UCRL 8787

UNIVERSITY OF CALIFORNIA

Ernest O. Lawrence

Radiation Laboratory

SOLUTION OF MULTISTAGE SEPARATION PROBLEMS BY USING DIGITAL COMPUTERS

BERKELEY, CALIFORNIA

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-8787

Chemistry - General

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

SOLUTION OF MULTISTAGE SEPARATION PROBLEMS BY USING DIGITAL COMPUTERS

John H. Duffin
(Thesis)

August 1959

Printed for the U. S. Atomic Energy Commission

Printed in USA. Price $4.00. Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

SOLUTION OF MULTISTAGE SEPARATION PROBLEMS BY USING DIGITAL COMPUTERS

Contents

	Page
Abstract	10
I. Introduction and Consideration of Variables and Data Functions	11
Design Variable	12
Data Functions	24
II. Mass-Balance Methods	28
Equations — Method I	28
Feed Quality	35
Alternate Equations — Method I	37
Equations — Method II	46
Improving Rate of Convergence — Method I	56
III. Energy-Balance Methods	65
Method I	65
Method II	76
The Flash Process	84
The Corrective Energy-Flow Extrapolation Process	87
Application of Method II	90
IV. Calculations With Variable Other Than Bulk Separation Set and Held, and Calculations with Complex Columns	100
Component Separation as a Set Variable	100
Composition-Dependent Variable as a Set Variable	108
Complex Columns Three or More Products	118
Complex Columns Two or More Feeds	125
V. Stripping and Absorption Columns	133
Simple Stripping Column	133
Refluxed Stripper	158

Contents (cont'd.)

Page

Refluxed Stripper with Side Stripper 170

Simple Absorber 182

Reboiled Absorber 191

VI. Infinite-Mixture Calculations 206

VII. Effect of Nonideality in Multistage Calculations 224

VIII. Liquid-Liquid Extraction Calculations 245

Acknowledgments 259

Nomenclature 260

References 265

LISTING OF EXAMPLES, FIGURES, AND TABLES

Example	Figure	Table	Page	Remarks
--	1	--	14	Various types of reflux production in distillation columns used for indepdent-variable analysis
--	2	--	17	Complex distillation columns for independent variable analysis
--	--	I	21	Listing of independent variable from Description Rule for columns of Fig. 1.
--	3	--	36	Methods of introducing feed at various thermal conditions into distillation columns
--	4	--	39	Column used to illustrate mass-balance method in Example 1
--	5	--	40	Schematic computer program for Method I mass balance
1	--	--	38	Simple distillation mass balance by Method I
1	--	II	43	Results for Example 1 for four-component nine-stage system
1		III	44	
1		IV	45	
2	6	--	51	Method II mass-balance results on same system as Example 1
2	7	--	52	
2	8	--	53	
2	--	V	55	
--	9	--	59	Φ-function plot
3	--	VI	61	Results for Method I mass balance of system of Example 1, using Φ factor
3	--	VII	62	
--	--	VIII	64	Product estimation using Φ factor extrapolation
4	--	--	75	Simple distillation using Method I mass balance and Method I energy balance in the calculation
--	10	--	70	Schematic computer program for Method I energy-balance calculations

Example	Figure	Table	Page	Remarks
4	--	IX	71	Results for Example 4 for a four-component nine-stage system
4	--	X	72	
4	--	XI	73	
--	11	--	77	Illustrations for Method II energy-balance considerations
--	12	--	82	Schematic computer program for energy balance by Method II
--	13	--	86	Qualitative behavior of (C_V/C_L) ratio
--	14	--	88	Method II energy-balance reflection process
5	--	--	98	Simple distillation using Method I mass balance and Method II energy balance in the calculation
5	--	XII	92	Results for Example 5 for six-component ten-stage system using various damping factors
5	15	--	94	Effect of Φ factor also illustrated
5	16	--	95	
5	17	--	96	
5	18	--	97	
6	--	--	105	Simple distillation holding product purity and recovery
6	--	XIV	103	Results for Example 6 for four-component nine-stage system using Method I mass balance only
6	--	XV	104	
7	--	--	109	Simple distillation holding reboiler temperature and composition
7	--	XVI	112	Results for Example 7 for six-component nine-stage system using Method I mass balance only
7	--	XVII	113	
8	--	--	114	Simple distillation holding reboiler temperature and duty
8	--	XVIII	115	Results for Example 8 for six-component nine-stage system using Method I mass balance only
8	--	XIX	116	
		XX	117	
--	19	--	119	Complex column illustrations
9	--	--	124	Column with side-draw product

Example	Figure	Table	Page	Remarks
9	--	XXI	122	Results of Example 9 for four-component
9	--	XXII	123	22-stage system with side stripper by Method I mass balance only
--	20	--	126	Distillation column with two feeds
10	--	--	132	Column with two feeds
10	--	XXIII	131	Results for Example 10 for four-component
10	--	XXIV	132	16-stage system by modified Method I mass balance only
--	21	--	134	Typical stripping columns
11	--	--	139	Simple stripper--flow corrections only
11	--	XXV	140	Results for Example 11 for five-component
11	--	XXVI	140	plus steam - 4 stage system. Method I mass balance used in the calculation
12	--	--	142	Simple stripper--mass and energy balance
--	22	--	143	Schematic computer program for strippers
	Path (a)			Flow correction only
	Path (b)			Temperature correction only
12	--	XXVII	146	Results for Example 12 for same system
12	--	XXVIII	146	as Example 11. Method I mass balance
12	--	XXIX	147	plus flow correction and Method II energy balance
12	23	--	144	
12	24	--	145	
13	--	--	149	Simple stripper--temperature correction only
13	--	XXX	148	Results for Example 13 for same system as Example 12 but with Method I mass balance only
14	--	--	149	Simple stripper--temperature correction and energy balance
14	--	XXXI	150	Results for Example 14 for same system
14	--	XXXII	150	as Example 12. Temperature corrected
14	--	XXXIII	150	by dew point, energy balance by Method
14	25	--	151	II, mass balance by Method I, results
14	26	--	152	with and without Φ factor
14	27	--	153	

Example	Figure	Table	Page	Remarks
15	--	--	158	Simple stripper--Method I energy balance
15	--	XXXIV	157	Results of Example 15 for system of Example 11
15	--	XXXV	158	Shows failure of Method I energy balance
16	--	--	159	Refluxed stripper--steam as a component
16	--	XXXVI	160	Results for Example 16 for four-component
16	28	--	161	plus steam - 9 stage system. Method II
16	29	--	162	mass balance only used in the calculation
17	--	--	164	Refluxed stripper--mass and energy
17	30	--	166	balance. Instability of double-flow-correction solution of Example 17
17	--	XXXVII	171	Results for Example 17 for six-component
17	--	XXXVIII	172	plus steam - 8 stage system. Method I
17	31	--	167	mass balance and Method II energy balance
17	32	--	168	used in the calculation together with
17	33	--	169	double-temperature-corrections
--	34	--	173	Refluxed stripper with side stripper.
--	35		174	Meshing side stripper into Method II energy balance
18	--	--	176	Refluxed stripper with side stripper
18	--	XXXIX	180	Results for Example 18 for six-component
18	--	XL	181	plus steam - 8 stage system. Method I mass balance and Method II energy balance used in the calculation
18	36	--	177	Double-temperature-correction solution
18	37	--	178	
18	38	--	179	
--	39	--	183	Typical absorbers
19	--	--	189	Simple absorber--mass and energy balance
19	--	XLI	188	Results for Example 19 for six-component
19	--	XLII	189	four-stage system with modified Method
19	40	--	185	I mass balance and Method II energy balance
19	41	--	186	
19	42	--	187	
20	--	--	197	Reboiled absorber--mass and energy balance

Example	Figure	Table	Page	Remarks
20	--	XLIII	195	Results for Example 20 for six-component eight-stage system with modified Method I mass balance and Method II energy balance. Results of various damping factors shown
20	--	XLIV	196	
20	--	XLV	197	
20	43	--	192	
20	44	--	193	
20	45	--	194	
21	--	--	199	Comparison of results of Method I and Method II mass balance on reboiled absorber
21	46	--	200	
22	--	--	205	Reboiled absorber--mass and energy balance
22	--	XLVI	204	Results for Example 22 for same feed and system as Example 20, but with Method II mass balance and Method II energy balance
22	--	XLVII	204	
22	--	XLVIII	205	
22	47	--	202	
22	48	--	203	
--	49	--	207	Infinite-mixture function representation
--	50	--	210	True boiling point (TBP) and TBP stage curves
--	51	--	214	Typical TBP product curves
23	--	--	222	Infinite mixture in simple distillation
23	--	XLIX	220	Results for Example 23 for 17-component nine-stage system with mass (I) and energy (I) balance using Method I mass balance and Method I energy balance in the calculation
23	52	--	216	
23	53	--	217	
23	54	--	218	
23	55	--	221	
--	56	--	229	Schematic computer program for nonideal calculations
24	--	--	230	Simple distillation with nonideal liquid phase
24	--	L	231	Results for Example 24 for three-component five-stage system with mass (I) balance using only Method I mass balance in the calculation
24	57	--	232	
24	58	--	233	
25	--	--	235	Same as Example 24 but with different split and stages

Example	Figure	Table	Page	Remarks
25	--	LI	236	Results for Example 25 for three-component eleven-stage system with mass (I) balance using only Method I mass balance in the calculation.
25	59	--	237	
25	60	--	238	
26	--	--	239	Same as Example 24 except for different split and stages
26	61	--	240	Results for Example 26 for three-component 24-stage system showing instability of Method I mass balance
27	--	--	243	Same as Example 26 but with Method II mass balance
27	62	--	241	Results for Example 27 for three-component 24-stage system. Method II mass balance only used in the calculation
27	63	--	242	
--	64	--	244	Converged temperature gradients for Examples 25, 26, and 27
--	65	--	249	Schematic computer program for liquid-liquid extraction
28	--	--	250	Single-stage extraction
28	--	LII	252	Results for Example 28 for three-component one-stage system with Method II mass balance and corrective mass flow
28	66	--	251	
29	--	--	258	Multiple-stage liquid-liquid extraction
29	--	LIII	257	Results for Example 29 for three-component three-stage system with Method II mass balance and corrective mass flow
29	--	LIV	258	
29	67	--	254	
29	68	--	255	
29	69	--	256	

SOLUTION OF MULTISTAGE SEPARATION PROBLEMS BY USING DIGITAL COMPUTERS

John H. Duffin

Lawrence Radiation Laboratory and Department of Chemical Engineering
University of California, Berkeley, California

June 1959

ABSTRACT

Methods of solving various problems in multistage separation operations are presented. These methods are illustrated by solving specific problems using both medium (IBM 650) and large (IBM 701) digital computers.

Separations by distillation normally encountered in the petroleum and chemical industries are covered in detail from the initial considerations of variable analysis to the final convergent solution of a given problem. Various methods of attacking a problem are presented and combinations of these methods that produce convergent solutions are suggested and illustrated. By means of appropriate equations, an operating unit is simulated on a computer and its behavior is studied as a steady-state or convergent solution is approached.

Problems in distillation occur where an infinite rather than a discrete mixture is used, and methods of attack and illustrations are given for problems of this type. By using these methods it is possible to simulate such complex industrial units as crude-oil distillation columns.

Nonideal equilibrium problems are also covered; methods of attack are presented as well as illustrations for a specific problem.

Since methods developed for distillation operations should apply, with appropriate modifications, to any multistage process, liquid-liquid extraction is considered finally. A method of attack for problems of this type is developed and solutions of problems are given.

I. INTRODUCTION AND CONSIDERATION OF VARIABLES AND DATA FUNCTIONS

In the past, a large amount of effort has been expended in studies of calculational procedures for certain problems in multistage separation processes. In distillation, for example, the classic problem which has received most attention is the design of a column for a specified separation of two components of a mixture. For this problem, the reflux flow is set at a value greater than the minimum for the separation, and an attempt is made to estimate the product amounts for all components other than the two specified. The number of stages required is then calculated, usually by a stage-to-stage procedure from one or both ends of the column. Unfortunately, except for relatively few problems, the calculations are not easily done, but the hard work of such approaches is now done by digital computers. If the equilibria are nonideal, the product compositions cannot be estimated with any certainty, and, in addition, stage-by-stage calculations become complex and difficult. Again, if the column is producing more than two products from a multicomponent mixture, the necessary estimation of the product compositions is difficult.

In addition to these difficulties, the calculational procedures developed for the solution of the classic problems are not well adapted to the solution of other common and equally important problems which arise in the operating of existing columns. Examples of this type of problem are (a) the analysis of the operation of an existing unit to determine whether a separation might be improved and how this might be done, (b) the calculation of the capacity of an available column when put into use for a specified separation, or (c) the effect of a change in feed stock or some other variable on a series of interconnected columns. Any of these problems could be of considerable importance in determining the optimum use of equipment. With the growing prominence of linear programming and operations research methods, the solution of problems such as these becomes increasingly important.

Calculation methods for existing columns are presented in this work. The basic equations and procedures employed in some of these methods

have been discussed by Thiele and Geddes,[35] Hummel,[19], Donnell and Turbin,[7] and others,[1,8,14,16,23,29] but the usefulness of the methods has not been widely appreciated because of the lack of elaboration of the techniques of solution. The advent of small and large digital computers has stimulated interest in the solution of these problems and has brought to light many difficulties in obtaining convergent solutions for problems involving the myriad variations in column types, column feeds, product requirements, etc., which commonly occur in industrial practice.

Design Variables

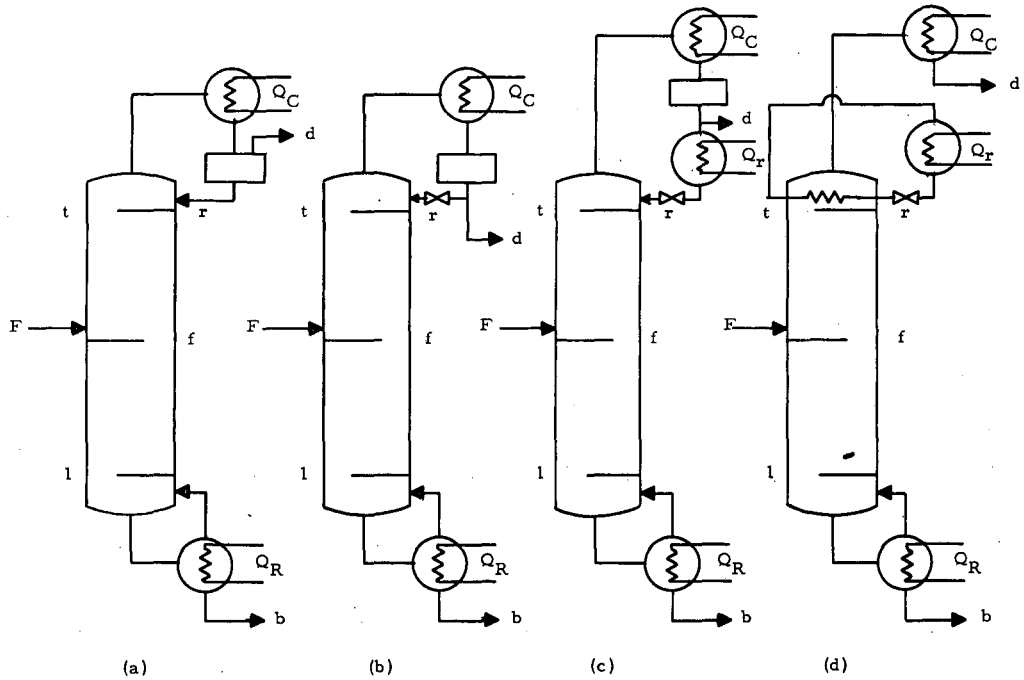
The calculation procuedres to be discussed in subsequent sections offer a means of solution to a wide variety of separation problems. The very fact that they are so versatile, however, requires that in their utilization a thorough understanding be had of the formulation or setting up of the separation problems. Setting up or describing the fractionation to be calculated is essentially a matter of assigning values to the number of independent variables needed to define the problem. The calculation then yields the values of all the dependent variables.

Although it is quite as important as the calculation, the subject of problem description has, until recently, been neglected in distillation literature. Gilliland and Reed,[13] and Kwauk[20] have presented papers giving a rigorous treatment of problem description, and Robinson and Gilliland[28] touch on the subject in their book. The great bulk of the literature has been concerned with development of calculation methods suitable to the design of columns, and the problem set up to test the methods has almost inevitably been the same, viz., the independent variables have been two separation specifications, the reflux or reflux ratio and the stipulation that the feed plate was to be located at the optimum point. Here, then, calculations are made primarily to obtain values for the number of enriching and stripping stages, although they also yield the separation that will result for each component of the feed. This problem has been illustrated so often

that its formulation is intuitive to one working in distillation design. However, the simple, general rule which governs what and how many variables are independent and must be set to define a separation problem is not well known. Therefore it becomes desirable to state and discuss the rule. The rule as discussed here is, in essence, the same as the elegant formulations of Kwauk but is much easier and quicker to apply.

Associated with any fractionation problem is a number of variables which describe the column and its operation. These variables are flows, temperatures, separation specifications, number of stages, column diameter, and in general, any quantity that satisfies the requirement of describing the column or its operation. Obviously, not all these variables are independent and can be arbitrarily set, and the number of independent ones changes with the column used and the operation performed. A simple general problem-description rule, called the Description Rule, can be stated, and the rule will hold for any multistage contacting unit. It is as follows: To completely describe the separation operation, a number of independent variables must be set equal to the number that can be set by construction or controlled by external means. Setting a lesser number in the problem description yields an infinitude of answers in solving for values of the remaining variables, whereas setting a greater number may lead to no answer.

The use of the rule is extremely simple, but the terms variables which can be set by construction or controlled by external means are unfortunately vague and can best be clarified by use of examples. A simple distillation column is shown in Fig. 1a, and the process of drawing the figure is tantamount to construction. Any feature of the column drawn has been set by construction and hence is an independent variable. Not all the features of the column, however, enter the fractionation equations which can be written, and so these extraneous features can be neglected. The important independent variables that can be set in the figure are the numbers of theoretical stages in each column section. The fractionation equations written must, of course, recognize such a structural stiplulation as a partial condenser, but



MU-17904

Fig. 1

the influence of the bulk of the structural details on the fractionation can at present be only implicitly expressed in the estimate of the overall stage efficiency for each section.

In addition to being able to construct the column of Fig. 1a with any desired number of theoretical stages in the two sections, there are a number of variables which can be externally controlled and which can be determined by simply looking at the figure. It is apparent that an arbitrary amount of feed material may enter the column, that (within limits) an arbitrary amount of energy or heat may enter the reboiler, and also that an arbitrary amount of energy or heat may be withdrawn at the condenser. There are, then, three additional independent variables. Lastly, it is apparent that the pressure at some point in the column can be arbitrarily set and controlled and that the feed may have any composition and energy content.

The total list of independent variables which must be fixed to completely describe the problem is then

	Number of independent variables
Feed composition (N components)	N-1
Feed amount	1
Feed enthalpy	1
Condenser duty	1
Reboiler duty	1
Theoretical enriched stages	1
Theoretical stripping stages	1
	$\Sigma = N+6$.

Defining the fractionation problem with the N+6 specific independent variables above would almost never be done. In general, from the variables listed, setting the condenser and reboiler duties is of least interest, and setting the other variables is also of little interest. Instead, it is usually preferable to specify something about the separation. Of course this can be done, since, for this example, all the listed independent variables can be replaced, in describing the problem, with an equal number of any other independent variables;

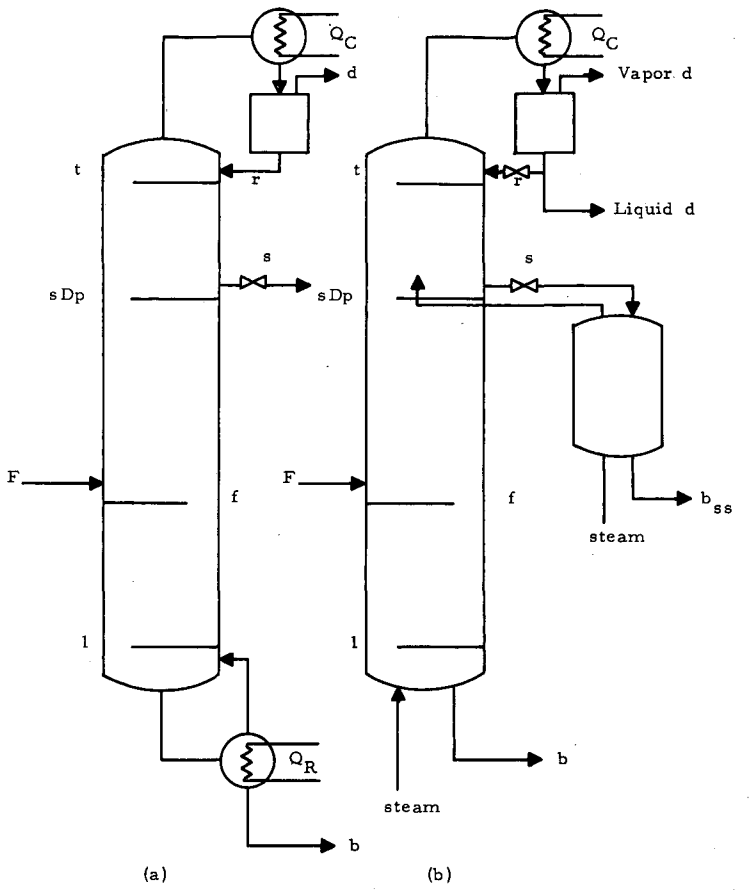
variables are chosen which are most pertinent to the problem at hand. The Description Rule serves to tell how many of these independent variables must be set. The ones used are then, at least in part, a matter of free choice.

Practical limitations enter, however, in the selection of independent variables, because the calculations are too difficult to carry out unless certain variables are set. Thus it is imperative that variables describing the feed and also the column-pressure variable be set in order to do calculations, and it becomes convenient in thinking about the Description Rule to consider these as always set, as indeed they are in almost all practical problems. For the column of Fig. 1a, the last four variables of the above list are available for replacement by other variables in a specific problem description.

The Description Rule is just as easily applied to more complex operations. As a further example, Fig. 2a shows a distillation column with a side stream, S, withdrawn from a stage (sDp) in the enriching section. Again, the column may be fed with feed of any amount, composition, and enthalpy, and may be operated at any pressure; these independent variables can be considered as arbitrarily set. From inspection of Fig. 2a, the remaining independent variables are

	Number of independent variables
Condenser duty	1
Reboiler duty	1
Enriched stages	1
Intermediate stages (between side-drawn and feed stages)	1
Stripping stages	1
Side-drawn amount	1
	$\Sigma = 6$.

Thus, there are six independent variables (in addition to feed variables and column pressure) compared to four for the column and operation of Fig. 1a.



MU-17905

Fig. 2

Probably the most complex column and operation that will normally encountered is a crude-oil distillation column, a somewhat simplified illustration of which is shown in Fig. 2b. Again, all the feed variables and the column pressure are set, and the remaining variables are written down by simply inspecting the figure and noting the points that may be controlled.

	Number of independent variables
Main stripping-steam amount	1
Main stripping-steam enthalpy	1
Side stripping amount	1
Side stripper-steam enthalpy	1
Enriched stages	1
Intermediate stages	1
Stripping stages	1
Side-stripper stages	1
Side-draw amount	1
Condenser duty	1
Reflux amount	1
	$\Sigma = 11$.

The Description Rule may be applied with ease to any multistage operation such as distillation, absorption, extraction, etc., and will yield the number of independent variables that must be set in defining a problem. However, as pointed out, the variables listed in applying the rule are those which are fixed either through construction or through direct external control; these are not necessarily of greatest interest in the definition of a specific problem. When they are replaced with other independent variables, four considerations enter:

(a) The replacement variables must be independent;

(b) The variables listed in the problem description must be set at values which lie within the limiting range of possible values;

(c) Because all the remaining independent variables can usually be replaced by others (more convenient or more pertinent), there is not a completely free choice of substitution;

(d) Those variables should be chosen which allow a reasonably easy calculation of a problem. Each of these considerations needs further discussion.

Variables are independent if they are not defined through a mass balance, an energy balance, or a fractionation equation defining the relation between concentrations, stages, and flows. The column of Fig. 1a serves to illustrate these points. Consider the column operating to separate a given amount of feed (an N-component mixture of specified composition and enthalpy) into a top product d and a bottom product b. It is apparent that the amount of component, 1, in the top product, $d(x_1)_d$, and the amount of the same component in the bottom product, $b(x_1)_b$, are not both independent, since we have

$$F(x_1)_F = d(x_1)_d + b(x_1)_b.$$

However, one of the two [say, $d(x_1)_d$] is independent. In the same way as for other components, $d(x_2)_d$, $d(x_3)_d$, and $d(x_4)_d$ are independent variables, since they are not connected through mass balances. It might be assumed that the amounts of all other components in the top product are also independent, but the Description Rule allows only four independent variables; the remaining variables are thus dependent through fractionation relations.

Variables may also be dependent through energy balance. This can be determined for specific varibales only by writing the appropriate energy balance. However, because composition, amount, and temperature are needed to define an enthalpy flow, and since it is uncommon to set all these variables, this is seldom of concern. To illustrate again with Fig. 1a, it is possible (although it seems at first glance unlikely), to set arbitrarily the temperatures of any four stages, since they are all independent variables. However, such a fractionation-problem definition would be unusual to say the least.

The second consideration is sometimes of concern, because it is not always easy to find the limits within which certain variables must be set. Again, the column of Fig. 1a, separating an N-component mixture, serves as an illustration. For purposes of this illustration, a useful variable for describing the separation of a specified component is introduced, viz., the recovery fraction of that component in a product.

The recovery fraction of component "i" in the top product is defined as the fraction of that component in the feed which appears in the top product, and therefore for component "i" the recovery fraction becomes $d(x_i)_d/F(x_i)_F$ and is assigned the symbol $(/i)_d$. The recovery fraction of a component in any other product, in this case the bottom product, is defined in a similar manner: $(/i)_b \equiv b(x_i)_b/F(x_i)_F$. If (as here) there are only two products, then we have $(/i)_d + (/i)_b = 1$, and only one of the variables is independent.

A set of independent variables describing the problem might then be $(/1)_d$, $(/2)_d$, $(/3)_d$, and reflux amount. Although these can all be set arbitrarily — that is, they can take on an infinitude of values — there are certain limitations on these values. If the vapor-liquid equilibria for the system of components are not highly nonideal and components 1, 2, and 3 are progressively less volatile, it is apparent that $(/1)_d$ must be greater than $(/2)_d$, which in turn must be greater than $(/3)_d$. If $(/1)_d$ and $(/2)_d$ are set first, they are limited only to values between 0 and 1. If reflux quantity is set next, it is limited to values between the minimum necessary to effect the specified separation on 1 and 2 and infinite reflux. If reflux is then set at some value within these limits, $(/3)_d$ is now limited to values within those obtained with either a maximum number of enriched stages or a maximum number of stripping stages (usually an infinity of stages in either section). These limits could all be obtained by calculation, and if a separation problem were to be described by the four variables used above, it would be necessary to be certain that the values chosen were within the allowed limits. Fortunately, in the description of most fractionation problems, the independent variables employed are such that the limiting values for them are determined fairly easily and the problem can usually be set up very quickly,

The third consideration states that although all the variables obtained through the Description Rule are independent, they are not necessarily all replaceable with a completely free choice of other independent variables. This can best be shown by considering columns a, b, and c, of Fig. 1, for which it will be understood that all feed variables

and the pressure have been set. The only difference among these columns is that 1a has a partial condenser, 1b has a total condenser, and 1c has a total condenser plus a reflux cooler. The Description Rule will correctly predict the number of remaining independent variables that must be set to define a problem for each of these columns. These variables are shown in Table I.

Table I

Independent variables from Description Rule
(in addition to feed variables and column pressure)

Figure 1a	Figure 1b	Figure 1c
Enriching stages	Enriching stages	Enriching stages
Stripping stages	Stripping stages	Stripping stages
Reboiler duty, Q_R	Reboiler duty, Q_R	Reboiler duty, Q_R
Condenser duty, Q_C	Condenser duty, Q_C	Condenser duty, Q_C
	Reflux amount, r	Reflux amount, r
		Reflux cooler duty, Q_r

Regarding column 1a, all the variables listed in Table I have direct bearing on the fractionation being done, i.e., if any one of the variables is changed, the separation will be changed. If the feed contains four components (1, 2, 3, 4, or more), then each of the variables listed could be replaced with the recovery fraction of one of the components or with variables that are functions of concentrations, such as four stage temperatures. Thus, in theory at least, it would be possible to design a column like 1a to perform a set separation on four components.

With the column of 1b, it might be expected that five independent recovery fractions could be set, and (in like manner) six for 1c. However, it is possible to represent 1b and 1c by the column shown in 1d. In this last column the reflux stream has been separated from the top-product stream, as in reality this is what is occurring for the reflux streams of 1b and 1c, since they can be considered as following a closed cycle about the column tops. In all three cases, then, the

reflux streams have the same effect in producing liquid flow off the top stage. Also, in 1d, the top product has been shown as condensing in a separate condenser. Thus, if the top product and reflux leave their condensers at the same temperature, 1d becomes equivalent to 1b; and if they leave at different temperatures, 1d is equivalent to 1c. It is apparent that the top-product condenser of 1d has no influence on the fractionation, since it is completely removed from it. Also, it is apparent that the amount of reflux flow around the closed loop of 1d is irrelevant to the fractionation. The only variable relevant to the fractionation is the refluxing condenser duty, Q_r, or the heat extracted at the top stage; this can be accomplished with an infinitude of external reflux flows, depending on subcooling. Hence, this heat load can be replaced in both 1b and 1c by a separation variable or -- what is the same thing -- the condenser load of which it is a part can be replaced. Alternatively, the variables associated with the condenser might be taken as reflux amount and reflux temperature, in which case one or the other could be replaced by a fractionation variable but not both. In all three cases, then (1a, 1b, and 1c), only four separation variables can be set.

With the columns of 1b and 1c, if the reflux amount were set, it would still be necessary to set the reflux temperature in the problem description. In 1c, in addition to the reflux temperature out of the condenser, the reflux temperature from the cooler would also have to be set.

Problem descriptions in which recovery fractions for several components are to be set would be very uncommon, and actually these requirements cannot usually be met in operation if the feed conditions are invariant. Design equations do not correspond to operation because of lack of knowledge of plate efficiency, hence the operation must be adjustable to correct for this lack. By adjustment of condenser and reboiler duties, two separation variables can be controlled. Within limits that are normally quite restrictive, additional separation variables can be controlled by changing feed enthalpy or feed stage location or by adding or removing heat within the fractionating part of the column, i.e., in reboiler vapor, in reflux from a partial condenser, or within the column proper.

The fourth consideration, that the variables chosen must be such as to lead to a reasonably easy calculation, is probably the most important. If the variables are chosen to do this, the first two considerations are usually easily satisfied, since simplicity of calculation and simplicity of problem description usually occurs simultaneously.

In discussing the courth consideration, it might be best to direct emphasis to the type of problems to be discussed in subsequent sections of this work. The problems to be discussed are those for which a column already exists or for which column design is to be effected by use of the alternate method of calculating the separation obtainable from a series of likely columns and picking the one giving the desired separation. In the setting up of fractionation problems of this type, then, the numbers of theoretical stages in each column section are always independent variables and are set in the problem description. If the calculation is to be done with any ease at all, as already noted, all feed variables and column pressure must be set, The number of independent variables remaining usually is small. For the column of Fig. 1a there are only two; in more complex columns there are still relatively few remaining. However, as the calculations presented later will show, it is almost imperative that only one of the remaining variables be chosen as a separation variable for an individual component or the temperature at a particular point in the column, and that the remaining variables be chosen primarily as flows. In this case the independence and possible range of values of the variables are easily determined.

With these restrictions, it might seem that the usefulness of the methods to be presented would be seriously limited. However, although the restrictions are sweeping, the calculations can still be applied to a very large number of problems. In fact, they can be applied to any problem and can be used with considerable facility on problems that are virtually impossible by other procedures.

Data Functions

In the calculations to be presented in subsequent sections, two basic types of data are required. The first is equilibrium data expressing the ratio of the mole fraction of a component in the vapor phase to its mole fraction in liquid phase when both phases are in equilibrium; this ratio is

$$\left(\frac{y}{x}\right)_i = K_i ,$$

where y = vapor-phase mole craction of component "i",
x = liquid-phase mole fraction of component "i",
K = equilibrium constant for component "i".

The constant K is, in general, a function of temperature, pressure, and composition. However, the composition dependence of K is usually neglected on the basis of the assumption that hydrocarbon mixtures behave in an ideal manner in the liquid phase. When mixture compositions are such that ideal behavior can no longer be assumed, special means are available for calculating K values, and these cases are covered in Section VII of this work. Liquid-liquid extraction calculations will also be considered, and here again equilibrium data are needed. In this latter case, nonideal conditions in both phases is almost a certainty, and K-value determinations once more must be done in a special manner, as will be shown in Section VIII. For the remainder of the calculations covered in Sections II through VI, K values will be assumed to be a function of only temperature and pressure.

Generally, in distillation work, columns are designed in such a way that pressure drop experienced in passage through the column is quite small. When the pressure drop is small, it is possible to assume that, for all practical purposes, the column is operating at a constant pressure arbitrarily set at that obtaining at either end of the column or at some average of these values. The assumption of constant pressure reduces the K value to dependence on temperature only.

It should be noted that these assumptions, although they are reasonably good in most hydrocarbon calculations, are made primarily to

facilitate the setting up and programming of a problem for solution on a digital computer. The pressure dependence of K as well as the composition dependence could be retained in any arbitrary functional form desired, and convergent solutions to problems would be available no matter what these forms were. These forms would, however, tend toward a high degree of complexity and would involve much additional computational effort and require large blocks of additional computer storage space. In most cases, either the lack or inaccuracy of available data does not justify this additional effort, and calculations based on the above assumptions will be quite satisfactory for practical engineering solutions to given problems.

Assuming that K values are functions of temperature only, it remains, then, to determine a functional form which will best represent available literature data. The form used will have no effect on the ability of proposed calculational methods to give convergent solutions, therefore the prime considerations for any functional form is ease of programming and minimum storage for computer use. Most equilibrium data can be fitted to a polynomial function for each component in the form

$$K_{ip} = \alpha_i + \beta_i T_p + \gamma_i T_p^{\,2} + \cdots \omega_i T_p^{\,n}, \qquad (I.2)$$

where α_i, β_i, γ_i, $\cdots$ are characteristic of the component "i" and the total pressure. It has been found, however, that data plotted by an equation of a type first proposed by Calingaert and Davis[6] gives essentially a straight line when plotted on semilog paper. The equation is

$$\ln K_i = \frac{A_i}{T + 400} + B_i , \qquad (I.3)$$

where A_i and B_i are characteristic of component "i" and the total pressure, as above, and T is expressed in ^{o}F. The constant 400 is an arbitrary one selected only because when it is used the plotted data give the best straight-line fit across the desired system temperature range. Equation (I.3) is used in this work and the A_i and B_i were determined by plotting equilibrium data from one of several sources,[10,15,25,26,38]

and determining those values giving the best fit across the temperature range expected in a given problem. If it is desired to account for the slight curvature evident in such plots, Eq. (I.2) may be used with that polynomial power which gives the best fit.

The second type of basic data required is enthalpy data. As with K values, the assumption of ideal behavior is made so that heats of solution (data for which are generally not available) can be neglected. Enthalpies, also, are functions of composition, temperature, and pressure; and since pressure has been assumed constant, the functional form used will involve only composition and temperature. Once again, polynomials may be used to represent available data as follows,

$$h_{ip} = l_i + k_i T_p + j_i T_p^2 \tag{I.4}$$

and

$$H_{ip} = w_i + u_i T_p + s_i T_p^2 , \tag{I.5}$$

where

h_{ip} = liquid-phase enthalpy for component "i" at temperature T_p for any stage p,

H_{ip} = vapor-phase enthalpy for component "i" at temperature T_p for any stage p,

and the constants j_i, k_i, l_i, s_i, u_i, and w_i are characteristic for component "i" and the total pressure, and T is defined as ($^{\circ}F$ + 400) in order to be consistent with K-data temperatures.

Data taken from Maswell[25] were replotted to obtain values of the coefficients in Eqs. (I.4) and (I.5), and only a slight curvature was found when the data were plotted over system temperatures used. As a result, Eqs. (I.4) and (I.2) were used with the coefficients j_i and s_i set equal to 0. If it is desired to account for the slight curvature in such plots, these latter coefficients may be retained and evaluated. The form of the function used will in no way affect the convergence ability of the calculation methods to be presented.

The remaining coefficients (k_i, l_i, u_i, w_i) were determined by fitting the best straight line to the replotted data of Maxwell for the

temperature range expected in a given system. The mixture enthalpies were then obtained from these individual component enthalpies as follows,

$$h_p = \sum_i h_{ip} x_{ip} \tag{I.6}$$

and

$$H_p = \sum_i H_{ip} y_{ip} , \tag{I.7}$$

where h_p = liquid molar enthalpy for composition at stage p represented by x_{ip},

H_p = vapor molar enthalpy for composition at stage p represented by y_{ip}.

The x_{ip} and y_{ip} used in these equations must be normalized, that is, they must sum to 1, to produce the enthalpy per mole of mixture. With all data functions and sources defined, it is now possible to proceed with the development of calculation methods.

II. MASS BALANCE METHODS

The mass-balance methods to be presented here can be derived without regard to the previously presented variable analysis considerations. They are essentially mathematical descriptions of variable relationships, and they are unaffected by which independent variables are set and held while a particular problem is being solved.

However, there is one important feature of variable analysis which indirectly affects the use of the mass-balance methods. The number of theoretical stages in the various column sections always appears as a variable and can be arbitrarily set if desired. For mass-balance analysis, these variables are set, but this is not a necessary condition for the analysis to be carried out. Setting the number of theoretical stages involves the introduction of stage efficiency, which itself is a function of both the column design and the system to be separated. The sectional over-all plate efficiency must be evaluated, and the number of actual stages in the column sections is then converted to number of theoretical stages. Thus, the following mass-balance methods are to be applied to existing columns. In this respect, then, the methods to be presented are not primarily design methods but rather performance-evaluation methods which postulate the physical existence of an actual column. However, this does not preclude the use of these methods for design purposes, as indeed they could be if repeated solutions were carried out at various values for the number of theoretical stages in each column section.

Equations - Method I

The basic equations are those of Thiele and Geddes.[35] The equations are dimensionless in that they employ concentrations and flows always in ratio form. The individual stage concentrations are always referred to the product compositions at the column ends, and the first objective of the method becomes determination of the product composition ratio. In order that this may be done, the temperature, the product amounts, and the various internal and external system flows must be

preset. As was pointed out by Hanson and Rea,[16] the setting of the product amounts (d and b) and of the various flows (r; V_p; L_p; V_p'; L_p') will vary with which variables are set and held in a particular problem. However, no matter which variables are set and held, all the internal flows are determined on the basis of constant molal overflow. The equations also require the "guessing" of a temperature gradient before they can be used, since equilibrium relations are used across stages.

The basic equations following are for a column numbered from the bottom up; i.e., the bottom stage is stage number 1, m is any stage in the stripping section, n is any stage in the enriching section, and t is the top stage.

If a total condenser is used then, for any and each component, one has

$$y_t = x_d \ , \tag{II.1}$$

where

y_t = mole fraction of the component in the vapor leaving the top stage,

x_d = mole fraction of the component in the overhead liquid product.

The "bridging" relation across the top and each subsequent stage is the equilibrium relation which connects the vapor and liquid leaving that stage. For the top stage, this is given by

$$y_t = K_t \, x_t \ . \tag{II.2}$$

Combining Eqs. (II.1) and (II.2) gives

$$x_t = \frac{y_t}{K_t} = \frac{x_d}{K_t} \ ,$$

or

$$\frac{x_t}{x_d} = \frac{1}{K_t} \ . \tag{II.3}$$

A component material balance around the condenser and the top stage gives

$$V_{t-1}\, y_{t-1} = L_t\, x_t + d x_d$$

or

$$\frac{y_{t-1}}{x_d} = \frac{L_t}{V_{t-1}} \frac{x_t}{x_d} + \frac{d}{V_{t-1}}, \qquad \text{(II.4)}$$

where V_{t-1} = total moles vapor from stage t-1 into stage t,
L_t = total moles of liquid leaving stage t,
d = total moles of top product.

All flow quantities are defined in terms of moles flowing per mole of entering feed. An over-all material balance around the top stage and the condenser may be written

$$V_{t-1} = d + L_t$$

or

$$\frac{d}{V_{t-1}} = 1 - \frac{L_t}{V_{t-1}} \qquad \text{(II.5)}$$

Combining Eqs. (II.4) and (II.5), one has

$$\frac{y_{t-1}}{x_d} = \frac{L_t}{V_{t-1}} \left(\frac{x_t}{x_d} - 1 \right) + 1. \qquad \text{(II.6)}$$

Then, by equilibrium,

$$\frac{x_{t-1}}{x_d} = \frac{1}{K_{t-1}} \frac{y_{t-1}}{x_d} . \qquad \text{(II.7)}$$

Again, by material balances,

$$\frac{y_{t-2}}{x_d} = \frac{L_{t-1}}{V_{t-2}} \left(\frac{x_{t-1}}{x_d} - 1 \right) + 1. \qquad \text{(II.8)}$$

The process of alternating material balances and equilibrium relations is carried on down the column to the plate above the feed plate.

It is necessary to know all L_p/V_{p-1} ratios and stage temperatures to do this, but these have all been preset. Also, this is one of the two sections of the method in which the indirect effect of the variable analysis is felt, since the number of times the above "alternation" is carried out now becomes directly dependent on the number of theoretical stages above the feed stage.

The stripping-section equations are developed in a similar manner to those in the enriching section. The vapor leaving the reboiler may be calculated by the equilibrium relation

$$y_R = K_R \, x_R$$

or

$$\frac{y_R}{x_R} = \frac{y_R}{x_b} = K_R \, . \qquad \text{(II.9)}$$

A component material balance around the reboiler and the bottom stage gives

$$L_1 \, x_1 = V_R \, y_R + b x_b \, , \qquad \text{(II.10)}$$

where L_1 = total moles of liquid from stage 1, the bottom plate,
V_R = total moles of vapor from the reboiler,
b = total moles of bottom product.

As before, all flows are defined in terms of moles flowing per mole of entering feed. Now, combining Eq. (II.10) with a total material balance around the reboiler gives

$$\frac{x_1}{x_b} = \frac{V_R}{L_1} \left(\frac{y_R}{x_b} - 1 \right) + 1 \, . \qquad \text{(II.11)}$$

Then, by equilibrium,

$$\frac{y_1}{x_b} = K_1 \, \frac{x_1}{x_b} \, . \qquad \text{(II.12)}$$

Again, by material balance,

$$\frac{x_2}{x_b} = \frac{V_1}{L_2} \left(\frac{y_1}{x_b} - 1 \right) + 1 \, . \qquad \text{(II.13)}$$

Again the "alternation" process takes over and is continued up through the feed plate; the number of times the "alternation" is carried out is now directly dependent on the number of theoretical stages below the feed plate. Also, all the stage temperatures and V_p/L_{p+1} ratios have been preset.

The last ratios calculated are then

Ratio $\frac{y_f}{x_d}$, obtained by calculating down the column, and

Ratio $\frac{y_{f'}}{x_b}$, obtained by calculating up the column,

where y_f = mole fraction of component in vapor entering stage above feed stage,

$y_{f'}$ = mole fraction of component in vapor leaving the feed stage, and this vapor is in equilibirum with the liquid leaving the feed stage.

The first objective of determining the product-composition ratio may now be reached by matching the above ratios at the feed stage. The form of the matching equation is directly dependent on the thermal condition or quality of the feed, F. For illustration, saturated liquid feed will be considered. As will be shown later for this case, $y_{f'}$ obtained by calculating up is equal to y_f obtained by calculating down, and the product-composition ratio, (x_b/x_d), may be calculated for each component from the matching equation

$$\frac{x_b}{x_d} = \frac{y_f/x_d}{y_{f'}/x_b} \quad . \tag{II.14}$$

Once this ratio is obtained, the next objective of the method is to resolve the internal mole-fraction ratios, x_n/x_d and x_m/x_d, into component mole fractions at every stage in the column. These internal ratios are referred either to x_d or x_b, therefore the first step is the resolution of the external ratio into these two mole fractions. The over-all column component material balance gives the equation

$$x_d = \frac{Fx_F}{b\,(x_b/x_d) + d} \quad . \tag{II.15}$$

Values of x_d for each component are obtained from this equation, and the corresponding values of x_b are obtained from the product composition ratios x_b/x_d. These values of x_b and x_d may now be multiplied into the internal ratios to give the mole fractions of the components in the liquids at every stage of the column.

One check on the method is the summation of the individual mole fractions at every stage in the system. The convergence condition to be met might be

$$\left| \sum_i (x_i)_p - 1 \right| \leq (\epsilon_1)$$

for all p, including p = d, where ϵ_1 is some arbitrary predetermined small number. If the condition is not satisfied, then another iteration is necessary, and this in turn necessitates the corrective movement of some system variable. The flow ratios will be fixed if d (and hence b) is one of the preset variables. As Hanson and Rea have shown, the flow ratios may change from iteration to iteration if variables other than d have been preset, but they always change with the restriction of constant molal overflow. The remaining system variable available for corrective movement is temperature, since it implicitly appears in the method in the equilibrium relations. The final objective of the method is to correct the temperatures from their original assumed values and to correct them in such a way that the desired convergence condition is rapidly approached.

It has been found that bubble points calculated on the above values of plate compositions give excellent estimates of the correct temperature. The general method of calculation involves normalization of mole fractions for every stage before proceeding into the bubble-point section of the calculation. The summations and normalizations are carried out as one step of the method, with the general normalization being accomplished through the relation

$$[\,(x_i)_p\,]_{normalized} = \frac{(x_i)_p}{\sum_i (x_i)_p}$$

for all p.

When the normalized values of $(x\ )_p$ are used, the bubble-point relation becomes

$$\sum_i K_i \ [\ (x_i)_p\ ]_{normalized} = 1. \qquad (II.16)$$

In the carrying out of the bubble-point calculation, an extrapolation procedure is used wherein two values of T_p are arbitrarily assumed, and values of

$$\sum_i K_i \ [\ (x_i)_p\ ]_{normalized}$$

are calculated at these points and compared to 1. The condition to be satisfied is not imposed on the summation but on the temperature difference between any two successive T_p values resulting from the iterations within the bubble-point calculation. Thus the condition is

$$|(\ T_p)_{assumed} - (T_p)_{calculated}| \leq (\epsilon_2)\ ,$$

where (ϵ_2) is some arbitrarily predetermined small number. The method suggested for setting up the first two T_p values is to use the assumed temperature gradient for the first T_p value and to add one to this for the second T_p value. The extrapolation process automatically takes over until the above condition is satisfied. This calculation must be repeated for each stage in the column. Alternatively, dew points run on calculated vapor compositions on each stage could be used. However, little difference has been found in the correctness of the predicted temperature gradient using either bubble or dew points. For the sake of simplicity, it is suggested that bubble points be used throughout the column.

The iterative nature of the method now becomes apparent, since the whole calculation must be repeated with the corrected termperature gradient. If the convergence condition is not met, still another trial must be made, and so forth. The convergence criteria for termination of the iterative process may be based on several considerations. One would be the above-mentioned stage-summation test. Another could be the change of temperature gradient from one iteration to another. Still another could be the change in the recovery fractions of the individual

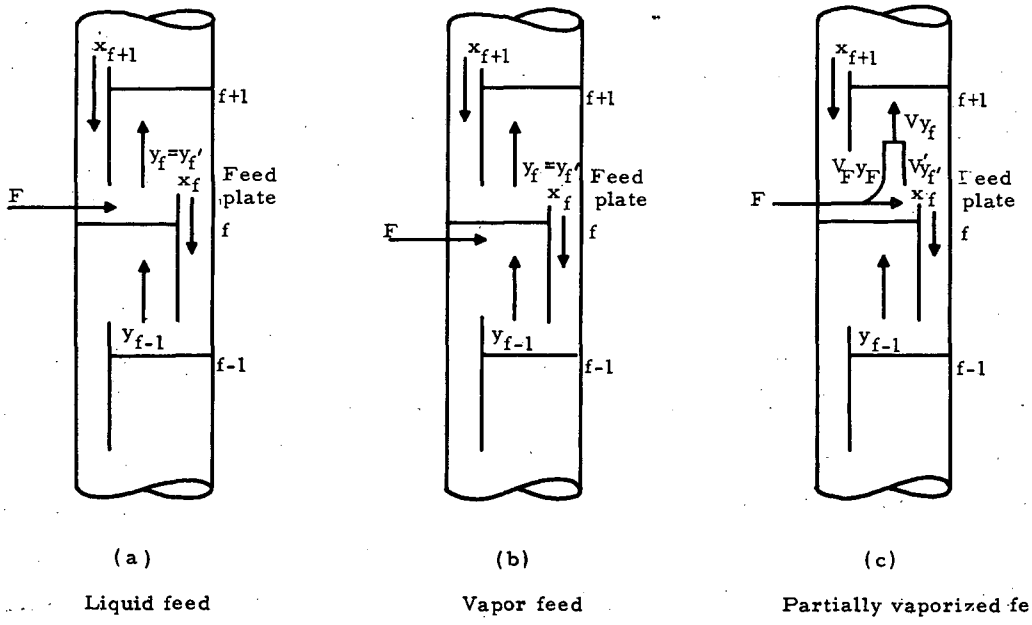
components in one or another of the products from one iteration to another. No rules exist for stating when the desired accuracy has been reached. This method is eminently suitable for use on medium or large digital computers so that acceptable error values, ϵ, can be made as small as desired within the limits of the particular computer's ability to store and work with meaningful significant figures. A small amount of experience in this type of calculation enables the calculator to judge when his specific requirements have been met.

Feed Quantity

In the method presented thus far, the feed has been considered saturated liquid and the feed-stage matching for this case is quite simple. However, matching must be considered for all three basic types of feed: namely, subcooled and saturated liquid, superheated and saturated vapor, and partially vaporized feed. These three types of feed and their points of entry are shown schematically in Fig. 3.

For subcooled or saturated liquid feed (Fig. 3a) the usual assumption made in distillation calculations is that the feed stage is the stage below the point of feed entry and that the liquid leaving the feed stage is in equilibrium with the vapor leaving the feed stage. This vapor is then fixed in composition regardless of the composition of the feed if calculations are made up the column to the feed stage. Similarly, the vapor leaving the feed stage is in material balance with the liquid leaving the stage above the feed stage, and again, the vapor composition is fixed regardless of the feed composition if calculations are made down the column to the feed stage. In Method I calculations, the ratio (y_f/x_d) is obtained by calculating down the column and the ratio $(y_{f'}/x_b)$ by calculating up. Since the feed has no effect on y_f in either case, then these two values are equal, and their ratios may be divided to give the component-distribution ratio.

For saturated or superheated vapor feeds the reasoning again holds if the feed stage is the stage <u>above</u> the point of entry of the



MU – 17906

Fig. 3

feed (Fig. 3b). Equation (II.14) may be used for the feed-stage match in this case.

For partially vaporized feeds, the matching calculation is more complex. Three conditions of feed entry are possible here. If the feed is separated before entering the column, the liquid being introduced above the feed stage and the vapor below the feed stage, then as in the above two cases the values of y_f are identical and the match is made with Eq. (II.14). However, the common method of introducing partially vaporized feed would be that shown in Fig. 3c, where liquid and vapor are both introduced above the feed stage. Under these conditions, a matching equation derived by Edmister[8] is convenient:

$$\frac{x_b}{x_d} = \frac{L_{f+1}\left(\frac{x_{f+1}}{x_d}\right) + d\left(1 - \frac{V_F y_F}{F x_F}\right)}{V_f\left(\frac{y_f}{x_b}\right) + b\left(\frac{V_F y_F}{F x_F}\right)} \qquad \text{(II.17)}$$

A third possibility of feed entry exists. The feed could be introduced in such a manner that the liquid portion entered almost directly into the downcomer from the feed stage and the vapor entered above the feed stage. Essentially, this amounts to feeding the liquid on the stage below the "feed" stage. Equations have not been developed for the match in such a case, and the match must be done by trial-and-error calculations around the feed stage.

Alternate Equations - Method I

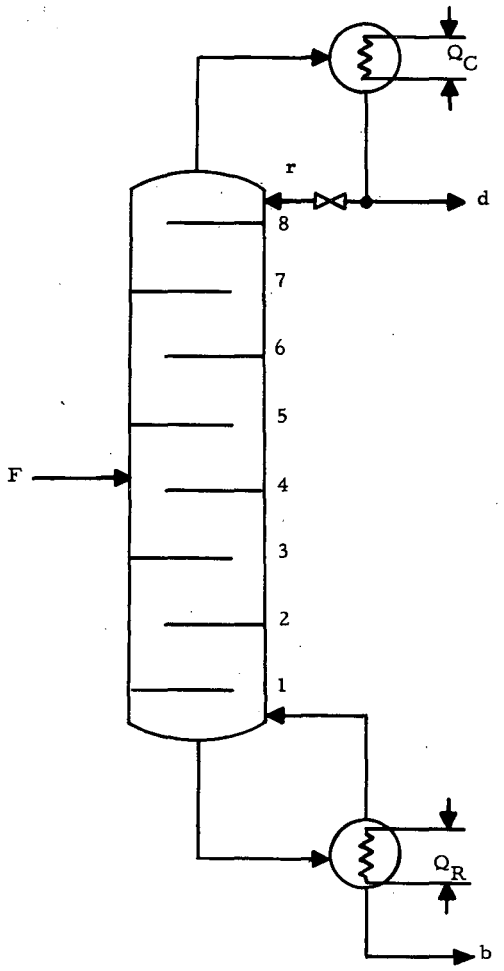
An alternate set of equations for iteration from stage to stage has been developed by Edmister.[8] These equations utilize the ratio of a flow of a component to the amount of that component in a product. These ratios take the place of the concentration ratios of Method I, but the two methods of iteration are essentially equivalent. The techniques of applying the alternate equations to various fractionation problems are identical with those of Method I.

Example I

To illustrate the use of Method I, the following example was calculated for the column shown in Fig. 4. The feed was specified as a four-component mixture of propane, butane, pentane, and hexane entering the column as saturated liquid at its bubble point. The specified pressure was 150 psia. The column contained four enriching and four stripping stages, counting the stage immediately below the point of feed entry as a stripping stage. The overhead vapors from the column were totally condensed.

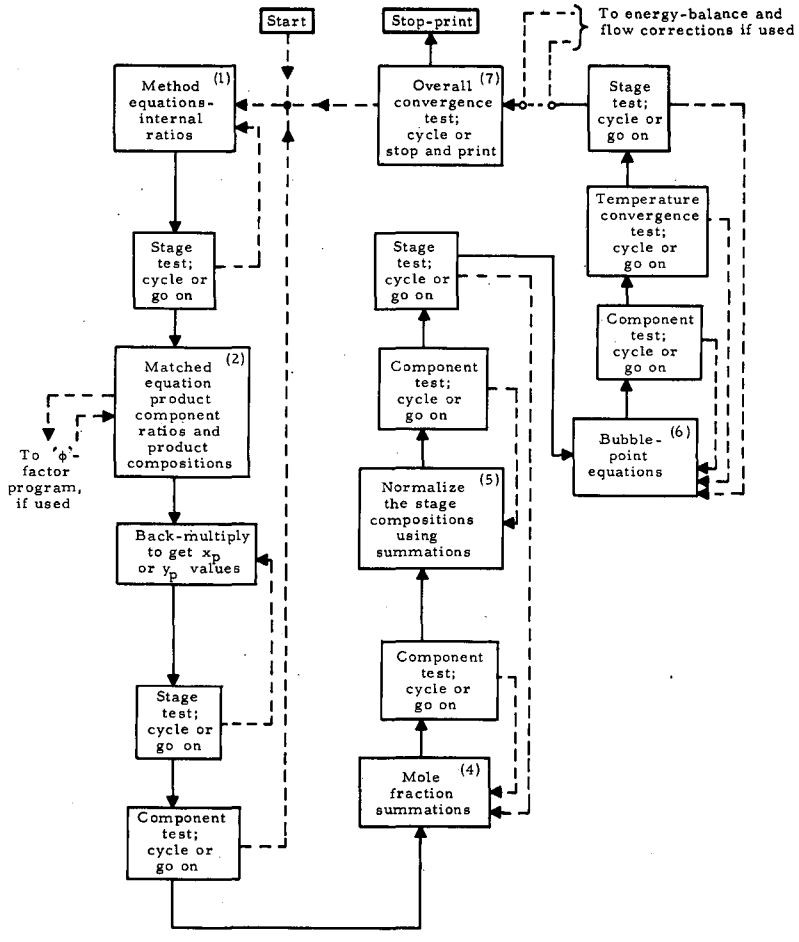
Variable analysis considerations by means of the Description Rule show that three variables remain to be fixed before Method I calculation can be started. The reflux temperature was set at its bubble point to fix one of the variables. The remaining two were set by fixing the total top-product amount and the reflux amount. As a convenient basis for calculation, the feed amount is always taken as one mole and the other streams are referred to this. Thus, flowing streams are expressed as moles per mole of feed. After the stage compositions have been determined by the converged calculation, the actual amounts of the streams flowing are simply proportional to the amount of feed. The feed capacity of a column of given diameter can be determined from whatever internal flow is limiting. It is apparent that the usefulness of the calculation procedure is determined by its convergence to the correct answer from a radically wrong set of initial temperatures. Since these and all subsequent calculations are to be carried out by using digital computers, another consideration for procedure usefulness is the number of iterations necessary for the degree of convergence desired. To illustrate that the method converges, even though the first guessed temperature gradient is completely wrong, Example I was started with the assumption that the temperature on all stages was the same. This temperature was approximately the bubble point of the feed.

The equations of Method I were translated to digital computer language, in this case an IBM 650, and the various equations were then interconnected by the necessary looping and logic decisions. The resulting computer program to do this is schematically shown in Fig. 5.



MU-17907

Fig. 4



MU-17908

Fig. 5

From the results of the first iteration in Example I, it is apparent that the temperature gradient "guessed" is radically wrong. However, this information cannot be obtained from

$$\sum_i (x_i)_d \quad \text{and} \quad \sum_i (x_i)_b ,$$

as they are very close to unity. The summations on all stages are substantially off unity, indicating that all stage totals must be examined to determine the degree of divergence of the results from the correct values. That

$$\sum_i (x_i)_d \quad \text{and} \quad \sum_i (x_i)_b$$

are close to unity indicates that the original temperatures were neither all too high nor all too low. Thus, some temperatures were high and some were low relative to their correct values.

In the Iteration 2 results of Example I, the stage summations are much closer to unity in all cases. The recovery fractions of C_4H_{10} and C_5H_{12} have changed considerably (as would be expected).

The stage summations of Iteration 3 are probably converged enough for practical use if the purpose of the calculation were to obtain a value for the separation to be expected for the variables set. However, in the analysis of columns, it is often of interest to determine how the separation will change with change in a variable. Thus, a high precision is desired in the calculation in order that the trend and perhaps the extent of the change can be determined with accuracy. The errors in Iteration 3 are the absolute value of ϵ, that is,

$$\left| \epsilon \right| \equiv \left| \sum_i (x_i)_p - 1.000 \right| ,$$

and they are large enough so that the degree of precision is doubtful for the above purposes.

If the calculation of Example I is continued past Iteration 3, a peculiarity of the method is brought out. Whenever the temperatures are predominantly low or high, the rate of convergence seems to be appreciably slowed. Whether this condition is true of a given iteration can be determined from the $\sum_i (x_i)_b$ or $\sum_i (x_i)_d$. If $\sum_i (x_i)_d$ is less than

unity, the temperatures are predominantly low and vice versa for $\sum_i (x_i)_d$ greater than unity. The reverse is true for $\sum_i (x_i)_b$. Predominantly low temperatures result in a value of $\frac{x_b}{x_d}$ that is too large; that is, x_d is too small and x_b is too large. Since this is true for each component, then the $\sum_i (x_i)_d$ and $\sum_i (x_i)_b$ follow the same pattern. Upon examining the results of Example I, as set forth in Tables II, III, and IV, one sees that the net effect of the errors in temperature in Iteration 1 is such as to balance better than the errors in Iterations 2 and 3. Because of this, $\sum_i (x_i)_d$ and $\sum_i (x_i)_b$ are closer to unity than in succeeding iterations, even though Iteration 1 temperatures and calculated separations are quite wrong.

Although bulk separations are not usually of interest as variables to define a separation problem, they nevertheless afford a simple calculation by means of which other problems may be solved. The method would be to use parameter networks obtained by varying the amount of top product and the reflux and cross-plotting the results. A working computer program could evaluate a large number of solutions of this type in a short time. The alternative is to develop computer programs for particular combinations of variables that are of interest.

Example 1

Feed	Fx_F
C_3H_8	0.25
C_4H_{10}	0.25
C_5H_{12}	0.25
C_6H_{14}	0.25
	1.00

Thermal condition of feed: saturated liquid.

Column pressure: 150 psia.

All stage temperatures are preset at 220°F.

Top product, d, is 0.5 mole per mole feed.

Reflux amount, r, is 1.0 mole per mole feed.

Constant molal flows assumed in each section gave the following flow ratios:

Table II

Results for Example 1: different mass-balance methods for components C_3, C_4, C_5, and C_6 (expressed in mole fractions)

Stage	Method I: Iteration 1				Iteration 2				Iteration 3				Iteration 12				Correct values from Φ function method				Method II after 52 iterations			
	C_3^-	C_4^-	C_5^-	C_6^-	C_3^-	C_4^-	C_5^-	C_6^-	C_3^-	C_4^-	C_5^-	C_6^-	C_3	C_4	C_5	C_6	C_3	C_4	C_5	C_6	C_3	C_4	C_5	C_6
d	.498	.434	.0738	.00260	.499	.454	.0292	.000325	.499	.456	.0268	.000266	.499	.463	.0344	.000351	.499	.464	.0361	.000372	.502	.470	.0275	.000280
8	.153	.292	.108	.008	.258	.575	.093	.002	.272	.614	.092	.002	.268	.612	.116	.003	.266	.610	.121	.003	.272	.631	.094	.002
7	.082	.228	.141	.018	.148	.551	.178	.010	.161	.620	.190	.010	.155	.603	.230	.012	.154	.596	.237	.012	.161	.636	.193	.010
6	.068	.199	.173	.039	.104	.474	.273	.031	.112	.538	.303	.032	.107	.507	.350	.038	.105	.498	.357	.039	.111	.548	.307	.034
5	.065	.186	.204	.082	.085	.383	.357	.084	.088	.421	.396	.088	.083	.388	.434	.096	.082	.381	.440	.097	.087	.425	.398	.090
4	.064	.181	.234	.167	.073	.293	.394	.187	.072	.308	.427	.192	.069	.283	.450	.198	.069	.278	.454	.199	.072	.308	.426	.194
3	.026	.147	.247	.171	.027	.228	.476	.217	.027	.235	.516	.227	.025	.209	.534	.233	.025	.205	.536	.235	.026	.235	.511	.228
2	.011	.117	.274	.186	.009	.156	.533	.270	.009	.155	.565	.282	.008	.135	.571	.288	.008	.131	.572	.289	.009	.154	.554	.283
1	.004	.090	.326	.248	.003	.093	.541	.365	.003	.089	.552	.371	.002	.076	.549	.375	.002	.074	.548	.375	.003	.089	.538	.371
b	.00154	.0658	.426	.497	.000751	.0465	.471	.500	.000679	.0439	.473	.500	.000602	.0371	.466	.500	.000590	.0360	.464	.500	.000660	.0436	.458	.497
x_b/x_d	.00309	.151	5.77	191.	.00151	.102	16.1	1538.	.00136	.0963	17.6	1880.	.00121	.0801	13.5	1425.	.00118	.0775	12.8	1342.	.00131	.0928	16.7	1775.

Table III

Results for Example 1: temperatures (^{o}F) and summations for various iterations using different mass balance methods

	Method I												Correct values from Φ function method[a]		Method II	
	Iteration 1		Iteration 2		Iteration 3		Iteration 4		Iteration 5		Iteration 12				52 iterations	
Stage	Temp.	$\sum_i (X_i)_p$	Temp.	$\sum_i (X_i)_p$	Temp.	$\sum_i (X_i)_p$	Temp.	$\sum_i (X_i)_p$	Temp.	$\sum_i (X_i)_p$	Temp.	$\sum_i (X_i)_p$				
d	--	1.009	--	.982	--	.982	--	.985	--	.988	--	.997	--	1.000	--	.999
8	220	.560	150.2	.929	144.3	.980	144.1	.989	144.5	.992	146.1	.998	146.7	1.000	144.7	1.000
7	220	.469	171.0	.887	164.0	.980	163.9	.993	164.5	.996	167.1	.999	168.0	.999	164.3	1.000
6	220	.479	184.1	.883	179.7	.985	180.2	.998	181.1	1.000	184.3	1.000	185.4	.999	180.6	1.000
5	220	.537	196.3	.910	195.5	.993	196.6	1.003	197.5	1.003	200.8	1.001	201.7	1.000	196.9	1.000
4	220	.646	211.4	.947	213.0	1.000	214.2	1.004	215.0	1.003	217.4	1.001	218.1	1.000	214.4	1.000
3	220	.591	232.5	.948	235.6	1.005	236.9	1.007	237.7	1.006	240.3	1.002	241.0	1.000	237.0	1.000
2	220	.588	248.1	.968	253.4	1.010	254.6	1.010	255.3	1.009	257.4	1.002	258.1	1.000	254.7	1.000
1	220	.668	262.9	1.002	268.9	1.015	269.7	1.013	270.2	1.011	271.8	1.003	272.3	1.000	270.0	1.000
b	220	.991	281.7	1.018	284.1	1.018	284.5	1.015	284.8	1.012	285.8	1.003	286.1	1.000	284.8	1.000

[a]Values obtained by phi-function method are correct to three significant figures.

Table IV

Results for Example 1: product recovery fractions from various iterations using mass balance Method I

Component	Method I												Correct values*		Method II	
	Iteration 1		Iteration 2		Iteration 3		Iteration 4		Iteration 5		Iteration 12				52 iterations	
	$(\gamma)_d$	$(\gamma)_b$	$(\gamma)_d$	$(\gamma)_b$	$(\gamma)_d$	$(\gamma)_b$	$(\gamma)_d$	$(\gamma)_b$	$(\gamma)_d$	$(\gamma)_b$	$(\gamma)_d$	$(\gamma)_b$	$(\gamma)_d$	$(\gamma)_b$	$(\gamma)_d$	$(\gamma)_b$
C_3-	.997	.003	.998	.002	.998	.001	.999	--	.999	--	.999	--	.999	--	1.004	--
C_4-	.868	.132	.907	.093	.913	.087	.915	--	.918	--	.926	--	.928	--	.941	--
C_5-	.147	.853	.058	.942	.054	.946	.056	--	.058	--	.069	--	.072	--	.055	--
C_6-	.005	.995	.001	.999	.000	1.000	.001	--	.001	--	.001	--	.001	--	.001	--

*Values correct to 3 significant figures--these values obtained by phi function methods.

Enriching section: $(L/V) = 1.0/1.5 = 0.667$,
Stripping section: $(V'/L') = 1.5/2.0 = 0.750$.

The following values for the constants A and B were used in the equation for equilibrium value, K:

Feed	A	B
C_3H_8	-2553.	5.299
C_4H_{10}	-3106.	5.408
C_5H_{12}	-3828.	5.797
C_6H_{14}	-4502.	6.159

The value assigned $|\epsilon_2|$, the acceptable error in the bubble-point relation, was $0.1^{\circ}F$.

The problem was not terminated automatically, and printouts were taken at every iteration. In normal operation, a programmed error scanner would automatically terminate the problem when all $|\epsilon_1|$ were within the preset limit. The error, ϵ_1, can be defined on any variable desired, such as stage summations or temperatures or component recovery fractions, and so forth.

Equations - Method II

The equations of Method I are fairly simple to formulate and apply as long as the column to which they are being applied is fairly simple. A simple column is here defined as one not having multiple feeds or multiple side-draw stages or any combination of feed and side-draw stages. These combinations, can, in essence, be handled by the algebraic techniques of Method I; but the simplicity of the expressions is quickly lost as the column becomes complex, and it becomes necessary for the computer to evaluate long, unwieldy mathematical expressions. In addition, as will be shown later, there is the danger of loss of significant figures as a result of differences of very small numbers. This loss prevents the convergence of problems of this type and necessitates special programming to obtain convergence. As a result, the desirability of another method of mass balance is greatly enhanced.

Amundson and Pontinen have circumvented the above difficulties by writing the complete steady-state network of mass-balance equations in matrix notation.[1] The solution to a problem is then obtained by repeated matrix inversion, and this requires a very large, fast computer. Others avoid the above difficulties by techniques which sometimes introduce their own peculiar troubles. Rose et al. solve these problems by relaxation techniques using basic difference equations,[29] and here again a fast computer is required. Greenstadt et al. have developed a general program of stage-to-stage calculations[14] utilizing Newton's method of root finding. It appears to be quite lengthy and subject to convergence difficulties, even though the authors propose a special convergence-inducement scheme that will force convergence in any problem.

The method proposed here is one derived from the basic differential equation of the system, and will be called the Method of Successive Flashes (for reasons that will become apparent in its development). The unsteady-state equation for any component i on any stage p of the column of Fig. 4 would be

$$S_{Vp}\left(\frac{dy_p}{d\theta}\right) + S_{Lp}\left(\frac{dx_p}{d\theta}\right) = V_{p-1}\, y_{p-1} + L_{p+1}\, x_{p+1} - (V_p y_p + L_p x_p)\ , \qquad \text{(II.18)}$$

where S_{Vp} = vapor holdup at stage p, assumed constant,
S_{Lp} = liquid holdup at stage p, assumed constant,
θ = time.

If the equilibrium relation is introduced into this equation and the further assumption made that S_{Vp} is much smaller than S_{Lp}, then for any component one has

$$S_{Lp}\left(\frac{dx_p}{d\theta}\right) = V_{p-1}\, K_{p-1}\, x_{p-1} + L_{p+1}\, x_{p+1} - x_p\,(V_p K_p + L_p). \qquad \text{(II.19)}$$

Substituting the definition

$$\tau = \theta/S_{Lp} \qquad \text{(II.20)}$$

$$\text{or } d = d\theta/S_{Lp}$$

into Eq. (II.19) results in

$$\frac{dx_p}{d\tau} = V_{p-1}\, K_{p-1}\, x_{p-1} + L_{p+1}\, x_{p+1} - x_p\, (V_p\, K_p + L_p). \qquad \text{(II.21)}$$

Defining $\lambda = (V_{p-1}\, K_{p-1}\, x_{p-1} + L_{p+1}\, x_{p+1})$ and $\beta = (V_p\, K_p + L_p)$ and putting these terms into Eq. (II.21) and separating variables lead to

$$d\tau = \left(\frac{dx_p}{\lambda - x_p\, \beta}\right) . \qquad \text{(II.22)}$$

An iterative type of solution of Eq. (II.22) can be obtained by integrating from the point x_p at iteration $\underline{r}$ to the point x_p at iteration $\underline{r+1}$ with the corresponding finite difference in τ being $\Delta\tau$. The assumption needed to carry out this integration is that λ and β are constant across the iteration. The resulting equation is

$$\frac{\lambda - (x_p)_{r+1} \cdot \beta}{\lambda - (x_p)_r} \approx \exp\,(-\beta\Delta\tau). \qquad \text{(II.23)}$$

Equation (II.23) can be rearranged as follows:

$$(x_p)_{r+1} \approx (x_p)_r \exp\,(-\psi) + \frac{\lambda}{\beta}\ [1 - \exp\,(-\psi)], \qquad \text{(II.24)}$$

where $\psi = \beta\Delta\tau$.

If it is arbitrarily assumed that the values of ψ are chosen so that one has $\exp\,(-\psi) \approx 0$ for each iteration, then the very simple basic expression for the $\underline{r+1}$st value of (x_p) becomes

$$(x_p)_{r+1} \approx \frac{\lambda}{\beta} = \frac{V_{p-1}\, K_{p-1}\, x_{p-1} + L_{p+1}\, x_{p+1}}{V_p\, K_p + L_p} . \qquad \text{(II.25)}$$

Equation (II.25) has the exact form of the well-known flash equations, so that repeated application of this equation across iterations leads to the naming of this method as the Method of Successive Flashes. Indeed, in the solution of a mass-balance problem by this method, a "reverse" flash of the system is just exactly what is accomplished. In the normal solution of a flash equation, feed concentrations

are fixed and values of V and L obtained corresponding to these concentrations. The Method of Successive Flashes reverses this procedure in that V and L are fixed and concentrations are obtained corresponding to these flows. In addition, the results are for an interconnected network of stages rather than for a single stage.

Another form of iteration equation, (II.25), allows error ϵ scanning as the solution proceeds, and is the form actually programmed for the computer. Starting with Eq. (II.24) and manipulating and using the same assumptions used to obtain Eq. (II.25) results in

$$(x_p)_{r+1} \approx (x_p)_r + \left(\frac{\epsilon}{\beta}\right), \qquad \text{(II.26)}$$

where $\epsilon = [\lambda - (x_p)_r \beta]$.

Here ϵ represents the input-output mass discrepancy for a component at any stage and as the iteration proceeds ϵ approaches 0. It can be used as a criterion for cessation of the iterative process or as information on the progress of the problem toward its steady-state solution.

As in Method I, it is necessary to preset all stage temperatures as well as all vapor and liquid flows before a solution is attempted. Here additional starting information is needed; that is, the starting composition on every stage must be known or assumed. The values actually used are immaterial, since the steady-state solution is independent of any starting compositions. One way of starting would be to fill every stage with feed material at its bubble point. If the starting variables are such that the flow ratios will change from iteration to iteration, the methods of Hanson and Rea can be used for changing these ratios. However, as pointed out previously, which of variables are set and held has no effect on the form of the above equations.

The Method of Successive Flashes has a distinct advantage over Method I in nonsimple or complex columns. At a feed or side-draw stage, the λ term of Eq. (II.25) or (26) has one additional term added, and, in this simple manner, accomplishes what is done by the sometimes

very complex matching equations of Method I. It is a mathematically very stable, slow-moving process which has the disadvantage of being much slower in its convergence than is Method I.

In actual use, Method II proceeds much the same as Method I. In the schematic computer program of Fig. 5, the boxes 1, 2, and 3 would be replaced by one box, labeled Method I Equations, which would cycle on stages first and components second. The criterion for stopping the iteration process could be the aforementioned ϵ value if these values are recorded, or the criteria listed under Method I could be used. However, since the convergence rate of Method II is inherently slow, the rate of movement of summation, temperatures, or recovery fractions, etc., would also be quite slow except at the very start of the problem. For this reason, the values of ϵ are suggested as the best criteria for stopping a problem.

Example 2

The Method of Successive Flashes is illustrated for the same physical column and with the same feed and variables set as in Example 1. For purposes of comparison, the temperature behavior on every stage is plotted versus iteration in Fig. 6 for the Method of Successive Flashes and in Fig. 7a for Method I mass balance. The nearly exact temperature values for this system are shown in Fig. 7b, the source of which will be explained shortly. The slow-moving nature of the Method of Successive Flashes quickly becomes evident, since even after 52 iterations some temperatures in the center section of the column are as much as 4.8° from convergence. A very large number of iterations will be needed to reach convergence throughout the column.

Tables II, III, and IV show further results for Example 2, and in Fig. 8 are plotted the recovery fractions in the top product versus iterations for each component for both Methods I and II mass balance. It is obvious from these plots that convergence is being asymptotically approached, and that an exact solution is available if the computer is allowed to run long enough. However, the driving force toward convergence has established itself at a very small value and

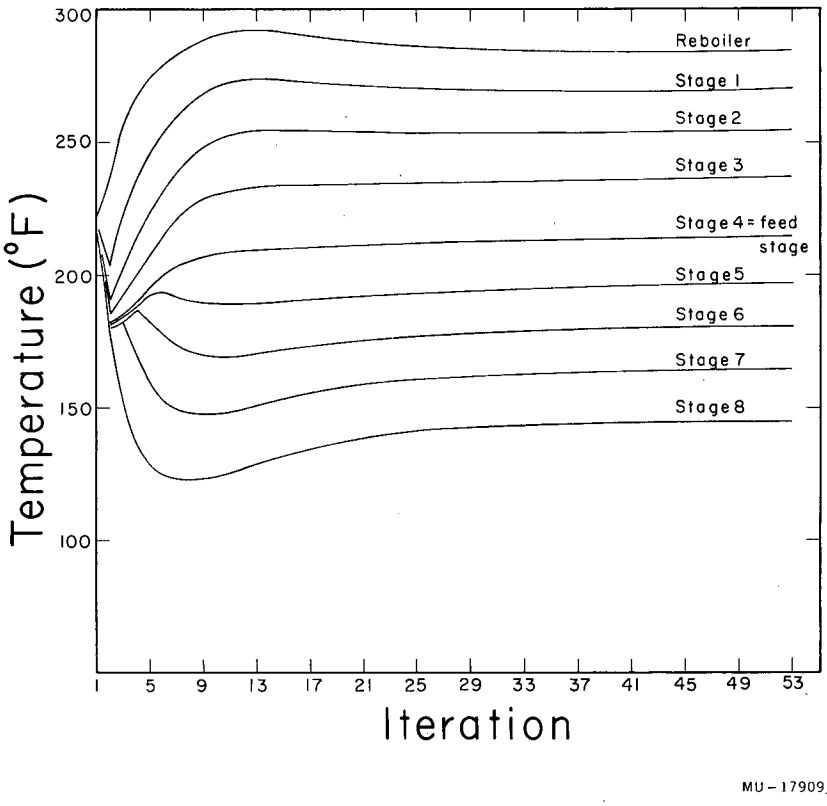
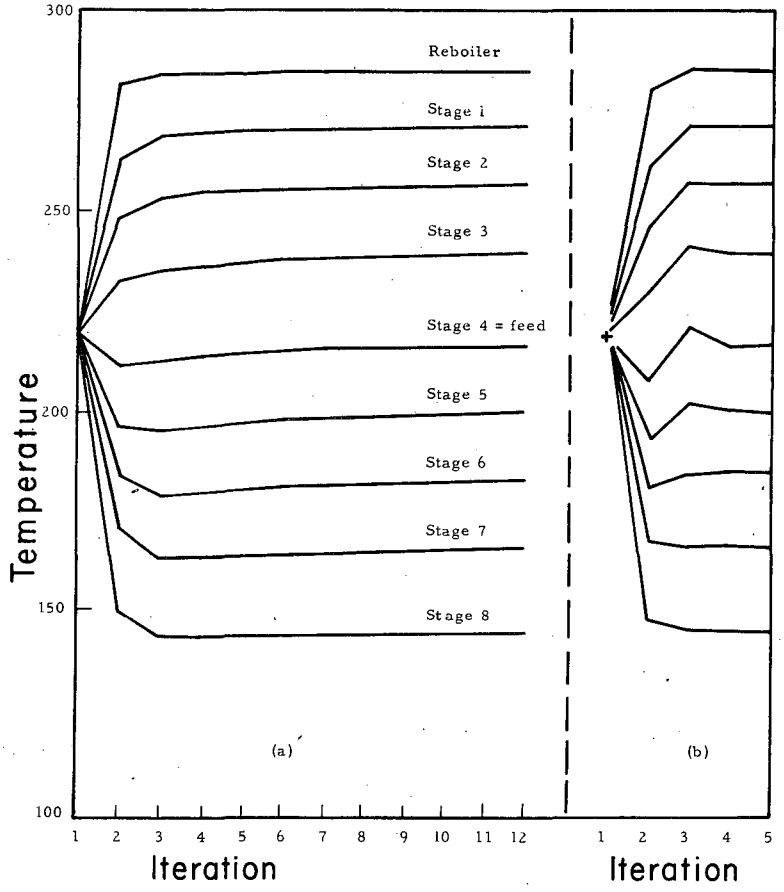


Fig. 6. Example 2 results.



MU-17910

Fig. 7. (a) Example 1 results.
(b) Example 3 results.

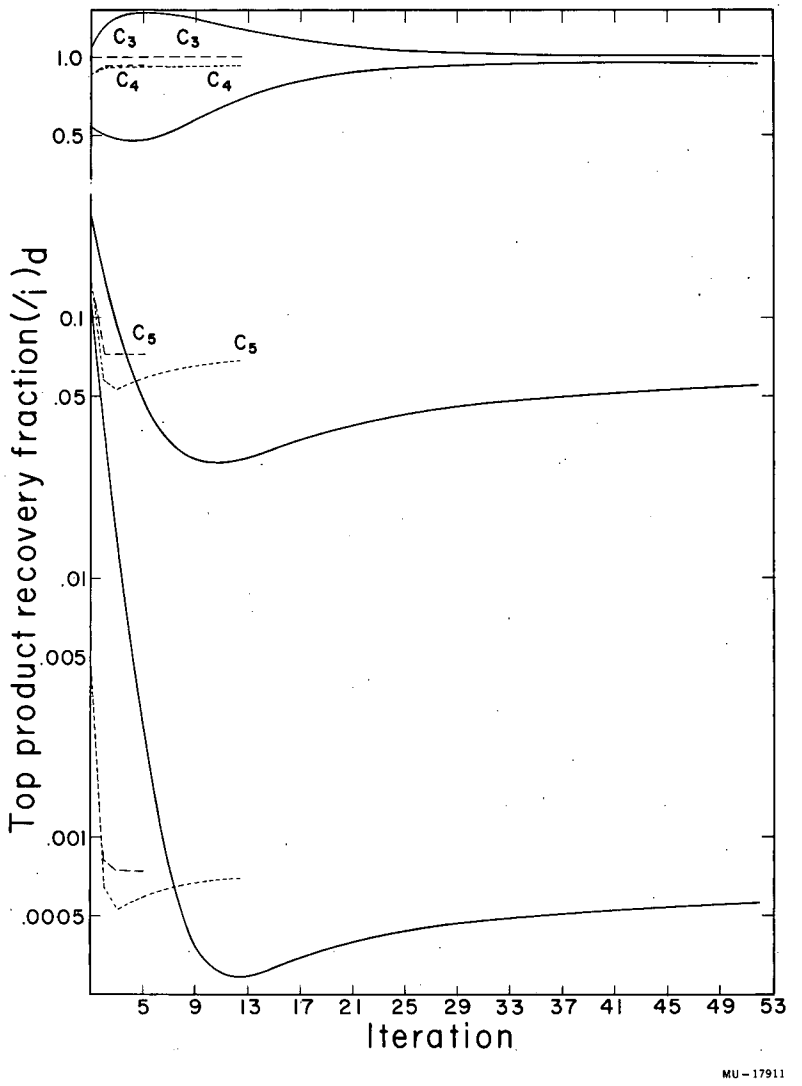


Fig. 8. Mass balance by different methods; same feed and same column for all examples.

⊙ Example 1, Method I.

△ Example 2, Method II.

\+ Example 3, Method I with Φ factor.

therefore has drastically limited the rate of convergence. It should be noted that in Fig. 8 the sensitivity of the curves for the C_5 and C_6 hydrocarbons is greatly enhanced because of their small value. On a plot of bottom-product recovery fractions, these two components would behave in the same manner as the C_3 and C_4 hydrocarbons do in Fig. 8, and it is the accuracy of the values in the nonsensitive areas close to 1.0 that is of importance.

Table V shows the input-output mass unbalances, that is, the ϵ values of Eq. (II.26) for the 52nd iteration. From this table and the other tables and plots it is quite evident that the ends of the column are appreciably nearer to their converged value than is the central section of the column. Also, an over-all mass balance shows that the lightest and heaviest components are appreciably nearer their convergence values than are the other components. This would be expected because of the "cumulative error" characteristic of the method. That is, unbalances in the inner areas of the column tend to "accumulate" into a large error in the products for a given component. Table V shows that the largest unbalance errors occur for the C_4 and C_5 hydrocarbons; and on the basis of an over-all mass balance these hydrocarbons are approximately 3% off, in contrast to only 0.5% for the C_3 and C_6 hydrocarbons.

It is essentially a matter of experience and judgment in deciding when to terminate a Successive Flash calculation. There are means available for extrapolating results ahead, and the accuracy of the extrapolation will be a direct function of the method used. Perhaps the simplest possible extrapolation would be a simple two-point linear method used. If such a method were applied to Example 2, results for the 49th and 52nd iterations would give a C_3 recovery fraction of 0.9994 for an over-all ϵ of 10^{-4} and 0.9990 for an over-all ϵ of 10^{-5}. The corresponding figures for the C_4 hydrocarbon would be 0.9344 and 0.9343 at the same ϵ values. These recovery-fraction estimates are appreciably improved. Three- or four-point extrapolation formula could be used, but it is very questionable.

Table V

Input-output mass unbalances, ϵ, for the 52nd iteration of example 2 (error as $\epsilon \times 10^4$)

Stage	Component			
	C_3	C_4	C_5	C_6
8	-7	-10	+6	+1
7	-6	-17	12	5
6	-5	-22	16	1
5	-4	-22	16	2
4	-4	-24	17	2
3	-2	-26	19	3
2	-1	-22	17	3
1	-4	-15	13	2
R	-1	-6	+6	+2

whether or not the increased work is justified. Another method of predicting the steady-state values would be to use, for the unsteady-state equation, (II.21), the solution form

$$(x - x_{ss}) = C \exp(-\eta), \qquad \text{(II.27)}$$

where x_{ss} = steady-state value of mole fraction,

η = time-dependent variable (in this case, iterations).

The x values in Eq. (II.27) would be those from any portion of a plot of mole fraction versus iteration. The method of using the equation would be to assume a value of x_{ss} and, using this value and any number of values of x, form differences $x - x_{ss}$. Plotting these differences on semilog paper would give a straight line for the correct value of x_{ss} and a curved line for other values of x_{ss}. The process could be repeated for another portion of the x-versus-iteration plot to check the x_{ss} value, and so forth. It can be seen that this process soon becomes lengthy itself, even though it is basically a much more sound approach than simple two-point extrapolation.

It should be remembered that the Method of Successive Flashes was derived primarily for use with nonsimple columns or for those cases, as will be shown later, for which Method I fails. It would never be used in a simple distillation system such as that of Examples 1 and 2.

Improving Rate of Convergence - Method I

The results of Example 1 illustrate that the rate of convergence is appreciably retarded if the temperature gradient becomes predominantly low or high. If successive iterations indicate the existence of such a condition, an arbitrary adjustment of all temperatures in the proper direction definitely aids the rate of convergence. However, such adjustments require judgment, and for use with digital computers, it would be desirable to have an automatic correction method built into the program. It will be noted in Example 1 that the rate of change of the product-composition ratios x_b/x_d rapidly falls, while a relatively much slower rate of change occurs for the recovery fractions of those

components appearing in the top or bottom product in major amounts. While this behavior is only part of the mechanism contributing to the slow convergence rate, it does suggest the possibility of modifying the product-composition ratios in some manner such that the rate of convergence is appreciably increased. The simple method proposed here for modifying these ratios is to introduce a factor Φ into Eq. (II.15) as follows:

$$x_d = \frac{Fx_F}{b\left[\left(\frac{x_b}{x_d}\right)\Phi\right] + d} , \qquad \text{(II.28)}$$

where Φ is a correction factor giving $\sum_i (x_i)_d = \sum_i (x_i)_b = 1$. In the normal course of a calculation, these summations can be appreciably different from 1 so that the purpose of Φ is to modify the product-composition ratio in such a way that the summations are 1 even though the calculation is far from convergence. The values of x_b to be used in Method I are then obtained by

$$x_b = x_d\left[\left(\frac{x_b}{x_d}\right)\Phi\right] , \qquad \text{(II.29)}$$

where, as in Eq. (II.28), the same value of Φ applies to all components. This same approach has been proposed by Lyster et al.[23]

Some insight into the behavior of Φ can be determined by defining a function $f_1(\Phi)$ as

$$f_1(\Phi) = \sum_i \frac{F(X_i)_F}{b\left[\frac{(x_i)_b}{(x_i)_d}\Phi\right] + d} - \sum_i (x_i)_d . \qquad \text{(II.30)}$$

Since, in a physical sense, all values of mole fractions must be either 0 or positive, it follows that the same limitations apply for Φ. The behavior of the function $f_1(\Phi)$ is best shown by a plot of $f_1(\Phi)$ versus

Φ, and for this purpose it would perhaps be better to use Eq. (II.30) in the form

$$f(\Phi) = \sum_i \frac{F(X_i)_F}{\frac{b}{d}\left[\frac{(x_i)_b}{(x_i)_d}\Phi\right] + 1} - d \qquad \text{(II.31)}$$

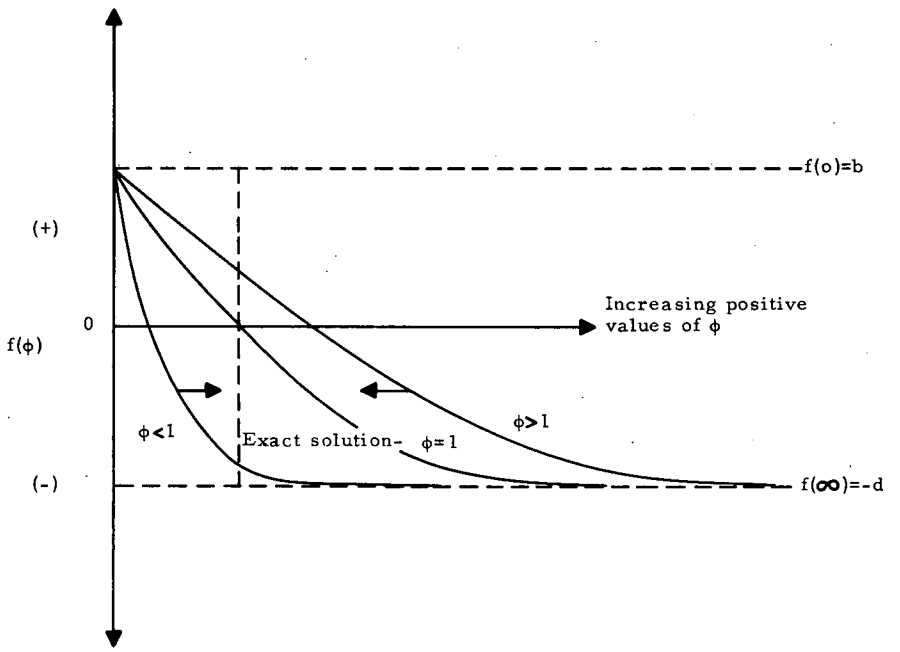
and to plot $f(\Phi)$ rather than $f_1(\Phi)$ versus Φ. Figure 9 is such a plot.

As shown in Fig. 9, there is a unique curve and Φ root at $f(\Phi) = 0$ for each set of product-composition ratios, but the exact solution to a given calculation occurs only when absolute convergence has been obtained, that is, when the Φ root is 1 at $f(\Phi) = 0$. A common point for all these curves is $f(\Phi) = b$ at $\Phi = 0$. On the other hand as Φ goes to ∞, the curves asymptotically approach the value $f(\Phi) = -d$ and would, of course, reach that value in the limit. If the Φ factor is to be of use, subsequent predictions must rapidly converge on the exact solution. As is shown shortly, this is exactly how the Φ factor behaved.

Unfortunately, for every set of product-composition ratios it is necessary to find the root value of Φ for which $\sum_i (x_i)_d = 1$, and there are several ways in which this could be done. The method used here is a simple two-point linear extrapolation which involves the original assumption of two Φ values. At the start of the process one of the Φ values is implicitly set at 1 and the other is set at the first value of $\sum_i (x_i)_d$ obtained from Method I mass balance. By use of these two values of Φ and the resulting two values of $\sum_i (x_i)_d$, a third value of Φ and of $\sum_i (x_i)_d$ is calculated, and the process is repeated until the following condition is satisfied:

$$\left|\sum_i (x_i)_d - 1\right| \leqslant (\epsilon_\Phi),$$

where ϵ_Φ is an arbitrarily predetermined small number. The value of ϵ_Φ normally used was 1×10^{-4}, and the number of iterations required to satisfy the above condition normally ranged from 4 to 6. The value



MU-17912

Fig. 9. Plot of the Φ function.

assigned ϵ_Φ is dependent upon the accuracy desired in the mole fractions. It is possible for the two-point linear extrapolation to get into trouble if it predicts a negative value for Φ. This difficulty is circumvented by building a sign test into the computer program to watch for this condition, and if it is found, Φ is set equal to 0 and the process continued. The Φ correction appears in the computer schematic diagram as an auxiliary operation on Box 2 of Fig. 5.

Example 3

Example 3 was run by using the same feed, set variables, and physical setup as Example 1, and the results are summarized in Tables VI and VII and plotted in Figs. 7b and 8. Comparing calculations made with and without the Φ factor shows two distinct advantages when Φ is used. When the calculation without Φ gives a predicted temperature gradient that is essentially all low, the rate of convergence falls off appreciably from iteration to iteration. The same calculation using Φ develops the same type of gradient at Iteration 2 but automatically corrects for it, with the result that the next predicted temperature gradient is much closer to the correct value and therefore the convergence rate is appreciably increased. Even more striking is the fact that correcting for the character of the temperature gradient also makes the calculated recovery fractions much closer to the correct value. Essentially, the separation given by Iteration 2 is correct to a part in a thousand, and only one more iteration is needed to confirm it. A basic property of the Φ-factor method is also illustrated in that from iteration to iteration the value of Φ alternates above and below 1, and it is this property which brings about convergence in the minimum number of iterations.

In the normal use of Eq. (II.28), b and d are fixed and the product-composition ratios and Φ move. If the amount, d, of top product (and hence b) is changed, the product-distribution ratio is appreciably changed for each component, but it has been found that the relative values of the ratios to one another remain quite constant. This then suggests the use of Eq. (II.28) for exploring the variation of product

Table VI

Results for Example 3: temperatures (^{o}F) and summations from five iterations

Stage	1		2		3		4		5	
	Temp.	$\sum_i (X_i)_p$	Temp.	$\sum_i (X_i)_p$	Temp.	$\sum_i (X_i)_p$	Temp.	$\sum_i (X_i)_p$	Temp.	$\sum_i (X_i)_p$
d	--	1.000	--	1.000	--	1.000	--	1.000	--	1.000
8	220	.550	149.1	.976	146.6	1.001	146.7	1.000	146.7	1.000
7	220	.457	169.5	.968	167.8	1.004	168.1	.999	168.0	.999
6	220	.464	182.3	1.007	185.5	1.005	185.6	.998	185.4	.999
5	220	.517	194.2	1.087	203.1	.993	201.9	.997	201.7	1.000
4	220	.665	209.1	.834	222.4	1.014	217.7	.998	218.1	1.000
3	220	.606	230.5	.867	242.7	1.003	240.8	.999	241.0	1.000
2	220	.599	246.4	.912	258.4	1.000	258.0	1.000	258.1	1.000
1	220	.678	261.7	.967	272.2	1.000	272.2	1.000	272.3	1.000
b	220	1.000	280.8	1.000	286.0	1.000	286.0	1.000	286.1	1.000

Table VII

Results for Example 3: top product recovery fractions from five iterations

Components	1	2	3	4	5
C_3	.998	.999	.999	.999	.999
C_4	.860	.928	.928	.928	.928
C_5	.139	.073	.073	.072	.072
C_6	.005	.001	.001	.001	.001
Φ	1.076	.701	1.061	.997	1.000

recovery fractions as a function of total product d. For example, if the distribution ratios are known for a given value of d, the approximate compositions of the top and bottom products at other values of d can easily be determined if one assumes that, for the desired variation d, the ratios of the product-composition ratios are set and held at those obtaining for the given value of d. Substituting the composition ratios and the new values of d and b into Eq. (II.28) gives a Φ value for which $\sum_i (x_i)_d = 1$ within the desired limits. This is done in the usual manner by using the two-point extrapolation method as set forth previously. The individual values of x_d calculated with this new value of Φ give the composition of the new top product.

Although no such extrapolation can be correct in general, it can be a very useful approximation. An idea of the error encountered can be obtained from Table VIII, for which the exact top-product compositions were calculated for several values of top product using the feed, physical setup, and reflux flow of Example 1. The exact calculated recovery fractions are compared with predicted recovery fractions by using the above extrapolation based on the converged product-composition ratios of Example 1 as shown in Table II. Although the character of the fractionation changed greatly, and the values of Φ changed by a factor of approximately 20 in each direction, it can be seen that results are remarkably close for this case. Unfortunately, not enough information exists to define the limits within which such agreement can be expected. The best use for the extrapolation is as an approximation method to reduce the number of exact calculations, and in this respect it is very helpful. It is shown later that the extrapolation property of the Φ factor can be quite useful in those calculations in which product d is not one of the variables set and held.

Table VIII

Prediction of change in product composition with change in product amount
(values of d=0.5 and r=1 product-composition ratios used for extrapolating)

Components	Top-product component-recovery fractions for various top-product amounts, d													
	0.3		0.4		0.45		0.5		0.55		0.6		0.7	
	Approx.	Exact	Approx.	Exact	Approx.	Exact	Approx.	Exact	Approx.	Exact	Approx.	Exact	Approx.	Exact
C_3	.955	.982	.990	.994	.996	.997	--	.999	1.000	.999	1.000	1.000	1.000	1.000
C_4	.217	.243	.601	.559	.783	.787	--	.928	.979	.968	.991	.982	.998	.994
C_5	.001	.002	.009	.006	.021	.016	--	.072	.219	.229	.403	.410	.771	.765
C_6	--	--	--	--	--	--	--	.001	.003	.003	.006	.008	.031	.040
Φ	--	17.19	--	5.713	--	2.931	--	1.000	--	.3401	--	.1734	--	.0541
	Product-composition ratios (X_b/X_d)													
C_3	--	.00778	--	--	--	--	--	.000118	--	--	--	--	--	.000331
C_4	--	1.55	--	--	--	--	--	.0775	--	--	--	--	--	.0132
C_5	--	413.	--	--	--	--	--	12.8	--	--	--	--	--	.712
C_6	--	44268.	--	--	--	--	--	1342.	--	--	--	--	--	55.1

III. ENERGY-BALANCE METHODS

In Section II, the mass-balance equations were derived by use of the assumption of constant molal overflow. For separations in which the components involved have latent heats whose spread is not large, there is a reasonable justification for the above assumption. However, in addition to a low latent-heat spread, there should be small variation in temperature from top to bottom and the mixture properties of the components should approach ideality in that heats of solution and volume changes, etc., should be negligible. If the separation being considered reasonably meets these requirements then use of the mass-balance equations alone will provide the desired information. If the mixture-property effects alone are assumed negligible, then the use of energy-balance plus mass-balance equations will give some idea of the variation of flow quantities in the system.

In general, if enthalpy data are available for the system of components being considered, calculations involving both energy and mass balance are not difficult. There is a resulting "extension" of the calculations in that more iterations are required than for mass balance alone, but in general this extension is quite small.

Another consideration that could make it desirable to run energy balances is column capacity. If the capacity of an existing column is known to be large relative to the feed expected and to the flows needed for the separation desired, then there is little reason to run an energy balance. On the other hand, if the column capacity is closely approached for the desired feed amount and separation, then an energy balance may become quite desirable. Also, if a design calculation is being done, then an energy balance is needed.

Method I

Since energy balances will be made by using enthalpies of flowing streams, it will always be necessary to precede these balances by mass-balance and bubble-point (or dew point) calculations in order that temperature and composition of the various streams be known.

Having obtained the molal enthalpy of all streams associated with the column, one may calculate the flow amounts of these streams to fit the variables set.

In the calculation of the flow of the various streams, a convenient quantity for use in energy balancing at any point is the "net heat flow," defined as ΔQ. In any column section, assuming adiabatic conditions relative to its surroundings, the net heat flow is given by

$$\Delta Q = V_p H_p - L_{p+1} h_{p+1}, \qquad \text{(III.1)}$$

where V_p = molal vapor flow from general stage p,
H_p = molal enthalpy of stream V_p,
L_{p+1} = molal liquid flow from stage above stage p,
h_p = molal enthalpy of stream L_{p+1}.

This quantity should be a constant between any two stages in a given section of column.

The variable analysis of Section I plays a more important role here than in the mass-balance equations. Setting and holding ΔQ at some point in the column is desirable, since all new flows will now be calculated by using this value of ΔQ. A variable analysis will indicate to what degree this is possible. Consider the column of Example I, in which--in addition to the feed amount, composition and enthalpy, column pressure, and stages in each section--the following variables were set:

Top-product amount, d,

Reflux amount, r,

Reflux and top-product temperature (total condenser).

The net heat flow in the enriching section can be obtained, based on these set variables, from

$$\Delta Q_{es} = V_t H_t - rh_r = Q_c + dh_d, \qquad \text{(III.2)}$$

where V_t = molal vapor flow from top stage,
Q_c = condenser duty.

The molal-enthalpy terms of Eq. (III.2) are all obtained from the temperatures and compositions resulting from the mass-balance

equations. It should be noted that with the above variables set and held, ΔQ is not fixed as a specific number, since from iteration to iteration both Q_c and h_d change as a result of temperature and composition changes. However, the rate of change is quite small and rapidly approaches 0, so that although it is impossible to absolutely fix and hold ΔQ, it is possible to insure that it is a reasonably stable number.

The numerical value and sign of the net heat flow are meaningless. Actually, the quantity calculated is the net enthalpy flow, as it properly should be, and the value and sign of the enthalpy are directly dependent upon the temperature base chosen for the component enthalpies. The net heat flow is merely a convenient mathematical tool for conducting enthalpy balances, and is in no way to be construed as a fundamental quantity.

Having established a value for ΔQ in the enriching section, one then may determine values of vapor and liquid flows between stages in two forms for use with the two different methods of mass balancing. Mass-balance Method I uses the flows in ratio form, and these can be obtained from

$$\frac{L_{p+1}}{V_p} = \frac{\frac{\Delta Q_{es}}{d} - H_p}{\frac{\Delta Q_{es}}{d} - h_{p+1}} , \qquad \text{(III.3)}$$

whereas mass-balance Method II, using the flows in explicit form, would require the equation

$$L_{p+1} = \frac{\Delta Q_{es} - d\,H_p}{H_p - h_{p+1}} . \qquad \text{(III.4)}$$

Thus flows can be calculated down to those above the feed plate. In order to continue the flow calculations, a new value of net heat flow must be used, since the feed introduces energy into the system at this point. The net heat flow is thereafter that for the stripping section,

and is defined by

$$\Delta Q_{ss} \equiv \Delta Q_{es} - Fh_F, \qquad \text{(III.5)}$$

where Fh_F = enthalpy of the feed.

In continuation of the calculations down the column equation, it will be recalled that Method I uses the flow ratios in the form (V'/L'), and the counterpart of Eq. (III.3) for the stripping section becomes

$$\frac{V'_p}{L'_{p\pm1}} = \frac{\frac{\Delta Q_{ss}}{b} + h_{p+1}}{\frac{\Delta Q_{ss}}{b} + H_p}, \qquad \text{(III.6)}$$

and the corresponding explicit form is

$$V'_p = \frac{\Delta Q_{ss} + bh_{p+1}}{H_p - h_{p+1}}. \qquad \text{(III.7)}$$

The calculation down is stopped at $p = R$, and the last quantities obtained would be (V'_R/L'_1) or V'_R. When the explicit forms are used, Eq. (III.4) and (III.7), the other flow is obtained by a simple overall flow balance.

If the set variables had been specified at the bottom of the column, the analysis would proceed as above except that the direction of movement is reversed. Variables such as the amount of reboiler vapor, V'_R, and amount of bottom product, b, would define the stripping-section net heat flow as

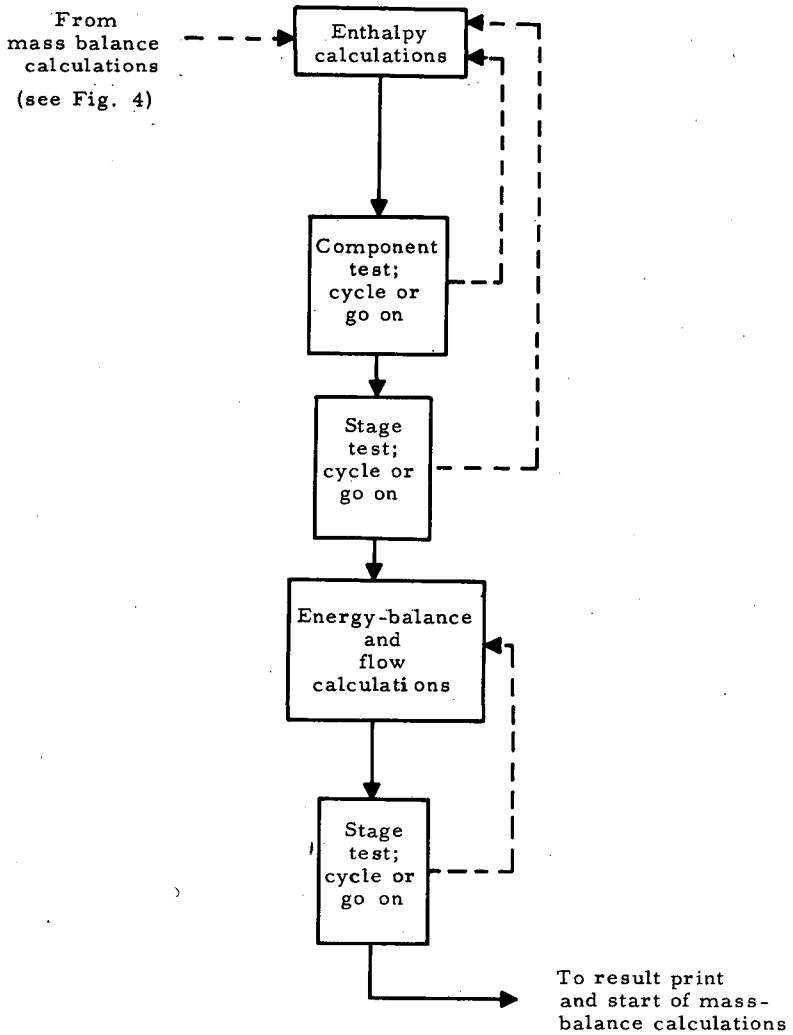
$$\Delta Q_{ss} = Q_R - bh_b, \qquad \text{(III.8)}$$

where Q_R = reboiler duty. At the feed stage, there is a shift from ΔQ_{ss} to ΔQ_{es}, and the calculation then proceeds on up the column to the top stage. In general, the set variables are used along with the available estimates of composition, temperature, and enthalpy to establish values of the net heat flows in the various column sections.

New estimates of flows are then obtained for further fractionation calculations using either of the two mass-balance methods.

The method of conducting the entire calculation should be given some further consideration, since the calculations could be run in a number of ways. One way might be to run two or more mass-balance iterations, holding a certain set of flows, until the concentrations are relatively correct for these flows. Then energy-balance calculations might be made to establish a new set of flows and the pattern repeated. Alternatively, one mass-balance iteration may be followed by one energy balance, and this pattern continued. Because of the diversity of cases that can arise, no set answer to this problem can be stated that is optimum for all cases. When Method I mass-balance equations are used, the movement of concentrations towards their correct values is very fast even if radically wrong "guesses" of flow and temperature gradients have been made. Therefore, under these conditions, it is recommended that a "one-to-one" type of pattern be followed. When the Method of Successive Flashes is used for mass balancing, however, the rate of concentration movement is relatively slow, so that a different pattern must be followed. It is recommended for this case that one reduces the "input-output" error ϵ below some arbitrarily preset small number for all stages by repeated iteration before proceeding with an energy balance. The pattern actually used under these conditions will vary with the number of stages, since as a rough estimate the minimum number of iterations needed to meet reasonable values of ϵ is equal to the number of stages in the system. As the calculation approaches convergence, it is quite possible for a "one-to-one" pattern to develop.

Example 4 was calculated by using Method I mass-balance equations and a one-to-one pattern for energy balancing. The calculation proceeds as indicated in the computer schematic program, Fig. 5, up to the completion of the bubble-point cycling, at which time the program branched into the energy section to calculate new flows. Figure 10 shows schematically the linkages and program flow for this area of the calculation. The example uses the same feed and physical column as Example



MU-17913

Fig. 10. Schematic computer program for energy-balance calculations by net-heat-flow method.

Table IX

Results for Example 4: Temperatures (^{o}F) and stage summations from five iterations

Stages	1		2		3		4		5	
	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$
d	--	1.000	120.6	1.000	119.3	1.000	119.3	1.000	119.3	1.000
8	220°F	.550	149.1	.981	147.1	1.005	147.6	.998	147.5	1.000
7	220	.457	169.5	.978	165.4	1.013	169.5	.994	169.0	1.001
6	220	.464	182.3	1.020	186.1	1.011	186.4	.990	185.8	1.003
5	220	.517	194.2	1.098	203.3	.985	200.8	.994	200.7	1.004
4	220	.665	209.1	.852	220.7	1.038	212.9	.987	215.9	1.003
3	220	.606	230.5	.877	241.1	1.017	237.1	.994	238.5	1.001
2	220	.599	246.4	.918	257.3	1.007	255.5	.997	256.2	1.000
1	220	.678	261.7	.970	271.6	1.002	270.8	.999	271.1	1.000
R	220	1.000	280.8	1.000	285.7	1.000	285.4	1.000	285.5	1.000

Table X

Results from Example 4: stages flows from five iterations

	1		2		3		4		5	
Stage	V	L	V	L	V	L	V	L	V	L
	--	1.000	--	1.000	--	1.000	--	1.000	--	1.000
8	1.500	1.000	1.500	.951	1.500	.929	1.500	.927	1.500	.929
7	1.500	1.000	1.451	.950	1.429	.876	1.427	.884	1.429	.886
6	1.500	1.000	1.450	.921	1.376	.818	1.383	.852	1.386	.846
5	1.500	1.000	1.421	.857	1.318	.759	1.352	.834	1.346	.799
4	1.500	2.000	1.357	1.901	1.259	1.900	1.334	1.853	1.299	1.871
3	1.500	2.000	1.401	1.968	1.400	1.951	1.353	1.926	1.371	1.935
2	1.500	2.000	1.468	1.980	1.451	1.986	1.426	1.977	1.435	1.980
1	1.500	2.000	1.480	1.938	1.486	2.003	1.477	2.000	1.480	2.001
b	1.500	.500	1.438	.500	1.503	.500	1.500	.500	1.501	.500

Table XI

Results from Example 4:
top product recovery fractions from five iterations

Components	1	2	3	4	5
C_3H_8	.997	.999	.998	.999	.999
C_4H_{10}	.860	.923	.919	.921	.921
C_5H_{12}	.139	.077	.081	.080	.080
C_6H_{14}	.005	.001	.001	.001	.001
ΔQ_{es}	--	12146	12174	12208	12196
ΔQ_{ss}	--	8813	8841	8875	8863
Φ Factor	1.076	.725	1.119	.965	1.008

3. It is apparent from the iteration results shown in Tables IX, X, and XI that convergence is reached essentially as rapidly as in Example 3, for which constant flows are assumed.

In the energy-balance equations, (III.3) or (III.4), it would be of great interest to know under what conditions negative flows can results. There is, of course, no physical conception of a negative flow; and though the mass-balance equations can methematically handle negative flows, it has been generally found in the work presented here that the appearance of negative flows heralds unstable conditions which prevent convergence of the calculations. By using Eq. (III.2) the following energy balance expression can be derived

$$V_p = \frac{Q_c + d\,(h_p - h_{p+1})}{H_p - h_{p+1}} = \frac{r\,(H_t - h_r) + d\,(H_t - h_{p+1})}{H_p - h_{p+1}}. \quad \text{(III.9)}$$

This expression holds across all p up to the feed stage, and at this point becomes

$$V_p = \frac{Q_r + b\,(h_p - h_b)}{H_p - h_{p+1}}. \quad \text{(III.10)}$$

The denominator terms will never be negative, as H_p is always greater than h_{p+1}. The source of negative values in these expressions is then the numerator term. The terms $r\,(H_t - h)$ and $b\,(h_p - h_b)$ are always positive, and their magnitudes depend upon the values of r and b set or assumed. Since there are limits on r and d, this discussion assumes that these quantities have been set within these limits. The term $(H_t - h_{p+1})$ is generally positive although it could conceivably go negative if temperatures and compositions toward the bottom of the column were such that (h_{p+1}) were greater than H_t. Even though Eq. (III.9) produces positive values, they may be so small that when they are used in the liquid-flow calculation,

$$L_{p+1} = V_p - d, \quad \text{(III.11)}$$

negative values of L_{p+1} result. Thus Eqs. (III.9) and (III.10) depend upon temperature and composition movements found by using the mass-balance and equilibrium equations. For systems with a high degree of temperature sensitivity, such as may be encountered when relatively very heavy or very light components are present, it is quite possible that negative flows may result. Ordinarily, the flow variables set and held are within their limits and column feeds are such that the temperature gradients are orderly and not subject to large fluctuation, so that the net-heat-flow concept works well.

Example 4

Enthalpy-value constants (referred to liquid 100°F)

	Fx_F	k	l	u	w
C_3H_8	0.25	30.90	-15430	21.80	-4830
C_4H_{10}	0.25	40.10	-20050	27.00	-4910
C_5H_{12}	0.25	49.10	-24530	29.90	-3790
C_6H_{14}	0.25	55.60	-27790	36.60	-5040
	1.00				

Thermal condition of feed: saturated liquid.

Column pressure: 150 psia.

Reflux temperature: bubble point.

Top-product amount: 0.50 mole per mole of feed.

Reflux amount: 1.00 mole per mole of feed.

Enriching stages: 4 (not including the feed stage).

Stripping stages: 4 (including the feed stage).

A and B constants: same as those of Example 1.

Allowable error in bubble point: $|\epsilon_2| \leqslant 0.1°F$.

Total condenser used.

It would appear desirable, then, to develop another approach to energy balances. One reason for this has just been mentioned, namely, systems which contain a component that is highly volatile or highly nonvolatile relative to the other components. Systems of this type become quite temperature-sensitive, with the result that the enthalpy functions and therefore the flows move markedly from iteration to iteration. Another reason is found in the variables set and held.

When the variables set and held are such that the external flows, r and d, "float" (in the sense that they must be guessed), the net-heat-flow concept leads to internal-flow corrections based on these "floating" values. The external flows cannot be corrected by the ΔQ method, since it inherently corrects only internal flows. In simple distillation problems, resort can be had to the over-all column energy balance for an expression to correct d. As is shown later, in the case of stripping-type columns, this over-all column energy balance completely fails when used in combination with the ΔQ method. Thus, a method that corrects not only the internal flows of the system but the external flows as well would be desirable, and the following development presents such a method.

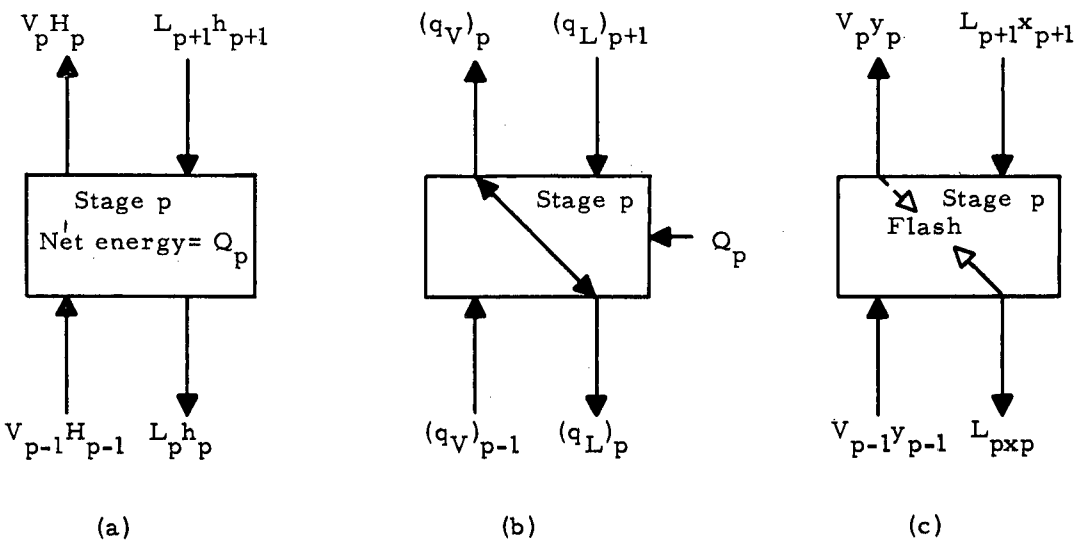
Method II

Consider the general stage p shown in Fig. 11a. A total energy balance about this stage (assuming adiabatic conditions) leads to

$$(V_{p-1} H_{p-1} + L_{p+1} h_{p+1}) - (V_p H_p + L_p h_p) = \text{net energy} \equiv Q_p. \quad \text{(III.12)}$$

There is, then, a Q_p term for every stage p in the system being considered, and if these terms are calculated after any iteration of the mass-balance equation, they give the magnitude of the individual-stage energy unbalances as well as the total system unbalance, $\sum_p Q_p$. At steady state all Q_p must be zero, as must $\sum_p Q_p$. If, in some manner, all Q_p can be "relaxed" to zero, the system will be in energy balance at this instant and the next step of the iterative procedure may be done.

The method of doing this as presented here is to first consider a "feedback" process whereby all the individual stage unbalances, Q_p, are fed back into the stage as corrections superimposed upon the energy streams leaving and entering that stage. The net energy fed back at any one stage appears in the streams leaving that stage, as shown in Fig. 11b. The over-all expression for stage p is



MU-17914

Fig. 11. (a) General representation of stage p.
(b) Relationship indicated between $(q_V)_p$ and $(q_L)_p$ is $(q_V)_p/(q_L)_p = a/b$.
(c) Input feed for flash calculations is the two streams indicated.

$$\left[V_{p-1}H_{p-1} + (q_V)_{p-1} + L_{p+1}h_{p+1} + (q_L)_{p+1}\right] -$$

$$\left\{\left[V_pH_p + (q_V)_p\right] + \left[L_ph_p + (q_L)_p\right]\right\} = 0, \qquad \text{(III.13)}$$

where q = that corrective value of energy flow which when added to its accompanying main-stream energy flow makes $Q_p = 0$.

If, now, Eq. (III.12) is subtracted from Eq. (III.13), the relation between the corrective flows q and the total stage unbalance Q_p is

$$(q_V)_{p-1} + (q_L)_{p+1} - \left[(q_V)_p + (q_L)_p\right] + Q_p = 0 \text{ for all p.} \qquad \text{(III.14)}$$

The equation for the over-all system of stages would be

$$\sum_p Q_p = (q_V)_{top} + (q_L)_{bottom} = (q_V)_{top} + \left(\frac{C_L}{C_V}\right) (q_V)_{bottom}. \qquad \text{(III.15)}$$

If, now, a connection between q_V and q_L can be found, then a system of calculation is possible whereby either $(q_V)_{top}$ or $(q_L)_{bottom}$ is assumed, and the recurrence equation, (III.14), after modification by some as yet unknown $(q_V)_p$, $(q_L)_p$ relation, C_L/C_V, is used to calculate from one end of the system to the other. The result of this calculation would be $(q_V)_{top}$ if $(q_L)_{bottom}$ were assumed, and vice versa. The calculated value would be obtained from Eq. (III.12), and this would be compared with the assumed value to satisfy the condition

$$\left| (q_V)_{assumed} - (q_V)_{calculated} \right| \leq \epsilon_c,$$

where ϵ_c is some arbitrarily predetermined small number for use with corrective heat flows. If the condition were not met, another arbitrary assumption of $(q_V)_{top}$ or $(q_L)_{bottom}$ would be made and another calculation and test would be conducted. Should the second comparison not be within the imposed limit, a process of linear extrapolation can be used to predict the next value of $(q_V)_{top}$ or $(q_L)_{bottom}$ to be used. This process can then be repeated for as many times as necessary to satisfy the imposed condition. It has been found

that the number of extrapolations necessary to satisfy conditions is seldom greater than 2 or 3, and quite often the first extrapolated value is sufficient.

When the energy unbalance Q_p is fed back to stage p, it can result in a change in temperature on the stage as well as a change in the exit flows. Thus, both latent-heat and heat-capacity effects are involved in the corrective flow terms $(q_V)_p$ and $(q_L)_p$. Letting ΔT be any arbitrary temperature change on any stage p, it is possible to define the term

$$C_V = \frac{(V_p H_p)_{T+\Delta T} - (V_p H_p)_T}{\Delta T}, \qquad \text{(III.16)}$$

where C_V = change in total energy content of the vapor stream per degree temperature change. If a value can be calculated for C_V, then it is possible to calculate the specific temperature change associated with stage p, since one has

$$(q_V)_p = C_V\ (\Delta T)_p, \qquad \text{(III.17)}$$

where $(\Delta T)_p$ = the temperature change on stage p resulting from feeding back the net energy Q_p of that stage.

In like manner, the corresponding equation for the liquid stream would be

$$C_L = \frac{(L_p h_p)_{T+\Delta T} - (L_p h_p)_T}{\Delta T}, \qquad \text{(III.18)}$$

and $(q_L)_p = C_L\ (\Delta T)_p$. (III.19)

On the assumption, then, that values can be obtained for C_L and C_V, Eqs. (III.17) and (III.19) give the relationship between $(q_V)_p$ and $(q_L)_p$ needed for use in the recurrence equation, (III.14). Thus

$$\frac{(q_V)_p}{(q_L)_p} = \frac{(C_V)}{(C_L)} = \frac{(V_p H_p)_{T+\Delta T} - (V_p H_p)_T}{(L_p h_p)_{T+\Delta T} - (L_p h_p)_T}. \qquad \text{(III.20)}$$

Equation (III.20) allows resolution of the Q_p into the individual corrective flows as outlined above. Having obtained the individual

values of (q_V) or $(q_L)_p$, one can then obtain the actual value of $(\Delta T)_p$ from either Eq. (III.17) or (III.19). When the value of $(\Delta T)_p$, has been obtained, it can be used to change the exit flows from stage p if an expression is available for rate of change of flow with temperature. Such an expression would be defined as

$$\frac{\Delta V_p}{\Delta T} = (V_p)_{T+\Delta T} - (V_p)_T, \qquad \text{(III.21)}$$

with a corresponding expression for $\frac{\Delta L_p}{\Delta T}$.

The method used to evaluate the terms C_V, C_L, and $\left(\frac{\Delta V_p}{\Delta T}\right)$ or $\left(\frac{\Delta L_p}{\Delta T}\right)$ is to perform flash calculations at two different temperatures. However, one basic assumption is necessary to carry out the two-point flash. By recalling the two alternate forms of the flash equation,

$$\sum_i \frac{F(x_i)_F}{1 + \left(\frac{L}{V}\right)_p \frac{1}{K_i}} = \sum_i V_p y_i = V_p$$

or

$$\sum_i \frac{F(x_i)_F}{1 + \left(\frac{V}{L}\right)_p K_i} = \sum_i L_p x_i = L_p, \qquad \text{(III.22)}$$

it can be seen that the term Fx_F must be fixed at every stage p before the flash equations can be utilized. For the general stage p it is assumed that the Fx_F term is composed of the two streams <u>leaving</u> the plate, as is indicated in Fig. 11c. With Fx_F fixed and held as indicated, it is a straight-forward calculation to determine any of the quantities $(V_p;\ L_p;\ y_i;\ x_i)$ at temperature T and again at $T+\Delta T$. The value of ΔT being artibrary, some judgment must be used in its choice. The value of T used for the first flash is also somewhat arbitrary. However, just before the corrective heat-flow calculation is entered, equilibrium bubble-point (or dew point) temperatures have been established, so that one useful choice for a first flash T would be these temperatures. It can easily be shown that if the equilibrium

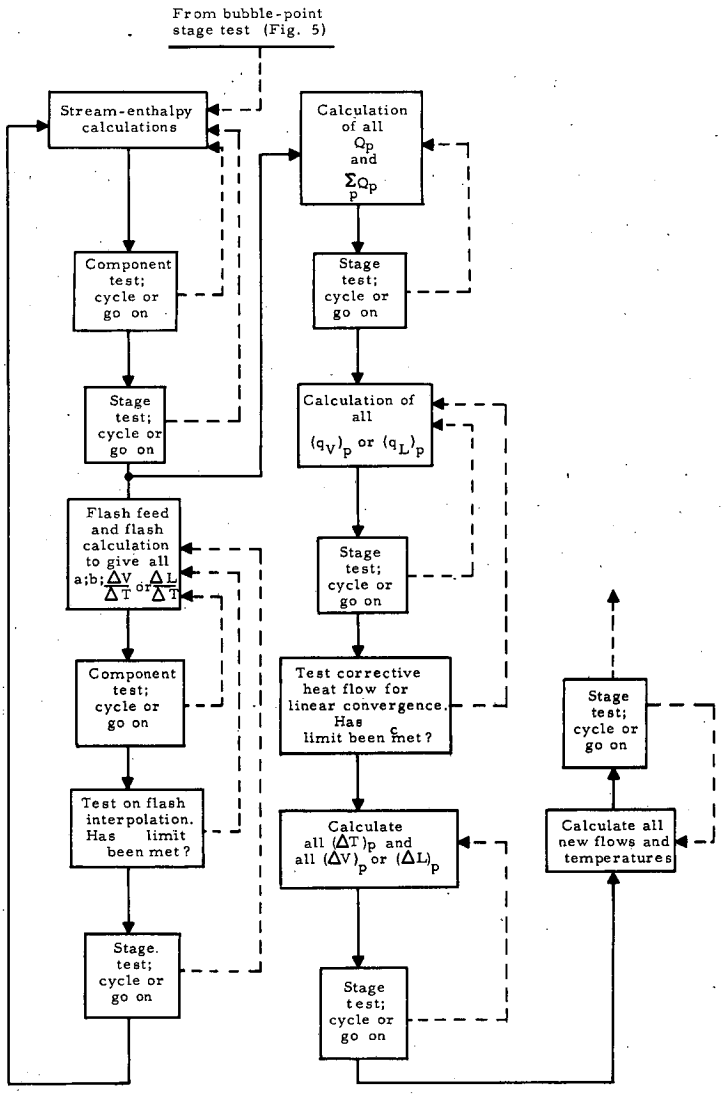
temperature is to be the first flash T, then no flash calculation need be run at this temperature because the flash equation will do nothing but reproduce the V_p and L_p already existing for stage p.

The calculation as outlined here and schematically programmed in Fig. 12 is to first calculate all the V_pH_p and L_ph_p terms at the temperatures and compositions from the mass-balance and equilibrium equations. Following this, a flash calculation is run, using the $F(x_i)_F$ indicated above and with a temperature equal to the equilibrium temperature plus the arbitrary ΔT. The flash equation gives the information $[(V_p)_{T+\Delta T}]$ and all $[V_p(y_i)_p]_{T+\Delta T}$, and this latter term, when combined with $[F(x_i)_F]_p$, gives all the $[L_p(x_i)_p]_{T+\Delta T}$. Thus the calculation of $(V_pH_p)_{T+\Delta T}$ and $(L_ph_p)_{T+\Delta T}$ can now be carried out and these, in turn, will provide the C_V and C_L terms required. The flash calculation gives the additional information needed to evaluate $\left(\frac{\Delta V_p}{\Delta T}\right)$ by Eq. (III.21). In carrying out the flash calculation, an extrapolation procedure is used wherein two values of V_p are arbitrarily assumed and then compared with values of V_p calculated from the flash equation. The condition to be satisfied is

$$\left|(V_p)_{assumed} - (V_p)_{calculated}\right| \leq (\epsilon_F),$$

where $(\epsilon)_F$ is some arbitrarily predetermined small number. The method suggested for setting up the first two V_p values is to use the value of V_p used in the mass-balance equation when the flash calculation is first started and then to use the V_p from the first flash calculation itself as the second value.

At this point, all the information needed for actual corrective heat-flow calculation is available. The first step in the calculation of all $(q_V)_p$ or $(q_L)_p$ is to determine all Q_p, using Eq. (III.12). Next, the recurrence relation and extrapolation procedure previously described are used repeatedly until the conditions imposed by ϵ_c are met. The form of the recurrence relation actually used at this point is that obtained by solving Eq. (III.20) for $(q_V)_p$ or $(q_L)_p$ and substituting into Eq. (III.14). Solving for $(q_V)_p$ gives the form



MU-17915

Fig. 12. Schematic computer program for energy-balance calculations by corrective-heat-flow method.

$$(q_V)_{p-1} = \left[1 + \left(\frac{C_L}{C_V}\right)_p\right] (q_V)_p - \left(\frac{C_L}{C_V}\right)_{p+1} (q_V)_{p+1} - Q_p. \qquad \text{(III.23)}$$

The $(q_V)_p$ are converted to $(\Delta T)_p$ by Eq. (III.17), and these $(\Delta T)_p$ are in turn converted to ΔV_p by using Eq. (III.21) and being careful to take into account the relation between the arbitrary ΔT and the calculated $(\Delta T)_p$. Finally, all new vapor flows are calculated by using ΔV_p, and the new vapor flows are used to calculate new liquid flows by a simple flow balance.

As was previously pointed out, the choice of a value for ΔT for use in the flash calculation is arbitrary. For all the work presented here, ΔT was chosen as $+ 1.0^\circ$. Quite often it would be better to choose a larger value for ΔT. The reason is that the method may very well predict a large value of $(\Delta T)_p$, and to apply the values obtaining for a ΔT of 1.0° across a large value of $(\Delta T)_p$ will often lead to trouble in the form of negative-flow predictions, as is shown later. The basic fault lies in trying to extrapolate conditions holding for a very narrow temperature range across a very wide temperature range. Even though the extrapolation may fail, a very useful piece of information is obtained, namely, the <u>direction</u> that the correction should take. For the sake of simplicity in problem layout and programming, the approach used here is to always accept the direction of correction indicated by using a ΔT of 1.0° and to alter the magnitude only if negative flows are predicted. A very simple and direct way of doing this is to apply a so-called "damping factor" in the form of a fractional multiplier of the $(\Delta T)_p$ predicted. In general, its value ranges from 1 down to 1/5, and the variation is primarily a function of the components present and the correctness of the original variable assumptions and--to a lesser degree--a function of the physical setup. There are other reasons for using a "damping factor." As is shown later, a varying C_V/C_L ratio should theoretically be used in the corrective heat-flow extrapolation process using Eq. (III.14); but, in actual use, this ratio was assumed constant and equal to that value obtained from

the flash process. The "damping factor" helps compensate for this assumption. As convergence is approached, however, both $(\Delta T)_p$ (predicted) and $(q)_p$ (calculated) diminish and pass through 1 and approach 0 in the limit, and therefore in this region the fractional multiplier can be set to 1. Thus a variable fractional multiplier should be used to obtain convergence in the minimum number of iterations, but doing this would require a fairly large amount of additional computer program and its value is questionable. For the most part, in the work presented here, a multiplier value was selected that gave positive flows, and this multiplier was used right up to the convergence point.

The choice of a ΔT of 1° for the flash calculation has a direct bearing on the value of ϵ_F used in terminating the flash extrapolation process. The $(\Delta V)_{T+\Delta T}$ predicted for $\Delta T = +1$ is quite small, and generally it was found to be in the range 10^{-1} to 10^{-3}. To insure a sufficient number of significant figures for $(\Delta V)_{T+\Delta T}$, ϵ_F was arbitrarily set at 1×10^{-5}.

The values of the total stream energy flows, $V_p H_p$ and $L_p h_p$, depend on the temperature base for the component enthalpies with the normal magnitudes within the range -10^{-5} to $+10^{-5}$. However, even though initial values of Q_p and q_p may be of the same order of magnitude as the stream energy flows, as convergence is approached all Q_p and q_p approach 0 so that the arbitrary value ϵ_c was set near 0--specifically, 1×10^{-1}.

The Flash Process

Since the flash process provides the two important relations needed to effectively use the corrective heat flow principle, some further consideration of this process is in order. The first important relation obtained from the process is C_V/C_L, defined by Eq. (III.20). The limits of this ratio can be obtained from the limits of the actual physical process of adding energy to a two phase system whose equilibrium compositions and thermodynamic conditions are those of the exit streams of a given stage p. The addition of energy must result in both an increase in vapor and an increase in temperature as long as

more than one component is present and equilibrium conditions are maintained. The amount of energy absorbed in these two increases varies according to the boiling range of the components present. For wide boiling ranges, heat-capacity effects would predominate. In any case, the values of C_V as defined by Eq. (II.16) will always be positive and will normally be something less than 10^3. Since the feed to the flash process is fixed, any increase in the vapor phase as a result of energy addition must lead to a numerically equal decrease in the liquid phase according to the equation

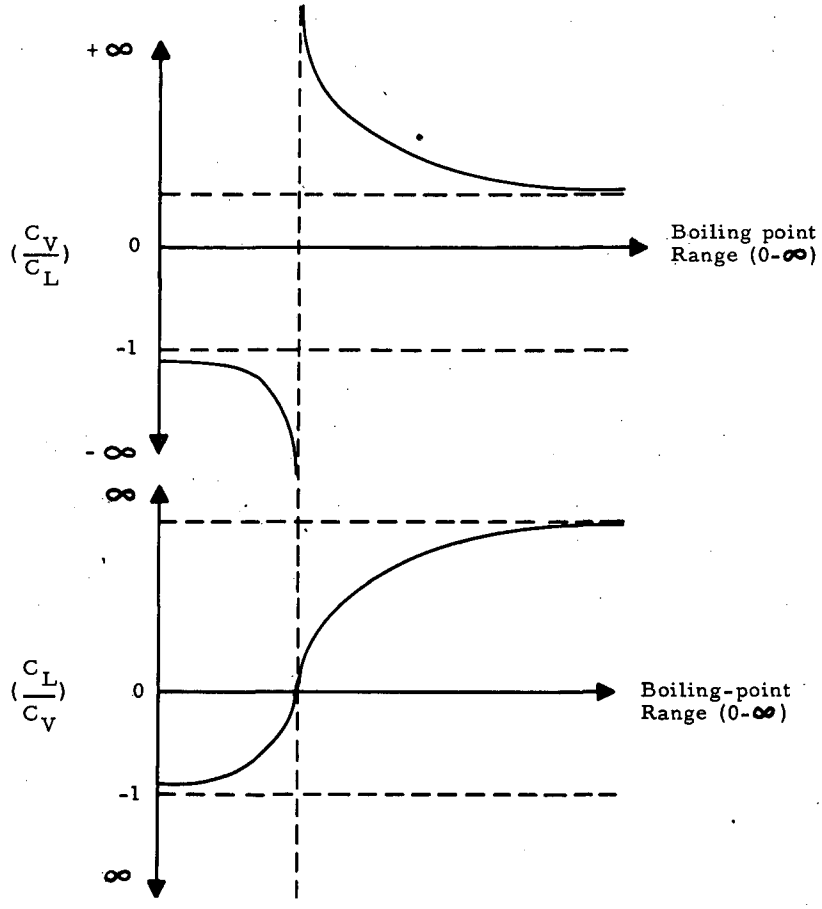
$$+\Delta V = -\Delta L. \qquad \text{(III.24)}$$

Thus, we are brought to a consideration of the C_L term defined by Eq. (III.18). Since $(L_p)_{T+\Delta T}$ is always less than $(L_p)_T$ for energy added (ΔT of +1), C_L will be positive only if the enthalpy or heat-capacity effects are greater than the flow-change or latent-heat effects. Where latent-heat effects predominate, as in the narrow boiling systems, it is possible for C_L to become negative. The limit of this process would be the complete disappearance of the liquid stream, and the ratio C_V/C_L would become

$$\frac{C_V}{C_L} = \frac{(V_p H_p)_{T+\Delta T} - (V_p H_p)_T}{-(L_p h_p)_T} .$$

As C_L varies from some positive number to its negative limit, the ratio C_V/C_L and its inverse behaves as indicated in Fig. 13. The ratio can have no value in the region 0 to -1 because this would imply $C_V \leqslant -C_L$, which means that either no energy can be put into the system ($C_V = -C_L$) or energy is being <u>removed</u> from the system ($C_V < -C_L$), and both these conditions contradict the condition necessary for $\Delta T = +1$, that is, that energy is being added to the system. The point $C_L/C_V = 0$ or $C_V/C_L = \pm\infty$ occurs when $(L_p h_p)_{T+\Delta T}$ approaches $(L_p h_p)_T$ and finally becomes identical with it.

The second important relation provided by the flash process is the $\Delta V/\Delta T$ figure defined by Eq. (III.21). As pointed out above, this



MU-17916

Fig. 13. Qualitative behavior of C_V/C_L ratio and its increase.

will always be positive and its magnitude will be a function of the boiling range of the components involved in any given separation.

Qualitative considerations indicate, then, that in simple distillation columns in which boiling-point ranges are not large latent heat effects would predominate, and that because of this C_V/C_L would tend to be positive and large. However, it may well be negative toward the stripping end of a column, where an essentially pure component exists at high temperature. On the other hand (as is shown later), for absorbers and strippers where wide boiling ranges are involved, heat-capacity effects predominate and the operating point shifts to the right in Fig. 13. This means that the C_V/C_L ratios will be small, and indeed they are quite often found to range near +1.

The Corrective Energy-Flow Extrapolation Process

The process of extrapolation using Eq. (III.14) is essentially a complex reflection process in which stream-corrective energy flow, q, entering a given stage p is reflected into the exit streams from that stage. In a cascade of stages, the reflection process becomes complex but is nevertheless capable of being carried out as previously outlined. A typical schematic reflection process is shown in Fig. 14. The flash process provides a value of C_L/C_V for use in Eq. (III.23), and this ratio is assumed constant until the (ϵ_c) condition has been satisfied. It should be noted, however, that the ratio applies only for a pure energy feedback to a stage. This energy feedback creates mass changes, and in the resulting reflection network combined mass- and energy-corrective flows should enter and leave stages so that the C_L/C_V ratio for pure energy would not apply for combined mass and energy flows except by chance. The exact values of these ratios would be available if mass effects were taken into account at every step in the reflection network, but this would involve flas-process calculations at every step. To do this would unduly expand and complicate the calculation and therefore the method actually used is a compromise one wherein one flash calculation is used as the basis for running out the reflection network, with the assumption that C_L/C_V is constant for all streams and

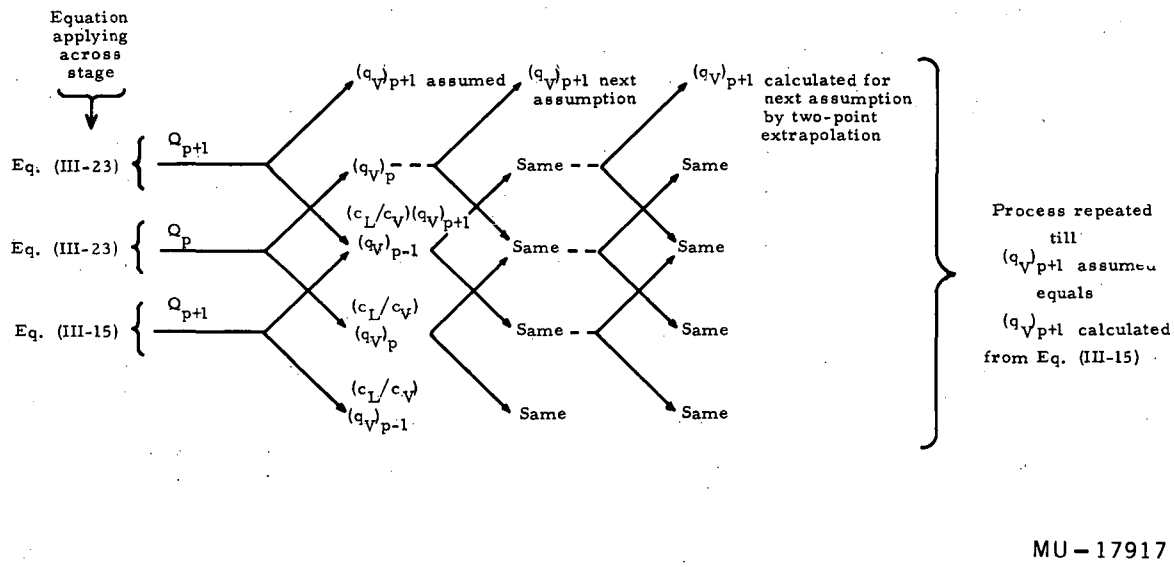


Fig. 14. Schematic energy-reflection or extrapolation process.

is equal to the value from the flash process. Note that the constancy is <u>within one iteration only</u> and that the ratio changes from iteration to iteration. The "damping factor" previously mentioned helps take care of the errors introduced by this assumption. As convergence is approached, the assumption is still incorrect, but the q values have become very small, and as they approach 0, the effect of this or any other assumption becomes negligible.

Although Eq. (III.23) is explicit in q_V it could equally well have been written for q_L. The question of which form to use is immaterial from a purely mathematical standpoint, since either form will lead to satisfaction of the ϵ_c condition. However, there is justification for the use of the q_V form if both mass and energy are considered, and this can be found in following a reflection-network runout. In the course of such a runout, one condition must never be violated, viz.: the sign of the corrective energy flow and its corresponding corrective mass flow must always be the same in the <u>vapor phase</u>. The only way to assure this is to calculate q_V and then make the mass correction dependent on the sign of the q_V calculated. It can be shown that if the q_L values calculated are used as a basis for a reflection runout, it is quite possible for opposite signs to appear on energy- and mass-corrective flows in the vapor phase. This is a physical impossibility, since if there is an energy increase in the vapor stream, there must be a mass increase and vice versa. The same is true for a decrease.

In the corrective energy-flow process as used here, no mass-flow considerations are involved until all the corrective energies have been resolved to satisfy ϵ_c. It is at this point that a choice must be made, since the path of arrival at this point is independent of whether q_V or q_L was used. Based on the above arguments, the only sound choice for correcting the system flows is to use q_V and a combination of Eqs. (III.17) and (III.21). This is not to say that using q_L and Eqs. (III.19) and (III.21) to correct the system flows will fail. What is implied is that the choice of q_V is theoretically sound and will always lead to convergence. The fact that q_L works indicates only that it has

succeeded in generating the right direction to bring about convergence, although the magnitude of the correction is questionable. The risk involved in using q_L and calculating ΔL from the q_L value lies in that the correct direction of the flow correction may not be generated. If the direction is correct, questionable magnitudes may be compensated for by the aforementioned damping factor.

The fact that the corrective energy flow process is independent of which q is used to satisfy ϵ_c has some utility in its actual use. As is shown later, for strippers it is convenient to use q_V whereas, for absorbers, q_L is more convenient. For simple distillation columns, it makes little difference which is used. In all cases, though, the flow corrections should be based on q_V, and if q_L was actually calculated, it should first be converted to q_V by Eq. (III.2) before flow corrections are made. In summation, then, the use of q_V will always produce a ΔV for which the direction of movement is correct although the magnitude may have to be altered by the use of a damping factor.

Application of Method II

Method II, the corrective-energy-flow method, can be applied to all types of columns, but it is especially useful for absorbers and strippers. Using the method involves careful consideration of the variable analysis since the Q for every stage p must be capable of evaluation. For those columns with a reboiler, in order to determine Q_R, the reboiler duty must be one of the variables set and held. In effect then for these columns, use of Method II removes a degree of freedom since it is no longer possible to substitute another fractionation variable for the reboiler duty. At the top or condenser end of the column, it is not necessary to explicitly set the condenser duty, Q_c, since the only requirement for the top stage is a knowledge of energy in the reflux stream. For simple absorbers and strippers, there are no condenser or reboiler duties to consider, but a refluxed stripper will involve a condenser duty while a reboiled absorber will involve a reboiler duty. In general, although Method II can be used for simple or complex distillation columns, Method I is recommended, since it will give a convergent solution in a smaller number of iterations.

As a first illustration of the use of Method II, it is applied to a simple distillation column of the type shown in Fig. 4. In Example 5, the reboiler duty is set so that after all feed variables, stages per column section, and the column pressure are additionally set, the Description Rule indicates the possibility of setting the remaining variables

Condenser duty,

Reflux amount,

but for this example these were replaced with

Saturated liquid reflux,

Top-product amount.

The results of Example 5 are shown in Tables XII, XIII and Figs. 15-18. It was necessary to use a damping factor in this case and the first value that gave a stable solution was 1/3. Factors of 1 and 1/2 were tried but both gave negative flows. The typical divergent behavior of a nonstable factor is shown in Fig. 16 for a factor of 1/2 together with the behavior of the factors 1/3 and 1/5; all results were obtained by using a Φ factor as well as a damping factor.

The effectiveness of the Φ factor is shown in Table XII and Fig. 15. The use of the Φ factor brings about a rapid establishment of the correct temperatures and recovery fractions at approximately the 6th or 7th iteration, but it is necessary to do 20-plus iterations to reduce all Q values to some small number, in this case, 10. However, as can be seen from Fig. 18, the iterations from 6 on are moving only the third significant figure in the numbers representing vapor flows, and for all practical purposes, this degree of accuracy is unwarranted. The additional time and effort to reduce Q values from the largest value of 100+ at Iteration 6 to a value of < 10 for all stages at Iteration 14 has negligible effect on the recovery fractions. The value below which all Q should fall for a given calculation is a matter of judgment and experience.

The behavior of the three stages lagging behind all others in the reduction of Q values is shown in Fig. 17. This figure and Fig. 16

Table XII

Results for Example 5: top product recovery fraction from various iterations

Components	1	2	3	4	5	6	7	8	9	10	15	20
	No Φ Factor - Damping Factor = 1/5											
C_4H_{10}	1.030	1.035	1.029	1.023	1.019	1.015	1.011	1.008	1.006	1.004	1.001	1.000
C_5H_{12}	1.023	1.033	1.026	1.021	1.016	1.012	1.009	1.007	1.004	1.002	.998	.998
C_6H_{12}	.903	.897	.909	.911	.911	.911	.910	.910	.909	.908	.906	.905
C_7H_{16}	.154	.052	.050	.056	.063	.069	.075	.080	.084	.087	.095	.096
C_8H_{18}	.005	--	--	--	--	--	.001	.001	.001	.001	.001	.001
C_9H_{20}	--	--	--	--	--	--	--	--	--	--	--	--
	With Φ Factor - Damping Factor = 1/5											
C_4H_{10}	1.000	1.000	--	1.000	--	1.000	--	1.000	--	1.000	1.000	1.000
C_5H_{12}	.995	.998	--	.998	--	.998	--	.998	--	.998	.998	.998
C_6H_{14}	.917	.912	--	.914	--	.911	--	.909	--	.907	.906	.905
C_7H_{16}	.182	.089	--	.087	--	.092	--	.093	--	.094	.096	.096
C_8H_{18}	.006	.001	--	.001	--	.001	--	.001	--	.001	.001	.001
Φ Factor	.790	.828	1.089	1.000	1.003	1.004	1.004	1.003	1.002	1.002	1.000	1.000
	With Φ Factor - Damping Factor = 1/3											
C_4H_{10}	1.000	1.000	--	1.000	--	1.000	--	1.000	--	1.000	1.000	--
C_5H_{12}	.995	.998	--	.998	--	.998	--	.998	--	.998	.998	--
C_6H_{14}	.917	.913	--	.913	--	.908	--	.906	--	.905	.905	--
C_7H_{16}	.182	.088	--	.089	--	.094	--	.096	--	.096	.096	--
C_8H_{18}	.006	.001	--	.001	--	.001	--	.001	--	.001	.001	--
Φ Factor	.790	.815	1.158	.937	1.039	.994	1.007	1.000	1.000	1.000	1.000	--

Table XIII

Results for Example 5: (C_L/C_V); (C_V); $(\Delta V/\Delta T)$ from various iterations

	(C_L/C_V)			(C_V)			$(\Delta V/\Delta T)$
Stage	1	6	14	1	6	14	14
9	.320	.370	.370	364	299	300	.031
8	.232	.238	.235	403	464	460	.041
7	.201	.187	.187	391	456	446	.038
6	.175	.156	.156	371	417	408	.033
5	.145	.128	.129	344	363	354	.027
4	.204	.207	.211	480	501	492	.038
3	.065	.033	.037	734	919	901	.061
2	-.010	-.060	-.057	998	1408	1380	.087
1	-.065	-.121	-.120	1281	1841	1812	.107
R	-.158	-.192	-.191	1008	1298	1286	.067

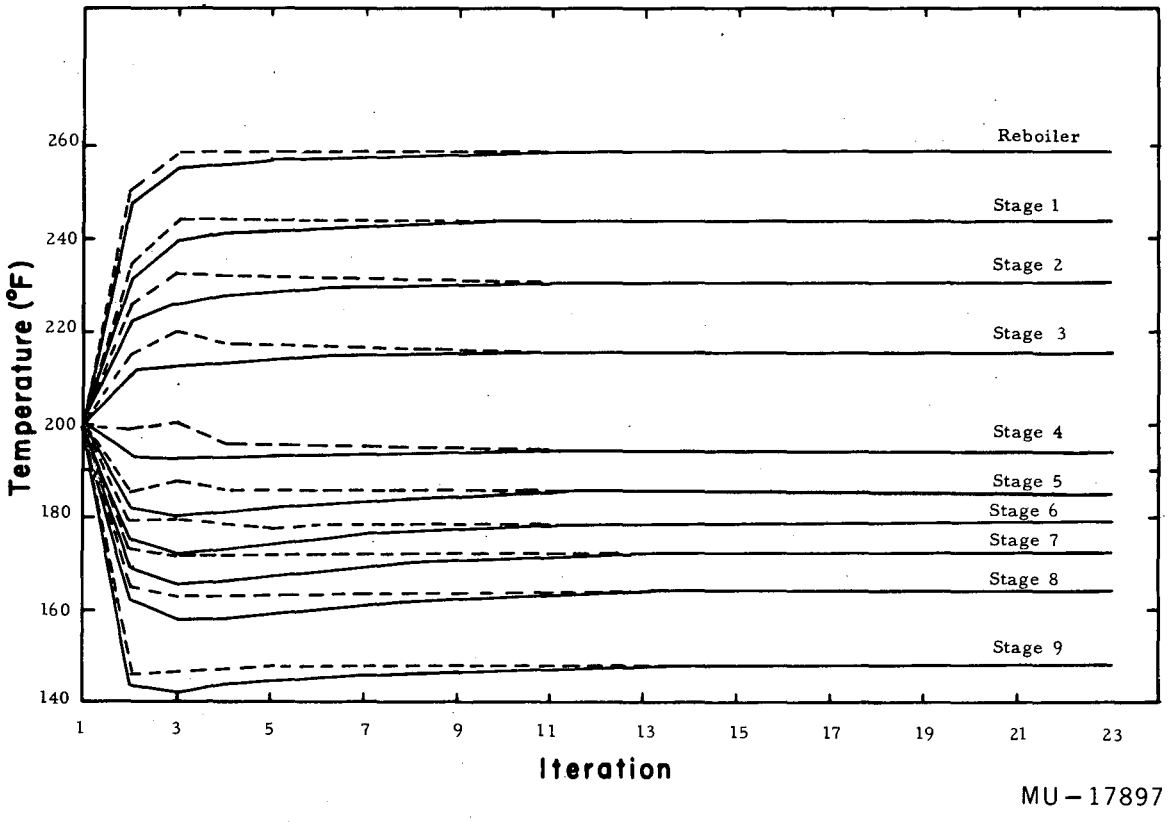
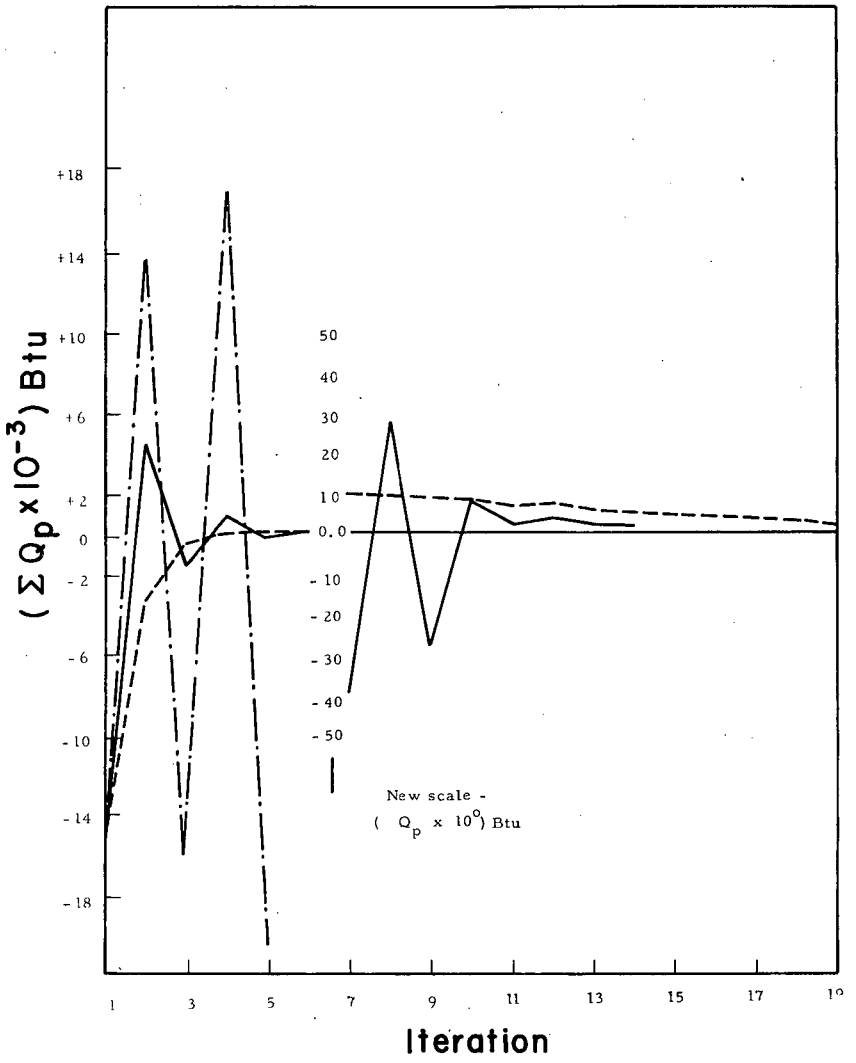


Fig. 15. Results for Example 5: temperature vs. iteration for each stage.
--- Φ factor used.
—— no Φ factor.



MU-17918

Fig. 16. Results for Example 5: summation of energy unbalances vs. iteration.
—— damping factor = 1/3.
--- damping factor = 1/5.
—·—· damping factor = 1/2.

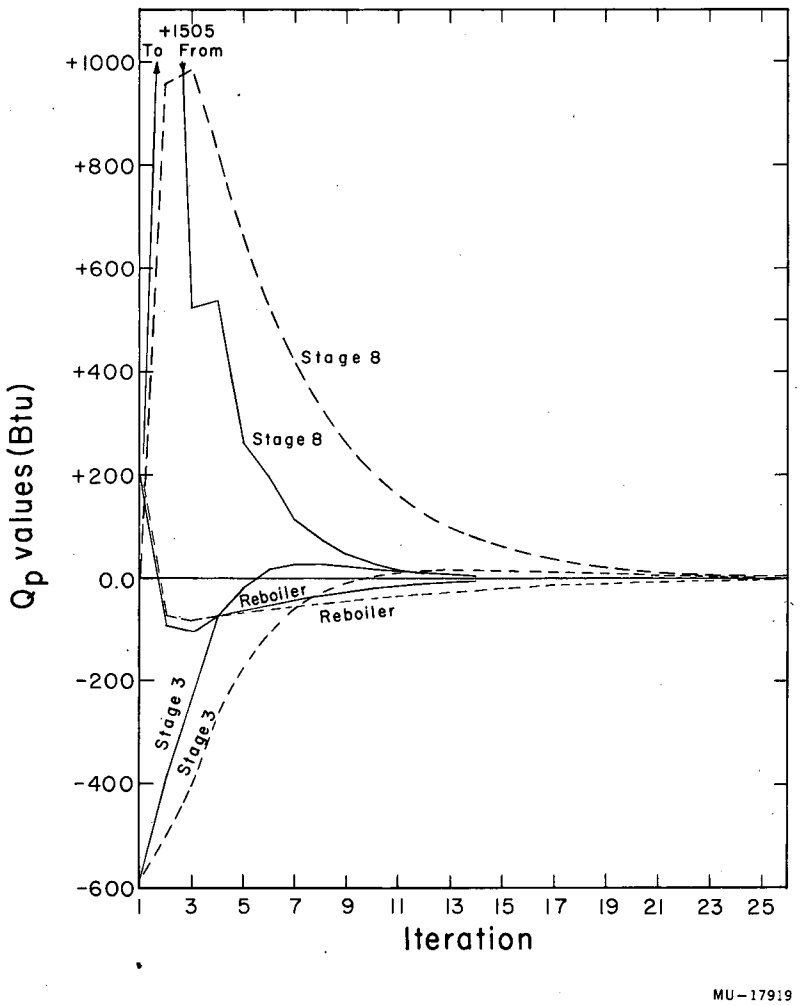


Fig. 17. Results for Example 5: energy unbalance vs. iteration for selected stages.
—— damping factor = 1/3.
--- damping factor = 1/5.

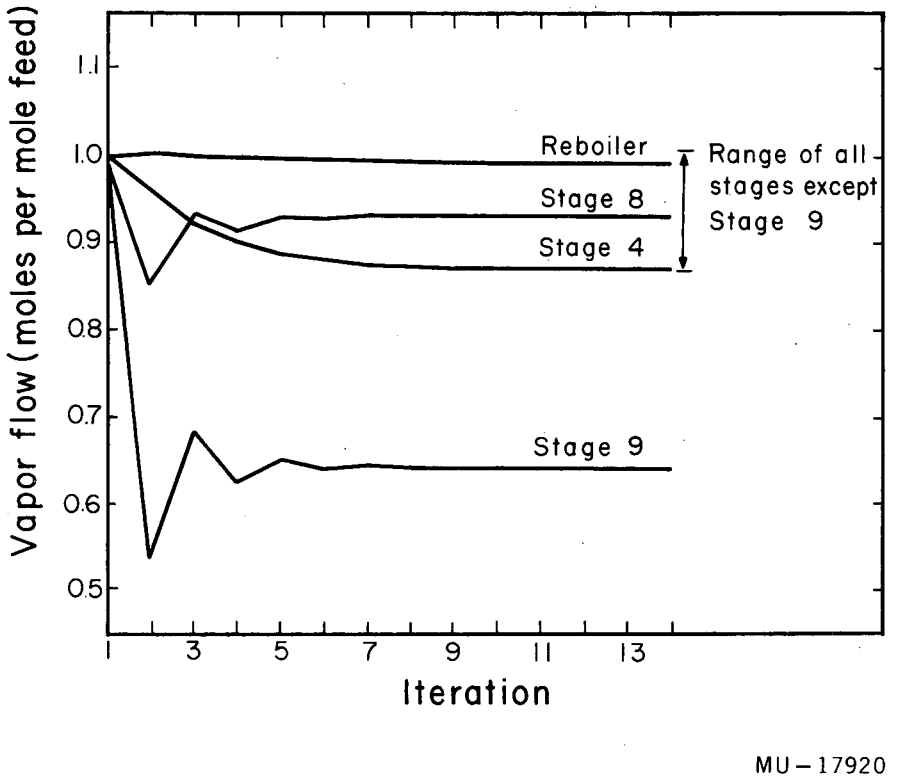


Fig. 18. Results for Example 5: vapor flow vs. iteration for selected stages; damping factor = 1/3.

indicate the effect of varying the damping factor. Smaller factors appreciably slow down the rate of convergence and bring about an asymptotic approach to the $Q = \Sigma Q = 0$ axis. From the standpoint of the minimum computer time, that damping factor which just gives a stable solution should be used, but there is no a prior way to predict what this value will be. A factor of 1 should always be tried first, and the factor can then be reduced in some arbitrary manner if unstable solutions develop.

Table XIII shows that values of C_L/C_V can and do go negative even if the end effect represented by the reboiler is neglected. This merely reflects the movement of the composition toward pure heavy material, with the result that high values of the equilibrium value cause flash calculation to be made in that area of the general flash curve where there is a large movement in the amount of vapor when energy is added to the system. Thus, latent-heat effects are predominating in this area and the large change in vapor is such that the C_L term is negative, since the change in liquid enthalpy cannot compensate for the decrease in liquid.

Example 5

		Equilibrium-value constant		Enthalpy-value constants			
Feed	Fx_F	A	B	k	l	u	w
C_4H_{10}	0.1	-3848	8.358	41.27	-24762	29.64	-10170
C_5H_{12}	0.2	-4002	7.833	52.67	-31602	36.79	-12189
C_6H_{14}	0.2	-4997	8.665	58.60	-35160	42.23	-13533
C_7H_{16}	0.2	-5595	8.847	66.13	-39678	50.10	-16232
C_8H_{18}	0.2	-6300	9.261	73.10	-43860	58.25	-19188
C_9H_{20}	0.1	-7295	10.078	76.94	-46164	62.84	-19879
	1.0						

Thermal condition of feed: saturated liquid

Column pressure: 1 atmosphere

Reflux temperature: bubble point

Top-product amount: 0.5 mole per mole feed

Reboiler duty: 15,000 Btu per mole feed

Enriching stages: 5(not including feed stage)

Stripping stages: 4 (including feed stage)

Total condenser used

Allowable error in dew point: $|\epsilon_2| \leqslant 0.1^{\circ}F$

Allowable error in flash: $|\epsilon_F| \leqslant 1 \times 10^{-5}$ mole

Allowable error in corrective-energy-flow calculation:

$|\epsilon_c| \leqslant 0.1$ Btu.

Enthalpy-value constants are referred to liquid at $200^{\circ}F$

Original flow gradient assumed;

Enriching section: $L/V = 0.5/1.0 = 0.5$

Stripping section: $V/L = 1.0/1.5 = 0.333$

IV. CALCULATIONS WITH VARIABLES OTHER THAN BULK SEPARATION SET AND HELD, AND CALCULATIONS WITH COMPLEX COLUMNS

For the most part the discussion and illustrations of Sections II and III involved bulk separation and a column flow as the variables set and held during a calculation. These variables were used for a simple distillation column, such as that of Fig. 4, for which the total list of variables set would be

Feed composition and amount
Feed thermal condition
Column pressure
Enriching stages
Stripping stages
Condenser (reflux) temperature
Reflux amount
Total top-product amount

Quite often it is desirable to make calculations in which total top-product amount is not a variable of primary interest. More likely, the recovery fraction of a certain component or the separation between two components will be of interest. This latter case would require the setting of the recovery fractions of both components. Still another possibility is the setting of a variable which is a function of the composition existing at some stage in a column. Although the following calculational procedures are developed for these non-bulk-separation variables, any problem can be solved with bulk separation used as a parameter, as was pointed out in Section II. Enough values of r and d would be assumed, for instance, to give a sufficient number of calculations to build up a network of answers. It becomes a matter of individual preference and judgment as to what approach is utilized for the solution of a given problem.

Component Separation as a Set Variable

When the recovery fraction of a certain component is desired as a fixed variable, quite convenient calculational procedures can be devised no matter what the system of components. In addition, for many hydrocarbon systems encountered, the fixing of two recovery fractions--

that is, the separation of two components--also permits convenient calculation of the system.

The technique used is perhaps best illustrated by means of an example; consider Example 6. A feed of four components is to be fed to an existing column such as that of Fig. 4. The recovery and purity of C_4H_{10} in the top product are of primary interest, and these variables are used in place of reflux and top-product amounts of a typical bulk separation. However, setting the recovery and purity of a component in a product fixes the total amount of that product. The net result then is that only the reflux amount has been replaced.

Setting the column flows and stage temperatures allows calculation using Method I mass balance. The beginning step in this calculation is, then, the prediction of the column temperature gradient. The simplest possible gradient is one in which all stage temperatures are set at the bubble point of the feed, since it has been shown in Section II that convergence is very fast when this is done. To spend additional effort on predicting a "better" gradient is a matter of judgment. Example 6 provides an opportunity to make a "better" prediction, if desired, for with the system of components involved a very close estimate of product compositions can be made. Assuming C_3H_8 goes completely into the top product and C_6H_{14} completely into the bottom product, one can calculate the split of C_5H_{12} into the products. Thus, good estimates can be made for the top-stage and reboiler temperatures; they were found to be 142°F and 247°F respectively for Example 6. The first assumed temperature gradient was simply taken as a straight line between these two temperature values. In many systems the end temperatures would be much more difficult to predict, so that the simple constant gradient mentioned above would serve as the first prediction.

Following the temperature-gradient assumption, a flow is assumed and calculation can proceed. Based on the assumption of a reflux flow, Method I mass-balance calculations are made <u>only</u> for the control component whose recovery fraction is fixed. The control-component distribution ratio resulting is then used in the following form of the

over-all mass balance equation,

$$dx_d = \frac{Fx_F}{\frac{b}{d}\left(\frac{x_b}{x_d}\right) + 1}, \qquad \text{(IV.1)}$$

which gives directly the amount of the control component in the top product. If the desired separation for the control component is not obtained, another value of reflux is assumed and the calculation is repeated. A simple and rapid method for doing this is the two-point extrapolation method previously mentioned. In Example 6, then, these calculations were first made for component C_4H_{10}.

By using the proper value of reflux and the first predicted temperature gradient, Method I mass-balance calculations are now made for all components present. New temperatures are obtained and the whole procedure repeated.

In the first trial of Example 6 a reflux value of 0.574 moles per mole of feed was found to give the desired top-product recovery fraction of 0.900 for C_4H_{10}. With this value of reflux used to predict the internal flows, the calculation was done for all components with the ϕ-factor form of the over-all mass balance equation, Eq. (II.28). The value of the ϕ factor is, of course, unknown at the time the control-component calculations are run, so that the factor does not appear in Eq. (IV.1). The effect of the factor in the over-all mass-balance equations for all components is to accelerate convergence to the correct temperature gradient, and therefore ϕ should be used. A value of ϕ other than 1 will displace the control-component recovery fraction from the value obtained in the control-component calculation. In the first trial of Example 6 the value of ϕ was 1.070 and consequently the recovery fraction of C_4H_{10} calculated was 0.894 rather than 0.900. In subsequent trials, as ϕ approached 1 and the temperature gradient became more correct, this discrepancy died out and the two recovery fraction values became identical. The results are presented in Tables XIV and XV.

Table XIV

Results for Example 6: temperature (^{o}F) and summations from five iterations

	1		2		3		4		5	
Stage	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$
d	--	1.000	134.8	1.000	134.4	1.000	134.4	1.000	134.4	1.000
8	142	1.024	144.3	.989	143.2	1.000	143.2	1.001	143.3	1.000
7	155	1.008	154.3	.978	152.9	1.000	152.9	1.001	153.0	1.000
6	168	.986	166.1	.973	164.9	1.001	165.0	1.002	165.0	1.000
5	181	.978	179.7	.978	179.2	1.003	179.4	1.002	179.5	1.000
4	195	1.049	194.4	.992	195.3	.998	195.5	1.001	195.4	1.000
3	208	1.044	204.1	.993	204.8	.999	205.0	1.001	204.9	1.000
2	221	1.025	216.1	.995	216.7	1.000	216.8	1.000	216.8	1.000
1	234	1.005	230.2	.997	230.8	1.000	230.8	1.000	230.8	1.000
b	247	1.000	246.1	1.000	246.6	1.000	246.6	1.000	246.6	1.000

Table XV

Results for Example 6:
top product recovery fraction from five iterations

Component	1	2	3	4	5
C_3H_8	.998	.998	.998	.998	.998
C_4H_{10}	.894	.900	.900	.900	.900
C_5H_{12}	.111	.101	.101	.102	.102
C_6H_{14}	.002	.001	.001	.001	.001
Reflux	.574	.645	.633	.630	.630
Φ factor	1.070	.997	.995	1.000	1.000

Example 6

Feed	Fx_F	Equilibrium-value constants A	B
C_3H_8	0.01	-2553	5.704
C_4H_{10}	0.35	-3106	5.813
C_5H_{12}	0.24	-3828	6.202
C_6H_{14}	0.40	-4502	6.564

Thermal condition of feed: saturated liquid

Column pressure: 100 psia

Reflux temperature: bubble point

Enriching stages: 4(not including feed stage)

Stripping stages: 4(including feed stage)

Recovery fraction of C_4H_{10} in top product: 0.90

Purity of C_4H_{10} in top product: 90%

Calculated top product d = 0.35 mole per mole feed

Acceptable bubble-point error: $|\epsilon_2| \leqslant 0.1^{\circ}F$

It is interesting to note that in Example 6 the second-iteration value of the reflux was within 4% of the correct value and that the separation on all components was correct to within 1%. Iteration 3 confirmed this result and for all practical purposes Iterations 4 and 5 need not have been run. Example 6 did not include an energy-balance calculation, but if an energy balance were desired, Method I of Section III would be recommended.

The results of a calculation such as that of Example 6 allow the specification of the flows in a column for any given amount of feed. On the other hand, by using the diameter and capacity of an existing column, it is possible to calculate the amount of feed that can be handled. If the calculation is being used as a design method, it is possible to determine the column size that will handle a given amount of feed.

The use of the calculation as a design method may at first seem somewhat backward, but it is just as logical to set the number of stages to be used at some arbitrary figure greater than the minimum number stages at total reflux as it is to set the reflux to be used at some arbitrary amount greater than minimum reflux, as is commonly done.

If a given problem description is to include the recovery and purity of a component, then the calculation procedure as exemplified by Example 6 is immediately applicable. If the problem description is to include the recovery fractions of two components, there is no change in the basic calculational procedure but there is a change in starting the procedure. The amount of product that will yield the second recovery fraction should be estimated and calculations made as in Example 6. It is difficult to vary the total product amount to match the second recovery fraction by using the above calculational procedure. It is suggested that for a given value of top-product amount, two control-component calculations be made, one for each component. The reflux values from each calculation should be the same for correct conditions. If the values do not match, the two-point extrapolation procedure may again be called upon to find that value of top product which will give identical reflux values from the individual control-component calculations. In many hydrocarbon systems, it is easy to estimate total product amounts; for other systems a few calculations are required but in either case a minimum amount of effort is required.

Another problem description of a similar type is of interest. With the recovery of a given component set, and the amount of feed to be fractionated known, the questions arise as to what product purity can be obtained for this component or what sharpness of separation from the other components can be obtained. From the size of the column to be used, the vapor or liquid capacity of the column--whichever is limiting--can be estimated. Then, as an example, the amount of vapor that can be used per unit amount of feed can be estimated and set as the second variable, with the control-component recovery fraction as the first set variable. For this case the amount of top product is assumed and calculations are

made on the control component as in Example 6 until that value of the product is found which gives the correct answer for the recovery of the control component. The procedure from this point on is straightforward. In like manner, calculations to determine how much of a product of given purity can be obtained can be made in which the purity of a control component and an internal column flow are held.

Problems of this latter type can be solved by another, more convenient procedure than that of Example 6. For these problems a variable such as the recovery fraction of the control component is set and in addition a column flow is set. What must be solved for is the amount of total product that will yield the required separation on the control component. Here, then, a value of the total product is assumed and Method I mass-balance calculations are made on all components until the temperature gradient is correct. The calculation therefore proceeds as in Example 1. There results a value of the recovery fraction which is correct for the assumed product amount but which is most likely not correct in comparison with the desired value. To find that value of total product which is approximately correct for the desired recovery-fraction value, Eq. (II.28) is used as described in Section II. That is, d (and hence b) is varied, with the restriction $\sum_i (x_i)_d = 1.0$, until a value of d is found which gives the correct control-component recovery fraction. The product-composition ratios used in Eq. (II.28) are those existing when the above correct temperature gradient is obtained. The new temperature gradient and approximate product value are then used in the next iteration, and the whole process repeated until convergence. The rate of convergence for such a calculation is quite rapid and the amount of product calculated is correct. From this point of convergence further extrapolation for the change in control-component separation with small movements in total product amount may be made with a high degree of confidence.

Composition-Dependent Variable as a Set Variable

Instead of the recovery and (or) purity of a given component, it is often of interest to specify a product variable which is dependent upon the composition of that product. Such a variable might be octane number, which could be calculated from the composition of the product and the blending numbers of the components. Another such variable might be the vapor pressure at a certain temperature, and this could be estimated from the boiling point of the product at the column pressure. In general, any variable that can be obtained from a knowledge of the composition can be set and held in the calculations just as was the recovery and (or) purity of a control component.

Calculations holding a composition-dependent variable are generally more difficult than those holding a component recovery and (or) purity. Consider a problem description in which the amount of the bottom product and the reboiler temperature are set. A temperature gradient and a reflux (or some other flow) are assumed. Calculations proceed on all components to obtain the bottom-product composition. If the bubble-point temperature based on this composition is not that set for the reboiler, another value of reflux is assumed and the calculation repeated. This procedure is carried out repeatedly, holding the assumed temperature gradient, until the bottom bubble-point temperature is within the desired limit. At this point the temperature gradient is corrected and the whole procedure repeated until the recovery fractions of all components become constant from iteration to iteration. This type of calculation will consume more computer time because of the necessary iteration-within-iteration pattern, and this would also be true for cases in which recovery and (or) purity variables are set. Nevertheless digital computer solutions proceed extremely fast and make this type of calculation quite feasible.

In contrast to setting a composition-dependent variable and a product flow, consider the problem description in which a column flow and a composition-dependent variable are set. As will be shown, this latter combination affords an appreciable simplification in calculations. This is best illustrated by an example.

In Example 7 a hydrocarbon stream is to be debutanized in a column similar to that of Fig. 4 to produce a bottom product with a Reid vapor pressure of 9 psig. As the separation is predominantly between C_4H_{10} and C_5H_{12}, a reflux is set which is typical for such separations, viz. 0.5 mole per mole of feed. What is desired, then, is the amount of product that can be made in a specified column. In all such problems in which the amount of a product is unset, very effective use can be made of Eq. (II.28), as described in Section II and pointed out previously. When one Method I mass-balance calculation has been made on all components at an assumed temperature gradient, all component-distribution ratios are available. These ratios are then used to vary the product composition with product amount until the desired bottom bubble-point temperature is obtained. This is an approximation, but (as was pointed out in Section II) it is quite accurate. Once the bottom product has been determined, the temperature gradient can be corrected and the procedure repeated to convergence.

Example 7

Feed	Fx_F	Equilibrium-value constants A	B
C_3H_8	0.040	-2553	5.522
C_4H_{10}	0.320	-3106	5.631
C_5H_{12}	0.285	-3828	6.020
C_6H_{14}	0.155	-4502	6.382
C_7H_{16}	0.090	-5750	7.698
C_8H_{18}	0.110	-6510	8.286
	1.000		

Thermal condition of feed: saturated liquid

Column pressure: 120 psia

Reflux temperature: bubble point

Enriching stages: 4(not including feed stage)

Stripping stages: 4(including feed stage)

Reid vapor pressure of bottom product: 9 psig

Reflux flow: 0.5 mole per mole feed

Reboiler temperature: 280°F (based on estimated vapor pressure of bottom product of 120 psia at 280°F)

Acceptable bubble-point error: $|\epsilon_2| \leqslant 0.1°F$

For the first iteration, the initial separation estimate led to the assumption of b = 0.7 mole per mole feed. This also led to the following assumed first temperature gradient:

Stage	Temperature
8	150°F
7	167
6	183
5	199
4	215
3	231
2	247
1	263
Reboiler	280°F

A Method I mass-balance calculation for all components gave the following product distribution ratios:

Component	Distribution ratio (x_b/x_d)
C_3H_8	0.001778
C_4H_{10}	0.07396
C_5H_{12}	3.991
C_6H_{14}	23.95
C_7H_{16}	16270.
C_8H_{18}	617700.

These ratios were then used in Eq. (II.28) to determine the bubble point of the bottom product at various values of b. A simple two-point extrapolation process suffices to quickly find the correct value for the given bubble point. In this case the initial value of b was 0.7 and the value of ϕ that gave $\sum_i (x_i)_d = 1$ was 1.801, and the

resulting bottom-product composition gave a bubble point of 262.7°F vs 280°F desired. Further iterations at this point and their results are as indicated:

$$b = 0.6, \qquad \phi = 0.6248, \qquad T_b = 282.5^{\circ}F;$$
$$b = 0.6124, \qquad \phi = 0.7151, \qquad T_b = 280.3^{\circ}F.$$

The last value of T_b was sufficiently close to 280°F. Therefore, the values of x_d and x_b calculated at this point were used to obtain the compositions of the individual-stage liquids, and from these a new temperature gradient was determined. Calculations were then continued with these new temperatures and with b = 0.6124. The results of the iterations are given in Tables XVI and XVII, and it is evident that the results of Iteration 3 are sufficiently converged for all practical purposes. As is also evident, the calculation quickly converged to the correct bottom product.

Another type of problem very similar to that of Example 7 is of interest. It may well be that the capacity of an existing column is limited not by a flow but by the heat-transfer capacity of either the reboiler or the condenser. As would be expected, energy balancing is involved in this type of problem and the second variable set and held would be the duty of the limiting heat exchanger.

Thus, after a composition-dependent variable and an exchanger duty were set, the calculation would proceed exactly as in Example 7 except that energy balances by Method I of Section III are included in every iteration. As an illustration of this kind of problem, Example 8 was calculated for the same feed and physical setup as in Example 7. The feed to the column was to be stabilized to produce a bottom product whose boiling point at the column pressure of 120 psia was to be 280°F. The limiting duty of the reboiler was used as the second variable set, and the value of Q_R was set at 11,000 Btu per mole of feed. The results of the calculation are the composition and amount of bottom product it is possible to make with these set variables. As in Example 7 the initial assumed amount of bottom product was $\phi = 0.7$. The amount of reboiler vapor was estimated to be equal to one mole per mole of feed.

Table XVI

Results for Example 7: temperatures ($^{\circ}F$) and summations for five iterations

Stage	1		2		3		4		5	
	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$
d	--	1.000	145.1	1.000	146.7	1.000	146.6	1.000	146.6	1.000
8	150	1.168	165.3	1.001	167.8	.998	167.6	1.000	167.6	1.000
7	167	1.263	180.5	1.020	181.5	.994	180.9	.999	180.9	1.000
6	183	1.292	193.8	1.048	191.6	.990	190.9	1.000	190.9	1.000
5	199	1.284	207.7	1.085	201.4	.991	201.0	1.002	201.1	1.000
4	215	.972	230.5	.939	215.8	.994	218.2	.999	218.2	1.000
3	231	1.010	238.0	.993	228.1	.999	229.0	.999	229.1	1.000
2	247	1.019	247.0	1.024	240.5	1.000	240.7	1.000	240.8	1.000
1	263	.999	259.0	1.025	255.5	.999	255.6	1.000	255.6	1.000
b	280	1.000	280.3	1.000	280.0	1.000	280.1	1.000	280.2	1.000

Table XVII

Results for Example 7:
bottom product recovery fraction from five iterations

Component	1	2	3	4	5
C_3H_8	.002	.002	.002	.002	.002
C_4H_{10}	.077	.087	.086	.086	.086
C_5H_{12}	.819	.785	.786	.785	.785
C_6H_{14}	.996	.994	.994	.994	.994
C_7H_{16}	1.000	1.000	1.000	1.000	1.000
C_8H_{18}	1.000	1.000	1.000	1.000	1.000
'b' used	.700	.6124	.6055	.6055	.6055
'b' calculated	.6124	.6055	.6055	.6055	.6055
T_b calculated	280.3	280.0	280.1	280.2	280.2
Φ factor	.7151	1.282	.977	.999	1.000

As mentioned above, the calculational procedure is exactly the same as that of Example 7 up to the point where a corrected temperature gradient has been obtained. New flow gradients are now calculated by the net-energy-flow process of Section III, and for this purpose the $\Delta Q_{ss} = Q_R - bh_b$ would be calculated first, and flows would be calculated starting at the bottom of the column and proceeding to the top stage.

From the results given in Tables XVIII, XIX, and XX it is apparent that convergence is quite rapid and, as in Example 7, the correct value of b is quickly established. Again, for all practical purposes, the degree of convergence of Iteration 3 is sufficient even though the third-place figure of the flows is still in doubt. The enthalpy data and assumptions necessary to use the net-energy-flow process do not justify iteration to determine the flows to one part in a thousand.

Example 8

		Enthalpy constants used			
		Liquid		Vapor	
Feed	Fx_F	k	l	u	w
C_3H_8	0.040	30.90	-15430	21.80	-4830
C_4H_{10}	0.320	41.27	-24672	29.64	-10170
C_5H_{12}	0.285	52.67	-31602	36.79	-12189
C_6H_{18}	0.155	58.60	-35160	42.23	-13533
C_7H_{16}	0.090	66.13	-39678	50.10	-16232
C_8H_{18}	0.110	73.10	-43860	58.25	-19188
	1.000				

Thermal condition of feed: liquid at 200°F

Column pressure: 120 psia

Reflux temperature: bubble point

Enriching stages: 4(not including feed stage)

Stripping stages: 4(including feed stage)

Reboiler temperature: 280°F

Reboiler duty: 11,000 Btu per mole feed

Acceptable bubble-point error: $|\epsilon_2| \leqslant 0.1°F$

A and B constants same as Example 7

Table XVIII

Results from Example 8: temperatures (^{o}F) and summations from five iterations

Stage	1		2		3		4		5	
	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$
d	--	1.000	143.0	1.000	144.8	1.000	144.8	1.000	144.8	1.000
8	150	1.168	160.8	1.036	164.3	.998	164.1	1.000	164.1	1.000
7	167	1.263	175.3	1.054	178.4	.993	177.9	1.000	177.9	1.000
6	183	1.292	189.3	1.038	189.8	.988	188.9	1.001	189.1	1.000
5	199	1.284	204.3	.983	200.0	.991	199.9	1.002	200.0	.999
4	215	.972	227.4	1.102	212.6	.983	217.9	1.004	216.1	.999
3	231	1.010	236.5	1.057	226.0	.994	228.4	1.001	227.9	1.000
2	247	1.019	246.4	1.023	239.4	.999	240.3	1.000	240.1	1.000
1	263	.999	258.9	1.004	255.3	1.000	255.5	1.000	255.5	1.000
b	280	1.000	280.7	1.000	280.0	1.000	280.1	1.000	280.1	1.000

Table XIX

Results for Example 8:
bottom product recovery fraction from five iterations

Component	1	2	3	4	5
C_3H_8	.001	.002	.002	.002	.002
C_4H_{10}	.063	.078	.077	.077	.077
C_5H_{12}	.864	.824	.824	.824	
C_6H_{14}	.998	.996	.996	.996	
C_7H_{16}	.999	1.000	1.000	1.000	1.000
C_8H_{18}	1.000	1.000	1.000	1.000	1.000
'b' used	.700	.621	.614	.614	.614
'b' calculated	.621	.614	.614	.614	.614
T_b calculated	280.7	280.0	280.1	280.1	280.1
Φ factor	.770	1.271	.941	1.018	.994
ΔQ_{ss}	--	9715.	9807.	9805.	9805.
ΔQ_{es}	--	4717.	4808.	4807.	4807.

Table XX

Results for Example 8: flows from five iterations

	1		2		3		4		5	
Stage	L	V	L	V	L	V	L	V	L	V
d	.300	--	.379	--	.386	--	.386	--	.386	--
reflux	.700	--	.687	--	.675	--	.676	--	.676	--
8	.700	1.000	.652	1.066	.648	1.061	.652	1.062	.651	1.062
7	.700	1.000	6.14	1.031	.628	1.034	.631	1.038	.630	1.037
6	.700	1.000	.573	.993	.610	1.013	.608	1.017	.607	1.016
5	.700	1.000	.500	.952	.590	.996	.554	.994	.566	.993
4	1.700	1.000	1.696	.879	1.601	.975	1.650	.940	1.632	.951
3	1.700	1.000	1.709	1.075	1.641	.987	1.664	1.036	1.658	1.018
2	1.700	1.000	1.716	1.088	1.662	1.027	1.672	1.050	1.670	1.044
1	1.700	1.000	1.680	1.095	1.643	1.048	1.646	1.057	1.645	1.056
b	.700	1.000	.621	1.059	.614	1.029	.614	1.032	.614	1.031

Calculations for Complex Columns--Three or More Products

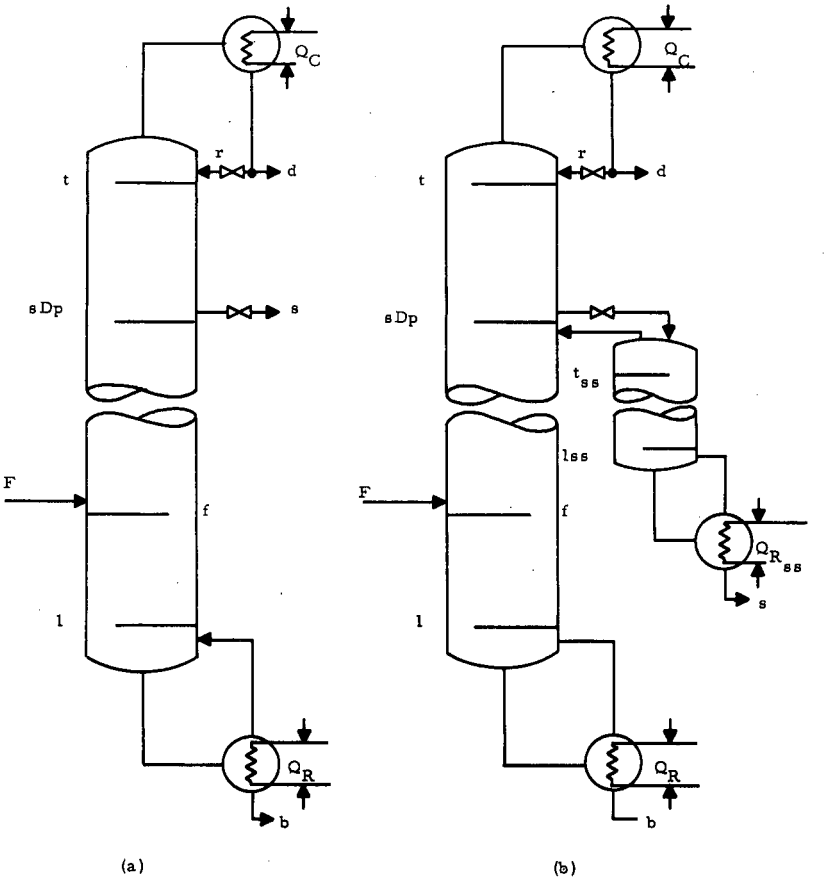
Columns containing more than two main plate sections, or more than one feed, or more than two products frequently occur in fractionation problems. Such problems are readily solvable by a Method I mass-balance calculation or the Edmister procedure. However, these complex columns are approaching an area where it may become feasible to use the Method II mass-balance procedure. As will be seen shortly, the entry or removal of additional streams from a column materially increases the complexity of the Method I mass-balance equations, and when more than two such streams are called for, the notational and programming ease of Method II may well outweigh the speed of convergence of Method I.

Typical columns in which more than one product is removed might be as indicated in Fig. 19. Example 9 is based upon the column of part (b) of this figure. Three products are being removed as indicated; the top and bottom products are being removed from the main column in the usual manner, but in addition a side product is withdrawn at the bottom of a side stripper. The additional plate section allows the setting of more variables than in a simple two-section two-product column. On the basis of the description rule, the number of stages per column section, all variables connected with the feed, and the column pressure are set. In addition the following variables can be set:

Condenser duty
Reboiler duty
Side-stripper reboiler duty
Reflux amount
Side-draw amount

These variables can be replaced with an equivalent list if desired. The simplest set of variables--the variables actually used for Example 9--would be:

Total top-product amount
Side-stripper product amount
Side-stripper reboiler vapor flow
Reflux amount
Reflux temperature



MU-17921

Fig. 19. Typical complex columns.

Having assumed a temperature gradient and all internal column flows, one starts Method I mass-balance calculations. From the bottom stage of the main column to the feed stage, the calculation is carried out as outlined in Section II; the last ratio calculated is $y_{f'}/x_b$. Again, from the top of the column to the side-draw stage, the calculation is as previously outlined. However, the last ratio calculated is for the side-draw stage, Stage 12 in Example 9, and will be x_{12}/x_d. In order to continue the calculation down to the feed plate, the side stripper must in some manner be meshed into the calculational scheme. This is accomplished by starting another series of ratio calculations at the bottom of the side stripper with all stage compositions being referred to x_s, the side-stripper product composition, and the last ratio calculated will be that of the side-draw stage to the bottom product, x_{12}/x_s for Example 9. At this point it becomes convenient to define a new combined top product in order to make mass balances on those stages from just below the side-draw stage to the feed stage. This section of the column is here termed the intermediate section. From Fig. 19b, the first stage in this section is Stage 11 and its mass-balance equation is

$$V_{11}y_{11} = L_{12}x_{12} + dx_d + sx_s = L_{12}x_{12} + Px_P \qquad \text{(IV.2)}$$

The newly defined product P now appears in all equations from Stage 11 to the feed stage. Equation (IV.2) is first put in the form

$$\frac{y_{11}}{x_P} = \frac{L_{12}}{V_{11}}\left(\frac{x_{12}}{x_P} - 1\right) + 1, \qquad \text{(IV.3)}$$

and if the ratio x_{12}/x_P is available, calculation down to the feed plate can proceed in the normal manner. One can readily show

$$\frac{x_{12}}{x_P} = \frac{d + s}{\dfrac{d}{\left(\dfrac{x_{12}}{x_s}\right)} \dfrac{x}{\left(\dfrac{x_{12}}{x_s}\right)}}, \qquad \text{(IV.4)}$$

and therefore all quantities are available to calculate the ratio. Calculations are continued down to the feed stage and the proper matching equation used to obtain the product distribution ratio x_b/x_P. Having obtained the product-distribution ratios for all components, one uses the over-all material balance relation, Eq. (II.28), but its nomenclature is now

$$x_P = \frac{Fx_F}{b\left[\left(\frac{x_b}{x_P}\right)\phi\right] + d} \quad . \tag{IV.5}$$

Thus all x_P and $x_b = x_P\,[x_b/x_P)\phi]$ can be determined under the usual restriction $\sum_i (x_i)_P = 1$. In this type of column a similar relation exists for x_d, and it is

$$x_d = \frac{Px_P}{s\,\frac{x_s}{x_d}\,\phi' + d} \quad . \tag{IV.6}$$

Finally, then, all x_d and $x_s = x_P\,[(x_s/x_d)\phi]$ are determined under the restriction $\sum_i (x_i)_d = 1$. The distribution ratios x_s/x_d are all obtained from the known ratios x_{12}/x_d and x_{12}/x_s. The value of ϕ' is not necessarily equal to the value ϕ of Eq. (IV.5) except at the point of convergence, which is, of course, a unique point at which all $\phi = 1$.

These values of x_d, x_b, x_s allow calculation of compositions at all stages and thus a corrected temperature gradient. Also, internal flows may be corrected at this point by energy-balance Method I if desired. The over-all calculation is now repeated and the iteration is continued until the desired degree of convergence is obtained. The results of Example 9, as presented in Tables XXI and XXII, indicate that such a calculation converges rapidly.

If the bulk separation-column flow-variable combination discussed above is not desired, it is quite possible to specify setting a control-component separation or setting a composition-dependent variable, since for these variables the calculational procedures previously outlined can be used. It is even possible to effectively set and hold more

Table XXI

Results for Example 9:
temperature (^{o}F) and summations from four iterations

Stage	1		2		3		4	
	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$
d	--	1.000	--	1.000	113.0	1.000	113.1	1.000
17	110°F	1.076	117.5	1.008	118.3	1.002	118.5	1.000
16	121	1.119	126.3	1.019	127.6	1.004	127.8	1.001
15	131	1.193	139.8	1.026	140.9	1.005	141.2	1.001
14	142	1.318	156.0	1.021	155.9	1.006	156.1	1.002
13	153	1.490	157.1	.998	168.9	1.006	169.0	1.001
12	164	1.673	183.4	.957	178.5	1.008	178.8	1.001
11	175	1.130	186.6	1.023	188.8	.996	188.2	1.001
10	186	1.148	195.4	1.005	194.7	.994	194.2	1.001
9	196	1.124	202.0	.983	199.7	.995	199.3	1.001
8	207	1.063	207.7	.966	204.4	.998	204.4	1.001
7	218	.987	212.8	.957	209.3	1.004	209.9	1.001
6	229	.960	217.2	1.025	215.1	.987	216.4	.999
5	240	.917	235.5	1.014	233.4	.990	234.3	.998
4	251	.897	250.8	1.005	249.2	.993	249.8	.998
3	262	.891	264.6	1.000	263.8	.995	264.3	.999
2	273	.901	278.1	.999	277.9	.997	278.3	.999
1	284	.923	291.6	1.000	291.8	.999	292.1	1.000
b	295	1.000	306.1	1.000	306.1	1.000	306.2	1.000
5ss	171	.935	185.4	1.020	182.0	1.002	182.0	1.001
4ss	178	.966	188.4	1.014	186.0	1.002	185.8	1.001
3ss	186	.988	192.1	1.010	190.3	1.002	190.0	1.001
2ss	193	1.004	196.1	1.007	194.7	1.002	194.5	1.001
1ss	200	1.010	200.3	1.003	199.2	1.001	199.0	1.000
s	207	1.000	204.9	1.000	204.2	1.000	204.0	1.000

Table XXII

Results for Example 9:
various recovery fractions from four iterations

Component	Top product recovery fraction			
	1	2	3	4
C_3H_8	.951	.945	.944	.943
C_4H_{10}	.037	.042	.042	.043
C_5H_{12}	--	--	--	--
C_6H_{14}	--	--	--	--
	Side draw product recovery fraction			
C_3H_8	.049	.055	.056	.057
C_4H_{10}	.908	.904	.904	.904
C_5H_{12}	.109	.109	.107	.107
C_6H_{14}	.001	.002	.001	.001
	Bottom product recovery fraction			
C_3H_8	--	--	--	--
C_4H_{10}	.055	.055	.054	.053
C_5H_{12}	.891	.891	.893	.893
C_6H_{14}	.999	.998	.999	.999
Φ factor	1.060	1.063	.975	1.000
Φ' factor	.539	1.074	.993	1.000

than one control-component separation. A case in point using the system of Example 9 would be to set and hold the following variables:

Recovery of C_3H_8 in the top product
Purity of C_3H_8 in the top product
Recovery of C_5H_{12} in the bottom product
Purity of C_5H_{12} in the bottom product
Reflux temperature

Example 9

Feed	Fx_F	Equilibrium constant values A	B
C_3H_8	0.30	-2553	5.011
C_4H_{10}	0.40	-3106	5.120
C_5H_{12}	0.20	-3828	5.509
C_6H_{14}	0.10	-4502	5.871
	1.00		

Thermal condition of feed: saturated liquid
Column pressure: 200 psia
Reflux temperature: bubble point
Enriching stages: 5(not including side-draw stage)
Intermediate stages: 6(not including feed stage)
Stripping stages: 6(including feed stage)
Side-stripper stages: 5
Top-product amount: 0.3 mole per mole feed
Reflux amount: 0.4 mole per mole feed
Side-stripper product amount: 1.5 moles per mole feed
Side-stripper reboiler vapor: 0.5 mole per mole feed
Acceptable bubble-point error: $|\epsilon_2| \leqslant 0.1^{\circ}F$

Since stages are numbered from the bottom of the column upward, for this example the feed stage is 6, the side-draw stage is 12, and the top stage in the main column is 17. The designation "ss" is used for side-stripper stages, and thus the top stage in the side stripper becomes 5ss. See Fig. 19b.

Fixing these variables automatically sets all product amounts so that what is required is the calculation of all internal column flows.

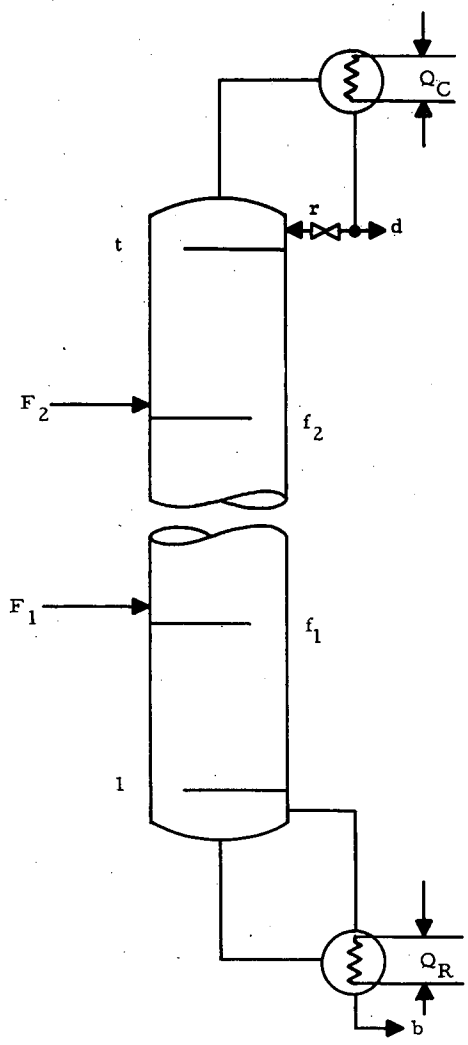
It is apparent that the internal flow that will have the greatest effect on the recovery of C_3H_8 will be the vapor flow in the side stripper. Similarly, that flow which will affect the C_5H_{12} recovery the most will be the liquid flow in the intermediate section. Consequently these two flows can be varied essentially independently and calculations made alternately on the two components to produce the desired recoveries. To hold the recovery and purity of C_4H_{10}, which appears in appreciable quantity in all products, is more difficult but can be done by the same procedure. In general, the techniques previously presented for two-section columns can be used here.

In the generalization of this procedure for more than three products, as for example a crude-oil distillation column with two or more side strippers, Eq. (IV.2), (IV.3), (IV.4), (IV.5), and (IV.6) must be repeated for every side-draw product. For each additional side product another term appears in Eq. (IV.2) and (IV.4) and another ϕ must be evaluated. Although in principle this presents no difficulties, the programming and calculations become rather involved and it is recommended that Method II mass-balance procedures be used rather than Method I. If such a column is further complicated by more than one feed input, the use of Method II mass-balance procedure is strongly recommended.

Calculations for Complex Columns--Two or More Feeds

The simplest column of this type is that illustrated in Fig. 20. Using this figure and applying the description rule, one can see that if the two feeds are completely specified and if in addition the number of stages per section and the column pressure are specified then the three following variables can be set:

Condenser duty
Reboiler duty
Reflux amount



MU-17922

Fig. 20. Typical two-feed distillation column.

The simplest set of variables that can be used would involve replacing the exchanger duties as follows:

Total top-product amount
Reflux temperature
Reflux amount

Example 10 uses this latter set of variables. For each component, the Method I mass-balance procedure is started after assumption of a temperature gradient and all internal column flows. Calculations from the column bottom to the lower feed stage, f_1, yield the ratio (y_{f_1}/x_b). Calculations from the column top to the upper feed stage, f_2, yield the ratio (x_{f_2}/x_d), and below this feed stage it would be desirable to continue calculating down, using some combined product, as was done for three-product columns. Unfortunately, concentration ratios based on a combined product cannot be expressed as a pure number, as they could for the side-product column. The unknown concentration ratio (x_{f_2}/x_d) appears at feed stage f_2 and must be carried along in any calculations continuing down the column.

Consider first the mass balance below Stage f_2. In Example 10 the upper feed stage is number 11 and the lower feed stage is number 2, and in the subsequent equations actual stage numbers are used to simplify the subscriptings. Consider, then, the first mass balance to involve F_2. At Stage 11 this is

$$V_{10}y_{10} = L_{11}x_{11} + dx_d - F_2x_{F_2} , \qquad \text{(IV.7)}$$

which can be written in the following two alternate forms

$$\frac{y_{10}}{x_d} = \frac{L_{11}}{V_{10}}\left(\frac{x_{11}}{x_d}\right) + \frac{V_{10} - L_{11} + F_2}{V_{10}} - \frac{F_2}{V_{10}}\left(\frac{xF_2}{x_d}\right), \qquad \text{(IV.8)}$$

$$\frac{y_{10}}{x_d} = \left[\frac{L_{11}}{V_{10}}\left(\frac{x_{11}}{x_d} - 1\right) + 1\right] + \left[\frac{F_2}{V_{10}}\left(1 - \frac{xF_2}{x_d}\right)\right]. \qquad \text{(VI.9)}$$

Equation (IV.9) is recognized as a combination of a normal Method I mass-balance equation and a carrying term for the unknown

(x_{F_2}/x_d) ratio. To simplify the nomenclature, Eq. (IV.9) is newly defined as

$$\frac{y_{10}}{x_d} = G_{10} + J_{10}\left(1 - \frac{x_{F2}}{x_d}\right), \tag{IV.10}$$

where the G and J functions are calculable numbers. Using the equilibrium relation results in

$$\frac{x_{10}}{x_d} = \frac{G_{10}}{K_{10}} + \frac{J_{10}}{K_{10}}\left(1 - \frac{x_{F2}}{x_d}\right), \tag{IV.11}$$

and this equation in turn can be newly defined as

$$\frac{x_{10}}{x_d} = g_{10} + j_{10}\left(1 - \frac{x_{F2}}{x_d}\right), \tag{IV.12}$$

where the g and j functions are also calculable numbers. The continuation of this procedure yields, for Stage 9,

$$\frac{y_9}{x_d} = \left[\frac{L_{10}}{V_9}(g_{10} - 1) + 1\right] + \left[\frac{L_{10}}{V_9}(j_{10})\frac{F_2}{V_9}\right]\left(1 - \frac{x_{F2}}{x_d}\right) \tag{IV.13}$$

or

$$\frac{y_9}{x_d} = G_9 + J_9\left(1 - \frac{x_{F2}}{x_d}\right), \tag{IV.14}$$

and so on down the column. Thus the generalized expressions for these newly defined functions are

$$G_p = \frac{L_{p+1}}{V_p}(g_{p+1} - 1) + 1, \tag{IV.15}$$

$$J_p = \frac{L_{p+1}}{V_p}(j_{p+1}) + \frac{F_2}{V_p}, \tag{IV.16}$$

$$g_p = \frac{G_p}{K_p}, \tag{IV.17}$$

$$j_p = \frac{J_p}{K_p}, \tag{IV.18}$$

and the complexity of these functions is directly dependent upon the number of stages existing in the intermediate section between the two feed stages. As noted, these functions are numbers and as such are calculated and stored for each stage in the intermediate section. As will be shown, they also appear in the matching relation existing at the lower feed stage, f_1.

In starting the calculation of these functions at the upper feed stage, we have $g_{f_2} = (x_{f_2}/x_d)$ and $j_{f_2} = 0$ for feeds which are all liquid or all vapor. For partially vaporized feeds, the relations are slightly more complex but can be readily derived.

Stage-to-stage calculations in the intermediate section finally yield values of g and j for the stage immediately above the lower feed stage or values of G and J for the lower feed stage. The matching equation on the lower feed tray can be written using these functions. Thus, for all-liquid or all-vapor feeds, the matching equation would be

$$\frac{x_b}{x_d} = \frac{G_{f_1} + J_{f_1}\left(1 - \frac{x_{F2}}{x_d}\right)}{(y_{f_1}/x_b)} . \tag{IV.19}$$

However, the value of x_d must be known before this equation can be used, so that it becomes necessary to set up an over-all mass-balance relation explicit in x_d. Upon substituting Eq. (IV.19) into the over-all mass balance relation, one obtains

$$x_d = \frac{F_1 x_{F_1} + F_2 x_{F_2}}{b\left[\frac{G_{f_1} + J_{f_1}\left(1 - \left(\frac{x_{F2}}{x_d}\right)\right)}{(y_{f_1}/x_b)}\right] + d.} \tag{IV.20}$$

Solving Eq. (IV.20) for x_d yields

$$x_d = \frac{F_1 x_{F_1} + F_2 x_{F_2} + b\left[\dfrac{J_{f_1}\ x_{F_2}}{(y_{f_1}/x_b)}\right]}{b\left[\dfrac{G_{f_1} + J_{f_1}}{(y_{f_1}/x_b)}\right] + d} \quad . \tag{IV.21}$$

All the numbers in Eq. (IV.21) are known, and therefore values of x_d can easily be obtained for each component. Values of x_b can then be calculated by using Eq. (IV.19). However, before one proceeds to calculate the individual stage compositions, it is best to use these values in component-distribution-ratio form for the ϕ-factor calculation such as that described in Section II. The form of the ϕ-factor equation here is

$$x_d = \frac{F_1 x_{F_1} + F_2 x_{F_2}}{b\left(\dfrac{x_b}{x_d}\right) + d} \quad . \tag{IV.22}$$

Thus all x_d and $x_b = x_d\left[\left(\dfrac{x_b}{x_d}\right)\phi\right]$ are determined in the usual way with the restriction $\sum_i (x_i)_d = 1$, and stage compositions can be obtained. Following this the temperature gradient is corrected and the flows, if desired, can be corrected by the Method I energy-balance procedure.

Calculations with two feeds are more difficult than with one feed only in that two numbers must be carried through the intermediate section between the feed plates rather than one number as is normally done. As can be seen from the results of Example 10 in Tables XIII and XXIV, the rate of convergence is quite rapid. All of the variables that can be held successfully in the calculation of ordinary columns can be held also.

It is possible to extend the use of these G, J, g, and j functions to the case of three feeds without unduly complicating the calculation, but this would represent the limit of their usefulness.

Table XXIII

Results for Example 10: temperature (°F) and summations from five iterations

Stage	1		2		3		4		5	
	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$	Temp.	$\sum_i (x_i)_p$
d	--	1.000	171.6	1.000	172.1	1.000	172.2	1.000	172.2	1.000
15	172	1.084	180.6	1.009	181.6	1.000	181.6	1.001	181.6	1.000
14	177	1.141	186.9	1.011	187.6	1.000	187.6	1.001	187.7	1.000
13	182	1.178	192.7	1.002	192.4	1.000	192.4	1.001	192.4	.998
12	187	1.209	198.8	.978	196.2	1.000	196.3	1.001	196.4	.999
11	193	1.235	205.8	.935	199.4	1.004	199.8	1.001	199.9	.999
10	198	1.206	213.7	.932	212.7	1.010	213.5	1.003	213.6	.999
9	203	1.211	222.2	.964	225.5	1.017	226.5	1.004	226.6	.999
8	208	1.259	230.9	1.012	236.0	1.024	236.9	1.004	236.9	.999
7	213	1.355	239.1	1.053	243.6	1.027	244.2	1.004	244.2	1.000
6	218	1.498	246.2	1.077	248.9	1.028	249.2	1.003	249.1	1.000
5	223	1.687	252.0	1.082	252.8	1.025	252.8	1.002	252.6	1.000
4	229	1.908	257.3	1.070	256.3	1.022	256.1	1.001	255.9	1.000
3	234	2.197	263.3	1.043	260.5	1.017	260.2	.999	260.0	1.000
2	240	.760	271.4	1.018	266.1	1.001	266.0	1.001	265.8	1.000
1	245	.832	275.4	1.006	272.9	1.000	272.8	1.000	272.7	1.000
b	250	1.000	283.0	1.000	281.8	1.000	281.7	1.000	281.7	1.000

Table XXIV

Results for Example 10:
top product recovery fractions from five iterations

Component	1	2	3	4	5
C_3H_8	1.000	1.000	1.000	1.000	1.000
C_4H_{10}	.983	.973	.973	.972	.972
C_5H_{12}	.095	.109	.110	.111	.111
C_6H_{14}	.002	.001	.001	.001	.001
Φ factor	.292	1.022	.987	1.003	1.002

For more than three feeds the use of the Method II mass-balance procedure is strongly recommended.

Example 10

Feed	$F_1x_{F_1}$	$F_2x_{F_2}$	Equilibrium-value constants A	B
C_3H_8	--	0.05	-2553	5.299
C_4H_{10}	0.20	0.80	-3106	5.408
C_5H_{12}	0.60	0.10	-3828	5.797
C_6H_{14}	0.40	0.05	-4502	6.159
	1.20	1.00		

Thermal condition of feed: saturated liquid

Column pressure: 150 psia

Reflux temperature: bubble point

Enriching stages: 4(not including upper feed stage)

Intermediate stages: 9(not including lower feed stage)

Stripping stages: 2(including lower feed stage)

Top-product amount: 1.10 moles per 2.20 moles feed

Reflux amount: 1.00 mole per 2.20 moles feed

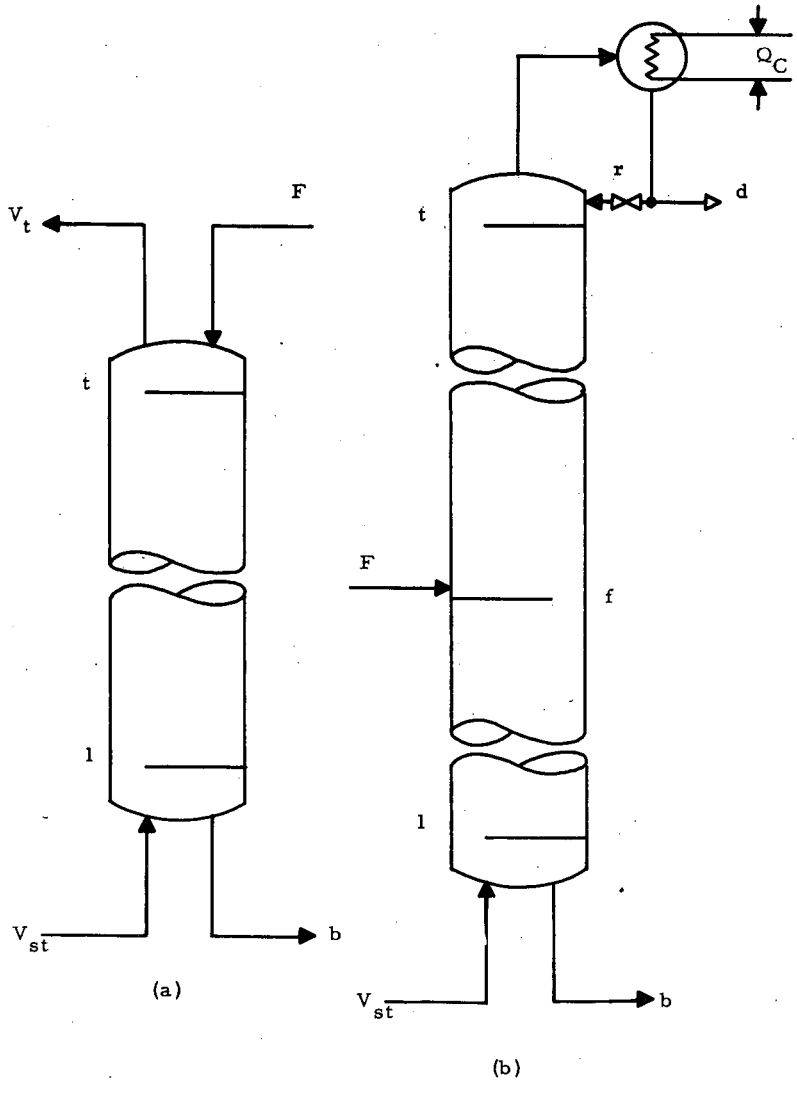
Acceptable bubble-point error: $|\epsilon_2|$ 0.1°F.

V. STRIPPING AND ABSORPTION COLUMNS

The boiling-point range of feed material to the simple and complex columns discussed in the preceding sections has generally been limited to a small value. Fairly large values of the boiling-point range are not ordinarily encountered except when it is desired to accomplish some special-purpose separations. Stripping and absorption fall in this latter category, and for this reason are discussed separately here. The recovery of valuable hydrocarbons from multicomponent gaseous mixtures by absorption with a lean solvent oil followed by steam stripping of the enriched solvent is an important operation in the natural-gasoline and petroleum-refining industries. In the absorption process there is present, then, a component or a mixture--the lean oil--whose boiling point will be appreciably higher than that of those components remaining after absorption. On the other hand, in the stripping process, steam will have a much lower boiling point than those components remaining after stripping. Unfortunately, in the solution of problems based on these systems, the use of digital computers brings to light convergence difficulties not ordinarily encountered in "approximation" methods such as those of Souders and Brown,[5] Horton and Franklin,[12] Sherwood and Pigford,[33] Edmister,[9] and others, where exact solutions are not desired. The methods developed and presented here are convergent and therefore give exact solutions to problems involving absorption and stripping columns.

Simple Stripping Column

In a simple stripping column, such as that shown in Fig. 21, steam entering at the bottom proceeds up the column and becomes saturated with hydrocarbon vapor at the temperature and pressure existing at any given point. Since the operation is adiabatic, the energy required to vaporize hydrocarbon must come from the sensible heat of the liquid stream. Thus, the temperature gradient, instead of rising from top to bottom, drops off, and this is another important feature in which a stripping column differs from an ordinary distillation column.



MU-17923

Fig. 21. Typical stripping columns.

In the mathematical mass-balance analysis to follow, it is always assumed that thermodynamic conditions in the stripping column are such as to preclude the condensation of any steam at any point in the column. At the very outset of any analysis, the presence of steam poses the necessity of deciding how to handle it in the calculational scheme developed.

The first decision is to make a choice from two available treatments, viz., to treat the steam as merely another component in the system or to recognize that steam is not a hydrocarbon and so treat it as a diluent not entering into the general fractionation pattern. In the development to follow, steam has been treated as a diluent and the general computer programs for stripping columns were usually based on this choice. However, as is shown later, the treatment of steam as another component is actually a more desirable approach. Fortunately either approach is acceptable, since the convergence of a problem is unaffected by which approach is used.

The necessity of a second decision exists only if the choice is made to treat steam as a diluent. Since that choice was made in the analysis to follow, a decision must be made as to the basis upon which to define vapor mole fractions. The choice here lies in defining vapor mole fractions on total mass flow or on only the hydrocarbon mass flow. Once again, fortunately, either approach is acceptable from the convergence standpoint, so that the only basis for a decision would be the relative ease of programming for a computer. Both approaches were used here, and it was found that they required approximately the same storage space and the same execution time in a computer. In the equations to follow, then, all vapor flows are total mass flows, that is, they include both hydrocarbons and steam, and consequently all vapor mole fractions are defined on this total mass flow.

The Description Rule for this case indicates that in addition to all the feed variables, column pressure, and number of stages, it is possible to set two other variables. They would be the amount and enthalpy of the stripping steam. When all these variables have been set,

it becomes necessary to predict the top- and bottom-product amounts as well as all internal column flows. Also, a temperature gradient must be predicted. As is shown later, it is not necessary to expend a lot of effort in making an initial prediction, since convergence will result even with an absurd prediction. Predictions based on the "approximate" methods of Horton and Franklin or Souders and Brown may be used if desired, but they will result in a relatively small reduction of computer time needed for a calculation.

It would be desirable to use the Method I mass-balance procedure, and for this purpose, the combined bottom product is defined by

$$P \equiv L_1 - V_{st} = b - V_{st}, \tag{V.1}$$

where V_{st} = moles of steam entering the stripping column per mole feed. The individual-component mass balance becomes

$$Px_P = bx_b - V_{st}y_{st}, \tag{V.2}$$

or, since we have $y_{st} = 0$ for all the hydrocarbon components,

$$\frac{x_b}{x_P} = \frac{x_1}{x_P} = 1 - \frac{V_{st}}{b} \quad . \tag{V.3}$$

Starting from Eq. (V.3) and proceeding up the column in the manner of Method I mass balance, it is possible to obtain the component ratio (y_t/x_P) for each component. This ratio is the actual component-distribution ratio, since y_t is the mole fraction in the top product in this case. The over-all mass balance equation,

$$x_P = \frac{Fx_F}{V_t\left(\frac{y_t}{x_P}\right) + P} \quad , \tag{V.4}$$

makes use of this ratio to obtain all x_P values. The V_t of Eq. (V.4) is in reality d, the top product, for this column, and therefore $y_t = x_d$ and Eq. (V.4) can be written as

$$x_p = \frac{Fx_F}{d\left(\frac{x_d}{x_p}\right) + P} \quad . \tag{V.5}$$

As noted above, this equation holds for all the hydrocarbons, and the x_p values resulting from it are used to resolve all the component ratios into the actual stage compositions. It is now possible to use these individual stage compositions either to move the temperatures while holding the flows constant at their preset values or to move the flows while holding the temperature constant at their present value. This latter possibility exists only because steam is present and is treated as a diluent rather than as another component.

Some further discussion of these two possibilities is in order because of their effect on the energy-balance procedure to be used for stripping columns. As is shown later, the Method I energy-balance procedure fails altogether in this case. Method II energy-balance procedure does work, but if the choice is made to hold the temperatures and move the flows, then the method differs from that of Section III in that the flows, rather than the temperatures, are moved twice. That is, there is a flow-correction calculation made prior to entering the energy balance calculation, and another flow correction is made as a result of the flash calculation within the energy balance.

For the moment, then, let the choice be made to hold the temperatures and move the flows, and let this be done with the view in mind of accomplishing only a mass balance rather than both mass and energy balances. If the assumption is made that the mole fraction ratios of the hydrocarbon portion of the vapor are correct, then it is possible to find how much of this hydrocarbon vapor will be required to saturate the steam at the temperatures set and held. Thus a variation in total vapor flow is implicit, and it is necessary to have an expression for $(V_p)_{NEW}$, the corrected vapor flow at any stage p.

The ratio of mole fractions in the hydrocarbon portion of the vapor is $(y_i/\sum_i y_i)$, where the summation is on the hydrocarbons only.

At the unknown new value of V_p there will be a new value of y_{st} and therefore the new value of (y_i) hydrocarbon can be written

$$[1 - (y_{st})_{NEW}]\ (y_i/\sum_i y_i) = (y_i)_{NEW}, \tag{V.6}$$

and using this expression in the dew-point relation leads to

$$\sum_i \frac{[1 - (y_{st})_{NEW}]\ (y_i/\sum_i y_i)}{K_i} = \sum_i x_i = 1 \tag{V.7}$$

or

$$(y_{st})_{NEW} = 1 - \frac{\sum_i y_i}{\sum_i y_i/K_i}, \tag{V.8}$$

where i in Eqs. (V.6), (V.7), and (V.8) runs across the hydrocarbon only. Dew points are used here because the vapor-phase compositions give a more sensitive temperature indication than do the liquid-phase compositions. Now $\sum_i y_i$ can be replaced by its equivalent expression,

$$\sum_i y_i = \sum_i (y_i)_{TOTAL} - (y_{st})_{OLD}, \tag{V.9}$$

where i in $(\sum_i y_i)_{TOTAL}$ includes the steam. Substituting Eq. (V.9) into Eq. (V.8) gives the expression

$$(y_{st})_{NEW} = 1 - \frac{(\sum_i y_i)_{TOTAL} - (y_{st})_{OLD}}{\sum_i y_i/K_i} \tag{V.10}$$

At any given iteration in a calculation, all quantities necessary to evaluate either Eq. (V.8) or (V.10) are available and $(y_{st})_{NEW}$ is then used to calculate $(V_p)_{NEW}$ as indicated

$$(V_p)_{NEW} = \frac{V_{st}}{(y_{st})_{NEW}}\ . \tag{V.11}$$

Following the calculation of all $(V_p)_{NEW}$, the $(L_p)_{NEW}$ are obtained by a simple flow balance, and the calculation returns to the start of the mass-balance equations, and iterations are carried out to the desired degree of convergence. When convergence is reached, there results a set of flows and compositions for every stage, and they are correct for the temperature gradient assumed and held.

This procedure is illustrated in Example 11, in which a four-stage column similar to that illustrated in Fig. 21 is used. It is desired to strip light hydrocarbons out of a feed stream consisting essentially of C_9H_{20}. This is to be done with 0.1 mole of steam per mole feed. A Horton and Franklin approximate calculation was used to set the initial temperature and flow gradients for the results shown in Table XXV. The flow gradient was next set at an absurd condition and the example rerun, with the results shown in Table XXVI. It is apparent in both cases that the procedure is rapidly convergent.

Example 11

	Equilibrium-value constants		
Feed	Fx_F	A	B
C_3H_8	0.0121	-2747.	7.143
C_4H_{10}	0.0236	-3302.	7.189
C_5H_{12}	0.0166	-4879.	8.920
C_6H_{14}	0.0149	-4974.	8.259
C_9H_{20}	0.9328	-7737	10.592
	1.0000		

Steam flow: 0.1 mole per mole feed

Steam temperature: 270°F

Column stages: 4

Column pressure: 30 psia

Table XXV

Results for Example 11:
flows and summations for four iterations with a calculated initial flow gradient

Stage	1			2			3			4		
	V	L	$\sum_i (y_i)_p$	V	L	$\sum_i (y_i)_p$	V	L	$\sum_i (y_i)_p$	V	L	$\sum_i (y_i)_p$
4	.23	.96	.965	.214	.955	1.011	.219	.955	.996	.217	.955	1.001
3	.19	.93	.937	.169	.938	1.015	.173	.936	.996	.172	.937	1.001
2	.16	.90	.974	.152	.927	1.011	.155	.923	.997	.154	.925	1.001
1	.13	.87	1.061	.141	.886	1.005	.142	.881	.999	.141	.883	1.000

Table XXVI

Results for Example 11:
flows and summations for four iterations with no initial flow gradient

Stage	1			2			3			4		
	V	L	$\sum_i (y_i)_p$	V	L	$\sum_i (y_i)_p$	V	L	$\sum_i (y_i)_p$	V	L	$\sum_i (y_i)_p$
4	.25	1.00	.913	.213	.954	1.012	.218	.955	.997	.217	.955	1.001
3	.25	1.00	.780	.167	.937	1.024	.174	.937	.996	.172	.937	1.001
2	.25	1.00	.713	.150	.925	1.023	.155	.923	.997	.153	.924	1.000
1	.25	.85	.683	.138	.887	1.018	.142	.882	.998	.141	.883	1.000

Initial Assumptions

Stage	Temperature gradient	First flow gradient		Second flow gradient	
		Liquid	Vapor	Liquid	Vapor
4	280°F	0.96	0.23	1.00	0.25
3	254	0.93	0.19	1.00	0.25
2	250	0.90	0.16	1.00	0.25
1	245	0.87	0.13	0.85	0.25

The component-recovery fractions in the bottom product are as listed:

Component	Bottom-product recovery fraction
C_3H_8	.005
C_4H_{10}	.064
C_5H_{12}	.265
C_6H_{14}	.593
C_9H_{20}	.931

Whether or not the initial gradients were established by approximation methods, it is very desirable to run energy-balance calculations on stripping columns, since flow variation could have an appreciably effect on the separation. For energy-balance purposes Method II of Section III was used. It will be recalled that this method corrects both the temperature and the flows, so that in a typical iteration the sequence of calculations might be

(a) Method I mass-balance calculation modified for strippers.

(b) Flow-correction calculation as just outlined.

(c) Method II energy-balance calcuation to correct both flow and temperature.

The pattern followed in a calculation is arbitrary. Steps 1 and 2 above might be repeated a number of times before Step 3 was done, and this was tried. A pattern involving Steps 1, 2, and 3 in sequence was also tried. The best pattern to use in any given case is a matter of judgment and experience, but it has been found that in most cases a Step 1, 2, 3 sequential pattern will converge just about as rapidly as any other pattern.

The feed and column of Example 11 were used for a complete calculation, Example 12, using both mass and heat balances in a sequential pattern. The schematic diagram of the computer program to accomplish this is shown in Fig. 22, where path (a) is used. It should be noted that the normalizing of the vapor mole fractions is done after Step 2 flow correction and before Step 3 energy balance. The purpose of this is to use $(y_{st})_{NEW}$ in the normalization process. The results of Example 12 are given in Tables XXVII, XXVIII, and XIX as well as in Fig. 23 and 24. Once again the rate of convergence is good, since the results of Iteration 4 or 5 are sufficient for all practical purposes even though the initial flow and temperature gradients were pure "guesses."

Example 12

Feed and column variables as in Example 11; also A and B constants.

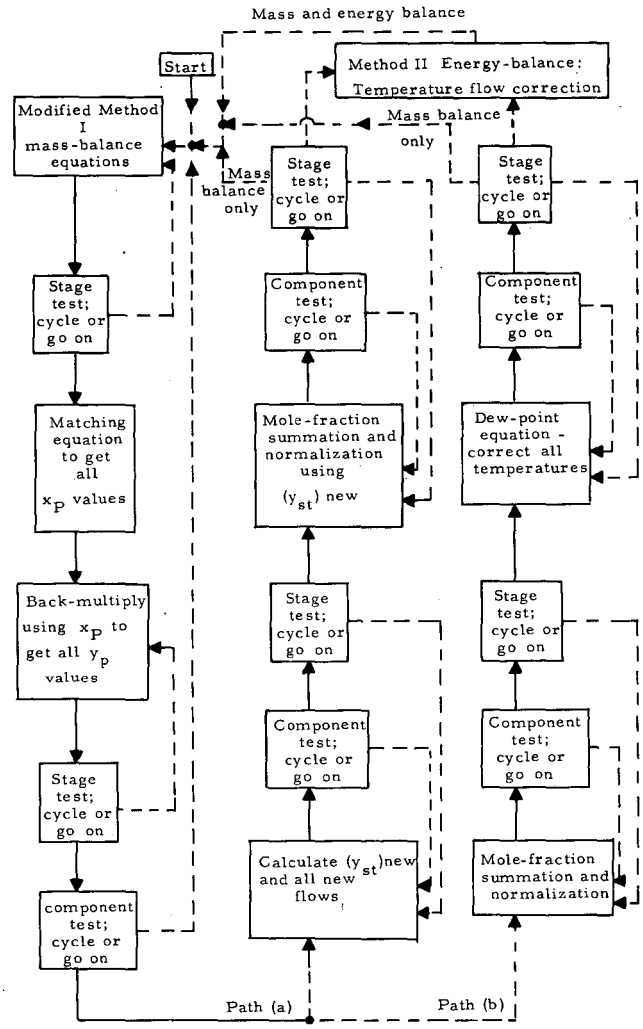
Enthalpy-value constants

(Referred to liquid at 200°F)

Feed	k	l	u	w
C_3H_8	31.75	-19050	22.04	-7712
C_4H_{10}	41.27	-24762	29.64	-10170
C_5H_{12}	52.67	-31602	36.79	-12189
C_6H_{14}	58.60	-35160	42.23	-13533
C_9H_{20}	76.94	-46164	62.84	-19879
Steam	--	--	9.2	-5220

Initial assumptions

Stage	Temperature Gradient	Flow gradients Liquid	Vapor
4	270°F	0.20	1.00
3	270	0.20	1.00
2	270	0.20	1.00
1	270	0.20	0.90



MU-17964

Fig. 22. Schematic computer program for stripper.

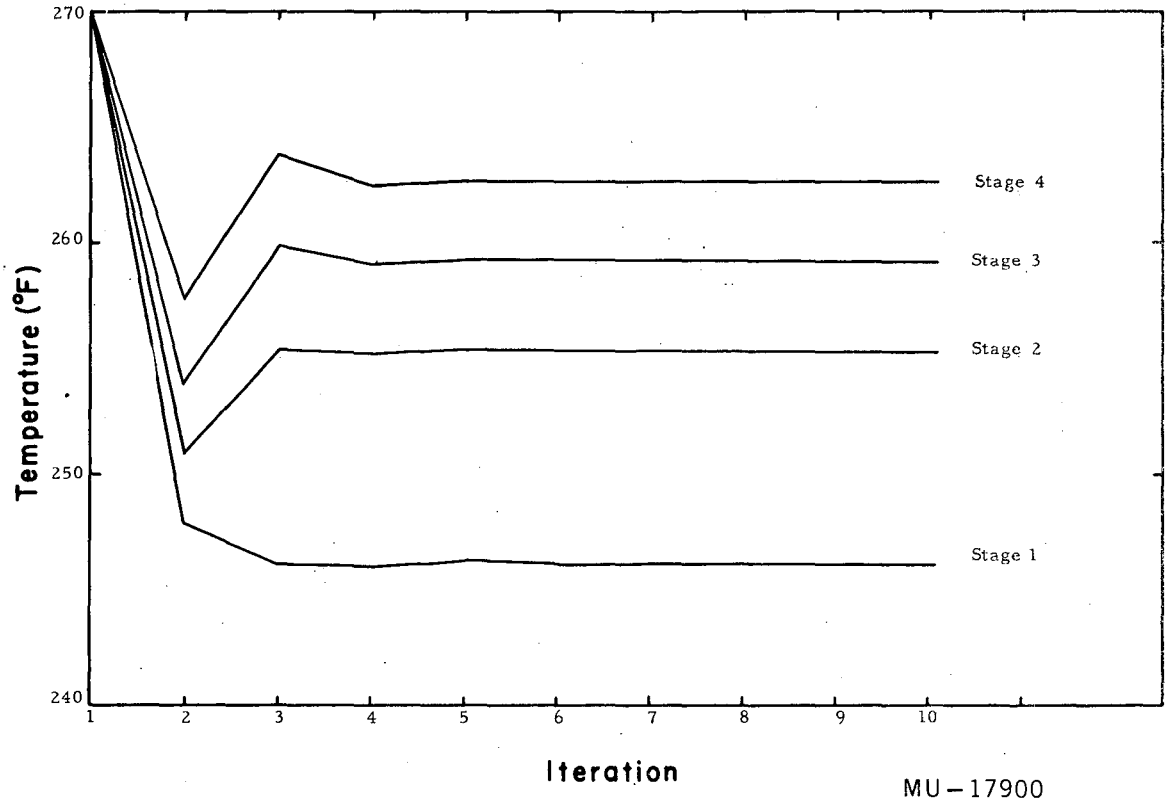
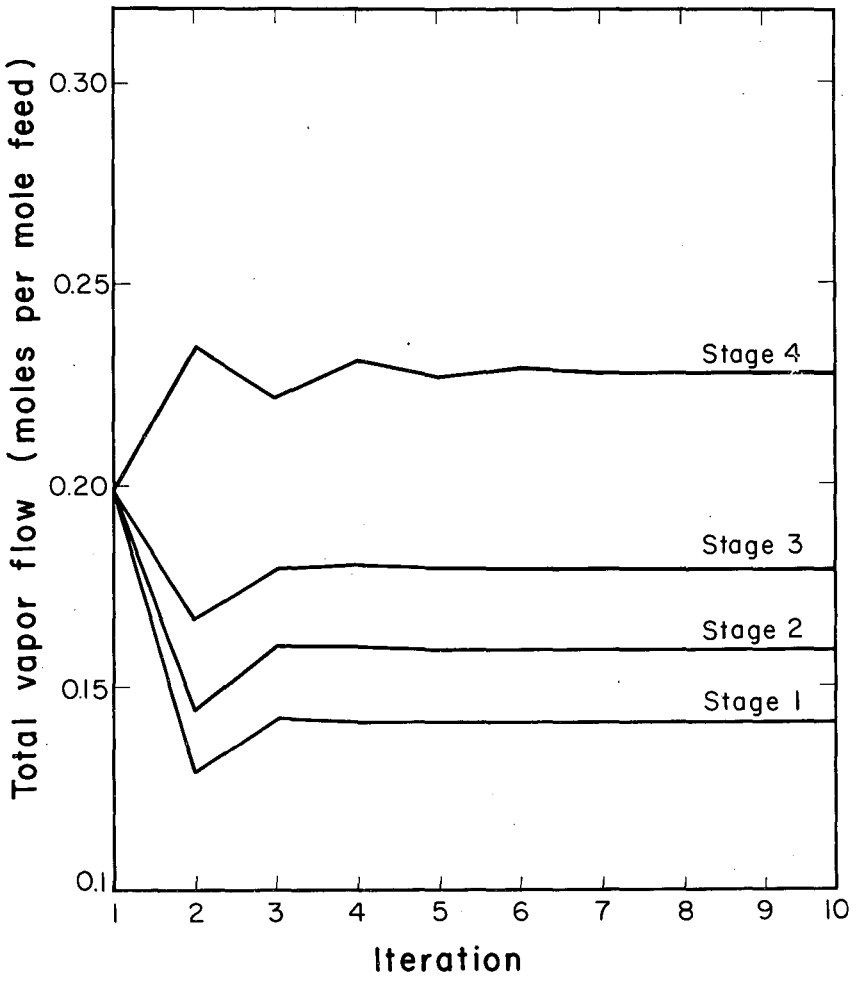


Fig. 23. Results for Example 12: temperature vs. iteration for all stages.



MU-17924

Fig. 24. Results for Example 12: vapor flow vs. iteration for all stages.

Table XXVII

Results for Example 12: temperatures (^{o}F) and summations from various iterations

Stage	1		2		3		4		5		10	
	Temp.	$\sum_i (y_i)_p$	Temp.	$\sum_i (y_i)_p$	Temp.	$\sum_i (y_i)_p$	Temp.	$\sum_i (y_i)_p$	Temp.	$\sum_i (y_i)_p$	Temp.	$\sum_i (y_i)_p$
4	270°F	1.134	257.5	.953	263.8	1.023	262.5	.991	262.8	1.004	262.7	1.000
3	270	1.011	253.9	1.017	259.9	1.005	259.1	.996	259.3	1.002	259.2	1.000
2	270	.950	250.9	1.058	255.4	.997	255.2	.998	255.4	1.001	255.3	1.000
1	270	.916	247.9	1.084	246.1	.995	246.0	.999	246.3	1.001	246.2	1.000

Table XXVIII

Results for Example 12: vapor flow and energy unbalance from various iterations

Stage	1		2		3		4		5		10	
	V	Q	V	Q	V	Q	V	Q	V	Q	V	Q
4	.200	-707	.235	+495	.222	-131	.231	+36.0	.227	-12.3	.228	-.10
3	.200	-250	.166	+83.5	.179	+.70	.180	-7.0	.179	+.90	.179	+.00
2	.200	-151	.144	+75.0	.160	+32.0	.160	-.10	.159	+2.3	.159	+.00
1	.200	-1197	.129	-456	.142	+6.80	.141	+7.7	.141	-2.5	.141	+.00
ΣQ	--	-2305	--	+197	--	-91.6	--	+36.6	--	-18.0	--	+.20

Table XXIX

Results for Example 12:
top product recovery fraction from various iterations

Component	1	2	3	4	5	6
C_3H_8	.998	.995	.996	.996	.996	.996
C_4H_{10}	.965	.940	.947	.950	.949	.949
C_5H_{12}	.816	.749	.768	.775	.771	.772
C_6H_{14}	.451	.429	.438	.447	.442	.444
C_9H_{20}	.077	.076	.079	.080	.079	.080

As mentioned previously, it is possible to calculate this type of problem by holding the flows and moving the temperatures by a dew-point calculation before proceeding with an energy balance. This approach assumes that y_{st} is correct and finds that value of the temperature for which

$$\sum_i \frac{(y_i)\ \dfrac{1-(y_{st})}{\sum_i (y_i)}}{K_i} = \sum_i x_i = 1.0, \qquad \text{(V.12)}$$

where i runs across hydrocarbons only and where

$$(y_i)\ \frac{1-(y_{st})}{\sum_i (y_i)} = (y_i)_{\text{NORMALIZED}}. \qquad \text{(V.13)}$$

Having found that value of the temperature which satisfies Eq. (V.12), one carries out an energy balance, and there results another temperature change as well as a flow change. Path (b) of Fig. 22 shows the computer program for this approach, and Example 13 was done by using dew points and mass balance only for the same feed and physical column as that of Example 12. The results of Example 13 are shown in Table XXX from which it can be seen that convergence is fairly rapid.

Table XXX

Results for Example 13: temperatures (^{o}F) and summations from eight iterations

	Stage summations $\sum_i (y_i)_p$															
	1		2		3		4		5		6		7		8	
Stage	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ
1	1.267	1.134	.992	.995	.999	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
2	1.082	1.011	.990	1.002	.998	1.004	1.000	1.002	1.000	1.001	1.000	1.000	1.000	1.000	1.000	1.000
3	.992	.950	.994	1.017	.998	1.009	1.000	1.004	1.000	1.002	1.000	1.001	1.000	1.000	1.000	1.000
4	.941	.916	1.008	1.049	1.000	1.019	1.000	1.008	1.000	1.003	1.000	1.001	1.000	1.001	1.000	1.000
Stage	Stage temperatures															
1	270°F	270°F	277.4	279.1	278.3	279.1	278.5	278.8	278.5	278.6	278.5	278.5	278.5	278.5	278.5	278.5
2	270	270	270.2	278.6	271.3	272.8	271.5	272.1	271.5	271.8	271.5	271.6	271.5	271.6	271.5	271.6
3	270	270	261.1	266.6	261.6	264.1	261.9	262.9	261.9	262.4	261.9	262.1	261.9	262.0	261.9	262.0
4	270	270	246.4	254.8	245.5	249.3	245.5	247.0	245.4	246.1	245.4	245.7	245.4	245.5	245.4	245.5
Φ factor	.652	--	.985	--	.999	--	1.000	--	1.000	--	1.000	--	1.000	--	1.000	--

Example 13

Feed and column variables, A and B constants, and all initial assumptions are the same as those of Example 12.

Allowable dew-point error: $|\epsilon_2| \leqslant 0.1^{\circ}F$.

The use of the Φ factor in absorber and stripper calculations will be discussed shortly, but the factor does speed up the convergence in Example 13. However, the temperature gradient obtained is completely wrong when compared with that from a mass and energy balance, therefore this calculation is done next.

A complete calculation using the sequence

(a) Method I mass-balance calculation modified for strippers,

(b) Temperature correction by dew-point procedure,

(c) Method II energy-balance calculation to correct both flow and temperature,

is illustrated in Example 14. In the first attempt to solve this example no damping factor was used, but the results of the very first iteration produced so much movement in the vapor flow that a value of (y_{st}) greater than 1 resulted. This situation is physically impossible, as the upper limit on (y_{st}) is 1 for pure steam. The results reported in Tables XXXI, XXXII, and XXXIII and Figs. 25 and 26 are based upon a damping factor of 1/2 applied to the temperature correction as outlined in Section III. As can be seen from the results, there has been very little slowing down of the rate of convergence as a result of carrying out energy balances, since, for all practical purposes, the results of Iteration 6 or 7 would be acceptable.

Example 14

Feed and column variables, A and B constants, all initial assumptions, and the enthalpy-value constants are the same as those of Example 12.

Allowable dew-point error: $|\epsilon_2| \leqslant 0.1^{\circ}F$,

Damping factor: 1/2.

Table XXXI

Results for Example 14: summations from nine iterations

	1		2		3		4		5		6		7		8		9	
Stage	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ
4	1.267	1.134	.981	1.039	.994	1.011	.997	1.002	.999	.999	.999	.999	1.000	.999	1.000	1.000	1.000	1.000
3	1.082	1.011	.983	1.039	.984	.998	.992	.993	.997	.995	.999	.997	.999	.999	1.000	.999	1.000	1.000
2	.992	.950	1.040	1.075	.995	1.001	.995	.994	.998	.996	.999	.998	1.000	.999	1.000	1.000	1.000	1.000
1	.941	.916	1.058	1.068	.999	1.000	.997	.996	.999	.998	.999	.999	1.000	1.000	1.000	1.000	1.000	1.000

Table XXXII

Results for Example 14: energy unbalances (Q_Φ) and their algebraic sums from nine iterations

	1		2		3		4		5		6		7		8		9	
Stage	Φ	No Φ	Σ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ
4	+2025	+1338	+1019	+1223	+469	+702	+224	+373	+110	+187	+531.1	+89.9	+26.3	+41.7	+12.6	+18.9	+5.8	+8.4
3	-926	-744	-277	-77.1	-244	-129	-170	-128	-103	-95.7	-57.9	-60.3	-31.4	-35.2	-16.5	-19.4	-8.5	-10.2
2	-547	-422	+448	+361	+334	+257	+189	+143	+101	+78.5	+52.7	+43.5	+27.3	+24.0	+14.1	+13.2	+7.3	+7.2
1	-2109	-2009	-1029	-1267	-461	-629	-214	-300	-100	-139	-47.6	-63.7	-22.9	-29.4	-11.1	-13.7	-5.4	-6.5
Σ Q	-1558	-1836	+161	+241	+97.7	+201	+30.4	+88.5	+7.4	+32.3	+0.3	+9.3	-0.7	+1.3	-0.9	-1.0	-0.7	-1.2

Table XXXIII

Results for Example 14: top product recovery fractions from various iterations

	Without Φ factor							With Φ factor								
Component	1	2	3	4	5	6	12	1	2	3	4	5	6	7	8	9
C_3H_8	.777	.986	1.015	1.013	1.007	1.002	.996	1.031	1.050	1.021	1.007	1.002	.998	.997	.997	.997
C_4H_{10}	.751	.919	.953	.958	.957	.954	.949	.980	.984	.964	.956	.953	.951	.950	.950	.950
C_5H_{12}	.635	.690	.737	.761	.770	.772	.772	.767	.746	.761	.769	.772	.772	.773	.773	.773
C_6H_{14}	.351	.360	.401	.425	.436	.441	.444	.361	.396	.423	.436	.440	.442	.444	.444	.444
C_9H_{20}	.060	.058	.067	.073	.077	.078	.080	.053	.063	.072	.076	.078	.079	.079	.079	.079
Φ factor	--	--	--	--	--	--	--	.652	1.039	1.012	1.005	1.003	1.002	1.001	1.000	1.000

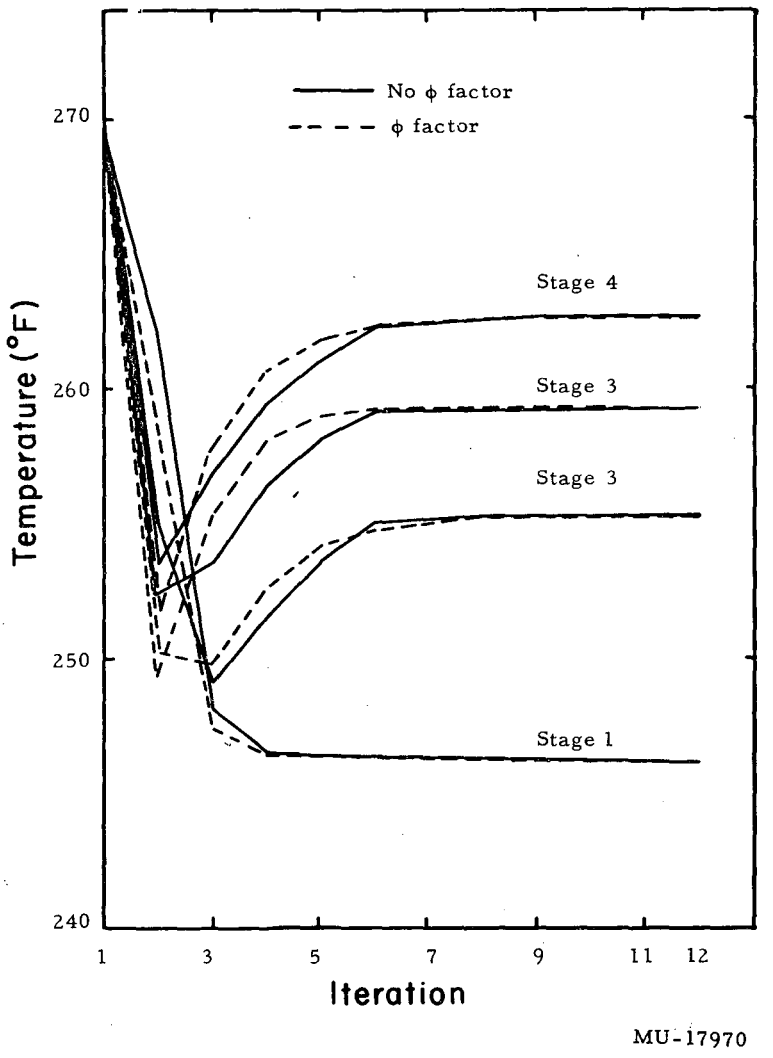


Fig. 25. Results for Example 14: temperature vs. iteration for all stages.
—— no Φ factor.
--- Φ factor used.

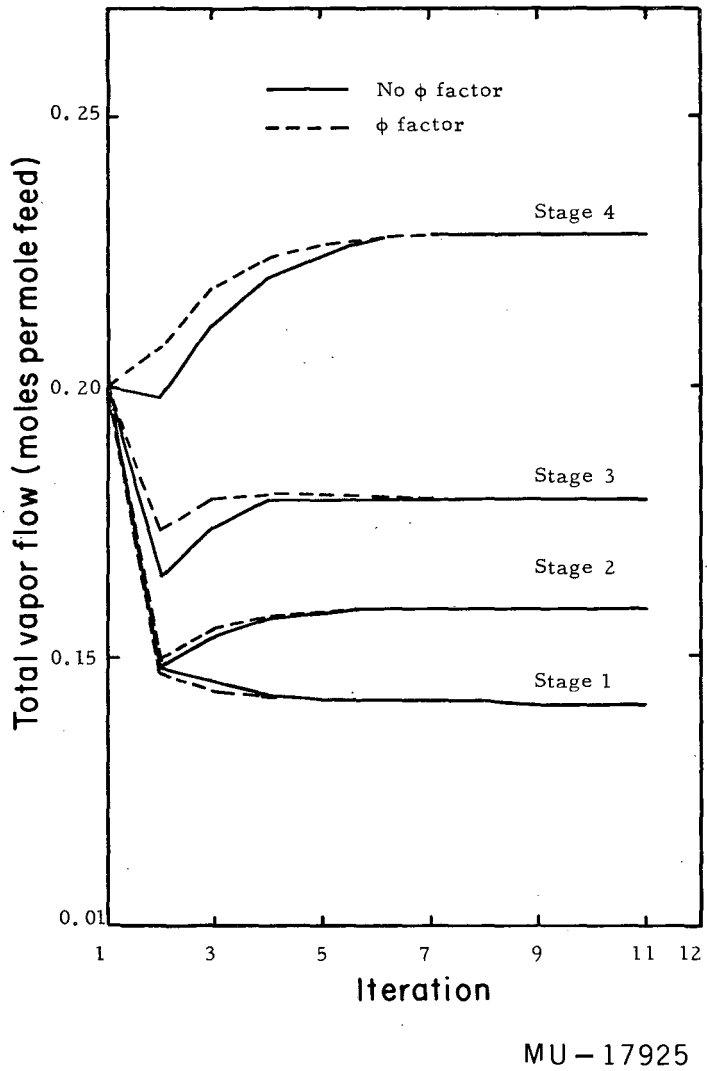
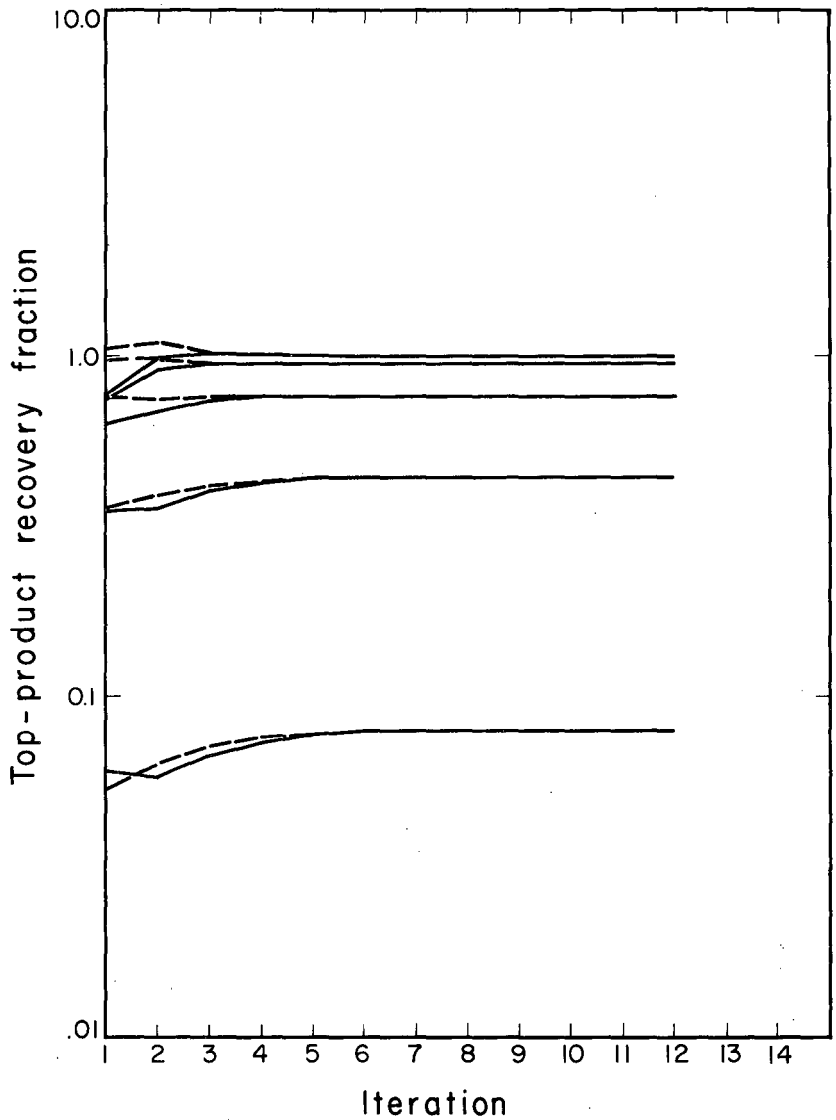


Fig. 26. Results for Example 14: total vapor flow vs. iteration for all stages.
—— no Φ factor.
--- Φ factor used.



MU-17926

Fig. 27. Results for Example 14: top-product recovery fraction vs. iteration for all stages.
—— no Φ factor.
--- Φ factor used.

The results of Examples 12 and 14 bring out a rather striking difference in the rate of relaxation of the energy unbalances, Q_p, on each stage. The double correction of the flows quickly relaxes all Q_p to zero without ever generating an impossible condition and without requiring a damping factor. The use of a damping factor when doing double corrections of the temperatures appreciably slows down the rate of convergence but assures that no impossible physical condition arises. As was pointed out for the Φ factor, any time a solution alternates about its correct value, convergence will be reached in a minimum number of iterations, and this is the case for the double flow correction. However, the asymptotic behavior of the double temperature correction is equally capable of giving an exact answer but at a cost of additional iterations. Unfortunately, the double-flow-correction approach is possible only when a component, such as steam, can be treated as a diluent. As is shown later, this approach breaks down when a more complex column is involved and the liquid flow is very small in one section of the column.

It is also of interest to note the following results from Example 12, as these values reflect the predominantly heat-capacitive nature of the system when it absorbs energy via the flash equation.

	(C_L/C_V) Ratio		C_V		$(\Delta V/\Delta T)$	
Stage	Initial	Final	Initial	Final	Initial	Final
4	1.511	.968	44.9	61.7	.0020	.0027
3	1.111	1.484	57.5	42.3	.0025	.0018
2	.910	1.927	66.9	33.2	.0028	.0014
1	.674	2.744	74.9	23.1	.0030	.00098

These values should be compared to those of Table XIII, which show the same results for a simple distillation column with a relatively narrow-boiling-range feed.

The use of the Φ factor for stripping and absorption calculations is somewhat controversial. If it is used when steam is treated as a diluent and flow corrections are made with temperature held, as in Examples 11 and 12, it would be expected to be of little use because of the inherently rapid convergence of this approach. In actual use,

the Φ values diverged rather than converged. When used where flows were held and temperatures varied, the Φ factor would be useful if the temperatures were predominantly low or high. Table XXX for Example 13 shows exactly this behavior, and the use of Φ quickly corrected the temperature gradient except for an absurd set of flows with a resultant completely wrong temperature gradient compared with the final values when energy balances are done. Since the simplest and most general method of approach to problems of this type is to make a pure "guess" of the flow and temperature gradients, it is always necessary to do both mass and energy balances to get the correct answer. The effectiveness of the Φ factor is greatly diminished when both balances are run, as in Example 14. A damping factor was necessary to obtain a convergent solution, and approximately eight iterations were needed to establish the flows to the third decimal place. The Φ factor did cause a closer approach to the convergence values in the early iterations, but its effect quickly died out and was for all practical purposes nonexistent by the 5th iteration.

When the Φ factor is used, Eq. (V.5) takes the form

$$x_P = \frac{Fx_F}{d\left[\frac{x_d}{x_P}\,\Phi\right] + P}, \qquad \text{(V.14)}$$

and care must be exercised in the two-point extrapolation process to take account of $\sum_i (x_i)_P \neq 1$ but $[1 + (x_P)_{st}]$. The range of values of component distribution ratios is markedly different from those for simple distillation columns, as the following shows.

$\left(\frac{x_d}{x_P}\right)$ Typical values from Example 14		$\left(\frac{x_d}{x_b}\right)$ Typical values from Example 1	
C_3H_8	1757.	C_3H_8	.00118
C_4H_{10}	111.	C_4H_{10}	.0775
C_5H_{12}	17.7	C_5H_{12}	12.8
C_6H_{14}	3.29	C_6H_{14}	1342.
C_9H_{20}	.333		

In Fig. 9, the $f(0)$ and $f(\infty)$ limits would shift upward for strippers and that for $f(\infty)$ would approach the $f(\Phi) = 0$ axis if d were quite small, as it is here. While this limit shifting in no way affects the ability of the two-point extrapolation process to find the Φ roots, it is suggested that the shifting of the component distribution ratios using these Φ values loses a large part of its effectiveness when movements in flow gradients are included in a calculation, as they must be for strippers and absorbers.

Since it is necessary to use Method II energy balances with damping factors, and because there is some doubt of the effectiveness of the Φ factor in stripper calculations, subsequent examples for refluxed strippers and for refluxed strippers with side strippers do not include the Φ factor.

Method I energy balance, the net-energy-flow (ΔQ) method, was tried for the simple stripper problem, but proved incapable of producing any solution, let alone a convergent solution. When ΔQ is defined for a stripper, it may be done for any stage, but the most likely stage to use would be the top stage, where

$$\Delta Q_{STRIPPER} = V_t H_t - F h_F \tag{V.15}$$

and Fh_F is a relatively large fixed quantity. The mass balance and equilibrium relations give the information necessary to obtain H_t, so that V_t must be obtained from another relation, in this case the overall mass-energy-balance relation, which gives

$$V_t = d = \frac{F(h_F - h_b) + V_{st}\,(H_{st} - h_b)}{(H_t - h_b)} . \tag{V.16}$$

Again, the mass-balance and equilibrium relations make it possible to determine h_b, so that all quantities needed are known, and therefore V_t is known. Since any vaporization in an adiabatic stripper must take place at the expense of sensible heat of the fluid flowing, the temperature must drop from top to bottom of the column. Thus, the term $(H_t - h_b)$ will always be positive and the term $(H_{st} - h_b)$ will always

be negative, so that the term $(h_F - h_b)$ must always be positive and such that we have $V_t > (V_{st})_t$ to maintain physically plausible conditions. Since the liquid flowing is essentially pure heavy component, $h_F > h_b$ can be true only for $T_F > T_b$, and therefore temperature movement becomes very important. Unfortunately, there is a high degree of temperature sensitivity with steam as a diluent and only small hydrocarbon vapor flows, so that this effect can and does reflect in large variations in V_t and hence in ΔQ. Also, since all internal flows must be calculated from this ΔQ, they in turn will reflect large variations in V_t. It is impossible to set and hold V_t=d as a variable if complete specification of the stripping steam is assumed. Thus, internal flows are based upon a quantity which is itself subject to large variations, with the result that a convergent calculation is highly improbable. In Example 15, the ΔQ approach was tried on the feed and column of Example 11, and the starting gradients were purposely obtained by an approximation to see if the ΔQ method could converge given excellent starting conditions. The results shown in Tables XXXIV and XXXV clearly indicate the instability of the ΔQ calculation for a pure stripper. The approach was tried on refluxed strippers, and on refluxed strippers with side strippers, and equally poor results were obtained. Historically speaking, it was the failure of the ΔQ approach to give convergent solutions which led to the development of Method II energy balance, and this method was specifically developed for strippers and absorbers, and application to other types of columns was a secondary consideration.

Table XXXIV

Results for Example 5:
temperatures (°F) and summations from four iterations

Stage	1		2		3		4		Correct value*
	Temp.	$\sum_i (y_i)_p$	Temp.	$\sum_i (y_i)_p$	Temp.	$\sum_i (y_i)_p$	Temp.	$\sum_i (y_i)_p$	
4	258°F	.965	261.5	.777	283.8	.358	341.9	--	262.7°F
3	254	.938	262.4	.719	284.7	.330	333.9	--	259.2
2	250	.974	255.0	.373	298.4	.303	338.2	--	255.3
1	245	1.061	233.1	.262	324.6	.323	346.9	--	246.2

*Correct values from converged solution of Example 12

Table XXXV

Results for Example 15: vapor flows from four iterations showing failure of Method I energy balance

Stage	1	2	3	4	Correct value*
4	.230	.355	-1.227	-.372	.228
3	.190	.272	-1.157	-.088	.179
2	.160	.462	-.734	-.125	.159
1	.130	3.051	-.328	-.082	.141
ΔQ	--	-1831	-16931	-11289	-3020

*Correct values from converged solution of Example 12.

Example 15

All variables and constants as in Example 12, but with the following initial assumptions:

Stage	Temperature gradient	Flow gradients V	Flow gradients L
4	258°F	.230	.96
3	254	.190	.93
2	250	.160	.90
1	245	.130	.87

Refluxed Stripper

A typical refluxed stripping column is that shown in Fig. 21b, for which a total condenser is used. Two examples are given to illustrate the calculation for this case, the first uses a total condenser and the second uses a partial condenser.

As was pointed out previously, it is quite possible to treat the steam as just another component and so let it enter into the general fractionation scheme. This approach obviates the necessity of any special handling in the mass-balance equations or the dew- (or bubble-) point equation. To accomplish this, steam is merely assigned some arbitrarily high equilibrium value which assures that its concentration in the liquid is always some very small number. Example 16 illustrates

this approach together with the Method of Successive Flashes for mass balancing. The column used is that of Fig. 21b, and the feed was 70% vaporized. The Description Rule for this case states that in addition to all feed variables, stages per section, and column pressure, these variables also can be set:

Condenser duty

Reflux amount

Stripping-steam amount

Stripping-steam enthalpy

For Example 16, condenser duty is replaced by top-product amount, d, but all other variables indicated are set. Since only mass balancing is to be done, the stripping-section flows are estimated by an approximate method--that of Horton and Franklin, for this case--and the enriching-section flows are set by assuming constant molal overflow. The stages all were assumed to initially contain liquid of feed composition at its bubble point. Also, bubble points were used for correcting the temperatures. The results given in Table XXXVI and Figs. 28 and 29 show that convergence is fairly slow and that practical values of the separation are available somewhere near the 50th iteration.

Example 16

	Equilibrium-value constants				
Feed	$L_F x_{LF}$	$V_F y_{VF}$	A	B	
C_5H_{12}	0.0077	0.0923	-4002	7.833	(Enthalpy-value constants same as those of Example 5)
C_6H_{14}	0.0309	0.1691	-4997	8.665	
C_7H_{16}	0.0864	0.2136	-5595	8.847	
C_8H_{18}	0.1750	0.2250	-6300	9.261	
	0.3000	0.7000			

Thermal condition of feed: 70% vapor at 220°F (from feed flash)

Column pressure: 1 atmosphere

Enriching stages: 4(including vapor feed stage but not liquid feed stage)

Stripping stages: 5(including liquid feed stage)

Top product amount: 0.36 mole per mole feed

Reflux amount: 0.50 mole per mole feed

Table XXXVI

Results for Example 16: mass balance error array at 81st iteration

Component	Stage 0	1	2	3	4	5	6	7	8
C_5H_{12}	$5x10^{-9}$	$-5x10^{-8}$	$-6x10^{-8}$	$-6x10^{-8}$	$8x10^{-9}$	$-3x10^{-7}$	$-2x10^{-7}$	$-4x10^{-7}$	$5x10^{-6}$
C_6H_{14}	$1x10^{-7}$	$-3x10^{-7}$	$-4x10^{-7}$	$-3x10^{-7}$	$-5x10^{-8}$	$-1x10^{-6}$	$-2x10^{-6}$	$-3x10^{-6}$	$7x10^{-6}$
C_7H_{16}	$8x10^{-7}$	$-9x10^{-7}$	$-9x10^{-7}$	$-9x10^{-7}$	$-1x10^{-7}$	$-2x10^{-6}$	$-2x10^{-6}$	$-9x10^{-7}$	$1x10^{-5}$
C_8H_{18}	$4x10^{-6}$	$1x10^{-6}$	$1x10^{-6}$	$1x10^{-6}$	$2x10^{-6}$	$1x10^{-6}$	$4x10^{-6}$	$4x10^{-6}$	$6x10^{-6}$

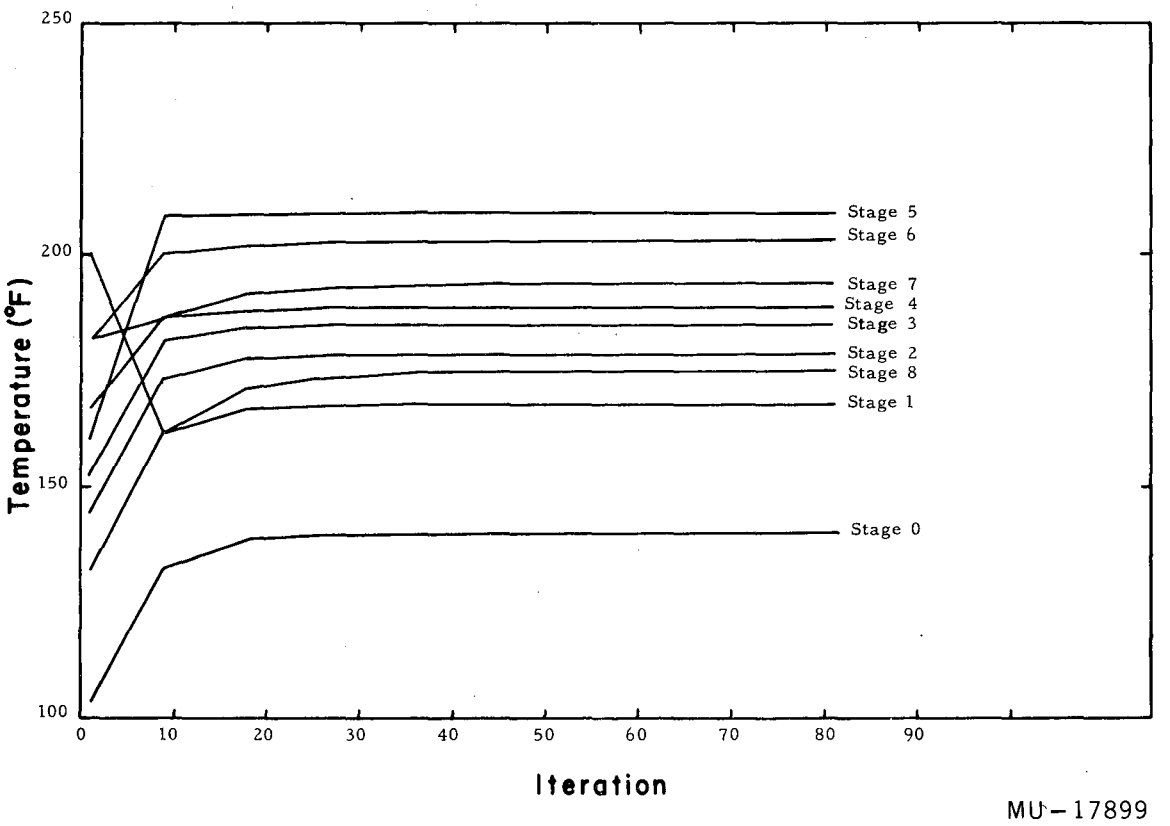


Fig. 28. Results for Example 16: temperature vs. iteration for all stages.

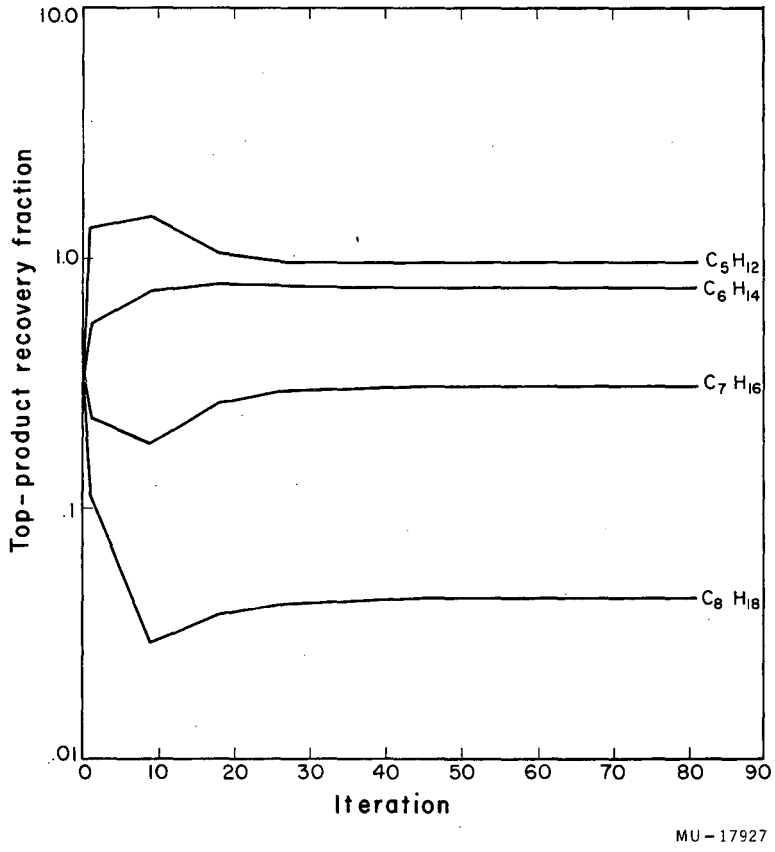


Fig. 29. Results for Example 16: top-product recovery fraction vs. iterations for all stages.

Stripping steam amount: 0.10 mole (at 270°F) per mole feed
Acceptable bubble-point error: $|\epsilon_2| \leqslant 0.1°F$
'A' value assigned steam was 0, and 'B' value was such that all $K_{steam} \approx 10^6$

As can be seen from Table XXXVI, the largest mass-balance errors remaining in the system after 81 iterations are those of component C_8H_{18}, but the over-all mass-balance check on this component is less than 0.1% in error, so that the solution is fairly close to exact for the flows assumed, which were

Stage	Flow gradient V	Flow gradient L
Reflux	--	0.500
8	0.960	0.500
7	0.960	0.500
6	0.960	0.500
5	0.960	0.500
4	0.260	0.767
3	0.227	0.735
2	0.195	0.705
1	0.165	0.670
0	0.130	0.640
Steam	0.100	--

When combined mass and energy balance is run, it is convenient to use a partial condenser and to specify the condenser duty indirectly by setting either top product or reflux amount. This allows determination of the reflux composition and enthalpy by a flash calculation using the condenser input as the fixed feed. Usually the hydrocarbon reflux amount is small and the steam leaves the system as a vapor. Example 17 was set up in this fashion, with the reflux from the partial condenser set at a small value so that the separation would tend to minimize the heavy component in the top product.

Example 17

Feed	Equilibrium value constants Fx_F	A	B	Enthalpy-value constants k	l	u	w
C_4H_{10}	0.0053	-3848	8.358	41.27	-24762	29.64	-10170
C_5H_{12}	0.0106	-4002	7.833	52.67	-31602	36.79	-12189
C_6H_{14}	0.0324	-4997	8.665	58.60	-35160	42.23	-13533
C_7H_{16}	0.0832	-5595	8.847	66.13	-39678	50.10	-16232
C_8H_{18}	0.2810	-6300	9.261	73.10	-43860	58.25	-19188
C_9H_{20}	0.5875	-7295	10.078	76.94	-46164	62.84	-19879
	1.0000						

Constants u and w for steam same as in Example 12

Enthalpy-value constant referred to liquid at 200°F

Thermal condition of feed: saturated liquid

Column pressure: 20 psia

Reflux amount: 0.05 mole per mole feed

Enriching stages: 4(not including the partial condenser)

Stripping stages: 4

Allowable errors:

Dew point: $|\epsilon_2| \leqslant 0.1^{\circ}F$

Flash: $|\epsilon_F| \leqslant 1 \times 10^{-5}$ mole

Corrective energy flow: $|\epsilon_c| \leqslant 0.1$ Btu

Stripping steam amount: 0.1 mole (at 270°F) per mole feed.

Initial gradient assumptions

Stage	Temperature	Vapor	Liquid
Reflux	--	--	0.05
8	270°F	0.25	0.05
7	270	0.25	0.05
6	270	0.25	0.05
5	270	0.25	0.05
4	270	0.25	1.05
3	270	0.25	1.05
2	270	0.25	1.05
1	270	0.25	0.90

In view of the success with the double-flow-correction approach on simple strippers, this approach was tried first in this Example. It was found that negative flows were predicted at the first iteration when flow correction without energy balance was attempted. This behavior could be attributed to the very high temperature assumed for the top stages, forcing a large amount of hydrocarbon into the vapor, with the result that liquid flows disappear and even become negative. This condition was not recognized by arbitrarily changing the temperature gradient, but by combining the energy-balance and flow-correction calculations. The results of this double flow correction did not give negative flows, but neither did a convergent solution appear. Figure 30 shows the behavior of vapor flows at certain stages and indicates the instability of the double-flow-correction approach. The combined temperature and flow movements from the energy-balance calculation are incapable of compensating for the effect of high temperatures of the top stages. The most likely cause of the difficulty is that the flash calculation is carried out at a temperature far removed from the saturation temperatures in the upper stages of the column, and the corrections predicted under these conditions are quite wrong and lead finally to a divergent result. The small liquid flow in the upper column section is another source of difficulty, since it is subject to large errors as a result of being obtained as the difference of two relatively large numbers which oscillate markedly as shown. Also, the temperature movements resulting from the flash calculation do not move the temperature gradient toward saturation conditions. For these reasons, the double-flow-correction approach was abandoned and the double temperature correction was tried in hopes that this approach would allow the calculation to be made even if a poor temperature gradient was originally assumed.

The results of the double-temperature calculation are given in Figs. 31, 32, and 33 and Tables XXXVII and XXXVIII. The sequence used within every iteration was

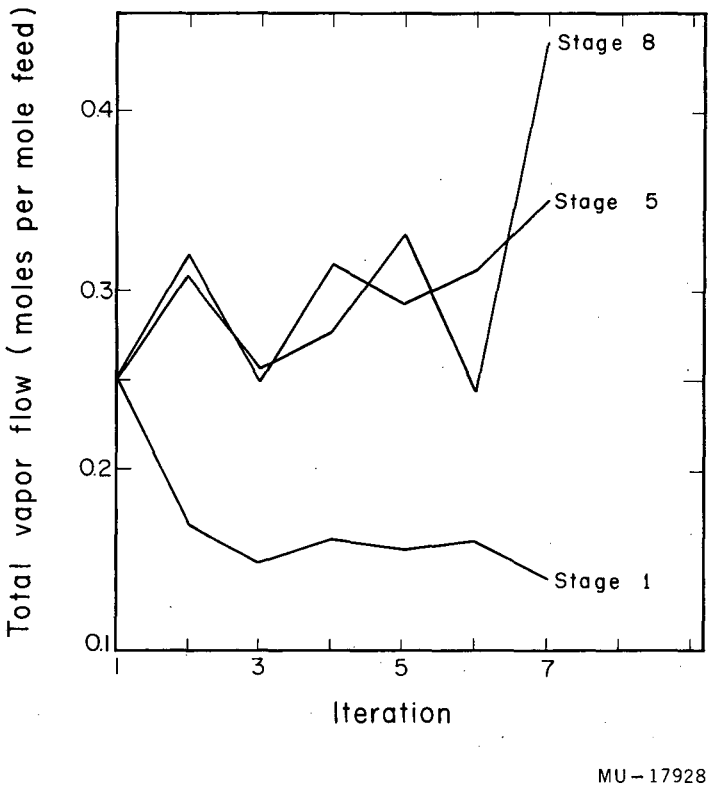
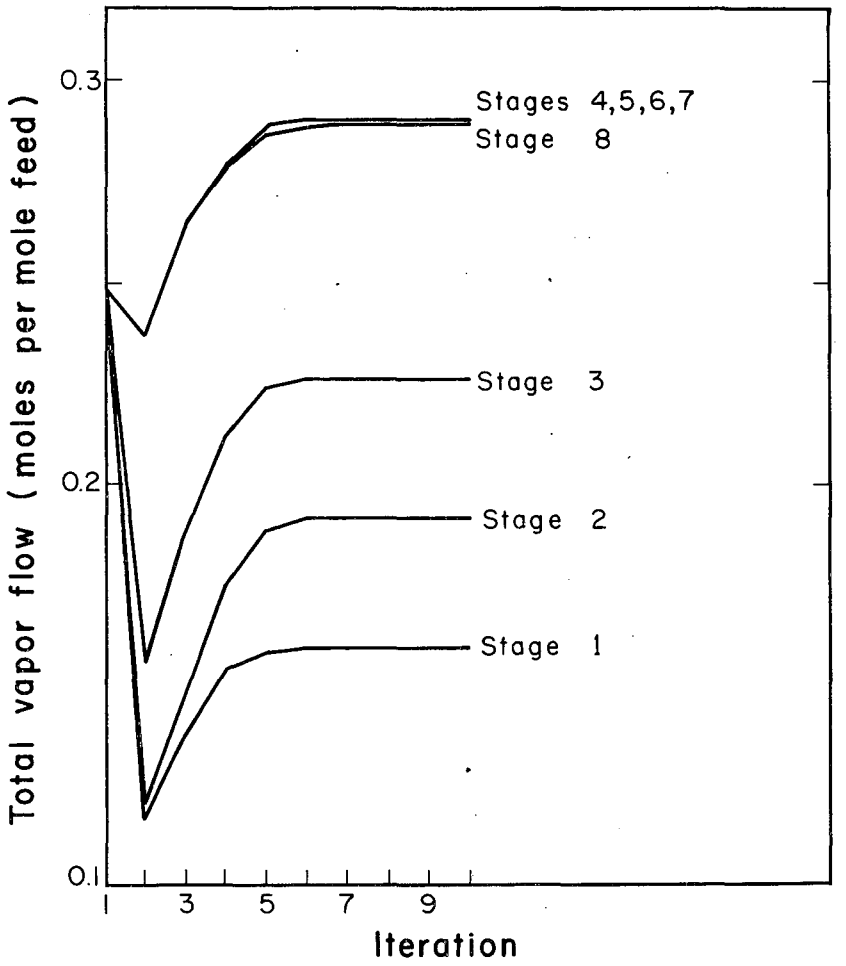
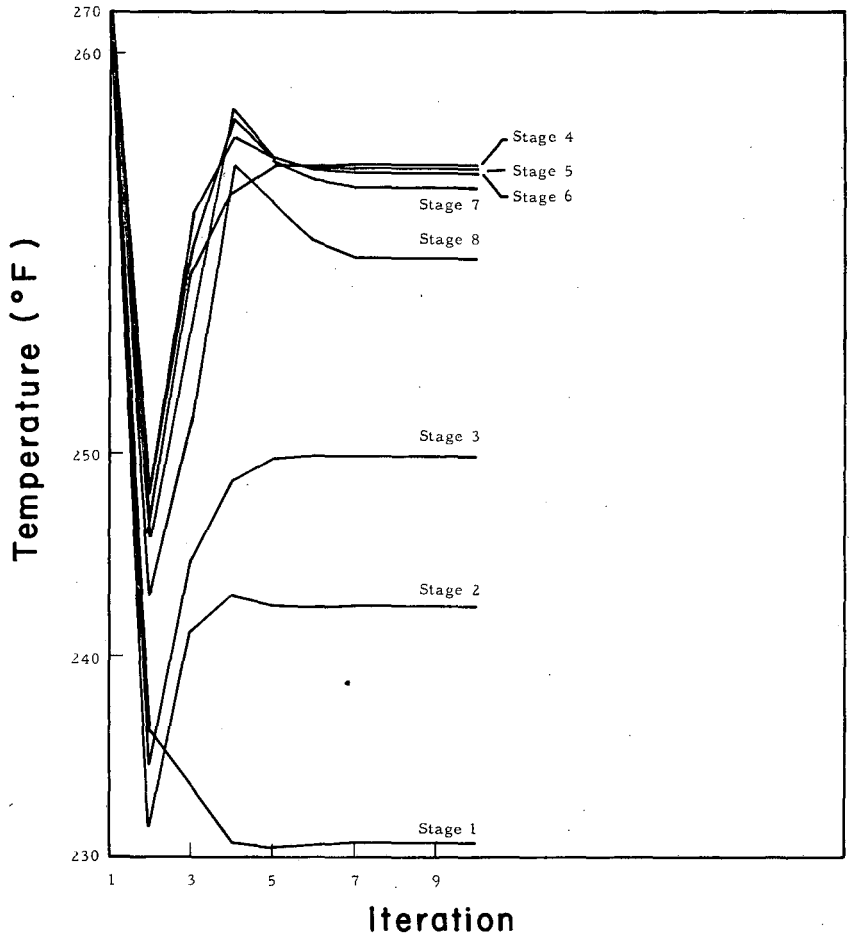


Fig. 30. Results for Example 17: instability of solution with double flow correction.



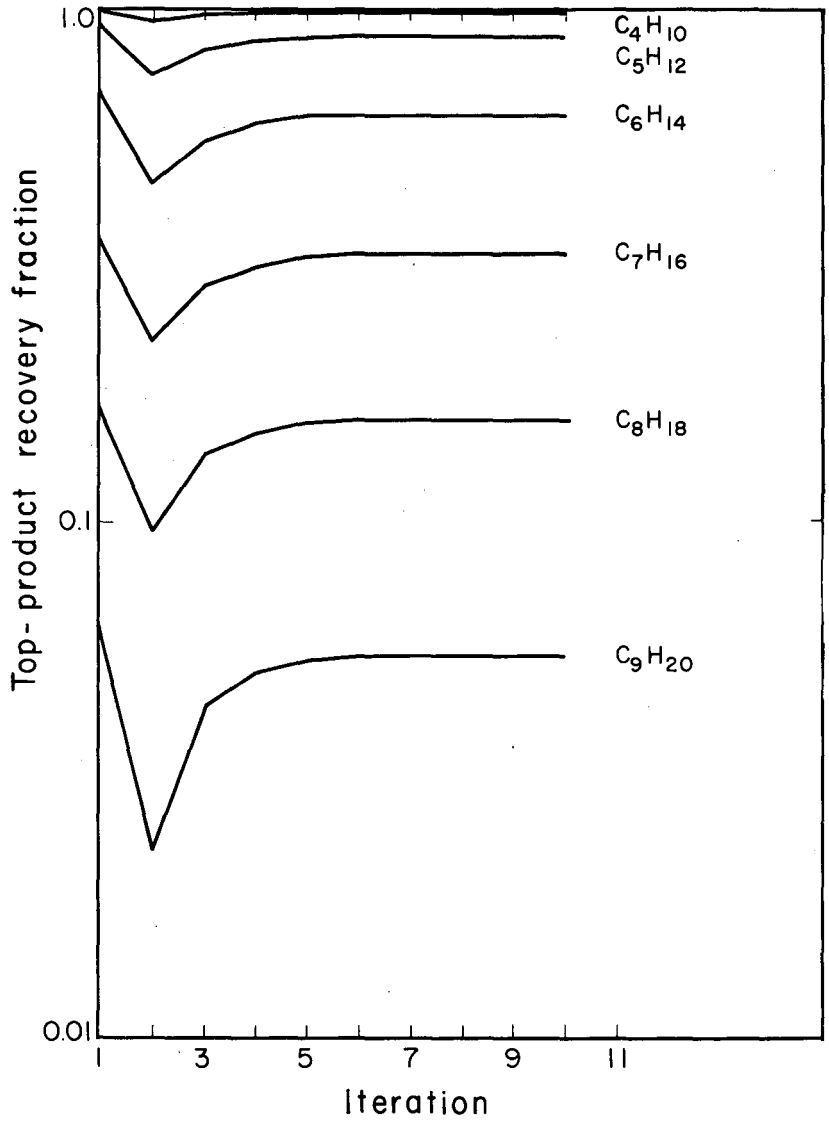
MU-17929

Fig. 31. Results for Example 17: total vapor flow vs. iteration for all stages, with Method II energy balance and double temperature correction.



MU-17930

Fig. 32. Results for Example 17: temperature vs. iteration for all stages, with Method II energy balance and double temperature correction.



MU-17931

Fig. 33. Results for Example 17: top-product recovery fraction as iteration.

(a) Mass balance by Method I equations,

(b) Dew point using equilibrium equation,

(c) Energy balance by corrective-energy-flow method,

and the results show a rapid convergence. For all practical purposes the calculation could have been terminated at the 4th or 5th iteration.

As before, relaxing all Q_p to a very small number is not necessary, so that the last iterations could be dispensed with unless a very exact solution were desired. Also, it is interesting to note the values of $(\Delta V/\Delta T)$ and the (C_L/C_V) ratios in Table XXXVIII. Even though the liquid flows are very small in the refluxed section of the column, the flow change resulting from the flash overshadows the enthalpy effect, and in this area latent heat effects predominate and the (C_L/C_V) are negative and very close to 0.

Refluxed Stripper with Side Stripper

Columns of this type are quite common in the petroleum industry, and their principal usage is for crude-oil separations. A simple column of this type is shown in Fig. 34 in which only one side stripper is indicated but the normal crude distillation column will have as many as four or five side strippers. To illustrate calculational methods only one side stripper is used, since it is a simple matter to extend the method for two or more side strippers. The normal boiling-point range of feed material to these columns is quite large even without steam present, and therefore the general form of the calculation proceeds just as in simple strippers.

As pointed out in Section IV, there are a number of additional variables that can be set for columns of this type. In Example 18, the column of Fig. 34 is used and the Description Rule indicates that--in addition to all feed variables, column pressure, and stages per column section--the following variables can be set,

Main-column steam: amount and enthalpy,

Side-stripper steam: amount and enthalpy,

Reflux amount,

Side-draw amount,

Combindened condenser duty, $Q_r + Q_c$,

Table XXXVII

Results for Example 17: summations and energy unbalance from seven iterations

	1		2		3		4		5		6		7	
Stage	$\sum_i (y_i)_p$	Q_p	$\sum_i (y_i)_p$	Q_p	$\sum_i (y_i)_p$	Q_p	$\sum_i (y_i)_p$	Q_p	$\sum_i (y_i)_p$	Q_p	$\sum_i (y_i)_p$	Q_p	$\sum_i (y_i)_p$	Q_p
8	1.163	-35.4	.965	+29.4	1.096	-77.5	1.032	-31.7	1.012	-16.4	1.002	+0.6	1.000	+0.5
7	1.182	+5.3	.984	+0.5	1.057	-35.5	1.013	-2.0	1.003	+0.7	1.000	+0.1	1.000	-0.0
6	1.192	+2.5	.998	+10.4	1.038	-25.6	1.008	+10.7	1.002	+1.7	1.000	+1.1	1.000	-0.1
5	1.196	+0.1	1.008	-13.1	1.026	+25.6	1.007	+30.1	1.002	+14.9	1.000	+4.1	1.000	+0.9
4	1.198	+1490	1.015	-433	1.017	+56.3	1.008	+13.3	1.002	+2.6	1.000	+3.1	1.000	+1.4
3	1.146	-207	1.116	+1353	1.067	+457	1.025	+107	1.004	+4.3	1.001	-3.7	1.000	-0.4
2	1.100	-154	1.269	+2553	1.166	+1230	1.058	+429	1.009	+88.4	1.001	+11.3	1.000	+0.4
1	1.039	-2631	1.287	+250	1.130	-80.4	1.028	-151	1.001	-39.1	1.000	-3.4	1.000	-0.7
ΣQ_p	--	-1530	--	+4617	--	+1550	--	+406	--	+57.1	--	+11.9	--	+2.0

Table XXXVIII

Results from Example 17:
ratio (C_V/C_L) values from various iterations

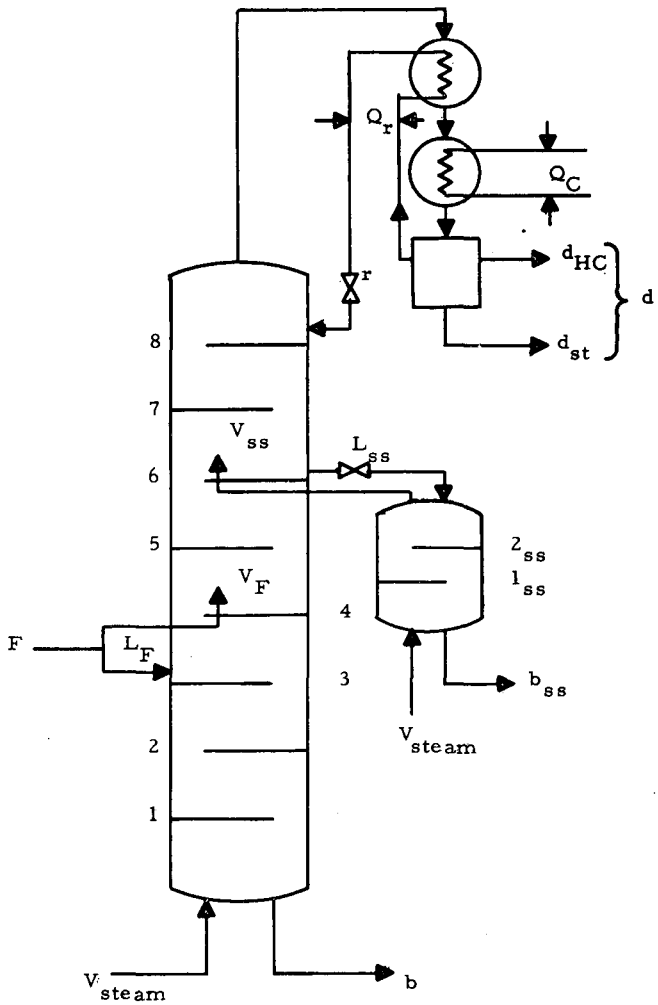
Stage	1	3	5	7	$(\Delta V/\Delta T)^*$
8	-.106	-.136	-.144	-.144	.0042
7	-.113	-.139	-.148	-.150	.0043
6	-.116	-.138	-.150	-.151	.0043
5	-.117	-.132	-.149	-.151	.0043
4	+.660	+.496	+.370	+.364	.0061
3	.589	1.346	.751	.731	.0037
2	.540	3.021	1.227	1.158	.0024
1	.406	3.746	2.029	1.995	.0015

*Typical values at 5th iteration

and for this example the steam amounts and enthalpies are retained, as is the side-draw amount. Reflux amount is replaced by the combined top product, d, and the combined condenser duty is replaced by a total condenser with the hydrocarbon reflux stream at its bubble-point temperature. Thus, the reflux and two bottom-product amounts are unspecified and will be determined by the calculation.

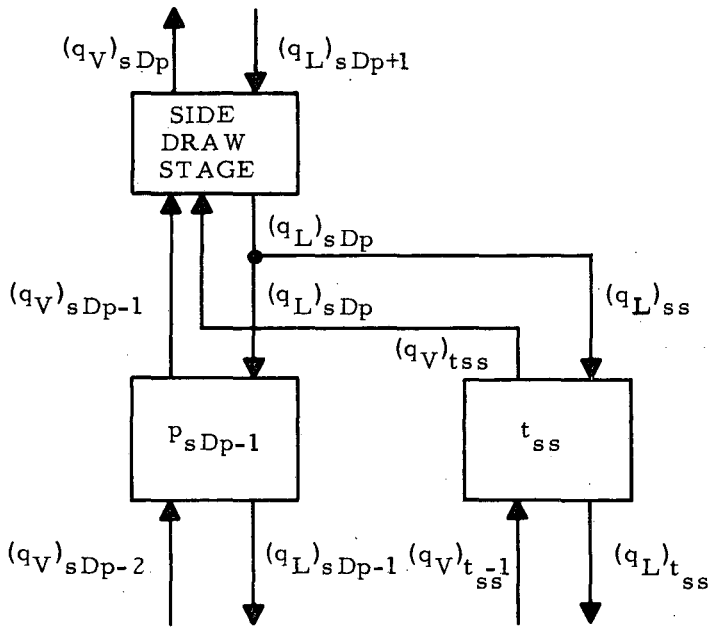
The equations previously given in Section IV for a side-stripped column apply here, and two combined bottom products are now used rather than one, both having the form of Eq. (V.1). The Method I mass-balance equations then apply in a straightforward manner, but the Method II energy balance must be handled in a slightly different manner because of the presence of the side stripper. There are corrective energy streams to and from the side stripper, as shown in Fig. 35, and these must be meshed in with the main-column corrective energy flows. Thus, the recurrence relation, Eq. (III.23), for this point in the column becomes

$$(q_c) \equiv (q_v)_{sDp-1} + (q_v)_{tss} = \left[1 + \left(\frac{C_L}{C_V}\right)_{sDp}\right](q_v)_{sDp} - \left[\left(\frac{C_L}{C_V}\right)q_v\right]_{sDp+1} - Q_{sDp}, \qquad (V.17)$$



MU-17932

Fig. 34. Refluxed stripper with side stripper. Column used for Example 18.



MU-17933

Fig. 35. Corrective energy-flow meshing at a side-draw stage.

where the number (q_c) can be determined but must be broken down into its component parts before calculation can proceed either in the main column or the side stripper. Fortunately, this can be done, but at the cost of an additional two-point extrapolation calculation for each side stripper present on a given column.

The following relations exist at the side-draw stage:

$$(q_L)_{sDp} = (q_L)_{sDp'} + (q_L)_{ss}, \tag{V.18}$$

$$(q_L)_{ss} = \frac{L_{ss}}{L_{sDp}} \left[(C_L/C_V)\ (q_V)\right]_{sDp}, \tag{V.19}$$

where $(q_L)_{ss}$ can be calculated as a number and used in the expression

$$(q_V)_{tss} = \left[1 + \left(\frac{C_L}{C_V}\right)_{tss}\right] (q_V)_{tss} - (q_L)_{ss} - Q_{tss}. \tag{V.20}$$

The only unknown quantity in Eq. (V.20) is $(q_V)_{tss}$, and if this is known, a normal corrective energy-flow calculation can be run on the side stripper by means of the two-point extrapolation procedure. When the desired value of $(q_V)_{tss}$ is available, $(q_V)_{sDp-1}$ is obtained from Eq. (V.17) and $(q_L)_{sDp'}$ from Eq. (V.18) and the calculation for the main column is done. This latter calculation, it will be recalled, is itself done by a two point-extrapolation procedure. Thus, a value of $(q_V)_{tss}$ must be assumed for use in Eq. (V.20), and the most obvious first assumption is

$$\left[(q_V)_{tss}\right]_{ASSUMED} = \left(\frac{V_{tss}}{V_{tss} + V_{sDp-1}}\right) q_c;$$

the second assumption is some arbitrary number times the first assumption, and the limit of convergence, $(\epsilon_c)_{ss}$, for the whole calculation is set at the same value as that for the main column, ϵ_c, and is usually 0.1 Btu. The number of extrapolation calculations needed for convergence in the side stripper is small--on the order of 3 or 4.

When the number of side strippers is three or more, the two-point extrapolation process may be replaced by an approach involving matrix solution of the corrective energy equations. This approach has not been used in this work because even with three side strippers the calculation proceeds quite rapidly by use of the extrapolation process. In a very complex column of this type, Method II mass-balance equations are recommended; and since rates of convergence are quite slow for this method, any approach that will appreciably speed up the corrective-energy-flow section of the over-all calculation is desirable. Whether or not a matrix approach will do this is questionable.

The general computer program for refluxed strippers with side strippers follows that shown in Fig. 22, path (b). The only additions necessary are in the energy-balance area and are a bubble-point subprogram to give the temperature and enthalpy of the reflux, and a two-point extrapolation subprogram for each side stripper.

The results of Example 18 are given in Tables XXXIX and XL and Figs. 36, 37, and 38. Damping factors of 1 and 1/2 both gave negative flows, and the next factor tried was 1/5, which gave the results shown. A factor of 1/3 will probably be stable and would certainly speed up the convergence. Even so, a practical solution to the problem is available in the neighborhood of the 12th iteration. All Q_p were less than 100 at the 19th iteration and less than 10 at the 29th iteration, but the last 10+ iterations were establishing the third place in the flows, and this is not necessary.

Example 18

Feed	Fx_F	$V_F y_{VF}$
C_4H_{10}	0.10	.0956
C_5H_{12}	0.20	.1811
C_6H_{14}	0.20	.1627
C_7H_{16}	0.20	.1328
C_8H_{18}	0.20	.0976
C_9H_{20}	0.10	.0302
	1.00	.7000

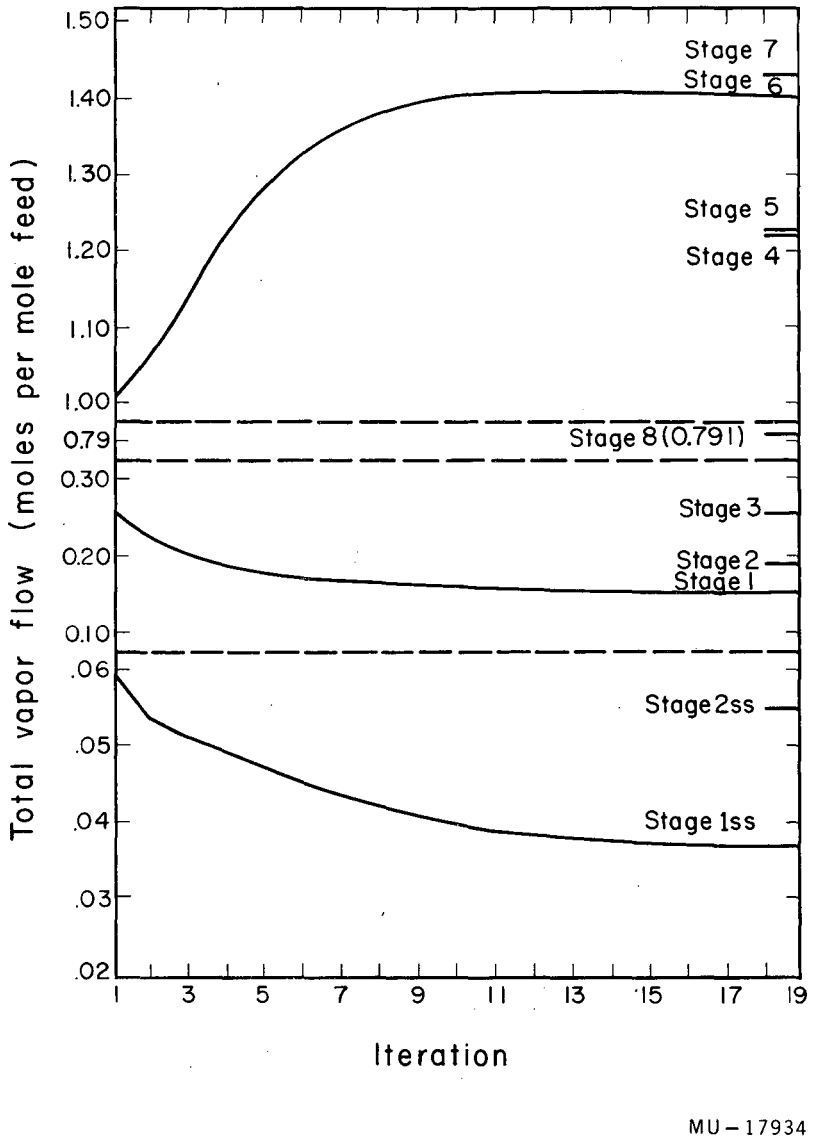


Fig. 36. Results for Example 18: total vapor flow vs. iteration for all stages.

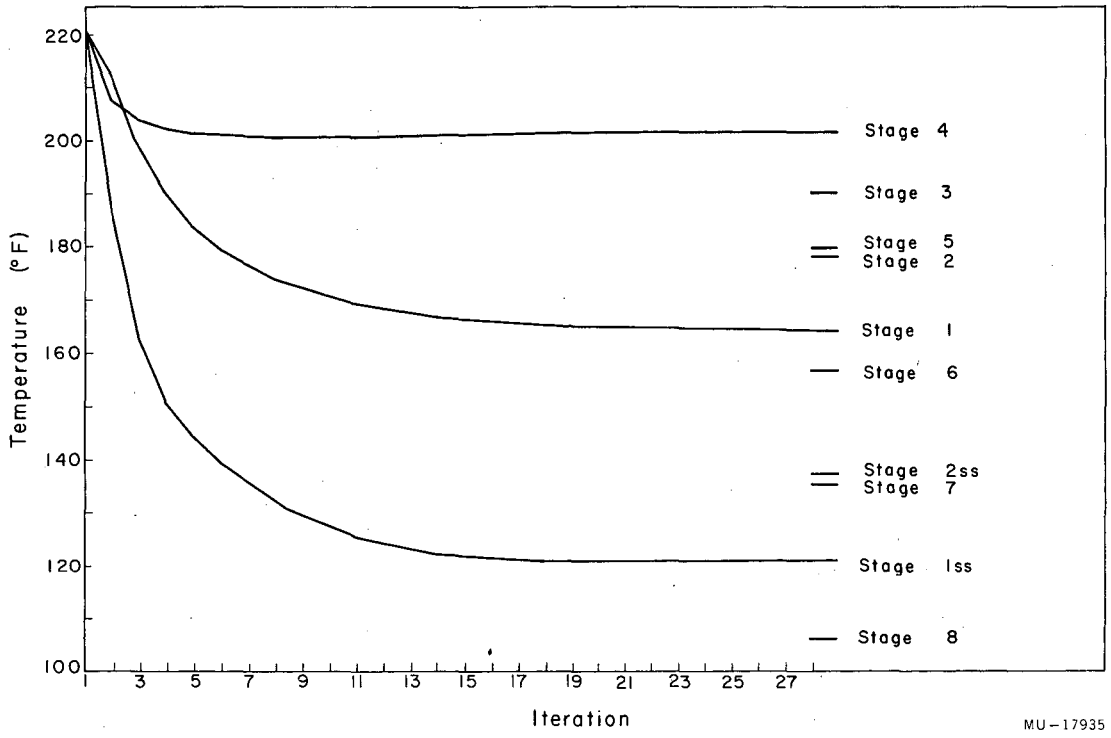


Fig. 37. Results for Example 18: temperature vs. iteration for all stages.

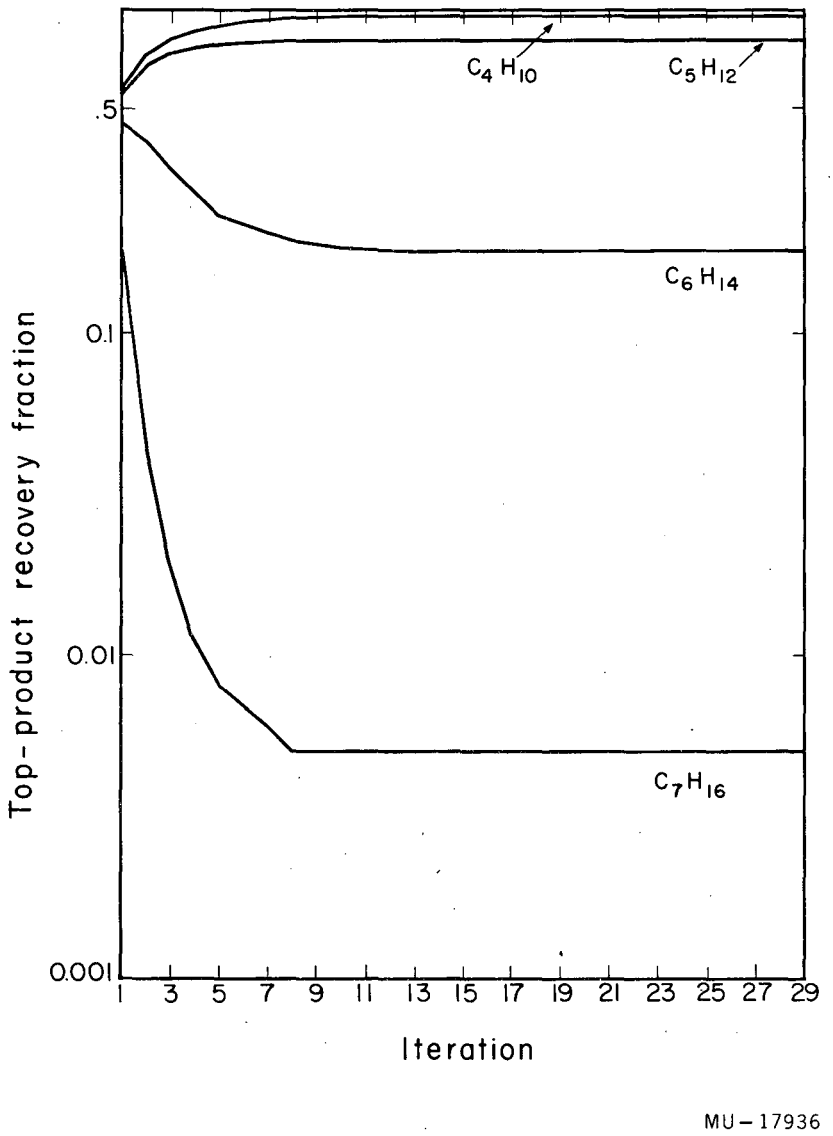


Fig. 38. Results for Example 18: top-product recovery fraction vs. iteration.

Table XXXIX

Results for Example 18: summations and energy unbalances from various iterations

	1		3		5		7		9		11		13		15		20	
Stage	$\sum_i (y_i)_p$	Q_p	$\sum_i (y_i)_p$	Q_p	$\sum_i (y_i)_p$	Q_p	$\sum_i (y_i)_p$	Q_p	$\sum_i (y_i)_p$	Q_p	$\sum_i (y_i)_p$	Q_p	$\sum_i (y_i)_p$	Q_p	$\sum_i (y_i)_p$	Q_p	$\sum_i (y_i)_p$	Q_p
8	1.613	-16564	1.167	-3587	1.071	-2171	1.032	-1257	1.013	-696	1.004	-372	1.000	-190	.998	-90.7	.998	-6.1
7	1.009	-169	1.084	+1244	1.035	+1131	1.017	+931	1.006	+703	1.001	+496	.999	+332	.998	+212	.999	+59.2
6	.928	+176	1.000	+307	.998	-116	.998	-314	.997	-347	.997	-307	.998	-243	.998	-180	1.000	-70.3
5	.937	+287	.964	+265	.983	+47.6	.992	-61.6	.995	-83.3	.997	-67.6	.999	-43.4	.999	-22.6	1.000	+2.7
4	.974	+3916	.967	+2595	.982	+1620	.991	+1004	.996	+619	.998	+378	.999	+229	1.000	+137	1.000	+35.7
3	1.099	+777	.989	+635	.985	+343	.991	+171	.994	+72.9	.997	+20	.998	-6.5	.999	-17.9	1.000	-18.8
2	.972	-238	.993	-105	.985	-122	.990	-124	.994	-108	.997	-86.0	.998	-64.9	.999	-47.1	1.000	-18.3
1	.870	-2680	.998	-1636	.992	-964	.995	-581	.997	-354	.999	-217	.999	-133	1.000	-80.9	1.000	-22.2
2ss	.958	+131	.995	+39.4	.984	-88.6	.992	-123	.995	-111	.997	-85.2	.998	-59.6	.999	-39.0	1.000	-105
1ss	.801	-653	.988	-370	.985	-24.4	.995	-150	.999	-83.1	1.000	-40.5	1.000	-15.8	1.000	-3.0	1.000	+5.0
ΣQ_p		-15019		-613		-565		-505		-388		-280		-195		-131		-43.6

Table XL

Results for Example 18:
ratios (C_L/C_V) and ($\Delta V/\Delta T$) from various iterations

Stage	1		15		29	
	C_L/C_V	$\Delta V/\Delta T$	C_L/C_V	$\Delta V/\Delta T$	C_L/C_V	$\Delta V/\Delta T$
8	.358	.0228	.895	.0332	.892	.0330
7	.230	.0234	.497	.0552	.491	.0548
6	.188	.0217	.332	.0500	.329	.0492
5	.117	.0171	.187	.0345	.183	.0345
4	.083	.0158	.065	.0228	.061	.0228
3	.761	.0042	.743	.0041	.757	.0040
2	.636	.0045	1.367	.0022	1.433	.0020
1	.399	.0046	2.292	.0012	2.449	.0011
2ss	.857	.0013	1.148	.0013	1.231	.0012
1ss	.593	.0013	2.445	.0005	2.557	.0005

All equilibrium and enthalpy-value constants are the same as those of Example 17.

Thermal condition of feed: 70% vaporized

Column pressure: 20 psia

Top-product amount: 0.42 mole per mole feed (includes 0.12 mole steam)

Reflux temperature: bubble point of hydrocarbon

Enriching stages: 2(not including side-draw stage)

Intermediate stages: 2(including side-draw stage but no feed stage)

Stripping stages: 4(including both feed stages)

Main-column stripping steam amount: 0.1 mole (at 270°F) per mole feed

Side-stripper stripping steam amount: 0.02 mole (at 270°F) per mole feed

Side-stripper stages: 2

Allowable errors:

Dew point: $|\epsilon_2| \leqslant 0.1^{\circ}F$

Flash: $|\epsilon_F| \leqslant 1 \times 10^{-5}$ moles

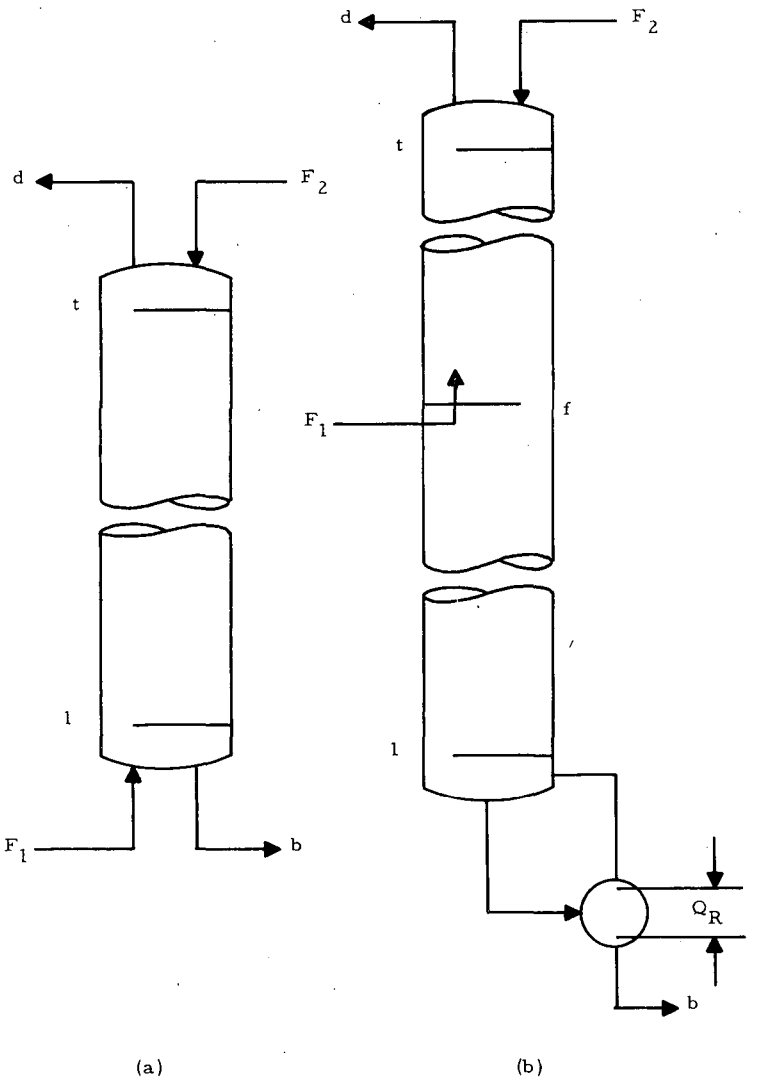
Corrective energy flow: $|\epsilon_c|$ and $|\epsilon_c|_{ss} \leqslant 0.1$ Btu

Simple Absorber

In the simple absorber shown in Fig. 39a heavy components are absorbed from the primary feed material, F_1, into the lean absorbing oil, F_2, which can be considered as a second feed to the column. Since only hydrocarbons are present, no special handling of any one component need be considered here. Also, the temperature gradient will rise from top to bottom for an adiabatic system because of the condensation accompanying the absorption and the resultant release of latent heat in the fluid stream.

The lean oil will usually be a heavy material, relative to the components present in the vapor feed, but it may contain small amounts of light material which will appear in both the vapor and the liquid leaving the column. Any method of calculation must be capable of handling this common component (or components), and the methods of Sections II and III do this quite nicely.

One difficulty that can arise in absorber calculations does require special handling in computer application. Since an absorber is essentially a two-feed column, the two-feed equations of Section IV are used, but they are just a variation of Method I mass balance. In the calculation of the G, g, J, and j functions of the two feed equations, difficulties can arise if stage temperatures are such that heavy components in the lean oil have very small equilibrium values. Under these conditions, the G, g, J, and j functions become large numbers very fast as calculations proceed from stage to stage. In the process of resolving the individual-stage component ratios into concentrations, these large value functions give rise to a condition involving the subtraction of two very large numbers in the lower stage region. The average digital computer carries only eight places when operating in a floating-point mode; and in



MU-17937

Fig. 39. Typical absorbers.

the carrying out of the subtraction and the rounding off of the result, enough significant figures were lost so that convergence was prevented.

There are several ways to handle this difficulty. One possibility is to use double-precision numbers for all calculations, so that 18 places are carried rather than 8. Another possibility is to use Method II mass balance, since numbers requiring even eight-place accuracy never occur in this method. In the calculations that follow both approaches were used with success. They both suffer the disadvantage of requiring additional computer time to arrive at a solution, and the double-precision approach has the further disadvantage of requiring a large additional block of computer storage space needed for operation in that mode.

In starting an absorber problem, approximation methods previously mentioned can be used for the initial assumptions as to temperature and flow gradients, or a pure "guess" can be made for these gradients, since a convergent solution will result no matter what the assumption. The Description Rule indicates that after all feed variables, column pressure, and the number of stages are set, the column is completely specified and calculation can begin.

In Example 19, the flow and temperature gradients were approximated by the method of Souders and Brown and all calculations were done in the double-precision mode in the computer. The results of this example, given in Tables XLI and XLII and Figs. 40, 41, and 42 indicate a small tendency for the solution to oscillate, although the third-place figure of the variables has been fairly well established at approximately the 11th iteration. This tendency to oscillate slowly damps out if enough iterations are run; but doing this is hardly justified, as iterations beyond the 11th establish only the third or fourth significant figure, and this is not necessary for a practical solution. An oscillation also develops in solutions for reboiled absorbers, as will be seen shortly, and this behavior appears to be a characteristic of the combination of two feed equations with corrective energy flows.

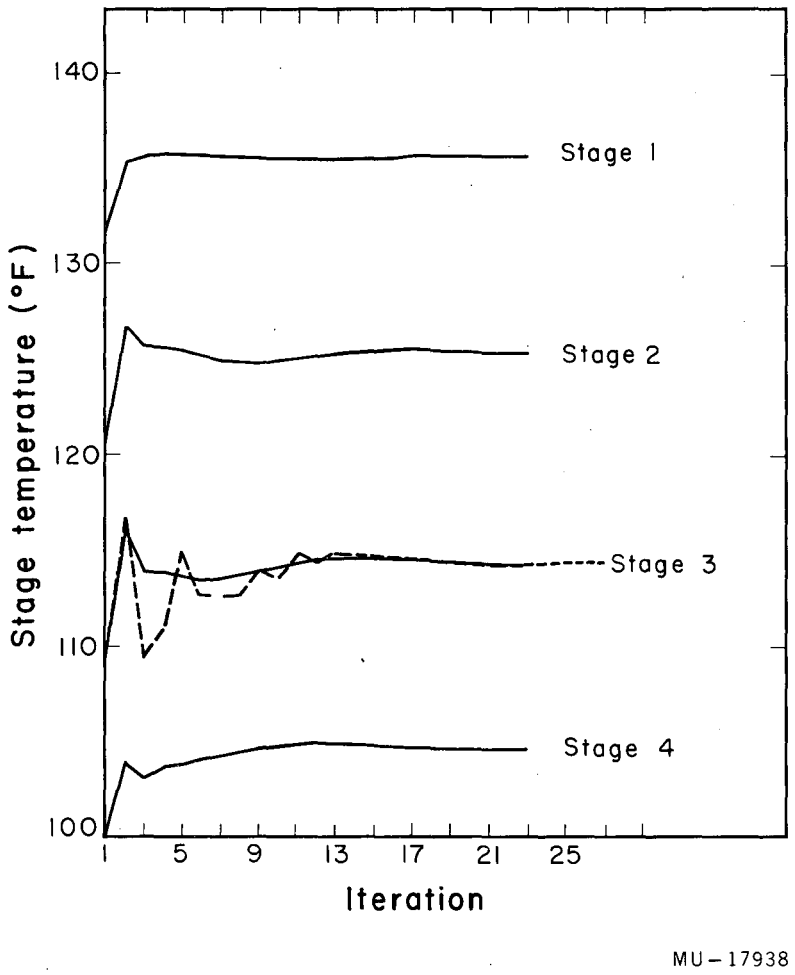
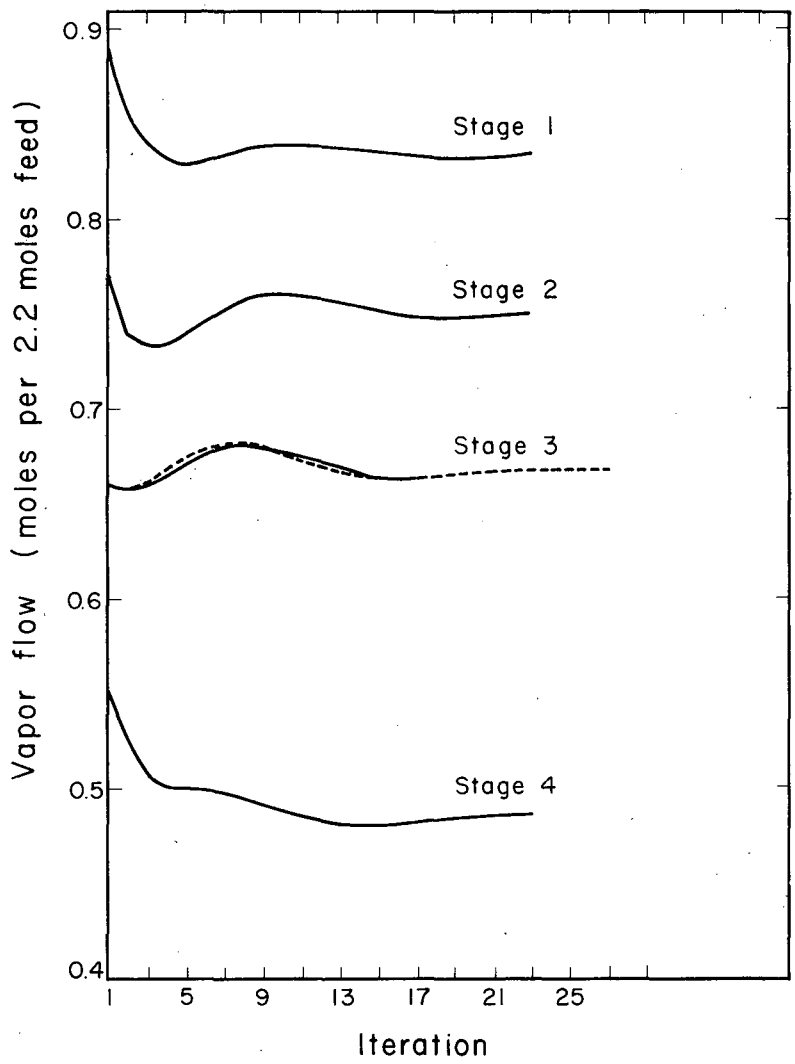


Fig. 40. Results for Example 19: temperature vs. iteration for all stages.
—— damping factor = 1.
--- damping factor = 3/2.



MU-17939

Fig. 41. Results for Example 19: vapor flow vs. iteration for all stages.
—— damping factor = 1.
--- damping factor = 3/2.

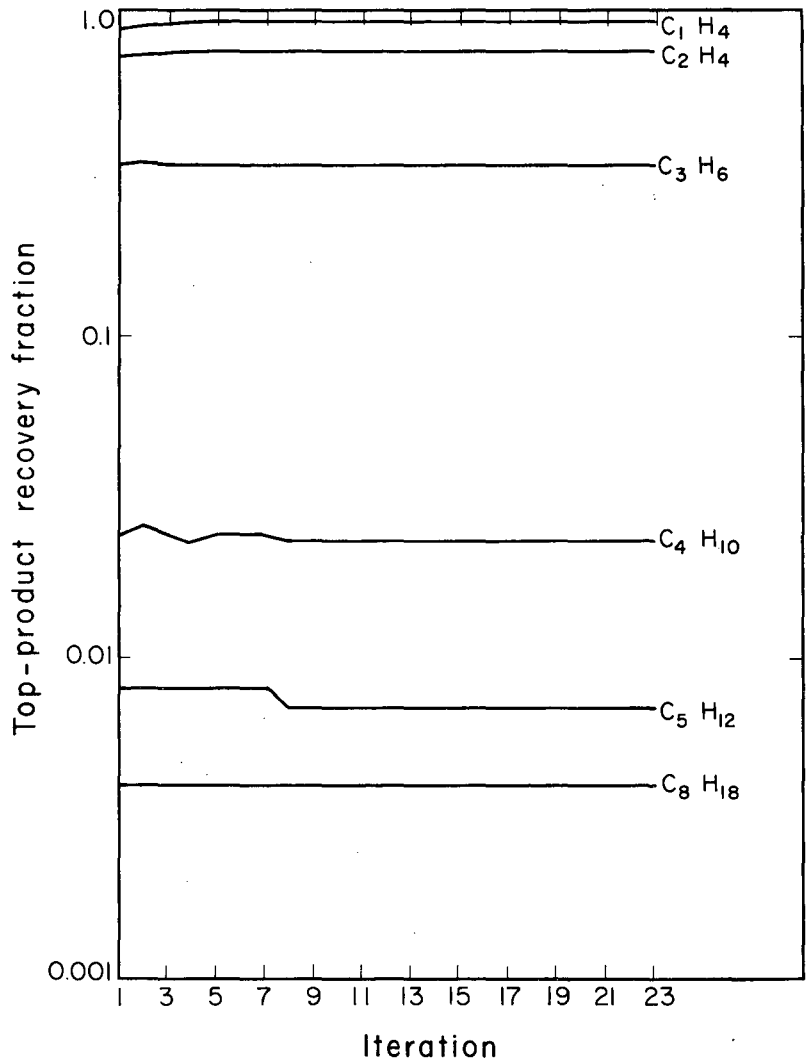


Fig. 42. Results for Example 19: top-product recovery fraction vs. iteration.

Table XLI

Results for Example 19: summations and energy unbalances from various iterations

	1		3		5		7		9		11		13		15		23	
Stage	$\sum_i (x_i)_p$	Q_p	$\sum_i (x_i)_p$	Q_p	$\sum_i (x_i)_p$	Q_p	$\sum_i (x_i)_p$	Q_p	$\sum_i (x_i)_p$	Q_p	$\sum_i (x_i)_p$	Q_p	$\sum_i (x_i)_p$	Q_p	$\sum_i (x_i)_p$	Q_p	$\sum_i (x_i)_p$	Q_p
4	1.043	-1744	1.017	-649	1.005	-347	.999	-182	.996	-26.8	.996	+78.5	.998	+107	1.000	+75	1.000	-28.8
3	1.033	+1447	1.025	+270	1.015	+12.7	1.006	-58.5	.998	-77.7	.995	-64.4	.996	-32.9	.998	-1.9	1.001	+6.0
2	1.014	+515	1.013	+428	1.013	+233	1.008	+85.6	1.002	-1.6	.997	-38.1	.996	-38.2	.997	-20.0	1.001	+9.5
1	1.034	-1041	1.012	-296	1.008	+10.4	1.006	+61.5	1.003	+27.4	1.000	-12.6	.998	-30.3	.998	-25.9	1.000	+9.1
ΣQ_p		-823		-247		-91		-93		-78		-37		-5.6		+27		-4.2

Table XLII

Results for Example 19:
ratios (C_V/C_L) and ($\Delta V/\Delta T$) from various iterations

	1		12		23	
Stage	C_V/C_L	$\Delta L/\Delta T$	C_V/C_L	$\Delta L/\Delta T$	C_V/C_L	$\Delta L/\Delta T$
4	.243	-.0014	.190	-.0014	.193	-.0014
3	.332	-.0022	.324	-.0023	.325	-.0023
2	.462	-.0031	.445	-.0030	.444	-.0030
1	.742	-.0046	.647	-.0044	.645	-.0044

The general computer program for absorbers follows that of Fig. 22, with bubble ponints replacing dew points of Path (b) and with liquid rather than vapor mole fractions being recorded. In the flash equation of the corrective-energy-flow process, the ratio (C_V/C_L) was used and ΔL was calculated and used to correct the liquid flows, and the vapor flows were corrected by a simple over-all flow balance. It was found that a damping factor of 1 gave a stable solution. As can be seen from the values of Table XLII, the system has a predominantly heat-capacitive nature.

Example 19

	Feed		Equilibrium-value constants		Enthalpy-value constants (Referred to liquid at 90°F)			
	F_1x_{F1}	F_2x_{F2}	A	B	k	l	u	w
C_1H_4	0.285	--	-1355	6.356	11.55	-5659	9.15	-3144
C_2H_5	0.158	--	-2110	6.158	21.65	-10608	14.13	-2608
C_3H_8	0.240	--	-2419	5.671	30.43	-14911	19.84	-3046
C_4H_{10}	0.169	--	-3281	6.288	38.94	-19081	25.57	-3503
C_5H_{12}	0.148	0.012	-4544	7.627	45.45	-22270	32.47	-4597
C_8H_{18}	--	1.188	-6989	9.312	65.11	-31904	51.39	-7796
	1.000	1.200						

Allowable errors: same as Example 18, except dew point, which was inadvertently set at $|\epsilon_2| < 0.00001^{\circ}F$

Thermal condition of feeds: F_1, saturated vapor
F_2, liquid at $90^{\circ}F$

Column pressure: 5 atmospheres

Number of stages: 4

Feed amounts as indicated above and initial-gradient assumptions as below

	Temperatures		Vapors		Liquids	
Stage	1st	2nd	1st	2nd	1st	2nd
4	$100^{\circ}F$	$100^{\circ}F$	0.55	0.75	1.31	1.45
3	110	100	0.66	1.00	1.42	1.45
2	121	100	0.77	1.00	1.54	1.45
1	132	100	0.89	1.00	1.64	1.45

Example 19 was restarted with the second set of initial assumptions and reached the same convergence values, but required more iterations to do so. What initial gradient to use is a matter of judgment and experience.

In an attempt to speed up the convergence of Example 19, the damping factor was set at 3/2 and the problem restarted. Typical stage behavior under these conditions is shown in Figs. 38 and 39. The disturbance is pronounced in the early iterations but soon dies out and behaves exactly as the factor-1 results in the later iterations, with the net result of no gain in the convergence rate.

The Φ factor also was combined with the two-feed equations, and an attempt was made to use it. The process of finding the Φ root was in no way affected, but consecutive root values diverged quickly and the whole calculation "blew up." The exact reason for this behavior is not known, but it is in some manner a result of the very large numbers calculated for the G, g, J, and j functions in the two feed equations, causing large oscillation of the Φ roots.

Reboiled Absorber

A typical reboiled absorver is that shown in Fig. 39b. The purpose of the enriching section is to recovery more of the light products, or--what is in effect the same thing--to enrich the heavy products. The addition of a reboiling section introduces more variables into the system, and the Description Rule indicates that in addition to all feed variables, column pressure, and stages per column section, one additional variable can be set; that is reboiler duty. Since Method II energy-balance equations are used, reboiler duty must be the set variable. It is quite possible to replace this variable with a product flow and attempt to do energy balances by Method I equations but, as is shown later, this approach fails.

In Example 20, a combination of Method I mass balance and Method II energy balance was used to obtain a convergent solution. Also, to avoid the special form of the two-feed equations required with Method I mass balance, a combination of Method II mass balance and Method II energy balance was used, and the results of this approach appear in Example 21.

The results of Example 20 are given in Figs. 43, 44, and 45 and Tables XLIII, XLIV, and XLV. The oscillating property of the solutions is quite evident, but a reasonably exact solution is available if enough iterations are run. In Figs. 40 and 41 only results for certain stages are plotted, as they are typical of the behavior of the other stages. Final values of the other stages are indicated in the figures. It would appear that even practical solutions to this type of problem require a relatively large number of iterations, approximately 35 or 40 here, and that the actual number for a given case is at least partly a function of the damping factor used and of the most sensitive stage in the system. As can be seen, larger damping factors appreciably reduce the amplitude of the oscillations at the expense of increased frequency, but in this case, this behavior actually improves the rate of convergence. The top stage in the system is the worst actor in the sense that its oscillations are the last to die out. It is intuitively evident that the top stage

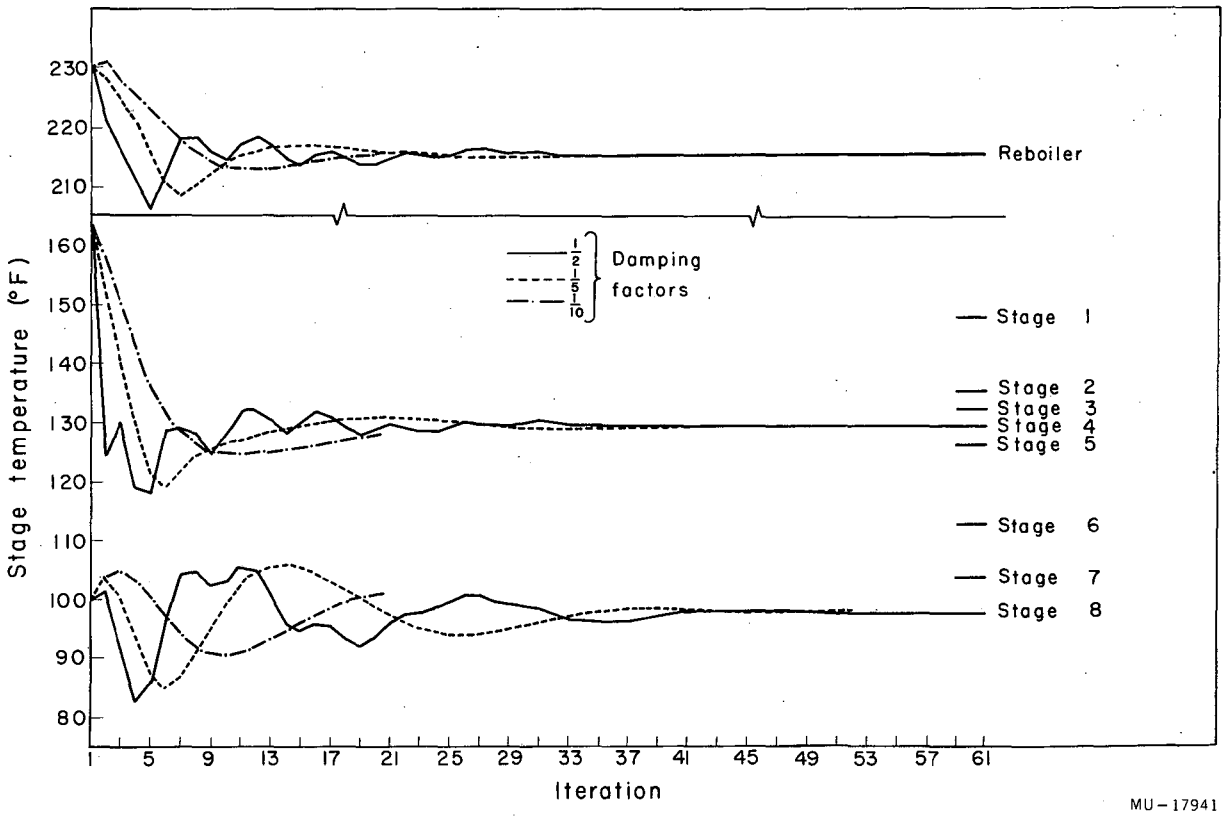
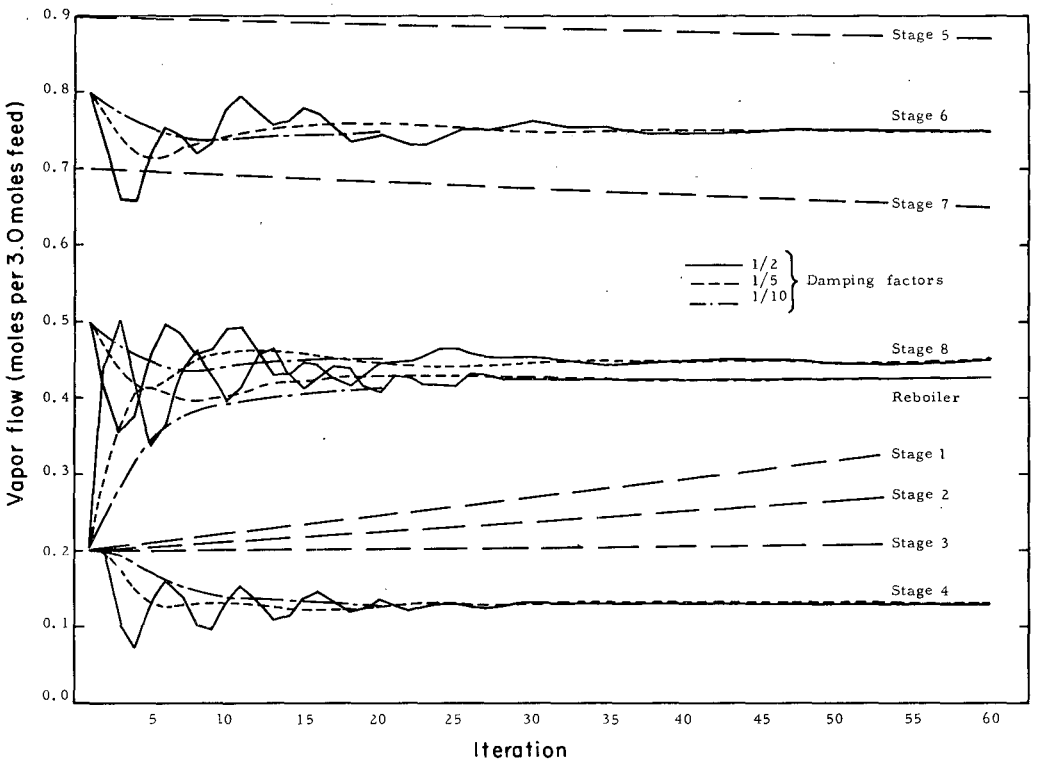


Fig. 43. Results for Example 20: temperature vs. iteration for selected stages.
—— damping factor = 1/2.
--- damping factor = 1/5.
-·-· damping factor = 1/10.



MU-17942

Fig. 44. Results for Example 20: vapor flow vs. iteration for selected stages.
—— damping factor = 1/2.
--- damping factor = 1/5.
-·-· damping factor = 1/10.

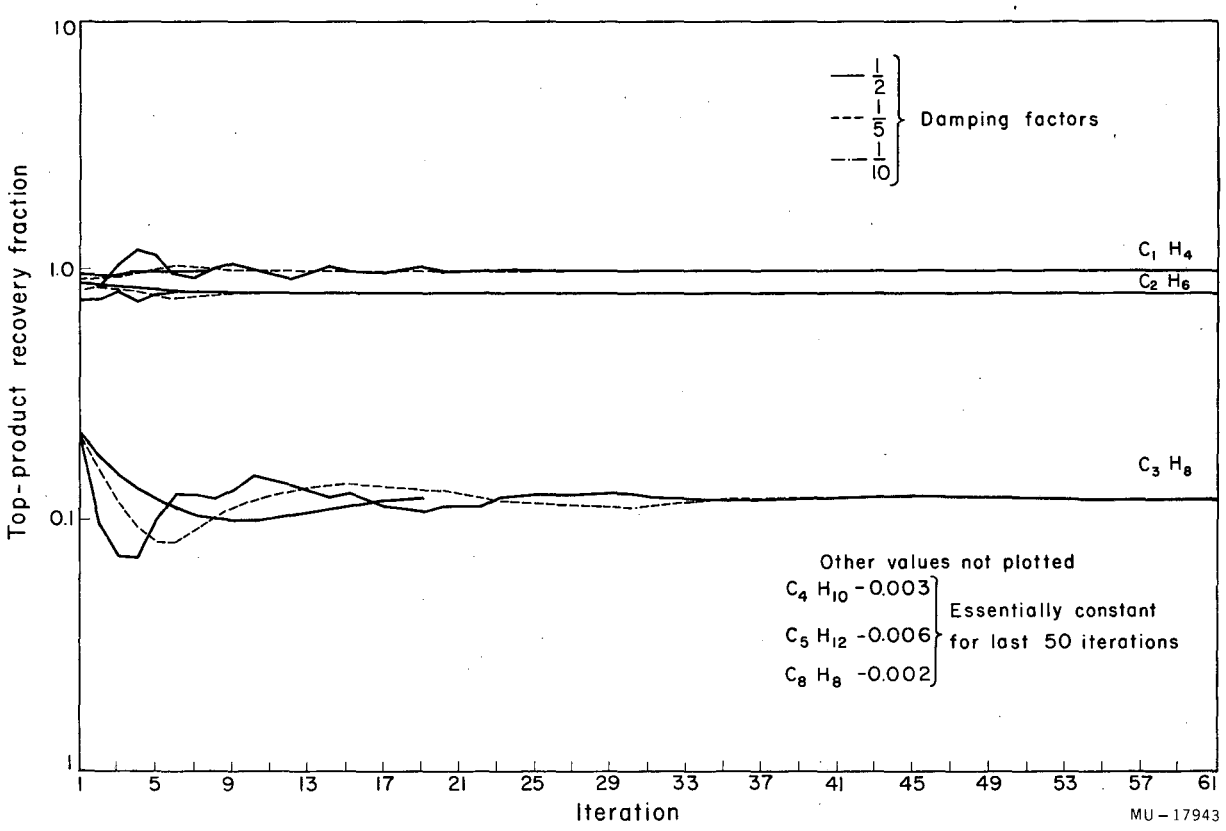


Fig. 45. Results for Example 20: top product recovery fraction vs. iteration.

—— damping factor = 1/2.

--- damping factor = 1/5.

-·-· damping factor = 1/10.

Other values not plotted: C_4H_{10} = 0.003, C_5H_{12} = 0.006, C_8H_8 = 0.002 } essentially constant for last 50 iterations

Table XLIII

Results for Example 20: summations and energy unbalances from various iterations

Stage	1	5	10	15	20	25	30	35	40	45	50	66	60
						Q_p values - Damping factor (1/2)							
8	-716	-92	-2073	+693	+348	-876	-146	+363	-134	-208	+107	+63	-81
7	-48	+761	+199	-421	+343	+294	-173	-35	+150	-3	-65	+29	+15
6	-742	-1500	+428	-436	-94	+325	-6	-141	+71	+68	-51	-16	+31
5	+328	+162	+540	-111	-308	+146	+127	-105	-22	+74	-5	-34	+21
4	-4563	-947	-865	-992	-411	-152	-232	-143	+1	-10	-39	--	+18
3	-1559	-2220	-548	-153	-357	-208	+19	-26	-74	+1	+23	-14	-2
2	-1178	+498	+479	+220	-86	-53	+33	-30	-56	-4	+4	-17	-1
1	-1758	+1592	+804	+720	+269	+60	+114	+63	-24	-7	+18	-6	-11
R	+7400	+1989	+812	+440	+486	+323	+80	+66	+92	+19	-13	+13	--
Stage						$\sum_i (x_i)_p$ values							
8	1.021	1.010	.996	.997	1.005	1.000	.998	1.000	1.001	.999	1.000	1.001	1.000
7	1.032	1.014	1.000	.992	1.005	1.004	.997	.999	1.002	1.000	.999	1.000	1.000
6	1.036	1.015	1.008	.992	1.002	1.006	.999	.998	1.002	1.001	.999	1.000	1.000
5	1.001	1.006	1.009	.995	.999	1.004	1.000	.998	1.001	1.001	.999	1.000	1.000
4	1.004	1.000	1.006	.993	.998	1.003	.999	.998	1.001	1.001	.999	1.000	1.000
3	1.009	1.001	1.006	.993	.997	1.003	.999	.998	1.001	1.001	.999	1.000	1.000
2	1.010	1.007	1.009	.995	.998	1.003	.999	.998	1.000	1.001	.999	1.000	1.000
1	1.000	1.012	1.011	.997	.999	1.004	1.000	.998	1.001	1.001	.999	1.000	1.000
R	1.002	1.012	1.014	.999	1.000	1.005	1.000	.998	1.001	1.001	.999	1.000	1.000

Table XLIV

Results for Example 20: summations and energy unbalances from various iterations

Q_p values

	Damping factor (1/5)											Damping factor (1/10)				
Stage	1	5	10	15	20	25	30	35	40	45	50	1	5	10	15	19
8	-716	+2029	-904	-1082	+157	+590	+189	-181	-166	-3	+66	-716	+121	+930	-18	-454
7	-48	-315	+504	-30	-280	-58	+141	+112	--	-43	-18	-48	+86	-93	+113	+80
6	-742	-668	+35	+27	-310	+279	-38	+89	+54	-13	-28	-742	-320	-551	-311	-207
5	-328	+840	+718	+631	+131	-173	-127	+15	+58	+19	-16	-1328	+1575	+917	+748	+682
4	-4563	+593	+217	+328	-8	-140	-53	+13	+42	+3	-16	-4563	-1687	-260	+73	+186
3	-1559	+748	-493	-109	+99	+58	-38	-50	-10	+15	+10	-1559	-42	+109	-165	-192
2	-1178	+455	+80	+179	+198	+77	-21	-30	--	+14	+7	-1178	-600	+285	+297	+270
1	-1758	-2416	-690	-320	-5	+55	+2	-31	-16	+6	+9	-1758	-2685	-1754	-1032	-765
R	+7400	-186	+616	+57	-99	-37	+38	+34	-1	-15	-6	+7400	+2628	+853	+557	+363
ΣQ_p	-2836	+1080	+79	-319	-117	+93	+93	-29	-39	-16	+8	-2836	-924	+436	+212	-38
Stage	$\sum_i (x_i)_p$ values											$\sum_i (x_i)_p$ values				
8	1.021	1.002	1.000	.997	.999	1.001	1.001	1.000	1.000	1.000	1.000	1.021	1.000	1.001	1.000	.999
7	1.032	1.000	1.003	.997	.997	1.000	1.001	1.001	1.000	1.000	1.000	1.032	1.000	1.001	1.000	.999
6	1.036	.999	1.006	1.000	.997	.999	1.001	1.001	1.000	1.000	1.000	1.036	1.000	1.001	1.002	1.001
5	1.001	.996	1.005	1.001	.998	.999	1.000	1.001	1.000	1.000	1.000	1.001	.998	1.000	1.002	1.001
4	1.004	1.000	1.005	1.001	.998	.999	1.000	1.001	1.000	1.000	1.000	1.004	1.000	1.000	1.002	1.001
3	1.009	1.006	1.005	1.001	.998	.999	1.000	1.001	1.000	1.000	1.000	1.009	1.000	1.000	1.001	1.001
2	1.010	1.007	1.004	1.001	.998	.999	1.000	1.001	1.000	1.000	1.000	1.010	.999	1.000	1.001	1.001
1	1.000	1.001	1.004	1.001	.998	.999	1.000	1.001	1.000	1.000	1.000	1.000	.998	1.000	1.001	1.001
R	1.002	.993	1.005	1.001	.998	.999	1.000	1.001	1.000	1.000	1.000	1.002	.996	1.000	1.002	1.001

Table XLV

Results for Example 20:
ratios (C_V/C_L) and ($\Delta L/\Delta T$) from various iterations

	1		30		60	
Stage	C_V/C_L	$\Delta L/\Delta T$	C_V/C_L	$\Delta L/\Delta T$	C_V/C_L	$\Delta L/\Delta T$
8	.125	-.0017	.097	-.0014	.096	-.0014
7	.218	-.0028	.172	-.0023	.167	-.0022
6	.311	-.0037	.244	-.0032	.237	-.0031
5	.440	-.0053	.379	-.0048	.373	-.0048
4	.332	-.0045	.177	-.0035	.172	-.0034
3	.430	-.0055	.279	-.0051	.276	-.0052
2	.515	-.0061	.361	-.0063	.358	-.0064
1	.628	-.0066	.474	-.0075	.470	-.0075
R	.973	-.0069	.988	-.0072	.967	-.0072

should behave in this manner since the two-feed equations are solved from the top of the column down, and the top-stage concentrations are obtained by back-multiplying. Any errors occurring in the lower stages thus tend to "accumulate" into the results for the top stage.

The relaxation of the stage energy unbalances, Q_p, need not have been carried as far as 60 iterations, since the last 20 to 25 iterations once again establish only the third-place figure of the flow numbers. However, the computer time required for these latter iterations is somewhat less than that for the initial iterations because of fewer trials needed for the extrapolation processes within the calculation. How far a given calculation should be carried and what damping factor should be used are matters of judgment and experience.

Example 20

Feed	F_1x_{F1}	F_2x_{F2}
C_1H_4	0.285	--
C_2H_6	0.158	--

Feed	$F_1 x_{F1}$	$F_2 x_{F2}$
C_3H_8	0.240	--
C_4H_{10}	0.169	--
C_5H_{12}	0.148	0.02
C_8H_{18}	--	1.98
	1.000	2.00

Allowable errors: same as Example 18

All equilibrium- and enthalpy-value constants same as those of Example 19.

Thermal condition of feeds same as those of Example 19.

Number of absorbing stages: (4 including vapor-feed stage).

Number of stripping stages: 4

Reboiler duty: 14000 Btu per 3.0 moles feed

Feed amounts as indicated above

Initial gradient assumptions as below:

Stage	Temperatures	Vapors	Liquids
8	100°F	0.5	2.2
7	116	0.7	2.3
6	132	0.8	2.4
5	148	0.9	2.7
4	164	0.2	2.7
3	180	0.2	2.7
2	196	0.2	2.7
1	212	0.2	2.7
R	230	0.2	2.5

All results up to this point have been obtained by using the two-feed modification of Method I mass-balance equations. To eliminate the necessity for the double-precision mode of computer calculation, Method II mass balance was tried in Example 21. It is necessary to estimate initial compositions on every stage for this approach in addition to the usual flow and temperature gradients. Mass balance without energy balance was tried first in order to obtain some idea of the convergence behavior under these conditions.

The results are shown as a temperature plot for certain stages in Fig. 46. For comparison, the Method I solution is plotted in the same figure. The totally absurd starting temperature and composition gradient used for Method II unfortunately resulted in an oscillatory behavior which appears to compare unfavorably with the behavior of Method I. What is important is that both approaches converge and, as would be expected, Method I converges at a faster rate than Method II. It will be recalled that a distrubance takes a number of iterations--roughly equal to the number of system stages--to propagate through the system, so that the rate of convergence of Method II should not be judged too harshly.

Example 21

Allowable bubble-point error: $|\epsilon_2| \leqslant 0.1^{\circ}F$

Feed, physical column, and constants as in Example 20.

Initial gradient assumptions:

	Temperature		Vapor		Liquid	
Stage	I	II	I	II	I	II
8	100°F	180°F	0.5	S	2.2	S
7	116	180	0.7	A	2.3	A
6	132	180	0.8	M	2.4	M
5	148	180	0.9	E	2.7	E
4	164	180	0.2		2.7	
3	180	180	0.2		2.7	
2	196	180	0.2		2.7	
1	212	180	0.2		2.7	
R	230	180	0.2		2.5	

The starting composition on every stage was synthesized from the two-feed streams and was as follows:

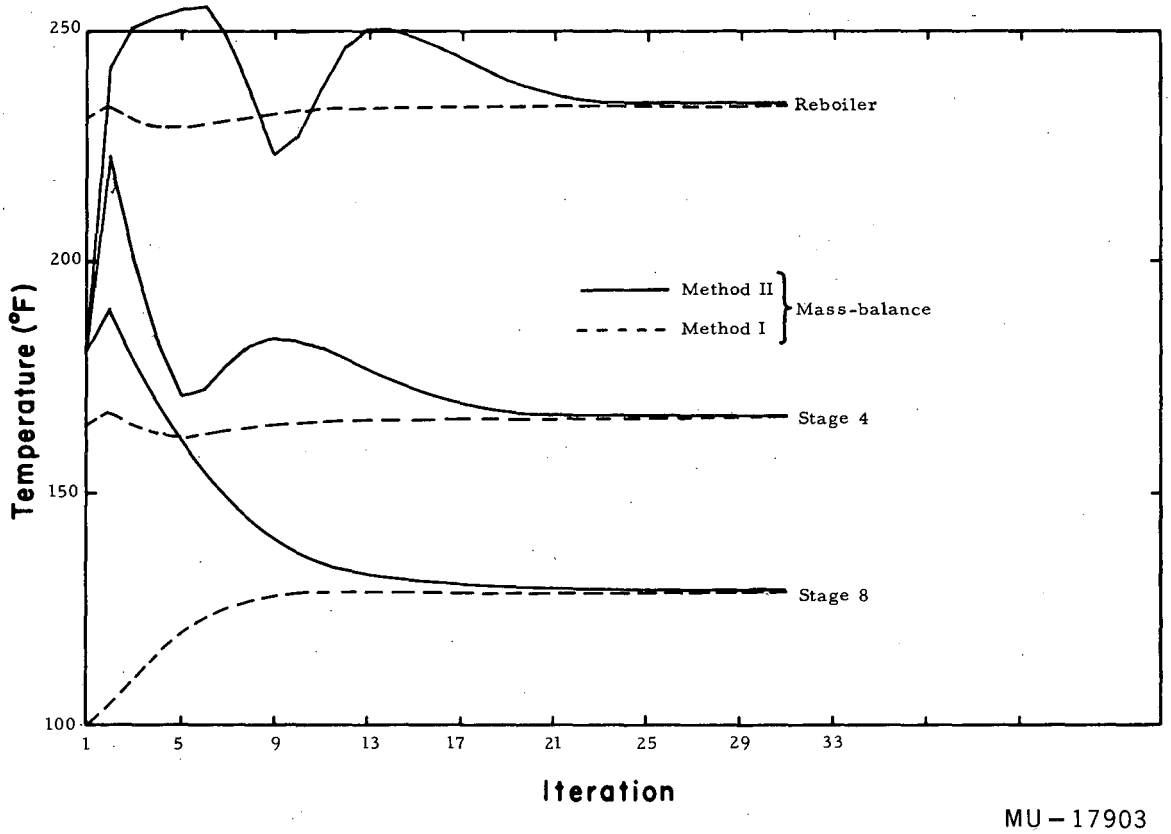


Fig. 46. Results for Example 21: comparison of results for Method I and II mass balance on reboiled absorber.

Feed	Liquid mole fraction
C_1H_4	0.0015
C_2H_6	0.0076
C_3H_8	0.0350
C_4H_{10}	0.0746
C_5H_{12}	0.2206
C_8H_{18}	0.6607
	1.0000

When Method II mass balance is combined with Method II energy balance, it must be done in a very definite pattern. The first pattern attempted was a one-to-one approach in which an energy balance was made after every material balance. This pattern failed completely even though damping factors as high as 1/200 were used. The reason for failure lies in the very slow movement of the concentrations in the mass-balance equations. With the starting conditions above, the initial concentrations and temperatures are so badly out of balance that the corrections generated in the energy-balance equations are far enough wrong that divergence quickly sets in and the problem "blows up" even with very high damping factors.

This behavior suggests a technique that would allow the Method II mass-balance equations to reduce the unbalance errors, ϵ, to a value less than some arbitrarily set small number before allowing an energy balance to be carried out. In this manner, it should be possible to avoid the divergent behavior of a one-to-one pattern, and this is what was done in Example 22. The number of iterations needed to meet the condition on ϵ should be large in the initial stages of the calculation but should reduce to its limit of one as convergence is approached. Thus, in effect, the arbitrary limitation on ϵ introduces a variable pattern into the system, since the number of mass-balance iterations per energy-balance iteration will vary from some large number to one as the calculation progresses.

The results of Example 22 are given in Figs. 47 and 48 and Tables XLVI, XLVII, and XLVIII. The "variable-pattern" technique gives

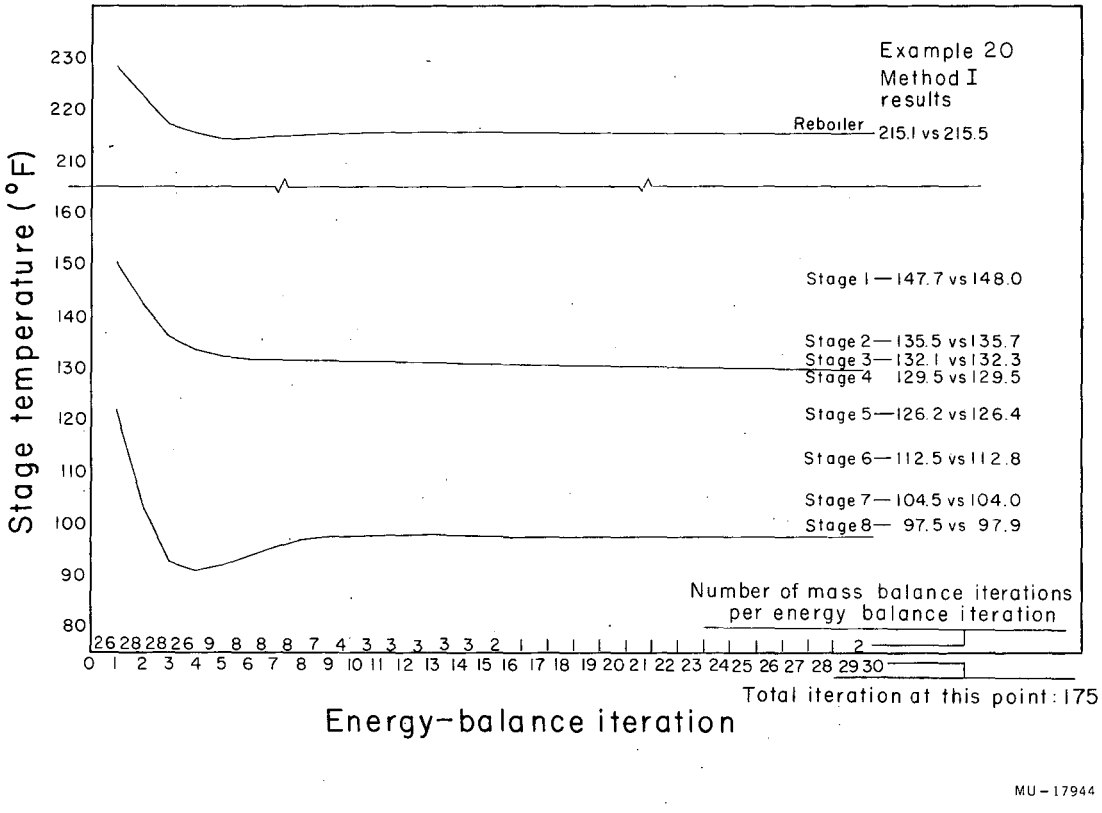


Fig. 47. Results for Example 22: temperature vs. energy-balance iteration for all stages, using a damping factor = 1/5.

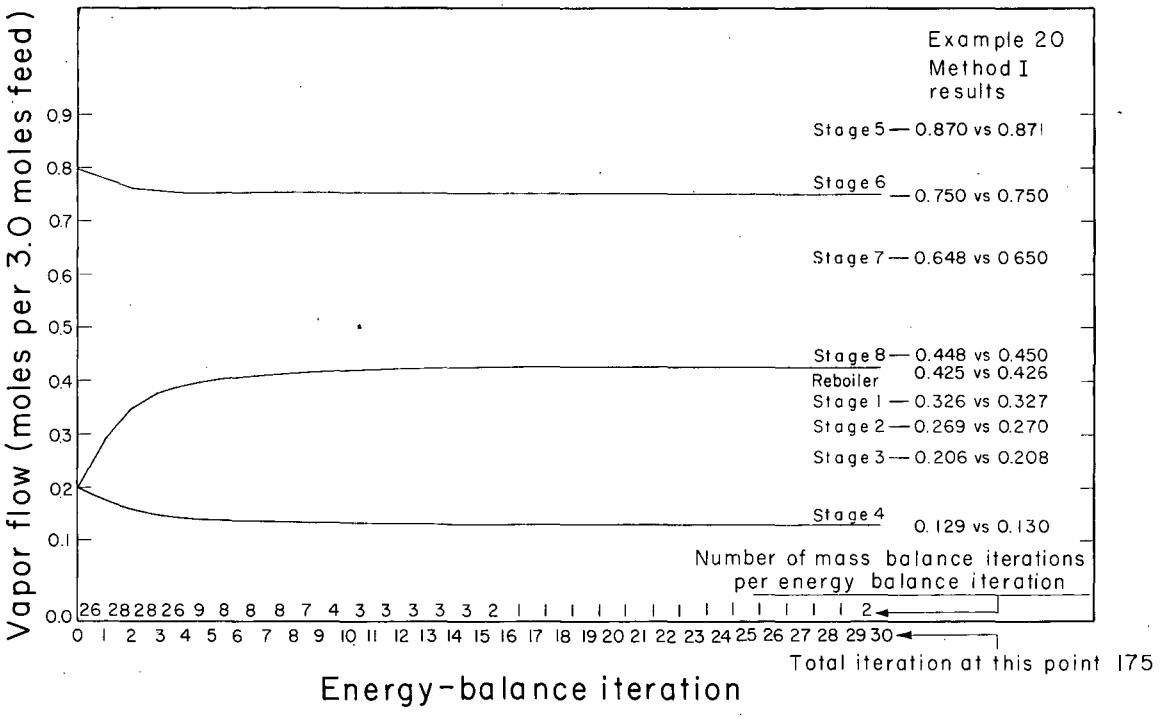


Fig. 48. Results of Example 22: vapor flow vs. energy-balance iteration for all stages, using a damping factor = 1/5.

a stable solution for this case, but at the expense of a marked increase in the number of total iterations needed for convergence. Fortunately, the mass-balance iterations are much faster than energy-balance iterations, so that the extension of computer time required by this technique is not as large as it appears. The combination of the slow-moving Method II mass balance and a damping factor of 1/5 have all but eliminated the oscillatory behavior evident when Method I mass balance is used.

Table XLVI

Results for Example 22:
top product recovery fractions from various iterations

Component	Method II values 5	10	15	20	25	30	Method I value
C_1H_4	1.005	1.000	.999	1.000	1.000	1.001	1.000
C_2H_6	.815	.822	.817	.814	.816	.815	.818
C_3H_8	.108	.124	.123	.122	.122	.122	.123
C_4H_{10}	.003	.003	.003	.003	.003	.003	.003
C_5H_{12}	.006	.006	.006	.006	.006	.006	.006
C_8H_{18}	.002	.002	.002	.002	.002	.002	.002

Table XLVII

Results for Example 22:
energy unbalances (Q_p) from various iterations

Stage	Damping factor (1/5) 1	5	10	15	20	25	30
8	-3921	+1007	+39	+55	+93	+42	+16
7	+575	-160	+9	+9	+11	+43	+25
6	+77	-730	-365	-229	-128	-54	-18
5	+2629	+819	+477	+121	+51	+13	+9
4	-5107	-1434	-550	-303	-186	-125	-24
3	-1922	+1651	+460	+212	+125	+76	+31
2	-1167	+177	+375	+202	+88	+16	+18
1	-1354	-2034	-664	-203	+28	-21	+8
R	+7196	+971	+228	+27	--	+4	--
ΣQ_p	-2995	+268	+8	-39	+26	-6	+68

Table XLVIII

Results for Example 22:
mass unbalance errors ($\epsilon x10^5$)

Stage	Component					
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_9H_{18}
8	-1.0	-11.0	-7.0	-0.2	--	+8.9
7	+2.6	-10.8	-13.0	-0.7	+0.1	+10.9
6	+4.2	-8.5	-19.4	-1.9	-0.4	+20.2
5	+4.2	-3.1	-14.7	-1.3	+0.3	+14.6
4	+2.9	+0.8	-17.0	-4.5	-0.5	+24.2
3	+3.3	+16.8	-15.7	-5.2	-1.4	+12.1
2	+1.5	+29.2	-17.3	-8.1	-1.9	+25.2
1	+0.5	+47.3	-17.9	-8.4	-6.8	-10.5
R	+0.1	+29.2	+41.1	+2.6	-2.8	-70.2

For all practical purposes, the results of the 15th energy-balance iteration could be accepted as a reasonably exact solution to the problem, with the additional iterations serving only to establish third-place figures in the flows and other variables.

Example 22

Feed, physical column, and constants as in Example 20

Starting gradients are those of Example 21, Method II

Allowable errors: same as Example 18 except bubble-point error, which was restored to $|\epsilon| \leq 0.1^{o}F$

The value below which all $|\epsilon|$ must be reduced before proceeding with an energy balance was set at 0.0009. The values of this mass-unbalance error, ϵ, existing at the 30th iteration for this example are given in Table XLVII.

The slight discrepancy of the converged temperature and flow values indicated in Figs. 44 and 45 is due mainly to the use of different values of the ϵ in the bubble-point part of the program in each case and--to a slight degree--is due to not carrying out the Method II

solution for a very large number of iterations. In any case, an exact solution can be obtained by either approach.

VI. INFINITE-MIXTURE CALCULATIONS

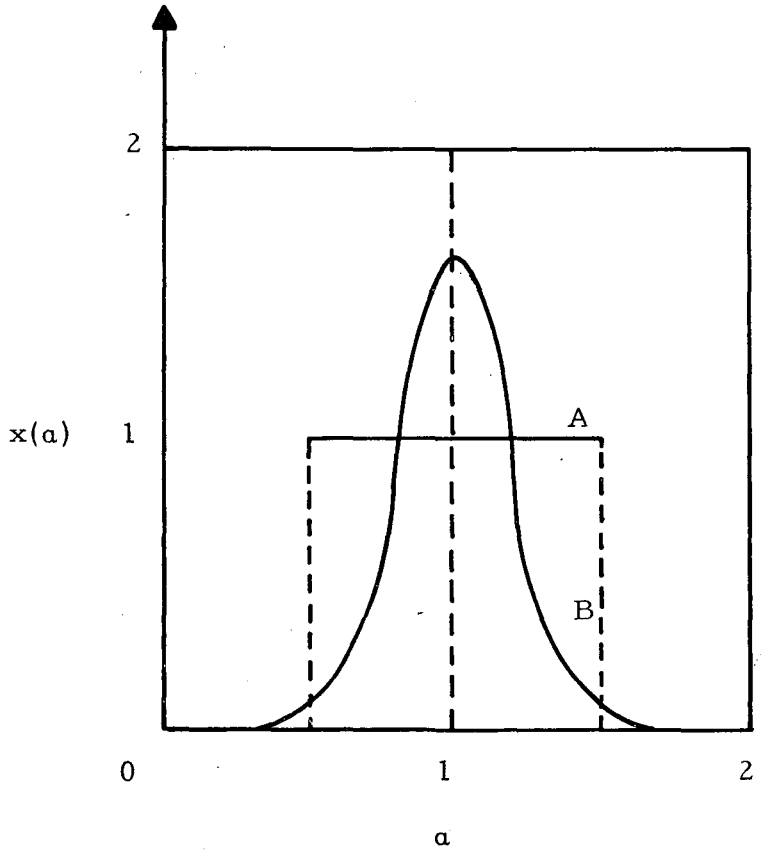
In the usual calculational approaches for multicomponent separation processes, compositions are specified by a discrete set of numbers, the mole fraction concentrations. However, it is quite possible that a continuum mixture of an indefinite number of components may compose the feed to a separation process. Mathematically, the transition to a continuum of components is essentially a formal one in which it is necessary to define a system variable in such a way that it can be integrated rather than summed.

For problems involving a continuum or infinite mixture, recourse must be had to the curve for the true boiling point (TBP) or to some other function based on this curve. Bowman[3,4] and Edmister[11] defined a function $x(\alpha)$, based on relative volatility, and showed that this function can represent mole fractions for the range of relative volatility α to $\alpha + \delta\alpha$ by the product $x(\alpha)\delta\alpha$. This approach effectively sets up α as a component-designating variable, and gives to function $x(\alpha)$ a physical interpretation as the reciprocal of the slope of the TBP curve.

Normally the function $x(\alpha)$ is continuous, as indicated in Fig. 49, which shows curves for two typical mixtures. Curve A represents a mixture containing an infinite number of components uniformly distributed with respect to (α), while Curve B represents a mixture rich in intermediate-boiling components with fast-dwindling amounts of high- and low-boiling components. A very important property of these differential representation curves is that the area under them must be unity, that is,

$$\int_0^\infty x(\alpha)\delta\alpha = 1, \qquad \text{(VI.1)}$$

which corresponds to the normal $\sum_i (x_i) = 1$. The use of this function in



MU-17946

Fig. 49. Representation of infinite-mixture function.

various distillation calculations is set forth in some detail by both Bowman and Edmister.

Another very similar approach, and--with some modification--the one used in this work, is that due to Harbert.[17] For direct use in digital computer calculation, the TBP must be put in the form of the differential curve ($\delta x/\delta T_{bp}$) versus T_{bp}, where x represents mole fraction and T_{bp} is the boiling temperature. Such a curve would provide the relation between total moles, component mole fractions, and vaporization properties required for calculations and at the same time allow characterizing infinitesimal amounts of a component by its boiling point. Thus, the mole fraction of that component whose boiling range is (T_{bp}) to ($T_{bp} + \delta T_{bp}$) is $x\delta T_{bp}$.

The TBP curve is usually available in the form of liquid volume percent distilled over plotted against column top temperature or boiling point, that is, T_{bp} vs v. It is necessary to convert this to the form of the differential curve above before calculation can be started. The basic relation used to do this is

$$\frac{\delta v/\delta T_{bp} \cdot (\rho/mw)}{\int_{T_{bp1}}^{T_{bp2}} (\delta v/\delta T_{bp}) \cdot (\rho/mw)\delta T_{bp}} = \delta x/\delta T_{bp}, \qquad \text{(VI.2)}$$

where

mw = molecular weight,

v = liquid volume percent of total mixture,

ρ = liquid density,

and the values of the derivatives are for the infinitesimal fractions of the mixture boiled over at an average temperature T_{bp}. Derivatives are, then, the inverse slope at any point of the T_{bp}-vs-v curve in the range T_{bp1} to T_{bp2}. Obviously the value of the integral in the denominator is the total moles present, and the numerator represents the infinitesimal moles of that component whose boiling point is T_{bp}. For one mole of

material, the numerator becomes identical with the mole fraction.

A typical true-boiling-point curve, together with molecular-weight and liquid-density curves, is shown in Fig. 50a, and the derived curve for $(\delta x/\delta T_{bp})$ vs T_{bp} is shown in Fig. 50b. Curve A is the basic-data curve, while Curves B and C must be estimated in some manner. These latter curves may be obtained by using the Universal Oil Products characterization factor,[37] which relates six commonly available laboratory inspections. The derived curve is then the starting point for the computer calculations. The process of obtaining this curve would be

(a) Differentiation of Curve A, with the inverse of the slopes obtained being plotted and smoothed.

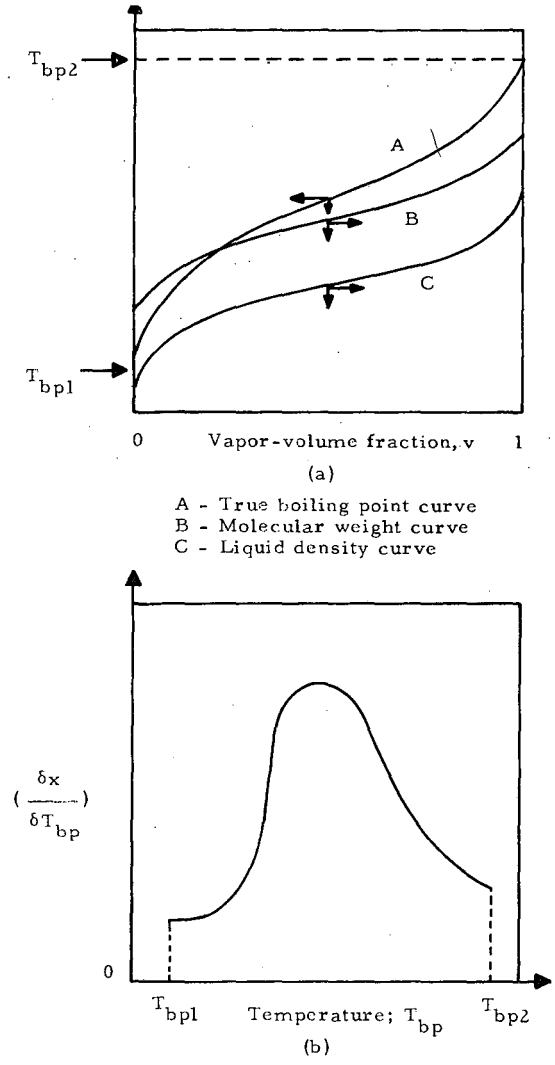
(b) Use of Curves B and C together with Eq. (VI.2) to obtain the smoothed curve for $(\delta x/\delta T_{bp})$ vs T_{bp}.

The area under the curve of Fig. 50b must meet the condition

$$\int_{T_{bp1}}^{T_{bp2}} (\delta x/\delta T_{bp})\, ST_{bp} = 1.0. \qquad \text{(VI.3)}$$

The manner in which step (a) above is accomplished is entirely arbitrary. It may be done either by analytical or graphical methods, but in this work an analytical approach was used. Rutledge[30] presented formulas for numerical differentiation based on the assumption that any give set of data can be represented by a fourth- (or lower-) power polynomial, and these formulas were used to differentiate the TBP curve. The smoothed results from this differentiation were then used in Step (b).

In order to use these slopes in multicomponent distillation calculations, equilibrium values for the hypothetical components characterized by T_{bp} are required. These may be obtained from vapor pressures, fugacities, or empirical correlations of observed equilibrium (K) values. In Example 23 (to follow), the A and B constants of the



MU-17947

Fig. 50. (a) A = true boiling point,
B = molecular weight,
C = liquid density.
(b) differentiated true boiling point.

equilibrium-value relation were determined by plotting empirical K data, given by Edmister,[10] on semilog paper. The temperature spread covered in the plot corresponds to the T_{bp1} to T_{bp2} spread, and though the lines on semilog paper were not quite straight, they were nearly enough so that they could be approximated by straight lines. Lines were plotted for a number of T_{bp} within the over-all spread, and the A and B constants from all these lines were in turn plotted vs T_{bp} and a best-fit straight line drawn through these points. The resulting plot gives the A and B constant for any component whose T_{bp} is specified within the range covered.

Since Example 23 also includes heat balances, it is necessary to know the enthalpy-value constants for these T_{bp}-characterized components. These were obtained by plotting the enthalpy data of Maxwell[25] for known hydrocarbons whose boiling points bracketed the T_{bp} spread involved. These data were plotted for two different temperatures, and a straight line was drawn through these points for extrapolation to other system temperatures. Following this, interpolated straight lines were fitted for each T_{bp} component, and the slopes of these lines then gave the desired values of the enthalpy constants, either liquid or vapor. Since Maxwell's data for enthalpy are in Btu per pound, it was converted to Btu per mole by using molecular weights obtained from Curve B of Fig. 50a. As with equilibrium data, nearly straight lines are obtained when enthalpy data are plotted, and therefore the assumption of a straight line across the system temperature spread is ordinarily quite satisfactory. Mixture enthalpies must now be obtained by integration rather than by Eqs. (I.6 and I.7), so that the enthalpy expressions become

$$h_p = \int_{T_{bp1}}^{T_{bp2}} h_{ip} \left(\frac{\delta x_i}{\delta T_{np}}\right) \delta T_{bp} \qquad \text{(VI.4)}$$

and

$$H_p = \int_{T_{bp1}}^{T_{bp2}} H_{ip} \left(\frac{\delta y_i}{\delta T_{bp}}\right) \delta T_{bp} \, . \qquad \text{(VI.5)}$$

where all terms are defined as in the Section I enthalpy expressions.

In using a slope plot for infinite mixtures, such as Fig. 50b, with Method I or II mass balance, the equations are the same as for discrete mixtures but with slopes replacing mole fractions. The equilibrium relation becomes

$$\frac{\delta y_p}{\delta T_{bp}} = K_p \frac{\delta x_p}{\delta T_{bp}}, \qquad \text{(VI.6)}$$

and a typical internal relation would be

$$\frac{(\delta y_{p-1}/\delta T_{bp})}{(\delta x_d/\delta T_{bp})} = \frac{L_p}{V_{p-1}} \left(\frac{\delta x_p/\delta T_{bp}}{\delta x_d/\delta T_{bp}} - 1\right) + 1, \qquad \text{(VI.7)}$$

but it will be noted that in these equations as well as all other equations describing the system, the differential temperature δT_{bp} drops out. The computer program for calculations using slope plots follows that of Fig. 5 with summations being replaced by integrations. Other than this replacement the programs are identical.

The normalization procedure and the reverse process of obtaining the TBP curves of the product and stage materials and the evaluation of mixture enthalpies all require integration to obtain areas under the slope curves. These must be done by the digital computer with a fair degree of accuracy, and therefore some method of numerical integration must be programmed. Integrations using the trapezoidal rule[31] and Gaussian quadrature formulas[31] were tried but discarded because of the necessity of breaking up the T_{bp} range into too many increments to get the accuracy desired. The best compromise finally adopted was the use of Simpson's Rule,[31] with the number of characterizing components being arbitrary and with the condition imposed on values of

$$\int_{T_{bp1}}^{T_{bp2}} (\delta x/\delta T_{bp})\delta T_{bp}$$

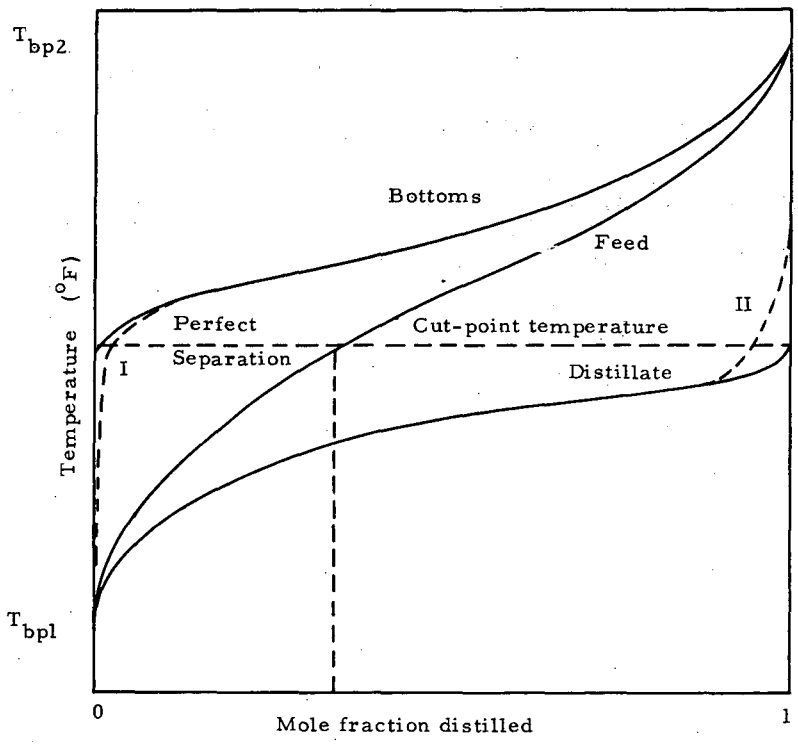
at convergence being of the same order as for discrete components. As a rough approximation, the number of characterizing components is

usually chosen in such a way that the temperature gap between any two adjacent components is of the order of 15 to 20 degrees, and the total number must be odd for use with Simpson's Rule.

The net result of the fractionation process of infinite mixture feeds is to produce a series of curves similar to that of Fig. 50b, with the peaks moving upward and to the left in the enriching section and upward and to the right in the stripping section. These curves in turn would integrate into true-boiling-point curves located below that of the feed for enriching-section liquids and above that of the feed for stripping-section liquids. The limit of this resolution process would be a pure component (at one or both ends of the column) requiring a peak of infinite height in the slope-curve representation and having a horizontal line for a true-boiling-point curve. Of course, no practical column will ever approach this condition.

A perfect separation for an infinite-mixture feed would be two (or more) products whose ending and beginning boiling points exactly coincided as indicated in Fig. 51. In actual practice, this ideal is never reached, since theoretically the ends of the TBP curves of the products must all coincide with T_{bp1} or T_{bp2}, as indicated by Curves I and II of Fig. 51. This behavior will have some affect on the decision of what temperature increment to use between any two adjacent components, since the region where reasonably good accuracy is desired is that for the boiling curves I and II. It is quite possible to break up integrations into two regions with an arbitrary temperature increment within each. The technique used in a given case is a matter of judgment and experience.

The laboratory inspection of a given product is more often an ASTM[37] distillation curve, and the end points of this type of curve would appear respectively above and below the bottoms and distillate cut-point temperature of Fig. 51, with a resulting gap between ending- and starting-product temperatures. This behavior results because ASTM distillations tend to average the product temperatures.



MU-17948

Fig. 51. Typical true-boiling-point curves.

The combination of infinite-mixture calculations using Method I mass-balance equations and Method I energy-balance equations will always give product compositions as true-boiling-point curves. However, these curves should really be interpreted in terms of their equivalent ASTM curves when conclusions are being drawn as to separation achieved and cut-point temperatures since, as pointed out above, most laboratory inspection of products is done in terms of ASTM distillations.

True-boiling-point curves with plateaus representing discrete amounts of a given component can easily be handled by a combination of the method presented in this Section and the methods for discrete components given in Section II This means that both integrations and summations must be done in a given calculation. Other than increasing the complexity of a calculation, mixed feeds present no additional difficulties.

The results of Example 23 are given in Table XLIX and Figs. 6, 7, 8, and 9. The feed for this problem (shown in Fig. 54), was arbitrarily broken up into 17 characterizing components, including the two limits of T_{bp}, so that the increment between components was 20°F. As can be seen, convergence was quite rapid without a ϕ factor, and the use of the ϕ factor actually retarded the convergence of the internal stages of the column. This behavior of the ϕ factor was encountered in strippers when the double flow correction, which converged very fast without ϕ, was used. In that case, the use of ϕ actually caused divergence.

Figures 52 and 53 show the converged values of temperatures and flows for all stages, and the complete plots for only certain stages that are indicative of the general behavior of the other stages. Figure 54 is interesting because it gives the slope curves for the components at all the system stages. When dealing with infinite mixtures, it is possible to visualize a distillation surface, such as that shown, which is a unique surface for any combination of feed, physical column, temperatures, and flows. This surface is shifted about by the mass- and energy-balance equations, with the restriction that the integrated areas under all slope curves must be $1 \pm \epsilon$, where ϵ is some arbitrarily

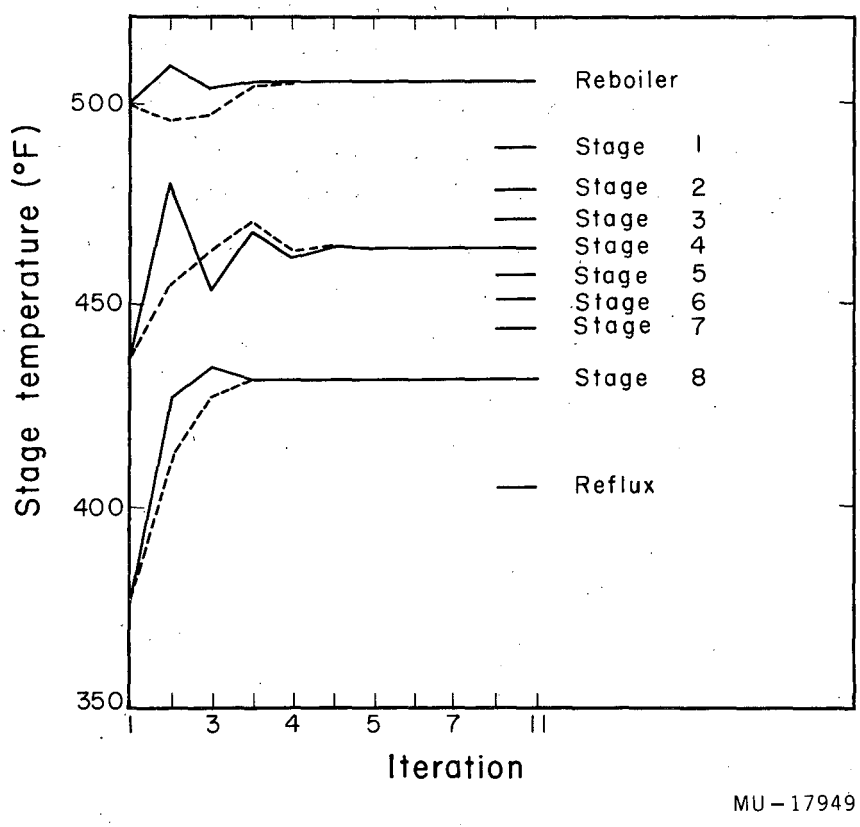
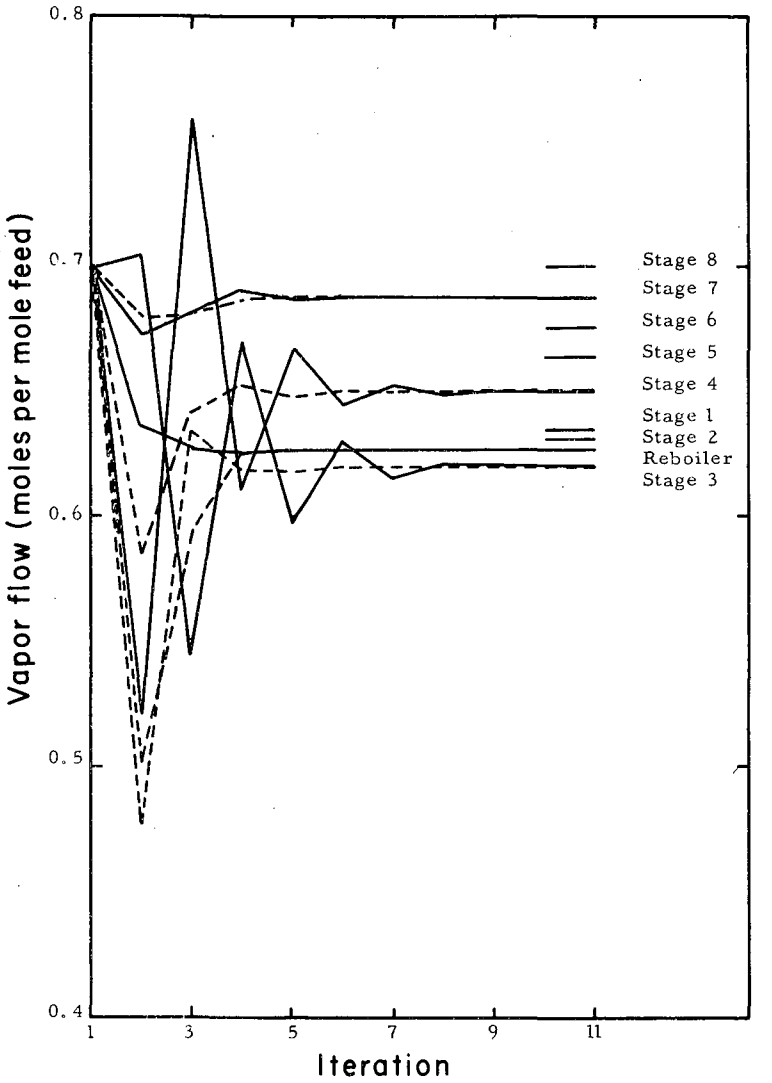


Fig. 52. Results for Example 23: temperature vs. iteration for all stages.
—— Φ factor.
--- no Φ factor.



MU-17950

Fig. 53. Results for Example 23: vapor flow vs. iteration for all stages.
—— Φ factor.
--- no Φ factor.

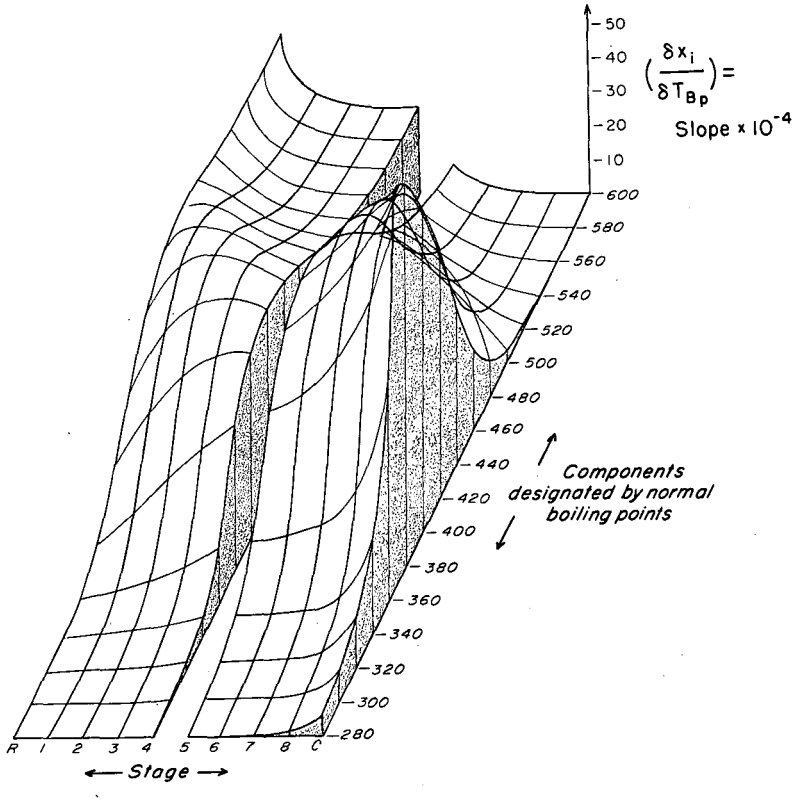


Fig. 54. Results for Example 23: slope vs. stage-component network for all stages.

predetermined small number. The shifting of the peaks of the slope curve upward and to the left is quite evident in the enriching section of the column, while the shifting of the peaks upward and to the right is not nearly so pronounced in the stripping section. This behavior is to be expected because of the shape of the feed-slope curve and the point of introduction of feed into the column.

Figure 55 gives the integrated TBP curves for the liquid products from various stages of the system, and includes the feed curve for reference purposes. Since a bulk split of 40% top product was set and held, the perfect separation or cut temperature would be approximately 432°F for the feed used. That this was not achieved is quite evident, but in terms of the equivalent ASTM distillation curves of the products, the overlap would be appreciably diminished. There are, however, ways in which the TBP separation could be improved. The reflux ratio for this example is quite low and the number of stages is quite small, while in crude-oil columns, where infinite-mixture feeds generally occur, both the stages and reflux ratio would be appreciably above those used here. Increasing both these quantitites would definitely improve the separation obtained.

It is possible, then, by means of the calculational techniques presented here and those of previous sections to simulate a crude-oil distillation column on a computer, and to obtain reasonably accurate predictions of the compositions of the streams at every point in the system as well as the stream amounts and stage temperatures.

Table XLIX

Results for Example 23: individual stage integrals from nine iterations

	1		2		3		4		5		6		7		8		9	
Stage	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ	Φ	No Φ
8	.945	1.217	1.030	1.086	.996	.986	1.001	.997	1.001	1.001	1.001	1.000	1.001	1.001	1.001	1.000	1.001	1.001
7	.905	1.238	1.065	1.076	.990	.970	1.001	.993	1.001	1.001	1.000	1.000	1.001	1.000	1.001	1.000	1.001	1.000
6	.847	1.208	1.113	1.062	.978	.967	1.003	.995	1.001	1.000	1.000	1.000	1.001	1.000	1.001	1.000	1.001	1.000
5	.785	1.146	1.188	1.046	.955	.976	1.015	.998	.998	1.001	1.001	1.000	1.001	1.000	1.001	1.000	1.001	1.000
4	2.782	1.205	.997	1.163	.922	.978	1.042	.993	.980	1.004	1.008	1.000	.997	1.001	1.001	1.000	1.000	1.001
3	2.687	1.289	1.117	1.175	.906	1.010	1.028	.985	.993	1.005	1.000	1.000	1.000	1.000	1.000	1.001	1.000	1.001
2	2.423	1.291	1.138	1.128	.936	1.027	1.009	.988	1.000	1.003	.999	1.001	1.000	1.000	1.000	1.001	1.000	1.001
1	1.806	1.085	1.086	1.021	.972	1.017	1.001	.994	1.001	1.001	.999	1.001	1.000	1.000	1.000	1.000	1.000	1.001
R	1.000	.720	1.000	.856	1.000	.973	1.000	.994	1.000	.998	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Φ factor	.2658	--	1.5798	--	.8430	--	1.0739	--	.9759	--	1.0102	--	.9974	--	1.0022	--	1.0001	--
ΔQ_{es}	26709	25543	27207	26697	26976	26984	26993	26972	26997	26989	26995	26994	26994	26996	26994	26996	26994	26996
ΔQ_{ss}	-14484	-15650	-13986	-14496	-14216	-14209	-14200	-14220	-14196	-14203	-14198	-14199	-14198	-14197	-14198	-14197	-14198	-14197

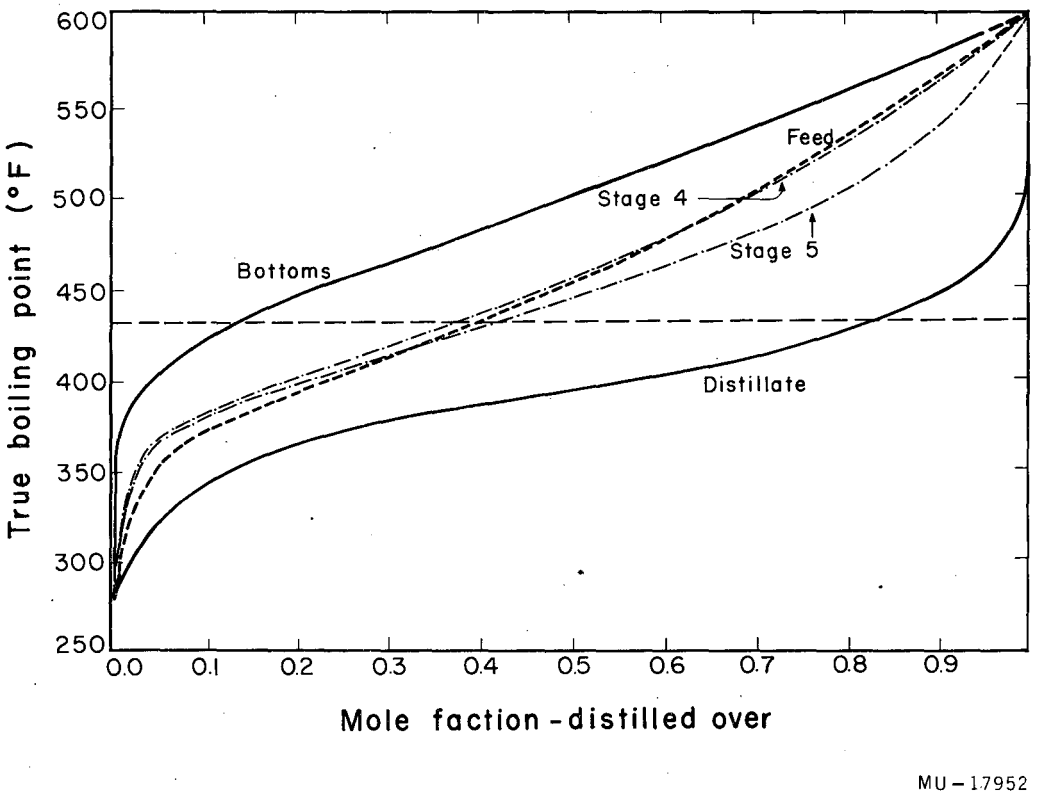


Fig. 55. Results for Example 23: selected TBP product curves.

Example 23

Component characterizing temperature, T_{bp}	Feed-slope value ($\delta x/\delta T_{bp} \times 10^4$)	Equilibrium-value constants		Enthalpy-value constants			
		A	B	k	l	u	w
280°F	2.739	-5375	8.055	71.12	-32844	55.30	-6700
300	4.084	-5760	8.285	75.47	-35719	58.00	-7050
320	6.225	-6160	8.515	77.84	-36738	61.00	-7470
340	11.056	-6560	8.750	81.40	-38307	64.00	-7885
360	24.602	-6960	8.980	84.24	-39528	67.00	-8300
380	50.199	-7350	9.205	88.32	-41588	70.30	-8820
400	51.295	-7750	9.435	92.38	-43657	73.70	-9360
420	50.000	-8145	9.565	95.00	-44464	77.20	-9900
440	46.813	-8545	9.900	98.07	-45443	81.00	-10600
460	42.530	-8945	10.130	101.82	-47021	84.70	-11230
480	38.546	-9345	10.360	106.38	-49311	88.90	-12040
500	34.960	-9745	10.585	110.92	-51606	93.00	-12800
520	32.171	-10140	10.820	115.44	-53622	97.30	-13620
540	30.528	-10540	11.050	119.31	-55289	101.7	-14530
560	29.681	-10940	11.280	123.69	-57201	106.2	-15420
580	29.233	-11335	11.510	128.00	-59071	110.8	-16270
600	28.984	-11735	11.740	132.24	-60900	115.1	-16970

Thermal condition of feed: saturated liquid

Column pressure: 1 atmosphere

Reflux temperature: bubble point

Reflux amount: 0.3 mole per mole feed

Top-product amount: 0.4 mole per mole feed

Enriching stages: 4(not including feed stage)

Stripping stages: 4(including feed stage)

Total condenser used with equilibrium reboiler

Allowable error limits:

Integration: $|\epsilon| \leqslant 1 \times 10^{-3}$

Bubble point: $|\epsilon_2| \leqslant 0.1^{\circ}F$

Initial gradient assumptions:

Stage	Temperature	Flows	
		Vapor	Liquid
8	377°F	0.7	0.3
7	390	0.7	0.3
6	407	0.7	0.3
5	422	0.7	0.3
4	436	0.7	1.3
3	453	0.7	1.3
2	467	0.7	1.3
1	483	0.7	1.3
R	500	0.7	0.6

VII. EFFECT OF NONIDEALITY IN MULTISTAGE CALCULATIONS

The equilibrium values used in calculations presented up to this point have been empirical ones based on general correlations available in the literature. These equilibrium or K values are correlated as functions of temperature and pressure, and as usually presented are in no way dependent upon composition. The composition dependence can be disregarded if the assumption of ideal behavior is postulated for the liquid phase, and this assumption is generally a good one for paraffinic and olefinic hydrocarbon mixtures. However, for mixtures containing aromatic hydrocarbons, water, alcohols, etc., the departure from ideal behavior in the liquid phase is pronounced enough so that it must be accounted for in some manner. It is the purpose of this section to present a method for doing this and to show how this method can be used with the calculational methods of Section II.

As Robinson and Gilliland,[28] Perry,[26] and others[22,36] have shown, departures from ideal conditions may occur in both the vapor and liquid phases under certain specified conditions. Vapor-phase departures occur at high pressures because the volume and molecular-force effects become large enough to preclude ideal gas behavior and therefore fugacity replaces pressure in the vapor-liquid relationship. The Lewis and Randall fugacity rule[36] is normally used for mixtures in the vapor phase, so that the fugacity of component i is

$$f_{Vi} = y_i f_{\pi i}, \qquad \text{(VII.1)}$$

where $f_{\pi i}$ is the fugacity of the pure component at the same temperature and pressure as the mixture.

Deviations from the ideal solution laws are more important for the liquid phase than for the vapor phase because they occur even at low pressures and their magnitudes are larger. In the dense liquid phase, the molecular volumes and intermolecular forces are always significant and lead to at least two main types of deviations, such as

(a) those resulting because vapor does not obey the perfect gas law,

(b) those due to special phenomena connected with the liquid phase, such as chemical association.

Robinson and Gilliland have shown that Type a deviations can be calculated by an equation of the form

$$f_{Li} = x_i \, f_{pi} \exp\left[\bar{v}_i \, (\pi - P_i)/RT\right], \qquad \text{(VII.2)}$$

where f_{Li} = fugacity of component i in the liquid phase,

f_{pi} = fugacity of pure liquid i under its own vapor pressure,

$\bar{v}_i$ = partial molal volume of component i,

π = total system pressure,

P_i = vapor pressure of component i at the temperature of the mixture,

T = absolute temperature,

R = gas law constant.

Type b and other liquid-phase deviations can be summed up in what is termed an activity coefficient, which is a term inserted in the fugacity equality at equilibrium, as follows:

$$f_{Vi} = f_{Li}$$

or

$$y_i \, f_{\pi i} = \gamma_i \, x_i \, f_{pi} \exp\left[\bar{v} \, (\pi - P_i)/RT\right]. \qquad \text{(VII.3)}$$

In this manner, pure liquids before mixing serve as a reference base, and deviations resulting from mixing are accumulated as the departure factor or activity coefficient γ. The general expression relating vapor- and liquid-phase mole fractions becomes

$$\frac{y_i}{x_i} = \gamma_i \left\{ \frac{f_{pi}}{f_{\pi i}} \exp\left[\bar{v}_i \, (\pi - P_i)/RT\right] \right\} = K, \qquad \text{(VII.4)}$$

where K is the normal equilibrium constant. The fugacities in this expression can be determined in various ways, such as from generalized plots or from various equations of state, and the exponential term requires partial molal volume data. No matter what form the expression takes for these quantities, a K value calculated from them would cause no difficulties in the mass-balance methods of Section II, since these expressions are essentially independent of composition. The γ term, however, is composition-dependent, since it involves molecular interactions, and the effect on the fractionation calculations of this composition dependence is what is of interest.

In the presentation to follow, then, the system pressures are assumed low enough that fugacity becomes identical with pressure, and under these conditions Eq. (VII.4) reduces to

$$\bar{p}_i = y_i \pi = \gamma_i P_i x_i , \qquad \text{(VII.5)}$$

where $\bar{p}_i$ = partial pressure of component i.

This form of equation is quite suitable for studying the effect of γ_i on the fractionation calculations, and the ideal equilibrium value P_i/π becomes the modified value

$$K_{MODIFIED} = \gamma_i K_{IDEAL} = \left[\gamma_i \left(\frac{P_i}{\pi}\right)\right] . \qquad \text{(VII.6)}$$

There have been many proposals of methods for calculating the activity coefficient; probably the most widely used are those of Margules[24] and van Laar.[21] More recent methods proposed are those due to Scatchard and Hamer,[32] Redlich and Kister,[27] Wohl,[39] and others. The method used by Wohl in his derivation of the ternary and quaternary three-suffix Margules equations was used to derive a three-suffix Margules equation for N components. Similar N-component equations can be derived for the van Laar approach as well as the other approaches, but the Margules equation is simplest in application and is quite adaptable to use with digital computers. The three-suffix Margules equation proposed here is, then, for component a in a mixture of N components, where a = 1, 2, 3,... N as follows:

$$\ln\gamma_a = 2x_a \sum_{i=1}^{N} x_i A_{ia} + \sum_{j=1}^{N} (x_j)^2 A_{aj} + \frac{1}{x_a} \sum_{\substack{j=1 \\ a\neq j\neq k \\ a\neq k \\ j<k}}^{N} \sum_{k=1}^{N} x_a x_j x_k A^*_{ajk} -$$

$$2\sum_{i=1}^{N} [(x_i)^2 \sum_{j=1}^{N} x_j A_{ij}] - 2 \sum_{\substack{i=1 \\ i\neq j\neq k \\ i\neq k \\ j<k}}^{N} \sum_{j=2}^{N} \sum_{k=3}^{N} x_i x_y x_k A^*_{ijk}. \qquad \text{(VII.7)}$$

This equation can be written in symbolic form as

$$\ln \gamma_a = 2x_a\omega_{ia} + \psi_{aj} + \frac{1}{x_a} \nu_{ajk} - 2\eta - \mu, \qquad \text{(VII.8)}$$

and one can show

$$\mu = 2/3 \sum_{i=1}^{N} \nu_{ajk} \qquad \text{(VII.9)}$$

The implied definitions of the functions (ω_{ia}, ψ_{aj}, ν_{ajk}, η, and μ) is obvious, and the latter two, η and μ, are actually constants applying to all γ values calculated. The above equations show the dependence of γ values on composition as well as binary interaction data A_{ij} and A^*_{ijk}, where the latter term as defined as actually dependent on binary interaction data as follows:

$$A^*_{ijk} = 1/2\ (A_{ij} + A_{ji} + A_{ik} + A_{ki} + A_{jk} + A_{kj}) + C^*_{ijk} \qquad \text{(VII.10)}$$

The term C^*_{ijk} represents actual ternary data, and normally these data are not available. Following Wohl, then, this term is set equal to zero, and there is some justification for this on the basis of meager data available, which indicate the magnitude of the term to be quite small.

The following suffix permutation relation holds,

$$A^*_{ijk} = A^*_{jki} = A^*_{kij}$$

so that the number of A^* terms that exist for N components is $[\frac{N!}{(N-3)!3!}]$ which implies a minimum value of 3 for N.

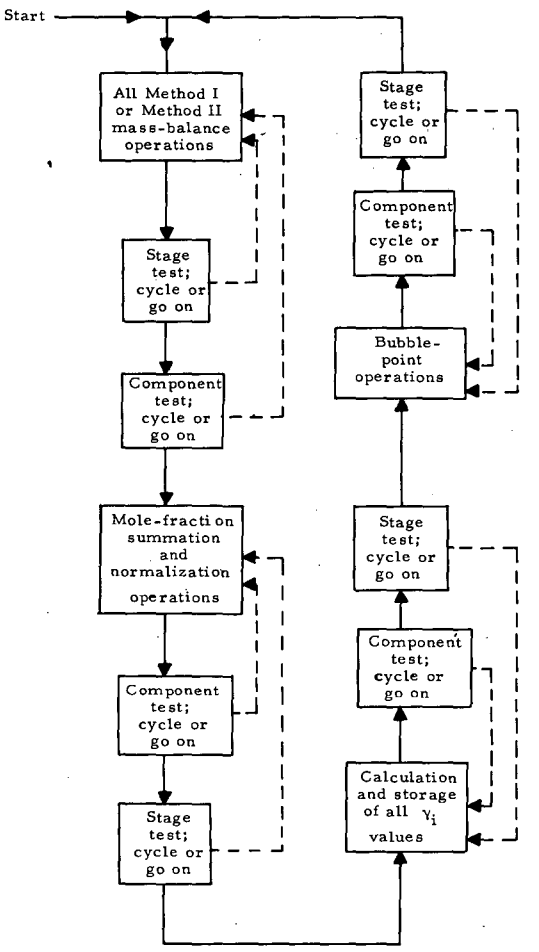
Thus, if binary-interaction data are available for all the binary pairs possible in a mixture of N components, it is possible to calculate the activity coefficient for any component as a function of composition and these binary-interaction constants, A_{ij}. The individual values of A_{ij} are the limits of ln γ_i as x_i approaches 0 in a mixture of j and i; that is, they are the terminal values of ln γ_1. Similarly, the A_{ji} value would be the limit of ln γ_i as x_j approaches 0. In actual use, the A_{ij} data are stored in a computer as a two-dimensional i,j array from which ω_{ia} terms are obtained as row summations and ψ_{aj} terms as column summations. The η term is the sum of $(x_i)^2$ terms times the ω_{ia} terms, and the μ term is obtained by Eq. (VII.9) involving ν_{ajk} terms. These latter terms are derived from a special two-dimensional array of A^*_{ijk} terms made in accordance with the limitations on the suffix combinations indicated in Eq. (VII.7). By use of this special array, the ν_{ajk} terms become column summations.

The over-all calculation involves the use of either Method I or Method II mass-balance equations in which $K_{MODIFIED}$ values from Eq. (VII.6) are used. Following this, a bubble-point calculation is made to correct the stage temperatures, and the bubble point-relation used is

$$\sum_i K_{MODIFIED} (x_i)_{NORMALIZED} = 1.0. \qquad \text{(VII.11)}$$

When new temperatures have been obtained, the next step in the calculation is to use the mass-balance equations for another iteration. A schematic computer program for doing one iteration is shown in Fig. 56.

Treybal[36] and others have pointed out the dependence of the γ value on temperature and noted that data on partial molal heat of solution are needed to calculate the change in γ value with temperature. These heat-of-solution data are also required if any attempt is made to make energy balances and flow corrections for a given system. Such data are not generally available and therefore, for calculations done in this work, the temperature dependence of γ was neglected and constant molal overflow was assumed.



MU-17953

Fig. 56. Schematic computer program using activity coefficient, γ_i.

One of the primary advantages of calculations using modified K values is that they predict the formation of azeotropes which cannot be predicted in any other way. The formation of these azeotropes at some point in a distillation column is much more a function of composition than of flows, and therefore the neglect of flow changes that would result from energy balances is reasonable even if not rigorously justifiable. If heat-of-solution data and other energy data were available, energy balances could easily be made by the methods of Section III with appropriate modifications.

In Example 24, a ternary solution of ethyl alcohol, propyl alcohol, and water is fed to a column similar to that of Fig. 4 and containing four stages plus an equilibrium reboiler with saturated liquid feed entering at Stage 2. Method I mass-balance equations were used and the results are shown in Table L and Figs. 57 and 58. The setting of the bulk split in this and subsequent problems in this section was purely arbitrary; the only purpose of the problem was to ascertain the behavior of the mass-balance equations with values of $K_{MODIFIED}$. It is not to be inferred that the separations obtained represent any practical solution to the separation problem proposed. However, the calculational techniques given here can be used for studying separations obtainable by varying the available independent variables for a given system.

As can be seen from the results of Example 24, the convergence is not as fast as that using empirical K values. However, if enough iterations are run, an exact solution is available.

Example 24

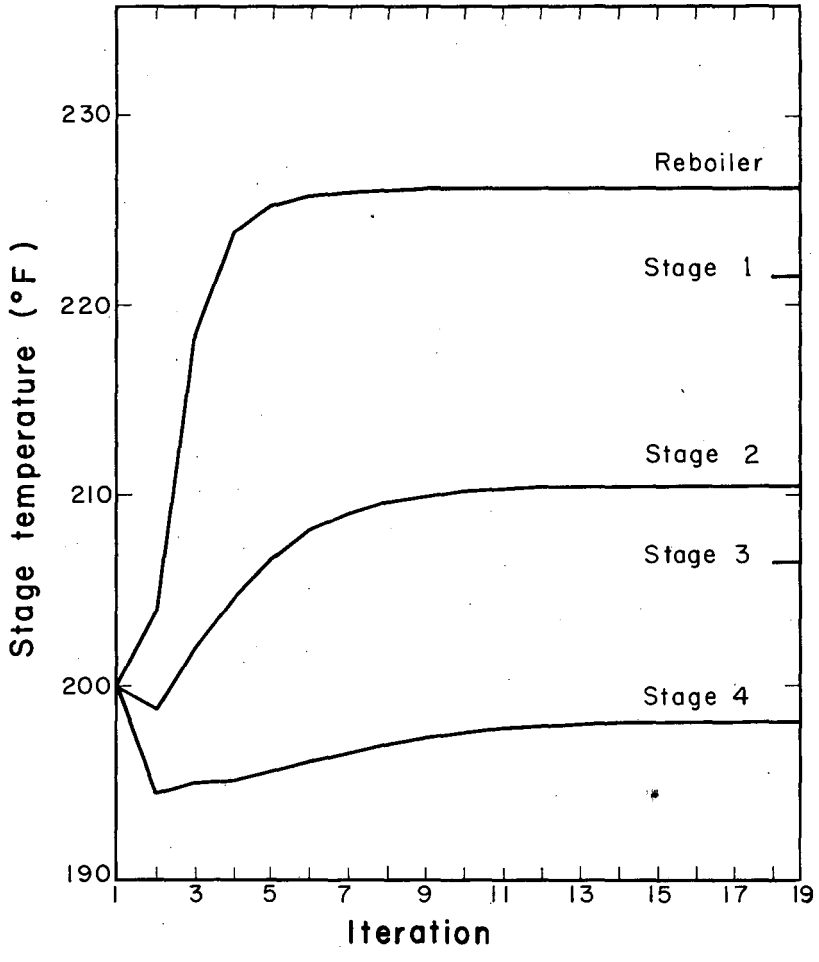
Feed	Fx_F	Vapor-pressure constants* A	B
C_2H_5OH	0.239	-7319.2	15.4563
C_3H_7OH	0.045	-8076.3	15.9924
HOH	0.716	-7450.9	14.8618
	1.000		

*These constants were obtained in the usual manner and used in the equation

Table L

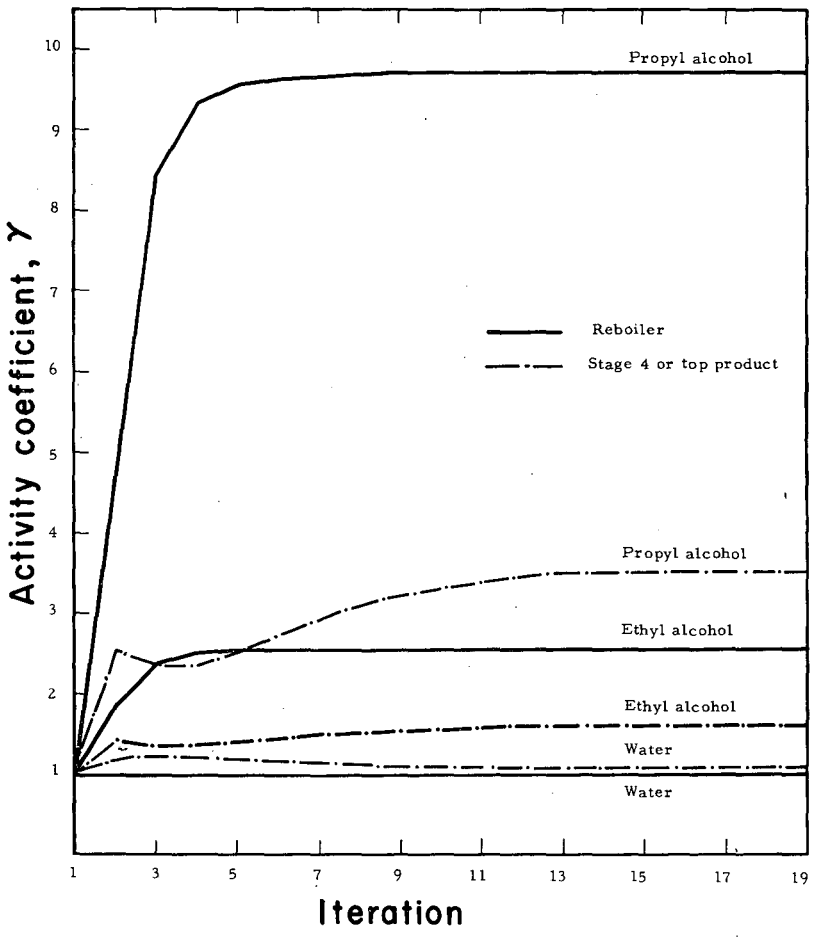
Results for Example 24: summations and top-product recovery fractions from various iterations

	Stage summations $\sum_i (x_i)_p$												
Stage	1	2	3	4	5	6	7	8	10	12	14	16	18
4	.708	.799	.884	.947	.978	.994	1.001	1.003	1.003	1.002	1.001	1.000	1.000
3	.845	.850	.920	.983	1.011	1.019	1.018	1.014	1.007	1.003	1.001	1.000	1.000
2	.978	.924	.974	1.014	1.022	1.018	1.013	1.009	1.004	1.002	1.001	1.000	1.000
1	1.088	.982	1.042	1.054	1.040	1.028	1.018	1.012	1.005	1.002	1.001	1.000	1.000
R	1.410	1.195	1.118	1.073	1.047	1.031	1.020	1.013	1.005	1.002	1.001	1.000	1.000
Component	Top-product recovery fraction												
Ethyl alcohol	1.152	1.129	1.094	1.054	1.030	1.015	1.005	.999	.992	.989	.988	.987	.987
Propyl alcohol	.357	1.165	1.121	1.073	1.045	1.028	1.018	1.010	1.003	1.000	.998	.998	.998
Water	.291	.248	.263	.279	.289	.295	.299	.301	.304	.305	.306	.306	.306



MU-17954

Fig. 57. Results for Example 24: temperature vs. iteration for all stages.



MU-17955

Fig. 58. Results for Example 24: activity coefficient vs. iteration for selected stages.
—— reboiler.
--- stage 4 or top product.

$$\ln P_i = \frac{A_i}{T} + B_i$$

to obtain values of P_i.

Thermal condition of feed: saturated liquid

Column pressure: $\pi = 20$ psia (assumed constant)

Reflux amount: 0.5 mole per mole feed

Top product amount: 0.5 mole per mole feed

Enriching stages: 2(not including feed stage)

Stripping stages: 2(including feed stage)

Total condenser used;

Equilibrium reboiler used

Allowable bubble-point error: $|\epsilon_2| \leqslant 0.1^{\circ}F$

Binary interaction constant array

i	1	2	3
j	Ethyl alcohol	Propyl Alcohol	Water
Ethyl alcohol	A_{11} = 0.00	A_{21} = 0.00	A_{31} = 1.05
Propyl alcohol	A_{12} = 0.00	A_{22} = 0.00	A_{32} = 1.05
Water	A_{13} = 0.95	A_{23} = 2.30	A_{33} = 0.00

Three-suffix constant

$A^*_{123} = A^*_{231} = A^*_{312} = 2.675$

These data were estimated from information available in Treybal[36] and Horsley.[18]

Initial-gradient assumptions

Stage	Temperature	Flows Vapor	Flows Liquid
4	200°F	1.0	0.5
3	200	1.0	0.5
2	200	1.0	1.5
1	200	1.0	1.5
R	200	1.0	0.5

In Example 25, the same feed was fed to Stage 5 of a 10-stage column with the top product amount cut to 0.3 mole per mole feed and a reflux ratio of 1.0 maintained. The results are given in Table LI and Figs. 59 and 60; and indicate that an oscillatory behavior in the early iterations is possible and quite pronounced. Fortunately, it does damp out and an exact solution becomes possible, but some doubt is raised as to the behavior of the Method I mass-balance approach with larger numbers of stages present in the column.

Example 25

Same feed, vapor pressure constants, binary interaction, and three-suffix constants as Example 24. Column conditions are the same except for

Enriching stages: 5(not including the feed stage)
Stripping stages: 5(including the feed stage)
Reflux amount: 0.3 mole per mole feed
Top-product amount: 0.3 mole per mole feed

For initial gradients all temperatures were set at 200°F, $L/V = 0.3/0.6 = 0.5$ in the enriching section, and $V'/L' = 0.6/1.3 = 0.462$ in the stripping section.

The results of Example 25 further indicate that as more stages are added and the bottom product shifts toward higher water content, oscillations of the propyl alcohol activity coefficient show up and the values of the coefficient become large. The oscillations are quite marked at first, but finally damp out. The temperature profile for the system based on the split set indicates that stripping stages in the area of the feed stage are doing very little fractionation, while the last stage and the reboiler are doing a relatively large amount of fractionation. This large movement at one end of the column apparently is the major cause of the initial large oscillation, which fortunately then damps out.

Even though the bulk split and flow gradients set do not give an efficient column (as evidenced by the presence of several stages where

Table LI

Results for Example 25: summations and top product recovery fractions from various iterations

	Stage summations $\sum_i (x_i)_p$														
Stage	1	3	5	7	9	10	13	15	17	19	21	23	25	27	29
10	.602	1.049	1.093	.975	.977	1.018	.996	1.003	1.000	.995	1.003	1.001	.998	1.000	1.000
9	.681	.994	1.101	.965	.978	1.013	.996	1.004	1.000	.995	1.003	1.001	.999	1.000	1.000
8	.766	.941	1.101	.956	.988	1.007	.995	1.004	1.001	.995	1.002	1.001	.999	1.000	1.000
7	.846	.928	1.063	.960	.998	1.006	.992	1.004	1.002	.996	1.001	1.001	.999	1.000	1.000
6	.917	.948	1.021	.973	1.003	1.008	.992	1.001	1.003	.998	1.001	1.000	1.000	1.000	1.000
5	.979	.981	1.024	.997	.993	1.009	.998	.999	1.002	.999	1.000	1.001	.999	1.000	1.000
4	.977	.963	1.043	1.012	.973	1.014	1.000	.996	1.003	.998	1.000	1.001	.999	1.000	1.000
3	.975	.938	1.048	1.042	.964	1.013	1.007	.993	1.004	.998	.999	1.003	.999	1.000	1.001
2	.980	.918	1.028	1.074	.958	1.005	1.013	.993	1.004	.998	.998	1.003	.999	.999	1.001
1	1.018	.925	.990	1.064	.971	.996	1.012	.995	1.002	1.000	.997	1.002	1.000	.999	1.000
R	1.189	.974	.960	1.011	1.005	.992	1.002	.999	1.000	1.002	.999	1.000	1.001	1.000	1.000
Component	Top-product recovery fraction														
Ethyl alcohol	.850	.826	.776	.713	.772	.771	.756	.757	.757	.761	.761	.758	.758	.760	.759
Propyl alcohol	.167	.893	.830	.565	.760	.788	.725	.735	.732	.738	.748	.735	.734	.741	.739
Water	.125	.087	.108	.146	.114	.112	.121	.120	.120	.119	.118	.120	.120	.119	.119

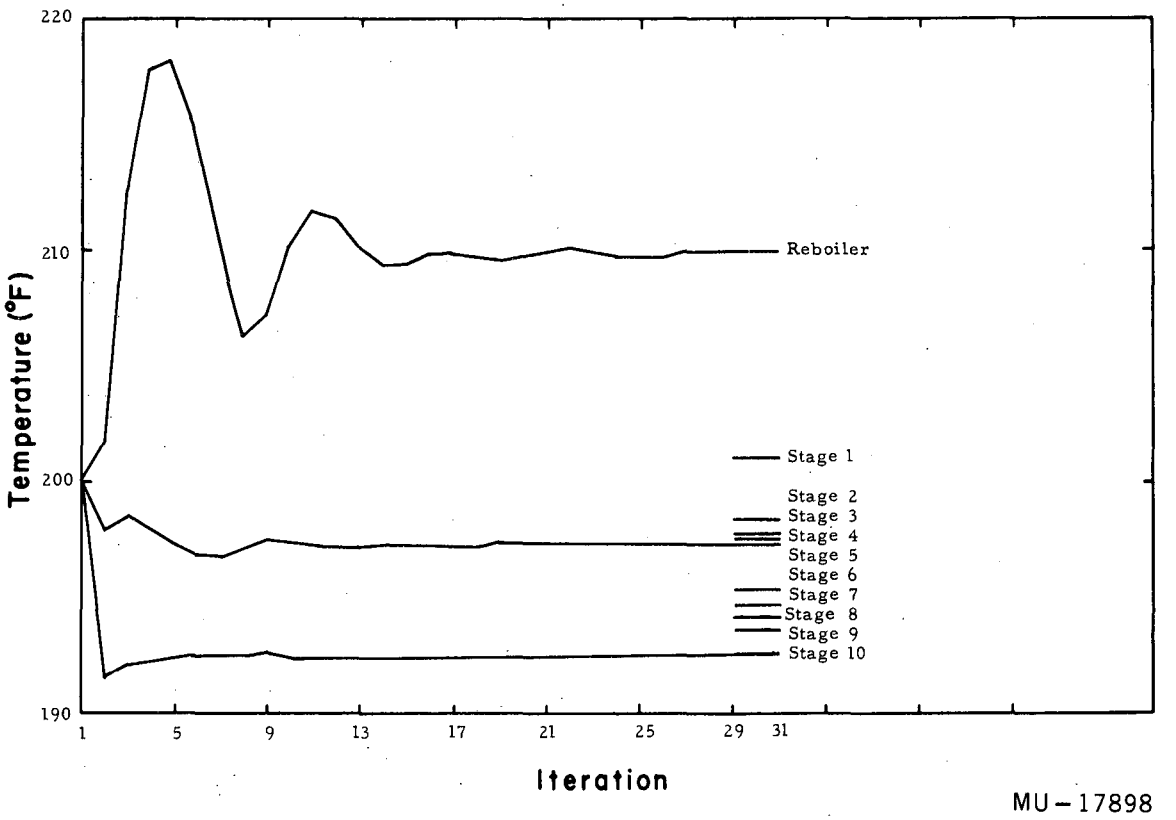


Fig. 59. Results for Example 25: temperature vs. iteration for all stages.

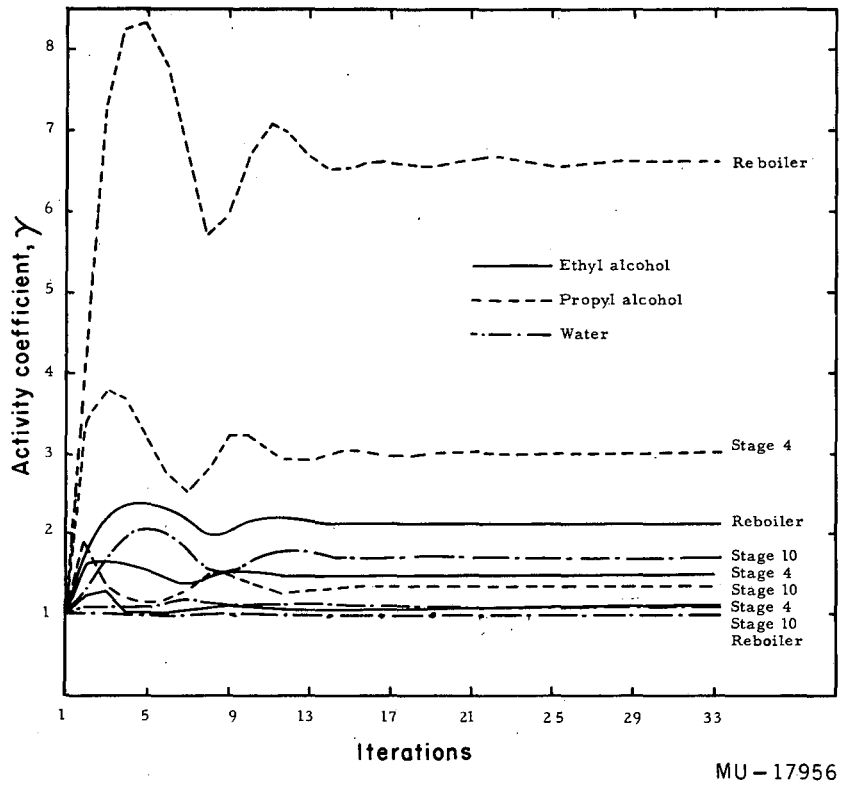


Fig. 60. Results for Example 25: activity coefficient vs. iteration for selected stages.
—— ethyl alcohol.
--- propyl alcohol.
-·-·- water

very little fractionation takes place), it is important to have a calculational method that will always converge so that bulk splits, flow gradients, and numbers of stages may be varied and problem solutions cross-plotted. Example 26 uses the feed of Examples 24 and 25 but increases the number of stages to 23 with liquid feed on the 11th stage. The bulk separation is changed to 0.25 mole top product per mole feed with a reflux ratio of 1. Typical results given in Fig. 61 show that under these condition Method I mass-balance equations are incapable of giving a convergent solution, so that recourse must be had to Method II equations. The combination of Method II equations with $K_{MODIFIED}$ normally gives convergent solutions if enough iterations are run on the computer.

Example 26

Same feed, vapor pressure constants binary interation, and three-suffix constants as Example 24. Column conditions are the same with the only system changes

Enriching stages: 12(not including feed stage)
Stripping stages: 11(including feed stage)
Reflux amount: 0.25 mole per mole feed
Top-product amount: 0.25 mole per mole feed
All temperatures initially 200°F
Enriching section: $L/V = 0.25/0.5 = 0.5$
Stripping section: $V^1/L^1 = 0.5/1.25 = 0.4$

Example 27 is a rerun of Example 26 but with Method II mass-balance equations used rather than Method I equations. The results are given in Figs. 62 and 63, where only specific stage temperatures and activity coefficients are plotted as they are typical of the behavior of all other stages. The use of slow-moving Method II has essentially removed all oscillation from both the temperature and activity-coefficient values, and a practical convergent solution is available at approximately the 80th iteration. The over-all mass balance at the 100th iteration gave the following errors,

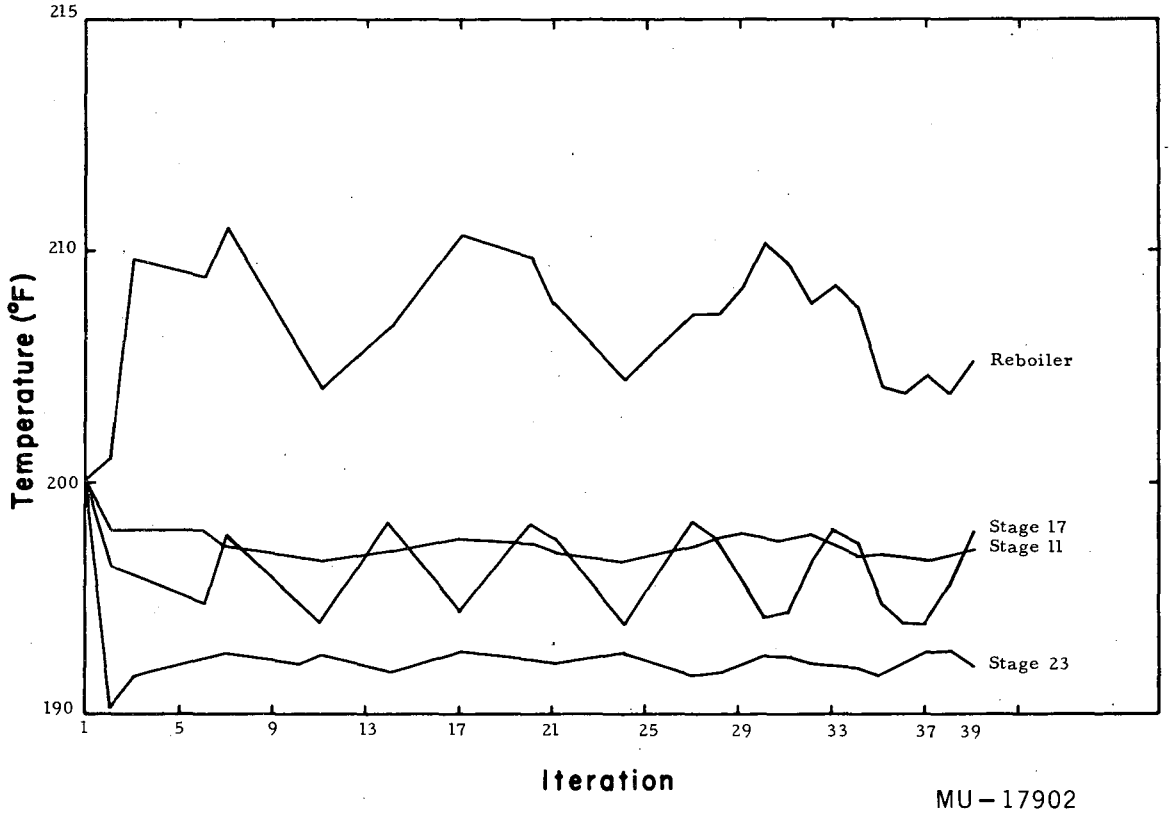


Fig. 61. Results for Example 26: temperature vs. iteration for selected stages.

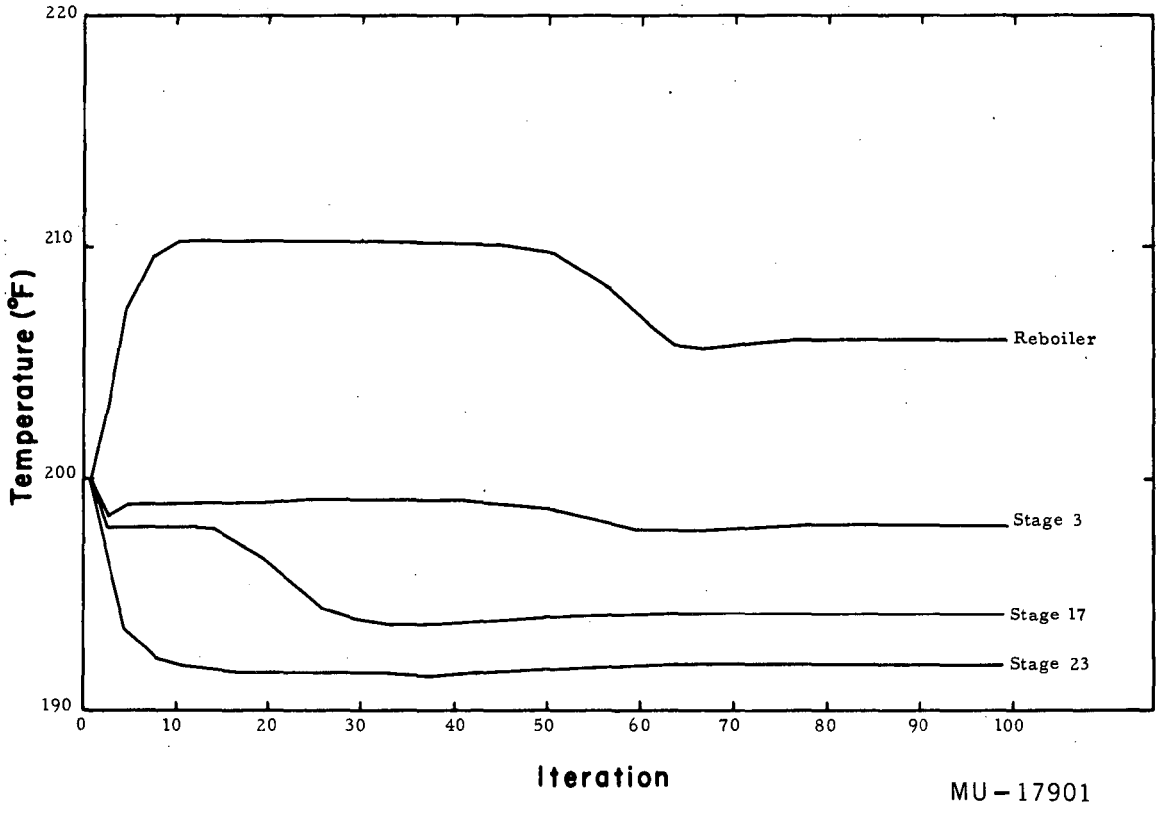
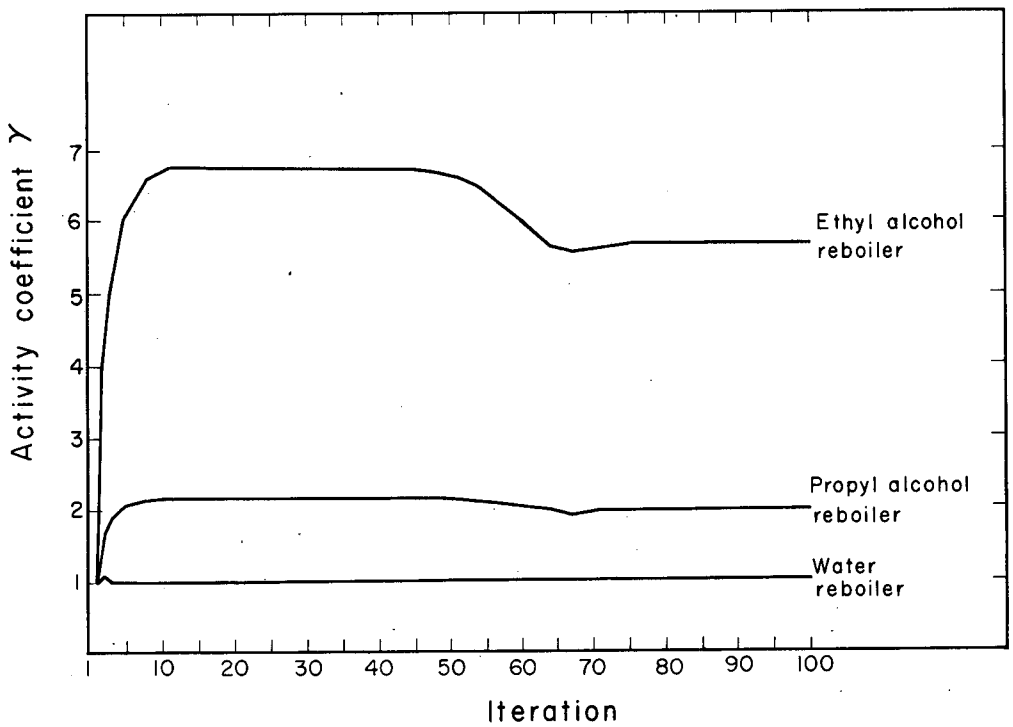


Fig. 62. Results for Example 27: temperature vs. iteration for selected stages.



MU-17957

Fig. 63. Results for Example 27: activity coefficient vs. iteration for reboiler only.

Ethyl alcohol - 0.12%,
Propyl alcohol - 0.53%,
Water - 0.01%.

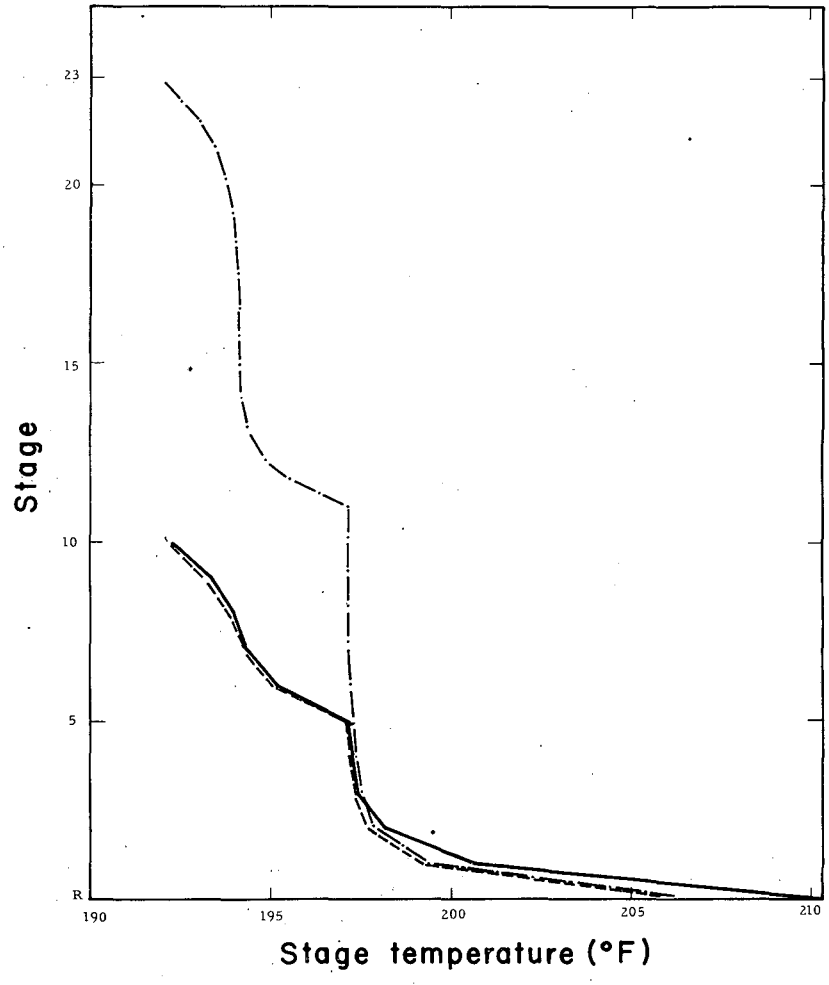
and these figures give an additional check on convergence.

Example 27

Exactly the same as Example 26 in all respects except one--that is, Method II mass-balance equations were used rather than those of Method I.

The converged temperature gradients for two bulk splits and two different columns are shown in Fig. 64 and are indicative of the inefficiency of the separation under the assumptions made. However, since no information is available on a ternary azeotrope for this three-component system, the arbitrary bulk splits indicated were assumed. It is very likely that any azeotrope would be such that smaller values of the top-product amount would have to be assumed and calculations made to see if the upper end of the temperature gradient curve became vertical, as it would be if an azeotrope were found. The shape of the gradient curve can also be changed by varying the reflux amount so that better fractionation efficiency is obtained.

In any case, calculational techniques have been presented which give convergent solutions as variables are assigned different values. Thus, it becomes possible to seek out azeotrope formation in multi-component systems and to make general calculations in systems exhibiting nonideal behavior in the liquid phase.



MU-17958

Fig. 64. Converged temperature gradients for Examples 25, 26, and 27.
—— 10 stages with top product = 0.3 mole.
--- 10 stages with top product = 0.25 mole.
-·-· 23 stages with top product = 0.25 mole.

VIII. LIQUID-LIQUID EXTRACTION CALCULATIONS

It is possible to apply the methods of Sections II, III, and VII to the general problem of liquid-liquid extraction, and it is the purpose of this section to illustrate how this might be done. There are obviously fundamental differences between the two processes which will require calculational techniques differing from those of the preceding sections.

In the general distillation problem, there is a process of vaporization and condensation which takes place at every stage; along with this process, the necessary mass transfer takes place to effect the desired component separation. Thus, of necessity, there is a temperature gradient in such a process, and this in turn allows mass and energy balances to be made.

It was a property of such processes that the composition-temperature interdependence allowed separation calculations to be made irrespective of the system flows, which were of course assumed constant. Further, when it was necessary to recognize flow changes, the energy-temperature interdependence provided a convenient basis upon which to make calculations.

In liquid-liquid extraction processes, the temperature is essentially constant from stage to stage if frictional and heat-of-solution effects are neglected and there are no arbitrary energy inputs or outputs. However, the mass-transfer process taking place requires that flows do change from stage to stage, and this flow variation must be taken into account in order to obtain a properly convergent solution for a given problem.

Method II mass-balance equations can be used to describe such a system if there is a means available for calculating the distribution coefficient or equilibrium value for the distributing component or components. Since it is assumed that two liquid phases are in equilibrium at any stage p, then the activity a of any component i must be the same in each phase, and this is expressed methematically as

$$(a_i)_V = (a_i)_L, \tag{VIII.1}$$

where

$(a_i)_V$ = activity of component i in phase V, and V is that phase ordinarily called the extract phase in liquid-liquid extraction literature.

$(a_i)_L$ = activity of component i in phase L, and L is that phase ordinarily called the raffinate phase in liquid-liquid extraction literature.

Since activity is defined as the product of activity coefficient and mole fraction, it follows, from Eq. (VIII.1) that we have

$$(\gamma_i y_i)_V = (\gamma_i x_i)_L, \tag{VIII.2}$$

and therefore

$$\frac{(y_i)_V}{(x_i)_L} = \frac{(\gamma_i)_L}{(\gamma_i)_V} = K_{LV}, \tag{VIII.3}$$

so that if the individual activity coefficients γ are known for each phase, it is then possible to use Method II mass-balance equations. These activity coefficients can be calculated from Eq. (VII.7) by assuming that all necessary data for the Margules binary-interation constants, A_{ij}, are available for a given set of components.

The equilibrium constant K_{LV} differs from that used in distillation calculations in that it is essentially temperature-independent. Activity coefficients do vary with temperature and pressure; but for all practical purposes, isothermal and isobaric conditions may be assumed in liquid-liquid extraction calculations so that K_{LV} becomes primarily a function of composition.

The change in the individual phase flows, which appear explicitly in the Method II mass-balance equations, must be calculated for every change in composition resulting from use of these equations, and energy effects cannot be used to do this. However, an equation parallel to Eq. (III.13), but involving only mass flows for component i, would be

$$(Vy_i)_{p-1} + (q_{iV})_{p-1} + (Lx_i)_{p+1} + (q_{iL})_{p+1} -$$

$$\left\{[(Vy_i)_p + (q_{iV})_p + (Lx_i)_p + (q_{iL})_p]\right\} = 0 \qquad \text{(VIII.4)}$$

where q_i = that corrective value of mass flow for component i which when added to its accompanying main-stream mass flow makes Eq. (VIII.4) identically 0.

Any stage mass unbalance would be defined for component i as

$$(Vy_i)_{p-1} + (Lx_L)_{p+1} - (Vy_i)_p + (Lx_i)_p = (Q_i)_p, \qquad \text{(VIII.5)}$$

and subtracting Eq. (VIII.5) from Eq. (VIII.4) leads to

$$(q_{iV})_{p-1} + (q_{iL})_{p+1} - (q_{iV})_p + (q_{iL})_p + (Q_i)_p = 0. \qquad \text{(VIII.6)}$$

This latter equation is identical with Eq. (III.14), but the q_i and Q_i now have totally different definitions. As in Section III, it is necessary to find or assume a relation between (q_{iV}) and (q_{iL}) before Eq. (VIII.6) can be effectively used. The previously proposed (C_V/C_L) ratio cannot now be derived from basic energy relations, so that recourse must be had to some other method of estimating (C_V/C_L).

One way of estimating this ratio, and the way proposed here, is to assume that any mass unbalance $(Q_i)_p$ that is fed back to a stage will split into two phases in a mass ratio equivalent to the mass ratio of component i in the two phases currently <u>leaving</u> that stage. It can be shown that this assumption cannot be rigorously correct except at the limit or convergence point, but it is nevertheless an excellent assumption, as any small feedback mass $(Q_i)_p$ splitting between two existing phases would split in some aribtrary manner heavily dependent on the respective masses of component i in each phase. For purposes of carrying out corrective mass-flow calculations, then, $(C_V/C_L)_i$ is set equal to the mass ratio of component i in the exit streams from each individual stage. On the basis of this assumption then, the following relationship is established:

$$(C_V/C_L)_i \equiv (Vy_i)/(Lx_i)_p. \qquad \text{(VIII.7)}$$

This relationship can now be used in Eq. (VIII.6), and a normal two-point extrapolation process can be run for each component i. This process operates exactly the same as the similar process described in Section III. The use of Eq. (VIII.6) with (q_{iL}) or (q_{iV}) being explicit is arbitrary; but, as will be shown later, the choice sometimes depends on the $(C_V/C_L)_i$ ratio values for certain components i.

If q_{iL} are calculated, they can be used directly to correct a component flow, since $q_{iL} = \Delta L_i$, and the following relations hold:

$$(Lx_i)_{NEW} = (\Delta L_i) + (Lx_i)_{OLD}, \qquad \text{(VIII.8)}$$

$$(Vy_i)_{NEW} = (C_V/C_L)_i \ (\Delta L_i) + (Vy_i)_{OLD}. \qquad \text{(VIII.9)}$$

Having calculated all values of $(Lx_i)_{NEW}$ and $(Vy_i)_{NEW}$, one can determine L_{NEW}, V_{NEW}, $(x_i)_{NEW}$, and $(y_i)_{NEW}$ for each stage p from the relations

$$L_{NEW} = \sum_i (Lx_i)_{NEW}, \qquad \text{(VIII.10)}$$

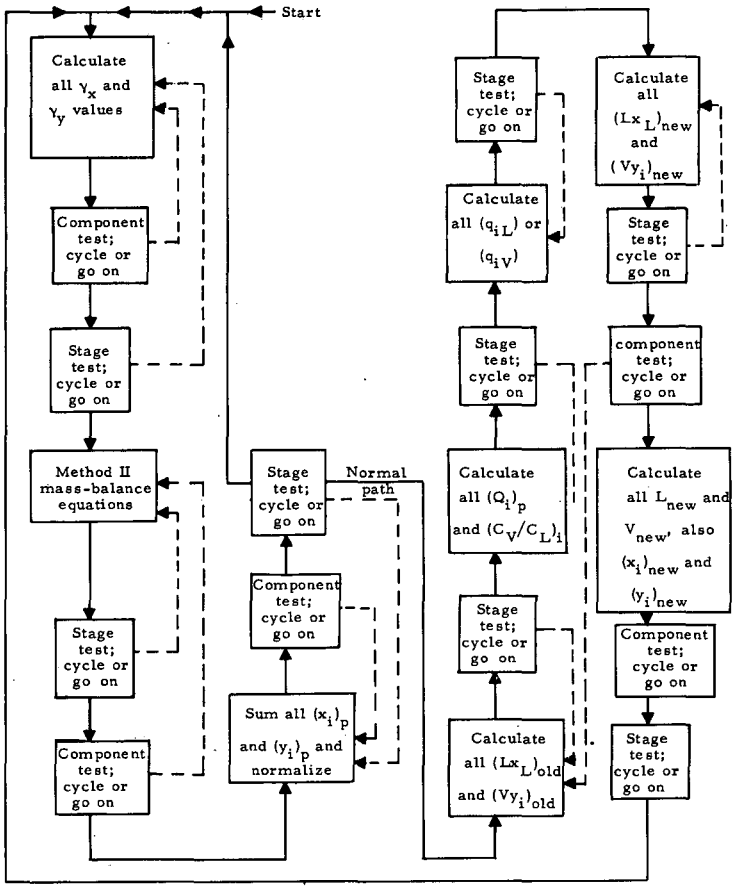
$$V_{NEW} = \sum_i (Vy_i)_{NEW}, \qquad \text{(VIII.11)}$$

$$(x_i)_{NEW} = \frac{(Lx_i)_{NEW}}{L_{NEW}}, \qquad \text{(VIII.12)}$$

$$(y_i)_{NEW} = \frac{(Vy_i)_{NEW}}{V_{NEW}}. \qquad \text{(VIII.13)}$$

When these relations are applied at each stage p, the final result is all new compositions and total stage flows.

The over-all program as set up for a digital computer is shown in Fig. 65, and the normal sequence in any given iteration would be one mass-balance step for each corrective-mass-flow step. It has generally been found that no damping factor is needed with this one-to-one pattern, but a factor could easily be inserted to multiply q_i if



MU-17959

Fig. 65. Schematic computer program for liquid-liquid extraction.

necessary. It also may be necessary, under certain conditions in a given problem, to run the mass-balance part of the iteration until the unbalance errors are reduced below some arbitrarily predetermined small number before moving on to the corrective mass flow. This type of operation would correspond to the variable pattern previously mentioned in Section V, and would be necessary when compositions changed rapidly (owing, most likely, to very poor guesses of starting gradients and compositions).

When Method II mass balance is being used, starting values of compositions must be assumed for all stages; the simplest possible assumption is that all V-phase streams have the composition of the extract solvent and all L-phase streams have the composition of the incoming feed containing the raffinate solvent and the distributing components. The initial flow gradients assumed should be selected with some care, since there are limits on these values outside which it is impossible to operate. Fortunately, if these limits are violated the calculation process itself will most likely give an indication of this condition and at what point in the column it has occurred.

To test the proposed method and the assumption regarding $(C_V/C_L)_i$, a two-component feed was fed to a single stage, as shown in Fig. 66a, and a pure solvent feed was used for extraction. This case is presented as Example 28, and the results are given in Fig. 66b and LII. The convergence is rapid, with practical results available at the third iteration. The range in values for $(C_V/C_L)_i$ is large because the V-phase solvent has a very small solubility in the L phase and vice versa for the L-phase solvent. These ratio values quickly reach an essentially constant value and stay there as the unbalance errors are reduced.

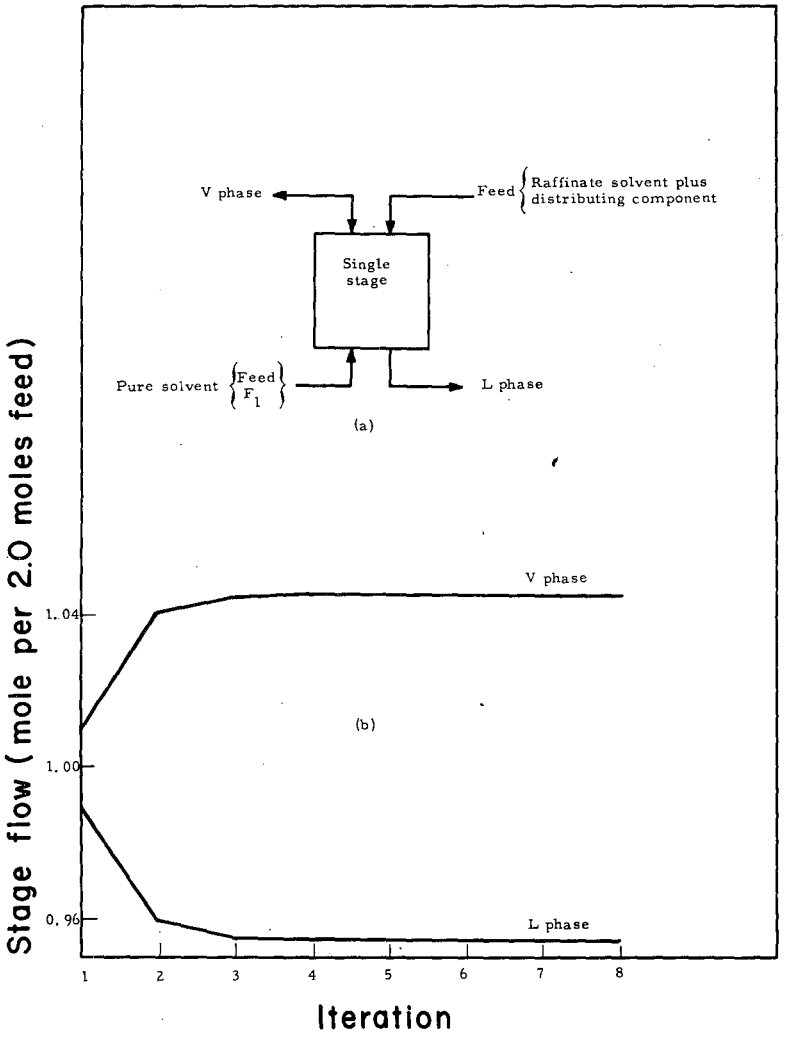
Example 28

	F_1y_1	F_2x_2
Component 1	1.0	0.0
2	0.0	0.1
3	0.0	0.9
	1.0	1.0

Margules binary interation constant (A_{ij}) array

j/i	1	2	3
1	0.0	0.5	9.0
2	0.5	0.0	0.2
3	10.0	0.2	0.0

$A^*_{123}=10.2$



MU-17960

Fig. 66. a. Stream flows for the single stage of Example 28.
b. Results for Example 28: stage flow vs. iteration.

Table LII

Results for Example 28:
parameter values from seven iterations

Summations	1	2	3	4	5	6	7
$\sum_i(x_i)$	.968	.995	.999	1.000	1.000	1.000	1.000
$\sum_i(y_i)$	1.032	1.004	1.001	1.000	1.000	1.000	1.000
Components	L-phase γ values						
1	7835.	11707.	12207.	12276.	12285.	12286.	12286.
2	1.165	1.191	1.193	1.194	1.194	1.194	1.194
3	1.003	1.001	1.001	1.001	1.001	1.001	1.001
Components	V-phase γ values						
1	1.000	1.001	1.001	1.001	1.001	1.001	1.001
2	1.633	1.585	1.579	1.578	1.578	1.578	1.578
3	7905.	5740.	5548.	5523.	5519.	5519.	5519.
Components	Mass-unbalance errors, ϵ_i						
1	-6.91	-.693	-.061	-.808	-.001	--	--
2	-.071	-.0078	-.0011	-.0001	--	--	--
3	+.0099	-.0001	--	--	--	--	--
Components	Flow-unbalance errors, Q_i						
1	+.031	+.0042	+.0006	+.0001	--	--	--
2	-.0006	-.0001	--	--	--	--	--
3	-.0003	-.0042	-.0006	-.0001	--	--	
Components	$(C_V/C_L)_i$ values						
1	7495.	12575.	13322.	13426.	13440.	13441.	13442.
2	.683	.807	.826	.828	.828	.828	.828
3	.0001	.0002	.0002	.0002	.0002	.0002	.0002
Components	Top-product recovery fraction						
1	.9999	.9999	.9999	.9999	.9999	.9999	.9999
2	.4057	.4467	.4522	.4530	.4531	.4531	.4531
3	.0001	.0002	.0002	.0002	.0002	.0002	.0002

The initial V- and L-phase masses were assumed as indicated in Fig. 66b and the compositions of these phases were set at those of F_1 and F_2 respectively. The A_{ij} values were arbitrarily assumed so as to have a high degree of immiscibility between components 1 and 3, with component 2 the main distributing component.

In Example 29, the same feeds were put into the three-stage column shown in Fig. 67a, and the results of this example are given in Tables LIII and LIV and Figs. 67b, 68, 69. Again the convergence is fairly rapid, with practical results available at the 5th or 6th iteration. These results were obtained with a corrective mass-flow allowable error, ϵ_c, of 0.01 for the two-point extrapolation process.

In the calculational process of Example 29, it was impossible to lower the value of ϵ_c to 0.001 or 0.0001 even though these values are more desirable than the one used. The reason that smaller values would not work is that in the two-point extrapolation process new values of q_{iL} are predicted in such a way that a difference-of-differences term occurs. The first difference is based upon numbers which are quite small, the q_{iL}, and this difference approaches the limit of significant figures that the computer can carry. When the differences of these difference terms is calculated, it is quite possible that total loss of significant figures can occur, and as this term is used as a division term, the computer automatically stops because in effect it is trying to divide by zero. There are two ways to get around this difficulty. The first is to use double-precision numbers that carry 18 rather than 8 places. The second and more desirable way is to switch to q_{iV} terms for any component that distributes essentially all into the V phase, since the order of magnitude of the q_{iV} is appreciably greater than that of the q_{iL}, and enough significant figures should be retained so that lower values of ϵ_c can be used. Unfortunately, this second approach requires some additional programming to seek out highly nondistributing components in order that a decision may be made on the use of q_{iL} or q_{iV}, with the logic being as follows:

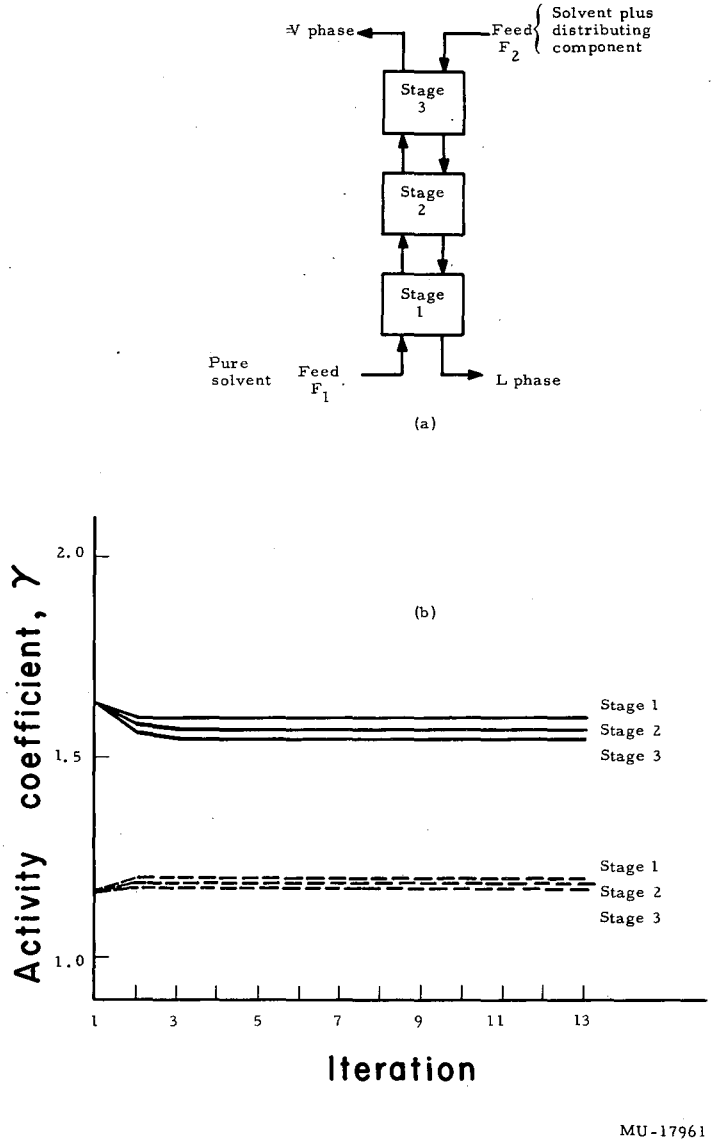
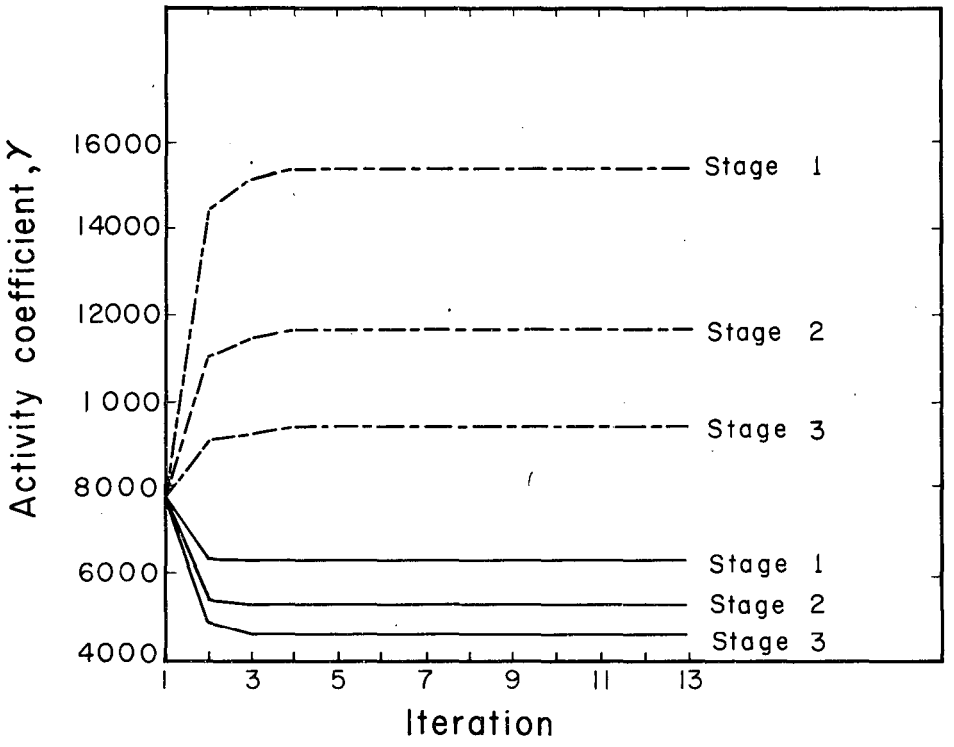
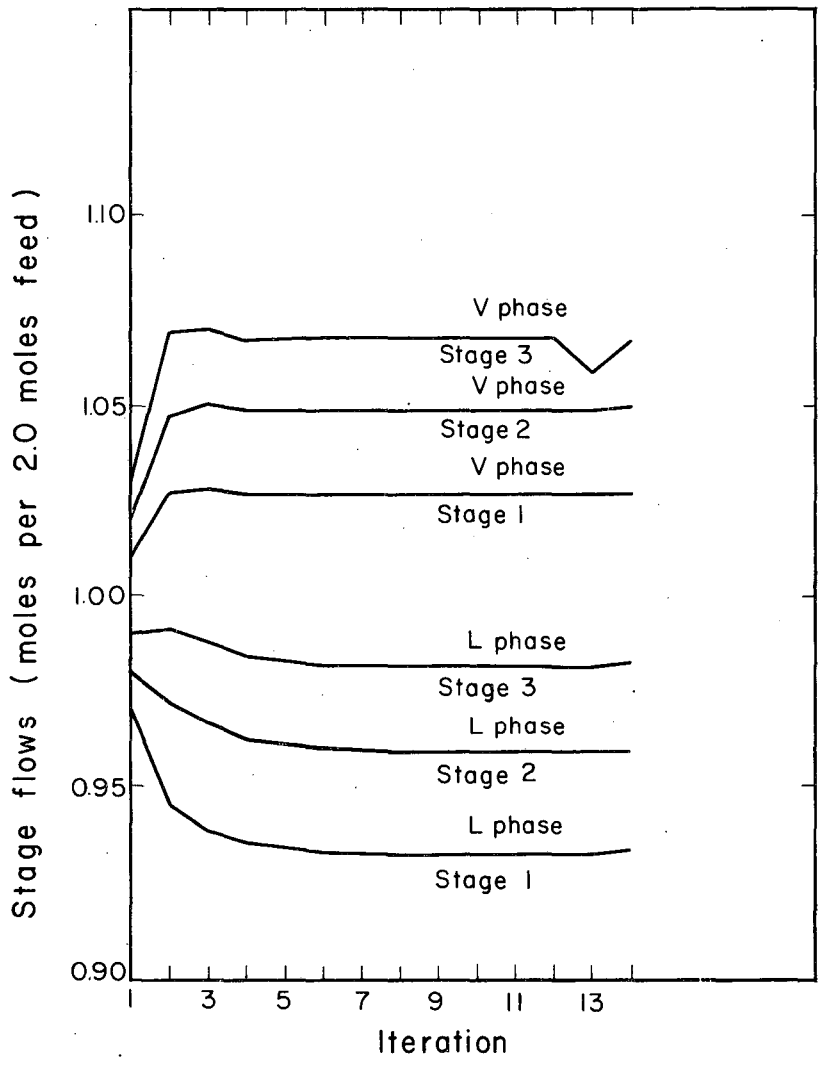


Fig. 67. a. Stream flows for the multiple stages of Example 29.
b. Results for Example 29: activity coefficient vs. iteration for component 2.
—— V phase.
--- L phase.



MU-17962

Fig. 68. Results for Example 29: activity coefficient vs. iteration for components 1 and 3.
—— L-phase solvent or component 3.
--- V-phase solvent or component 1.
All V-phase values of component 1 ≈ 1.001.
All L-phase values of component 3 ≈ 1.001.



MU-17963

Fig. 69. Results for Example 29: stage flow vs. iteration for all stages.

Table LIII

Results for Example 29: summations and top-product recovery fractions from various iterations

Phase mole-fraction summations $\sum_i (x_i)_p$ and $\sum_i (y_i)_p$

	1		2		3		4		5		6		7		8		12	
Stage	L	V	L	V	L	V	L	V	L	V	L	V	L	V	L	V	L	V
3	1.002	1.039	.992	.999	.994	.998	.997	1.000	.999	1.000	.999	1.000	1.000	1.000	1.000	1.000	1.000	1.000
2	.991	1.041	.997	1.005	1.000	1.001	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
1	.966	1.032	.997	1.003	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

Component	Top-product recovery fraction								
1	1.0075	1.0022	.9996	.9999	.9999	.9999	.9999	.9999	.9999
2	.6116	.6800	.6754	.6744	.6751	.6756	.6759	.6760	.6762
3	.0001	.0002	.0002	.0002	.0002	.0002	.0002	.0002	.0002

(a) If the component distributes heavily into the V phase, use q_{iV}.

(b) If the component distributes heavily into the L phase, use q_{iL}.

(c) For all other components, either q_i can be used.

These difficulties did not occur in distillation procedures because the value of the q term was normally quite large.

Table LIV

Results for Example 29:
mass unbalance errors, ϵ, from Iteration 13

	Component		
Stage	1	2	3
3	-5×10^{-5}	-6×10^{-7}	-4×10^{-9}
2	-6×10^{-5}	-9×10^{-7}	--
1	-11×10^{-5}	-4×10^{-6}	-2×10^{-5}

The small values of $q_{iL} = \Delta L$ cause another behavior quirk, as shown in Fig. 69. As the iterative process converges, all q_{iL} approach 0; and if an attempt is made to reduce all mass-balance errors, ϵ, to a very small number, difficulties with significant figures again arise. Table LIV shows values of ϵ for Iteration 13, and at that point the errors for Component 3 have been reduced below the eight-place carrying ability of the computer. Beyond this point, correction values calculated begin to oscillate. This behavior can be compensated for by the methods suggested in the preceding paragraph. However, the obvious solution to the problem is to recognize that practical convergence has set in long before Iteration 13 has been reached and to stop the iterative process, as reduction of ϵ to some very small value is not justified.

Example 29

The same feed and data as for Example 28. The starting flow gradients are as shown in Fig. 69, and the initial phase compositions at every stage were set equal to the F_1 composistion for the V phase and the F_2 composition for the L phase.

Liquid-liquid extraction in center-fed columns, refluxed columns, and other column variations can be handled by the calculational techniques presented here. The equilibrium data required can be calculated either by arbitrary empirical functions or from activity coefficients and used in the general calculational framework with no difficulty.

ACKNOWLEDGMENTS

The author is indebted to Professors Donald N. Hanson and Charles R. Wilke for their parts in directing this work, to Mrs. Robert Waite and Mrs. Edith Taylor for the numerous times they have assisted him, and particularly to his wife, Miriam, for her inestimable help and encouragement on many occasions of trial and tribulation.

Financial support was received through the Lawrence Radiation Laboratory from the U. S. Atomic Energy Commission.

NOMENCLATURE

$(a_i)_V$ = Activity of Component i in liquid phase V

$(a_i)_L$ = Activity of Component i in liquid phase L

A_{ij} = two-suffix Margules binary interaction constant

A^*_{ijk} = three-suffix Margules constant

A_i = coefficient for Component i in equilibrium expression, Eq. (I.3)

b = bottom-product amount from a column (moles per mole feed)

B_i = constant for Component i in equilibrium expression, Eq. (I.3)

C = column condenser

C_V = vapor-stream heat capacity defined by Eq. (III.16)

C_L = liquid-stream heat capacity defined by Eq. (III.18)

(C_V/C_L) = heat-capacity ratio or corrective mass-flow ratio

d = top-product amount from a column (moles per mole feed); or total differential symbol

f, f_1, f_2 = feed stages of a column or a general function

f_V, f_L = fugacity in vapor or liquid phases

F = amount of feed material entering a column (moles)

g = function for two-feed case, defined by Eq. (IV.17)

G = function for two-feed case, defined by Eq. (IV.15)

h_p = total liquid-stream enthalpy at stage p (Btu per mole)

h_{ip} = Component i enthalpy in liquid stream at stage p (Btu per mole)

H_P = total vapor-stream enthalpy at stage p (Btu per mole)

H_{ip} = Component i enthalpy vapor stream at stage p (Btu per mole)

j_i = coefficient for Component i in the equation (I.4) for liquid enthalpy

j = function for two-feed case, defined by Eq. (IV.18)

J = function for two-feed case, defined by Eq. (IV.16)

k_i = coefficient for Component in in the equation (I.4) for liquid enthalpy

K = equilibrium constant = y/x

l_i = coefficient for Component in in the equation (I.4) for liquid enthalpy

NOMENCLATURE (cont'd.)

L_p = liquid stream flowing off stage p (moles per mole feed)

m = number of stripping stages in a column

n = number of enriching stages in a column

o = number of intermediate stages in a column

p = general stage in a column

P = any combined column product or column pressure

q_V, q_L = corrective energy-flow or corrective mass-flow term in phase V or L

Q_R, Q_C, Q_r = heat-exchanger duties in reboiler, condenser, and reflux, respectively (Btu)

Q_p = net energy or net mass as defined by Eq. (III.12) or Eq. (VIII.5) (Btu or moles)

$\Delta Q_{es}, \Delta Q_{ss}$ = net energy flow in enriching section and stripping section respectively

r = reflux flow (moles per mole feed), or iteration number

R = column reboiler or gas constant

s = side-draw amount from a given stage; or bottom-product amount from a side stripper (moles per mole feed)

s_i = coefficient for Component i in the equation (I.5) for vapor enthalpy

sDp = any stage from which a side product is withdrawn

S_{Vp} = vapor-phase holdup at stage p (moles)

S_{Lp} = liquid-phase holdup at stage p (moles)

T = general stage temperature (^{o}F)

T_{bp} = characterizing temperature for boiling point of a component

TBP = true-boiling-point curve of a feed or product

u_i = coefficient for Component i in the equation (I.5) for vapor enthalpy

$\bar{u}_i$ = partial molal volume of Component i

V_p = vapor stream flowing off stage p or liquid off stage p in extraction - moles per mole of feed.

NOMENCLATURE (cont'd.)

V_{st} = amount of steam flow in a column (moles per mole of feed)

w_i = coefficient for Component i in vapor enthalpy, Eq. (I.5)

x = liquid-phase mole fraction

y = vapor-phase mole fraction or liquid-phase mole fraction in extraction

Greek Letters

α = general coefficient in equilibrium equation or relative volatility

β = general coefficient in equilibrium equation or defined as $V_p K_p + L_p$

γ = general coefficient in equilibrium equation or activity coefficient, Eq. (VII.3)

δ = total differential symbol

$\epsilon, \epsilon_1, \epsilon_2, \epsilon_C, \epsilon_F, \epsilon_\phi$ = general error or tolerance term, with 1, 2, C, F, ϕ representing allowable tolerances in mass-unbalance, bubble or dew point, corrective-energy or mass-flow, flash, and ϕ-factor evaluations, respectively.

η = defined symbol in Eqs. (II.7) and (VII.8)

Θ = time

λ = defined term = $V_{p-1} K_{p-1} x_{p-1} + L_{p+1} x_{p+1}$

μ = defined symbol in Eq. (VII.8)

ν = defined symbol in Eq. (VII.8)

π = total system pressure

ρ = density

τ = dimensionless group = $\Theta/S_L p$

Φ, ϕ, ϕ' = factors defined by Eq. (II.28) or (IV.6).

ψ = defined symbol in Eq. (VII.8)

ω = general coefficient in equilibrium equation; or defined symbol in Eq. (VII.8)

Δ = general difference symbol applied to V_p, L_p, and T

$\Sigma, \sum_i$ = general summation term or summation on components

NOMENCLATURE (cont'd.)

Subscripts

b	= value of variable in bottom product
c	= value of variable in any corrective process
C	= value of variable at condenser
d	= value of variable in top product
es	= value of variable in enriching section
f, f_1, f_2	= value of variable at various feed stages
F, F_1, F_2	= value of variable in various feeds or flash process
i	= general component, i = 1, 2, 3, ..., N.
L	= value of variable in liquid phase
m	= stage in stripping section
n	= stage in enriching section
NEW	= next sequential value of a variable
NORMALIZED	= value of variable giving $\sum_i (x_i)_p = 1$
o	= stage in intermediate section
OLD	= existing sequential value of a variable
p,p-1,p+1	= value of a variable at stage p = 1, 2, 3, ... or the stage below or above, respectively
P	= value of variable in any combined product
r	= iteration, r = 1, 2, 3, ..., ∞; or value of variable connected with reflux
R	= value of variable at reboiler
sdP,sDp+1,sDp-1	= value of variable in stream from side-draw stage and stage above and below, respectively
ss	= value of a variable at steady state, in a side stripper, or in the stripping section
st	= value of variable for steam
t,t-1	= value of variable at top stage of column and first stage below top
$T, T+\Delta T$	= value of variable at temperature T or temperature $T+\Delta T$
TOTAL	= value of a variable based on a total stream flow
V	= value of variable in vapor phase or liquid phase in extraction
π	= value of variable at total system pressure

NOMENCLATURE (cont'd)

Superscript ' = value of a variable below the feed stage

Miscellaneous

$(/_i)_d, (/_i)_b$ = recovery fraction of Component i in top or bottom product respectively

sDp' = part of side-draw stage liquid as defined in Fig. 35

ij = two-suffix constants in activity-coefficient equation

ijk = three-suffix constants in activity-coefficient equation

REFERENCES

1. N. R. Amundson and A. J. Pontinen, Ind. Eng. Chem. 50, 730 (1958).
2. M. Benedict, G. B. Webb, L. C. Rubin, and L. Friend, Kellogg Charts (M. W. Kellogg Co., New York, 1950).
3. J. R. Bowman, Ind. Eng. Chem. 41, 2004 (1949).
4. J. R. Bowman and W. C. Edmister, Ind. Eng. Chem. 43, 2625 (1951).
5. G. G. Brown and M. Souders, Jr., Ind. Eng. Chem. 24, 519 (1932).
6. G. Calingaert and D. S. Davis, Ind. Eng. Chem. 17, 1287 (1925).
7. J. W. Donnell and K. Turbin, Chem. Eng. 58, 112 (1951).
8. W. C. Edmister, A. I. Ch. E. Journal 3, 165 (1957).
9. W. C. Edmister, Ind. Eng. Chem. 35, 287 (1943).
10. W. C. Edmister, (California Research Corporation), private communication, 1954.
11. W. C. Edmister and D. H. Buchanan, Chem. Eng. Progr. Symposium 49, 69 (1953).
12. W. B. Franklin and G. Horton, Ind. Eng. Chem. 32, 1384 (1940).
13. E. R. Gilliland and C. E. Reed, Ind. Eng. Chem. 34, 551 (1942).
14. J. Greenstadt, Y. Brady, and B. Morse, Ind. Eng. Chem. 50, 1644 (1958).
15. S. T. Hadden, Chem. Eng. Progr. 25, 1373 (1933).
16. D. N. Hanson and H. E. Rea, Petrol. Refiner 31, 139 (1952).
17. W. D. Harbert, Ind. Eng. Chem. 39, 1118 (1947).
18. L. H. Horsely, Azeotropic Data, in Advances in Chem. Ser. 6 (1952).
19. H. H. Hummel, Trans. Am. Inst. of Chem. Engrs. 40, 445 (1944).
20. M. Kwauk, A. I. Ch. E. Journal 2, 240 (1956).
21. J. J. van Laar, Z. physik. Chem. 72, 723 (1910); 185, 35 (1929).
22. G. N. Lewis and M. Randall, Thermodynamics and Free Energy of Chemical Substances (McGraw-Hill Book Co. Inc., New, 1923).
23. W. N. Lyster, S. Sullivan, D. S. Billingsley, and C. D. Holland, Reprint, A. I. Ch. E. National Meeting, Salt Lake City, Utah, 1958.
24. M. Margules, Classe der Kaiserlichen Academie der Wissenschaften (Vienna) 104, 1243 (1895).

25. J. B. Maxwell, Data Book on Hydrocarbons (D. W. Van Nostrand Co., New York, 1950).

26. J. H. Perry, Chemical Engineering Handbook, 3rd Ed. (McGraw-Hill Book Co. Inc., New York, 1950).

27. O. Redlich and A. T. Kister, Ind. Eng. Chem. 40, 341 (1948).

28. C. S. Robinson and E. R. Gilliland, Elements of Fractional Distillation, 4th Ed. (McGraw-Hill Book Co. Inc., New York, 1950).

29. A. Rose, R. F. Sweeny, and V. N. Schrodt, Ind. Eng. Chem. 50, 737 (1958).

30. G. Rutledge, Phys. Rev. 40, 262 (1932).

31. J. B. Scarborough, Numerical Methematical Analysis, 2nd Ed. (The Johns Hopkin's Press, Baltimore (1950).

32. G. Scatchard and W. Hamer, J. Am. Chem. Soc. 57, 1805 (1935).

33. T. K. Sherwood and R. L. Pigford, Absorption and Extraction, 2nd Ed. (McGraw-Hill Book Co. Inc., New York, 1952).

34. Taylor and Parker, M.I.T. Charts (unpublished data), Massachusetts Institute of Technology, 1935.

35. E. W. Thiele and R. L. Geddes, Ind. Eng. Chem. 24, 289 (1933).

36. R. E. Treybal, Liquid Extraction, 1st Ed. (McGraw-Hill Book Co. Inc., New York, 1951.

37. K. M. Watson and E. F. Nelson, Ind. Eng. Chem. 25, 880 (1933).

38. R. R. White and G. G. Brown, Ind. Eng. Chem. 34, 1162 (1942).

39. K. Wohl, Trans. Am. Inst. Chem. Engrs. 42, 215 (1946); Chem. Eng. Progr. 49, 218 (1953).

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.