n = \sum_{i=h,l,L'} \left(\frac{Dx_{Di}/V_r}{K_i - L_r/V_r}\right) = 1$$

$$\text{or} \sum x_n = \sum_{i=h,l,L'} \left(\frac{x_{Di}}{(\alpha_i - 1)(L_r/D)_{min} + \alpha_i x_{hDI}/x_{hn}}\right) = 1$$

When the heavy key in the overhead is very small, less than 0.1 mol fraction, the last term of the denominator can be omitted.

$$\text{or} \sum x_n = \sum_{i=h,l,L'} \left(\frac{x_{Di}}{K_i + (K_i - 1)(L_r/V_r/D)_{min}}\right) = 1$$

Note that the calculations are only made for the heavy key, h; light key, 1; and all components lighter than it, L′. If there are split keys, the calculation is to include all components lighter than the heavy key.

Stripping pinch compositions:

$$\sum x_{Dsi} = \sum x_m = \sum_{i=H,h,l} \frac{Bx_{Bi}/V_s}{\frac{L_s}{V_s} - \alpha_i K_h} = 1 \qquad (10\text{-}483)$$

$$\text{or} \sum x_m = \sum_{i=H,h,l} \frac{Bx_{Bi}/V_s}{\frac{L_s}{V_s} - K_i} = 1$$

$$\text{or} \sum x_m = \sum_{i=H,h,l} \frac{\alpha_i x_{Bi}}{(\alpha_l - \alpha_i)(L_s/B)_{min} + \alpha_i x_{lB}/x_{ld}} = 1$$

Because the second term of the denominator is usually negligible when the light key in the bottoms is very small; (less than 0.1 mol fraction), this term is often omitted.

$$\text{or} \sum x_m = \sum_{i=H,h,l} \frac{x_{Bi}}{K_i + (1 - K_i) + (L_s/B)_{min}} = 1$$

Note that these calculations are made for the light key, l; heavy key, h; and all components heavier than the heavy key, H. For split key systems, the calculations are made for all components heavier than the light key.

10. Calculate mol fraction ratio:

a. Stripping pinch.

$$r_{ps} = \frac{\text{light key}}{\text{heavy key}}$$

b. Rectifying pinch

$$r_{pr} = \frac{\text{light key}}{\text{heavy key}}$$

c. $p = r_{ps}/r_{pr}$

11. Calculate for each component in pinch.

Rectifying: apply only to components lighter than light key, i = L'

$$\frac{(\alpha_i - 1)\alpha_i}{\alpha_i}$$

Read from Figure 10-97 value of C_{ni} for each component.

Calculate for each component:

$$(C_{ni})(x_{i_{pr}})$$

Sum these values:

$$\sum_{i=L'} C_{ni}\, x_{ip}$$

Stripping: apply only to components heavier than heavy keys, i = H.

$$(\alpha_l - 1)\ (\alpha_l)$$

Read from Figure 10-97 value of C_{mi} for each component.

Calculate for each component:

$$C_{mi}\alpha_i x_{i_{ps}}$$

Sum these values:

$$\sum_{i=H} C_{mi}\ \alpha_i\ x_{i_{ps}}$$

12. Calculate:

$$p' = \frac{1}{\left[1 - \sum C_n x_{ipr}\right]\left[1 - \sum C_m \alpha_i x_{ips}\right]} \qquad (10\text{-}481)$$

If the two values of p are not very nearly equal, this requires a retrial with a new $(L/D)_{min}$, and a follow through of the steps above.

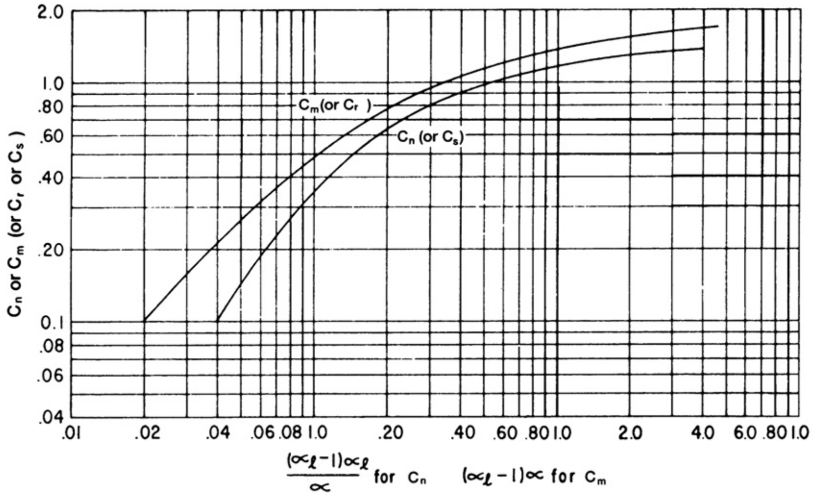


Figure 10-97 Colburn minimum reflux factors, above (Cn) and (Cm) feed point. Used by permission, Colburn, A. P., The American Institute of Chemical Engineers, Trans, Amer. Inst. Chem. Engr. Vol. 37, p. 805, (1941). All rights reserved.

When $r_{ps}/r_{pr} > p'$, the assumed $(L/D)_{min}$ is too high. Note that r_{ps}/r_{pr} changes rapidly with small changes in $(L/D)_{min}$, p' changes slightly. When $p = p'$, the proper $(L/D)_{min}$ has been found. Colburn reports the method is accurate to 1%. It is convenient to graph the assumed $(L/D)_{min}$ versus p and p′ in order to facilitate the selection of the correct $(L/D)_{min}$.

Example 10-45: Application of the Colburn Equation to Calculate the Minimum Reflux Ratio for a Multicomponent Mixture

A mixture of four components is as listed below, using n-butane as the base component.

Component	Relative Vol.	x_f	$(S_r)_i = Dx_D/Bx_B$
1	0.25	0.10	–
Heavy Key	0.50	0.225	0.05
n-butane	1.0	0.450	20.00
4	2.0	0.225	–

$$Dx_{Di} = \frac{(S_r)_i Fx_{Fi}}{1 + (S_r)_i}$$

$$S_r = \text{separation ratio} = \frac{Dx_{Di}}{Bx_{Bi}}$$

If all at top, $S_r = 1$
If all at bottom, $S_r = 0$

For component No.3; Basis; 1 mol feed,

$$Dx_{D3} = \frac{(20)[(1)(0.450)]}{1 + 20} = 0.428$$

For component No. 2,

$$Dx_{D2} = \frac{(0.05)(1 + 0.225)}{1 + 0.05} = 0.01072$$

Because this is at minimum reflux, and adjacent keys system,

$Fx_{FL} = Dx_{DL}$
$Fx_{FH} = Bx_{BH}$
Therefore, for component No.4, lighter than light key,
$Fx_{F4} = (1)\ (0.225) = 0.225$
Then, $Dx_{D4} = 0.225$
For component No.1, heavier than heavy key, this component will not appear in the overhead.
Bottoms:

$$Fx_{Fi} = Dx_{Di} + Bx_{Bi}$$

$$\frac{Fx_{Fi}}{Bx_{Bi}} = \frac{Dx_{Di}}{Bx_{Bi}} + 1$$

$$\frac{Fx_{Fi}}{Bx_{Bi}} = (S_r)_i + 1$$

$$(S_r)_i = \frac{Dx_{Di}}{Bx_{Bi}}, \text{ by definition}$$

$$\text{Then, } Bx_{Bi} = \frac{Fx_{Fi}}{(S_r)_i + 1}$$

Component No. 1:

$Fx_{Fi} = Bx_{Bi} = (1)\ (0.1) = 0.10$

Component No. 2:

$$(S_r)_i = \frac{Dx_{D2}}{Bx_{B2}} = 0.05$$

Substituting in equation previously established,

$$Bx_{B2} = \frac{(1)(0.225)}{(0.05) + 1} = 0.214$$

or, because Dx_{D2} has been calculated,

$$Bx_{B2} = \frac{Dx_{D2}}{(S_r)_i} = \frac{0.01072}{0.05} = 0.214$$

Component No. 3:

$$Bx_{B3} = \frac{Dx_{D3}}{(S_r)_i} = \frac{0.428}{20} = 0.0214$$

Component No. 4: This component will not be in the bottoms because it is lighter than the light key:

Overhead:

$Dx_{D1} + Dx_{D2} + Dx_{D3} + Dx_{D4} = D$

$0 + 0.01072 + 0.428 + 0.225 = D$

$D = 0.66372$ mols overhead product/mol feed

Composition of Overhead:

Component	Dx_{Di}	Mols%
1	0.0	0
2	0.01072	1.6
3	0.428	64.6
4	0.225	33.9
Total	0.66372	100.1

Composition of Bottoms:

Component	Bx_{Bi}	Mols%
1	0.10	29.9
2	0.214	63.8
3	0.0214	6.3
4	0.0	0
Total	0.3354	100.0

To have some idea of what value to use in Colburn's "exact" method for minimum reflux, use Colburn's "approximate" method to establish the order-of-magnitude of the minimum reflux:

$$\left(\frac{L}{D}\right)_{min} = \frac{1}{\alpha - 1}\left(\frac{x_D}{x_n} - \alpha\frac{x_{hD}}{x_{hn}}\right)$$

where

x_D and x_n = top and pinch compositions of a given light component

x_{hD} and x_{hn} = top and pinch compositions of the heavy key component

α = relative volatility of the given component with reference to the heavy key

Estimating Pinch Composition:

$$x_n(\text{approx}) = \frac{r_f}{(1 + r_f)(1 + \sum \alpha x_z)}$$

where

r_f = ratio of liquid composition of light to heavy key component on feed plate

x_n = mol fraction of a component in the liquid in the rectifying column pinch

x_z = mol fraction of a component in the liquid part of the feed where the feed is part vapor

$r_f = 0.450/0.225 = 2.0$

$\sum \alpha x_z = (0.5)\ (0.10) = 0.05$

$$\alpha_{light/heavy\ key} = \frac{1}{0.5} = 2.0$$

$$x_n(\text{approx}) = \frac{2.0}{(1 + 2.0)(1 + 0.05)} = \frac{2}{3.15} = 0.635$$

In terms of heavy key:

$\alpha_{l/h} = 2.0$

$\alpha_{l/l} = 0.25$

$\alpha_{l/h} = (\alpha_{l/h})\ (\alpha_{l/l}) = (2.0)\ (0.25) = 0.5$

$$\text{approx.}\left(\frac{L}{D}\right)_{min} = \frac{1}{(2.0 - 1)}\left(\frac{0.645}{0.635}\right)$$

$x_{D3} = 0.646$

$(L/D)_{min} = 1.017$ approx.

Now: Use Colburn's more detailed method:

$$\text{Assume}\left(\frac{L}{D}\right)_{min} = 1.017$$

$$\left(\frac{L}{V}\right)_{min} = \frac{1}{1 + \left(\frac{D}{L}\right)_{min}} = \frac{1}{1 + \frac{1}{1.017}}$$

$$\left(\frac{L}{V}\right)_{min} = \frac{1}{\frac{1.017 + 1}{1.017}} = 0.506$$

$V = L + D$

$$\frac{V}{L} = 1 + \frac{D}{L}$$

$$\frac{L}{V} = \frac{1}{1 + \frac{D}{L}}$$

$L_r = (0.506)\ (V_r)$

and:

$L_r = (1.017)\ (D_r)$

Then: $(0.506)\ V_r = (1.017)\ (D_r) = (1.017)\ (0.66372)$

$$V_r = \frac{(1.017)(0.6637)}{0.506} = 1.332 \text{ mols/mol feed}$$

$L_r = (1.017)\ (0.6637) = 0.674$ mols/mol feed.

The feed is a boiling point liquid from statement of problem:

$q = 1.0$

$L_s = L_r + qF$

Basis: 1 mol feed:

$L_{s\ (min)} = 0.674 + (1)\ (1) = 1.674$

$$\frac{L_r - V_s}{F} = 1 - q$$

$$\frac{1.332 - V_s}{1} = 1 - 1 = 0$$

$V_s = 1.332$

$$\frac{L_s}{V_s} = \frac{1.674}{1.332} = 1.255$$

Determine temperature of rectifying section pinch.

$$1 = \sum_{i=h,l,L} \frac{Dx_{Di}/V_r}{K_i - \frac{L_r}{V_r}}$$

Component	Dx_{Di}	$\frac{Dx_{Di}}{V_r}$	K_B @ 118°F	α_i	$\alpha_i K_B$	$\frac{L_r}{V_r}$	$K_i - \frac{L_r}{V_r}$	$\frac{Dx_{Di}/V_r}{K_i - (L_r/V_r)}$
h	0.01072	0.00805	1.06	0.50	0.53	0.506	0.024	0.333
l	0.428	0.321		1.0	1.06		0.554	0.580
L	0.225	0.169		2.0	2.12		1.614	0.104

Note: 0.225/1.332 = 0.169 $\sum = 1.017$

$K_i = \alpha_i\ K_B$

B = reference

Assume temperature at rectifying pinch. If the components were known, then the overhead dew point and bottoms bubble point could be determined, and from this an approximation could have been made of the pinch temperature. Because these cannot be calculated, trial-and-error must be used to obtain the correct pinch temperature.

Because the 1.017 $\approx$1.0, continue calculations composition of rectifying pinch:

$$x_{pri} = \frac{Dx_{Di}/V_r}{K_i - L_r/V_r} = \frac{Dx_{Di}/V_r}{\alpha_i K_B - L_r/V_r}$$

Component	$\frac{Dx_{Di}/V_r}{K_i - L_r/V_r}$	Revised Mol Fraction
2 = h	0.333	0.333/1.017 = 0.328
3 = l	0.580	0.572
4 = L	0.104	0.102
	1.017	1.002

Determine temperature of stripping section pinch:

$$1 = \sum_{i=H,h,l} \frac{Bx_{Bi}/V_s}{\frac{L_s}{V_s} - K_i} = \frac{Bx_{Bi}/V_s}{\frac{L_s}{V_s} - \alpha_i K_B}$$

Component	Bx_{Bi}	$\frac{Bx_{Bi}}{V_s}$	L_s/V_s	K_B @ 130°F	α_i	$\alpha_i K_B$	$L_s/V_s - \alpha_i K_B$	$\frac{Bx_{Bi}/V_s}{(L_s/V_s) - \alpha_i K_B}$
1 = H	0.10	$\frac{0.10}{1.332} = 0.0752$	1.255	1.23	0.25	0.308	0.947	0.0794
2 = h	0.214	0.1605			0.50	0.615	0.640	0.252
3 = l	0.0214	0.0160			1.0	1.23	0.025	0.640
								0.9714

Exact K_B must be between 1.23 and 1.24. Because there is a difference involved in calculation, the result is very sensitive to small changes in K.

Composition of Stripping Pinch:

Component	See Last Col. Above	Revised Mol Fraction
1 = H	0.0794	0.0794/0.9714 = 0.0817
2 = h	0.252	0.2585
3 = l	0.64	0.659
	0.9714	0.9992

Calculate C_r for each component lighter than light key.

There is only one component lighter than light key in this example, # 4

$$\left[\left(\frac{\alpha_l}{\alpha_h} - 1\right)\left(\frac{\alpha_l}{\alpha_L}\right)\right] = \left[\frac{1}{0.50} - 1\right]\left(\frac{1}{2}\right) = (2-1)\left(\frac{1}{2}\right)$$
$$= 0.50$$

Reading curve, $C_r = 1.0 = C_n$ (refer to Figure 10-97)

Evaluate C_s for No. 1:

$$\left[\left(\frac{\alpha_l}{\alpha_h} - 1\right)\alpha_H\right] = \left[\frac{1}{0.50} - 1\right](0.25) = (2-1)(0.25)$$
$$= 0.25$$

Reading curve, $C_s = 0.875$ (see Figure 10-97)

Now, substitute into Colburn correlation, for check,

$$\frac{x_{prl}\, x_{psh}}{x_{prh}\, x_{psl}} = \left(1 - \sum_L C_r\, x_{prl}\right)\left(1 - \sum \frac{\alpha_{psH}}{\alpha_{psh}} C_S\, x_{psH}\right)$$

$$\frac{(0.572)(0.2585)}{(0.328)(0.659)} = (1 - (1)(0.102))$$
$$\left(1 - \left(\frac{0.25}{0.50}\right)(0.875)(0.0817)\right)$$

$0.684 = (1 - 0.102)\ (1 - 0.0318) = (0.898)\ (0.9682)$

$0.684 \neq 0.868$

Because left side of equation is smaller than right side, $\left(\frac{L}{D}\right)_{min}$ assumed was too large. Try a smaller value around 0.95. Right side of equation is not so sensitive to change.

where

L = all components lighter than light key

$\sum_L$ = sum of all components lighter than light key, does not include light key

$\sum_H$ = sum of all components heavier than heavy key, does not include heavy key

p = pinch
r = rectifying
s = stripping
l = light key
h = heavy key
H = all components heavier than heavy key, not including the heavy key
L = all components lighter than light key, not including the light key
C_r, C_s = empirical constants

10.38 Scheibel-Montross Empirical: Adjacent Key Systems: Constant or Variable Volatility [61]

This method has not found as much wide acceptance, in use or in discussion in the literature; nevertheless it allows a direct approximate solution of the average multicomponent system with accuracy of 1–8% on average. If the key components are less than 10% of the feed, the accuracy is probably considerably less than indicated. If a split key system is considered, Scheibel reports fair accuracy when the split components going overhead are estimated and combined with the light key, the balance considered with the heavy key in the L/D relation.

$$(L/D)_{\min} = \frac{1}{x_{lF} + \sum x_{FL}}\left[x_{lF}R' + \left(x_{hF} + \sum x_{FH}\right)\right.$$
$$\left.\sum \frac{x_{FH}}{\frac{\alpha_l}{\alpha_L} - 1} + \sum \frac{x_{FL}}{\alpha_L}\left(1 + \frac{\alpha_l}{\alpha_L}\right)\right] \tag{10-485}$$

where

x_{lF} = mol fraction of light key in feed
Σx_{FL} = sum of all mol fractions lighter than light key in feed
R' = pseudo minimum reflux
Σx_{FH} = sum of all mol fractions heavier than heavy key in feed
x_{hF} = mol fraction heavy key in feed
α_l = relative volatility of light key to heavy key at feed tray temperature
α_H = relative volatility of components heavier than heavy key at feed tray temperature
α_L = relative volatility of components lighter than light key at feed tray temperatures
x_{it} = mol fraction liquid at intersection of operating lines at minimum reflux. (Calculated or from graph.)
x_{io} = mol fraction light key in overhead expressed as fraction of total keys in overhead

Pseudo minimum reflux:

$$R' = \frac{x_{io}}{(\alpha_i - 1)x_i} - \frac{(1 - x_i)(\alpha_i - 1)}{(1 - x_{io})\alpha_i} \tag{10-486}$$

When the overhead contains only a very small amount of heavy key, the second term in the equation may be neglected.

Intersection of operating lines at Equilibrium Curve:

$$x_{it} = \frac{\left[(\alpha_l - 1)(1+m)\left(\frac{x_{lF}}{x_{lF}+x_{hF}}\right) - \alpha_l - m \pm \sqrt{\left\{\left[(\alpha_l - 1)(1+m)\left(\frac{x_{lF}}{x_{lF}+x_{hF}}\right) - \alpha_l - m\right]^2 + 4m(\alpha_l - 1)(1+m)\left(\frac{x_{lF}}{x_{lF}+x_{hF}}\right)\right\}}\right]}{2m(\alpha_l - 1)} \tag{10-487}$$

The proper value for x_{it} is positive and between zero and one. Actually this is fairly straightforward and looks more difficult to handle than is actually the case.

Pseudo ratio of liquid to vapor in feed:

$$m = \frac{x_L - \sum x F_H}{x_v - \sum x F_L} = \frac{F_L - \sum F_H}{F_v - \sum F_L} \tag{10-488}$$

where

x_L = mol fraction of feed as liquid
x_v = mol fraction of feed as vapor
F_L = mols of liquid feed
F_v = mols of vapor feed
ΣF_H = total mols of components heavier than heavy key in feed
ΣF_L = total mol of components lighter than light key in feed.

Example 10-46: Scheibel-Montross Minimum Reflux [61]

A tower has the following all liquid feed composition:

Component	Feed Mols/hr	Overhead Mols/hr	Bottoms Mols/hr
A	30	30.	–
B (light key)	20	19.5	0.5
C (heavy key)	20	0.5	19.5
D	30	–	30.0
	100	50.0	50.0

Relative volatilities referenced to the heavy key, C:
$\alpha_A = 4.0$
$\alpha_B = 2.0 = \alpha_l$
$\alpha_C = 1.0 = \alpha_h$
$\alpha_D = 0.5$

$$\text{Calculate: } m = \frac{x_L - \sum x_{FH}}{x_v - \sum x_{FL}} = \frac{1.0 - 0.30}{0 - 0.30} = -2.33$$

Intersection of Operating Lines:

$$x_{it} = \frac{\left[(2-1)(1-2.33)\left(\frac{0.2}{0.2+0.2}\right) - 2 - (-2.33) \pm \sqrt{\left\{\left[(2-1)(1-2.33)\left(\frac{0.2}{0.2+0.2}\right) - 2 - (-2.33)\right]^2 + 4(-2.33)(2-1)(1-2.33)\left(\frac{0.2}{0.2+0.2}\right)\right\}}\right]}{2(-2.33)(2-1)}$$

$x_{it} = 0.610$, or -0.459 (not acceptable)

Pseudo minimum reflux ratio:

$$x_{lo} = \frac{19.5}{19.5 + 0.5} = 0.975$$

$$R' = \frac{0.975}{(2-1)(0.610)} - \frac{(1.0 - 0.975)(2)}{(1 - 0.610)(2-1)}$$

$R' = 1.472$

Minimum reflux ratio:

$$(L/D)_{min} = \frac{1}{0.2 + 0.3} \times \left[0.2(1.472) + (0.2 + 0.3)\left(\frac{0.3}{\frac{2}{0.5} - 1}\right) + \frac{0.3}{4}\left(1 + \frac{2}{4}\right)\right]$$

$(L/D)_{min} = 0.912$

10.39 Minimum Number of Trays: Total Reflux—Constant Volatility

The minimum theoretical trays at total reflux can be determined by the Fenske relation as previously given:

$$S_m = N_{min} + 1 = \frac{\log\left(\frac{x_{Dl}}{x_{Dh}}\right)\left(\frac{x_{Bh}}{x_{Bl}}\right)}{\log \alpha_{avg}} \qquad (10\text{-}489)$$

Note that N_{min} is the number of trays in the column and does not include the reboiler. When α varies considerably through out the column, the results will not be accurate using the α_{avg} as algebraic average, and the geometric mean is used in these cases.

$$\alpha_{avg} = [(\alpha_t)(\alpha_b)]^{1/2}$$

For extreme cases it may be necessary to calculate down from the top and up from the bottom until each section shows a fairly uniform temperature gradient between trays. Then the Fenske relation can be used for the remaining trays, using the conditions at the trays calculated as the terminal conditions instead of the actual overhead and bottoms.

10.39.1 Theoretical Number of Trays at Operating Reflux of a Multicomponent Mixture

The method of Gilliland [23] (Figure 10-49a or 10-93) is also used for multicomponent mixtures to determine theoretical trays at a particular operating reflux ratio, or at various ratios. The Brown and Martin [9] curve of Figure 10-98 is also used in approximate the same manner, and produces essentially the same results, but is based on internal vapor and liquid flows.

The values needed to use the graph include:

$$(L/V)_r = \frac{1}{1 + (D/L)} \qquad (10\text{-}490)$$

where $(D/L) = 1/\ (L/D)$

$$L_s = L_r + qF \qquad (10\text{-}491)$$

$L_r = (L/D)\ (D_r)$

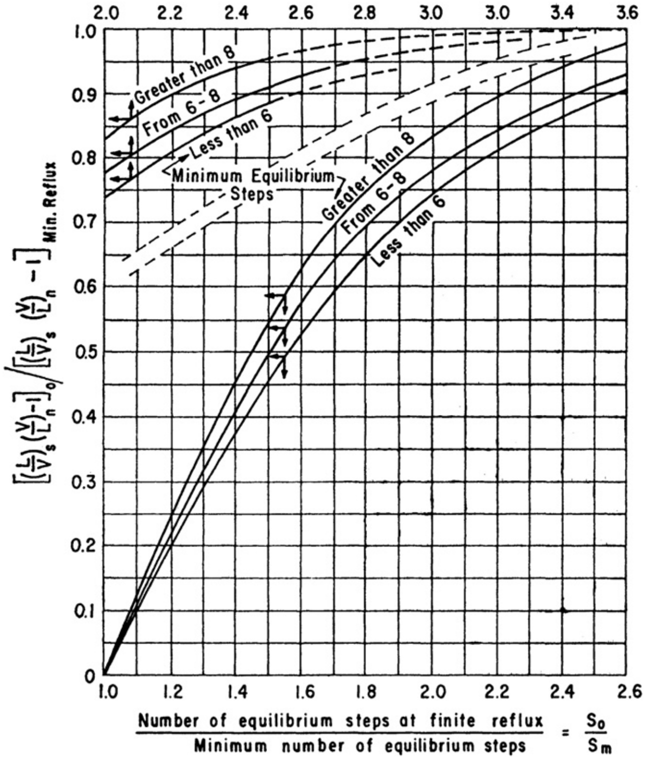


Figure 10-98 Brown and martin: operating reflux and stages correlated with minimum reflux and stages. Used and adapted by permission, Van Winkle, M., Oil and Gas Jour. V. 182, Mar. 23 (1953).

$$V_r = (L/D)D_r/(L/V) \tag{10-492}$$

$$V_s = V_r - F(1 - q) \tag{10-493}$$

Note that when $(L/D)_{min}$ is used as the starting basis, the L_r, L_s, V_r, V_s and their ratios will be for the minimum condition, and correspondingly so when the operating reflux is used.

The combined Fenske-Underwood-Gillilland (FUG) method developed by Frank [100] is shown in Figure 10-95. This relates product purity, actual reflux ratio, and relative volatility (average) for the column to the number of equilibrium stages required. This does not consider tray efficiency. It is perhaps more convenient to use in the design of new columns than for reworking existing columns, and should be used only on adjacent-key systems.

Eduljee [107] evaluated published data and corrected relationships for determining the number of actual trays versus actual reflux with reasonably good agreement:

First attempt:

when $1.1 < R/R_m \le 2.0$

$$(S/S_m)\ (R/R_m) = 2.82$$

when $R/R_m > 2.0$

$$(S/S_m)(R/R_m) = 0.7 + 1.06(R/R_m) \tag{10-494}$$

If the number of actual trays, S, calculates to be 27 or greater, then revert to the following for better accuracy:

Second attempt:

when $1.1 < R/R_m \le 2.0$

$$S = 2.71(R_m/R)(S_m) + 0.38 \tag{10-495}$$

when $R/R_m > 2.0$

$$S = [0.67(R_m/R) + 1.02](S_m) + 0.38 \tag{10-496}$$

where:

n = number of theoretical trays in the rectifying section
R = reflux ratio (O/D)
S = number theoretical trays in the column, including reboiler

Subscript

m = minimum

The feed plate location, for either rectifying or stripping sections:

For R/R_m from 1.2 to 3.6:

$$(n/n_m)(R/R_m) = 1.1 + 0.9\ (R/R_m) \tag{10-497}$$

Hengstebeck [224] presents a technique for locating the feed tray by plotting.

Example 10-47: Operating Reflux Ratio

The minimum reflux ratio $(L/D)_{min}$ has been determined to be 1.017. Using the Brown and Martin graph [9], evaluate the theoretical number of trays at an operating reflux of 1.5 times the minimum. The minimum number of stages was determined to be 22.1 including the reboiler. See Figure 10-98.

The column will have a total condenser. Product rate D is 0.664 mols/mol feed, and the feed is a boiling point liquid.

Minimum values:

$$\left(\frac{L}{V}\right)_{min} = \frac{1}{1 + (D/L)_{min}} = \frac{1}{1 + 1/1.017} = 0.506$$

$0.506V_r = 1.017\ (D_r) = 1.017\ (0.664)$
$V_r = 1.332$ mols per mol of feed
$L_r = 1.017\ (0.664) = 0.674$ mols/mol feed
$q = 1.0$
$L_s = (0.674) + (1)\ (1) = 1.674$ mols/mol feed
$V_s = 1.332 - (1)\ (1 - 1) = 1.332$ mols/mol feed

$$\left(\frac{L}{V}\right)_s = \frac{1.674}{1.332} = 1.255$$

Operating values:

Operating $(L/D)_o = (1.5)(1.017) = 1.525$

$$\left(\frac{L}{V}\right)_o = \frac{1}{1 + 1/1.525} = 0.603$$

$$V_r = \frac{(1.525)(0.664)}{0.603} = 1.68 \text{ mols/mol feed}$$

$L_r = (1.525)\ (0.664) = 1.013$ mols/mol feed

$q = 1.0$

$L_s = 1.013 + (1)\ (1) = 2.013$

$V_s = 1.68 - (1)\ (1 - 1) = 1.68$

$(L/V)_s = 2.013/1.68 = 1.198$

For graph:

$$\left[\left(\frac{L}{V}\right)_s\left(\frac{V}{L}\right)_r - 1\right]_o = 1.198\left(\frac{1}{0.603}\right) - 1 = 0.985$$

$$\left[\left(\frac{L}{V}\right)_s\left(\frac{V}{L}\right)_r - 1\right]_{min} = (1.255)\left(\frac{1}{0.506}\right) - 1 = 1.48$$

Read curve for "greater than 8" minimum equilibrium steps:

at 0.985/1,48 = 0.666

Curve reads: $S_o/S_M = 1.64$

Theoretical stages at reflux $(L/D) = 1.525$

$S_o = S_M\ (1.64) = 22.1\ (1.64)$

$S_o = 36.2$ stages

Theoretical trays at the operating reflux $(L/D) = 1.525$

$N_o = 36.2 - 1$ (for reboiler) $= 35.2$ trays in column

10.39.2 Actual Number of Trays

From the theoretical trays at operating reflux the actual trays for installation are determined:

$$N_{act} = N_o/E_o \tag{10-498}$$

The reboiler is considered 100% efficient, and likewise any partial condenser, if used. Therefore the value N_o represents the theoretical trays or stages in the column proper, excluding the reboiler and partial condenser. E_o represents the overall tray efficiency for the system based upon actual test data of the same or similar systems, or from the plot of Figure 10-54, giving operating information preference (if reliable).

10.39.3 Estimation of Multicomponent Recoveries

Yaws et al. [141] present a useful technique for estimating overhead and bottoms recoveries with a very good comparison with tray-to-tray computer calculations. The procedure suggested uses an example from the reference (with permission):

1. Plot relative volatility (α_i) and % desired recovery for LK and HK. Draw a straight line through these two points. The non-key component points will also be on this straight line.
2. Using α_i and the component distribution line, estimate % recovery of non-key components in distillate and bottoms.

From the references [124, 141]:

$$\log\ (d_i/b_i) = a + b \log \alpha_i \tag{10-499}$$

where

d_i = mols of component i in distillate

b_i = moles of component i in bottoms

α_i = relative volatility of component i

a, b = correlation constants

$\log\ (d_i/b_i)$ vs. $\log \alpha_i$ gives a straight line (Figure 10-99).

By superimposing a Y_{iD} scale over the d_i/b_i scale, $d_i/b_i = Y_{iD}/Y_{iB}$

where

Y_{iD} = % recovery of i in distillate

Y_{iB} = % recovery of i in bottoms

f_i = total mols of component i in distillate and bottoms

Then

$$Y_{iB} = 100 - Y_{iD} \tag{10-500}$$

$$\text{and}\ \ d_i/b_i = Y_{iD}(100 - Y_{iD}) \tag{10-501}$$

From Equation 10-501, Table 10-32 is constructed for selected values of d_i/b_i at various values of Y_{iD} from 99.9% to 0.1%.

10.39.4 Component Recovery Nomograph (Figure 10-99)

A nomograph is constructed by plotting d_i/b_i vs. α_i on log-log graph paper and then superimposing a Y_{iD} scale over the d_i/b_i scale, according to the values given in Table 10-33. The resulting nomograph, relating component recovered and component relative volatility, is given in Figure 10-100. This may be used to estimate component recovery in distillate and bottoms, as follows.

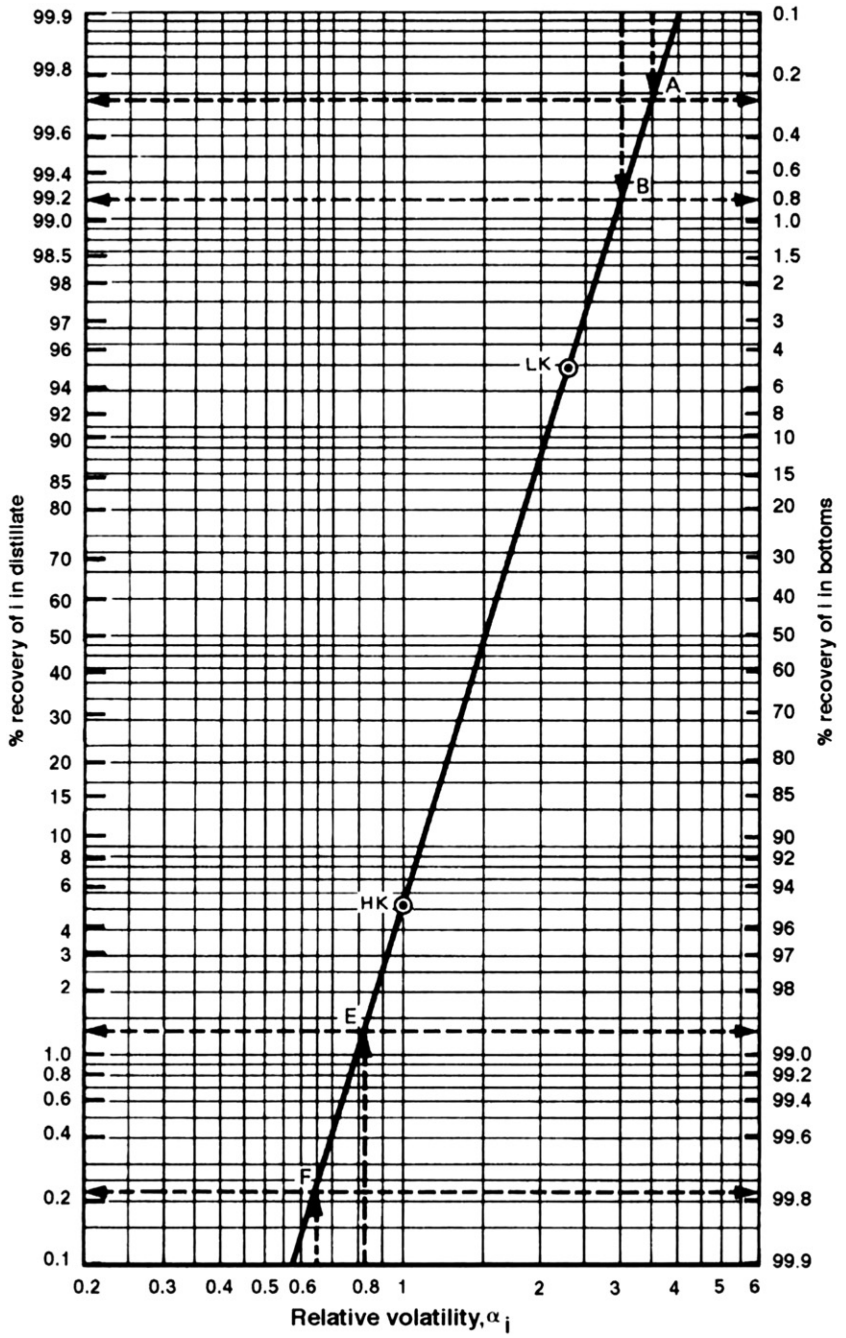


Figure 10-99 Estimation of recovery of non-key components using short-cut method of Yaws, et. al., Chem. Eng. Jan. 29, p. 101, (1979).

Example 10-48: Estimated Multicomponent Recoveries by Yaws' Method [141] (used with permission)

Component C is to be separated from Component D by distillation. A 95% recovery of both key components (LK, HK) is desired. Saturated-liquid feed composition and relative volatilities (at average column conditions) are given in Table 10-37.

Using the graphical short-cut method for component distribution, estimate the recovery of non-key components in distillate and bottoms.

Solution

1. α_i and % desired recovery are plotted for LK and HK ($\alpha_c = 2.3$, 95% recovery of C in distillate and $\alpha_D = 1$, 95% recovery of D in bottoms), as shown in

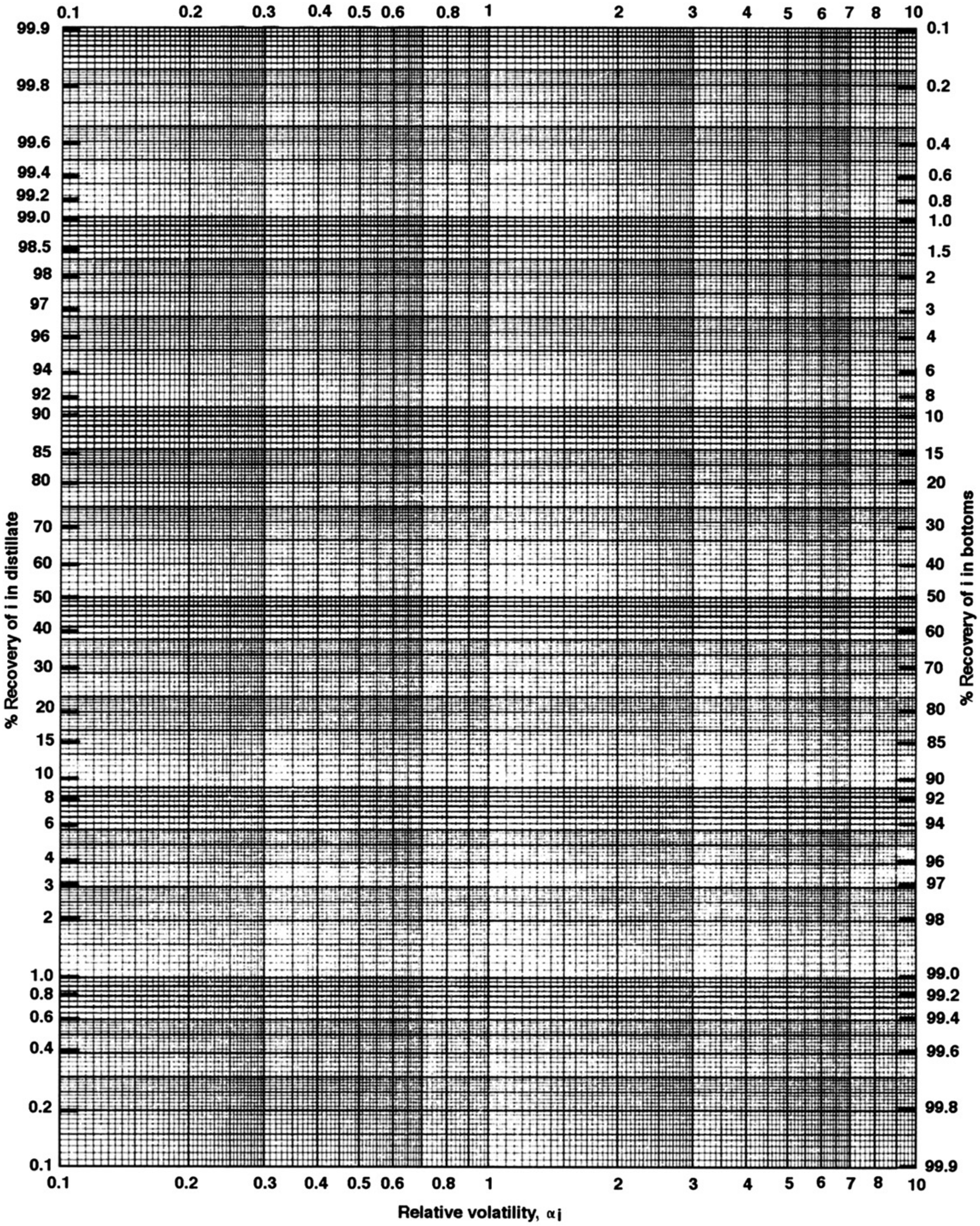


Figure 10-100 Working chart of Yaws, et. al. short-cut method for multicomponent distillation for estimating component recovery in distillate and bottoms. Used by permission, Yaws et al., Chem. Eng. Jan. 29, p. 101, (1979).

Figure 10-99. See Figure 10-100 for working chart. A straight line is then drawn through the two points.

2. Using $\alpha_A = 3.5$, $\alpha_B = 3.0$, $\alpha_E = 0.83$, $\alpha_F = 0.65$, and the component distribution line, the recovery of non-key components is estimated. The results are shown in Table 10-38.

Table 10-39 [141] illustrates the good agreement between the proposed method with the tray-to-tray calculations for Case I-High Recovery: 95% LK recovery in distillate, 94% HK in bottoms; Case II, Intermediate Recovery: 90% LK recovery in distillate, 85% HK recovery in bottoms; and Case III Low Recovery: 85% LK recovery in distillate, 81 % HK recovery in bottoms.

Table 10-37 Material Balance for Estimated Multicomponent Distillation Recoveries for Example 10-48 Using Method of Yaws, Fang, and Patel

Feed component	Composition, mol. fr.	Relative volatility	Keys
A	0.05	3.5	
B	0.20	3.0	
C	0.30	2.3	Light
D	0.25	1.0	Heavy
E	0.15	0.83	
F	0.05	0.65	
Distillate component	**Recovery desired, %**	**Recovery derived, %**	
A		99.72**	
B		99.20**	
C	95	-	
D	5	-	
E		1.30**	
F		0.22*	
Bottoms component	**Recovery desired, %**	**Recovery derived, %**	
A		0.28**	
B		0.80**	
C	5	-	
D	95	-	
E		98.70**	
F		99.78**	

Used by permission, Yaws, C. L., et al., Chem. Eng., Jan. 29 (1979), p. 101, All rights reserved.

* See calculations.

** From Figure 10-99.

Example 10-49: Estimated Multicomponent Recoveries by Yaws' Method [141]

Table 10-40 [141] shows case 1 (High recovery of 11 components), 94.70 % LK recovery and 95.52% HK recovery and case 2 (Low recovery of 13 components), 73.51 % LK recovery and 63.43% HK recovery. Using the short-cut method for component distribution, estimate the recovery of non-key components in distillate and bottoms.

Solution

Program PROG 104 is used to determine the recovery of non-key components in distillate and bottoms, using the thermal feed condition of saturated liquid, $q = 1$. The program (as illustrated earlier) determines the Underwood constant, the minimum reflux ratio, minimum number of stages, actual reflux ratio, the number of theoretical plates and the position of the feed plate. Tables 10-41 and 10-42 show the results of the program. Comparison of these results with plate-to-plate calculations is shown in Table 10-43. There is good agreement between them in both cases. Further, Microsoft Excel spreadsheet Example 10-49.xls is used to determine the number of theoretical stages using the Erbar-Maddox correlation and the Rusche Equation 10-452.

Table 10-38 Table of Y_{iD} Values for Solving Yaws, Fang, and Patel, Short cut Recoveries Estimate.

Y_{iD}	d_i/b_i	Y_{iD}	d_i/b_i	Y_{iD}	d_i/b_i	Y_{iD}	d_i/b_i
99.9	999	96	24.0	40	0.6670	2	0.02040
99.8	499	94	15.7	30	0.4290	1.0	0.01010
99.6	249	92	11.5	20	0.2500	0.8	0.00806
99.4	166	90	9.00	15	0.1760	0.6	0.00604
99.2	124	85	5.67	10	0.1110	0.4	0.00402
99.0	99.0	80	4.00	8	0.0870	0.2	0.00200
98.5	65.7	70	2.33	6	0.0638	0.1	0.00100
98.0	49.0	60	1.50	4	0.0417		
97.0	32.3	50	1.00	3	0.0309		

Used by permission, Chem. Eng., Yaws, C. L., et al Jan. 29 (1979), p. 101. All rights reserved.

Table 10-39 Comparison of Yaws, et al. Short Cut Nomograph Results vs. Plate-to-Plate Calculations

				Composition x_i	
	Component	**Nomograph**	**Plate to plate**	**Distillate nomograph**	**Bottoms plate to plate**
Case I High recovery (16 trays)	A	0.0901	0.0901	0.0002	0.0002
	B	0.3588	0.3591	0.0026	0.0023
	C (LK)	0.5197	0.5190	0.0269	0.0278
	D (HK)	0.0271	0.0271	0.5271	0.5271
	E	0.0041	0.0045	0.3314	0.3308
	F	0.0002	0.0002	0.1118	0.1118
Case II Intermediate recovery (13 trays)	A	0.0879	0.0880	0.0016	0.0012
	B	0.3466	0.3464	0.0128	0.0120
	C (LK)	0.4814	0.4770	0.0683	0.0726
	D (HK)	0.0668	0.0682	0.4839	0.4835
	E	0.0155	0.0187	0.3218	0.3187
	F	0.0018	0.0018	0.1116	0.1120
Case III Low recovery (9 trays)	A	0.0866	0.0872	0.0034	0.0028
	B	0.3376	0.3395	0.0250	0.0227
	C (LK)	0.4561	0.4552	0.1015	0.1027
	D (HK)	0.0844	0.0839	0.4606	0.4610
	E	0.0308	0.0295	0.3016	0.3031
	F	0.0045	0.0046	0.1079	0.1077

Used by permission, Chem. Eng., Yaws, C. L., et al Jan. 29 (1979), p. 101, all rights reserved.

10.39.5 Shortcut Methods: Reflux and Stages

The shortcut methods allow determination of the number of theoretical plates as a function of reflux ratio, minimum number of plates and minimum reflux. They are used to study the effect of reflux ratio on investment and operating costs with minimum computational effort. These methods are also useful for comparing other variables related to reflux ratio and number of stages. The Underwood [72] and Colburn [12] minimum reflux methods are used for more accurate calculation of minimum reflux, while the Brown-Martin [312] method is a suitable approximation. The Underwood [73] or Fenske methods are useful for estimating minimum number of stages, and the Brown-Martin [312] and Gilliland [23] correlations relate minimum reflux, minimum number of plates, operating reflux and number of theoretical plates.

The minimum number of stages at total reflux as given by Fenske's equation is:

$$N_m = \frac{\log\left[\left(\frac{x_{LK}}{x_{HK}}\right)_D \left(\frac{x_{HK}}{x_{LK}}\right)_B\right]}{\log\left(\alpha_{LK}/\alpha_{HK}\right)} \tag{10-182}$$

The Fenske's equation has been shown to be rigorous if

$$(\alpha_{LK/HK})_{avg} = \sqrt[N]{\alpha_{LK/HK,1}\ \alpha_{LK/HK,2}\cdots\cdots\cdots\alpha_{LK/HK,N}} \tag{10-502}$$

where $(\alpha_{LK/HK})_{avg}$ is usually obtained from one of the following approximations:

1. Evaluate $\left(\alpha_{LK/HK}\right)_{avg}$ at $T_{avg} = \left(T_{top} + T_{bot}\right)/2$ (10-502a)
2. $\left(\alpha_{LK/HK}\right)_{avg} = \left(\alpha_{top} + \alpha_{bot}\right)/2$ (10-502b)
3. $\left(\alpha_{LK/HK}\right)_{avg} = \alpha$ at feed tray temperature. (10-502c)
4. $\left(\alpha_{LK/HK}\right)_{avg} = \sqrt{\alpha_{top}\ \alpha_{bot}}$ (10-502d)
5. $\left(\alpha_{LK/HK}\right)_{avg} = \sqrt[3]{\alpha_{top}\ \alpha_{mid}\ \alpha_{bot}}$ (10-502e)

Table 10-40 ■

Component	f_i	α_i
Case 1. 11 components 94.70 % LK recovery and 95.52 % HK recovery.		
M	0.06	2.5
N	0.03	2.3
O	0.05	2.1
P	0.09	1.75
Q	0.13	1.60
R (LK)	0.15	1.45
S (HK)	0.14	1.00
T	0.11	0.90
U	0.10	0.83
V	0.08	0.75
W	0.06	0.70
Case 2. Low recovery (13 components) 73.51 % LK recovery and 63.43 % HK recovery.		
K	0.01	1.6
L	0.05	1.4
M	0.02	1.3
N	0.12	1.2
O	0.05	1.14
P	0.09	1.12
Q (LK)	0.16	1.10
R (HK)	0.17	1.00
S	0.04	0.98
T	0.11	0.94
U	0.09	0.90
V	0.06	0.80
W	0.03	0.65

Listed below is the preferred $(\alpha_{LK/HK})_{avg}$ by investigators, which is based upon the above conditions in Equations 10-502a–e.

Method	Recommendation
1	Maddox [112, 266]
2	Van Winkle [74]
3 or 4	King [319]
4	Thompson et al. [320], Treybal [321], Wankat [273], Ludwig [271]
4 or 5	Fair [322], Seader and Kurtyka [323], McCormick and Roche [324]

Douglas [325] proposed a criterion for testing the relative volatility approximation as:

$$\frac{\alpha_{top} - \alpha_{bot}}{\alpha_{top} + \alpha_{bot}} \le 0.1 \ln\left(\frac{\alpha_{top} + \alpha_{bot}}{2}\right) \qquad (10\text{-}503)$$

When the above inequality is obeyed, the relative volatility is reasonably constant throughout the column, and the simpler approximations such as 2 or 4 are suitable. The Fenske's equation applies to any pair of components and not necessarily to the light key and heavy key.

10.40 Smith–Brinkley (SB) Method [326]

Smith and Brinkley [326] developed a method for estimating the distribution of components in multicomponent separation processes. The method is based on an analytical solution of the finite-difference equations that can be written for multistage separation processes when stages and interstage flow rates are known. The Fenske-Underwood-Gilliland (FUG) method combines Fenske's total-reflux equation and Underwood's minimum reflux equation with a graphical correlation by Gilliland. The latter relates actual column performance to total and minimum reflux conditions for a specified separation between two key components. The method can be used for extraction and absorption processes as well as distillation. The SB and FUG methods are rating and design methods respectively, and both work best when mixtures are nearly ideal. Only the equations for distillation are presented here, as the derivation of the equations is given by Smith and Brinkley [326] and Smith [65]. For any component i (suffix i omitted in the equation for clarity).

$$\frac{b}{f} = \frac{(1 - S_r^{N_r - N_s}) + R(1 - S_r)}{(1 - S_r^{N_r - N_s}) + R(1 - S_r) + G S_r^{N_r - N_s}(1 - S_s^{N_s + 1})} \qquad (10\text{-}504)$$

where

b/f = the fractional split of the component between the feed and the bottoms.
N_r = number of equilibrium stages above the feed.
N_s = number of equilibrium stages below the feed.
S_r = stripping factor, rectifying section $= K_i V/L$.
S_s = stripping factor, stripping section $= K_i' V'/L'$.
V and L = total molar vapor and liquid flow rates, and the superscript′ denotes the stripping section
G depends on the condition of the feed.

If the feed is mainly liquid:

$$G_i = \frac{K_i'}{K_i}\frac{L}{L'}\left[\frac{1 - S_r}{1 - S_s}\right]_i \qquad (10\text{-}505)$$

and the feed stage is added to the stripping section.

Table 10-41 Input Data and Computer Results for Multicomponent Fractionation

Data Name: Data104.Dat

```
REL
 11
 0.06    2.50
 0.03    2.30
 0.05    2.10
 0.09    1.75
 0.13    1.60
 0.15    1.45
 0.14    1.0
 0.11    0.9
 0.10    0.83
 0.08    0.75
 0.06    0.7
 0.9470  0.9552
 71      1.15
```

Multicomponent System Fractionation

Component Number	Feed Moles	Rel Volatility Alpha	Distilattle %	Moles	Bottoms %	Moles
1	0.0600	2.5000	99.9991	0.0600	0.0009	0.0000
2	0.0300	2.3000	99.9965	0.0300	0.0035	0.0000
3	0.0500	2.1000	99.9850	0.0500	0.0150	0.0000
4	0.0900	1.7500	99.7243	0.0898	0.2757	0.0002
5	0.1300	1.6000	98.8541	0.1285	1.1459	0.0015
6	0.1500	1.4500	94.7000	0.1421	5.3000	0.0079
7	0.1400	1.0000	4.4800	0.0063	95.5200	0.1337
8	0.1100	0.9000	0.8622	0.0009	99.1378	0.1091
9	0.1000	0.8300	0.2376	0.0002	99.7624	0.0998
10	0.0800	0.7500	0.0471	0.0000	99.9529	0.0800
11	0.0600	0.7000	0.0156	0.0000	99.9844	0.0600

Component Number	Feed Moles	Mol Fract. XF	Distilattle Moles	Mol Fract. XD	Bottoms Moles	Mol. XB
1	0.0600	0.0600	0.0600	0.1182	0.0000	0.0000
2	0.0300	0.0300	0.0300	0.0591	0.0000	0.0000
3	0.0500	0.0500	0.0500	0.0984	0.0000	0.0000
4	0.0900	0.0900	0.0898	0.1767	0.0002	0.0005
5	0.1300	0.1300	0.1285	0.2531	0.0015	0.0030
6	0.1500	0.1500	0.1421	0.2797	0.0079	0.0162
7	0.1400	0.1400	0.0063	0.0124	0.1337	0.2717
8	0.1100	0.1100	0.0009	0.0019	0.1091	0.2216
9	0.1000	0.1000	0.0002	0.0005	0.0998	0.2027
10	0.0800	0.0800	0.0000	0.0001	0.0800	0.1625
11	0.0600	0.0600	0.0000	0.0000	0.0600	0.1219

```
The feed condition, Q:                               1.0
The heavy key compnent number is:                    7
Percentage recovery of the light key component
In the distillate is (%):                           94.70
Percentage recovery of the heavy key component
In the bottoms is (%):                              95.52
Total moles in the distillate:                       0.5078
Total moles in the bottoms:                          0.4922
Total moles in the feed:                             1.0000
Underwood constant:                                  1.1577
Factor for the reflux ratio:                         1.1500
Minimum reflux ratio:                                2.2977
Actual reflux ratio:                                 2.6424
Minimum number of stages is:                        16.0
Number of theoretical plates in the column:         36.2
The position of the feed plate is:                  18.9
```

Table 10-42 Input Data and Computer Results for Multicomponent Fractionation

```
Data name: Data104.Dat
REL
13
0.01                    1.6
0.05                    1.4
0.02                    1.3
0.12                    1.2
0.05                    1.14
0.09                    1.12
0.16                    1.10
0.17                    1.0
0.04                    0.98
0.11                    0.94
0.09                    0.90
0.06                    0.80
0.3                     0.65
0.7351                  0.6443
81                      1.5
```

Multicomponent System Fractionation

Component Number	Feed Moles	Rel Volatility Alpha	Distilattle %	Moles	Bottoms %	Moles
1	0.0100	1.6000	99.9370	0.0100	0.0630	0.0000
2	0.0500	1.4000	99.3979	0.0497	0.6021	0.0003
3	0.0200	1.3000	97.9181	0.0196	2.0819	0.0004
4	0.1200	1.2000	92.3776	0.1109	7.6224	0.0091
5	0.0500	1.1400	83.5591	0.0418	16.4409	0.0082
6	0.0900	1.1200	79.0165	0.0711	20.9835	0.0189
7	0.1600	1.1000	73.5100	0.1176	26.4900	0.0424
8	0.1700	1.0000	35.5700	0.0605	64.4300	0.1095
9	0.0400	0.9800	28.1639	0.0113	71.8361	0.0287
10	0.1100	0.9400	16.2144	0.0178	83.7856	0.0922
11	0.0900	0.9000	8.4782	0.0076	91.5218	0.0284
12	0.0600	0.8000	1.2437	0.0007	98.7563	0.0593
13	0.0300	0.6500	0.0373	0.0000	99.9627	0.0300

Component Number	Feed Moles	Mol Fract. XF	Distilattle Moles	Mol Fract. XD	Bottoms Moles	Mol. XB
1	0.0100	0.0100	0.0100	0.0193	0.0000	0.0000
2	0.0500	0.0500	0.0497	0.0958	0.0003	0.0006
3	0.0200	0.0200	0.0196	0.0378	0.0004	0.0009
4	0.1200	0.1200	0.1109	0.2138	0.0091	0.0190
5	0.0500	0.0500	0.0418	0.0806	0.0082	0.0171
6	0.0900	0.0900	0.0711	0.1371	0.0189	0.0392
7	0.1600	0.1600	0.1176	0.2268	0.0424	0.0880
8	0.1700	0.1700	0.0605	0.1166	0.1095	0.2275
9	0.0400	0.0400	0.0113	0.0217	0.0287	0.0597
10	0.1100	0.1100	0.0178	0.0344	0.0922	0.1914
11	0.0900	0.0900	0.0076	0.0147	0.0284	0.1711
12	0.0600	0.0600	0.0007	0.0014	0.0593	0.1231
13	0.0300	0.0300	0.0000	0.0000	0.0300	0.0623

The feed condition, Q:	1.0
The heavy key component number is :	8
Percentage recovery of the light key component In the distillate is (%)	73.51
Percentage recovery of the light key component In the bottoms is (%)	64.43
Total moles in the distillate:	0.5186
Total moles in the bottoms:	0.4814
Total moles in the feed:	1.0000
Underwood constant:	1.0438
Factor for the reflux ratio:	1.1500
Minimum reflux ratio:	5.2769
Actual reflux ratio:	6.0684
Minimum number of stages is:	16.9
Number of theoretical plates in the colum:	36.8
The position of the feed plate is:	17.3

Table 10-43 Short-cut versus plate – to – plate calculations.

			% recovery in dist. $100d_i/f_i$		% recovery in btms. $100b_i/f_i$		
Component	f_i	α_i	**Short-cut**	**Plate-to-Plate**	**Short-cut**	**Plate-to-plate**	**Absolute deviation $\lvert\Delta\rvert$, %**
Case 1. High recovery (11 components) 94.70 % LK recovery and 95.52% HK recovery.							
M	0.06	2.5	99.9991	99.999	0.0009	0.001	0.0001
N	0.03	2.3	99.9965	99.996	0.0035	0.004	0.0005
O	0.05	2.1	99.9850	99.986	0.0150	0.014	0.0010
P	0.09	1.75	99.7243	98.698	0.2757	0.302	0.0263
Q	0.13	1.6	98.8541	98.826	1.1459	1.174	0.0281
R (LK)	0.15	1.45	94.7	94.722	5.3000	5.278	0.0220
S (HK)	0.14	1.0	4.48	4.501	95.520	95.499	0.0210
T	0.11	0.9	0.8622	0.83	99.1378	99.170	0.0322
U	0.10	0.83	0.2376	0.221	99.7624	99.779	0.0166
V	0.08	0.75	0.0471	0.042	99.9529	99.958	0.0051
W	0.06	0.7	0.0156	0.013	99.9844	99.987	0.0026
							Avg. 0.0141 %
Case 2. (13 components) 73.51 % LK recovery and 64.43 % HK recovery.							
K	0.01	1.6	99.9253	99.911	0.0747	0.089	0.0143
L	0.05	1.4	99.3285	99.274	0.6715	0.726	0.0545
M	0.02	1.3	97.7574	97.745	2.2426	2.255	0.0124
N	0.12	1.2	92.0941	92.264	7.9059	7.736	0.1699
O	0.05	1.14	83.3346	83.677	16.6654	16.323	0.3424
P	0.09	1.12	78.8802	79.228	21.1198	20.772	0.3478
Q (LK)	0.16	1.10	73.5100	73.896	26.4900	26.104	0.3860
R (HK)	0.17	1.00	36.5700	36.264	63.4300	63.736	0.3060
S	0.04	0.98	29.2394	28.827	70.7606	71.173	0.4124
T	0.11	0.94	17.2097	16.818	82.7903	83.182	0.3917
U	0.09	0.90	9.2141	9.031	90.7859	90.969	0.1831
V	0.06	0.80	1.4349	1.491	98.5651	98.509	0.0561
W	0.03	0.65	0.0474	0.064	99.9526	99.936	0.0166
							Avg. 0.207 %

Note: Case 1: $N = 31$, $N_f = 17$, $D = 50.8$, $R = 3.05$

Case 2: $N = 28$, $N_f = 15$, $D = 52.2$, $R = 8.5$

(Source: Yaws, C. L., et al., Chem. Eng., p 101, Jan. 299, 1979).

If the feed is mainly vapor:

$$G_i = \frac{L}{L'}\left[\frac{1-S_r}{1-S_s}\right]_i \tag{10-506}$$

K_i and K'_i are determined at the effective top and bottom section temperatures. If the temperature profile is available (e.g. from a computer simulation), the effective temperature is the arithmetic average of all tray temperatures in the column section. Alternatively, an arithmetic average of the feed-stage and end-stage temperatures is also used.

$$t_r = \frac{t_{top} + t_{above\ feed}}{2} \tag{10-507}$$

$$t_s = \frac{t_{below\ feed} + t_{bot}}{2} \tag{10-508}$$

Application

The Smith-Brinkley method rates a column using the reverse sequence of steps. It takes the number of stages, reflux ratio and actual feed location, and determines the product compositions. Once a base case is given, small changes in variables can readily be made. For example, for a change in feed temperature, half the change is added to t_r and the other half to t_s. For a change in reflux rate, the extra liquid is added to S_s and S_r. If the changes are large, some trial-and-error calculation is required, in which t_s and t_r are varied. This is similar to an operator who adjusts the control temperature by trial and error until the desired end products are achieved. These features make the Smith-Brinkley method valuable for on-line optimization (e.g. using computer or microprocessor control).

Equation 10-505 is for a column with a total condenser. If a partial condenser is used, the number of stages in the rectifying section should be increased by one. The procedure for using the Smith-Brinkley method is as follows [327]:

1. Estimate the flow rates, L, V and L', V' from the specified component separations and reflux ratio.
2. Estimate the top and bottom temperatures by calculating the dew and bubble points for assumed top and bottom compositions.
3. Estimate the feed point temperature.
4. Estimate the average component K values in the stripping and rectifying sections.
5. Calculate the values of $S_{r,i}$ for the rectifying section and $S_{s,i}$ for the stripping section.
6. Calculate the fractional split of each component, and hence the top and bottom compositions.
7. Compare the calculated with the assumed values and check the overall column material balance.
8. Repeat the calculation until a satisfactory material balance is obtained. The usual procedure is to adjust the feed temperature up and down till a satisfactory balance is obtained.

The SB is a rating method, which is suitable for determining the performance of an existing column rather than a design method, as the number of stages must be known. It can be used for design if estimation of the number of stages is first accomplished by some other method. Equation 10-504 is then used to determine the top and bottom compositions. The estimated stages can thus be adjusted and the computations repeated until the required specifications are achieved. The Gedde-Hengstebeck method (as illustrated earlier) is easier to use and gives satisfactory results for preliminary design in estimating the component splits. Examples of the application of the Smith-Brinkley method are given by Smith [65].

Commercial process simulators have a wide range of distillation models with varying degree of sophistication. It is essential that the model is chosen for the problem type, the degree of information available and the level of detail required in the solution. The simplest distillation models are shortcut models, which use the Fenske-Underwood-Gilliland (FUG) or Winn-Underwood-Gilliland (WUG) method to determine the minimum reflux and the number of stages. Alternatively they determine the required reflux given a number of stages or the required number of stages for a given reflux ratio. The shortcut methods can also estimate the condenser and reboiler duties and determine the optimum feed stage. The minimum information required to specify a shortcut distillation model is:

- The component recoveries of the light and heavy key components.
- The condenser and reboiler pressures.
- Whether the column has a total or partial condenser.

There are instances where the designers can specify the purities of the light and heavy key components in the distillate and bottoms respectively. However, care must be taken when using purity as a specification, as it is easy to specify infeasible purities or combinations of purities.

The easiest way to use a shortcut distillation model is to start by estimating the minimum reflux ratio and number of stages. The optimum reflux ratio is usually between 1.05–1.25 times the minimum reflux ratio, however, $R = 1.15\ R_{min}$ is often used as initial estimate. Once the reflux ratio is specified, the number of stages and optimum feed stage can be determined. The shortcut model results can start as a basis for a rigorous distillation simulation. Shortcut models can be used to initialize fractionation columns with multiple products, as they are versatile and are solved rapidly. They do not give an accurate prediction of the distribution of non-key components and they do not perform well when there is significant liquid-phase non-ideality. The main disadvantage of shortcut models is that they assume constant relative volatility, which is usually calculated at the feed condition. Such models should not be used, if there is significant liquid or vapor phase nonideality, as this assumption does not hold at all well.

10.41 Retrofit design of distillation columns

Since distillation is an energy-intensive process requiring considerable capital investment, retrofit of distillation columns is often carried out in preference to installation of new equipment. Retrofits aim to reuse the existing equipment more effectively in order to increase profit and to reduce cost, for example, by increasing a unit's capacity. When such a revamp is carried out, it is important to make effective utilization of the existing equipment. If the capacity of a systems having two existing columns needs to be increased, then instead of replacing the existing columns with new ones, a third column might be added to the existing columns and the new system reconfigured. In carrying out a retrofit study, retrofit models are employed to fix the existing distillation design, as they are quicker to solve and more robust for optimization, especially when all design variables are being considered simultaneously. They can also be combined with detailed heat-integration models for improving the energy efficiency of distillation systems. Heat integration of distillation columns is reviewed later in the book.

Gadalla et al. [328] presented retrofit shortcut models for the design of reboiled and steam stripped distillation columns. These models are particularly valuable for evaluating retrofit design options, and for improving the performance of existing distillation systems. The models are based upon a modified Underwood method, the Gilliland correlation, the Kirkbride equation, the Fenske equation and the material balances. The models fix both column configurations and operating conditions such as the steam flow rates, and then calculate the product flow rates, temperatures and compositions, and the various heat duties.

These models account for the changes in relative volatility and molar overflow through the column, overcoming the underlying limitations of the previous shortcut models. The models are reliable for very complex configurations, including a – large number of components those having such as crude oil distillation. The models also apply to other distillation applications, such as naphtha fractionation and petrochemical separation. The retrofit models are suited for simple distillation columns, sequences of simple distillation columns, and complex distillation configurations including columns with side-strippers and side-rectifiers. They provide a basis for optimizing and improving operating conditions of existing columns for energy related, economic and environmental benefits. They can be applied to estimate the additional heating and cooling requirements for increased throughput to an existing distillation process. Detailed presentation of these methods is given by Gadalla [329] and Gadalla et al. [328].

Example 10-50 Shortcut method using Honeywell UniSim® simulation software

Estimate the number of ideal stages needed in the butane-pentane splitter defined by the compositions given in the table. The column will operate at a pressure of 120 psia (830 kPa), with a reflux ratio of 2.5. The feed is at its boiling point (q = 1).

Component	x_F	Feed (f_i)
Propane, C_3	0.05	5
Isobutane, iC_4	0.15	15
Normal butane, nC_4	0.25	25
Isopentane, iC_5	0.20	20
Normal pentane, nC_5	0.35	35

For a specification of not more than 1 mol of the light key in the bottoms product, and not more than 1 mol of the heavy key in the distillate product. Use the Peng-Robinson VLE package.

Solution

The Honeywell UniSim® simulation (Example 10-50) package is used to separate n-butane and i-pentane from the components in the feed entering at its boiling point condition and at 120 psia. The shortcut model in UniSim requires less data than the rigorous model; only five input parameters are required to solve the problem. These are:

1. Two key components: The light key (LK) in the bottoms and the heavy key (HK) in the distillate. The light key is defined as the most volatile component (eg. n-butane) to appear at the bottom of the column and the heavy key is defined as the least volatile component (e.g. i-pentane) to appear at the top of the column. The concentrations of the light and heavy key components must be specified.

NB: Setting these values too low will result in a large (tall) column with a high reflux, while choosing high values may result in poor product quality and a weak separation.

2. Two pressure specifications: The reboiler and condenser pressures should be specified, as the estimates of condenser and reboiler pressures have a direct relationship on the temperatures that UniSim will estimate in these locations. The reboiler pressure should be greater than the condenser pressure.

NB: Until the user is satisfied with making estimates about these values an initial guess of the pressures is required, and subsequent checks that the temperature estimates are reasonable need to be caried out.

The reflux ratio R: The actual reflux ratio should be specified.

Additionally, a fully defined feed stream is required to be setup. Once all the required data are entered, UniSim® simulation software will calculate the remaining column parameters, which can be found on the **Performance tab**. The user should then check the temperature estimates on this page and if necessary adjust the reboiler and condenser pressures.

The following screen shots from UniSim® software illustrate the procedure of carrying out this simulation process.

Step 1. Double click on UniSim icon to display the simulation window as shown in Figure 10-101.

Step 2. Open the file as a new case as in Figure 10-102 named simulation Basis Manager. Click on the Add button to select the components.

Step 3. Click on the Add Pure button to select the components as highlighted in Figure 10-103. Close the window.

Step 4. The Simulation Basis Manager window appears as shown in Figure 10-104. Click on Fluid Pkgs tab as shown in Figure 10-104.Then click on the **Add** button.

Step 5. Choose the required property package from the **Property Package Selection** menu. For this example, choose **Peng Robinson** as shown in Figure 10-105. Select **EOSs** from **Property Package Filter** and close the window.

Step 6. Close the window and return to the Simulation Basis Manager window as shown in Figure 10-106. Click on **Enter Simulation Environment** button as shown in Figure 10-106.

Step. 7. Here, the Process Flow Diagram (PFD) window appears, then from the palette, double click on the **blue** arrow and place it on the PFD window. Next, select the shortcut distillation icon in the palette by double clicking on it and place this on the PFD window as shown in Figure 10-107. This is named **T-100**. Double clicking on the arrow -1 gives the worksheet window.

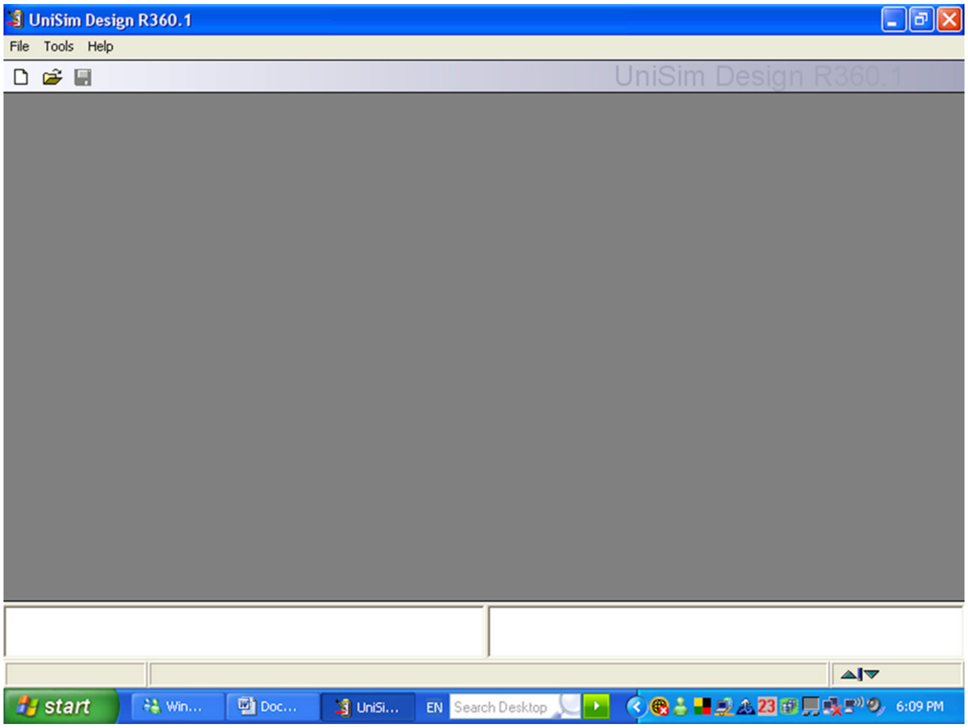


Figure 10-101 Snap shot of UniSim design window.

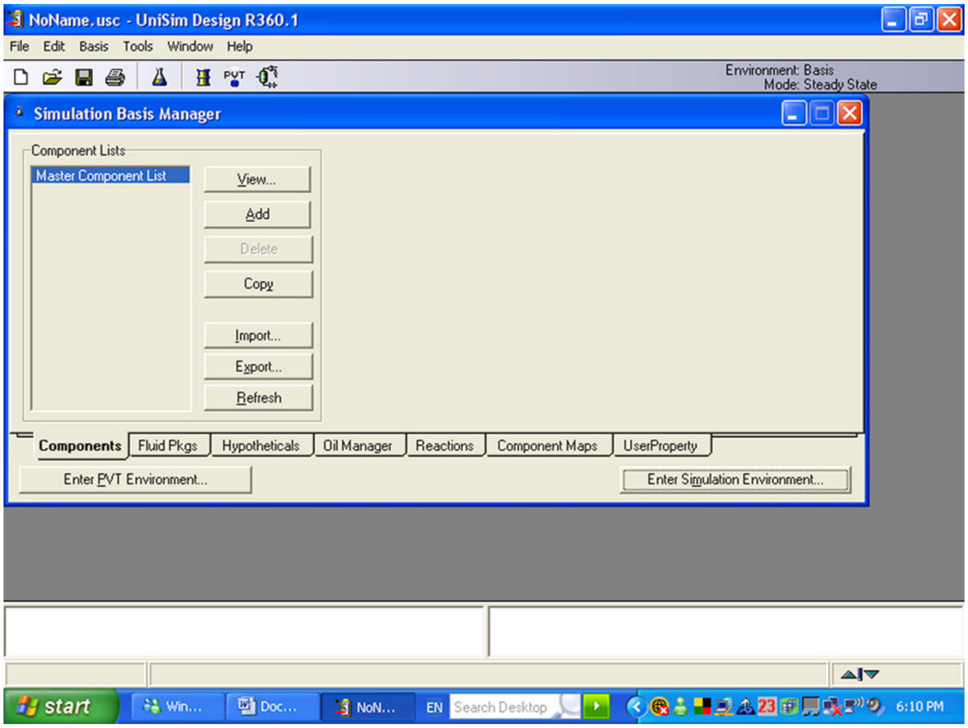
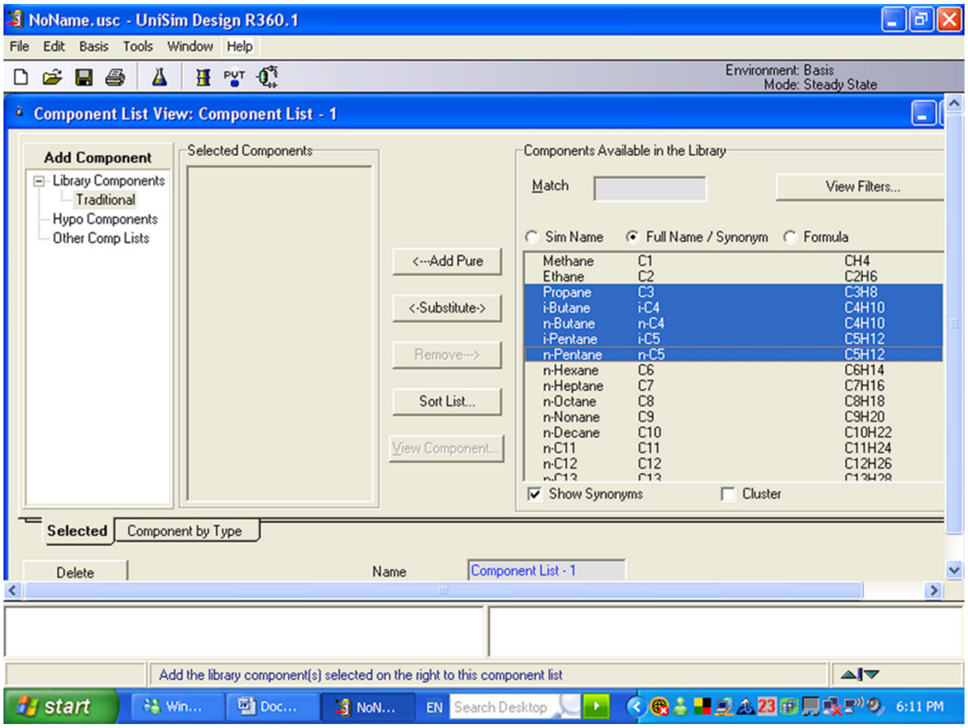


Figure 10-102 Snapshot window of Simulation Basis Manager.

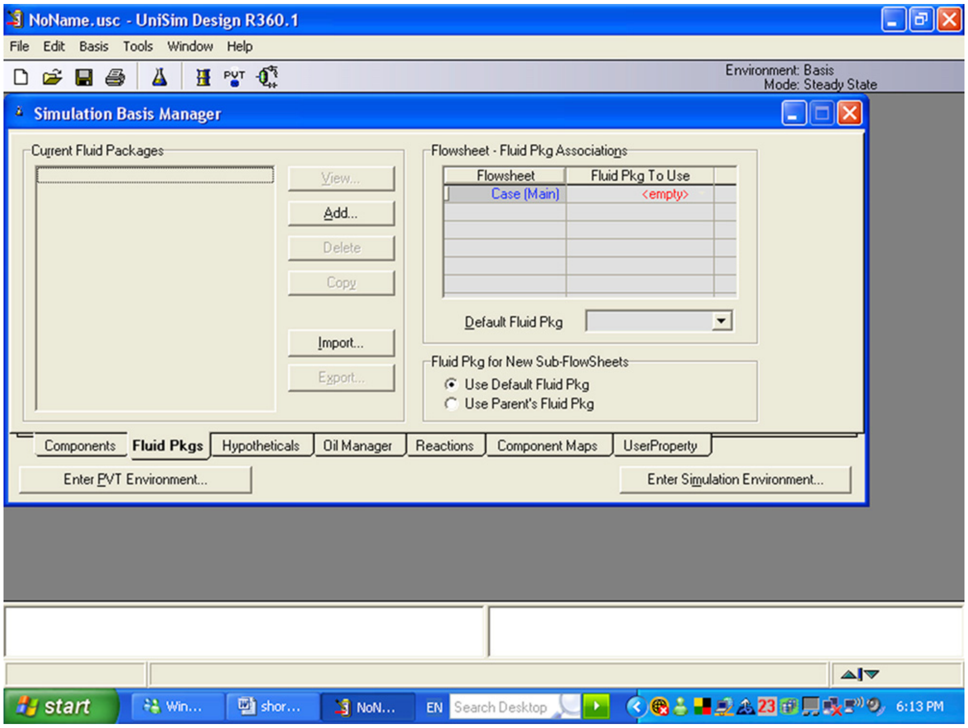


Methane	C1	CH4
Ethane	C2	C2H6
Propane	C3	C3H8
i-Butane	i-C4	C4H10
n-Butane	n-C4	C4H10
i-Pentane	i-C5	C5H12
n-Pentane	n-C5	C5H12
n-Hexane	C6	C6H14
n-Heptane	C7	C7H16
n-Octane	C8	C8H18
n-Nonane	C9	C9H20
n-Decane	C10	C10H22
n-C11	C11	C11H24
n-C12	C12	C12H26

Name: Component List - 1

Add the library component(s) selected on the right to this component list

Figure 10-103 Snapshot of the component List View window showing the components.

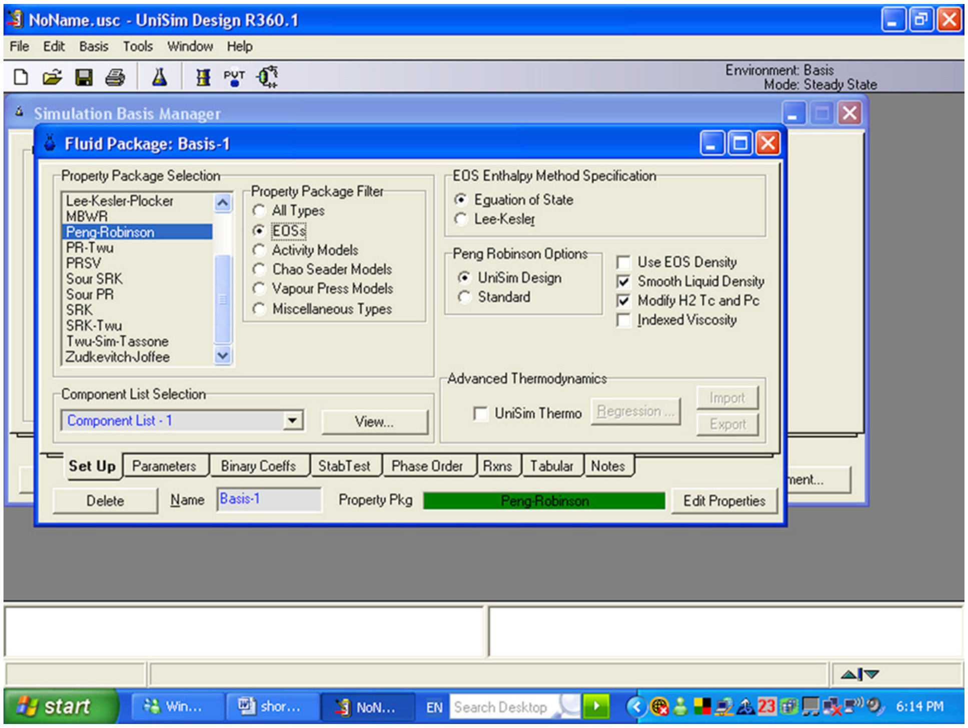


Flowsheet	Fluid Pkg To Use
Case (Main)	<empty>

Default Fluid Pkg

● Use Default Fluid Pkg
○ Use Parent's Fluid Pkg

Figure 10-104 Snapshot of Simulation Basis Manager window.



Property Package Selection:
- Lee-Kesler-Plocker
- MBWR
- Peng-Robinson
- PR-Twu
- PRSV
- Sour SRK
- Sour PR
- SRK
- SRK-Twu
- Twu-Sim-Tassone
- Zudkevitch-Joffee

Property Package Filter:
○ All Types
● EOSs
○ Activity Models
○ Chao Seader Models
○ Vapour Press Models
○ Miscellaneous Types

EOS Enthalpy Method Specification:
● Equation of State
○ Lee-Kesler

Peng Robinson Options:
● UniSim Design
○ Standard

☐ Use EOS Density
☑ Smooth Liquid Density
☑ Modify H2 Tc and Pc
☐ Indexed Viscosity

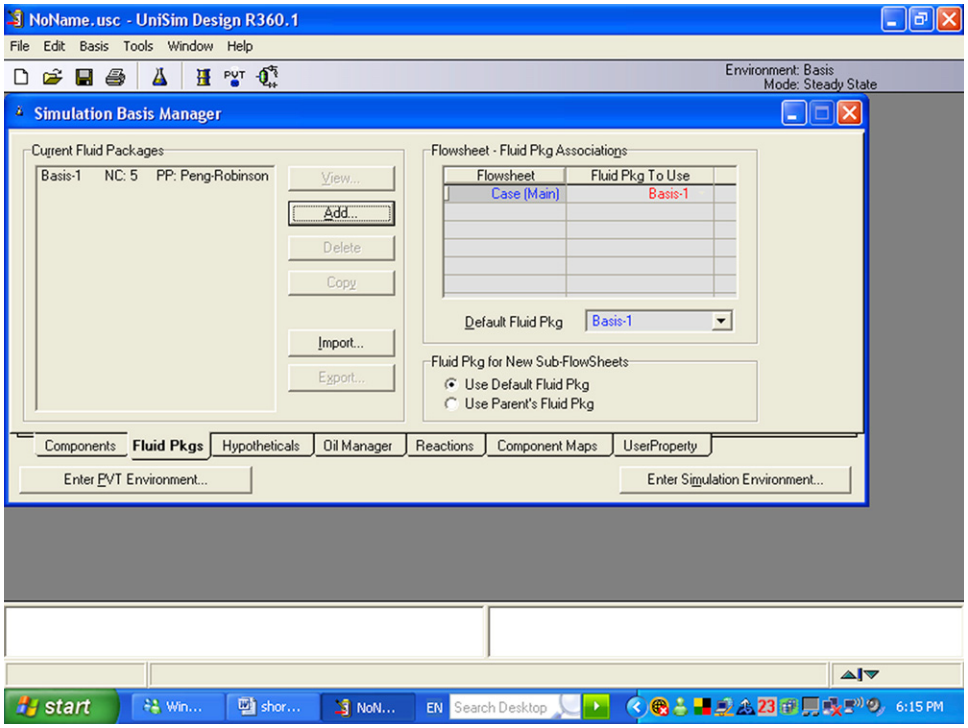
☐ UniSim Thermo

Component List Selection: Component List - 1

Name: Basis-1

Property Pkg: Peng-Robinson

Figure 10-105 Snapshot of Simulation Basis Manager window listing Property Package Selection.



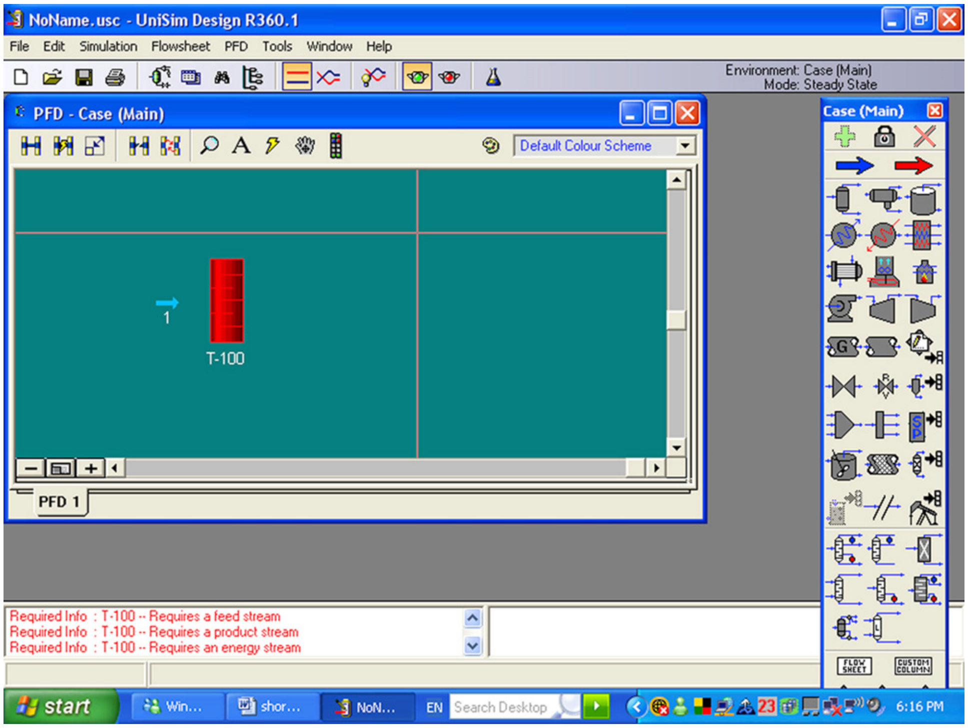
Basis-1 NC: 5 PP: Peng-Robinson

Flowsheet	Fluid Pkg To Use
Case (Main)	Basis-1

Default Fluid Pkg: Basis-1

● Use Default Fluid Pkg
○ Use Parent's Fluid Pkg

Figure 10-106 Snapshot of Simulation Basis Manager window.



Required Info : T-100 -- Requires a feed stream
Required Info : T-100 -- Requires a product stream
Required Info : T-100 -- Requires an energy stream

Figure 10-107 Snapshot of the feed stream 1 and distillation column T-100.

Step 8. Enter the **Stream Name**, **Pressure**, **Molar flow** from **Conditions** menu in the Worksheet of the Feed window as shown in Figure10-108.

Step 9. Next, select Composition menu from the Worksheet in the Feed window. This provides the five components C_3- C_5 that were previously selected for this example.

Step 10. Select **Mole fraction** tab from **Input Composition for Stream: Feed** window and input the data values of the components as shown in Figure 10-110. Click on **OK** button to close the window.

Step 11. The total Mole fraction is 1.0 as shown in Figure 10-111. Close this window and double click on the column icon on the PFD window.

Step 12. Double clicking on the Red icon of the column shows the Column window as shown in Figure 10-112. Click on the Design tab and enter the different streams: Feed, Distillate, Bottoms, Reb-Q, Cond-Q. Choose Liquid button for Top Product Phase from Connections as shown in Figure 10-112.

Step 13. Next, select the Parameter menu from Design window. Select light key in Bottoms and its Mole fraction tab, Heavy key in Distillate and its corresponding Mole fraction tab as shown in Figure 10-113. Notice the highlighted red comments displayed **"Unknown Key Components"** at the bottom of the window.

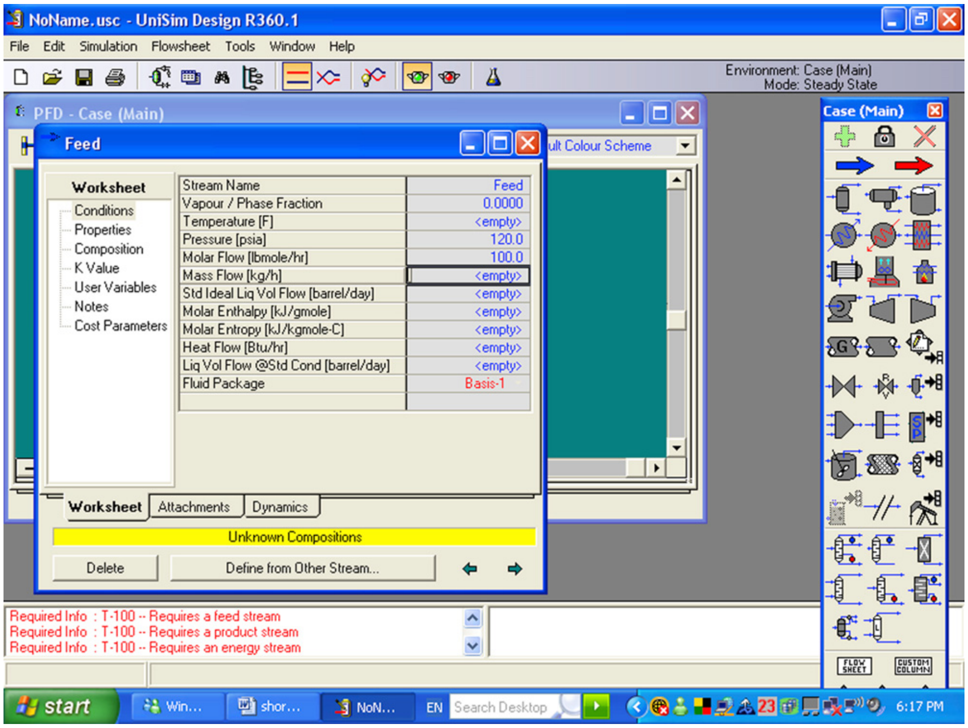
Step. 14. Input the Parameter values and notice the highlighted red comments displayed **"Unknown Pressure**" as shown in Figure 10-114

Step 15. Next, select **Parameters** from the **Design** window. Select Light Key in Component name from the list in Component "**Light key in Bottoms**" (e.g. n-Butane) and enter its value under Mole fraction label. Select Heavy Key component name from the list in Component "**Heavy Key in Distillate**" (e.g. i-Pentane) and enter its corresponding value under Mole fraction label. Enter Condenser and Reboiler Pressure (NB: The value of Reboiler pressure is greater than the value of Condenser pressure). Enter the value of External Reflux Ratio. This gives a highlighted green comment "**OK**" as shown in Figure 10-115.

Step16. The PFD window shows the results of shortcut simulation with **Feed**, **Distillate** and **Bottoms** and their corresponding values of **Temperature**, **Pressure** and **Molar flow rate** as shown in Figure 10-116.

Step 17. A summary of the printout of the data sheet can be obtained by right clicking on the column icon in Figure 10-117 to display a menu with **Print Datasheet** as shown in Figure 10-117. Then click on the **Print Datasheet** menu.

Step 18. Click on **Print Datasheet** to display "Select Data block(s) to Print for Shortcut Column" window as shown in Figure 10-118. Click on **Preview** button to view the Shortcut Column datasheet results or alternatively on **Print** button to print the hard copy of the results.

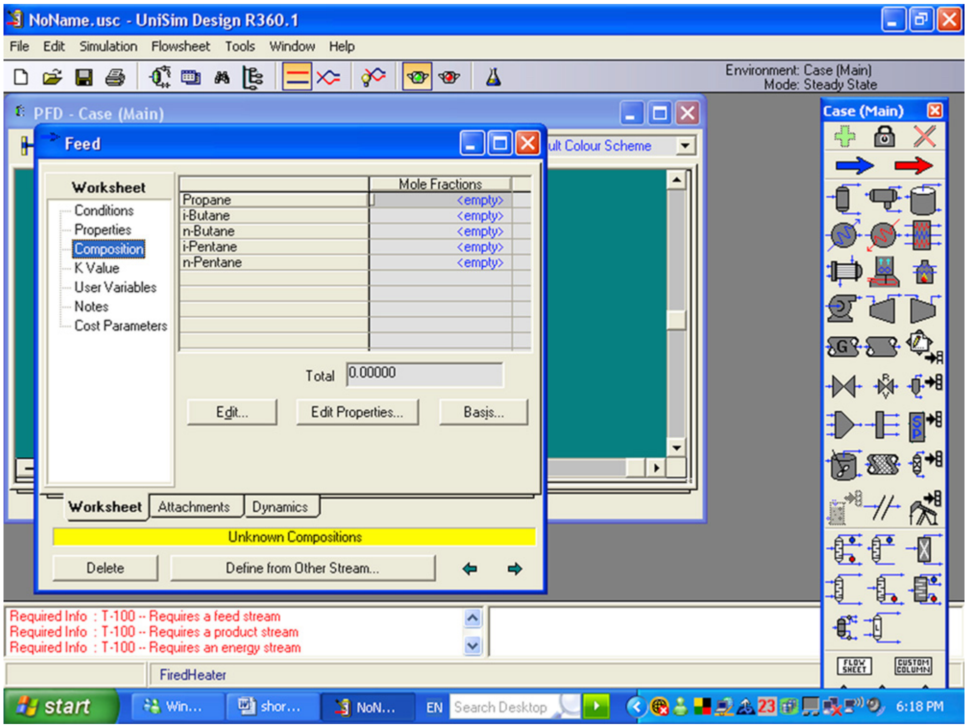


Stream Name	Feed
Vapour / Phase Fraction	0.0000
Temperature [F]	<empty>
Pressure [psia]	120.0
Molar Flow [lbmole/hr]	100.0
Mass Flow [kg/h]	<empty>
Std Ideal Liq Vol Flow [barrel/day]	<empty>
Molar Enthalpy [kJ/gmole]	<empty>
Molar Entropy [kJ/kgmole-C]	<empty>
Heat Flow [Btu/hr]	<empty>
Liq Vol Flow @Std Cond [barrel/day]	<empty>
Fluid Package	Basis-1

Unknown Compositions

```
Required Info : T-100 -- Requires a feed stream
Required Info : T-100 -- Requires a product stream
Required Info : T-100 -- Requires an energy stream
```

Figure 10-108 Snapshot of the Feed window showing the **Worksheet** parameters.



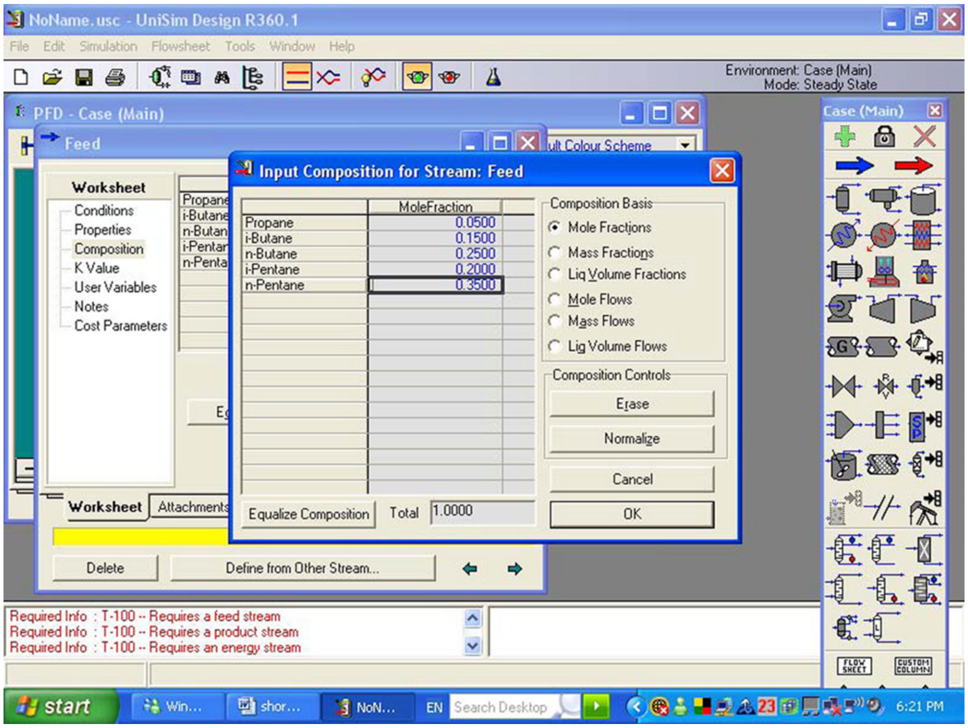
	Mole Fractions
Propane	<empty>
i-Butane	<empty>
n-Butane	<empty>
i-Pentane	<empty>
n-Pentane	<empty>

Total 0.00000

Unknown Compositions

Required Info : T-100 -- Requires a feed stream
Required Info : T-100 -- Requires a product stream
Required Info : T-100 -- Requires an energy stream

Figure 10-109 Snapshot of the Feed window with the selected five components.



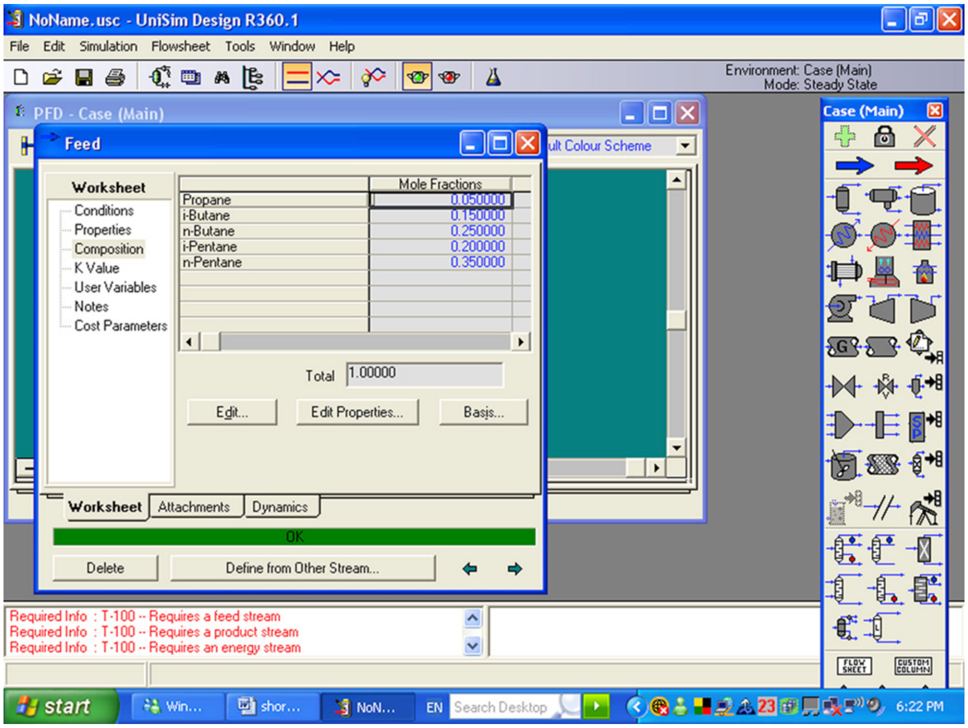
	MoleFraction
Propane	0.0500
i-Butane	0.1500
n-Butane	0.2500
i-Pentane	0.2000
n-Pentane	0.3500

Total 1.0000

Composition Basis
● Mole Fractions
○ Mass Fractions
○ Liq Volume Fractions
○ Mole Flows
○ Mass Flows
○ Liq Volume Flows

Required Info : T-100 -- Requires a feed stream
Required Info : T-100 -- Requires a product stream
Required Info : T-100 -- Requires an energy stream

Figure 10-110 Snapshot of **Input Composition For Stream: Feed** window.



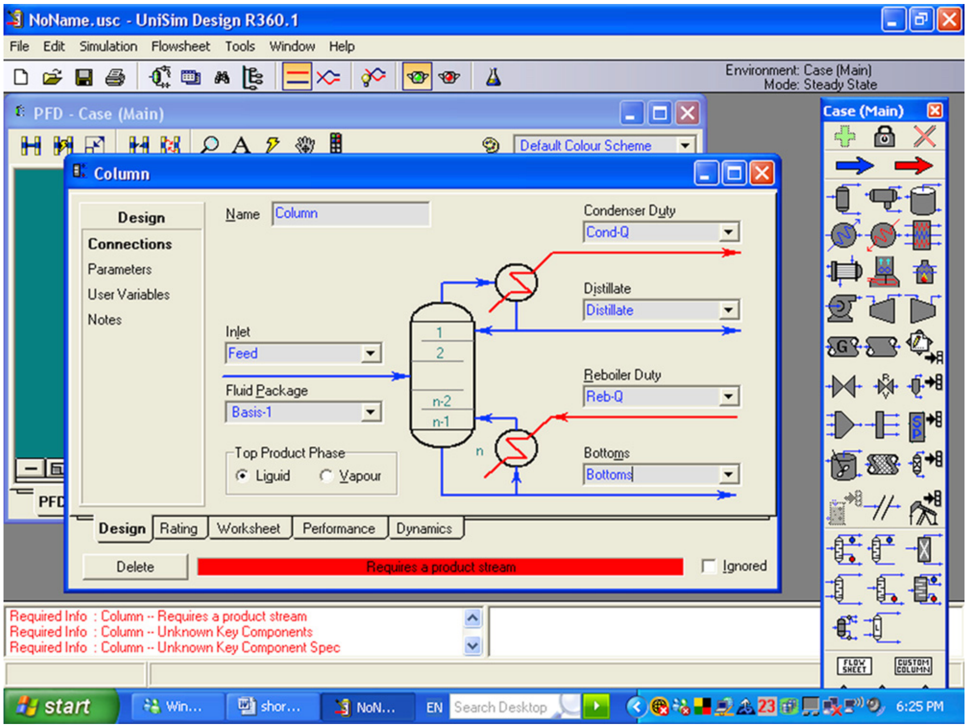
	Mole Fractions
Propane	0.050000
i-Butane	0.150000
n-Butane	0.250000
i-Pentane	0.200000
n-Pentane	0.350000

Total 1.00000

OK

Required Info : T-100 -- Requires a feed stream
Required Info : T-100 -- Requires a product stream
Required Info : T-100 -- Requires an energy stream

Figure 10-111 Snapshot of the Feed window showing the total mole fraction of the components.

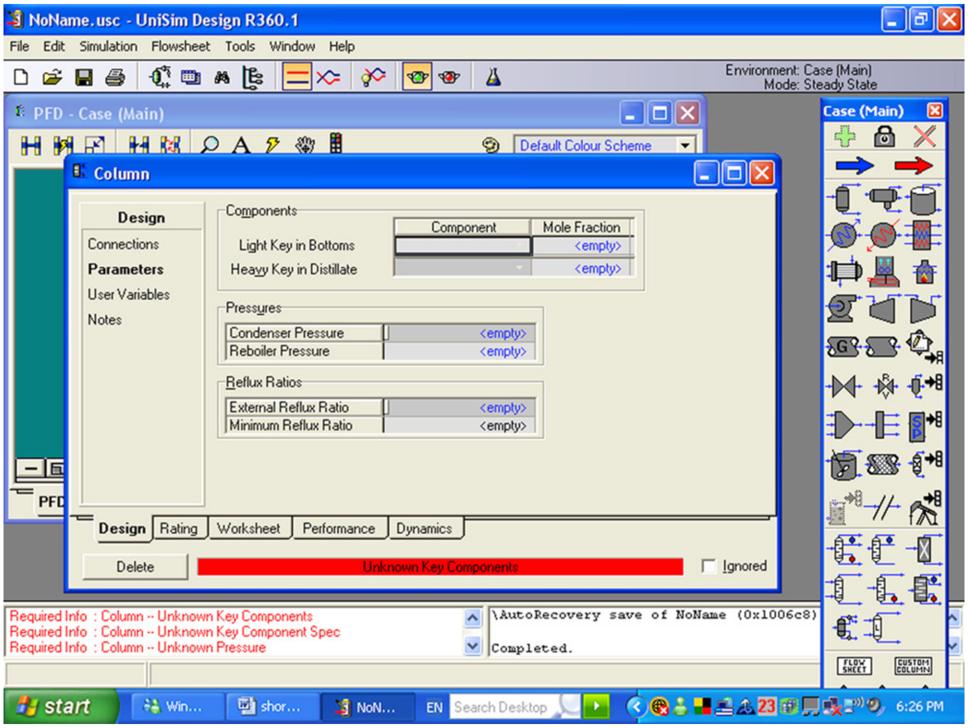


Name: Column
Inlet: Feed
Fluid Package: Basis-1
Top Product Phase: ● Liquid ○ Vapour
Condenser Duty: Cond-Q
Distillate: Distillate
Reboiler Duty: Reb-Q
Bottoms: Bottoms

Requires a product stream

Required Info : Column -- Requires a product stream
Required Info : Column -- Unknown Key Components
Required Info : Column -- Unknown Key Component Spec

Figure 10-112 Snapshot of **Column** window from **Design** tab in **Connections** menu.



Environment: Case (Main)
Mode: Steady State

Components

	Component	Mole Fraction
Light Key in Bottoms		<empty>
Heavy Key in Distillate		<empty>

Pressures

Condenser Pressure	<empty>
Reboiler Pressure	<empty>

Reflux Ratios

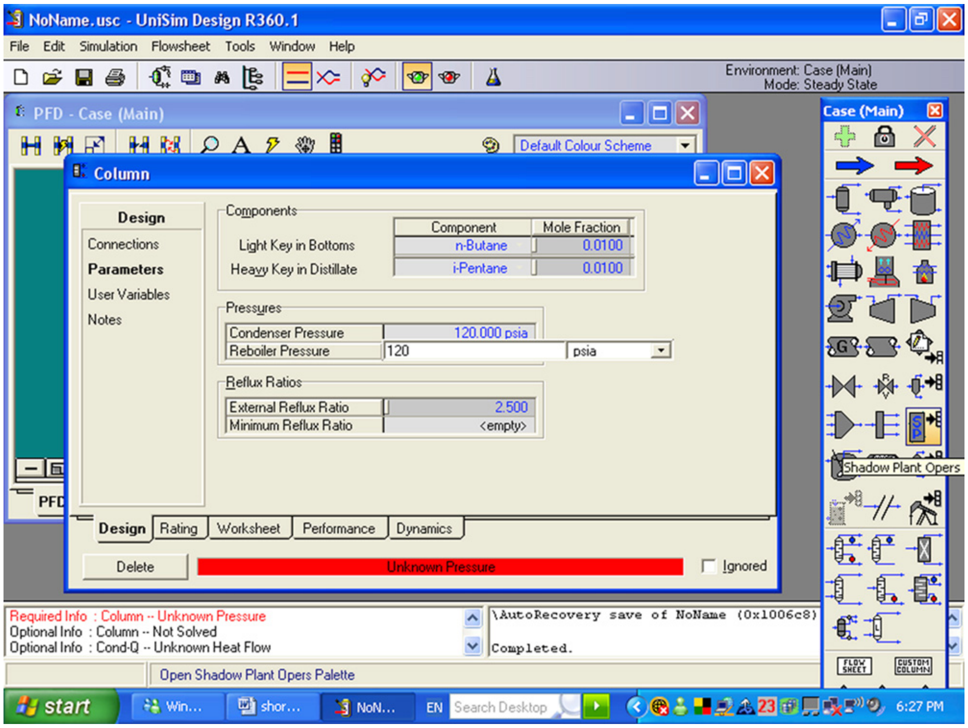
External Reflux Ratio	<empty>
Minimum Reflux Ratio	<empty>

Unknown Key Components

```
Required Info : Column -- Unknown Key Components
Required Info : Column -- Unknown Key Component Spec
Required Info : Column -- Unknown Pressure
```

```
\AutoRecovery save of NoName (0x1006c8)
Completed.
```

Figure 10-113 Snapshot of **Column** window showing **Parameters** menu.



Environment: Case (Main)
Mode: Steady State

Components

	Component	Mole Fraction
Light Key in Bottoms	n-Butane	0.0100
Heavy Key in Distillate	i-Pentane	0.0100

Pressures

Condenser Pressure	120.000 psia	
Reboiler Pressure	120	psia

Reflux Ratios

External Reflux Ratio	2.500
Minimum Reflux Ratio	<empty>

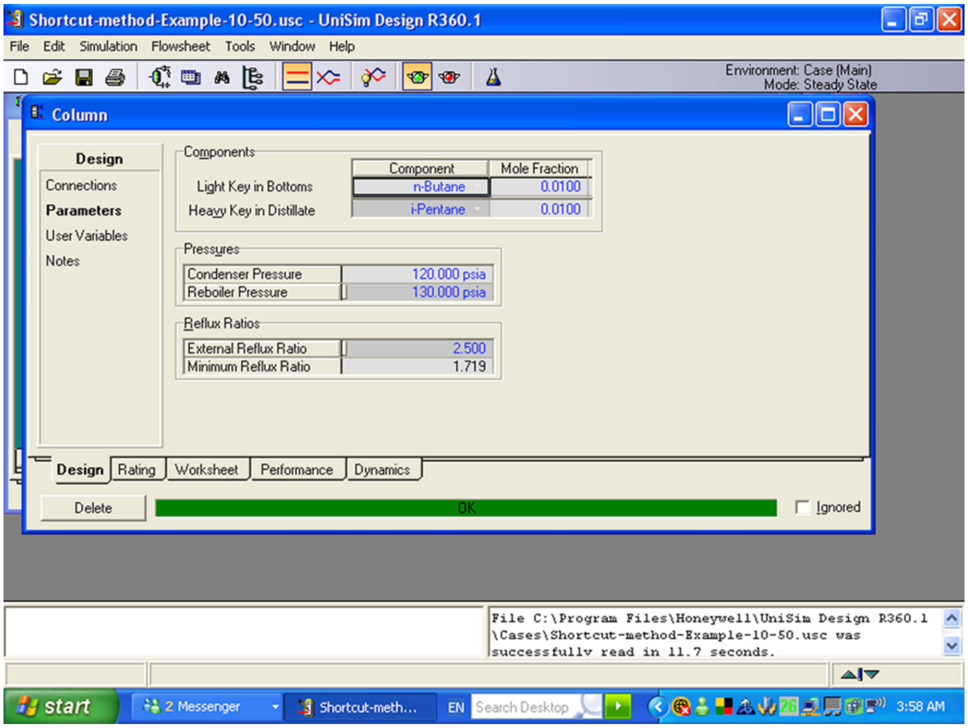
Unknown Pressure

```
Required Info : Column -- Unknown Pressure
Optional Info : Column -- Not Solved
Optional Info : Cond-Q -- Unknown Heat Flow
```

```
\AutoRecovery save of NoName (0x1006c8)
Completed.
```

Open Shadow Plant Opers Palette

Figure 10-114 Further snapshot of **Column** window showing **Parameters** menu.



Components

	Component	Mole Fraction
Light Key in Bottoms	n-Butane	0.0100
Heavy Key in Distillate	i-Pentane	0.0100

Pressures

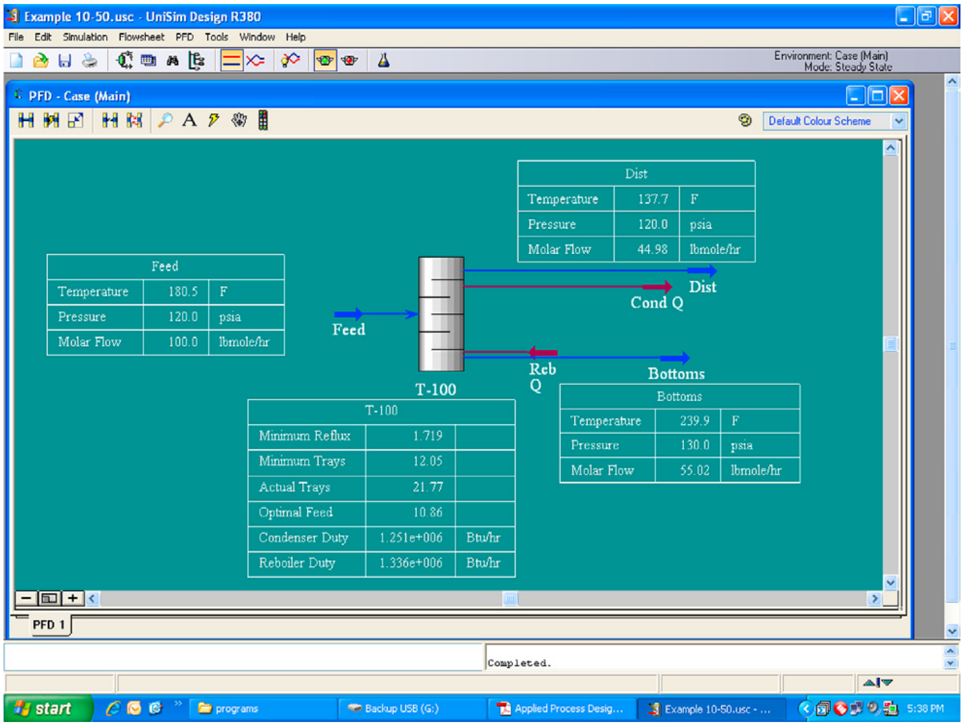
Condenser Pressure	120.000 psia
Reboiler Pressure	130.000 psia

Reflux Ratios

External Reflux Ratio	2.500
Minimum Reflux Ratio	1.719

```
File C:\Program Files\Honeywell\UniSim Design R360.1
\Cases\Shortcut-method-Example-10-50.usc was
successfully read in 11.7 seconds.
```

Figure 10-115 Snapshot of Column window with required Parameters.



Dist		
Temperature	137.7	F
Pressure	120.0	psia
Molar Flow	44.98	lbmole/hr

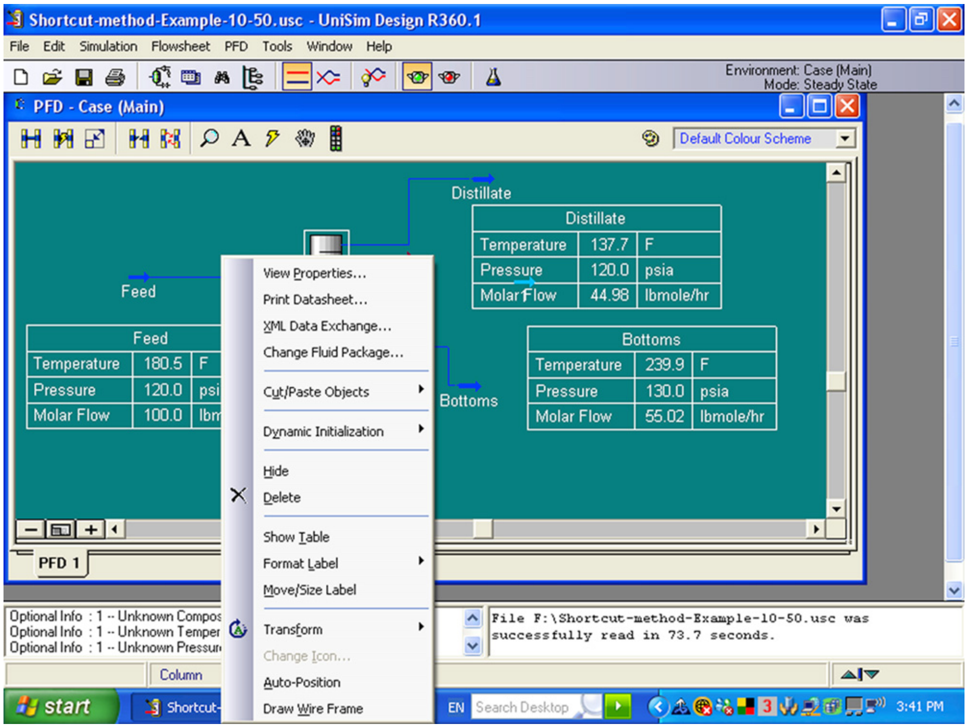
Feed		
Temperature	180.5	F
Pressure	120.0	psia
Molar Flow	100.0	lbmole/hr

T-100		
Minimum Reflux	1.719	
Minimum Trays	12.05	
Actual Trays	21.77	
Optimal Feed	10.86	
Condenser Duty	1.251e+006	Btu/hr
Reboiler Duty	1.336e+006	Btu/hr

Bottoms		
Temperature	239.9	F
Pressure	130.0	psia
Molar Flow	55.02	lbmole/hr

```
Completed.
```

Figure 10-116 Snapshot of PFD window showing the shortcut method simulation results of Example 10-50.



Distillate		
Temperature	137.7	F
Pressure	120.0	psia
Molar Flow	44.98	lbmole/hr

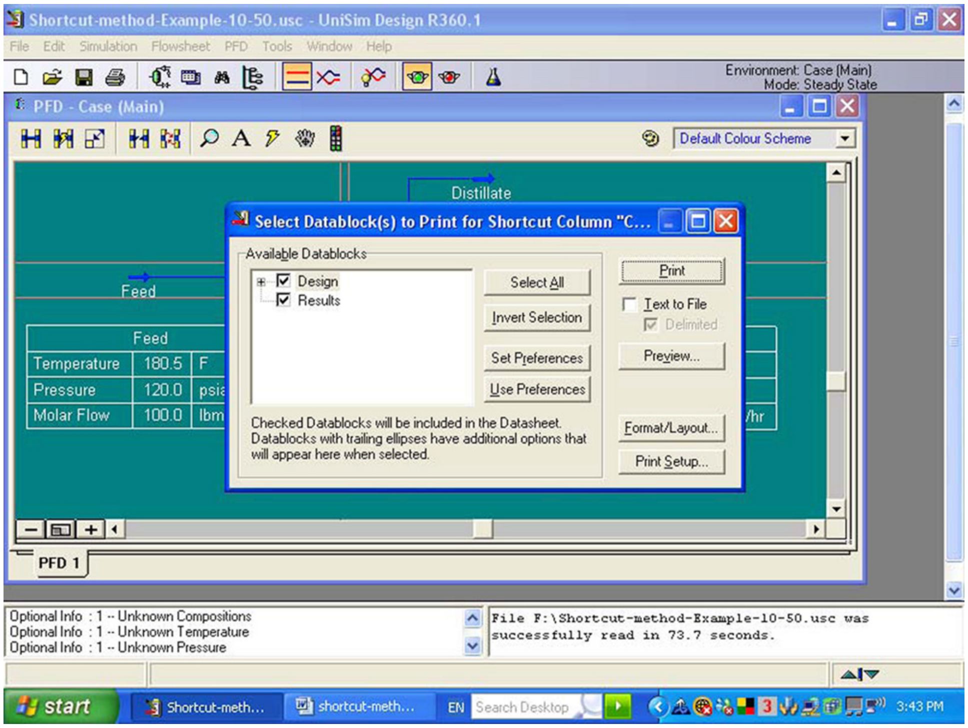
Feed		
Temperature	180.5	F
Pressure	120.0	psi
Molar Flow	100.0	lbm

Bottoms		
Temperature	239.9	F
Pressure	130.0	psia
Molar Flow	55.02	lbmole/hr

```
Optional Info : 1 -- Unknown Compos
Optional Info : 1 -- Unknown Temper
Optional Info : 1 -- Unknown Pressur
```

```
File F:\Shortcut-method-Example-10-50.usc was
successfully read in 73.7 seconds.
```

Figure 10-117 Snapshot of PFD window showing the **Print Datasheet** menu.



Checked Datablocks will be included in the Datasheet. Datablocks with trailing ellipses have additional options that will appear here when selected.

Feed		
Temperature	180.5	F
Pressure	120.0	psia
Molar Flow	100.0	lbm

```
Optional Info : 1 -- Unknown Compositions
Optional Info : 1 -- Unknown Temperature
Optional Info : 1 -- Unknown Pressure
```

```
File F:\Shortcut-method-Example-10-50.usc was
successfully read in 73.7 seconds.
```

Figure 10-118 Snapshot of **Select Data block(s) to Print for Shortcut Column**” window.

Step 19. Display results of the Shortcut Column simulation.

A summary of the results of the shortcut method obtained from both the UniSim simulation software and the developed computer program PROG104 is shown in Table 10-44. The results show that there is good agreement between them both.

Figure 110-119 shows the simulation results of Example 10-50.

10.42 Tray-by-Tray for Multicomponent Mixtures

Rigorous tray-by-tray computations for multicomponent mixtures of more than three components can be very tedious, even when made omitting a heat balance. Simulation software packages are type of this adept at dealing with detail and several computational methods are in use.

The direct-solution method of Akers and Wade [1] is among several that attempts to reduce the number of trial-and-error solutions. This has been accomplished and has proven quite versatile in application. The adaptation outlined here modifies the symbols and rearranges some terms for convenient use by the designer [3]. Dew point and bubble point compositions and the plate temperatures can be determined directly. Constant molal overflow is assumed, and relative volatility is held constant over sections of the column.

Rectifying section: reference component is heavy key, x_h

$$\left(\frac{x_i}{x_h}\right)_n = \frac{1}{\alpha_i}\left[\frac{(L/D)(x_i)_{n+1} + x_{Di}}{(L/D)(x_h)_{n+1} + x_{Dh}}\right] \qquad (10\text{-}509)$$

Table 10-44 Summary of the results of Example 10-50.

Parameters	Honeywell UniSim®	PROG104
Feed molar flow rate, lbmole/hr	100	100
Distillate molar flow rate, lbmole/hr	44.98	44.99
Bottoms molar flow rate, lbmole/hr	55.02	55.01
Minimum reflux ratio	1.719	1.5369
Actual reflux ratio	2.5	2.3054
Minimum number of stages	12.05	13.3
Actual number of stages	21.77	23.6
Optimum feed stage location	10.86	11.8

$\sum x_i = 1.0$ (including x_h)

$$\sum\left(\frac{x_i}{x}\right)_n = \left(\frac{1}{x_h}\right)_n$$

The compositions of each component are obtained from $(x_i/x_h)_n$ ratio.

The tray temperature is obtained from:

$$K_h = \frac{1}{\sum \alpha_i x_i} \qquad (10\text{-}510)$$

K_h is evaluated at the column pressure by use of suitable K charts.

Stripping section: reference component is heavy key, x_h, y_h

$$\left(\frac{y_i}{y_h}\right)_m = \alpha_i\left[\frac{(V_s/B)(y_i)_{m-1} + x_{Bi}}{(V_s/B)(y_h)_{m-1} + x_{Bh}}\right] \qquad (10\text{-}511)$$

$$\sum (y_i/y_h)_m = 1.0 \text{ (including } y_b)$$

The composition of each component on a tray is obtained from $(y_i/y_h)_m$.

The tray temperature is obtained from:

$$K_h = \Sigma y_i/\alpha_i \qquad (10\text{-}512)$$

At the column pressure using K charts for the heavy key or reference component.

Procedure

A. Rectifying Section

1. Determine material balance around column, including reflux L, distillate product D, bottoms product B.
    a. With total condenser, the reflux composition is equal to the condensed distillate product composition.
    b. With a partial condenser, the product D is a vapor, so a dew point must be run on its composition to obtain the liquid reflux composition.
2. Determine top tray temperature for use in relative volatility calculations by running a dew point on the overhead vapor. For total condenser its composition is same as distillate product. For a partial condenser, run a dew point on the column overhead vapor composition as determined by a material balance around the partial condenser, reflux, and product.
3. Determine $(x_i/x_h)_2$, for tray No.2 (second from top), for each component, using the x values for the reflux as the initial x_i $(n + 1)$.
4. Total this column to yield $\sum(x_i/x_h)$. This equals $1/x_h$.

5. Determine x_i for each component by:

$$x_i = \frac{(x_i/x_h)}{\sum(x_i/x_h)} \tag{10-513}$$

This is liquid composition on tray.

6. Continue down the column using the composition calculated for the tray above to substitute in Equation 10-509 to obtain (x_i/x_h) for the tray below.
7. Test to determine if α is varying to any great extent by calculating $\alpha_i x_i$ for a test tray. $\Sigma\alpha_i x_i = 1/K_h$. Determine temperature and evaluate corresponding values. Use new α_i if significantly different.
8. Continue the step-wise calculations until the ratio of light to heavy key on a tray equals (or nearly so) that ratio in the liquid portion of the feed. This is then considered the feed tray.
9. If there are components in the feed and bottoms which do not appear in the overhead product, they must gradually be introduced into the calculations. The estimated position above the feed tray to start introducing these components is determined by:

$$\frac{x_{Fi}}{x_a} = \left[\frac{1}{(1 + D/L)K_i}\right]^{p''} \tag{10-514}$$

where

x_{Fi} = mol fraction of a component in the feed that does not appear in the overhead

x_a = small arbitrary mol fraction in the liquid p'' plates above the feed plate

p'' = number of plates above the feed where introduction of components should begin

B. Stripping Section:

1. Determine the bubble point temperature of bottoms and composition of vapor, y_{Bi} up from liquid. Calculate relative volatility of light to heavy component at this temperature.
2. From these, calculate the vapor compositions, using Equation 10-511 calculate the ratio (y_i/y_h) for the first tray at the bottom.
3. Total $\Sigma(y_i/y_h)$ to obtain l/y_h
4. Calculate y_i for tray one

$$y_i = \frac{(y_i/y_h)}{\sum y_i/y_h}, \sum y_i/y_h = 1/y_h \tag{10-515}$$

$\Sigma y_i = 1.0$

5. Calculate (y_i/y_h) for the next tray, using the y_i values of tray one $(m - 1)$ in the equation to solve for $(y_i/y_h)_m$.
6. Test to determine if α_i is varying significantly by $K_h = \Sigma(y_i/\alpha_i)$. Evaluate the temperature of heavy component at the column bottoms pressure (estimated) using K charts or the equivalent. If necessary, calculate new α_i values for each component at the new temperature. Recheck every two or three trays if indicated.
7. Introduce components lighter than the light key which are not found in the bottoms in the same general manner as discussed for the rectifying section.

$$x_{Fi}/x_a = [(1 + D/L)K_i]p\prime \tag{10-516}$$

where p' is the number of trays below the feed tray where the component i is introduced in an assumed amount (usually small) x_a. Then x_{Fi} is the mol fraction of the component in the feed.

8. Continue step-wise calculations until ratio of light to heavy keys in the liquid portion of the feed essentially matches the same component ratio in the liquid on one of the trays.
9. The total number of theoretical trays in the column is the sum of those obtained from the rectifying calculations, plus those of the stripping calculations, plus one for the feed tray. This does not include the reboiler or partial condenser as trays in the column.

10.43 Tray-by-Tray Calculation of a Multicomponent Mixture Using a Digital Computer

Multicomponent distillation is much more common in process plants and refineries than the simpler binary systems. Many computer programs have developed to handle the many iterative calculations required when the system involves three to possibly ten individual components with the necessary degree of accuracy. To solve a multicomponent design properly, there should be both heat and material balance at every theoretical tray throughout the system.

To accommodate the step-by-step recycling and checking for convergence, requires input of vapor pressure relationships (such as those of Wilson, Renon, etc.) using the previously determined constants for latent heat of vaporization (equations) for each component (or enthalpy of liquid and vapor). Specific heat data for each component, and possibly special solubility or Henry's Law deviations may also be required.

There are several valuable references in the literature for developing and applying a multicomponent distillation program, including Holland [26, 27, 169], Prausnitz [52, 53], Wang and Henke [76], Thurston [167], Boston and Sullivan [6], Maddox and Erbar [115], and the pseudo-K method of Maddox and Fling [116]. Convergence of iterative trials to reach a given criterion requires careful evaluation [114]. There are several convergence techniques availiable – some requiring considerably less computational time than others.

Example 10-51: Tray-to-Tray Column Design for Multicomponent Mixture

A column is to be designed to separate the feed given below into an overhead of 99.9 mol % trichloroethylene. The top of the column will operate at 10 psig. Feed temperature is 158°F.

Note: the material balance for overhead and bottoms is based on:

a. 99.9 mol % trichloroethylene in overhead

b. 1.0 mol% trichloroethylene in bottoms.

c. 1.0 mol feed total

d. Light key = trichloroethylene

Heavy key = β trichloroethane

		Overhead		Bottoms	
Feed	**Mol Fraction**	**Mols**	**Mol Fraction**	**Mols**	**Mol Fraction**
(A) Trichloroethylene	0.456	0.451	0.999	0.00549	0.010
(B) β Trichloroethane	0.0555	0.00045	0.001	0.05505	0.101
(C) Perchloroethylene	0.3625	…	…	0.36250	0.661
(D) Tetras (1)	0.0625	…	…	0.0625	0.114
(E) Tetras (2)	0.0635	…	…	0.0625	0.114
	1.0000	0.45145	1.000	0.54804	1.000

Determine Overhead Temperature

Because trichloroethylene is 99.9% overhead, use it only to select boiling point from vapor pressure curves at 10 psig overhead pressure = 223°F (1,280 mm Hg abs).

Determine Bottoms Temperature (Bubble Point)

Allowing 10 psi column pressure drop, bottoms pressure = 20 psig (1,800 mm Hg abs)

Component	x_{iB}	Try t = 320°F Vapor Press. mm Hg	x_i (vp.)	$(y_i)_B$
A	0.01	4,500	45	0.0249
B	0.101	2,475	250	0.1382
C	0.661	1,825	1,210	0.67
D	0.114	1,600	183	0.1012
E	0.114	1,050	120	0.0664
			1,808 mm Hg abs.	1.0007

This compares quite well with the selected 1,800 mm bottoms pressure. Bottoms temperature is 320°F.

Relative volatilities: Light to Heavy key
At top:

$$\alpha = \frac{\text{v.p. Trichloroethylene}}{\text{v.p.}\beta\text{Trichloroethane}} = \frac{1280}{600} = 2.13$$

At bottoms:

$$\alpha = \frac{\text{v.p.Trichloroethylene}}{\text{v.p.}\beta\text{Trichloroethane}} = \frac{4500}{2275} = 1.98$$

α (average) = [(2.13) (1.98)]½ = 2.06

Minimum Stages at Total Reflux

$$S_M = N_{min} + 1 = \frac{\log(x_{D1}/x_{Dh})(x_{Bh}/x_{B1})}{\log \alpha_{avg}}$$

$$= \frac{\log(0.999/0.001)(0.101/0.01)}{\log 2.06}$$

$$= \frac{4.003}{0.318}$$

$$= 12.6 \text{ theoretical number of stages}$$

Minimum Stages Above Feed

$$S_r = \frac{\log(0.999/0.001)(0.0555/0.456)}{\log 2.13} = \frac{2.082}{0.328}$$

$$= 6.35 \text{ theoretical number of stages}$$

10.44 Thermal Condition of Feed

Feed temperature = 158°F

Calculated bubble point of feed = 266°F at assumed feed tray pressure of 15 psig.

$$\theta_c = 1.113 - (-0.2562/7.669) = 1.113 + 0.0334$$

$\theta_c = 1.146$ (this is sufficiently close to the original, to not require recalculation.)

The correct value of 1.146 should be used.

Check for balance:

$$1 - q = \sum \frac{x_{Fi}}{1 - \theta/\alpha_i} = \sum \frac{\alpha_i x_{Fi}}{\alpha_i - \theta} = -0.256$$

$$1 - 1.298 = -0.298 = -0.256$$

This could be corrected closer if a greater accuracy were needed. It is not as good a match as ordinarily desired.

$$q = \frac{\text{Heat to bring feed to boiling point} + \text{Heat to vaporize feed}}{\text{Latent Heat of one mol of feed}}$$

q = 1.298 (Calculations not shown, but handled in a similar manner to the example given in binary section, but all feed components considered, not just keys).

10.45 Minimum Reflux-Underwood Method, Determination of α_{Avg}. For Multicomponent Mixture

Assume pinch temperatures (usually satisfactory because α does not vary greatly) at $^1/_3$ and $^2/_3$ of over-all column temperature differences.

Lower pinch = 320 − $^1/_3$ (320 − 223) = 288°F

Upper pinch = 320 − $^2/_3$ (320 − 223) = 255°F

	@ 255°F		@ 288°F		
Component	**v.p.**	**α**	**v.p.**	**α**	**α_i (avg)**
A	2050	2.00	3050	1.91	1.955
B	1025	1.00	1600	1.00	1.00
C	750	0.732	1180	0.737	0.735
D	650	0.634	1035	0.647	0.641
E	390	0.380	650	0.406	0.393

To start, assume θ = 1.113 (it must lie between 1.00 and 1.955).

$$(L/D)_{min} + 1 = \frac{(\alpha_a x_a)_D}{\alpha_a - \theta} + \frac{(\alpha_b x_b)_D}{\alpha_b - \theta}$$

(for all distillate components)

$$(L/D)_{min} + 1 = \frac{(1.955)(0.999)}{(1.955 - 1.146)} + \frac{(1.00)(0.001)}{(1.00 - 1.146)}$$

$$= 2.41 + (-0.00685)$$

$$= 2.404$$

$$(L/D)_{min} = 2.404 - 1.0 = 1.40$$

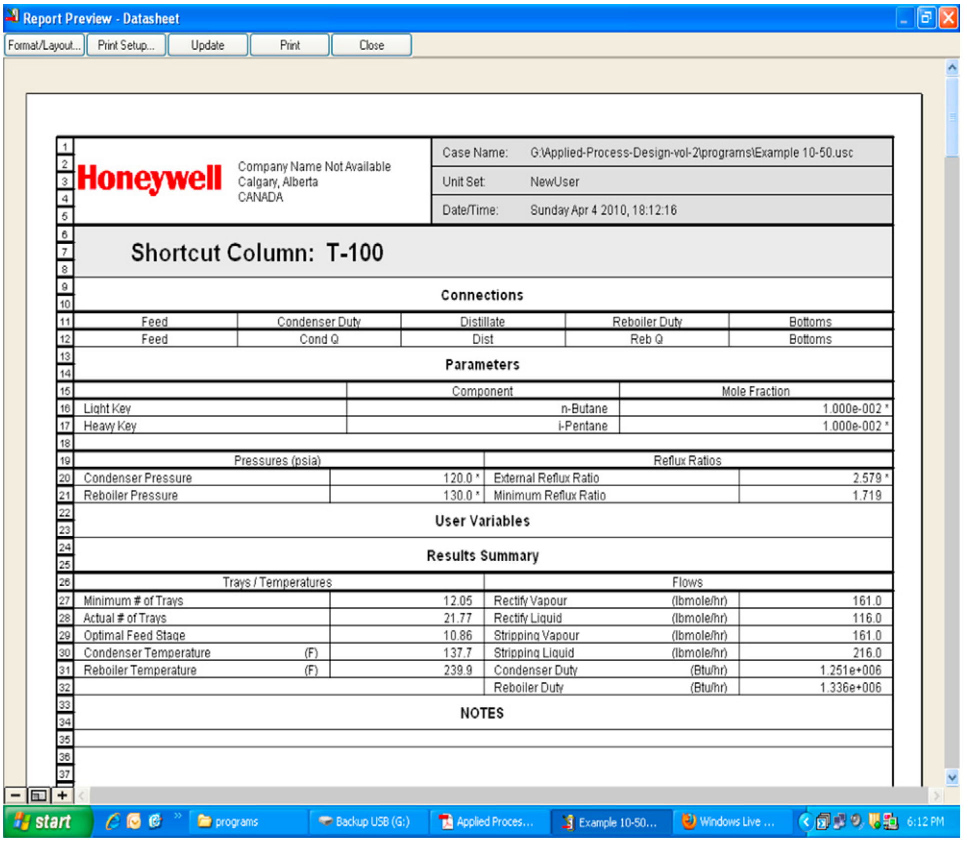
Operating Reflux and Theoretical Trays-Gilliland Plot

Min trays = S_M = 12.6

$(L/D)_{min}$ = 1.4

Assume $(L/D)_o$	**$\frac{(L/D)_o - (L/D)_M}{(L/D)_o + 1}$**	**Read: $(S - S_M)/(S + 1)$**	**Theoretical stages S**
1.4	0	∞	∞
1.6	0.0768	0.546	29
2.0	0.20	0.445	23.5
3.0	0.40	0.312	18.8
4.0	0.52	0.245	17
∞	–	–	12.6

Component	**x_{Fi}**	**$\alpha_i x_{Fi}$**	**$(\alpha_i - \theta)$**	**$\alpha_i x_{Fi}/(\alpha_i - \theta)$**	**$\alpha_i x_{Fi}/(\alpha_i - \theta)^2$**
A	0.456	0.891	0.842	1.058	1.252
B	0.0555	0.0555	−0.113	−0.491	4.33
C	0.3625	0.266	−0.378	−0.704	1.86
D	0.0625	0.0401	−0.472	−0.085	0.18
E	0.0625	0.0246	−0.720	−0.0342	0.0472
				Σ = −0.2562	Σ 7.669



Honeywell

Company Name Not Available
Calgary, Alberta
CANADA

Case Name:	G:\Applied-Process-Design-vol-2\programs\Example 10-50.usc
Unit Set:	NewUser
Date/Time:	Sunday Apr 4 2010, 18:12:16

Shortcut Column: T-100

Connections

Feed	Condenser Duty	Distillate	Reboiler Duty	Bottoms
Feed	Cond Q	Dist	Reb Q	Bottoms

Parameters

	Component	Mole Fraction
Light Key	n-Butane	1.000e-002 *
Heavy Key	i-Pentane	1.000e-002 *

Pressures (psia)		Reflux Ratios	
Condenser Pressure	120.0 *	External Reflux Ratio	2.579 *
Reboiler Pressure	130.0 *	Minimum Reflux Ratio	1.719

User Variables

Results Summary

Trays / Temperatures			Flows		
Minimum # of Trays		12.05	Rectify Vapour	(lbmole/hr)	161.0
Actual # of Trays		21.77	Rectify Liquid	(lbmole/hr)	116.0
Optimal Feed Stage		10.86	Stripping Vapour	(lbmole/hr)	161.0
Condenser Temperature	(F)	137.7	Stripping Liquid	(lbmole/hr)	216.0
Reboiler Temperature	(F)	239.9	Condenser Duty	(Btu/hr)	1.251e+006
			Reboiler Duty	(Btu/hr)	1.336e+006

NOTES

Figure 10-119 Snapshot of shortcut Column simulation results of Example 10-50.

These values are plotted in Figure 10-120. From the curve, the operating $(L/D)_o$ was selected, and the number of corresponding theoretical stages is 19. The spreadsheet Example 10-51.xls calculates the number of theoretical stages using the average value of the volatilities (α_{avg}) of the components at 288°F.

	α_{avg}
A	2.05
B	1.00
C	0.734

Tray-by-Tray Calculation-Ackers and Wade Method

Rectifying Section, $(L/D)_o = 3:1$

Light key = Trichloroethylene; Heavy key = β Trichloroethane

Relative Volatilities to start: Use average of top and feed

Neglect the heavier components than perchloroethylene in the rectifying section.

In order to carry the perchloroethylene, it is assumed at 0.0001 mol fraction in the overhead and reflux, the β-trichloroethane is reduced to 0.0005 mol fraction for these calculations being tighter specifications than the initial calculated balance. The overall effect will be small.

Component	$x_{iD} = x_i$ (Reflux)	$(x_i/x_h)_1$	$(x_i)_1$	$(x_i/x_h)_2$	$(x_i)_2$
A	0.9994	975.02	0.9984	545.5	0.9971
B	0.0005	1.00	0.001024	1.0	0.001828
C	0.0001	0.273	0.000280	0.359	0.000656
		$\Sigma = 976.293$	0.999704 (sufficiently close)	546.859	

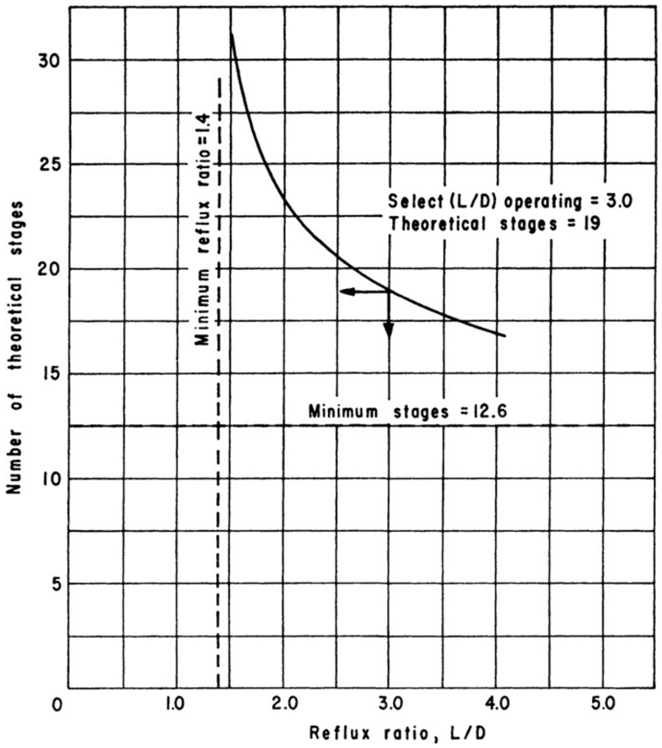


Figure 10-120 Gilliland plot for multicomponent for Example 10-48.

Typical calculations:

$$\left(\frac{x_i}{x_h}\right)_1 = \frac{1}{\alpha_i}\left[\frac{(L/D)(x_i)_{n+1} + x_{Di}}{(L/D)(x_h)_{n+1} + x_{Dh}}\right]$$

For component A: Tray 1

$$\left(\frac{x_i}{x_h}\right)_1 = \frac{1}{2.05}\left[\frac{(3)(0.9994) + (0.9994)}{(3)(0.0005) + 0.0005}\right] = 975.02$$

Component B:

$$\left(\frac{x_i}{x_h}\right)_1 = \frac{1}{1.00}\left[\frac{3(0.0005) + 0.0005}{3(0.0005) + 0.0005}\right] = 1.00$$

Component C:

$$\left(\frac{x_i}{x_h}\right)_1 = \frac{1}{0.734}\left[\frac{3(0.0001) + 0.0001}{3(0.0005) + 0.0005}\right] = 0.272$$

$(x_A)_1 = 975.02/976.293 = 0.9984$
$(x_B)_1 = 1.00/976.293 = 0.001024$
$(x_c)_1 = 0.273/976.293 = 0.000280$
Tray 2: Component A

$$\left(\frac{x_i}{x_h}\right)_2 = \frac{1}{2.05}\left[\frac{3(0.9984) + 0.9994}{3(0.00102) + 0.0005}\right] = 545.5$$

Component B:

$$\left(\frac{x_i}{x_h}\right)_2 = \frac{1}{1.00}\left[\frac{3(0.00102) + 0.0005}{3(0.00102) + 0.0005}\right] = 1.00$$

Component C:

$$\left(\frac{x_i}{x_h}\right)_2 = \frac{1}{0.734}\left[\frac{3(0.00028) + 0.0001}{3(0.0005) + 0.0005}\right] = 0.359$$

	$(x_i/x_h)_3$	$(x_i)_3$	$(x_i/x_h)_4$	$(x_i)_4$	$(x_i/x_h)_5$	$(x_i)_5$
A	325.24	0.9952	200.81	0.9916	126.61	0.9851
B	1.0	0.00306	1.0	0.004938	1.0	0.007781
C	0.514	0.001573	0.682	0.00337	0.908	0.007065
	326.754		202.492		128.518	

	$(x_i/x_h)_6$	$(x_i)_6$	$(x_i/x_h)_7$	$(x_i)_7$	$(x_i/x_h)_8$	$(x_i)_8$
A	80.60	0.9736	52.05	0.9520	33.97	0.9138
B	1.0	0.01208	1.0	0.01829	1.0	0.0269
C	1.213	0.01465	1.633	0.02987	2.21	0.05945
	82.813		54.683		37.18	

	$(x_i/x_h)_9$	$(x_i)_9$	$(x_i/x_h)_{10}$	$(x_i)_{10}$	$(x_i/x_h)_{11}$	$(x_i)_{11}$
A	22.47	0.8491	15.196	0.7501	7.716	0.5421
B	1.0	0.03779	1.0	0.04936	1.0	0.07026
C	2.994	0.1131	4.061	0.2005	5.516	0.3876
	26.464		20.257		14.232	

Ratio of keys in feed = 0.456/0.0555 = 8.2
Ratio of keys on Tray No. 10 = 0.7501/0.04936 = 15.2
Ratio of keys on Tray No. 11 = 0.5421/0.07026 = 7.7

Tray No. 11 should be used as the feed tray (counting down from the top). Note that since the relative volatility did not change significantly between top to feed trays, the same value was satisfactory over the range.

Stripping Section

Determine V_s: per mol of feed

$$(L/V)_r = \frac{1}{1+D/L} = \frac{1}{1+\frac{1}{3}} = 0.75$$

$$V_r = \frac{(L/D)D}{(L/V)} = \frac{3(0.45145)}{0.75} = 1.806$$

L_r = (L/D) (D) = 3(0.45145) = 1.35 mols/mol feed

L_s = $L_r + qF$ = 1.35 + 1.298 (1.0) = 2.648

V_s = $V_r - F(1-q)$ = 1.806 − (1.0) (1 − 1.298) = 2.104

V_s/B = 2.104/0.54804 = 3.84

Relative volatilities, α_i, determined at average temperature between bottom and feed of the column. Usually the pinch temperature gives equally satisfactory results.

Component	x_{iB}	y_{iB}	$(\alpha_i)_{avg}$	$(y_i/y_h)_1$	$(y_i)_1$	$(y_i/y_h)_2$	$(y_i)_2$
A	0.010	0.0249	1.905	0.319	0.0543	0.552	0.107
B	0.101	0.1382	1.00	1.000	0.170	1.00	0.194
C	0.660	0.6700	0.740	3.800	0.647	3.08	0.597
D	0.114	0.1012	0.648	0.517	0.088	0.389	0.0754
E	0.114	0.0664	0.411	0.241	0.0411	0.1476	0.0286
Total				5.877		5.1686	

Typical calculations: starting at the bottom and working up the column.

Tray 1: Component A

$$(y_i/y_h)_1 = \alpha_i\left[\frac{(V_s/B)(y_i)_{m-1} + x_{Bi}}{(V_s/B)(y_h)_{m-1} + x_{Bh}}\right]$$

$$= 1.905\left[\frac{(3.84)(0.0249) + 0.010}{3.84(0.1382) + 0.101}\right]$$

$(y_i/y_h)_1 = 0.319$
$(y_i)_1 = 0.319/5.877 = 0.0543$

Tray 2: Component A

$$(y_i/y_h)_2 = 1.905\left[\frac{(3.84)(0.0543) + 0.010}{3.84(0.170) + 0.101}\right] = 0.552$$

Continuation of the calculations gives an approximate match of ratio of keys on plate 10 to those in feed. Then feed tray is number 10 from bottom, which is number 11 from top.

Liquid mol fraction ratio from vapor mol fraction ratio:

$$(x_i/x_h) = \frac{(y_i/y_h)}{\alpha_{1/h}}$$

Ratio on tray no. 9 = 15.018/1.905 = (x_i/x_h) = 7.9
Ratio on tray no. 10 = 19.16/1.905 = 10.05
Ratio in feed = 8.2
Total theoretical trays = 11 + 10 − 1 (common feed tray count)
= 20 not including reboiler

Total theoretical stages = 20 + 1 (reboiler) = 21

This compares with 19 theoretical stages from Gilliland Plot.

Tray Efficiency

Use average column temperature of 271°F and feed analysis.

Component	x_{iF}	μ, cP	μ, $x_{iF,}$ cP	vp, mm Hg	$\alpha_{1/h}$
A	0.456	0.28	0.128	2500	1.94
B	0.0555	0.36	0.020	1290	
C	0.362	0.37	0.134		
D	0.0625	0.40	0.025		
E	0.0625	0.48	0.030		

$\Sigma = 0.337$

$\alpha\,\Sigma\,(\mu)\,(x_{iF}) = 1.94\,(0.337) = 0.654$

Using Figure 10-54
Drickamer and Bradford curve, $E_o = 46\%$
O'Connell curve, $E_o = 53.8\%$

In this case, recommend using:
$E_o = (46 + 53.8)/2 = 49.6\%$
Actual trays in column:
$N_{act} = 20/0.496 = 40.3$ trays

From tray-by-tray calculations, feed tray is $10/0.496 = 20.1$ trays from bottom, use 20.

Generally, in practice a column would be selected with extra trays, as a contingency e.g. a column with a total = 45 trays.

	Number of trays
Rectifying trays	22
Feed	1
Stripping	22
Total	45

Feed nozzles should be located on trays Nos. 21, 23, and 25 up from the bottom tray as No.1.

10.46 Heat Balance-Adjacent Key Systems with Sharp Separations, Constant Molal Overflow

Total Condenser Duty

Refer to Figure 10-121 (System (1)).

1. Assume or set condenser liquid product temperature, t_D.
2. Calculate condensing pressure, with t_D as bubble point (if subcooling exists, and t_D is below bubble point, use bubble point temperature for pressure calculation only).
3. $V_1 = L + D$

$$H_1V_1 = [L\,h_D + D\,h_D] + Q_c \qquad (10\text{-}517)$$

$$H_1 = \sum_1^1 H_{1i}y_{1i} \text{ at } t_1 \qquad (10\text{-}518)$$

$$h_D = \sum_1^i h_{Di}x_{Di} \qquad (10\text{-}519)$$

$$Q_c = V_1(H_1 - h_D) \qquad (10\text{-}520)$$

4. Calculate t_1 and x_1 by dew point on vapor V_1. Then determine H_1, referring to top tray as number one in this case, where

H_1 = total vapor enthalpy above reference datum for sum of all contributing percentages of individual components, i, in stream. Btu/lb, or Btu/mol

h_D = total liquid enthalpy above reference datum for sum of all contributing percentages of individual components, i, in product stream. (Also same as reflux), Btu/lb or Btu/mol.

For partial condenser: replace D_{hD} by DH_D in Step 3. A dew point calculation on compositions of y_D (vapor) gives t_D or total pressure. Also get liquid composition x_D (liquid reflux in equilibrium with product vapor y_D). Overhead vapor is the sum of compositions of y_D and x_p. A dew point calculation on this vapor (overhead from tray one top) gives top tray temperature, t_1.

$$V_1H_1 + Q_c = Lh_D + DH_D \qquad (10\text{-}521)$$

Reboiler Duty

Refer to Figure 10-121 (System (2)).

1. Determine bottoms temperature by bubble point on liquid x_B.
2. From feed condition determine enthalpy.

$$h_F = \frac{\sum V_F(H_iy_i)_F + \sum L_F(h_ix_i)_F}{F} \qquad (10\text{-}522)$$

3. Solve for Q_B, reboiler duty, Btu/hr

$$F\,h_F + Q_B = Dh_D + Bh_B + Q_c \qquad (10\text{-}523)$$

where

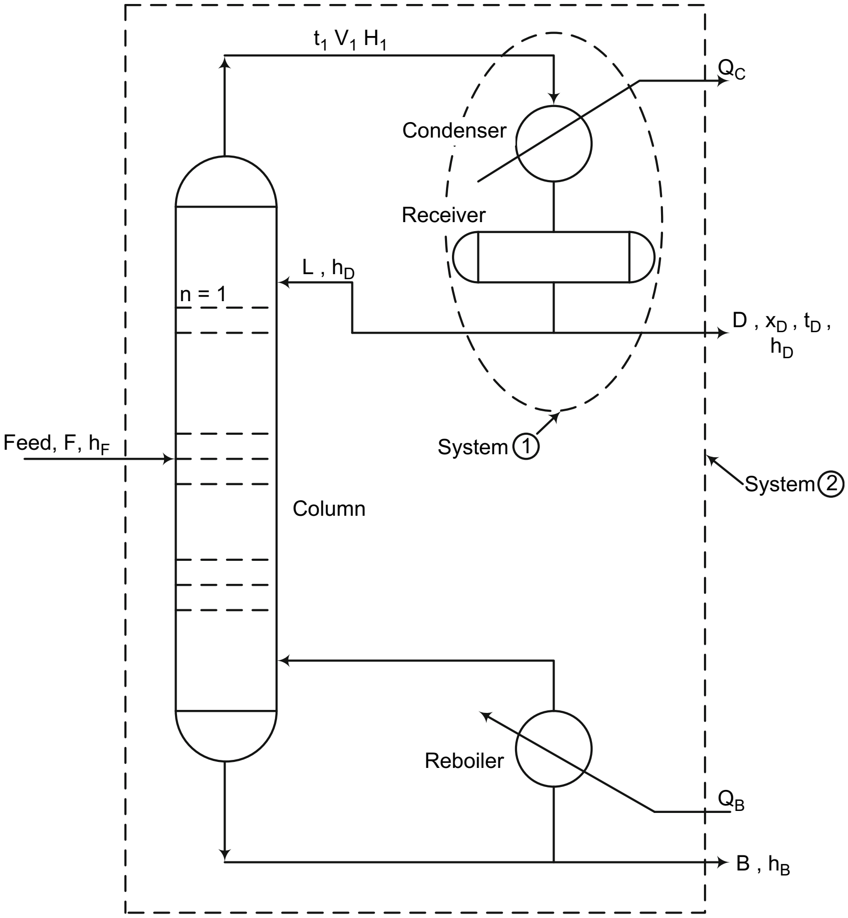


Figure 10-121 Heat balance diagram.

h_D = total enthalpy of distillate product, Btu/mol or Btu/lb
h_B = total enthalpy of bottoms product, Btu/mol or Btu/lb
h_F = total enthalpy of feed, But/mol or Btu/lb

10.47 Stripping Volatile Organic Chemicals (VOC) from Water with Air

Li and Hsiao [143] provide a useful approach to the environmental problem of stripping volatile organics from solution in a contaminated water stream by using fresh air as the stripping medium, in order to reduce atmospheric pollution. A number of industrial firms perform this stripping with steam. The mass balance on the VOC component around the column (trayed or packed) is shown in Figure 10-122 uses the symbols of Reference 143.

$$\frac{L}{V} = \frac{y_i - y_{n+1}}{x_o - x_N}\text{(slope of operating line)} \tag{10-524}$$

where

x_o = VOC mol fraction (ratio of number of mols of a specific VOC component in water solution to the total mols of all contaminants contained in the water)
x_N = mol fraction of VOC component in the stripped water
N = number of theoretical trays
y_i = mol fraction VOC component in exiting VOC contaminated air
y_{N+1} = mol fraction VOC component in the incoming fresh air, = 0 for fresh air
L = volumetric flow rate for incoming contaminated water
V = volumetric flow rate for incoming fresh air
V_{min} = minimum fresh air flow required based on slope of operating line L/V on x–y diagram
x_N = mol fraction VOC contaminant in exiting water stream, usually aimed at meeting the environmental regulations

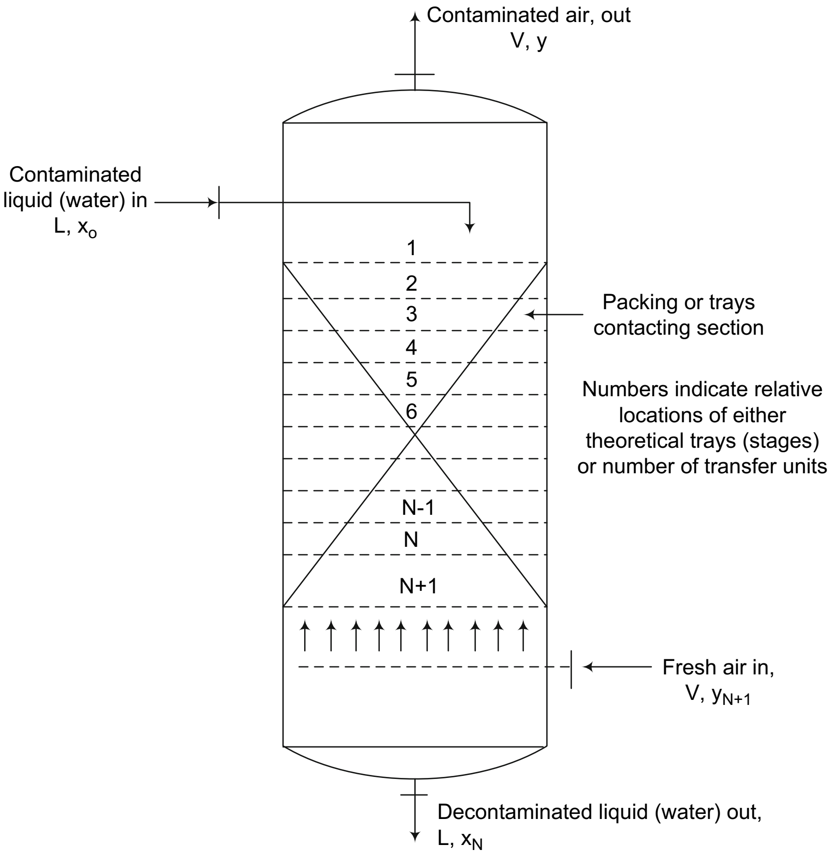


Figure 10-122 Schematic stripping tower using air to strip organics from water solution. Adapted and used by permission, Li, K. Y. and Hsiao, K.J., Chem. Eng., V. 98, No. 7, p.114 (1991).

S_{min} = minimum stripping factor at minimum flow rate for air

S_{opt} = optimum stripping factor, where treatment costs are a minimum, referenced to costs of utilities, maintenance, depreciation, labor, as economic conditions change one may need to adjust S_{opt}, see Reference 143

The concentrations of most of the VOC compounds in the contaminated water are usually expressed in ppm, as are the other residual compounds in the water exiting the tower. These are usually small values. As an approximation:

$$(L/V_{min}) = K$$

where

K = equilibrium constant (varies for each component)

$K = y^*/x^*$

y^* = equilibrium molar fraction of VOC components in air

x^* = equilibrium molar fractions of VOC components in water

Minimum stripping factor at corresponding minimum air flow rate:

$$S_{min} = K/(L/V_{min}) = 1.0 \tag{10-525}$$

$$V_{min} = L/K$$

The component with the lowest equilibrium constant is the key component in the stripping process, because it yields the largest value of V_{min}. This largest value is the "true" minimum air flow rate, whereas the actual air flow rate should be selected at 1.20 to 2.0 times the minimum. This is based upon an economic balance between the number of actual trays and air flow rate, which determines the column diameter.

It is relevant to evaluate the optimum stripping factor based on related costs, thus:

$$S_{opt} = K(L/V_{opt}) \tag{10-526}$$

$$V_{opt} = S_{opt}(V_{min}) \tag{10-527}$$

The Henry's Law constant, H, can be substituted for the equilibrium constant, K, when the system operates at or very close to atmospheric pressure:

$$H = p^*/x^* \tag{10-528}$$

Table 10-45 Henry's Law Constants and Optimum Stripping Factors for Selected Organic Compounds for Use with Packed Towers at 25°C (77°F).

Chemicals	Henry's Law constant	x_N/x_o %	L = 30 gpm	L = 300 gpm	L = 3,000 gpm
1,1,2,2 -Tetrachloroethane	24.02	4.75	1.39	1.66	1.84
		0.05	1.88	2.30	2.59
1,1,2-Trichloroethane	47.0	47.5	1.45	1.89	2.32
		0.05	2.00	2.79	3.37
1,2-Dichloroethane	61.2	4.75	1.46	1.97	2.54
		0.05	2.03	2.95	3.73
Propylene dichloride	156.8	4.75	1.6	2.43	3.9
		0.05	2.3	3.9	6.13
Methylene chloride	177.4	4.75	1.57	2.37	3.90
		0.05	2.23	3.87	6.20
Chloroform	188.5	4.75	1.59	2.46	4.10
		0.05	2.28	4.05	6.61
1,1,1-Trichloroethane	273.56	4.75	1.67	2.7	5.08
		0.05	2.43	4.62	8.37
1,2-Dichloroethane	295.8	4.75	1.65	2.68	5.08
		0.05	2.40	4.50	8.40
1,1-Dichloroethane	303.0	4.75	1.67	2.72	5.20
		0.05	2.40	4.63	8.66
Hexachloroethane	547.7	4.75	1.85	3.27	7.74
		0.05	2.7	6.0	13.6
Hexachlorobutadiene	572.7	4.75	1.88	3.48	8.1
		0.05	2.78	6.20	14.27
Trichloroethylene	651.0	4.75	1.82	3.27	7.78
		0.05	2.68	5.87	14.0
1,1-Dichloroethene	834.03	4.75	1.84	3.37	8.50
		0.05	2.70	6.10	15.9
Perchloroethane	1,596.0	4.75	2.10	4.20	13.2
		0.05	3.10	7.90	26.1
Carbon tetrachloride	1,679.17	4.75	2.06	4.2	13.2
		0.05	3.1	7.9	26.45

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where

p^* = the partial pressure, atm, of the contaminant in equilibrium with x^*

Tables 10-44 and 10-45 provide values for selected Henry's Law constants respectively [143].

The optimum stripping factor, S_{opt}, is expressed as a percent of residue, (100) (x_N/x_o), for water rates of 30 gpm, 300 gpm, and 3,000 gpm.

$$S_{opt} = 1 + {}_aH^b$$

Constants a and b were determined from a linear regression for $x_N/x_o = 4.75\%$ and x_N and $x_o = 0.05\%$ for the packed and tray towers. The optimum stripping factor decreases as the Henry's Law constant decreases. Due to the complex relationship between cost and performance, the authors [143] recommend caution in attempting to extrapolate from the water flow rate ranges shown.

Example 10-52: Stripping Dissolved Organics from Water in a Packed Tower Using Method of Li and Hsiao [143]

Using a packed tower, remove hexachloroethane (HCE) at a concentration of 110 ppm in water to 0.05 ppm using fresh air operating at essentially atmospheric pressure using a fan/blower generating up 1½ in. water pressure. The concentration of propylene dichloride (PDC) in the contaminated water is 90 ppm, and is to be reduced to 0.05 ppm in the exiting water. The water flow rate = 300 gpm. The required packing (or trays) must be determined by using a vapor-liquid equilibrium plot, setting slope L/V and stepping off the number of stages or transfer units. See Figure 10-122.

From Table 10-45 (Packed Tower):
Hexachloroethane: Henry's Law constant = 547.7 atm
Propylene dichloride: Henry's Law constant = 156.8 atm

1. For hexachloroethane: $x_N/x_o = 0.05$ ppm/100 ppm = 0.05%

   For propylene dichloride: $x_N/x_o = 0.05$ ppm/100 ppm = 0.05%
2. $S_{opt} = 6.0$ for HCE, and 3.9 for PDC.
3. For HCE:

   $V_{min} = L/K = (300)\ (8.33)\ (359\ \text{scf/mol})/(18\ \text{lb/mol})$
   $(547.7) = 91.1$ scf/minute
   For PDC:

   $V_{min} = L/K = (300\ \text{gpm})\ (8.33)\ (359)/(18)\ (156.8) = 317.8$ scf/min
4. Use the larger air rate as control required, which is the 317.8 scf/minute required for PDC, to calculate the optimum flow rate.
5. $V_{opt} = (3.9)\ (317.8) = 1{,}239.4$ scf/min

   $S_{opt} = K/(L/V_{opt})$

   $V_{opt} = S_{opt}\ (V_{min})$
6. Therefore, the operating conditions would be:

   L = 300 gpm
   V = 1,239 scf/min (minimum, may want to consider actually using 10–15% more for some assurance that the required conditions will be met.
7. Determine the tower diameter based on the flows of (6) above. See Chapter 13, this volume for packed tower design.

10.48 Rigorous Plate–to–Plate Calculation (Sorel Method [311])

The plate to plate calculation by Sorel using mole fractions is outlined as follows:

1. (a) For a total condenser as shown in Figure 10-123, the temperature of plate 1 is calculated as the dew point temperature of the vapor having the same composition as the distillate D. Therefore, a trial and error calculation is carried out until the relation:

$$\sum x_i = 1.0 = \sum \frac{y_i}{K_i} = \sum \frac{y_i\ \phi_i\ P_t}{\gamma_i\ P_i} \qquad (10\text{-}529)$$

is satisfied. This is carried out by selecting a number of temperatures (usually a minimum of three), and obtaining K or equivalent values at the column pressure and the selected temperature for each component, then summing the y/K values. This is followed by plotting the summation versus temperature and reading the temperature where the summation equals 1.0, as shown in Figure 10-124. The liquid composition in equilibrium with the vapor from plate 1 is calculated by obtaining the K values at the temperature and pressure on plate 1 and by evaluating y/K for each component.

(b) For a partial condenser as shown in Figure 10-125, the temperature of the vapor product and reflux liquid must be determined. This temperature is known as the dew-point of the vapor, and is calculated in the same manner as described in part 1(a). A plot of the summation versus temperature allows the temperature corresponding to the point where the sum equals unity to be read. The composition of the reflux liquid L_o is determined by obtaining K values for each component at the calculated temperature and pressure, and determining $x_i = y_i/K$.

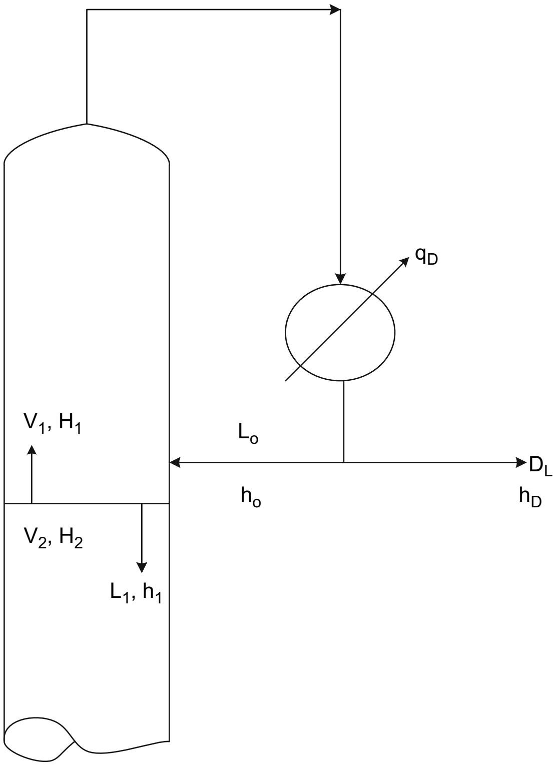


Figure 10-123 Total condenser.

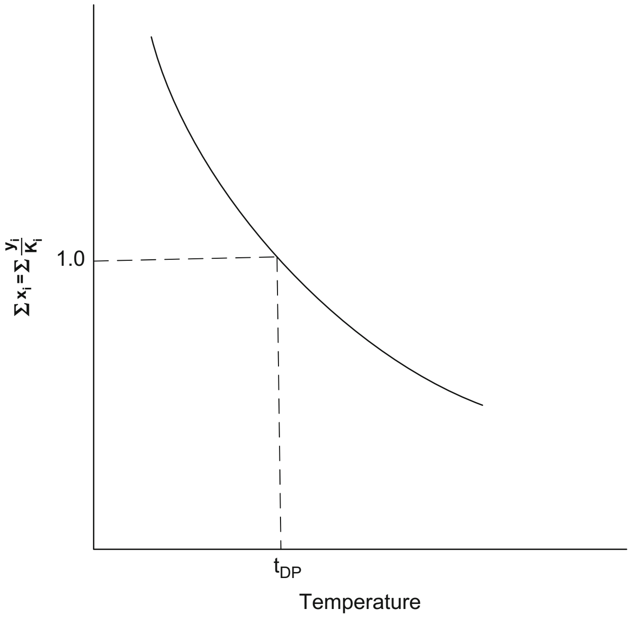


Figure 10-124 Determination of dew point.

2. The quantity of vapor rising from plate 1 is determined by material balance. Since L_O/D and D are known or fixed,

$$V_1 = L_o + D \quad (10\text{-}530)$$

or

$$V_1 = \left(\frac{L_o}{D} + 1\right) D \quad (10\text{-}531)$$

3. The condenser duty or heat removed in the condenser is then calculated by enthalpy balance, since all temperatures and pressures are known.

$$q_D = L_o h_o + D h_D - V_1 H_1 \quad (10\text{-}532)$$

4. The composition of the vapor V_2 rising to plate 1 (or V_1 in the case of partial condenser) is calculated by material and enthalpy balance. The equations for each case are illustrated as follows:

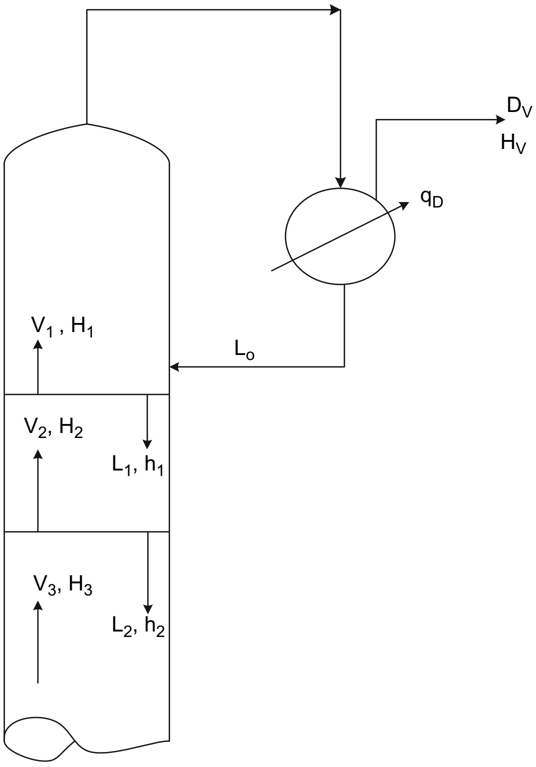


Figure 10-125 Partial condenser.

With a total condenser and reflux liquid cooled to a temperature below its bubble point, as shown in Figure 10-126, there are insufficient equations to determine the composition of V_2, quantity of V_2 and L_1, and the temperature T_2. Assuming that the molal latent heat of the mixture is essentially constant, and varies very little with temperature and composition, and that the molal heat capacities of the components in the system are essentially constant, and vary only slightly with temperature, then the following equations can be used to determine the solution:

$$V_C \lambda_1 = L_o C_{P_L} (T_o - T_1) \quad (10\text{-}537)$$

$$V_C + V_1 = V_2 \qquad L_o + V_C = L_1 \quad (10\text{-}538)$$

$$T_2 = \frac{D C_{P_L} (T_o - T_1) - q_D - V_2 \lambda_1}{V_2 C_{P_{V1}}} + T_1 \quad (10\text{-}539)$$

Total Condenser	Partial Condenser	
$V_2 = L_1 + D$	$V_1 = L_o + D$	(10-533)
$V_2 y_{i2} = L_1 x_{i1} + D x_{i\,D}$	$V_1 y_{i1} = L_o x_{io} + D x_{i\,D}$	(10-534)
$V_2 H_2 + q_D = L_1 h_1 + D h_D$	$V_1 H_1 + q_D = L_o h_o + D h_D$	(10-535)
$H_2 = f(y_{i2}, y_{j2}, y_{k2}, \ldots . T_2, P_t)$	$H_1 = f(y_{i1}, y_{j1}, y_{k1}, \ldots . T_1, P_t)$	(10-536)

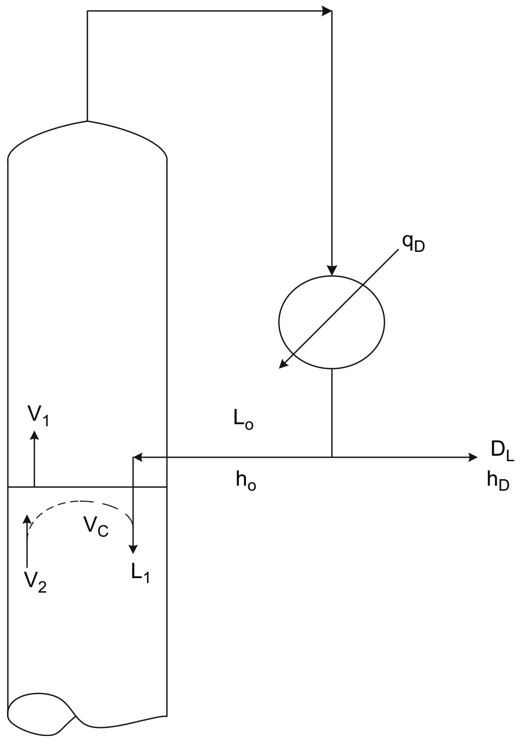


Figure 10-126 Reflux caused by supercooled liquid reflux from condenser.

5. With known V_2, the composition can be determined by Equation 10-534, since the quantities L_1 and D and the compositions x_{i1} and $x_{i\,D}$ are known.

   Note: Enthalpies of the streams may be calculated approximately by the following:

$$h_o = \sum_1^n \overline{h}_o$$
$$= x_{io}\, C_{pi}\,(T_o - T_r) + x_{jo}\, C_{pj}\,(T_o - T_r) + \ldots\ldots\ldots$$
$$+ x_{no}\, C_{p\,n}(T_o - T_r)$$

$h_O = h_D$ with a total condenser
For a partial condenser:

$$H_D = \sum_1^n \overline{H}_D = \sum_1^n x_i\,[\lambda_{i\,r} + C_{P\,v}\,(T_D - T_r)]$$

6. Determine the composition of L_2 in equilibrium with V_2 at T_2 and the column pressure by calculating the equilibrium concentrations x_{i2} by:

$$x_{i2} = \frac{y_{i2}}{K_{i2}} \qquad (10\text{-}540)$$

7. The vapor V_2 rising to plate 2 can be determined if the partial molal enthalpies of the components in the mixture are known from equations comparable to Equations 10-533 through 10-536. If the Lewis-Matheson assumptions of equimolal overflow and boilup are made, V_3 equals V_2.
8. Determine the composition of V_3 by component and material balance.
9. Calculate the temperature of V_3 by the equation comparable to Equation 10-539.
10. Repeat the calculations plate by plate until a vapor composition is reached which approximates the composition of the vapor portion of the feed, or until a liquid composition is reached that approximates the composition of the liquid portion of the feed.

    Note: As a guide, if the calculated ratio of the compositions of the key components approximately matches that of the ratio of keys in the feed, and if the calculated temperature essentially matches the temperature of the feed, the number of equilibrium stages is approximately correct [74].
11. From Figure 10-127, the quantity of liquid and vapor below the feed plate can be determined by:

$$\overline{L}_F = L_{F-1} + F \qquad (10\text{-}541)$$

$$\overline{V}_{F+1} = V_F - F_V \qquad (10\text{-}542)$$

12. Estimate the bubble-point temperature of the bottoms product B, if not determined above.
13. The composition of $\overline{V}_{n+1}$ is the equilibrium composition with B and is calculated by $y_{i_{n+1}} = (K_i\,x_i)_{n+1}$.

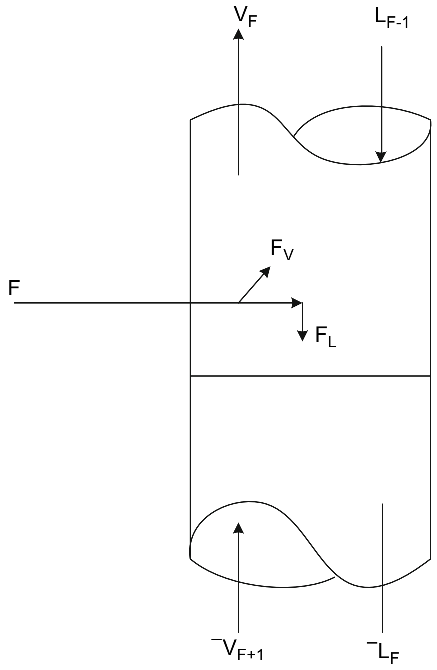


Figure 10-127 Condition at the feed.

14. Since the quantities of $\overline{L}_n$ and $\overline{V}_{n+1}$ are known, the composition of $\overline{L}_n$ can be determined by material balance:

$$x_{i_n} = \frac{\overline{V}_{n+1}\, y_{i_{n+1}} + B\, x_{i_B}}{\overline{L}_n} \tag{10-543}$$

15. The temperature of plate n is the bubble-point temperature of L_n and is calculated in the same manner as the reboiler temperature.
16. The calculations are then continued, plate by plate, up the column; determining liquid compositions by material balance, temperature by bubble point computation, and vapor composition by the equilibrium calculations until the liquid and vapor compositions approximate the compositions of the liquid and vapor portions of the feed, or until the key component ratio matches approximately that of the feed. This procedure and observations apply as to the computations proceeding down from the top of the column. The method is sufficient if the key component composition ratio approximately matches that of the feed and the plate temperature is essentially the same as that of the feed.

10.49 Multiple Feeds and Side Streams for a Binary Mixture

Simple binary distillation columns have been considered with single feed and two products, namely the distillate and bottoms. However, it is possible to have more than one feed or more than two product streams. For example, in the distillation of crude petroleum, several products such as natural gasoline, liquefied petroleum gas (LPG) propane, butane, motor gasolines, solvent naphtha, aviation fuels, kerosene, diesel oil, gas oils, lube oils, fuel oils and asphalts are all being withdrawn from the column at different points. The McCabe-Thiele method can be used to analyze such complex configurations.

Two Feed Streams

Consider a typical distillation column as shown in Figure 10-128 having two feeds F_1 and F_2; with an overhead and bottoms product D and B respectively. Figure 10-129 is the related McCabe-Thiele diagram showing the various operating lines. Each feed has its own q line, i.e. feed line. There are three distinct sections in Figure 10-128, namely:

Section I. The top section above the top feed tray.

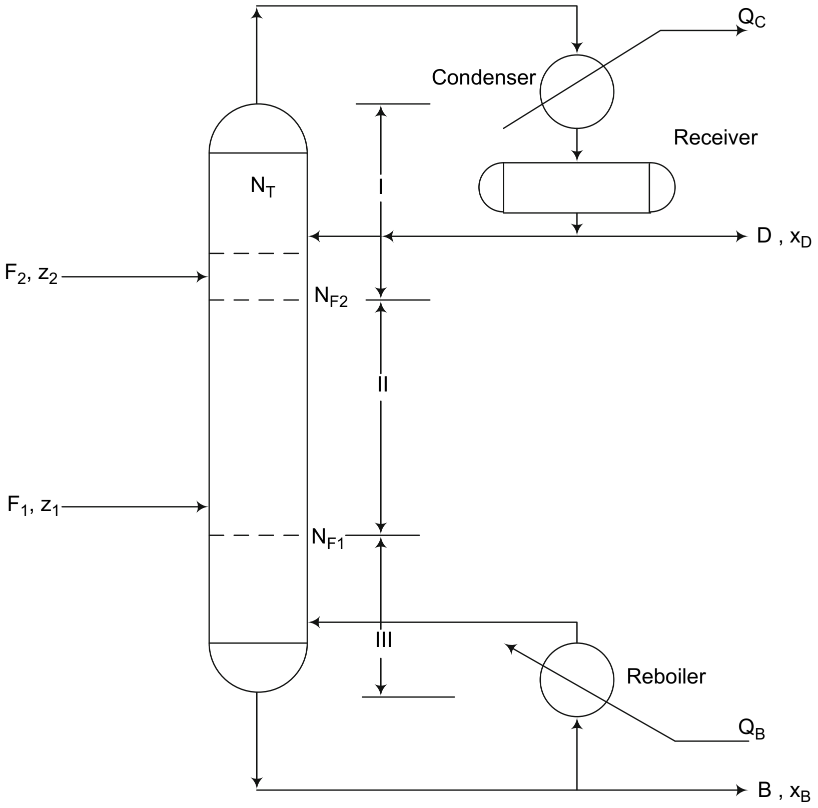


Figure 10-128 A two-feed column.

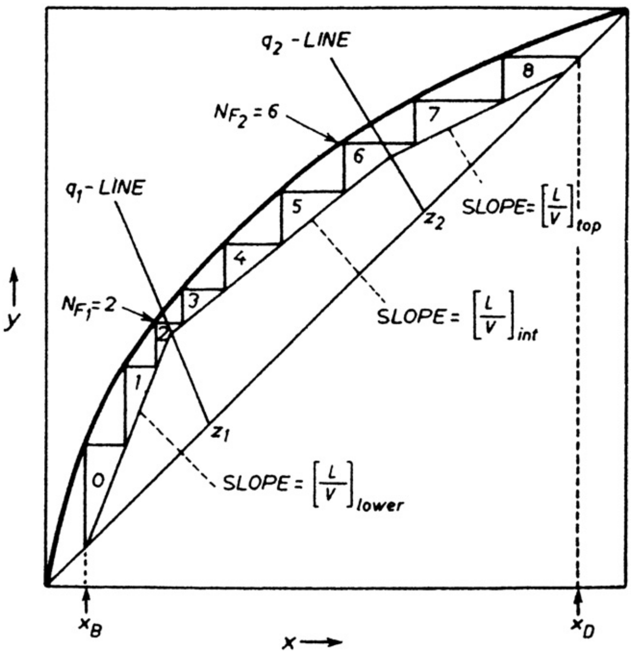


Figure 10-129 The McCabe-Thiele Diagram of a two-feed column.

Section II. The intermediate section between the two feed trays.

Section III. The bottoms section below the lower feed tray.

There are three operating lines in Figure 10 –129, each having different slopes (i.e. L/V ratio).

Side Stream Columns

Some columns receive feed at one point, but have one or more side streams drawing liquid or vapor product over the normal distillate and bottoms products – as in petroleum refineries. Figures 10–130a and c schematically represent a system in which a vapor or liquid side stream may be withdrawn. The removal of liquid from tray N_S reduces the liquid flow rate in the section below the side stream. Hence the L/V ratio is higher above the side stream than below it as shown in Figure 10–130b. Three additional variables, such as flow rate, S, type of side draw (liquid or vapor), and location or composition x_S or y_S must be specified. The operating equation for the middle section can be derived from the mass balances around the top or bottom section of the column. Further, the operating line changes the slope at the side stream tray. The material balance equations at the top, and the side stream assuming constant molal overflow are:

$$y = \frac{L}{V}x + \frac{D}{V}x_D \qquad (10\text{-}544)$$

and

$$y = \frac{L'}{V}x + \frac{Dx_D + Sx_S}{V} \qquad (10\text{-}545)$$

Equating the two operating line Equations (10-544) and (10-545), the intersection occurs at:

$$(L - L')x = Sx_S \qquad (10\text{-}546)$$

and since

$$L = L' + S \qquad (10\text{-}547)$$

the point of intersection becomes $x = x_S$

The intersection of the lines is:

$$y = \frac{L'}{V}x + \frac{Sx_S + Dx_D}{V} \qquad (10\text{-}548)$$

and $y = x$ intercept occurs at:

$$x = \frac{Sx_S + Dx_D}{S + D} \qquad (10\text{-}549)$$

Figure 10-130c schematically represents a system where a vapor side stream is withdrawn from tray N_S. The vapor flow rate in the section above N_S is lower than in the section below it. As the liquid flow rate, L remains unchanged, the L/V ratio above the side stream is higher than below it (Figure 10–130d). For a vapor side stream, the feed line is horizontal $(q = 0)$ at $y = y_S$. A balance on vapor flow rates gives:

$$V' = V + S \qquad (10\text{-}550)$$

As L remains unchanged, L'/V' can be calculated if L and V are known. If a specified value of x_S or y_S is desired, the problem becomes one of a trial and error.

Example 10-53

An ethanol–water mixture is to be separated by continuous fractionation in a sieve-plate distillation column operated at 101.325 kPa. A feed flow rate of 1000 kmol/h containing 28 mole % ethanol is to be separated into two ethanol-rich streams; a distillate containing 82.5 mole % ethanol, and a side stream containing 60 mol % ethanol. It is required to recover 98% of the ethanol in the feed in these two product streams.

The molar flow rate of the distillate will be twice that of the side stream. The feed will be liquid at its boiling point, and the product streams will be removed as liquids, also at their respective boiling points. An external reflux ratio of 2.5 to 1.0 will be applied at the top of the column. Stating clearly any assumptions, calculate:

a. The composition of the bottoms product.

b. Estimate the number of sieve plates required if the plate efficiency is 60%.

c. Indicate briefly how a distillate containing 99.5 mole % ethanol could be obtained.

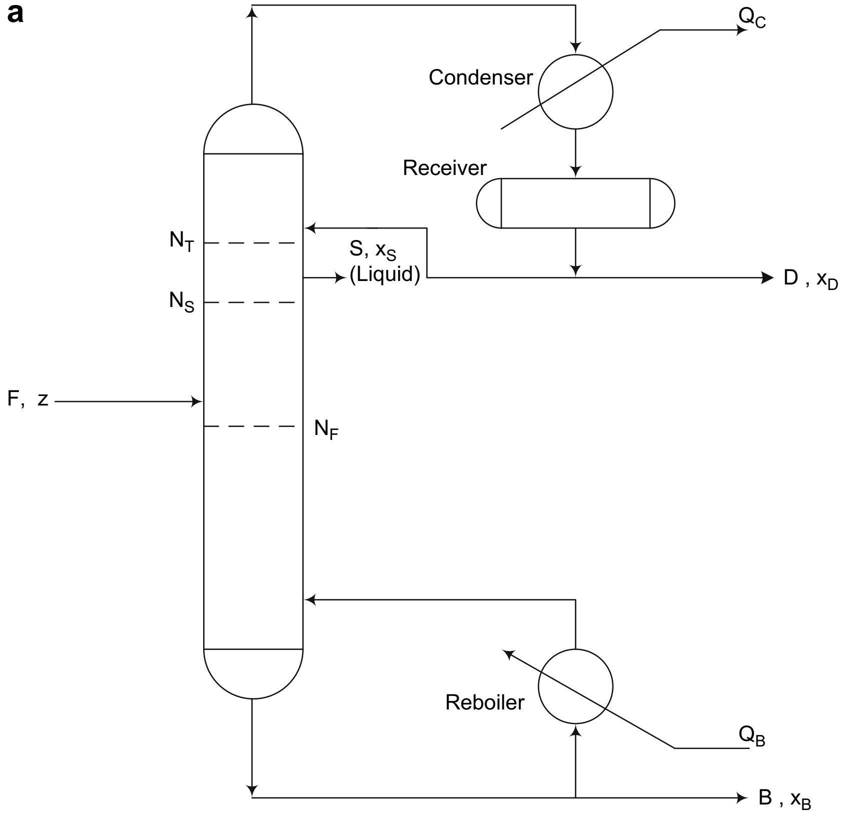
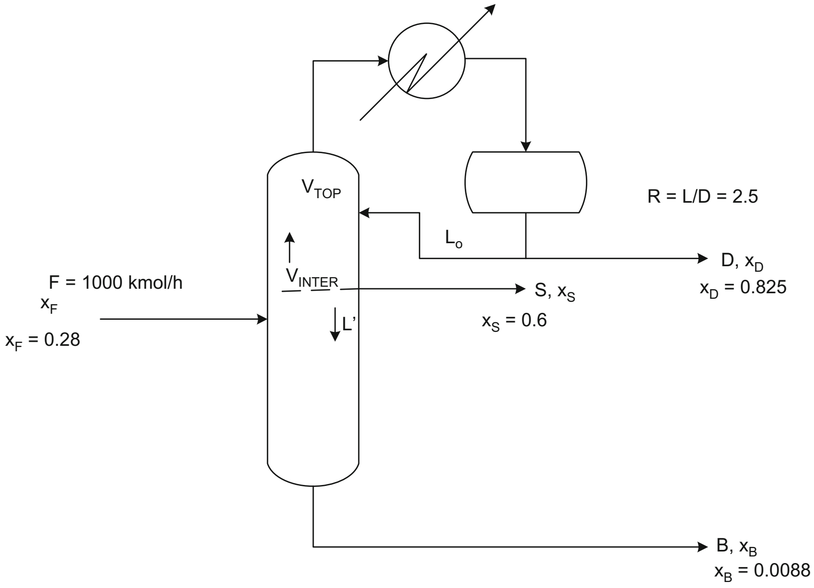


Figure 10-130a A liquid side stream column.

Solution



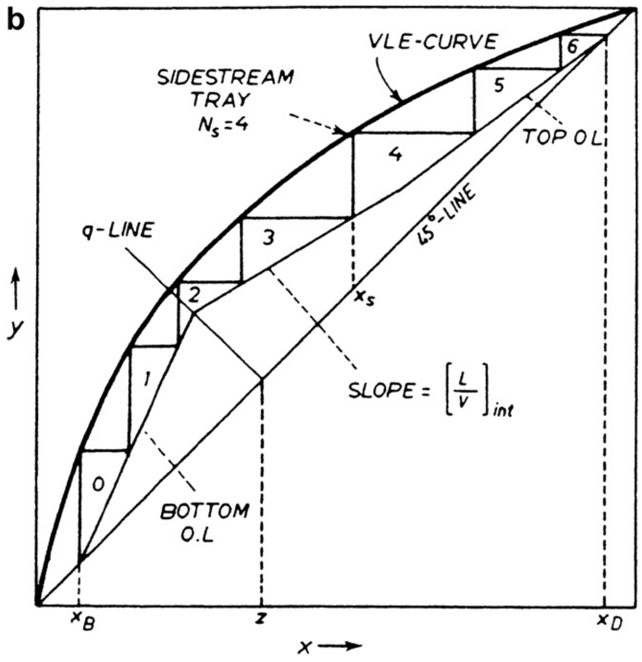


Figure 10-130b The McCabe-Thiele diagram with a liquid side stream column.

Assuming constant molal overflow:

(a) overall material

$$F = D + S + B \qquad (1)$$

The component balance on the more volatile component at the top of the column and side stream is:

$$Fx_F = Dx_D + Sx_S \qquad (2)$$

Since it is required to recover 98 % of the ethanol in the feed, then:

$$(0.98)\,(100)\,(0.28) = (0.825)D + 0.6S$$

Since the molar flow rate of the distillate is twice that of the side stream:

$$S = \frac{D}{2}$$

The feed is at its boiling point, $q = 1$ or $q/(q - 1) = \infty$

$274.4 = 0.825\ D + 0.3D$
Hence,
$D = 243.9$ kmol/h

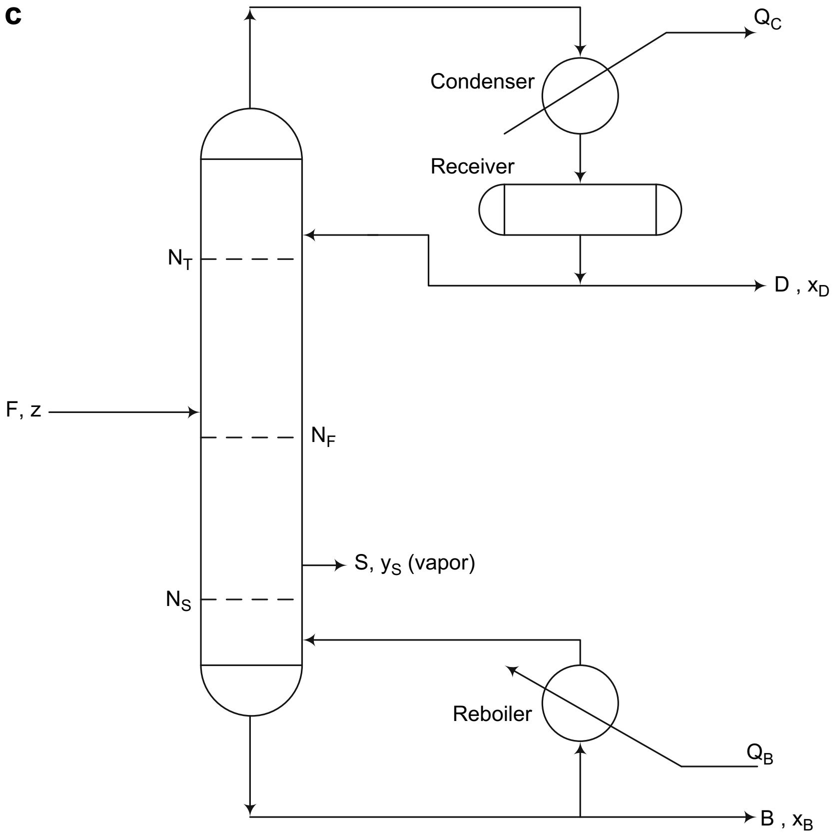


Figure 10-130c A vapor side stream column.

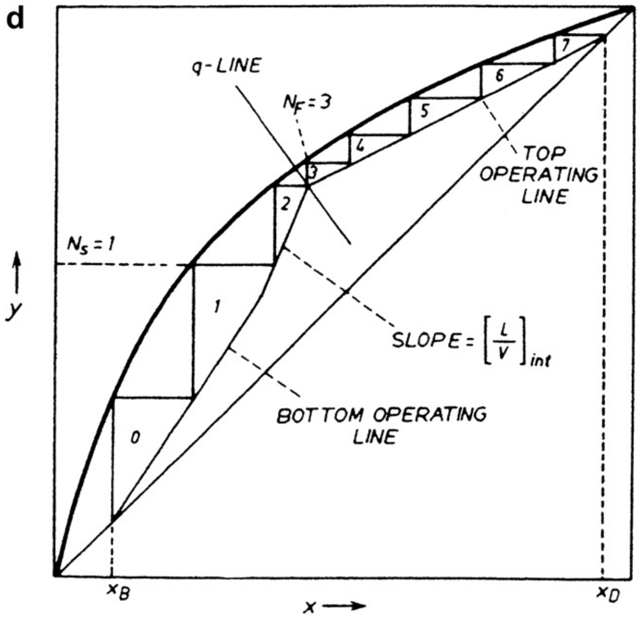


Figure 10-130d The McCabe-Thiele diagram with a vapor side stream column.

and

S = 243.9/2 = 121.95 kmol/h

Material balance on the upper operating line:

$$V = L + D$$

Component balance is:

$$V\,y = Lx + Dx_D$$

The equation of the upper operating line is:

$$y = \frac{L}{V}x + \frac{D}{V}x_D$$

where R = L/D or V = (R + 1)D

$$y = \frac{R}{(R+1)}\,x + \frac{x_D}{(R+1)}$$

The intercept of the upper operating line (UOL) is

$$I = \frac{x_D}{(R+1)} = \frac{0.825}{3.5} = 0.236$$

The bottoms flow rate is:

$$B = F - D - S$$

$$= 1000 - 243.9 - 121.95$$
$$= 634.15 \text{ kmol/h}$$

But 2 % of the ethanol in the feed is removed at the bottoms, that is:

$$0.02\ F\,x_F = B\,x_B$$

$$x_B = \frac{0.02 \times 1000 \times 0.28}{634.15}$$

$$= 0.0088$$

(b) The intermediate slope is L′/V′ assumed a constant molal overflow.

$$R = L_o/D = 2.5, L_o = 2.5\ D = 2.5 \times 243.9$$
$$= 609.75 \text{ kmol/h}$$

Mass balance at the top of the column is:

$$V_{Top} = L_o + D$$

$$= 609.75 + 243.9$$
$$= 853.65 \text{ kmol/h}$$

Side stream is liquid at its boiling point; therefore a mass balance on the side stream is:

$$V_{INTER} + L_o = S + L' + V_{TOP}$$

But $V_{INTER} = V_{TOP}$

Therefore $L' = L_o - S$

$= 609.75 - 121.95$

$= 487.8$ kmol/h

The slope of the side stream is:

$$\frac{L'}{V'} = \frac{487.8}{853.65} = 0.571$$

The number of sieve plates from the McCabe-Thiele diagram (Figure 10-131) is 13. The actual number of sieve plates with a plate efficiency of 60% is:

$$\text{Actual Number of plates} = \frac{\text{Number of plates}}{\text{Efficiency}}$$
$$= 13/0.60$$
$$= 21.6 \text{ sieve plates, i.e. } 22.$$

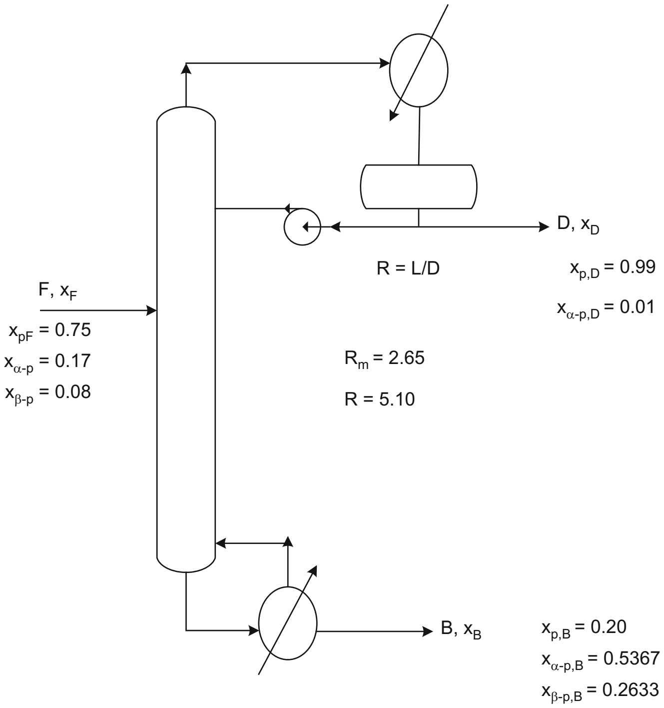
(c) Use an azeotrope extracting agent e.g. benzene, cyclohexane, or adjust the pressure to change the composition of the azeotrope. This will require a greater ΔP shift.

Example 10-54

The feed to a continuous distillation column operating at atmospheric pressure contains 75 mole per cent pyridine, 17 mole per cent α-picoline and 8 mole per cent β-picoline. The distillate contains 99 mole per cent pyridine, 1 mole per cent α-picoline, whilst the residue 20 mole per cent pyridine, 53.67 mole per cent α-picoline and 26.33 mole per cent β-picoline. The relative volatility of pyridine with respect to β-picoline is 2.32 and the relative volatility of α-picoline with respect to β-picoline is 1.54 at the mean column temperature. If the minimum reflux and actual operating reflux are 2.65:1 and 5:1 respectively, calculate:

- **a.** the approximate number of theoretical plates to accomplish the above separation
- **b.** the approximate location of the feed plate.

Solution



a. The approximate number of theoretical plates to accomplish the above separation is as follows:

Using Fenske's equation to determine the minimum number of stages at total reflux:

$$N_m = \frac{\log\left\{\left(\frac{x_{LK}}{x_{HK}}\right)_D \left(\frac{x_{HK}}{x_{LK}}\right)_B\right\}}{\log(\alpha_{LK}/\alpha_{HK})} \qquad (10\text{-}182)$$

where:

$$x_{LK,D} = 0.99, x_{HK,D} = 0.01,$$
$$x_{HK,B} = 0.5367, x_{LK,B} = 0.20$$
$$\alpha_{LK} = 2.32, \alpha_{HK} = 1.54$$

The minimum number of stages is:

$$N_m = \frac{\log\left\{\left(\frac{0.99}{0.01}\right)\left(\frac{0.5367}{0.20}\right)\right\}}{\log(2.32/1.54)}$$

$$= 13.6 \text{ (14 stages)}$$

$R_m = 2.65$, $R = 5.10$

Using Gilliland correlation, the abscissa is:

$$\frac{R - R_m}{R+1} = \frac{5.10 - 2.65}{(5.10+1)} = 0.40 \qquad (10\text{-}219)$$

The corresponding ordinate on Gilliland correlation is:

$$\frac{N - N_m}{N+1} = y = 0.27 \qquad (10\text{-}220)$$

$$N - N_m = y\ (N+1)$$

$$N = (N_m + y)/(1 - y) \qquad (10\text{-}453)$$

The number of theoretical plates is $N = \frac{N_m + y}{(1-y)} = \frac{13.6 + 0.27}{(1 - 0.27)}$

N = 19 stages.

b. The approximate location of the feed plate is:

Using the Kirkbride's equation for the feed plate location:

$$\log\left(\frac{m}{p}\right) = 0.206 \log\left\{\frac{B}{D}\left(\frac{x_{HK}}{x_{LK}}\right)_F \left[\frac{(x_{LK})_B}{(x_{HK})_D}\right]^2\right\} \qquad (10\text{-}462)$$

where

m = number of theoretical stages above the feed plate.
p = number of theoretical stages below the feed plate.

Basis of the feed flow rate, F = 100 kmol/h.

The overall mass balance of the column is:

$$F = D + B \qquad (1)$$
$$100 = D + B \qquad (2)$$
$$D = 100 - B \qquad (3)$$

Component balance on the more volatile component, pyridine (MVC) is:

$$F\,x_F = D\,x_D + B\,x_B \qquad (4)$$
$$100 \times 0.75 = D \times 0.99 + B \times 0.2 \qquad (5)$$

Substituting Eq. (3) into Eq. (5) gives:

$$75 = 0.99\,(100 - B) + 0.2B \qquad (6)$$
$$75 = 99 - 0.99B + 0.2B \qquad (7)$$

$B = 30.37$ kmol/h
$D = 100 - 30.37$
$= 69.63$ kmol/h

Substituting these values in Kirkbride's feed plate location equation gives:

$$\log\left(\frac{m}{p}\right) = 0.206 \log\left\{\frac{30.37}{69.63}\left(\frac{0.17}{0.75}\right)\left[\frac{0.2}{0.01}\right]^2\right\}$$

$$\log\left(\frac{m}{p}\right) = 0.329 \qquad (8)$$

$$m/p = 2.133 \qquad (9)$$
$$m = 2.133p \qquad (10)$$
$$m + p = 19 \qquad (11)$$

Substituting Eq. 10 into Eq. 11 gives:

$$2.133p + p = 19 \qquad (12)$$

$$3.133p = 19$$
$$p = 6.06 \text{ stages}$$
$$m = 12.94 \text{ (13 stages)}$$

The feed plate is between 12th – 13th stage from the top of the column.

Using Akashah et al. [317] Equation 10-462b to determine the location of the feed plate from Equation 10-462 or 10-462a:

$$\log\left[\frac{m}{p}\right] = 0.206 \log\left\{\left(\frac{B}{D}\right)\left(\frac{x_{HK}}{x_{LK}}\right)_F\left[\frac{(x_{LK})_B}{(x_{HK})_D}\right]^2\right\} \qquad (10\text{-}462)$$

or

$$\frac{m}{p} = \left\{\left(\frac{B}{D}\right)\left(\frac{x_{HK}}{x_{LK}}\right)_F\left[\frac{(x_{LK})_B}{(x_{HK})_D}\right]^2\right\}^{0.206} \qquad (10\text{-}462a)$$

$$m = p[\text{calculated from Eq.10} - 462a] - 0.5 \log N \qquad (10\text{-}462b)$$

where N = 19 and p = 6.06 from Kirkbride's Equation 10-462 or 10-462a, we have:

$$m = (6.06)\left\{\left(\frac{30.37}{69.63}\right)\left(\frac{0.17}{0.75}\right)\left(\frac{0.2}{0.01}\right)^2\right\}^{0.206} - 0.5 \log(19)$$

$$= 12.29 \text{ (12 stages)}$$

$$m + p = N \qquad (10\text{-}462c)$$

$$p = 19 - 12$$
$$= 7 \text{ stages}$$

10.50 Chou and Yaws Method [96]

This method for multicomponent distillation involving more than one feed and more than one side stream requires a reliable minimum reflux ratio.

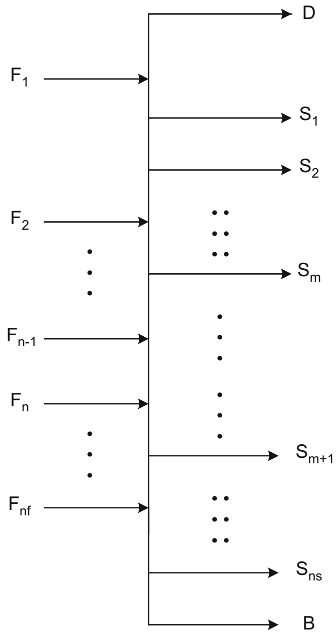
In summary, the calculation procedure is as presented by the authors.

For the systems rated above, the minimum reflux ratio is [96]:

$$R_{min} = R_F + R_{OF} + R_s \qquad (10\text{-}551)$$

$$R_{min} = R_F + \sum F_{FR,j}\, F_j + \sum F_{SR,\,k}\, S_k \qquad (10\text{-}552)$$

This includes recognizing the contribution from the feed (R_F), "other feeds" (R_{OF}), and sidestreams (R_S). The R_F portion is determined by assuming no other feeds or sidestreams are present. The R_{OF} and R_S parts represent the summation of the contributions of other feeds and sidestreams to the overall column minimum reflux ratio. The calculation sequence consists basically of three steps, here reproduced by permission of Chemical Engineering, Chou and Yaws, April 25, 1988, All rights reserved [96]:



The Column

1. Determine Underwood θ for each feed, using equation involving feed concentration:

   $\theta_1, \theta_2, \ldots.., \theta_{nf}$

$$1 - q_F = \sum_{i=1}^{c} \frac{\alpha_i\ z_i, F_n}{\alpha_i - \theta_n} \qquad (10\text{-}553)$$

2. Determine the “minimum reflux ratio” candidate for each feed:

   $R_{min,1}, R_{min,2}, \ldots\ldots.., R_{min,nf}$

$$\begin{aligned} R_{min,n} &= R_F + R_{oF} + R_S \\ &= R_{F,n} + \sum_{j=1}^{n-1} F_{FR,j}\ F_j + \sum_{k=1}^{m} F_{SR,k}\ S_k \qquad (10\text{-}554) \end{aligned}$$

$$\text{where: } R_{F,n} = \sum_{i=1}^{c} \frac{\alpha_i\ x_{i,D}}{\alpha_i - \theta_n} - 1$$

$$F_{FR,j} = -\frac{1}{D}\left(\sum_{i=1}^{c} \frac{\alpha_i\ Z_i, F_j}{\alpha_i - \theta_n} + q_{Fj} - 1\right)$$

$$F_{SR,k} = \frac{1}{D}\left(\sum_{i=1}^{c} \frac{\alpha_i\ Z_i, S_k}{\alpha_i - \theta_n} + q_{Sk} - 1\right)$$

3. Compare the candidates for minimum reflux ratio. The candidate having the largest (maximum) numerical value is the minimum reflux ratio for the column.

   $R_{min} = \mathrm{Max}(R_{min,1}, R_{min,2}, \ldots\ldots.R_{min,nf})$

Example 10-55: Distillation with Two Sidestreams Feeds

Data for Example 10-55, which includes two sidestreams.

		Mole Fraction				
		Feed		Distillate	Sidestream	
Component	**Relative Volatility α**	z_i , F_1	z_i , F_2	x_D	z_i , S_1	z_i , S_2
1 (LK)	2.0	0.38	0.45	0.999	0.975	0.900
2 (HK)	1.0	0.20	0.30	0.001	0.025	0.099
3 (HK + 1)	0.5	0.22	0.25	0	0	0.001

Feeds: $F_1 = 50$ mol/hr, $q_{F1} = 1$ (saturated liquid)
$F_2 = 100$ mol/hr, $q_{F2} = 0$ (saturated vapor)

Sidestreams: $S_1 = 20$ mol/hr, $q_{S1} = 1$ (saturated liquid)
$S_2 = 20$ mol/hr, $q_{S2} = 1$ (saturated liquid)

Distillate: $D = 36$ mol/hr

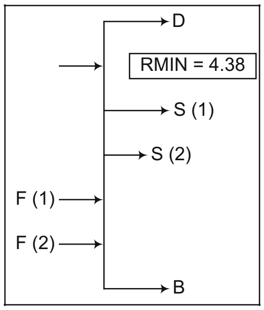
Minimum reflux and other results for Example 10-55.

1. UNDERWOOD THETAS:
   FOR FEED 1 THETA (1) = 1.164
   FOR FEED 2 THETA (2) = 1.485

2. MINIMUM REFLUX CANDIDATES:
   FOR FEED 1 RMIN (1) = 3.450271
   FOR FEED 2 RMIN (2) = 4.375502

3. TRUE MINIMUM REFLUX RATIO:
   RMIN = 4.38

Column representation of results of Example 10-55.



where

B = bottoms flowrate, mol/h
c = number of components
D = distillate flowrate, mol/h
F = flowrate of feed, mol/h
F_j = flowrate of feed j, mol/h

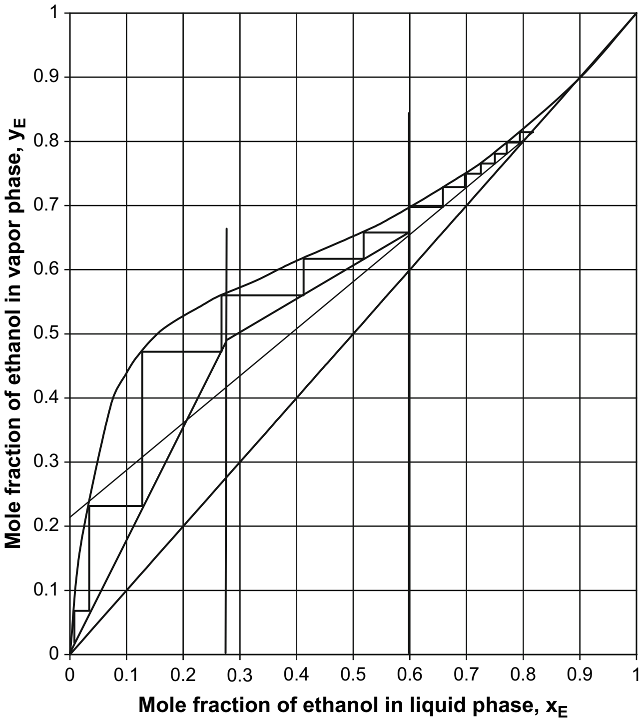


Figure 10-131 McCabe-Thiele diagram for Example 10-53.

F_{FR} = factor for contribution of other feed flow to minimum reflux
F_{FRj} = factor for contribution of feed j flow to minimum reflux
F_{SR} = factor for contribution of side stream flow to minimum reflux,
$F_{SR,k}$ = factor for contribution of sidestream k flow to minimum reflux
HK = heavy key component
L = liquid flowrate, mol/h
LK = light key component
nf = number of feeds
ns = number of sidestreams
m = number of sidestreams above feed n
q_F = thermal condition of feed
q_S = thermal condition of sidestream
R = reflux ratio
R_F = feed component of minimum reflux
$R_{F,n}$ = feed component of minimum reflux for feed n
R_{OF} = other feeds component of minimum reflux
R_{min} = minimum reflux ratio
R_S = sidestream component of minimum reflux
S = flowrate of sidestream, mol/h
S_k = flowrate of sidestream k, mol/h
V = vapor flowrate, mol/h
x_i = mole fraction of component i in liquid
y_i = mole fraction of component i in vapor
$z_{i,F}$ = mole fraction of component i in feed
$z_{i,Fj}$ = mole fraction of component i in feed j
$z_{i,S}$ = mole fraction of component i in sidestream
$z_{i,Sk}$ = mole fraction of component i in sidestream k
α = relative volatility
θ = Underwood parameter

Subscripts

B = bottoms
D = distillate
F = feed
F_j = feed j
F_n = intermediate feed

10.51 Optimum Reflux Ratio and Optimum Number of Trays Calculations

Van Winkle and Todd have developed shortcut graphical methods which are very useful for estimating the optimum reflux ratio RR_{opt}, and optimum number of stages N_{opt}, such to minimize operating and investment costs for a given separation of multicomponent systems in a fractionation operation. Their methods were based on:

1. Using the shortcut methods of Fenske for the minimum number of stages as shown in Figure 10-132.
2. Using the Underwood method for the minimum reflux ratio (Figures 10-133, 10-134, 10-135 and 10-136).
3. Using Gilliland's correlations for determining the relationship between theoretical stages and reflux ratio to their minimum value.

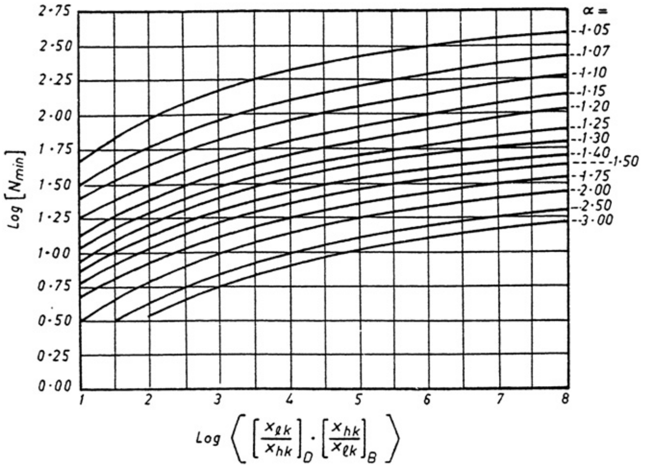


Figure 10-132 Graphical representation of Fenske equation for estimating minimum plates (Source: P. Chattopadhyay [293]).

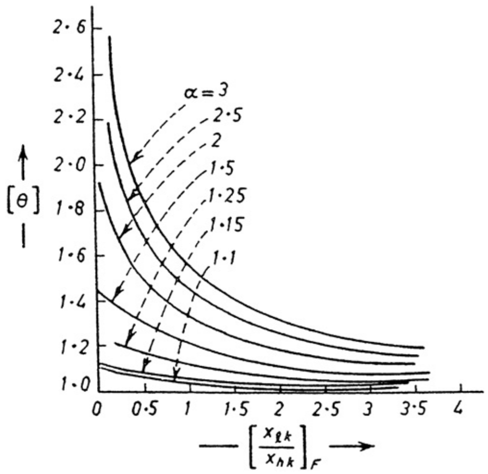


Figure 10-133 Underwood's parameter (θ) as a function of the ratio of the keys in the feed (Source: P. Chattopadhyay [293]).

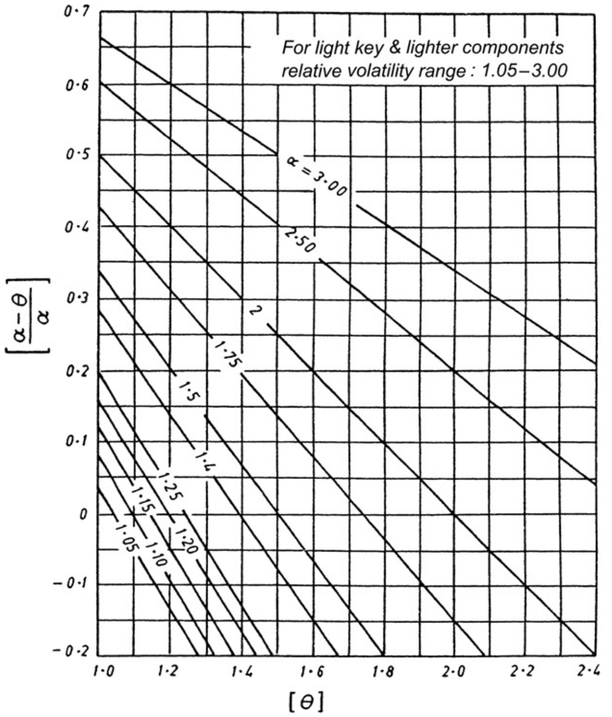


Figure 10-134 Dependence of $\left[\frac{\alpha-\theta}{\alpha}\right]$ on θ for the light key and lighter components for calculating underwood's ($RR_m + 1$) (Source: P. Chattopadhyay [293]).

This method has been tested on several hundred cases of multicomponent distillation in which α, $(x_{LK}/x_{HK})_F$, percent recovery of LK in the distillate and percent recovery of the HK in the bottoms were varied over a practical range. The following observations were made about the result:

Effect of Pressure: Pressure exerts no appreciable effect on the optimum values of total number of trays and reflux ratio.

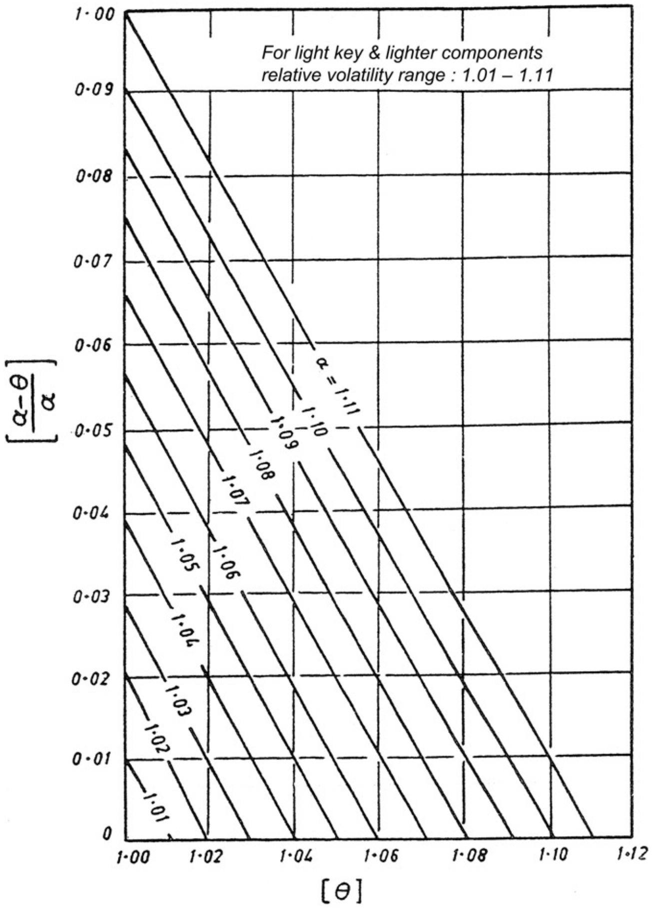


Figure 10-135 Dependence of $\left[\frac{\alpha-\theta}{\alpha}\right]$ on θ for the light key and lighter components for calculating underwood's ($RR_m + 1$) (Source: P. Chattopadhyay [293]).

Effect of Feed Rate: The optimum reflux ratio RR_{opt} and optimum number of stages N_{opt} vary with the changes in feed flow rates. The value of $(N/N_{min})_{opt}$ known as the tray factor increases with the increase in feed rate while the value of $(RR/RR_{min})_{opt}$ known as the reflux factor decreases at the same time.

Material of Construction: The materials of construction mainly used are plain carbon steel and stainless steel; Monel metal of tower and trays has a direct effect on $(N/N_{min})_{opt}$ and $(RR/RR_{min})_{opt}$. However, with the increase in the cost of material M_c, the optimum values of (N/N_{min}) and (RR/RR_{min}) decrease.

Utility Cost: The inclusion of utility cost (e.g. cost of steam + cost of cooling water + cost of electricity) in reducing the total cost greatly affects the RR_{opt} and N_{opt}. When the utility cost (also known as the operating cost) is taken into account, optimum level of (N/N_{min}) always increases whereas the optimum level of (RR/RR_{min}) always decreases.

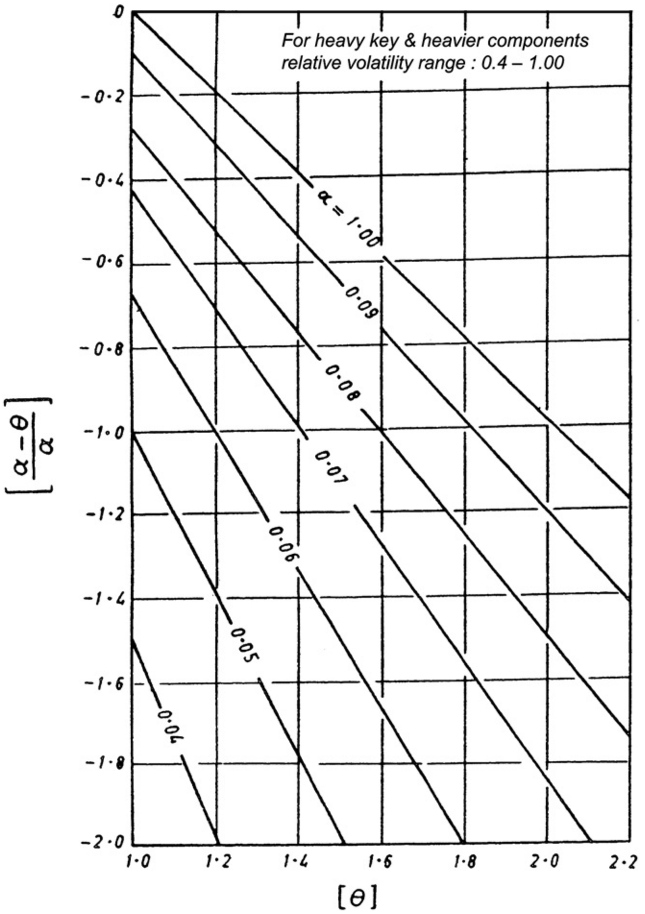


Figure 10-136 Dependence of $\left[\frac{\alpha-\theta}{\alpha}\right]$ on θ for the light key and lighter components for calculating underwood's ($RR_m + 1$) (Source: P. Chattopadhyay [293]).

Correlations

The overall procedure is based on the correlation of $(N/N_{min})_{opt}$ and $(RR/RR_{min})_{opt}$ for a given reference case. A base case is selected and then correction factors are correlated to take into account the effects of feed rates, cost of material and the number of years of equipment amortization.

Originally, the selected base case is:

A 3m diameter column of plain carbon steel as the material of construction, an operating pressure of 696 kPa and 2 year amortization. The optimum value of (N/N_{min}) for both the reference case and the range of conditions was correlated as a function of the Fenske separation factor, using α as the parameter as illustrated in Figure 10-137 to estimate $(N/N_{min})_{ref}$ values.

To account for the effects of various feed rates, the feed correction factor ϕ was correlated as a function of feed rate, using α as the parameter as shown in Figure 10-138. Figure 10-138 is used to evaluate the correction factor ϕ for $(N/N_{min})_{ref}$ and ϕ is used to calculate $(N/N_{min})_{opt}$ as:

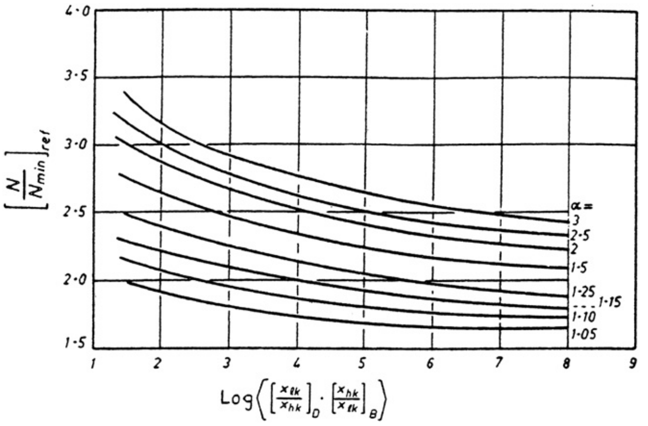


Figure 10-137 Correlation of the ratio of optimum to minimum number of trays as a function of Fenske separation factor (Source: P. Chattopadhyay [293]).

$$\left(\frac{N}{N_{min}}\right)_{opt} = \phi \cdot \Gamma \cdot \left(\frac{N}{N_{min}}\right)_{ref} \tag{10-555}$$

Γ is the correction factor for $(N/N_{min})_{ref}$ for the depreciation period and material of construction. This correction factor is obtained from Figure 10-139 which plots Γ as a function of (n/M_c) for various values of α. $(RR/RR_{min})_{opt}$ is obtained from Figure 10-140, and $(N/N_{min})_{ref}$ correction factor for feed ϕ is obtained from Figure 10-141; $(RR/RR_{min})_{opt}$ correction factor for amortization Δ is determined from Figure 10-142.

Procedure

In order to determine the optimum combination of reflux ratio and the number of stages based on minimum yearly operating cost, the following parameters are required:

1. Feed rate.
2. Feed condition and feed properties.
3. Operating pressure.
4. Operating temperatures.
5. Relative volatilities of the components.
6. Specified separation of key components.
7. Material costs.
8. Amortization years.

The algorithm is as follows:

1. Determine the value of N_{min}. Use either Figure 10-132 or Fenske equation (10-182).
2. Determine RR_{min} from Underwood's method. Use Figure 10-133 to determine the Underwood's

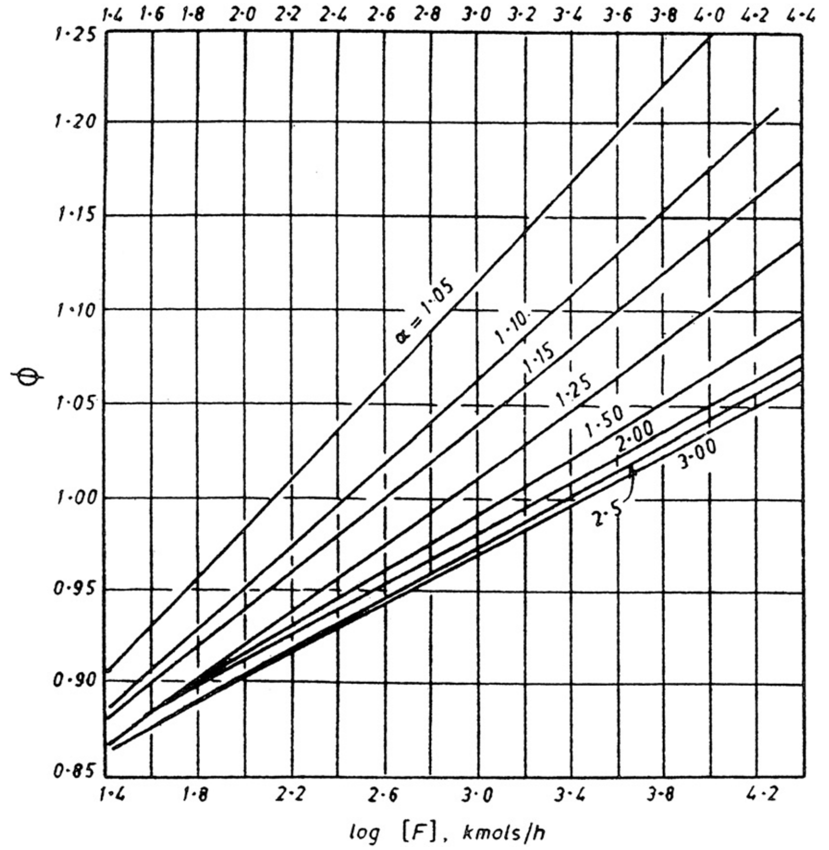


Figure 10-138 Feed rate correction factor for $(N/N_{mim})_{ref}$ (Source: P. Chattopadhyay [293]).

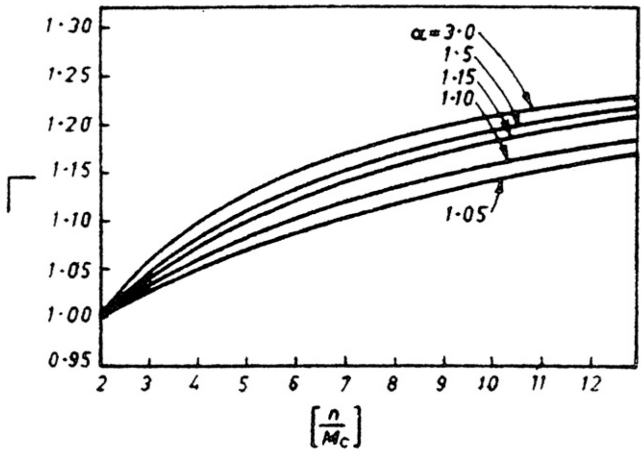


Figure 10-139 Correction factor for $(N/N_{mim})_{ref}$ for the number of years amortized (n), divided by the cost of materials (M_c) (Source: P. Chattopadhyay [293]).

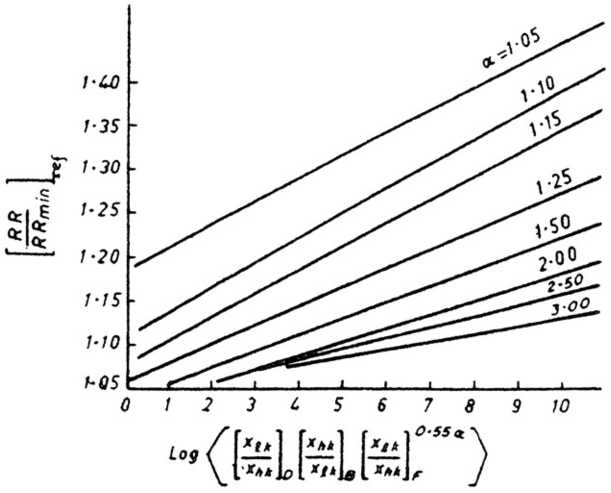


Figure 10-140 Correlation of optimum is to minimum reflux ratio for the reference case $(RR/RR_{mim})_{ref}$ (Source: P. Chattopadhyay [293]).

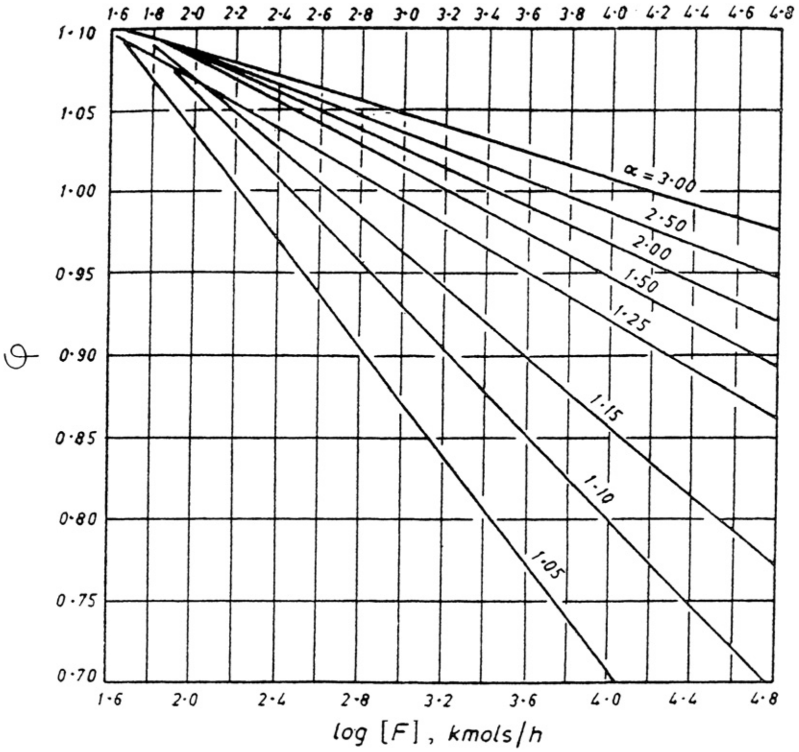


Figure 10-141 Feed rate correction factor for $(RR/RR_{mim})_{ref}$ (Source: P. Chattopadhyay [293]).

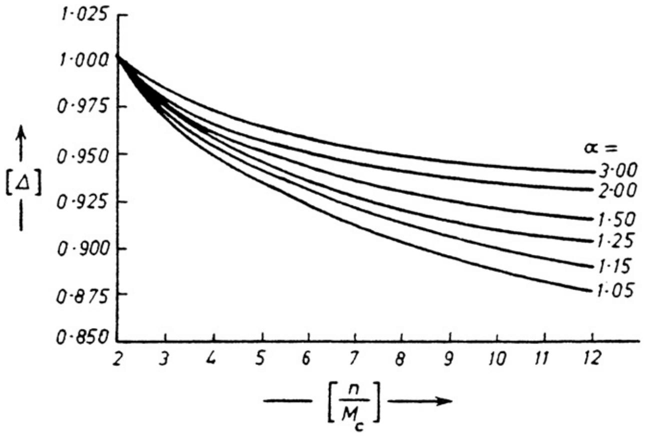


Figure 10-142 Correction factor for $(RR/RR_{mim})_{ref}$ for the depreciation period and material of construction (Source: P. Chattopadhyay [293]).

parameter θ. Alternatively use computer program PROG 104 or the spreadsheet program Example 10-41.xls. Use Equations 10-437 and 10-438 or Figures 10-134, 10-135, 10-136 to determine RR_{min}.

3. Obtain the reference value $(N/N_{min})_{ref}$ from Figure 10-137, using Fenske separation factor for the correct α.
4. Determine the feed correction factor ϕ from Figure 10-138. Use the correct feed rate (F) and α.
5. The amortization time (n) and the material cost factor (M_c) are used to obtain the (N/N_{min}) correction factor (Γ) for depreciation and material of construction, from Figure 10-139. Calculate the optimum value of N/N_{min} from:

$$\left(\frac{N}{N_{min}}\right)_{opt} = \phi \cdot \Gamma \cdot \left(\frac{N}{N_{min}}\right)_{ref} \tag{10-555}$$

6. Using the value of N_{min} from step 1 and the value of the RHS of Equation 10-555 in step 5, determine the optimum value of the number of theoretical stages required.
7. From Figure 10-140 determine $(RR/RR_{min})_{ref}$ on the basis of empirical separation factor (plotted in the abscissa).
8. From Figure 10-141 determine (RR/RR_{min}) correction factor φ for the feed. Use the correct feed rate (F) and α.
9. For the selected amortization time (n) and material cost factor (M_c), read out the correction factor Δ for (RR/RR_{min}) from Figure 10-142. Calculate the optimum value of (RR/RR_{min}) from

$$\left(\frac{RR}{RR_{min}}\right)_{opt} = \phi \cdot \Delta \cdot \left(\frac{RR}{RR_{min}}\right)_{ref} \tag{10-556}$$

10. With RR_{min} from step 2 and the value of the RHS of Equation 10-556, the optimum value of reflux ratio RR_{opt} is determined.

Generally, the optimum reflux ratio for a multicomponent system is obtained by comparing operating (energy) costs with the capital costs and then optimizing the two. Results of previous economic designs have been compiled, compared and reduced to a relationship of (RR/RR_{min}) or equivalently N/N_{min} based on the type of heat sink employed. Table 10-46 shows the economic ranges of reflux to minimum reflux and the resulting values of stages to minimum stages.

Example 10-56: Minimum and Optimum values of theoretical trays and reflux ratio

A multicomponent system comprising of four hydrocarbons: isobutane (iC_4H_{10}), n-butane (nC_4H_{10}), isopentane (iC_5H_{12}), and n-pentane (nC_5H_{12}) is to be separated as specified in the table.

Component	Feed moles	Equilibrium constant K	Relative volatility α	Distillate moles	Bottoms moles
iC_4H_{10}	0.06	2.15	2.5749	0.0596	0.0004
nC_4H_{10} (LK)	0.17	1.70	2.0359	0.1615	0.0085
iC_5H_{12} (HK)	0.32	0.835	1.0000	0.0160	0.3040
nC_5H_{12}	0.45	0.70	0.8383	0.0054	0.4446
Total	1.00			0.2425	0.7575

The column operating pressure = 103 kPa
Top temperature = 420 K
Bottom temperature = 470 K
95 per cent recovery of both keys is desired.
Feed is saturated liquid at its boiling point (q = 1).
Take: n-butane (nC_4H_{10}) as light key component
i-pentane (iC_5H_{12}) as heavy key component

Table 10-46 Economic R/R_{min} and N/N_{min} vs. Heat Sink Source

Method of condensing the reflux	R/R_{min}	N/N_{min}
Low-level refrigeration (−300 to 150°F)	1.05–1.10	2.0–3.0
High-level refrigeration (−150 to 50°F)	1.10–1.20	1.8–2.0
Cooling water at cost of circulation and limited treating	1.20–1.5	1.0–1.8
Air cooling	1.40–1.5	1.6–1.8

Input Data

Material of construction	= Carbon steel for all equipment
Material cost factor	= 1
Depreciation period	= 10 years
Feed rate	= 500 kmol/h
Tray efficiency	= 85%

Determine the following: $N_{min}, N_{opt}, R_{min}$ and R_{opt}.

Solution

Table 10-47 gives the computer results of PROG 104.

From Table 10-47:
Minimum reflux ratio, $RR_{min} = 2.8036$
Minimum number of stages, $N_{min} = 8.3$
Underwood constant, $\theta = 1.6213$
Relative volatility, $\alpha_{LK/HK} = 2.0359$

The following procedure is used to calculate N_{opt} and R_{opt}:

1. Graphical representation of Fenske equation for estimating minimum plates as:

$$\log\left[\left(\frac{x_{LK}}{x_{HK}}\right)_D \left(\frac{x_{HK}}{x_{LK}}\right)_B\right] \text{ from Figure 10-137:}$$

$$\log\left[\left(\frac{0.6660}{0.066}\right)\left(\frac{0.4013}{0.0112}\right)\right] = 2.558$$

2. Underwood constant, $\theta = 1.6213$

$$\left(\frac{x_{LK}}{x_{HK}}\right)_F = \frac{0.17}{0.32} = 0.5313$$

3. Correlation of the ratio of optimum to minimum number of trays as a function of Fenske separation factor from Figure 10-137

$$\text{At } \log\left[\left(\frac{0.6660}{0.066}\right)\left(\frac{0.4013}{0.0112}\right)\right] = 2.558, \text{ and}$$

$$\alpha_{LK/HK} = 2.0359$$

$$\left(\frac{N}{N_{min}}\right)_{ref} = 2.75$$

Table 10-47 Computer Output for Multicomponent System Fractionation.

```
Data name: Data104.Dat
EQUIL
0.06                2.15
0.17                1.70
0.32                0.835
0.45                0.70
0.95                0.95
3.1                 1.3
Component number  Feed moles  Rel. volatility alpha  Distillate %  Moles   Bottoms %  Moles
1                 0.0600      2.5749                 99.2532       0.0596  0.7468     0.0004
2                 0.1700      2.0359                 95.0000       0.1615  5.0000     0.0085
3                 0.3200      1.0000                 5.0000        0.0160  95.0000    0.3046
4                 0.4500      0.8383                 1.2067        0.0054  98.7633    0.4446
Component number  Feed moles  Mol fract. XF  Distillate moles  Mol fract. XD  Bottoms moles  Mol. fract. XB
1                 0.0600      0.0600         0.0596            0.2456         0.0004         0.0006
2                 0.1700      0.1700         0.1615            0.6660         0.0085         0.0112
3                 0.3200      0.3200         0.0160            0.0660         0.3040         0.4013
4                 0.4500      0.4500         0.0054            0.0224         0.4446         0.5869
The feed condition, Q:                                                      1.0
The heavy key component number is:                                          3
Percentage recovery of the light key component in the distillate is (%):   95.00
Percentage recovery of the heavy key component in the bottoms is (%):      95.00
Total moles in the distillate:                                              0.2425
Total moles in the bottoms:                                                 0.7575
Total moles in the feed:                                                    1.0000
Underwood constant:                                                         1.6213
Factor for the reflux ratio:                                                1.3000
Minimum reflux ratio:                                                       2.8036
Actual reflux ratio:                                                        3.6447
Minimum number of stages is:                                                8.3
Number of theoretical plates in the column:                                 16.2
The position of the feed plate is:                                          6.7
```

4. Correction factor ϕ for feed rate using Figure 10-138

$F = 500$ kmol/h
$\log(F) = \log(500) = 2.698$
From Figure 10-138, $\phi = 0.97$

5. Correction factor Γ for $(N/N_{min})_{ref}$ for the number of years amortized (n), divided by the cost of materials (M_c).

$n = 10$ years, $M_c = 1.0$

$$\frac{n}{M_c} = \frac{10}{1} = 10, \ \alpha_{LK/HK} = 2.0359$$

From Figure 10-139, $\Gamma = 1.185$

6. Optimum value of $\dfrac{N}{N_{min}}$ is:

$$\left(\frac{N}{N_{min}}\right)_{opt} = \phi \ \ \Gamma \ \left(\frac{N}{N_{min}}\right)_{ref}$$

$= (0.97)\ (1.185)\ (2.75)$
$= 3.16$

7. Optimum number of theoretical stages, where $N_{min} = 8.3$ (Table 10-47).

$$N_{opt} = N_{min}\left(\frac{N}{N_{min}}\right)_{opt}$$

$= (8.3)\ (3.16)$
$= 26.24$

8. Correlation of optimum to minimum reflux ratio for the reference case $(RR/RR_{min})_{ref}$ using composition values of LK and HK in Table 10-47.

$$\log\left[\left(\frac{x_{LK}}{x_{HK}}\right)_D \left(\frac{x_{HK}}{x_{LK}}\right)_B \left(\frac{x_{LK}}{x_{HK}}\right)_F^{0.55\ \alpha}\right]$$

$$= \log\left[\left(\frac{0.666}{0.066}\right)\left(\frac{0.4013}{0.0112}\right)\left(\frac{0.17}{0.32}\right)^{(0.55\ )(2.0359)}\right]$$

$= 2.25058$

From Figure 10-140, $\alpha_{LK/HK} = 2.0359$

$$\left[\frac{RR}{RR_{min}}\right]_{ref} = 1.06$$

Table 10-48 Economic Optimum Reflux Ratio For Typical Petroleum Fraction Distillation near 1 atm[a].

	Factor for optimum reflux **$f = (R_{opt}/R_m) - 1$** **$R_{opt} = (1 + f) R_m$**								**Factor for optimum trays** **N_{opt}/N_m**		
	$N_m = 10$			**$N_m = 20$**			**$N_m = 50$**		**$N_m = 10$**	**$N_m = 20$**	**$N_m = 50$**
	Rm			**R_m**			**R_m**		**R_m**	**R_m**	**R_m**
	1	**3**	**10**	**1**	**3**	**10**	**1**	**10**	**1 to 10**	**1 to 10**	**1 to 10**
Base case	0.20	0.12	0.10	0.24	0.17	0.16	0.31	0.21	2.4	2.3	2.1
Payout time 1 yr.	0.24	0.14	0.12	0.28	0.20	0.17	0.37	0.24	2.2	2.1	2.0
Payout time 5 yr.	0.13	0.09	0.07	0.17	0.13	0.10	0.22	0.15	2.7	2.5	2.2
Steam cost \$0.30/M lb	0.22	0.13	0.11	0.27	0.16	0.14	0.35	0.22	2.3	2.1	2.0
Steam cost \$0.75/M lb	0.18	0.11	0.09	0.21	0.13	0.11	0.29	0.19	2.5	2.3	2.1
$G_a = 50$ lb mole/(hr)(sq.ft)	0.06	0.04	0.03	0.08	0.06	0.05	0.13	0.08	3.1	2.8	2.4

[a] The "base case" is for payout time of 2 yr, steam cost of \$0.05/1000 lb, vapor flow rate Ga = 15 lb mol/(hr)(sq. ft.). Although the capital and utility costs are prior to 1975 and are individually far out of date, the relative costs are roughly the same so the conclusions of this analysis are not far out of line. Conclusion: For systems with nearly ideal VLE, R is approx. $1.2R_{min}$ and N is approx. $2.0 N_{min}$.
Source: Happen and Jordan, Chemical Process Economics, Decker, New York, 1975.

9. Correction factor φ for feed rate from Figure 10-141,

$$\log(F) = 2.70 \text{ at } \alpha_{LK/HK} = 2.0359$$

$$\varphi = 1.04$$

10. Depreciation and material of construction correction factor.

$n = 10$ years, $M_c = 1.0$, $n/Mc = 10$, $\alpha_{LK/HK} = 2.0359$

From Figure 10-142, $\Delta = 0.9375$

$$\left(\frac{RR}{RR_{min}}\right)_{opt} = \varphi \cdot \Delta \cdot \left(\frac{RR}{RR_{min}}\right)_{ref}$$

$$= 1.0335$$

11. Optimum reflux ratio, RR_{opt}, where $RR_{min} = 2.8036$ (Table 10-47).

$$RR_{opt} = RR_{min}\left(\frac{RR}{RR_{min}}\right)_{opt}$$

$$= (2.8036)\,(1.0335)$$
$$= 2.897$$

Generally, the reflux ratio affects the cost of the column, both in the number of trays and the diameter. It also affects the cost of operation, i.e. the costs of heat and cooling supply and power for the reflux pump. Therefore, the basis for choice of an optimum reflux ratio involves an economic balance. Table 10-48 summarizes an economic balance of optimum reflux ratio for typical petroleum fraction distillation. The conclusion may be drawn that the optimum reflux ratio is about 1.2 times the minimum, and also the number of trays is about twice the minimum. Figure 10-143 shows the temperature profiles of iC4, nC4, iC5, nC5 through the column using Sorel method of plate to plate calculation.

10.52 Tower Sizing for Valve Trays

Many types of trays are used in both fractionating and absorption columns. In a fractionating column, bubble caps with weirs and downcomers maintain a liquid level on the trays. Liquid flows across the tray via the downcomer and then across the next tray in the opposite direction, whilst vapor flows up through the cap and the slots, thus mixing with the liquid. Figures 10-144 and 10-145 show a section of a column distributor and different types of packings. Figure 10-146 illustrates vapor flow through the bubble cap, sieve and valve trays. The riser in a bubble cap can help to prevent liquid from "weeping" through the vapor passage. Sieve or valve trays control weeping by vapor velocity. The bubble cap tray has the highest turndown ratio designed to be 8:1 to 10:1. Such trays are commonly used in glycol dehydrating columns [290].

Valve and sieve trays are favored because of their lower cost and increased capacity compared to bubble cap trays for a given tower diameter. Sieve or perforated trays are plates with holes for vapor passage. Their simple construction makes them the least expensive of the three designs. Generally, sieve tray shave a higher capacity, but at low vapor rates, they are susceptible to "weeping" or dumping of the liquid through the holes. Furthermore, sieve trays are preferred in fouling applications, or when solids are present. They can have large holes which are highly resistant to clogging, and are easy to clean. In addition, its turndown ratio is limited.

Trayed columns give satisfactory operation over a wide range of liquid and vapor loadings. Correspondingly, valve trays can maintain high efficiencies over a wider range of operating liquid and gas rates than sieve trays. Valve units are more mechanically complex than sieve trays, and therefore are more expensive to make. The liquid and vapor rates can vary independently over a broad range in the column resulting in satisfactory operation. At low vapor rates, unsatisfactory tray dynamics may be evidenced by dumping of liquid, uneven distribution and vapor pulsation. Alternatively, at high vapor rates, the tower floods as the liquid backs up in the downcomers. Poor vapor-liquid contact can result at low liquid rates. Correspondingly, at high liquid rates, flooding and dumping can also result as liquid capacities are exceeded in the downcomers. Valve trays are designed to have better turndown properties than sieve trays, and therefore are more flexible for use with varying feed rates. At the design vapor rate, valve trays have about the same efficiency as sieve trays. They can be designed for a lower pressure drop (ΔP) than sieve trays. However, they are susceptible to fouling or plugging, if dirty solutions are distilled.

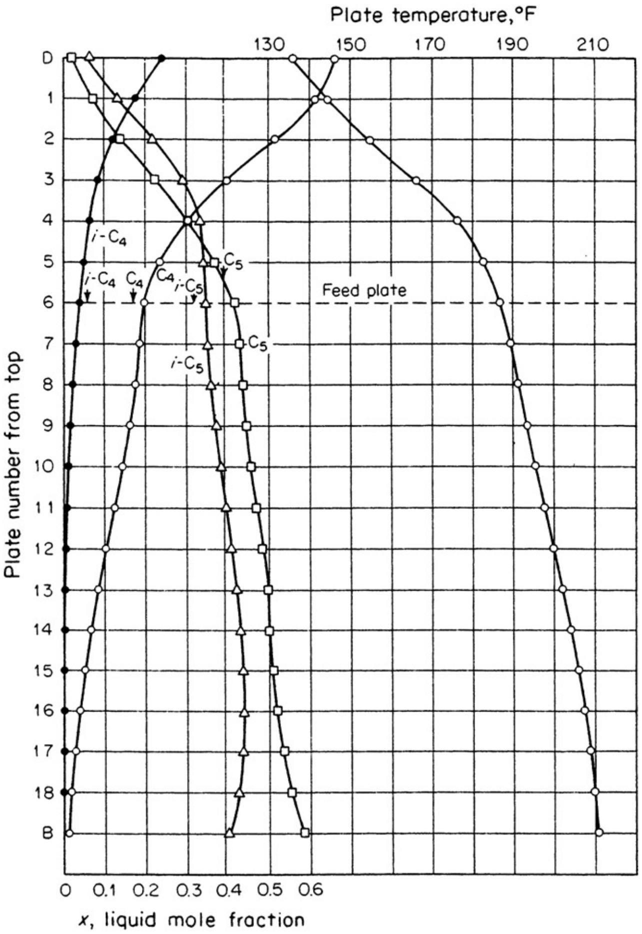


Figure 10-143 Typical concentration profiles in separation of light hydrocarbon mixtures when no substantial inversions of relative volatilities occur (Source: Van Winkle, Distillation, McGraw-hill, New York, 1967).

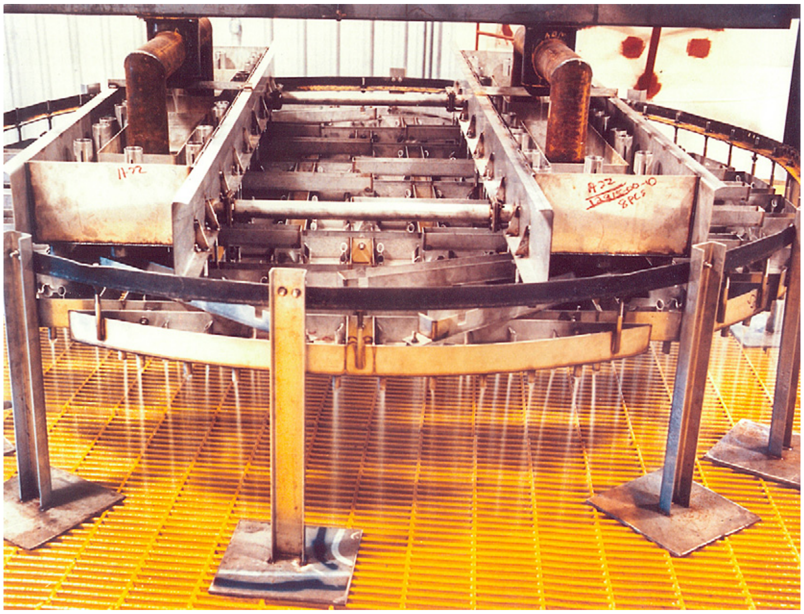


Figure 10-144 Nutter Engineering MTS - 109 multi-pan two stage liquid distributor. Courtesy of Nutter Engineering.

Figure 10-145 Nutter ring random packing. Courtesy of Nutter Engineering.

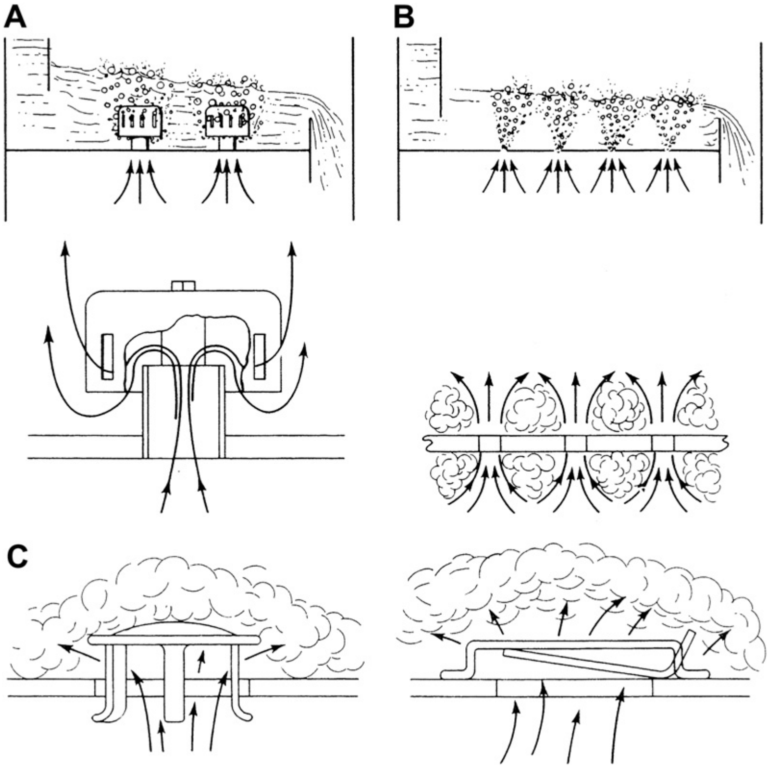


Figure 10-146 Flow through vapor passages. (A) Vapor flow through bubble cap. (B) Vapor flow through perforations. (C). Vapor flow through valves. (Source: Van Winkle, Distillation, McGraw-Hill, New York, 1967).

In these examples, valve trays are used for sizing a column. The procedure uses the Tower sizing graphs, and tables from Nutter [291] and Blackwell's [292] correlation.

The Equations

The following expressions are used for the design of valve trays columns:

The density radical R_D is defined by:

$$R_D = \left(\frac{\rho_V}{\rho_V - \rho_L}\right)^{0.5} \tag{10-557}$$

The velocity at zero liquid load is:

$$V = \exp\left[A + B(\ln X) - C(\ln X)^2 + D(\ln X)^3 - E(\ln X)^4\right] \tag{10-558}$$

where

$$X = \frac{\sigma}{\rho_V} \tag{10-559}$$

A, B, C, and D are constants

$A = 0.22982$

$B = 0.44605$

$C = 0.03452$

$D = 0.00415$

$E = 0.00017$

Equation 10-558 is valid for $0.1 \le X \le 3000$.

The tray spacing factor T_{SF} is defined by:

$$T_{SF} = G + H(\ln X) \tag{10-560}$$

where Equation (10-560) is valid for $0.1 \le X \le 5000$. The constants G and H for different tray spacing are given in Table 10-49. Figure 10-147 illustrates the plots of T_{SF} versus $X(\sigma/\rho_V)$ for different tray spacing.

The operating volumetric vapor flow rate Q_V is:

$$Q_V = \frac{W_V}{(3600)\ (\rho_V)},\ \text{ft}^3/\text{s}. \tag{10-561}$$

Table 10-49 Values of G and H for each tray spacing.

Tray spacing (inches)	G	H
12	0.77174	−0.02964
18	0.93655	−0.02310
24	$T_{SF} = 1$ for all values of X	
30	0.98057	0.03220
	$T_{SF} = 1.0X < 1.85$	
36	0.96583	0.06162
	$T_{SF} = 1$ when $X < 1.85$	

The operating volumetric liquid flow rate Q_L is:

$$Q_L = \frac{W_L}{(3600)\ (\rho_L)},\ \text{ft}^3/\text{s}. \tag{10-562}$$

The bubbling area A_b is:

$$A_b = \frac{(Q_V)\ (R_D) + Q_L}{(T_{SF})(V)\ (R_D)\ (\text{Foam fac})},\ \text{ft}^2 \tag{10-563}$$

Note: If $(V)\ (R_D) > 0.5$, then replace 0.5 for $(V)(R_D)$ in Equation (10-563). Table 10-50 gives recommended values of foam factor and residence time.

Using Table 10-50 to obtain both the foam factor (Foam fac) and the downcomer residence time τ, the downcomer area A_{DC} is:

$$A_{DC} = \frac{(\tau)\ (Q_L)\ (12)}{(\text{Faom fac})\ (T_s)},\ \text{ft}^2 \tag{10-564}$$

The expression for the safety factor S_{FAC} is:

$$S_{FAC} = K(X)^M \tag{10-565}$$

Equation (10-565) is valid for $3.0 \le X \le 50,000$. where

$K = 0.91146$

$M = -0.03821$

The tower area A_T is:

$$A_T = \frac{2(A_{DC}) + A_b}{S_{FAC}},\ f^2 \tag{10-566}$$

Table 10-51 shows the tower diameter versus its cross sectional area, and Tables 10-52 to 10-55 give the recommended downcomer area and bubbling area distribution ratios.

The column diameter D is:

$$D = \left(\frac{4\ A_T}{\pi}\right)^{0.5} \tag{10-567}$$

The number of tray passes required is determined from Table 10-56.

Figures 10-148 and 10-149 show the dimensions of the various downcomers and the distribution area for the number of passes.

10.52.1 Diameter of Sieve/Valve trays (F Factor)

The superficial vapor velocity above the tray not occupied by downcomers, is:

$$U = \frac{F}{\rho_V^{0.5}} \tag{10-568}$$

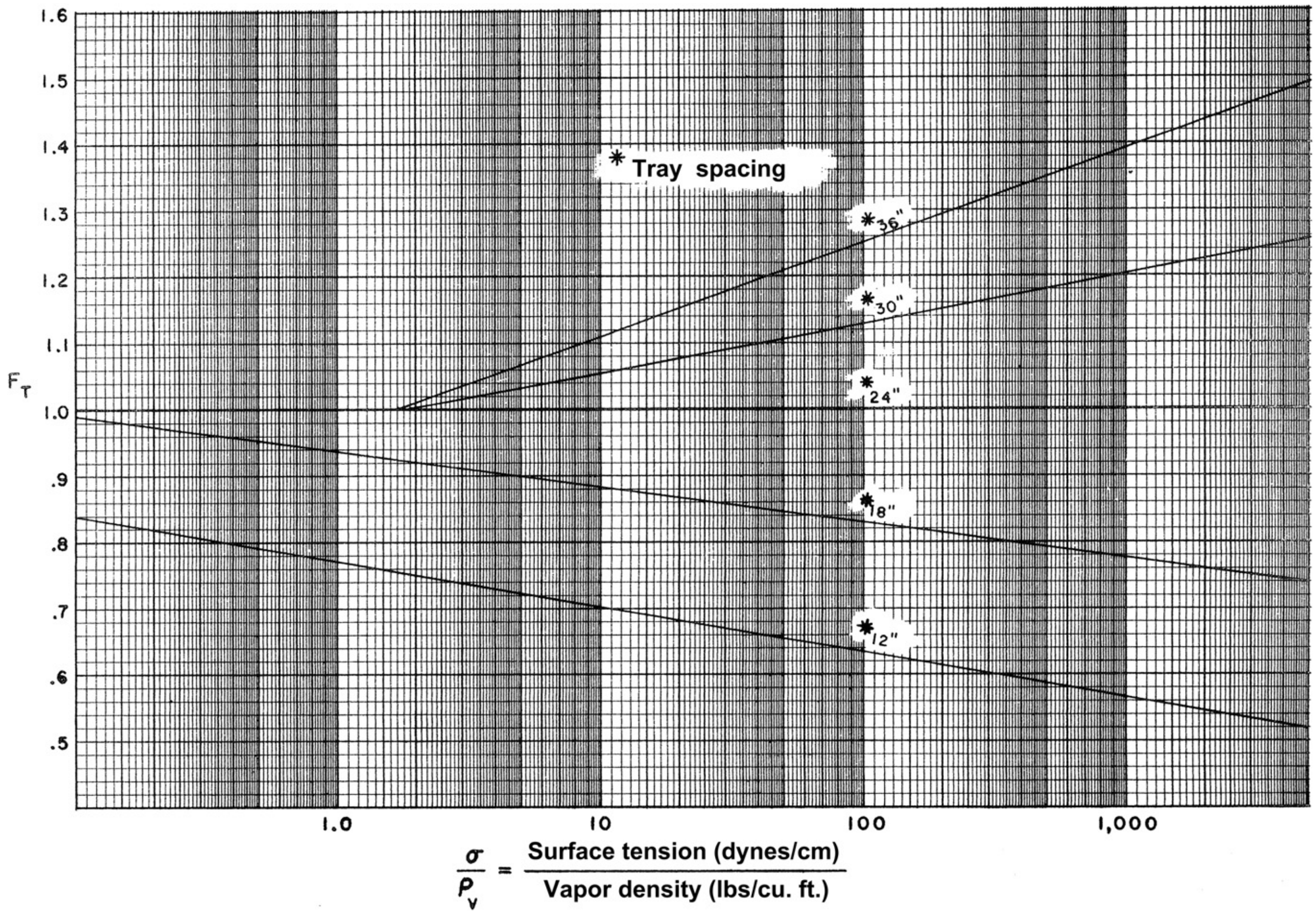


Figure 10-147 Plots of tray spacing vs. ratio of surface tension to vapor density. By permission of Nutter Engineering.

where F is the factor based on free column cross-sectional area (total column area minus the downcomer area). For foaming systems, the F-factor should be multiplied by 0.75. Figure 10-150 shows the F factor correlation as a function of column pressure for various tray spacings [284].

Branan [284] developed an equation for the F-factor as follows:

$$F = (547 - 173.2T + 2.3194T^2)\ 10^{-6}\ P$$
$$+0.32 + 0.0847T - 0.00078T^2 \quad (10\text{-}569)$$

Correlation ranges are:

F = 0.8 to 2.4
F = 0 to 220
F = 18 to 36

For estimating the downcomer area, Branan has developed an empirical equation to fit Frank's Figure 10-151 [284] as:

$$D_L = 6.667T + 16.665 \quad (10\text{-}570)$$

Clear liquid velocity (ft/s) through the downcomer is then found by multiplying D_L by 0.00223. The correlation is not valid if $(\rho_L - \rho_V) < 30\ \text{lb/ft}^3$ (very high pressure systems). For foaming systems, D_L should be multiplied by 0.7. Frank recommends segmental downcomers of at least 5% of total column cross-sectional area, regardless of the area obtained by this correlation. For final design, complete tray hydraulic calculations are required. For even faster estimates, Branan proposed the following rough F factor guidelines.

Situation	**F factor**
Fractionating column total cross section vapor velocity	1.0 – 1.5
Sieve tray hole velocity to avoid weeping	>12
Disengaging equipment for separating liquid droplets from vapor	<6

Table 10-50 Recommended Values for Foam Factor and Residence Time.

Fractionators	Foam factor	Downcomer res. time, sec.
Straight run		
Hydrocarbon	1.0	4.0
Low MW alcohols	1.0	3.5
Crude fractionator	1.0	4.5
Special		
Rich oil (top) demeth. or deeth.	0.85	4.5
Rich oil (BTM) demeth. or deeth.	1.0	4.5
Hydrocarbon still (top)	1.0	4.0
Hydrocarbon still (BTM)	1.0	4.5
MEA-DEA still	0.85	4.5
Glycol-DGA still	0.8	4.5
Sulfinol still	1.0	5.0
H_2S stripper	0.9	4.0
Sour water stripper	0.5–0.7	4.5
0_2 stripper	1.0	3.0
Refrigerated demeth. or deeth. (Top)	0.8	8.0
Refrigerated demeth. or deeth. (BTM)	1.0	5.0
Absorbers		
Oil – ambient temp. (above 0°F)	0.85	4.5
Oil – low temp. (below 0°F)	0.95	4.5
DGA-DEA-MEA (contactor)	0.75	4.5
Glycol contactor	0.65	5.0
Sulfinol contactor	1.0	5.0
Vacuum towers		
Crude vacuum	1.0	5.0

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10.52.2 Diameter of Sieve/Valve trays (Lieberman)

Lieberman [284] provides two rules of thumb for troubleshooting fractionators, which could also be used as checks on a design. The pressure drop (ΔP) across a section of trays must not exceed 22% of the space between the tray decks, to avoid incipient flood. This is expressed by:

$$\frac{\Delta P}{SG}(T_n)(T_s) < 22\% \qquad (10\text{-}571)$$

where

Δ P = Pressure drop in inches of water.
SG = Specific gravity of the liquid on the tray at the appropriate temperature.
T_n = Number of trays
T_s = Tray spacing, in

Table 10-51 Tower Diameter vs. Cross-Sectional Areas.

Tower Diameter		Area
Feet	**Inches**	**Sq. Ft.**
2′-0″	24″	3.142
2′-6″	30″	4.909
3′-6″	36″	7.069
3′-6″	42″	9.621
4′-0″	48″	12.566
4′-6″	54″	15.904
5′-0″	60″	19.635
5′-6″	66″	23.758
6′-0″	72″	28.274
6′-6″	78″	33.183
7′-0″	84″	38.485
7′-6″	90″	44.179
8′-0″	96″	50.266
8′-6″	102″	56.745
9′-0″	108″	63.617
9′-6″	114″	70.882
10′-0″	120″	78.540
10′-6″	126″	86.590
11′-0″	132″	95.033
11′-6″	138″	103.869
12′-0″	144″	113.098
12′-6″	150″	122.719
13′-0″	156″	132.733
13′-6″	162″	143.139
14′-0″	168″	153.938
14′-6″	174″	165.130
15′-0″	180″	176.715
15′-6″	186″	188.692
16′-0″	192″	201.062
16′-6″	198″	213.825
17′-0″	204″	226.980
17′-6″	210″	240.528
18′-0″	216″	254.469
18′-6″	222″	268.803
19′-0″	228″	283.529
19′-6″	234″	298.648
20′-0″	240″	314.159
20′-6″	246″	330.064
21′-0″	252″	346.361
21′-6″	258″	363.050
22′-0″	264″	380.133
22′-6″	270″	397.608
23′-0″	276″	415.476
23′-6″	282″	433.736
24′-0″	288″	452.389
24′-6″	294″	471.435

Table 10-51 Tower Diameter vs. Cross-Sectional Areas. (*Cont'd*)

Tower Diameter		Area
Feet	Inches	Sq. Ft.
25′-0″	300″	490.874
25′-6″	306″	510.705
26′-0″	312″	530.929
26′-6″	318″	551.546
27′-0″	324″	572.555
27′-6″	330″	593.957
28′-0″	336″	615.752
28′-6″	342″	637.940
29′-0″	348″	660.520
29′-6″	354″	683.493
30′-0″	360″	706.858
30′-6″	366″	730.617
31′-0″	372″	754.768
31′-6″	378″	779.311
32′-0″	384″	804.248
32′-6″	390″	829.577
33′-0″	396″	855.299
33′-6″	402″	881.413
34′-0″	408″	907.920
34′-6″	414″	934.820
35′-0″	420″	962.113
35′-6″	426″	989.798
36′-0″	432″	1017.876
36′-6″	438″	1046.347
37′-0″	444″	1075.210
37′-6″	450″	1104.466
38′-0″	456″	1134.115
38′-6″	462″	1164.156
39′-0″	468″	1194.591
39′-6″	476″	1225.417

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For sieve trays, a spray height of 15 in. is obtained when the jetting factor is 6 – 7.

$$\text{Jetting factor} = U^2\ \rho_V/\rho_L \qquad (10\text{-}572)$$

where

U = Hole vapor velocity, ft/s

ρ_L = Liquid density

ρ_V = Vapor density

For a 15-inch spray height, a tray spacing of at least 21 inch is recommended.

Table 10-52 Downcomer Dimensions.

H/DIA	L/DIA	A_d/A_t
.0000	.0000	.0000
.0005	.0447	.0000
.0010	.0632	.0001
.0015	.0774	.0001
.0020	.0894	.0002
.0025	.0999	.0002
.0030	.1094	.0003
.0035	.1181	.0004
.0040	.1262	.0004
.0045	.1339	.0005
.0050	.1411	.0006
.0055	.1479	.0007
.0060	.1545	.0008
.0065	.1607	.0009
.0070	.1667	.0010
.0075	.1726	.0011
.0080	.1782	.0012
.0085	.1836	.0013
.0090	.1889	.0014
.0095	.1940	.0016
.0100	.1990	.0017
.0105	.2039	.0018
.0110	.2086	.0020
.0115	.2132	.0021
.0120	.2178	.0022
.0125	.2222	.0024
.0130	.2265	.0025
.0135	.2308	.0027
.0140	.2350	.0028
.0145	.2391	.0030
.0150	.2431	.0031
.0155	.2471	.0033
.0160	.2510	.0034
.0165	.2548	.0036
.0170	.2585	.0037
.0175	.2622	.0039
.0180	.2659	.0041
.0185	.2695	.0042
.0190	.2730	.0044
.0195	.2765	.0046
.0200	.2800	.0048
.0205	.2834	.0050
.0210	.2868	.0051
.0215	.2901	.0053
.0220	.2934	.0055
.0225	.2966	.0057
.0230	.2998	.0059
.0235	.3030	.0061
.0240	.3061	.0063
.0245	.3092	.0065
.0250	.3122	.0067
.0255	.3153	.0069
.0260	.3183	.0071
.0265	.3212	.0073
.0270	.3242	.0075

(*Continued*)

Table 10-52 Downcomer Dimensions. (*Cont'd*)

H/DIA	L/DIA	A_d/A_t
.0275	.3271	.0077
.0280	.3299	.0079
.0285	.3328	.0081
.0290	.3356	.0083
.0295	.3384	.0085
.0300	.3412	.0087
.0305	.3439	.0090
.0310	.3466	.0092
.0315	.3493	.0094
.0320	.3520	.0096
.0325	.3546	.0098
.0330	.3573	.0101
.0335	.3599	.0103
.0340	.3625	.0105
.0345	.3650	.0108
.0350	.3676	.0110
.0355	.3701	.0112
.0360	.3726	.0115
.0365	.3751	.0117
.0370	.3775	.0119
.0375	.3800	.0122
.0380	.3824	.0124
.0385	.3848	.0127
.0390	.3872	.0129
.0395	.3896	.0132
.0400	.3919	.0134
.0405	.3943	.0137
.0410	.3966	.0139
.0415	.3989	.0142
.0420	.4012	.0144
.0425	.4035	.0147
.0430	.4057	.0149
.0435	.4080	.0152
.0440	.4102	.0155
.0445	.4124	.0157
.0450	.4146	.0160
.0455	.4168	.0162
.0460	.4190	.0165
.0465	.4211	.0168
.0470	.4233	.0171
.0475	.4254	.0173
.0480	.4275	.0176
.0485	.4296	.0179
.0490	.4317	.0181
.0495	.4338	.0184
.0500	.4359	.0187
.0505	.4379	.0190
.0510	.4400	.0193
.0515	.4420	.0195
.0520	.4441	.0198
.0525	.4461	.0201
.0530	.4481	.0204
.0535	.4501	.0207
.0540	.4520	.0210
.0545	.4540	.0212

Table 10-52 Downcomer Dimensions. (*Cont'd*)

H/DIA	L/DIA	A_d/A_t
.0550	.4560	.0215
.0555	.4579	.0218
.0560	.4598	.0221
.0565	.4618	.0224
.0570	.4637	.0227
.0575	.4656	.0230
.0580	.4675	.0233
.0585	.4694	.0236
.0590	.4712	.0230
.0595	.4731	.0242
.0600	.4750	.0245
.0605	.4768	.0248
.0610	.4787	.0251
.0615	.4805	.0254
.0620	.4823	.0257
.0625	.4841	.0260
.0630	.4859	.0263
.0635	.4877	.0266
.0640	.4895	.0270
.0645	.4913	.0273
.0650	.4931	.0276
.0655	.4948	.0279
.0660	.4966	.0282
.0665	.4983	.0285
.0670	.5000	.0288
.0675	.5018	.0292
.0680	.5035	.0295
.0685	.5052	.0298
.0690	.5069	.0301
.0695	.5086	.0304
.0700	.5103	.0308
.0705	.5120	.0311
.0710	.5136	.0314
.0715	.5153	.0318
.0720	.5170	:0321
.0725	.5186	.0324
.0730	.5203	.0327
.0735	.5219	.0331
.0740	.5235	.0334
.0745	.5252	.0337
.0750	.5268	.0341
.0755	.5284	.0344
.0760	.5300	.0347
.0765	.5316	.0351
.0770	.5332	.0354
.0775	.5348	.0358
.0780	.5363	.0361
.0785	.5379	.0364
.0790	.5395	.0368
.0795	.5410	.0371
.0800	.5426	.0375
.0805	.5441	.0378
.0810	.5457	.0382
.0815	.5472	.0385
.0820	.5487	.0389

Table 10-52 Downcomer Dimensions. (*Cont'd*)

H/DIA	L/DIA	A_d/A_t
.0825	.5502	.0392
.0830	.5518	.0396
.0835	.5533	.0399
.0840	.5548	.0403
.0845	.5563	.0406
.0850	.5578	.0410
.0855	.5592	.0413
.0860	.5607	.0417
.0865	.5622	.0421
.0870	.5637	.0424
.0875	.5651	.0428 .
.0880	.5666	.0431
.0885	.5680	.0435
.0890	.5695	.0439
.0895	.5709	.0442
.0900	.5724	.0446
.0905	.5738	.0449
.0910	.5752	.0453
.0915	.5766	.0457
.0920	.5781	.0460
.0925	.5795	.0464
.0930	.5809	.0468
.0935	.5823	.0472
.0940	.5837	.0475
.0945	.5850	.0479
.0950	.5864	.0483
.0955	.5878	.0486
.0960	.5892	.0490
.0965	.5906	.0494
.0970	.5919	.0498
.0975	.5933	.0501
.0980	.5946	.0505
.0985	.5960	.0509
.0990	.5973	.0513
.0995	.5987	.0517

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Example 10-57: Column Sizing Using Nutter's Valve Tray

Size an absorber tower for a methyl ethyl amine (MEA) system with the following conditions:

Vapor flow, lb/h	40,000
Vapor density, lb/ft^3	0.295
Liquid flow, lb/h	330,000
Liquid density, lb/ft^3	61.85
Foam factor	0.75
Residence time, s	4.5
Tray spacing, in.	24
Surface tension, dyne/cm.	57.6

Table 10-53 Downcomer Dimensions.

H/DIA	L/DIA	A_d/A_t
.1000	.6000	.0520
.1005	.6013	.0524
.1010	.6027	.0528
.1015	.6040	.0532
.1020	.6053	.0536
.1025	.6066	.0540
.1030	.6079	.0544
.1035	.6092	.0547
.1040	.6105	.0551
.1045	.6118	.0555
.1050	.6131	.0559
.1055	.6144	.0563
.1060	.6157	.0567
.1065	.6170	.0571
.1070	.6182	.0575
.1075	.6195	.0579
.1080	.6208	.0583
.1085	.6220	.0587
.1090	.6233	.0591
.1095	.6245	.0595
.1100	.6258	.0598
.1105	.6270	.0602
.1110	.6283	.0606
.1115	.6295	.0610
.1120	.6307	.0614
.1125	.6320	.0619
.1130	.6332	.0623
.1135	.6344	.0627
.1140	.6356	.0631
.1145	.6368	.0635
.1150	.6380	.0639
.1155	.6392	.0643
.1160	.6404	.0647
.1165	.6416	.0651
.1170	.6428	.0655
.1175	.6440	.0659
.1180	.6452	.0663
.1185	.6464	.0667
.1190	.6476	.0671
.1195	.6488	.0676
.1200	.6499	.0680
.1205	.6511	.0684
.1210	.6523	.0688
.1215	.6534	.0692
.1220	.6546	.0696
.1225	.6557	.0701
.1230	.6569	.0705
.1235	.6580	.0709
.1240	.6592	.0713
.1245	.6603	.0717
.1250	.6614	.0721
.1255	.6626	.0726
.1260	.6637	.0730
.1265	.6648	.0734
.1270	.6659	.0738

(*Continued*)

Table 10-53 Downcomer Dimensions. (*Cont'd*)

H/DIA	L/DIA	A_d/A_t
.1275	.6671	.0743
.1280	.6682	.0747
.1285	.6693	.0751
.1290	.6704	.0755
.1295	.6715	.0760
.1300	.6726	.0764
.1305	.6737	.0768
.1310	.6748	.0773
.1315	.6759	.0777
.1320	.6770	.0781
.1325	.6781	.0785
.1330	.6791	.0790
.1335	.6802	.0794
.1340	.6813	.0798
.1345	.6824	.0803
.1350	.6834	.0807
.1355	.6845	.0811
.1360	.6856	.0816
.1365	.6866	.0820
.1370	.6877	.0825
.1375	.6887	.0829
.1380	.6898	.0833
.1385	.6908	.0838
.1390	.6919	.0842
.1395	.6929	.0847
.1400	.6940	.0851
.1405	.6950	.0855
.1410	.6960	.0860
.1415	.6971	.0864
.1420	.6981	.0869
.1425	.6991	.0873
.1430	.7001	.0878
.1435	.7012	.0882
.1440	.7022	.0886
.1445	.7032	.0891
.1450	.7042	.0895
.1455	.7052	.0900
.1460	.7062	.0904
.1465	.7072	.0909
.1470	.7082	.0913
.1475	.7092	.0918
.1480	.7102	.0922
.1485	.7112	.0927
.1490	.7122	.0932
.1495	.7132	.0936
.1500	.7141	.0941
.1505	.7151	.0945
.1510	.7161	.0950
.1515	.7171	.0954
.1520	.7180	.0959
.1525	.7190	.9063
.1530	.7200	.0968
.1535	.7209	.0973
.1540	.7219	.0977
.1545	.7229	.0982

Table 10-53 Downcomer Dimensions. (*Cont'd*)

H/DIA	L/DIA	A_d/A_t
.1550	.7238	.0986
.1555	.7248	.0991
.1560	.7257	.0996
.1565	.7267	.1000
.1570	.7276	.1005
.1575	.7285	.1009
.1580	.7295	.1014
.1585	.7304	.1019
.1590	.7314	.1023
.1595	.7323	.1028
.1600	.7332	.1033
.1605	.7341	.1037
.1610	.7351	.1042
.1615	.7360	.1047
.1620	.7369	.1051
.1625	.7378	.1056
.1630	.7387	.1061
.1635	.7396	.1066
.1640	.7406	.1070
.1645	.7415	.1075
.1650	.7424	.1080
.1655	.7433	.1084
.1660	.7442	.1089
.1665	.7451	.1094
.1670	.7460	.1099
.1675	.7468	.1103
.1680	.7477	.1108
.1685	.7486	.1113
.1690	.7495	.1118
.1695	.7504	.1122
.1700	.7513	.1127
.1705	.7521	.1132
.1710	.7530	.1137
.1715	.7539	.1142
.1720	.7548	.1146
.1725	.7556	.1151
.1730	.7565	.1156
.1735	.7574	.1161
.1740	.7582	.1166
.1745	.7591	.1171
.1750	.7599	.1175
.1755	.7608	.1180
.1760	.7616	.1185
.1765	.7625	.1190
.1770	.7633	.1195
.1775	.7642	.1200
.1780	.7650	.1204
.1785	.7659	.1209
.1790	.7667	.1214
.1795	.7675	.1219
.1800	.7684	.1224
.1805	.7692	.1229
.1810	.7700	.1234
.1815	.7709	.1239
.1820	.7717	.1244

Table 10-53 Downcomer Dimensions. (*Cont'd*)

H/DIA	L/DIA	A_d/A_t
.1825	.7725	.1249
.1830	.7733	.1253
.1835	.7742	.1258
.1840	.7750	.1263
.1845	.7758	.1268
.1850	.7766	.1273
.1855	.7774	.1278
.1860	.7782	.1283
.1865	.7790	.1288
.1870	.7798	.1293
.1875	.7806	.1298
.1880	.7814	.1303
.1885	.7822	.1308
.1890	.7830	.1313
.1895	.7838	.1318
.1900	.7846	.1323
.1905	.7854	.1328
.1910	.7862	.1333
.1915	.7870	.1338
.1920	.7877	.1343
.1925	.7885	.1348
.1930	.7893	.1353
.1935	.7901	.1358
.1940	.7909	.1363
.1945	.7916	.1368
.1950	.7924	.1373
.1955	.7932	.1378
.1960	.7939	.1383
.1965	.7947	.1388
.1970	.7955	.1393
.1975	.7962	.1398
.1980	.7970	.1403
.1985	.7977	.1409
.1990	.7985	.1414
.1995	.7992	.1419
.2000	.8000	.1424
.2005	.8007	.1429
.2010	.8015	.1434
.2015	.8022	.1439
.2020	.8030	.1444
.2025	.8037	.1449
.2030	.8045	.1454
.2035	.8052	.1460
.2040	.8059	.1465
.2045	.8067	.1470
.2050	.8074	.1475
.2055	.8081	.1480
.2060	.8089	.1485
.2065	.8096	.1490
.2070	.8103	.1496
.2075	.8110	.1501
.2080	.8118	.1506
.2085	.8125	.1511
.2090	.8132	.1516
.2095	.8139	.1521

(*Continued*)

Table 10-53 Downcomer Dimensions. (*Cont'd*)

H/DIA	L/DIA	A_d/A_t
.2100	.8146	.1527
.2105	.8153	.1532
.2110	.8160	.1537
.2115	.8167	.1542
.2120	.8174	.1547
.2125	.8182	.1553
.2130	.8189	.1558
.2135	.8196	1563
.2140	.8203	.1568
.2145	.8210	.1573
.2150	.8216	1579
.2155	.8223	.1584
.2160	.8230	.1589
.2165	.8237	.1594
.2170	.8244	.1600
.2175	.8251	.1605
.2180	.8258	.1610
.2185	.8265	.1615
.2190	.8271	.1621
.2195	.8278	.1626
.2200	.8285	.1631
.2205	.8292	.1636
.2210	.8298	.1642
.2215	.8305	.1647
.2220	.8312	.1652
.2225	.8319	.1658
.2230	.8325	.1663
.2235	.8332	.1668
.2240	.8338	.1674
.2245	.8345	.1679
.2250	.8352	.1684
.2255	.8358	.1689
.2260	.8365	.1695
.2265	.8371	.1700
.2270	.8378	.1705
.2275	.8384	.1711
.2280	.8391	.1716
.2285	.8397	.1721
.2290	.8404	.1727
.2295	.8410	.1732
.2300	.8417	.1738
.2305	.8423	.1743
.2310	.8429	.1748
.2315	.8436	.1754
.2320	.8442	.1759
.2325	.8449	.1764
.2330	.8455	.1770
.2335	.8461	.1775
.2340	.8467	.1781
.2345	.8474	.1786
.2350	.8480	.1791
.2355	.8486	.1797
.2360	.8492	.1802
.2365	.8499	.1808
.2370	.8505	.1813

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Table 10-54 Downcomer Dimensions.

H/DIA	L/DIA	A_d/A_t
.2375	.8511	.1818
.2380	.8517	.1824
.2385	.8523	.1829
.2390	.8529	.1835
.2395	.8536	.1840
.2400	.8542	1845
.2405	.8548	.1851
.2410	.8554	.1856
.2415	.8560	.1862
.2420	.8566	.1867
.2425	.8572	.1873
.2430	.8578	.1878
.2435	.8584	.1884
.2440	.8590	.1889
.1445	.8596	.1895
.2450	.8602	.1900
.2455	.8608	.1906
.2460	.8614	.1911
.2465	.8619	.1917
.2470	.8625	.1922
.2475	.8631	.1927
.2480	.8637	.1933
.2485	.8643	.1938
.2490	.8649	.1944
.2495	.8654	.1949
.2500	.8660	.1955
.2505	.8666	.1961
.2510	.8672	.1966
.2515	.8678	.1972
.2520	.8683	.1977
.2525	.8689	.1983
.2530	.8695	.1988
.2535	.8700	.1994
.2540	.8706	.1999
.2545	.8712	.2005
.2550	.8717	.2010
.2555	.8723	.2016
.2560	.8728	.2021
.2565	.8734	.2027
.2575	.8745	.2038
.2580	.8751	.2044
.2585	.8756	.2049
.2590	.8762	.2055
.2595	.8767	.2060
.2600	.8773	.2066
.2605	.8778	.2072
.2610	.8784	.2077
.2615	.8789	.2083
.2620	.8794	.2088
.2625	.8800	.2094
.2630	.8805	.2100
.2635	.8811	.2105
.2640	.8816	.2111
.2645	.8821	.2116
.2650	.8827	.2122
.2655	.8832	.2128
.2660	.8837	.2133
.2665	.8843	.2139
.2670	.8848	.2145
.2675	.8853	.2150
.2680	.8858	.2156
.2685	.8864	.2161
.2690	.8869	.2167
.2695	.8874	.2173
.2700	.8879	.2178
.2705	.8884	.2184
.2710	.8890	.2190
.2715	.8895	.2195
.2720	.8900	.2201
.2725	.8905	.2207
.2730	.8910	.2212
.2735	.8915	.2218
.2740	.8920	.2224
.2745	.8925	.2229
.2750	.8930	.2235
.2755	.8935	.2241
.2760	.8940	.2246
.2765	.8945	.2252
.2770	.8950	.2258
.2775	.8955	.2264
.2780	.8960	.2269
.2785	.8965	.2275
.2790	.8970	.2281
.2795	.8975	.2286
.2800	.8980	.2292
.2805	.8985	.2298
.2810	.8990	.2304
.2815	.8995	.2309
.2820	.8999	.2315
.2825	.9004	.2321
.2830	.9009	.2326
.2835	.9014	.2332
.2840	.9019	.2338
.2850	.9028	.2349
.2855	.9033	.2355
.2860	.9038	.2361
.2865	.9043	.2367
.2870	.9047	.2872
.2875	.9052	.2378
.2880	.9057	.2384
.2885	.9061	.2390
.2890	.9066	.2395
.2895	.9071	.2401
.2900	.9075	.2407
.2905	.9080	.2413
.2910	.9084	.2419
.2915	.9089	.2424
.2920	.9094	.2430

Table 10-54 Downcomer Dimensions. (*Cont'd*)

H/DIA	L/DIA	A_d/A_t
.2925	.9098	.2436
.2930	.9103	.2442
.2935	.9107	.2448
.2940	.9112	.2453
.2945	.9116	.2459
.2950	.9121	.2465
.2955	.9125	.2471
.2960	.9130	.2477
.2965	.9134	.2482
.2970	.9139	.2488
.2975	.9143	.2494
.2980	.9148	.2500
.2985	.9152	.2506
.2990	.9156	.2511
.2995	.9161	.2517
.3000	.9165	.2523
.3005	.9170	.2529
.3010	.9174	.2535
.3015	.9178	.2541
.3020	.9138	.2547
.3025	.9187	.2552
.3030	.9191	.2558
.3035	.9195	.2564
.3040	.9200	.2570
.3045	.9204	.2576
.3050	.9208	.2582
.3055	.9212	.2588
.3060	.9217	.2593
.3065	.9221	.2599
.3070	.9225	.2605
.3075	.9229	.2611
.3080	.9233	.2617
.3085	.9237	.2623
.3090	.9242	.2629
.3095	.9246	.2635
.3100	.9250	.2640
.3105	.9254	.2646
.3110	.9258	.2652
.3115	.9262	.2658
.3125	.9270	.2670
.3130	.9274	.2676
.3135	.9278	.2682
.3140	.9282	.2688
.3145	.9286	.2693
.3150	.9290	.2699
.3155	.9294	.2705
.3160	.9298	.2711
.3165	.9302	.2717
.3170	.9306	.2723
.3175	.9310	.2729
.3180	.9314	.2735
.3185	.9318	.2741
.3190	.9322	.2747
.3195	.9326	.2753

(*Continued*)

Table 10-54 Downcomer Dimensions. (*Cont'd*)

H/DIA	L/DIA	A_d/A_t
.3200	.9330	.2759
.3205	.9333	.2765
.3210	.9337	.2771
.3215	.9341	.2777
.3220	.9345	.2782
.3225	.9349	.2788
.3230	.9352	.2794
.3235	.9356	.2800
.3240	.9360	.2806
.3245	.9364	.2812
.3250	.9367	.2818
.3255	.9371	.2824
.3260	.9375	.2830
.3265	.9379	.2511
.3270	.9382	.2842
.3275	.9386	.2848
.3280	.9390	.2854
.3285	.9393	.2860
.3290	.9397	.2866
.3295	.9401	.2872
.3300	.9404	.2878
.3305	.9408	.2884
.3310	.9411	.2890
.3315	.9415	.2896
.3320	.9419	.2902
.3325	.9422	.2908
.3330	.9426	.2914
.3335	.9429	.2920
.3340	.9433	.2926
.3345	.9436	.2932
.3350	.9440	.2938
.3335	.9443	.2944
.3360	.9447	.2950
.3365	.9450	.2956
.3370	.9454	.2962
.3375	.9457	.2968
.3380	.9461	.2974
.3385	.9464	.2980
.3390	.9467	.2986
.3400	.9474	.2998
.3405	.9478	.3004
.3410	.9481	.3010
.3415	.9484	.3016
.3420	.9488	.3022
.3425	.9491	.3028
.3430	.9494	.3034
.3435	.9498	.3040
.3440	.9501	.3046
.3445	.9504	.3053
.3450	.9507	.3059
.3455	.9511	.3065
.3460	.9514	.3071
.3465	.9517	.3077
.3470	.9520	.3083

(*Continued*)

Table 10-54 Downcomer Dimensions. (*Cont'd*)

H/DIA	L/DIA	A_d/A_t
.3475	.9524	.3089
.3480	.9527	.3095
.3485	.9530	.3101
.3490	.9533	.3107
.3495	.9536	.3113
.3119	.3500	.9539
.3505	.9543	.3125
.3510	.9546	.3131
.3515	.9549	.3137
.3520	.9552	.3143
.3525	.9555	.3150
.3530	.9558	.3156
.3535	.9561	.3162
.3540	.9564	.3168
.3545	.9567	.3174
.3550	.9570	.3180
.3555	.9573	.3186
.3560	.9576	.3192
.3565	.9579	.3198
.3570	.9582	.3204
.3575	.9585	.3211
.3580	.9588	.3217
.3585	.9591	.3223
.3590	.9594	.3229
.3595	.9597	.3235
.3600	.9600	.3241
.3605	.9603	.3247
.3610	.9606	.3253
.3615	.9609	.3259
.3620	.9612	.3265
.3625	.9614	.3272
.3630	.9617	.3278
.3635	.9620	.3284
.3640	.9623	.3290
.3645	.9626	.3296
.3650	.9629,	.3302
.3655	.9631	.3308
.3660	.9634	.3315
.3665	.9637	.3321
.3675	.9642	.3333
.3680	.9645	.3339
.3685	.9648	.3345
.3690	.9651	.3351
.3695	.9653	.3357
.3700	.9656	.3364
.3705	.9659	.3370
.3710	.9661	.3376
.3715	.9664	.3382
.3720	.9667	.3388
.3750	.9669	.3394
.3730	.9672	.3401
.3735	.9676	.3407
.3740	.9677	.3413
.3745	.9680	.3419

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Table 10-55 Downcomer Dimensions.

H/DIA	L/DIA	A_d/A_t
.3750	.9682	.3425
.3755	.9685	.3431
.3760	.9688	.3438
.3765	.9690	.3444
.3770	.9693	.3453
.3775	.9695	.3456
.3780	.9698	.3462
.3785	.9700	.3468
.3790	.9703	.3475
.3795	.9705	.3481
.3800	.0708	.3487
.3805	.9710	.3493
.3810	.9713	.3499
.3815	.9715	.3505
.3820	.9718	.3512
.3825	.9720	.3518
.3830	.9722	.3524
.3835	.9725	.3530
.3840	.9727	.3536
.3845	.9730	.3543
.3850	.9732	.3549
.3855	.9734	.3555
.3860	.9737	.3561
.3865	.9739	.3567
.3870	.9741	.3574
.3875	.9744	.3580
.3880	.9746	.3586
.3885	.9748	.3592
.3890	.9750	.3598
.3895	.9753	.3605
.3900	.9755	.3611
.3905	.9757	.3617
.3910	.9759	.3623
.3915	.9762	.3629
.3920	.9764	.3636
.3925	.9766	.3642
.3930	.9768	.3648
.3935	.9771	.3654
.3940	.9773	.3661
.3945	.9775	.3667
.3950	.9777	.3673
.3955	.9779	.3679
.3960	.9781	.3685
.3965	.9783	.3692
.3970	.9786	.3698
.3975	.9788	.3704
.3980	.9790	.3710
.3985	.9792	.3717
.3990	.9794	.3723
.3995	.9796	.3729
.4000	.9798	.3735
.4005	.9800	.3742
.4010	.9802	.3748
.4015	.9804	.3754
.4020	.9806	.3760

Table 10-55 Downcomer Dimensions. (*Cont'd*)

H/DIA	L/DIA	A_d/A_t
.4025	.9808	.3767
.4030	.9810	.3773
.4035	.9812	.3779
.4040	.9814	.3785
.4045	.9816	.3791
.4050	.9818	.3798
.4055	.9802	.3804
.4060	.9822	.3810
.4065	.9824	.3816
.4070	.9825	.3823
.4075	.9827	.3829
.4080	.9829	.3835
.4085	.9831	.3842
.4090	.9833	.3848
.4095	.9835	.3854
.4100	.9837	.3860
.4105	.9838	.3867
.4110	.9840	.3873
.4115	.9842	.3879
.4120	.9844	.3885
.4125	.9846	.3892
.4130	.9847	.3898
.4135	.9849	.3904
.4140	.9851	.3910
.4145	.9853	.3917
.4150	.9854	.3923
.4155	.9856	.3929
.4160	.9858	.3936
.4165	.9860	.3942
.4170	.9861	.3948
.4175	.9863	.3642
.4180	.9865	.3961
.4185	.9866	.3967
.4190	.9868	.3973
.4195	.9870	.3979
.4200	.9871	.3986
.4205	.9873	.3992
.4210	.9874	.3998
.4215	.9876	.4005
.4220	.9878	.4011
.4225	.9879	.4017
.4230	.9881	.4023
.4235	.9882	.4030
.4240	.9884	.4036
.4245	.9885	.4042
.4250	.9887	.4049
.4255	.9888	.4055
.4260	.9890	.4061
.4265	.9891	.4068
.4270	.9893	.4074
.4275	.9894	.4080
.4280	.9896	.4086
.4285	.9897	.4093
.4290	.9899	.4099
.4295	.9900	.4105

(*Continued*)

Table 10-55 Downcomer Dimensions. (*Cont'd*)

H/DIA	L/DIA	A_d/A_t
.4300	.9902	.4112
.4305	.9903	.4118
.4310	.9904	.4124
.4315	.9906	.4131
.4320	.9907	.4137
.4325	.9908	.4143
.4330	.9910	.4149
.4335	.9911	.4156
.4340	.9912	.4162
.4345	.9914	.4168
.4350	.9915	.4175
.4355	.9916	.4181
.4360	.9918	.4187
.4365	.9919	.4194
.4370	.9920	.4200
.4375	.9922	.4206
.4380	.9923	.4213
.4385	.9924	.4219
.4390	.9925	.4225
.4395	.9927	.4232
.4400	.9928	.4238
.4405	.9929	.4244
.4410	.9930	.4251
.4415	.9931	.4257
.4420	.9932	.4263
.4425	.9934	.4270
.4430	.9935	.4276
.4435	.9936	.4282
.4440	.9937	.4288
.4445	.9938	.4295
.4450	.9939	.4301
.4455	.9940	.4307
.4460	.9942	.4314
.4465	.9943	.4320
.4470	.9944	.4326
.4475	.9945	.4333
.4480	.9946	.4339
.4485	.9947	.4345
.4490	.9948	.4352
.4495	.9949	.4358
.4500	.9950	.4364
.4505	.9951	.4371
.4510	.9952	.4377
.4515	.9953	.4383
.4520	.9954	.4390
.4525	.9955	.4396
.4530	.9956	.4402
.4535	.9957	.4409
.4540	.9958	.4415
.4545	.9959	.4421
.4550	.9959	.4428
.4555	.9960	.4434
.4560	.9961	.4440
.4565	.9962	.4447
.4570	.9963	.4453

(*Continued*)

Table 10-55 Downcomer Dimensions. (*Cont'd*)

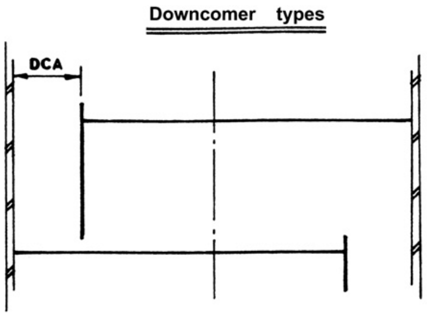
H/DIA	L/DIA	A_d/A_t
.4575	.9964	.4460
.4580	.9965	.4466
.4585	.9965	.4472
.4590	.9966	.4479
.4595	.9967	.4485
.4600	.9968	.4491
.4605	.9969	.4498
.4610	.9970	.4505
.4615	.9970	.4510
.4620	.9971	.4517
.4625	.9972	.4523
.4630	.9973	.4529
.4635	.9973	.4536
.4640	.9974	.4542
.4645	.9975	.4548
.4650	.9975	.4555
.4655	.9976	.4561
.4660	.9977	.4567
.4665	.9978	.4574
.4670	.9978	.4580
.4675	.9979	.4568
.4680	.9979	.4593
.4685	.9980	.4599
.4690	.9981	.4606
.4695	.9981	.4612
.4700	.9982	.4618
.4705	.9983	.4625
.4710	.9983	.4631
.4715	.9984	.4637
.4720	.9984	.4644
.4725	.9985	.4650
.4730	.9985	.4656
.4735	.9986	.4663
.4740	.9986	.4669
.4745	.9987	.4675
.4750	.9987	.4682
.4755	.9988	.4688
.4760	.9988	.4695
.4765	.9989	.4701
.4770	.9989	.4707
.4775	.9990	.4714
.4780	.9990	.4720
.4785	.9991	.4726
.4790	.9991	.4733
.4795	.9992	.4739
.4800	.9992	.4745
.4805	.9992	.4752
.4810	.9993	.4758
.4815	.9993	.4765
.4820	.9994	.4771
.4825	.9994	.4777
.4830	.9994	.4784
.4835	.9995	.4790
.4840	.9995	.4796
.4845	.9995	.4803
.4850	.9995	.4809
.4855	.9996	.4815
.4860	.9996	.4822
.4865	.9996	.4828
.4870	.9997	.4834
.4875	.9997	.4841
.4880	.9997	.4847
.4885	.9997	.4854
.4890	.9998	.4860
.4895	.9998	.4866
.4900	.9998	.4873
.4905	.9998	.4879
.4910	.9998	.4885
.4915	.9999	.4892
.4920	.9999	.4898
.4925	.9999	.4905
.4930	.9999	.4911
.4935	.9999	.4917
.4940	.9999	.4924
.4945	.9999	.4930
.4950	1.0000	.4936
.4955	1.0000	.4943
.4960	1.0000	.4949
.4965	1.0000	.4955
.4970	1.0000	.4962
.4975	1.0000	.4968
.4980	1.0000	.4975
.4985	1.0000	.4981
.4990	1.0000	.4987
.4995	1.0000	.4994
.5000	1.0000	.5000

Solution

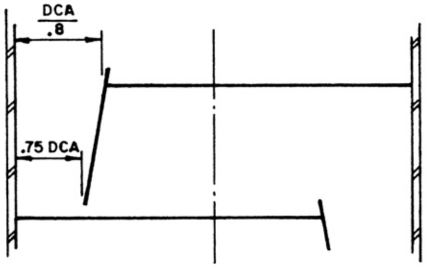
A computer program PROG105 has been developed to determine the parameters required for sizing a tower using valve trays. The program uses Nutter's Float Design Manual and calculates the bubbling area, downcomer area, tower area and diameter. The tower diameter may be rounded to an appropriate value and the area recalculated. Once the tower diameter is set, the downcomer

Table 10-56 Determining the Number of Tray Passes.

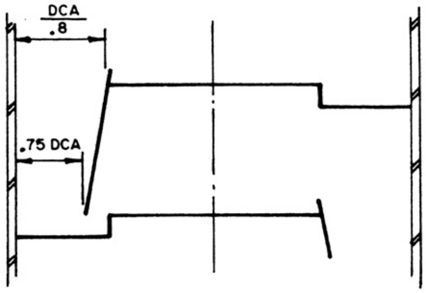
Tray spacing (inch)	Increase in number of passes if gpm/in. of weir exceeds
12	3
18	18
24	13



Vertical downcomer — Flat deck: Used as a standard unless process reasons dictate otherwise



Sloped downcomer — Flat deck: Used in high pressure systems where vapor disengagement out of the top portion of the downcomer is critical



Sloped downcomer — Recessed pan: (1) Used in high liquid rate systems to help alleviate hydraulic problems

(2) Used in low liquid rate systems to maintain positive downcomer seal

Figure 10-148 Dimensions of downcomer types. By permission of Nutter Engineering.

area ratio is determined and the downcomer height is then computed from Tables 10-52 to 10-55. Table 10-57 shows the input data and results for tower sizing using valve trays a tower area of 26.57 ft2 and a diameter of 5.82 ft.

Tray Geometry Sizing

From the tower size (normally obtained by increasing the diameter to the nearest 6-inch increment), the following procedure is used to calculate the downcomer dimensions.

The downcomer area ratio is:

$$R_{DCA} = \frac{A_{DC}}{(2A_{DC} + A_b)} \tag{10-573}$$

The calculated tower diameter is increased to 6.0 ft. and the tower area becomes:

$$A = \frac{\pi\, d^2}{4}, \text{ft}^2$$

$$= \frac{\pi \times 6^2}{4}$$

$$= 28.27 \text{ ft}^2$$

Using Tables 10-52 to 10-55 and R_{DCA} will allow direct computation of chord height for the side downcomer. This is rounded up to the nearest ½ in. increment dimension. Using this dimension, the corrected downcomer area is calculated from Tables 10-52 to 10-55. The

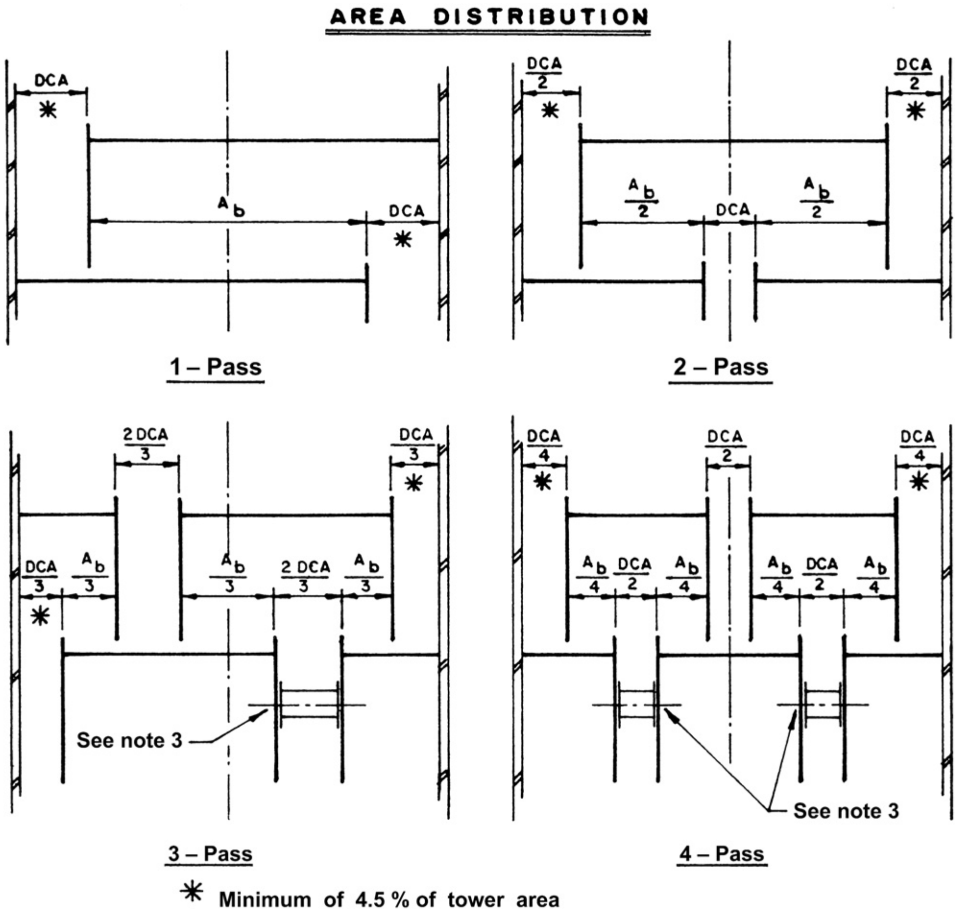


Figure 10-149 Area distribution for different pass types. By permission of Nutter Engineering.

NOTES:

(1) Trays are designed using as few passes as possible. Increasing number of passes decreases efficiency and increases cost.
(2) Multipass trays are designed with equal-bubbling areas. Weir lengths or heights can be adjusted to provide uniform tray hydraulics.
(3) Vapor equalizers are a recommended option to guarantee vapor equalization between compartments.

computed output of the tower used by the downcomer area ratio (R_{DCA}) is 0.2246.

That is

$$\frac{A_d}{A_t} = 0.2246$$

H/DIA	L/DIA	A_d/A_t
0.2760	0.8940	0.2246

The corresponding downcomer height to tower diameter ratio is 0.2760.

The downcomer height = (0.2760) (6) (12)
= 19.87 in. + ½ in.
= 20.4 in.

The new H/DIA = 20.4/72
= 0.2833

This gives a downcomer area to tower area ratio of 0.2329.

H/DIA	L/DIA	A_d/A_t
0.2830 Avg 0.28325 0.2835	0.9009 Avg 0.90115 0.9014	0.2326 Avg 0.2329 0.2332

That is:

$$\frac{A_d}{A_t} = 0.2329$$

The downcomer area A_d = (0.2329) (28.27)

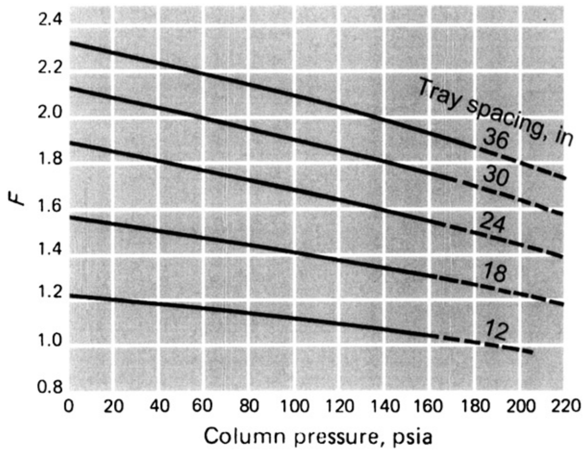


Figure 10-150 F Factor as a function of column pressure drop and tray spacing. (Source: Branan, C., "Rules of Thumb for Chemical Engineers", 4th Ed., Gulf Publishing Professional, 2005).

$= 6.584 \text{ ft}^2$

The weir height, L = (0.90115 × 72)

= 64.88 in (65 in.)

The computed liquid flow rate is:

$$= \frac{(33,0000)}{(61.82)\,(3600)}\left\{\frac{\text{lb}}{\text{h}}\cdot\frac{\text{ft}^3}{\text{lb}}\cdot\frac{\text{h}}{\text{s}}\right\}$$

$= 1.483 \text{ ft}^3/\text{s}$ (665.35 US gpm)

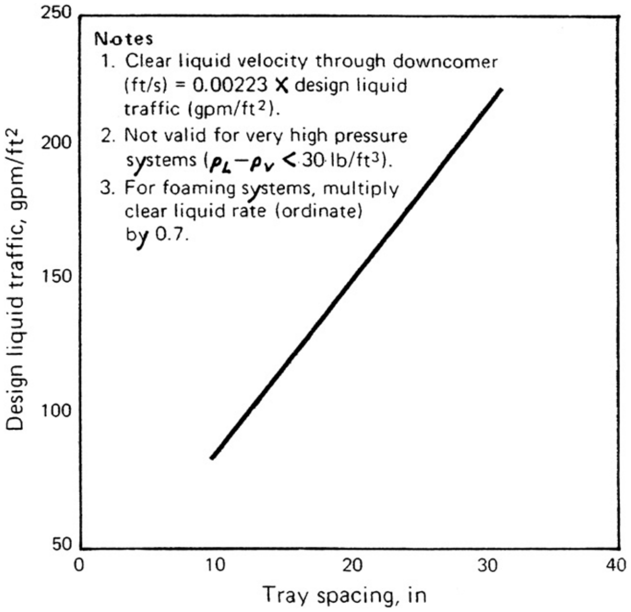
The liquid flow per inch of weir = 665.35/65 = 10.24 US gpm per inch of weir.

A single-pass tray is selected.

10.53 Troubleshooting, Predictive Maintenance and Controls for Distillation Columns

Troubleshooting currently is now much more sophisticated due to the technical tools that are available for investigating and analyzing performance. Radiation scanning referred to as distillation column scanning or "gamma scanning" is now in common use. This is the process of studying the process material inside a vessel by placing a moving radioactive source inside it, and moving radiation detector along the exterior of the vessel (Figure 10-152a). Such scanning enables the engineer to study tray or packing hydraulics inside the vessel at any set of online conditions as it provides essential data to:

- Track the performance – deteriorating effects of fouling, foaming, flooding and weeping.
- Optimize the performance of vessels.
- Identify maintenance requirements in advance of scheduled turnarounds
- Extend vessel run times.



Notes
1. Clear liquid velocity through downcomer (ft/s) = 0.00223 X design liquid traffic (gpm/ft²).
2. Not valid for very high pressure systems ($\rho_L - \rho_V < 30$ lb/ft³).
3. For foaming systems, multiply clear liquid rate (ordinate) by 0.7.

Figure 10-151 Estimation of downcomer area for a tray-type distillation column. (Source: Branan, C., "Rules of Thumb for Chemical Engineers", 4th Ed., Gulf Publishing Professional, 2005).

Figure 10-152b shows how the radiation source and the detector are aligned on opposite sides of a column or vessel. There are two typical alignments: one-pass trayed column and a packed tower respectively. The source and the detector are synchronized and lowered down the

Table 10-57 Input Data and Computer Output for Tower Design Using Valve Trays.

```
Data name: Data105.Dat
40000.0                     330000.0     61.85
0.295                       0.75         4.5
24.0                        57.6
              Tower Design for Value Trays

Vapor flow rate, 1b/hr.:               40000.0
Vapor volumetric rate, ft3/sec.:       37.665
Liquid flow rate, 1b/hr.:              330000.0
Liquid volumetric rate, ft3/sec.:      1.482
Liquid density, 1b/ft3. :              61.850
Vapor density, 1b/ft3. :               0.295
Foam factor:                           0.750
Downcomer residence time, sec.:        4.500
Tray spacing, in.:                     24.
Surface tension, dyne/cm.:             57 .60
Surface tension/vapor density (X):     195.254
Safety factor:                         0.745
Density radical:                       0.069
Bubbling area, ft2:                    10.905
Downcomer area, ft2:                   4.446
Tower area, ft2:                       26.571
Tower diameter, ft:                    5.816
Downcomer area ratio:                  0 .2246
```

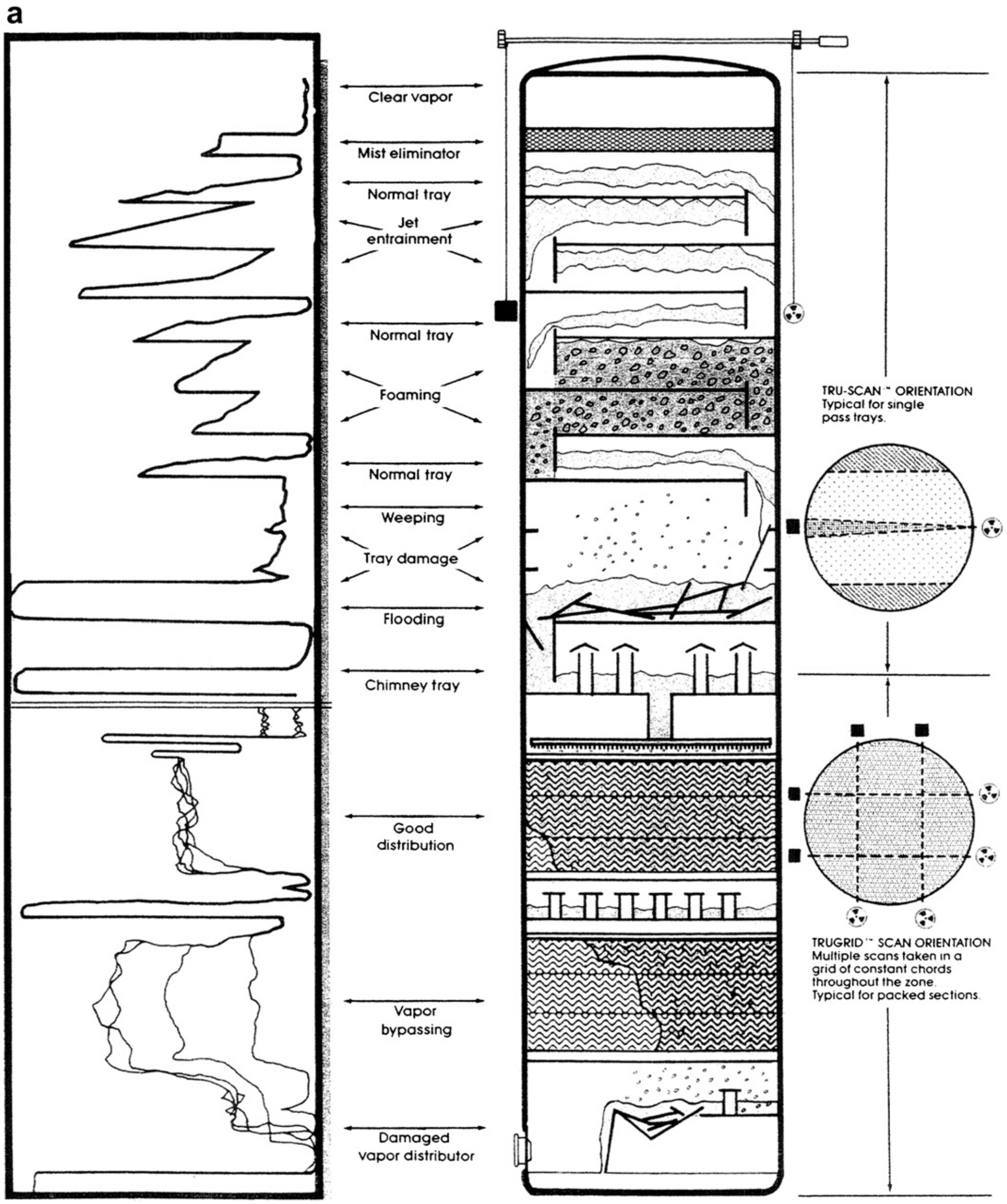


Figure 10-152a Distillation diagnostics. (Source: Tru-Tec Division, Koch Engineering Co. Inc.).

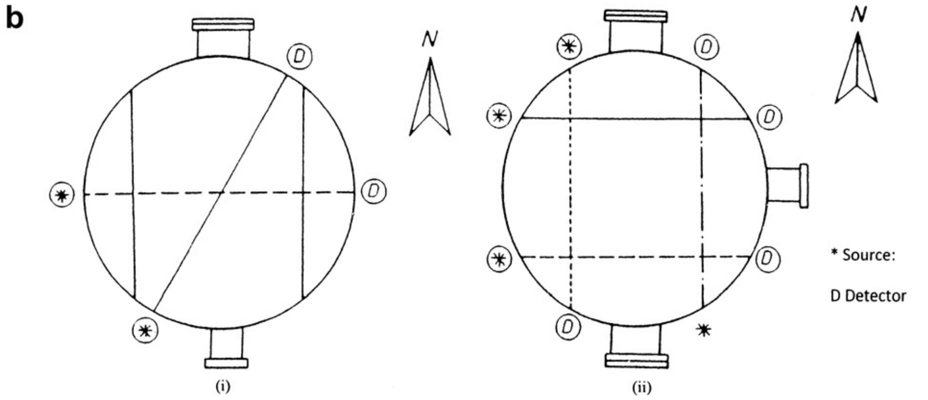
column, while intensity measurements are recorded at specified intervals. The variation in measured intensity depends on the changes in "absorber" thickness and density. The absorber is a composite of the vessel walls, insulation, column internal trays, packings, downcomers, support grids, gas/liquid distributors and process material inside the column. Thus, the difference in intensity that is detected is the result of process changes such as density differences between liquid and vapor within the column.

The scan produces a density profile that shows the relative density vs. column elevation. The results are then interpreted to show the behavior of the column, its performance and physical condition. Figure 10-152c illustrates how scan results are used to determine tray loading, extent of flooding and vapor space conditions. Tray locations and sources of external interference (e.g. welds, stiffening, rings or supports) are on the left side of the plot.

Flooding: Different extents of flooding occur on tray -1 in the region where scan profile flattens out and rises up.

Clear vapor region: Is marked by the bar line on the right side of the plot. It defines statistically what the relative density should be when only vapor is present.

Froth height intensity: The dotted line to the left of the clear vapor bar is labeled as froth height intensity. This is also referred to as the datum line through the



Double scan alignments for a single-pass trayed column. A single radiation source and a detector face each other along the column diameter in both alignments. They are moved synchronously up and down the column along its other surface.

Alignments for four separate scans of a packed tower. In such cases, scans are completed in a parallel and orthogonal 2 x 2 grid. The distance from source to detector must remain the same for all four scan lines. Therefore, the source and the detector are located at ends of each four equidistant chords oriented orthogonally in a north-to-south and east-to-west pattern.

Figure 10-152b Gamma ray scanning of a single-pass tray and of a packed tower.

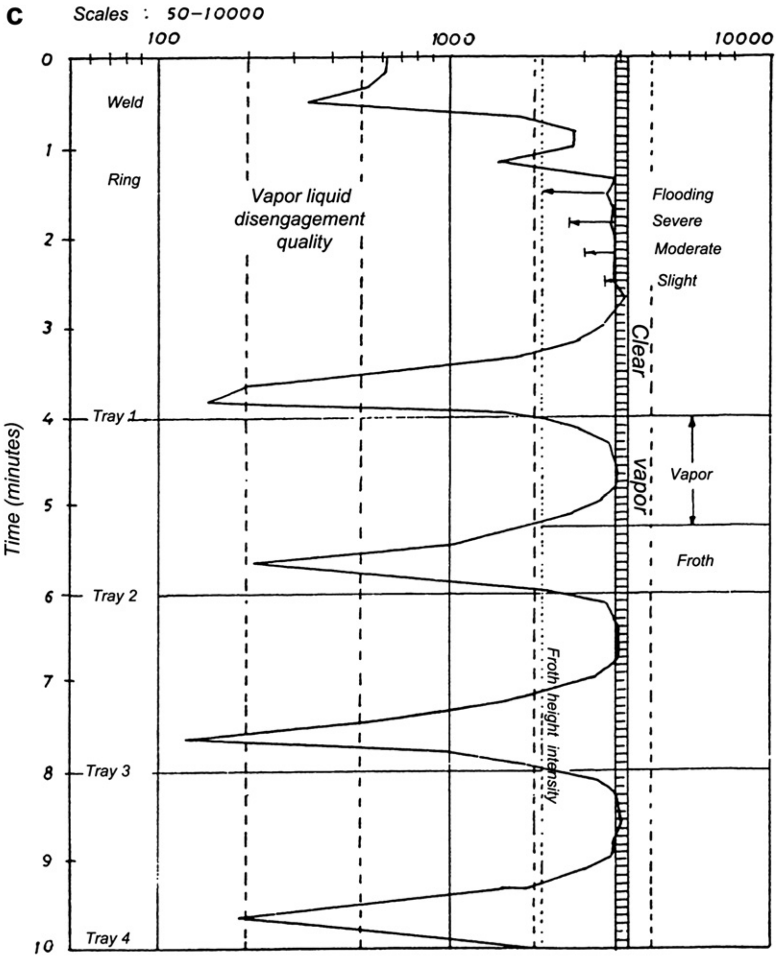


Figure 10-152c Gamma ray scanning profile of a distillation column. The profile is presented as a plot of time (and tray no.) vs. intensity of absorbed emission. The solid line depicts the actual scan data: the clear vapor region is marked by bar line. The dotted vertical lines to the left of the clear vapor bar represent froth height intensity. It is also called datum line. (Source: Bowman, J.D., Chem. Eng. Prog., Feb. 1991).

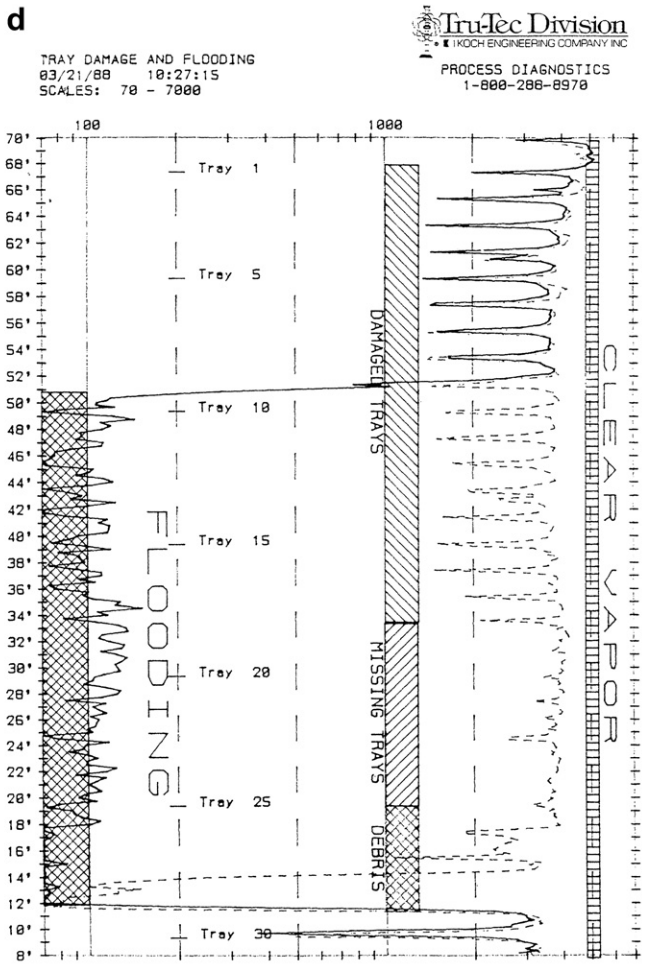


Figure 10-152d Gamma ray scanning "diagnostic diagnosis" of depropanizer column to evaluate performance. Used by permission, Tru-Tec Division, Koch Engineering Co. Inc.

statistical average of the relative vapor space densities and the liquid densities appearing on the tray active areas.

Froth height: Is the vertical distance between the deck and spray height level. This is depicted on tray - 2 on the right side of the vapor bar (Figure 10-152c). The tray is sustaining approximately 9 in. (229 mm) (±1in) of aerated froth.

Clear vapor height: Is the tray spacing minus froth height.

Experience with the techniques is important for its effective use combining it with a computer model can assist in both theoretical and practical design applications; best results are obtained by combining scan results and tray packing design [158, 182] it provides data that can aid significantly in determining whether a column is having liquid/vapor flow and or distribution problems. This system provides an accurate density profile of the operating fluids on each tray or through the packing of a packed column, which can be used to identify a number of column malfunctions, as shown in Table 10-58.

Table 10-58 Column Malfunctions Identifiable by Scanning.

Type of Malfunctions	Particulars
Process	Liquid hold up on tray/packing due to fouling or plugging Foaming Subcooled or superheated feed or reflux
Rate Related	Entrainment – slight, moderate, severe jet flooding Flooding Tray starvation Weeping
Mechanical	Damage to trays and packings Tray displacement Damage to trays due to corrosion Dislocation of liquid or vapor distributors Missing tray manways Level control problems in the base of the column

Figure 10-152d shows an example of using gamma scanning in a depropanizer column to evaluate its performance.

Other troubleshooting techniques include computer modeling, checking the reliability of instrumentation, measuring quality of product streams with varying reflux rates, measuring column tray temperatures at close intervals, stabilizing the feed rate, bottoms withdrawal and overhead condensing rates. Some surprising problems can be identified, including:

1. Trays may have damage to caps, valves, distributors, sieve holes, or packing for packed towers.
2. The contacting devices of (1) above may actually be missing, i.e., blown off one or more trays, so all that exists is a "rain-deck" tray with no liquid-vapor contact.
3. Crud, polymer, gunk and other processing residues, plus maintenance tools, rags, or overalls may be plugging or corroding the liquid flow paths.
4. Entrainment.
5. Weeping of trays, or flooding of packing or trays.
6. Foaming limitations.
7. Unusual feed conditions, unexpected or uncontrolled.
8. Many other situations, almost too odd to imagine. References on this topic include 159–166, 182, 238.

The topic of control of distillation columns has been discussed by many authorities with a wide variety of experience [117-120, 237], and is too specialized to be covered in this text.

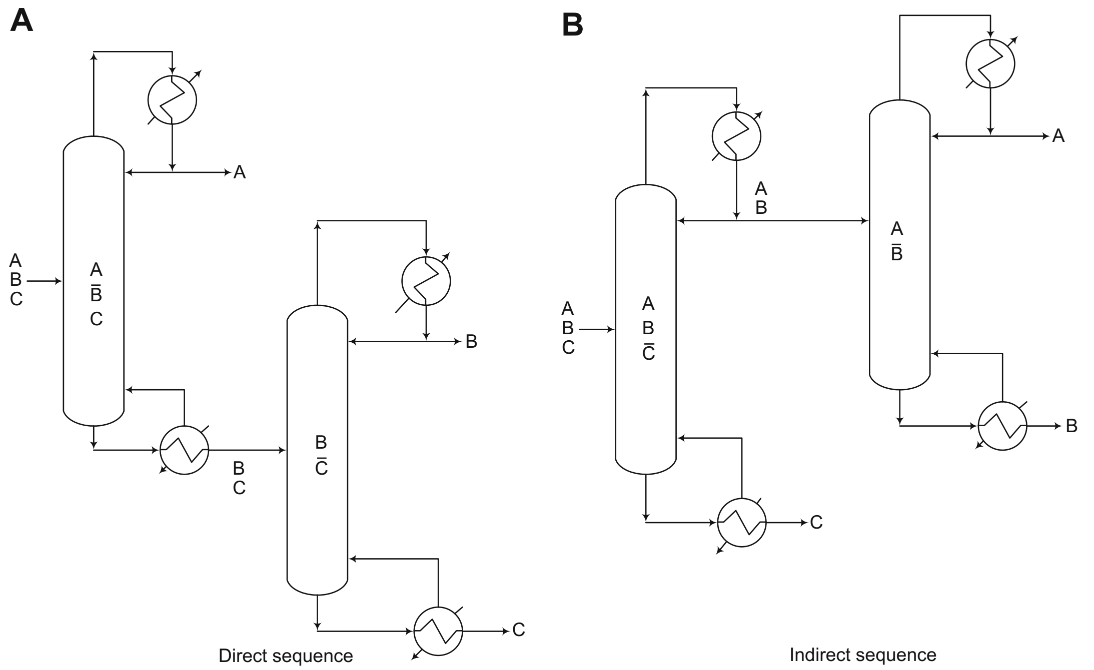
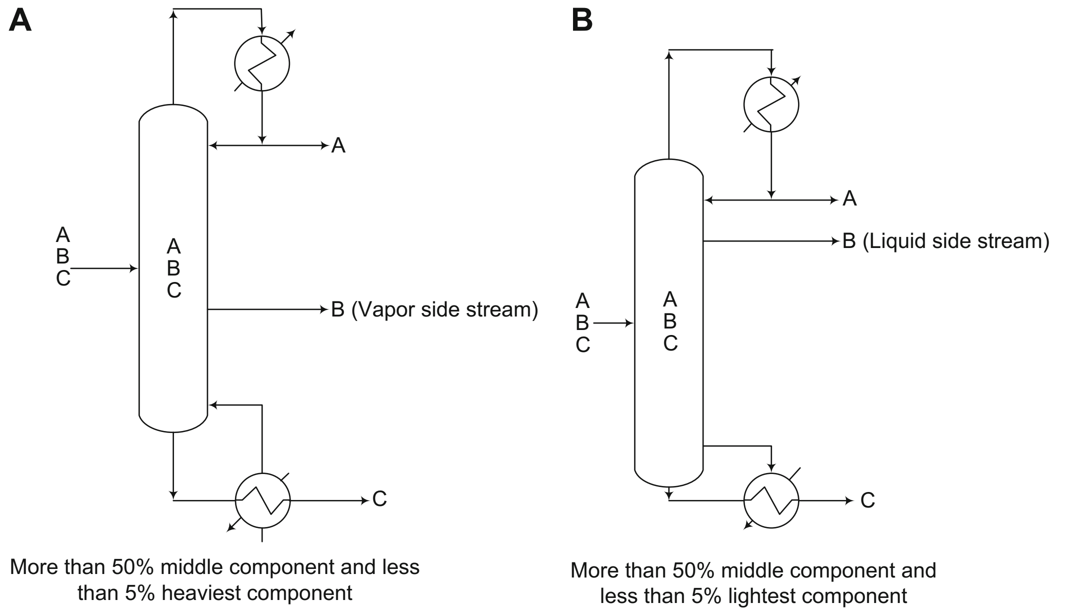


Figure 10-153 Alternative column sequences for a three-component separation.

10.54 Distillation Sequencing with Columns having More than Two Products

In the separation of multicomponent mixtures (more than two) using simple columns, there are only two possible sequences (see Figure 10-153). The sequence shown in Figure 10-153a is known as the direct sequence, in which the lightest component is taken overhead in each column. The indirect sequence as shown in Figure 10-153b. This removes the heaviest component as bottom product in each column. If we first consider the characteristics of simple columns, a single feed is split into two products. one alternative to two simple columns is shown in Figure 10-154. Here, three products are



More than 50% middle component and less than 5% heaviest component

More than 50% middle component and less than 5% lightest component

Figure 10-154 Distillation columns with three products. (Source: Smith and Linnhoff, Trans IChemE, ChERD. 66: 195, 1998).

taken from one column. The designs are feasible and cost effective when compared with simple arrangements utilizing reboilers and condensers operating on utilities for certain ranges of conditions. Where the feed is dominated by the middle product (i.e. >50 % of the feed) and the heaviest product is present in small quantities (i.e. <5 %), then the arrangement shown in Figure 10-154a can be an attractive option. The heavy product must find its way down the column past the sidestream. If the heavy product has a small flow and the middle product a high flow, a reasonably pure middle product cannot be achieved. In these situations, the sidestream is usually taken as a vapor product to obtain a reasonably pure sidestream.

If the feed is dominated by the middle product (i.e. >50%) and the lightest product is present in small amounts (i.e. <5 %), then the arrangement shown in Figure 10-154b can be an attractive choice. Here, the light product must find its way up the column past the sidestreams. Unless the light product is a small flow and the middle product a high flow, a reasonably pure middle product cannot be achieved. In this instance, the sidestreams is taken as a liquid product to obtain a reasonably pure sidestream [313].

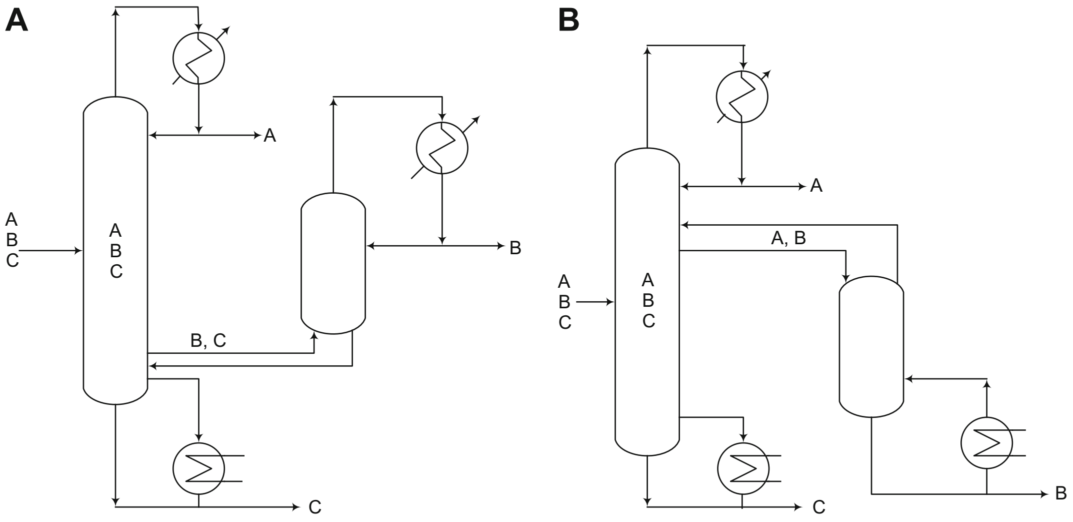
Generally, single-column sidestream arrangements can be attractive when the middle product is in excess and one of the other components is present only at small concentrations. Therefore, the sidestream column only applies to special cases of feed composition. More generally applicable arrangements are made possible by relaxing the restriction that separations must be between adjacent key components.

10.54.1 Thermally Coupled Distillation Sequence

The transfer of heat via direct contact is referred to as thermal coupling, and this is possible when materials flow in such a way as to provide some of the necessary heat transfer by direct contact. In the separation of a multicomponent mixture, thermally coupled distillation columns require less energy and fixed cost compared to conventional multicomponent mixture. To understand this process, first consider the separation of a ternary mixture having components A, B and C. A is the most volatile component and C is the least volatile component, while component B has intermediate volatility. Conventionally, the mixture would be separated by the mixture either via direct sequence or indirect sequence as shown in Figures 10-153a and 10-153b.

For the given ternary mixture, choice between these two arrangements depends on their boiling points, relative volatilities, composition of the ternary mixture, latent heat of vaporization, etc. By comparison, thermally coupled distillation columns need less energy and capital investment. Figures 10-155a and 155b show possible arrangements for the separation of the same ternary mixture of A, B and C by thermally coupled distillation. In the thermally coupled side column rectifier, a vapor stream is withdrawn from the stripping section of the main column and sent for rectification in a side column with an overhead condenser. Liquid stream from the bottom of the side column is then returned to the main column.

In the thermally coupled side column stripper, liquid stream from the main column is withdrawn and returned



Thermally coupled side column rectifier

Thermally coupled side column stripper

Figure 10-155 Alternative column sequences for a three-component separation.

to the side column for stripping where the reboiler is provided. Vapor stream from the side column is returned to the main column.

Selection between these two alternative arrangements depends on concentration profile of intermediate component B. If this reaches a maximum at any point of stripping section of the main or upstream column, and then the side column rectifier is selected. The distillation of B from either C or A is made much easier by withdrawing a side stream from the point at which the concentration of B is maximized.

Figure 10-156 compares conventional and a thermally coupled arrangements in terms of temperature and enthalpy. In the conventional arrangement the pressure of the two columns can be set independently, so allowing variation in temperatures of the two condensers or the two reboilers. Such freedom does not exist in the thermally coupled arrangement. Although thermally coupled arrangement requires a smaller heat load than the conventional arrangement, more of the duties are at extreme levels. These smaller duties favor the heat integration, but the more extreme levels work to its detriment. Therefore, if a thermally coupled arrangement is to be integrated, then the smaller loads and the more extreme levels may work to advantage or disadvantage depending on the situation. [314].

It is therefore recommended that simple columns should be used as a first option in the design process. Thermal coupling should be considered when the full heat integration context has been established.

An alternative to thermally coupled columns is a novel type of partitioned tray distillation column (also known as a divided-wall column or Petyluk column) for multicomponent systems. Figure 10-157 shows such a column, where a vertical baffle separates the feed location from that where intermediate boiling product is withdrawn. On the feed side of the partition, separation is achieved between the light (A) and heavy (C) fractions, while the intermediate boiling fraction (B) is allowed to migrate to the top and bottom sides of the partition. On the other side of the partition, the light fraction flows down, so intermediate boiling fraction (B) at the desired purity is

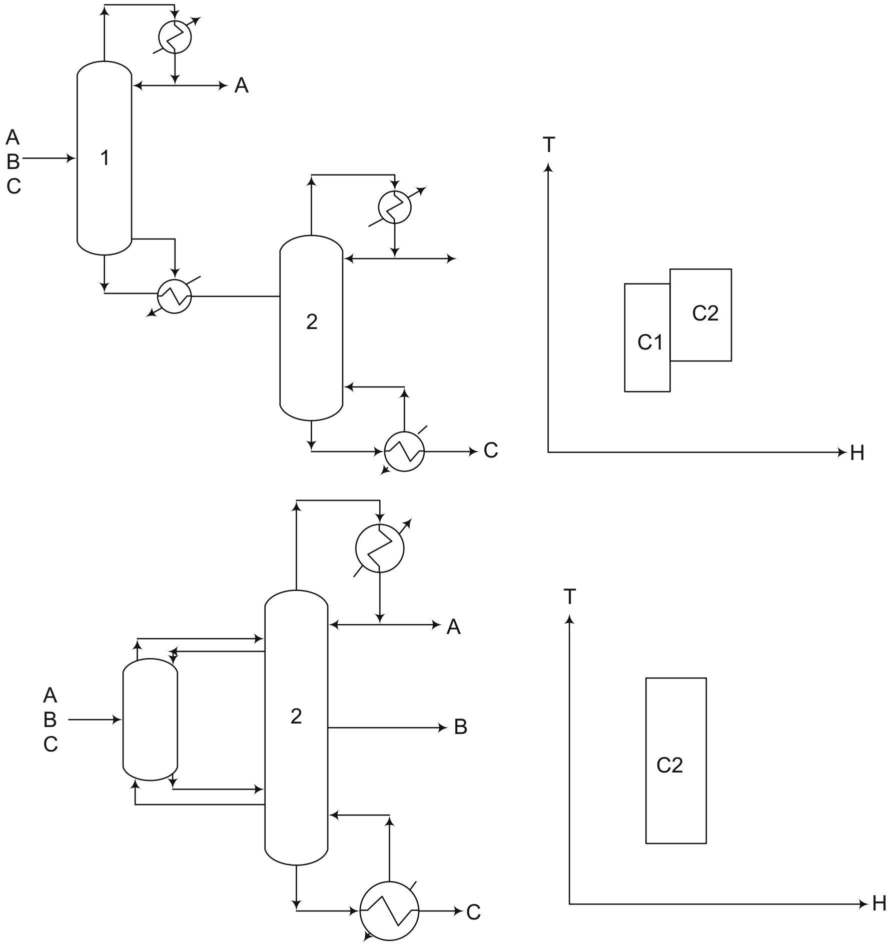


Figure 10-156 Relationship between heat load and level in simple and prefractionator sequences. (Source: Smith and Linnhoff, Trans IChemE, ChERD. 66: 195, 1998).

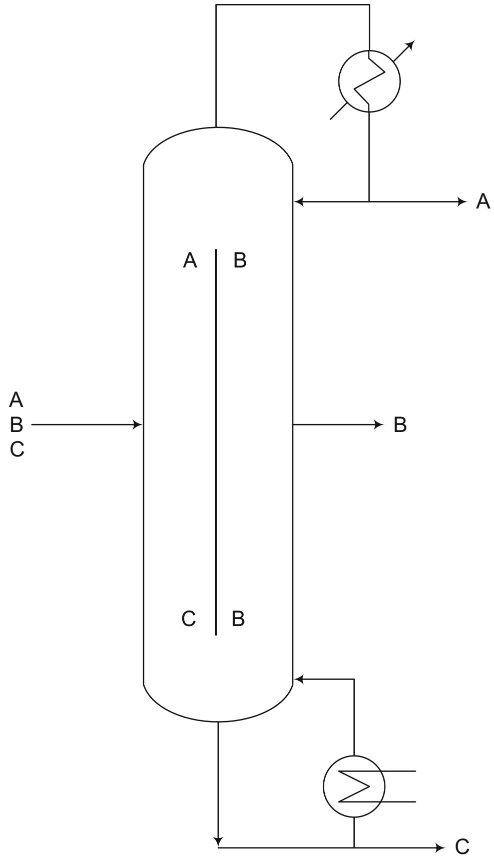


Figure 10-157 Partitioned Distillation Column.

withdrawn. Such a column has a larger diameter, but overall capital and operating costs are significantly lower (~30%) [313].

10.54.2 Practical Constraints in Sequencing Options

The following constraints limit the design options that are practically feasible [315]:

1. Corrosive components must be removed early to minimize the use of expensive, corrosion resistant in materials construction.
2. Reactive and heat sensitive components must be removed early to prevent product degradation.
3. Inhibitors are added to compounds that tend to polymerize when distilled. These tend to be nonvolatile, ending up in the column bottoms, and thus prevent finished products from being taken from the bottoms of columns.
4. Safety considerations often dictate that a particularly hazardous component be removed as early as possible from the sequence in order to minimize the inventory of that material.
5. When components in the feed to a distillation sequence are difficult to condense, total condensation of these components might require low-temperature condensation employing refrigeration and/or high operating pressures, and hence increased operating costs. Therefore, the light components are normally removed from the top of the first column to minimize the use of refrigeration and high pressures in the overall sequence.

10.54.3 Choice of Sequence for Distillation Columns

Many heuristics/rules of thumb have been proposed for the selection of the sequence for distillation columns, and these are summarized by the following [315]:

Heuristic 1.	Separations where the relative volatility of the key components is close to unity, or that exhibit azeotropic behavior should be performed in the absence of non-key components. That is, perform the most difficult separation last.
Heuristic 2.	Sequences that remove the lightest components individually in column overheads should be favored. i.e., favor the direct sequence.
Heuristic 3.	A component comprising a large fraction of the feed should be removed first.
Heuristic 4.	Favor splits in which the molar flow between top and bottom products in individual columns is nearly equal.

10.55 Heat Integration of Distillation Columns

Generally, the scope for integrating conventional distillation columns into an overall process is limited due to practical constraints. The grand composite curve is the curve where enthalpy residuals are displayed as a function of the interval temperatures, and the enthalpy residuals corresponding to the highest and lowest interval temperatures are the minimum heating and cooling utility duties (Figure 10-158). This curve provides a quantitative tool to access the integrating viabilities of the column. If the column cannot be integrated with the rest of the process or if the potential for integrating is limited by the heat flows in the background process, then the distillation process and its complex arrangements should be reviewed.

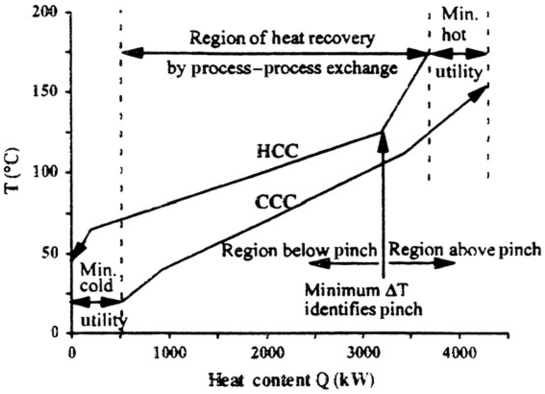
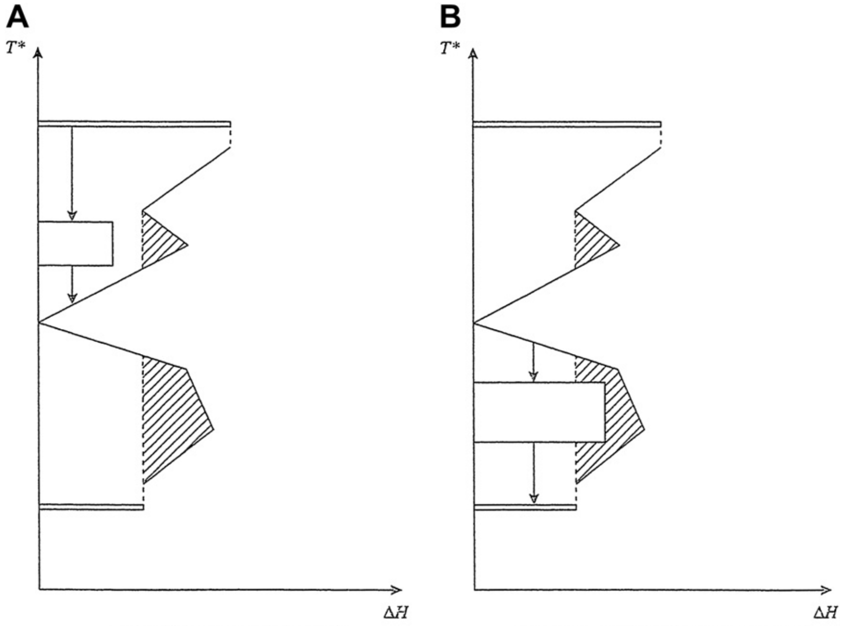


Figure 10-158 The hot composite curve (HCC) and cold composite curve (CCC) respectively show the heat availability and heat requirement for the overall process. (Source: Shenoy, Udah, V., Heat Exchanger Network Synthesis: Process Optimization by Energy and Resource Analysis, Gulf Publishing Co., Houston, 1995).

The pinch in this context is the point of minimum temperature difference, representing a bottleneck in heat recovery (i.e. the point of closest approach of composite curves in a "heating and cooling") problem. It divides the process into two thermodynamically separate regions, above which only hot utility is required, and its magnitude corresponds to the overshoot of the cold composite curve (CCC). Below the pinch, only cold utility is necessary and its magnitude is given by the overshoot of the hot composite curve (HCC). Where the two composite curves overlap, the hot process streams are in enthalpy balance with the cold process streams. The appropriate placement of distillation columns is when heat integration is not across the pinch. In an inappropriately placed column, if it is shifted above the pinch by an increase in pressure, the condensing stream which is a hot stream is shifted from below to above the pinch. The reboiler stream, which is a cold stream stays above the pinch. If the inappropriately placed column is shifted below the pinch by decreasing its pressure, then the reboiling stream, which is a cold stream is shifted from above to below the pinch. The condensing stream stays below the pinch, and therefore appropriate placement is a case of shifting streams, which is a particular case of the plus/minus principle indicated by Smith and Linnhoff [314].

However, when a distillation column is inappropriately placed across the pinch, its pressure may be altered in order to achieve appropriate placement. However, as the pressure changes, the shape of the "box" changes, since not only do the reboiler and condenser temperatures change but also the difference between the two. This affects the relative volatility, generally decreasing with increasing pressure and subsequently both the height and width of the box will change as the pressure changes.

Changes in pressure also affect the heating and cooling duties for column feed and products. Therefore, the



A column appropriately placed above the pinch

A column appropriately placed below the pinch

Figure 10-159 Distillation columns that fit against the grand composite curve. (Source: Smith, R. and B. Linnhoff., Trans. IChemE ChERD, 66, 195, 1988).

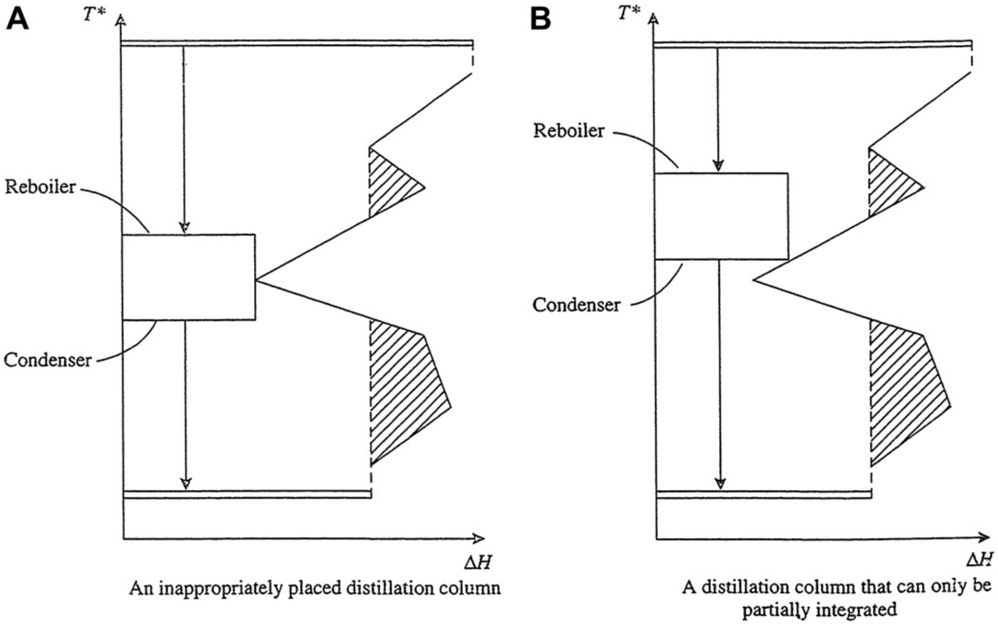


Figure 10-160 Distillation columns that do not fit against the grand composite curve. (Source: Smith, R. and B. Linnhoff., Trans. IChemE ChERD, 66, 195, 1988).

shape of the grand composite curve also changes as the column pressure changes. These effects will not be significant in most processes, since the sensible heat loads involved are small in comparison with the latent heat changes in condensers and reboilers. Figures 10-159 and 160 respectively show distillation columns that fit and do not fit against the grand composite curve. See Smith for detailed explanation [315].

If the distillation column will not fit either above or below the pinch, then other design options should be considered. One possibility is splitting the column feed and feeding to two separate parallel columns. The relative pressures in the columns are chosen such that the two columns can each be appropriately placed. The capital cost of such a scheme will be higher than that of a single column [314]. Use of an intermediate reboiler or condenser can also be considered. Reviews of this approach are presented elsewhere [316, 317, 318].

10.56 Capital Cost Considerations for Distillation Columns

Separators (e.g. distillation columns, evaporators and dryers) are energy intensive. Their efficiency in terms of the overall process can be improved if they are properly heat integrated. In distillation, the major design parameters must be ascertained to allow the design to proceed. The first decision is the operating pressure. As this is raised:

1. Condenser temperature increases.
2. Vapor density increases, resulting in a smaller column diameter.
3. Reboiler temperature increases with a limit often set by thermal decomposition of the material being vaporized. This results in excessive fouling.

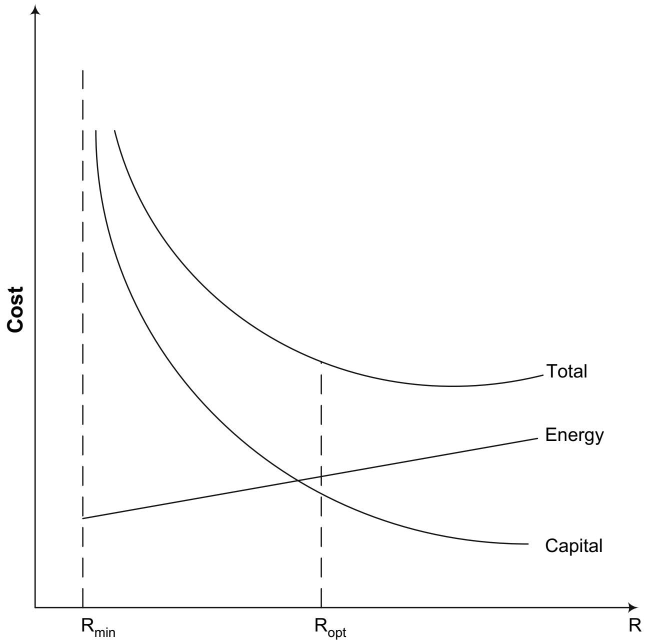


Figure 10-161 The capital energy tradeoff for stand-alone distillation columns.

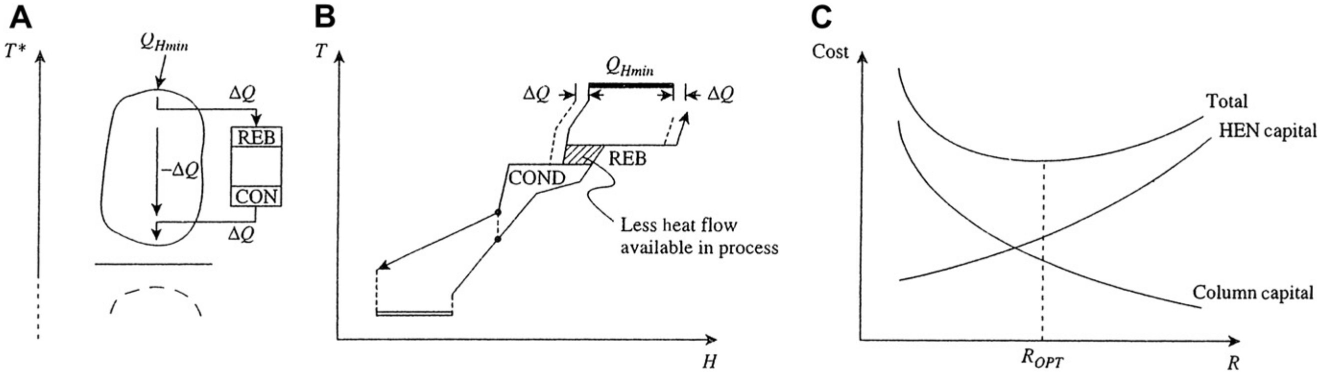


Figure 10-162 The capital/capital tradeoff for an appropriately integrated distillation column. (Source: Smith and Linnhoff, Trans IChemE, ChERD. 66: 195, 1998).

4. Latent heat of vaporization decreases, i.e. reboiler and condenser duties become lower.
5. Separation becomes more difficult (relative volatility, α decreases), i.e. more plates or reflux are required.

Correspondingly, as the operating pressure is lowered these effects are reversed, and the lower limit is often set by the desire to avoid:

- Refrigeration in the condenser
- Vacuum operation.

The use of refrigeration and vacuum operation incurs further capital and operating costs and thus increase the complexity of the design. It is essential, therefore to set distillation pressure to as low a pressure above ambient as allows cooling water or air cooling to be used in the condenser. The pressure should be fixed such that the bubble point of the overhead product is 10°C above the summer cooling water temperature, or to atmospheric pressure if using vacuum operation. When distilling high molecular weight material, process constraints dictate that vacuum operation be used in order to reduce the boiling point of the material to below where product decomposition occurs.

Reflux ratio is also needs to be chosen for distillation. Figure 10-161 illustrates a capital-energy tradeoff in a stand-alone distillation column. As the reflux ratio increases from its minimum, the capital cost decreases initially as the number of plates reduces from infinity, but the utility costs then increase as more reboiling and condensation are required. The optimal ratio of actual to minimum reflux is often less than 1.1, but designers are reluctant to design columns closer to minimum reflux than 1.1 except in special circumstances. This is because a small error in design or small alteration in operating conditions might result in an infeasible design. If the column is properly heat integrated with the rest of the process, the reflux ratio can often be increased without changing the overall energy consumption, as illustrated in Figure 10-162a. Increasing the heat flow through the column decreases the number of plates required, but increases the vapor rate. The corresponding decrease in heat flow through the process (shown in Figure 10–162b) will have the effect of decreasing temperature driving forces and increasing the capital cost of the heat exchanger network. Therefore, the tradeoff for an appropriately integrated distillation column becomes one between the capital costs of the column and the capital cost of the heat exchanger network- as shown in Figure 10-162c.

The nature of the tradeoffs change and the optimal reflux ratio for the heat-integrated column can be very different from that for a stand-alone column and thus the optimal reflux ratio for an appropriately integrated distillation column will be problem-specific.

For more examples, please visit: http://www.elsevierdirect.com/companions/9780750683661

Nomenclature for Part 1: Distillation Process Performance

A, B thru K = Constants developed in original article
a, b, c = Correlation constants (distillation recoveries [141])
A′, B′, C′ = constants in generalized Antoine equation (Table 10-5)
a = Activity of component
a_i = Activity of component, i
av or avg = Average
$a_{SRK}(T)$ = attraction function in SRK equation 10-75, $cm^6 - bar/mol^2$
$a_{C,SRK}$ = constant value of $a_{SRK}(T)$ at the critical point, $cm^6 - bar/mol^2$
B, C, D = Virial coefficients, Equation 10-11

B = Bottoms product or waste, lb mols/hr, also = W

B_b = Mols of component, b, used as reference for volatility, after a given time of distillation

B_{bo} = Mols of component, b, used as reference for volatility, at start of distillation

B_i = Mols of component, i, after a given time of distillation

B_{io} = Mols of component, i, at start of distillation

B_{Ti} = Total mols of liquid in bottoms of still at time, T_1

B_{To} = Total mols liquid (not including any steam) in bottom of still at start time T_o (batch charge)

b = y intercept of operating line; or constant at fixed pressure for Winn's relative volatility

b = intercept of a straight line with the y-axis

b_i = Mols of component, i, in bottoms

b_{SRK} = volume parameter in SRK equation 10-76, cm^3/mol.

C = No. components present, phase rule; or no. components, or constant

C_{mi} = Factor in Colburn Minimum Reflux method, pinch conditions, stripping

C_{ni} = Factor in Colburn Minimum Reflux method, pinch conditions, rectifying

C = Specific heat, Btu/lb (°F)

C_{mi} = Mols of distillate or overhead product, lb mols/hr; or batch distillation, mols

C_p = heat capacity, Btu/(lb mole °F)

c = constant defined by Equation 10-253

D = moles distillate per unit time

d_i = Mols component, i, in distillate

E = Vaporization efficiency of steam distillation

E_G = Overall column efficiency

E_o = Overall tray efficiency

$E^*_{MV} = Eoc$ = Murphree point efficiency, fraction

$E_{MV}O$ = Murphree plate/tray efficiency, = EM

F = Degrees of Freedom, phase rule; or, charge to batch still, mols

F = Feed rate to tower, lb mols/hr; or, mols of feed, (batch distillation) entering flash zone/time all components except non-condensable gases

F_{FR} = Factor for contribution of other feed flow to minimum reflux

F_L = Mols of liquid feed

F_v = Mols of vapor feed

$F_t = F + V_s$ = mols feed plus mols of non-condensable gases

$F_R = F_{SR,k}$ = Factor for contribution of side stream, k, flow to minimum reflux

F_{SR} = Factor for contribution of sidestream flow, to minimum reflux

F_{FRJ} = Factor for contribution of feed, j, flow to minimum reflux

f = Fugacity at a specific condition

f = acentric factor function, $f_{SRK}(\omega)$ in Table 10-5, $f_{PR}(\omega)$ in Table 10-6, dimensionless

f_ω = acentric factor dimensionless in Equation 10-77.

$f_{SRK}(\omega)$ = acentric factor function for SRK equation, dimensionless.

$f_{PR}(\omega)$ = acentric factor function for PR equation, $= 0.37464 + 1.54226\omega - 0.26992\omega^2$ dimensionless

$f\upsilon$ = Fugacity at reference standard condition

f_i = Feed composition,. i,; or, = total mols of component, i, in distillate and bottoms

G = Boilup rate, mols/hr

H = Total enthalpy, above reference datum, of vapor mixture at tray or specified conditions, Btu/lb mol, or Btu/lb

$H' = H_{ij}$ = Henry's Law constant, lb mols/(cu ft)(atm)

H_n = Total molal enthalpy of vapor at conditions of tray, n, entering tray; $H_n = \Sigma H_{ni} (y_{ni})$

H_s = Total enthalpy of steam, Btu/lb mol, or Btu/lb

HK = Heavy key component in volatile mixture

h = Enthalpy of liquid mixture or pure compound at tray conditions of temperature and pressure, or specified point or condition, Btu/lb mol, or Btu/lb

h = ratio of parameter b_{SRK} to molar volume, Equation 10-81, dimensionless

h_n = Total molal enthalpy of liquid at conditions of tray, n; $h'_n = h_{ni}(x_{ni})$

h_D = Molal enthalpy of product or total liquid enthalpy above reference datum for sum of all contributing percentages of individual components

h_{n+1} = Molal enthalpy of liquid leaving plate n + 1

h_a = Total molal enthalpy of liquid at conditions of tray, n; $hn = \Sigma h_{ni} (x_{ni})$

K = Equilibrium constant for a particular system (= y/x)
K′ = Equilibrium constant for least volatile component, K′ = y/x
K_i = Equilibrium distribution coefficient for component, i, in system
k = Experimentally determined Henry's Law constant, also can be K
k = Value of x at intersection of operating line and equilibrium curve on x–y diagram (batch operation)
k = composition of the liquid where the operating line intersects the equilibrium line
kpa = Metric pressure
L = Liquid flow rate return to tower as reflux, lb mols/hr, mols component in liquid phase; or, L_1, L_2 = Latent heat of vaporization; or, volumetric flow rate for incoming contaminated water (stripping VOC with air); or mols liquid produced from F per unit time, leaving flash zone, or moles liquid per unit time, rectifying section
$\bar{L}$ = moles liquid per unit time, stripping section.
L_F = moles liquid from feed plate per unit time.
L_o = moles reflux liquid returned to plate 1 per unit time.
L_r = Liquid flow rate down rectifying section of distillation tower, lb mols/hr
L_s = Liquid flowrate down stripping section of distillation tower, lb mols/hr
LK = Light key component in volatile mixture
L/V = Internal reflux ratio
L/D = Actual external reflux ratio
$(L/D)_{min}$ = Minimum external reflux ratio
M = Molecular weight of compound
M_s = Total mols steam required
m = Number of sidestreams above feed, n
N = Number of theoretical trays in distillation tower (not including reboiler) at operating finite reflux. For partial condenser system N includes condenser; or number theoretical trays or transfer units for a packed tower (VOC calculations) N_B = Number of trays from tray, m, to bottom tray, but not including still or reboiler
N_{min} = Minimum number of theoretical trays in distillation tower (not including reboiler) at total or infinite reflux. For partial condenser system, N_{min} includes condenser; also, minimum value of N
N_n = Number of theoretical trays above feed, or reference plate, n, but not including n
N_m = Number of theoretical trays before feed tray
N_{im} = Mols of immiscible liquid
N_o = Mols of non-volatile material present; or, number of theoretical trays/stages in column only, not reboiler or condenser
N_s = Mols of steam
n = Number of theoretical trays in rectifying section or number of components, or minimum number of equilibrium trays
n = number of plates between any two points in the column under consideration.
n_f = Number of feeds
n_s = Number of sidestreams
P = Pressure, atmospheres; or, vapor pressure of component, atm.; or,
P = number of phases; or, P = for batch operations, percentage draw-off
P_i = Vapor pressure of each component
P_s = Vapor pressure of steam, absolute
P_b = Vapor pressure of reference more volatile component, b
p = Pi = Partial pressure of one compound in liquid, absolute units, or, ratio rps/rpr; also, P_i = partial pressure of solute (Henry's Law)
p = Total pressure of system = π
p′ = Number of trays below feed where introduction of light components should begin, Akers-Wade calculation method
P_i^* = Vapor pressure component, i, in pure state at temperature
P_{ii}^* = Similar to above by analogy
p″ = Number of trays above feed where introduction of heavy components should begin. Akers-Wade calculation
p_{im} = Pure component vapor pressure of immiscible liquid, mm Hg
p_s = Partial pressure of steam, mm Hg
P_t = total pressure.
Q_B = Net heat in through reboiler duty, Btu/hr; or heat added in still or bottoms
Q_c = Net heat out of overhead condenser, Btu/hr, = w cp $(t_i - t_o)$
q = qF = Thermal condition of feed, approximately amount of heat to vaporize one mol of feed at feed tray conditions divided by latent heat qf vaporization of feed

q_B = reboiler duty, Btu/hr.

q_D = condenser duty, Btu/hr.

q_v = Thermal condition of sidestream (s)

R = Reflux ratio = External reflux ratio for a given separation, = L/D, L = liquid rectifying column

R = reflux ratio, reflux per unit time divided by moles of distillate per unit time

R = Actual reflux ratio, O/D

R_m = Minimum reflux ratio, O/D

R′ = Pseudo minimum reflux ratio

R_{min} = Minimum external reflux ratio for a given separation

R_F = Feed component of minimum reflux

$R_{F,n}$ = Feed component of minimum reflux for feed, n

R_{OF} = Other feed components of minimum reflux

R_s = Sidestream component of minimum reflux

r_{ps} = Ratio of light to heavy keys, stripping pinch

r_{pr} = Ratio of light to heavy keys, rectifying pinch

r_f = Ratio mol fraction light key to heavy key in feed

S = Steam flowrate, lb1lhr or lb mols/hr; or theoretical stages at actual reflux (Figure 10-49a) including reboiler and partial condenser, if any; or batch, mols in mixture in still kettle at time θ

S_n = Theoretical stages at minimum reflux

S_M = Minimum theoretical stages at total reflux from bottoms composition through overhead product composition, including reboiler and any partial condenser (if used); or minimum stripping fat for at minimum flowrate of air

S_k = Flowrate of sidestream, k, mols/hr

S_o = Theoretical stages at a finite operating reflux; or batch, mols originally charged to kettle

S_r = Theoretical stages in total rectifying section, including partial condenser, if used

S_s = Theoretical stages in total stripping section, including reboiler

S_t = Theoretical trays/stages at actual reflux, L/D, including reboiler and total condenser

S_{opt} = Optimum stripping factor

$(SR)_i$ = Separation factor

s = Pounds (or mols) steam per pound (or mol) of bottoms; or flowrate of sidestream, mols/hr

T = Temperature, °Abs R

t_B = Bottoms temperature, °F

t_i = Temperature in, °F

t_o = Temperature out, oF; or overhead temperature, °F

$V = V_t$ = Total vapor leaving flash zone/unit time at specific temperature and pressure; or total overhead vapor from tower, mols/hr; or mols of component in vapor phase; or volumetric flowrate for incoming fresh air

V = Quantity of vapor, mols

V_C = moles of vapor condensed necessary to heat reflux liquid to t.

V_F = moles vapor per unit time rising from feed plate.

V_r = Vapor flow rate up rectifying section of tower, lb mols/hr

V_s = Vapor flowrate up stripping section of tower, lb mols/hr; or mols non-condensable gases entering with feed, F, and leaving with vapor, V/time

V_{min} = Minimum fresh air flow based on slope of operating line, L/V, on x–y diagram

v = Vapor flow rate, mols/hr; or molar volume

W = Bottoms product, or still bottoms, or kettle bottoms, mols; also see B; or mols/hr bottoms product; or mols of residue or bottoms/unit time (Ponchon heat balance)

W = Weight of material in vapor (steam distillation)

W_1 = Mols final content in still

W_{il} = Contents of still pot or kettle at any point, 1, after start for components, i, mols

W_{io} = Initial contents of kettle or still pot, mols, for component, i

W_o = Mols liquid mixture originally charged to still pot

w = Pounds coolant per hour

x_B = mole fraction in the bottoms.

x_D = mole fraction in the distillate.

$x_i = x$ = Mol fraction of component in liquid phase; or mol fraction solute in solution (Henry's Law)

$x_f = x_{lF}$ = Mol fraction of any component in feed, vapor + liquid, F_t; $x_f = Fx_f/F_t$

x′ = Mol fraction of least volatile component

x'_1 = $x_l - k$
x'_p = $x - k$
x = Mol fraction more volatile component in liquid
x_1 = Mol fraction of component, i, in liquid mixtures as may be feed distillate or bottoms, B_T, at any time, T_l; or mol fraction more volatile in vapor entering column at any time (or in distillate)
x_{it} = Mol fraction liquid at intersection of operating lines at minimum reflux, Scheibel-Montross equation
x_{hf} = Mol fraction heavy key in feed
x_n = Pinch composition and light component mol fraction
x_N = Mol fraction VOC component in the stripped water exiting, usually targeted at meeting environmental regulations
x_{iD} = Mol fraction light key component in overhead product; or, any light component Colburn)
x_{iB} = Mol fraction light key component in keys in original charge
x_{io} = Mol fraction light key in overhead expressed as fraction of total keys in overhead
x_{1B} = Mol fraction most volatile component in bottoms
x_{hD} = Overhead composition of heavy key component, mol fraction
x_{hn} = Pinch composition of heavy key component, mol fraction
x_l = Mol fraction of component in liquid phase; or mol fraction more volatile component in vapor entering column at any time
x_s = Mol fraction of a more volatile in kettle at time θ
x_{si} = Value of xs when distillate receiver is first filled
x_{so} = Mol fraction more volatile in kettle at time θ
x_w = Mol fraction more volatile component in bottoms residue (final); or, composition of liquid in still, mol fraction
x_{wo} = Initial mol fraction of more volatile component in liquid mixture
x_F = Mol fraction more volatile component in feed
x_D = Mol fraction more volatile component in final distillate = mol fraction in distillate leaving condenser at time θ
x_p = Mol fraction of more volatile component in liquid leaving column at any time
x_L = Mol fraction of feed as liquid, Scheibel-Montross
x_{lo} = Mol fraction light key in overhead expressed as fraction of total keys in overhead, Scheibel-Montross equation
x_m = Tray liquid mol fraction for start of calculations (most volatile component)
x_o = Mol fraction of component, i, in bottoms B_{To} at start time, T_o; or VOC mol fraction
x_v = Mol fraction of feed as vapor, Scheibel-Montross equation
$y = y_i$ = Mol fraction of component in vapor phase, as may be feed, distillate, or bottoms; or Henry's Law, y_i = mol fraction solute in vapor
y_i = Mol fraction VOC component in the exiting VOC contaminated air
y' = Mol fraction of least volatile component
y^* = Equilibrium value corresponding to x_i
y_n = Average light key mol fraction vapor leaving plate, n
y_{n-1} = Average light key mol fraction vapor entering plate, n + 1
y_{n-1} = Mol fraction VOC component in the incoming fresh air (equals zero for fresh air)
y_j = Mol fraction solvent component in vapor
y_s = Mol fraction steam in vapor
Y_{iB} = Percent recovery of, i, in the bottoms
Y_{iD} = Percent recovery of, i, in the distillate
Z = Compressibility factor
z_F = mole fraction in the feed.
$z_{i,F}$ = Mol fraction component, i, in feed
$z_{i,Fj}$ = Mol fraction component, i, in feed, j
$z_{i,S}$ = Mol fraction component, i, in sidestream
$z_{i,Sk}$ = Mol fraction component, i, in sidestream, k

Greek Symbols

α, α_1 = Relative volatility of light key to heavy key component, or any component related to the heavy key component, except Equation 8-65, α_i is based on heavy key)
α_{avg} = Average relative volatility between top and bottom sections of distillation tower/column
α_j = Relative volatility of more volatile to each of other components (steam distillation)
α_i = Relative volatility of component, i

α_H = Relative volatility of components heavier than heavy key at feed tray temperature
α_i = Relative volatility of more volatile to each of other components
α_L = Relative volatility of components lighter than light key at feed tray temperature
β = Constant of fixed pressure in Wino's relative volatility, Equation 8-43
θ = Time from start of distillation to fill receiver, or value of relative volatility (Underwood Parameter) to satisfy Underwood Algebraic Method
θ_1 = Time for filling distillate receiver, hrs
θ_2 = Time for refluxed distillation (batch), hrs
μ = Viscosity, centipoise
υ = Activity, coefficient
π = total system pressure, absolute; atm, mm Hg, psia
π = 3.14159
Σ = Sum
Ψ = First derivative function
Ψ' = Second derivative function
ω_j = Function in Underwood's Algebraic method for minimum reflux ratio
Ω = Fugacity coefficient
ϕ = No. phases from phase rule
λ = Latent heat of vaporization, Btu/lb mole.

Subscripts

a, b, c, etc. = Specific components in a system or mixture
Avg, Av = Average
B = Any consistent component in bottoms product
B = b = Bottoms
b = Exponent in Winn's relative volatility equation
D = Any consistent component in condensed overhead product or distillate
eff = Effective
F = Feed
F_j = Feed, j
F_n = Intermediate feed, Scheibel-Montross method
F_L = FH = All mol fractions lighter than light key in feed, Scheibel-Montross method
FHK = Heavy key in feed
FLK = Light key in feed
HK = h = h_k = Heavy key component
H = Components heavier than heavy key
h = Heavy, or heavy or high boiling component in mixture; also heavy key component
i = Any component identified by subscripts 1,2, 3, etc, or by a, b, c, etc.; or initial condition, i
im = Immiscible liquid
j = Specific components in a system or mixture
l = lk = Light key component; or light or low boiling component in mixture
lh = Refers to light component referenced to heavy component
LK = Light key component
L = Liquid, Scheibel-Montross method only; or components lighter than light key
M = min = Minimum
m = No. trays in stripping section; or tray number
n = No. trays in rectifying section; or tray number
o = Initial conditions; or i; or operating condition
p_r = Pinch condition in rectifying section
p_s = Pinch condition in stripping section
P = For packed towers
w = Relates to bottoms or pot liquor, or kettle bottoms
r = Rectifying section; or component to which all the relative volatilities are referred
s = Steam, or stripping section of column
t = Top, or total
T = For tray towers
v = Vapor
1 = Initial, steam distillation
2 = Remaining, steam distillation
1, 2, 3, etc. = Tray numbers; or specific components in a system or mixture