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ON THE THEORY OF MULTICOMPONENT DISTILLATION AT MINIMUM REFLUX

(met een samenvatting in het Nederlands)

by/*door*

P. J. BRUIJN

Laboratory of Physics and Meteorology, Agricultural University, Wageningen, Netherlands

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CONTENTS

La théorie des colonnes à distiller est assez complexe.
Marcel PONCHON, (1921) [1])

CHAPTER I

INTRODUCTION

Distillation theory must still be considered a complex and difficult subject and the present state of affairs has been summed up well by N. R. AMUNDSON and A. J. PONTINEN, when they wrote: [2])

"...approximate and short-cut methods have been proposed in almost a continuous stream, with graphical techniques and empirical correlations. Plate by plate methods have been used to obtain semirigorous solutions. There is always some question as to what is meant by a solution to the multicomponent rectification problem. Most of the methods proposed do not give rigorous answers and cannot be made rigorous."

The present thesis exhibits a detailed study of the theory of multicomponent distillation at minimum reflux on the basis of the widely used model of constant relative volatilities and constant molal overflows. Only ideal columns, operated with a total condenser and a total reboiler, are considered.

The analysis is theoretical. No attempts have been made to derive short-cut approximations for practical purposes, nor has the applicability of the model been discussed. The object has been to remove some apparent obscurities and misinterpretations with respect to the main problem of specification, which still existed in distillation literature.

A thorough mathematical investigation of the consequences of the model is justified by three arguments: A complete and exact model

1. permits qualitative deductions of heuristic value.
2. offers means to check approximative methods founded on the basic assumptions underlying the model.
3. offers a solid base for extension of the model, by weakening of the restrictions imposed by, (or by generalization of), the basic assumptions.

In 1946 UNDERWOOD [4, 5] published his theorem which made possible the first straightforward computations in multicomponent distillation. Rigorous proofs for this theorem have been provided by different authors [1, 3]. At this stage it is possible, when given an a priori specification of the distribution of two key components and of the feed condition q, to compute on the basis of the mentioned model the product compositions and both the reflux ratio R_D and the reboil ratio R_B. To obtain correct results, however, the numbers of light and heavy components, which do not distribute, must be guessed. Moreover, an arbitrary a priori specification of two separation ratios does not necessarily permit a consistent solution but must satisfy conditions which are not easy to formulate explicitly. Finally, a criterion for the consistency of the computed results being non-existent, the computation of minimum reflux was lacking mathematical rigour and hence could easily lead to dubious answers (pseudo-solutions).

[1]) Tech. Moderne, *13*, (1921), 20.
[2]) Ind. Eng. Chem., *50*, (1958), 730.

It seems to be generally accepted that a (consistent) specification permits one and only one solution (uniqueness theorem). The present author, however, could not find a formal proof of this theorem in distillation literature.

Similarly, straightforward computations of the feed tray conditions on the basis of the present model are non-existent, though VAN WIJK and coworkers have developed an interative method for the case of two adjacent distributed components ("doublet separations") [10, 11, 12].

The present study can be divided into two parts. The first part (chapters 2, 3, 4 and 5) concentrates on the subject of specification. Topics are:

Classification

Introducing UNDERWOOD's theorem as a postulate, the resulting method of computation of minimum reflux separations is examined in chapter 3, which has a preparative character. The smallest roots of two "characteristic equations" are shown to be suitable independent parameters ("pinch parameters"). The separations are classified with respect to number of distributed components and the relation between classes and distinct intervals of the pinch parameters is established. (Fig. 12).

Geometrical representation

To gain a clear survey over the entire complex of all possible separations of a given multicomponent mixture, fed at various thermal conditions q to an infinite column, a geometrical representation is developed in chapter 4.

Minimum reflux separations are shown to be the points of a peculiarly shaped part of (q, R_B, R_D)-space, (*solid of minimum reflux*, Fig. 19).

Separations, pertaining to a fixed value of the feed condition parameter q, are represented by the points of a *multiplet diagram* (Fig. 16), i.e. a decomposition of the (R_B, R_D)-plane corresponding to the above mentioned classification. The multiplet diagram mirrors the nature and hence the principal difficulties of the mathematics of minimum reflux, which resembles in some respects the theory of continuation of analytic functions. The separation ratios s_{bk} (i.e. the quotients of the bottom rates over the feed rates), for instance, are continuous functions of the independent parameters R_B and R_D, (q constant). These functions, however, cannot be written explicitly, but are *per multiplet* solutions of a particular set of linear equations.

Interpretation of smallest root Ω_0 of UNDERWOOD*'s equation*

The smallest root Ω_0, which is never used in the computations of minimum reflux, can take any negative or positive value outside the range of reciprocal relative volatilities α_i^{-1}, in contradistinction with the other roots Ω_k of UNDERWOOD's equation. When $\Omega_0 > 0$, *it* determines an *empty zone* between the multiplet diagram and one of the coordinate axes. (Fig. 15). It is shown in section 4.3 that in these cases all roots play formally the same role, which is satisfactory from the theoretical point of view.

Vertex-separations a priori specificable

Specification is the selection of the feed condition q and two separation ratios $s_{b\mu}$ and $s_{b\nu}$. To compute the solution, however, the components which go entirely either to top or bottom and the possibility of the prescribed combination ($s_{b\mu}$, $s_{b\nu}$) must be known in advance. And hence part of the solution must be known before the computation can be initiated.

Exceptions to this rule are the separations represented by the vertices of the multiplet diagram. A vertex-separation can be completely specified by the selection of the non-distributed components only. The vertex-separations, therefore, constitute a rigid basis of the diagram of multiplets.

Linear interpolation

Linear equations play an important part in the theory. Separations in points of the boundaries (and hence the points themselves) are obtained by linear interpolation between vertices; separations in interior points are obtained by linear interpolation between suitable points of the boundaries.

Criterion of consistency

An adequate criterion of consistency follows directly from the one-to-one correspondence between the separations and the combinations of pinch parameters (chapter 5).

Monotony and uniqueness theorem

The ordering of the components with respect to volatility induces monotony theorems concerning the lines of constant s_{bk} and the boundaries of the diagram of multiplets. Rigorous proofs are given in the appendices. From the monotony theorems the uniqueness of a solution pertaining to a consistent specification is derived in section 4.8.

Specification diagram

In chapter 5 a definitive discussion of the specification problem is given. A diagram is introduced, consisting of a number of distinct quadrangles corresponding to the domains of distribution ratios, total bottom liquid rate and total bottom product rate, pertaining to the separations of one same multiplet, (Fig. 28). Specification and solution are combined into one simple ruler construction, which is based on the essential linearity of the equations of the underlying part of the theory. The inevitable numerical evaluations, *preceding* the construction, consist of the computation of the four vertex-separations of the multiplet to which the specification diagram belongs, and can be readily performed by a digital computer because of the above mentioned a priori specificability of vertex-separations.

The second part of this thesis (chapters 6 and 7) concerns the computation of the compositions and equilibrium constants throughout infinite columns. Topics of this part are:

Formulation of the theory

The present formulation of the theory is an extension of the formulation given by VAN WIJK, who published analytical solutions of the basic equations for the distillation of discrete multicomponent mixtures several years prior to ACRIVOS and AMUNDSON (compare [8] and [1]). To overcome characteristic difficulties in the computation of feed tray conditions, VAN WIJK's formulation is appended by a complementary "mirror-formulation" in chapter 6. As a result, a definitive theory of infinite columns can be given and a rigorous and entirely straightforward computation of the physical conditions throughout infinite columns can be derived in chapter 7.

Uniqueness of pinches

The pinches are defined to be regions of infinite extension, in which the phys-

ical conditions are uniform. It is shown in section 7.15 that one and only one pinch occurs in the bottom section and similarly one and only one pinch in the top section.

Types of pinch location

The trays, adjacent to condenser, feed tray or reboiler, may (but need not), belong to the pinches. In this respect 9 types of pinch location are to be distinguished (Fig. 31), of which type 9 pertains to absolute separations of binary mixtures only.

UNDERWOOD'S *theorem*

UNDERWOOD'S theorem is shown to be a direct consequence of the uniqueness of the pinches. (section 7.5).

Linear equations for feed tray conditions of infinite columns[1])

Hitherto the feed tray conditions could only be computed by iterative procedures [10, 11, 12]. In section 7. 7, however, a set of linear equations is derived from which the exact values of the compositions and of the absorption factor of the reference component at the feed tray can be obtained by straightforward solution.

Pinch paradox

A paradox, resulting from the discontinuity of the pinch parameters at the multiplet boundaries, is examined and resolved in section 7.16.

CHAPTER 2

PRELIMINARIES

2.1. NOMENCLATURE

Usually a distillation column is a vertical array of flat, in some way perforated, devices (plates or trays) locked up in a cylindrical enclosure. Liquid flows continuously down the column from tray to tray and across the trays. At the same time vapour travels up the column from tray to tray. On the trays exchange of heat and matter takes place. The trays are designed to give intimate contact between the two phases. As a result the vapour and the liquid, leaving the same tray, are more or less in thermodynamic equilibrium. If this equilibrium is perfectly established, the trays are said to be ideal or theoretical.

For continuous operation, the multicomponent mixture (feed), which is separated into a distillate and a residual fraction, is introduced on a tray (feed tray) somewhere between the top and the bottom of the column. The feed tray divides the column into two sections, the lower part (stripping section or bottom section) and the upper part (enriching, top or rectifying section). Part of the bottom product is returned to the column by the reboiler, part of the distillate is refluxed by the condenser. A distillation column is schematically represented in Fig. 1.

[1]) Note added in proof: It has come to the author's knowledge only recently that similar equations occur in UNDERWOOD'S original paper [5].

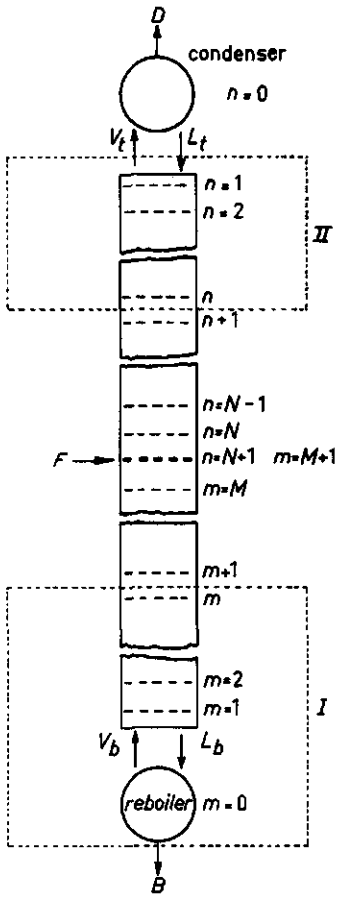

FIG. 1. Schematic representation of distillation column with M trays between reboiler and feed tray and N trays between feed tray and condenser. B, F and D represent total bottom product rate, total feed rate and total top product rate respectively. Rectangles I and II are drawn for application of law of conservation of matter (chapter 6). Total liquid rates L_b and L_t and total vapour rates V_b and V_t are constants.

2.2. MODEL OF CONSTANT MOLAL OVERFLOW AND CONSTANT RELATIVE VOLATILITIES

2.2.1. *Main characteristics*

Throughout this thesis steady state distillation is assumed and the well known model of constant molal overflow and constant relative volatilities is used.

The physical state in an ideal distillation column is determined by the law of conservation of matter, the law of conservation of energy and the condition of thermodynamic equilibrium on each plate of the column. The direct application of these laws, however, offers unsurmountable difficulties to rigorous mathematical analysis. Therefore, it has become common practice to substitute for the energy law the assumption of constant molal overflow, that is a constant value of L_b throughout the stripping section and likewise a constant L_t throughout the top section. This assumption, though widely used, contradicts the energy law.

W. R. VAN WIJK [7, 10] has developed methods to avoid this pitfall by taking full account of the heat balance while saving formally the present model. In-

troducing "generalized rates", a condition for the generalized total liquid rate in the bottom and for the generalized total vapour rate in the top is derived which is similar to the condition of constant molal overflow. To this purpose, [10], the molal vapour heat content must be approximated by a linear function of the equilibrium constant K of a reference component and the molal liquid heat content must be approximated by a linear function of $1/K$. In case of minimum reflux these approximations need only be valid in relatively narrow temperature ranges. It is possible in this way to preserve formally the assumption of constant molal overflow while actually the overflow may vary appreciably from tray to tray. The method is amply demonstrated in two subsequent articles [10, 11]. It is felt that these developments increase the importance of the restricted model treated in this thesis.

In the second place the customary assumption is made that the relative volatilities α_k are constant throughout the column.

2.2.2. *Additional assumptions and conventions*

The column is assumed to be ideal, (i.e. all the trays are ideal).

In this thesis only columns with an infinite number of trays in both sections are considered.

The components are arranged according to decreasing relative volatilities. The total feed rate F is taken to be unity.

The thermal condition of the feed is represented by the dimensionless parameter q, which is here defined by the quotient $(L_b - L_t)/F$ which comes to $L_b - L_t$ as $F = 1$, so

$$q = L_b - L_t$$

If the molal enthalpies of the liquid approaching and leaving the feed tray are identical and if the same holds for the molal enthalpies of the vapour, then q is exactly equal to the heat necessary to vaporize one mole of the feed divided by the latent heat of vaporization of the feed. Hence, the following feed conditions correspond approximately to the listed values of q.

$q < 0$	superheated vapour feed.
$q = 0$	all-vapour feed at boiling point.
$0 < q < 1$	partially vaporized feed.
$q = 1$	all-liquid feed at boiling point.
$q > 1$	cold liquid feed.

Throughout this thesis, the assumption is made that the reboil vapour has the same composition as the residue, $V_{b0,\,k} = R_B B_k$ for any component k, and also that the reflux liquid has the same composition as the distillate, $L_{t0,\,k} = R_D D_k$ for each component k.

2.3. General features of minimum reflux

In this section a number of well known features of a rectification, performed at minimum reflux, are resumed without proof.

Decrease of the reflux ratio R_D of a column with a finite total number of trays requires an increase of the numbers of trays in both sections, in order that the prescribed separation of the key components shall be preserved. There exists a lower boundary for this reflux ratio beneath which the separation cannot be performed. When R_D takes its minimum value the numbers of trays in both

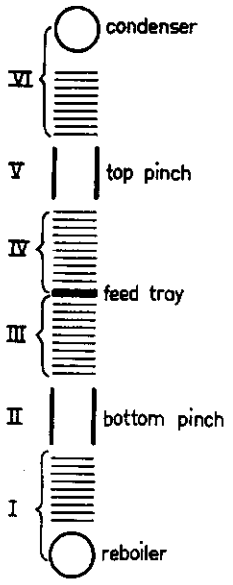

FIG. 2. Characteristic sections of infinite column.

sections have become infinite. The minimum value of R_D depends on the specified separation of the keys and also on the thermal condition parameter q of the feed.

A striking feature of an infinite column is the occurrence of six distinct regions (schematically drawn in Fig. 2), each region consisting of an infinite number of trays.[1]) These regions must be considered as limiting cases of less distinct zones to be distinguished in an ordinary column with large numbers of trays in both sections. In the regions I, III, IV and VI the physical conditions (composition and temperature) differ appreciably from tray to tray. These differences become smaller and smaller towards the regions II and V, called the pinches, where the conditions are identical on all the trays of one same pinch.

The pinches act as barriers to the separation. In fact, in most cases only a limited number of the components, penetrating at the feed tray, are able to pierce through both pinches.

These components occur in both product streams and are therefore called distributed components. The more volatile components are reflected at the bottom pinch and leave the column only in the distillate. The less volatile components are reflected at the top pinch and are present in the residue only.

The first monotony theorem (appendix I) states the monotonic increase of the separation ratios s_{bk} of the distributed components with respect to index k, that is with respect to decreasing volatility. Hence if l is the lightest distributed component and h the heaviest one, the inside components k with $l < k < h$ have ratios s_{bk} which satisfy

$$s_{bl} < s_{bk} < s_{bh}$$

From this it follows that none of the ratios s_{bk} vanishes and that hence all the components k between l and h are distributed. It is seen that the distributed components compose what may be termed a separation band, consisting of the *consecutive* components $l, l+1, \ldots, h-1, h$.

[1]) For exceptions see section 7.1.

2.4. Formulation of main problem

Summing up we can formulate the main problem, treated in this thesis, as follows.

Let be given

a) the feed composition $F_1, F_2, \ldots, F_J$.
b) the relative volatilities $\alpha_1, \alpha_2, \ldots, \alpha_J$.
c) the thermal condition parameter for the feed q.

Let be assumed

a) the total molal overflow is constant throughout each section.
b) the relative volatilities are constant throughout the column.
c) the column is ideal, (i.e. all trays are ideal).
d) the total numbers of trays in both sections are infinite.
e) the reboil vapour has the same composition as the residue and the reflux liquid has the same composition as the distillate.

Let be a priori specified

the separation ratios of an arbitrarily chosen pair of distributed components.

Then it is required

to compute the product compositions, the reflux ratios as well as the composition and the equilibrium constant of the reference component, at each tray of the column.

2.5. Numerical example

A large amount of numerical work has been carried out to elucidate the argumentation. The results are presented in several diagrams and tables in this thesis. The author has used to this purpose a system of ten components, which

Table 1. Ten component system of Murdoch and Holland. The order of the components has been reversed. (Component 7 is reference component).

component	F_k	α_k	component	F_k	α_k
1	0.05	3.00	6	0.14	1.15
2	0.08	2.00	7	0.13	1.00
3	0.14	1.50	8	0.05	0.90
4	0.16	1.35	9	0.12	0.70
5	0.08	1.25	10	0.05	0.40

was first used by Murdoch and Holland [3]. The order of the components has been reversed, taking here the most volatile component as the first one. The particulars of this system are listed in Table 1.

Chapter 3

Underwood's method

3.1. Characteristic equations

Various authors, [1, 3, 7] for instance, have carried out analytical investigations based on roots of what may be called *characteristic equations*. Though

the respective formalisms, developed by these writers, diverge widely, the characteristic equations are substantially the same. Adopting VAN WIJK's formalism, (chapter 6), we write the characteristic equation for the bottom section as

$$L_b = \sum_{i=l}^{J} B_i/(1 - \alpha_i s) \tag{3,1}$$

and for the top section as

$$V_t = \sum_{i=1}^{h} D_i/(1 - \alpha_i^{-1} s) \tag{3,2}$$

Here s is a mathematical variable. The right hand members of Eqs. (3,1) and (3,2) are conveniently termed *characteristic bottom function* and *characteristic top function* respectively. Typical for the graphs of these functions is the occurrence of the vertical asymptotes generated by the fractions constituting these functions. It follows from the first monotony theorem (section 2.3) that $B_i > 0$ if $B_l > 0$ and if $i \geqslant l$. Likewise $D_i > 0$ if $D_h > 0$ and if $i \leqslant h$. Therefore, there are $J - l + 1$ non-vanishing product streams B_i acting as numerators in the characteristic bottom function and hence $J - l + 1$ vertical asymptotes. The graph of the characteristic top function is seen to have h vertical asymptotes. These graphs are qualitatively represented for a ten component system in Figs. 3 and 4 respectively for the case of $l = 4$ and $h = 7$.

The functions are steadily increasing between and outside the vertical asymptotes. The s-axis itself is a horizontal asymptote in both graphs. The roots of the characteristic equations (3,1) and (3,2) are the points of intersection with a horizontal straight line at a height L_b or V_t respectively. A root occurs at the left hand side of each vertical asymptote. Hence all the roots are distinct and positive.[1]) The peculiar distribution of the roots may be loosely described by saying "every product stream has its own root". Each root is given the index k of the relative volatility determining the position of the asymptote at its right hand side, or, which comes to the same, the index k of the product stream in the numerator of the fraction generating this asymptote. Consequently the

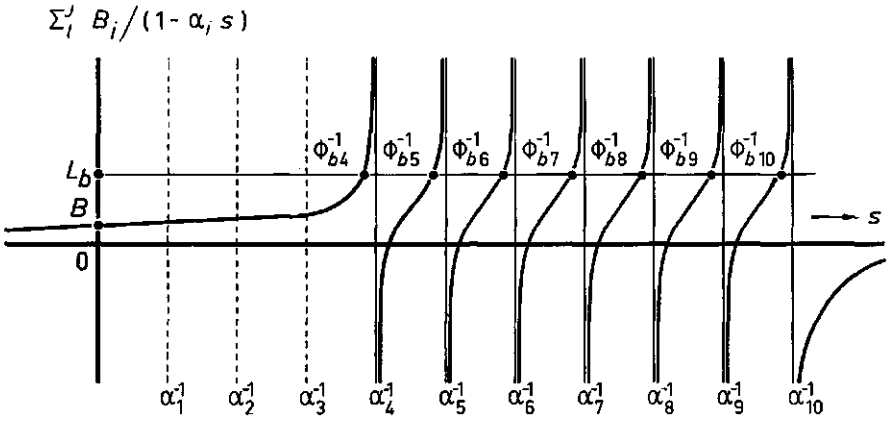

FIG. 3. Solution of characteristic bottom equation (schematical).

[1]) The graph of the characteristic bottom function intersects the positive part of the vertical axis at a height $B = \Sigma_i B_i$. As $L_b \geqslant B$, the first root is positive indeed except in the boundary case $L_b = B$ where this root is zero. Mutatis mutandis the same holds for the characteristic equation for the top section.

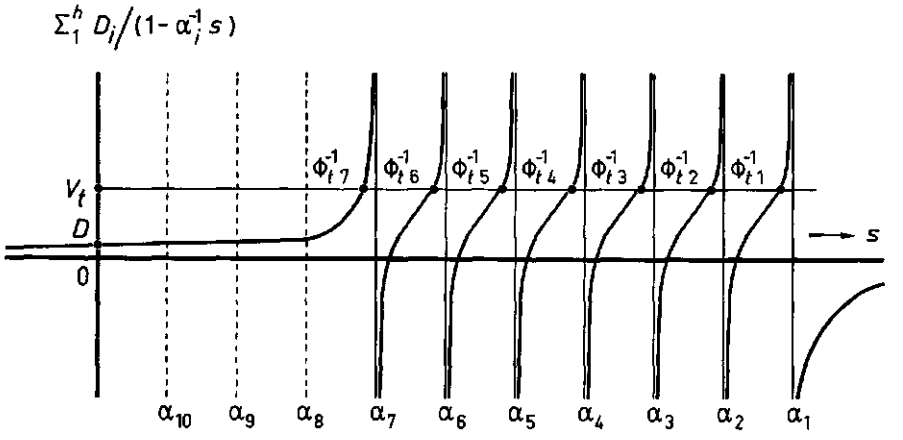

FIG. 4. Solution of characteristic top equation (schematical).

characteristic bottom equation (3,1) possesses $J - l + 1$ distinct and positive roots which will be denoted Φ_{bk}^{-1}. One has

$$\alpha_{k-1}^{-1} < \Phi_{bk}^{-1} < \alpha_k^{-1} \qquad \text{if } k > 1$$

and (3,3)

$$0 < \Phi_{b1}^{-1} < \alpha_1^{-1} \qquad \text{if } k = 1$$

Analogously the characteristic top equation (3,2) has h distinct and positive roots Φ_{tk}^{-1} obeying

$$\alpha_{k+1} < \Phi_{tk}^{-1} < \alpha_k \qquad \text{if } k < J$$

and (3,4)

$$0 < \Phi_{tJ}^{-1} < \alpha_J \qquad \text{if } k = J$$

In ordinary, finite, columns none of the product streams is exactly zero, strictly speaking. Then $l = 1$ and $h = J$ and the summations in Eqs. (3,1) and (3,2) must be carried out over all J components. Usually, however, the numerators in the characteristic functions are the object of the computation and hence are not simultaneously known in advance. Consequently the roots cannot be calculated a priori. Therefore, the majority of the analytical developments, based on roots of characteristic equations, merely result in a reshapement of the set of basic equations (conservation of matter and the like) with an enlarged number of unknowns. Especially the analytical "solutions", in which small product rates B_i and D_i are neglected in the characteristic equations without correction for their omission, are of little value.

For infinite columns, however, the situation is radically different. A. J. V. UNDERWOOD must be credited for discovering a third characteristic equation which provides a base for a *direct* computation of the unknown product rates of those columns.

3.2. UNDERWOOD'S THEOREM

According to the inequalities (3,3) and (3,4) the roots of the characteristic equations are imprisoned in their own intervals which are separated by the vertical asymptotes. From the viewpoint of these equations alone, no constraints

assumed to be imposed on the numerators B_i and D_i, a root may occupy any position in its interval and any combination of positions may occur.

The numerators, however, are to be interpreted as the terminal product streams of an infinite column. The numerators of both characteristic equations are therefore mutually dependent and this dependence is reflected in a surprisingly restricted behaviour of the roots.

Let us call *inside roots* the roots which are situated *between* the asymptotes associated with the lightest and heaviest distributed component l and h respectively. Then a theorem, discovered by UNDERWOOD [4, 5], states

The inside roots Φ_{bk}^{-1} *and* Φ_{tk-1}^{-1} *satisfy the relations* $\Phi_{bk}^{-1} = \Phi_{tk-1}$

$$(l + 1 \leqslant k \leqslant h) \tag{3,5}$$

Rigorous proofs of this theorem have been given by P. G. MURDOCH and C. D. HOLLAND [3] and independently by A. ACRIVOS and N. R. AMUNDSON [1]. A proof can also be found in section 7.5 of the present thesis.

3.3. UNDERWOOD'S EQUATION

It is convenient to denote the values of the inside roots of the characteristic bottom equation by Ω_k according to

$$\Omega_{k-1} = \Phi_{bk}^{-1} = \Phi_{tk-1} \qquad (l + 1 \leqslant k \leqslant h) \tag{3,6}$$

Then, clearly, Ω_{k-1}^{-1} is a root of Eq. (3,2), i.e.

$$V_t = \sum_{i=1}^{h} D_i/(1 - \alpha_i^{-1}\Omega_{k-1}^{-1}) \tag{3,7}$$

Application of the law of conservation of matter to the condenser leads to

$$V_t = L_t + \sum_{i=1}^{h} D_i \tag{3,8}$$

After equating the right hand members of Eqs. (3,7) and (3,8) it is easy to derive that

$$-L_t = \sum_{i=1}^{h} D_i/(1 - \alpha_i\Omega_{k-1}) \tag{3,9}$$

On the other hand Ω_{k-1} must satisfy Eq. (3,1)

$$L_b = \sum_{i=l}^{J} B_i/(1 - \alpha_i\Omega_{k-1}) \tag{3,10}$$

Recalling $F_i = B_i + D_i$ (conservation of matter applied to the entire column) and recalling $B_i = 0$ for $i < l$ and $D_i = 0$ for $i > h$, addition of Eqs. (3,9) and (3,10) yields

$$L_b - L_t = \sum_{i=1}^{J} F_i/(1 - \alpha_i\Omega_{k-1}) \tag{3,11}$$

Hence the values Ω_k are the roots of a third characteristic equation which is UNDERWOOD'S *equation*

$$q = L_b - L_t = \sum_{i=1}^{J} F_i/(1 - \alpha_i s) \tag{3,12}$$

It should be noted that one must write qF instead of q if the total feed rate F differs from unity!

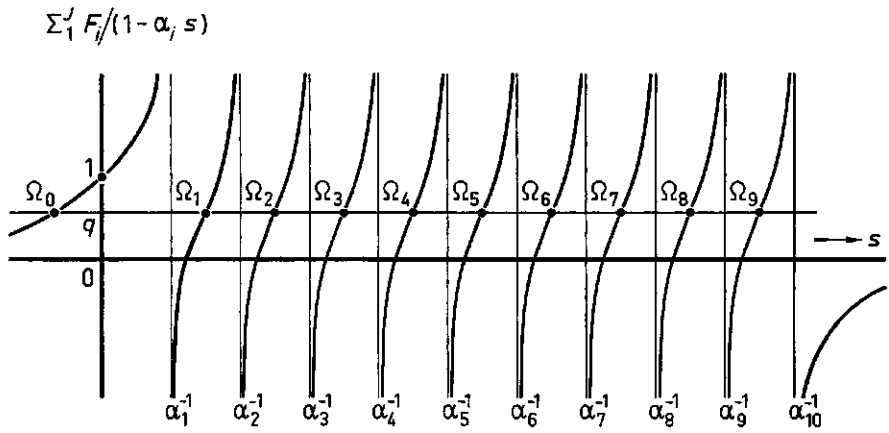

FIG. 5. Solution of UNDERWOOD's equation (schematical).

The graph of the function in the right hand side of Eq. (3,12) is qualitatively drawn in Fig. 5. This function is of the same type as the characteristic bottom function. All J components occur in Eq. (3,12) which has at least $J-1$ distinct and positive roots Ω_k obeying the inequality

$$\alpha_k^{-1} < \Omega_k < \alpha_{k+1}^{-1} \qquad (1 \leqslant k \leqslant J-1) \qquad (3,13)$$

The positive part of the vertical axis is intersected by the graph at a height $\Sigma_i F_i = 1$. Thus an additional root Ω_0 occurs which is negative for $0 < q < 1$, zero for $q = 1$, and positive for $q < 0$ or $q > 1$. The meaning of this root will become clear in section 4.3.

It is here that the above mentioned narrow freedom of the roots becomes manifest! Throughout this thesis the case is considered of *prescribed feed condition parameter q*. Then, by virtue of UNDERWOOD's equation (3,12), the inside roots Φ_{bk}^{-1} and Φ_{ik-1}^{-1} are nailed to the s-axis in the positions $s = \Omega_{k-1}$ and $s = \Omega_{k-1}^{-1}$ respectively, whatever the set of values of the product rates B_i and D_i may happen to be. Only the positions of the outside roots will be influenced by changes in the product rates B_i and D_i.

3.4. UNDERWOOD'S METHOD

The important feature of UNDERWOOD's equation (3,12) is the possibility, *once a value for q has been selected*, to calculate its roots Ω_k without a knowledge of the product rates B_i and D_i.

We no longer need to calculate roots of characteristic equations with estimated approximate values of the numerators B_i and D_i (which is the analytical routine for finite columns), but we substitute appropriate roots Ω_k of UNDERWOOD's equation into the characteristic bottom equation (3,1) and compute the bottom products B_i from the set of linear equations thus obtained.

For convenience we summarize the method in the following theorem, which is deliberately formulated in terms of the separation ratios $s_{bk} = B_k/F_k$ for the bottom products only:

If l and h are the indices of the lightest and heaviest distributed component

respectively and if $\Omega_l, \Omega_{l+1}, \ldots, \Omega_{h-1}$ *are the roots of* UNDERWOOD's *equation*

$$q = \sum_{i=1}^{J} F_i/(1 - \alpha_i s)$$

which satisfy the conditions

$$\alpha_k^{-1} < \Omega_k < \alpha_{k+1}^{-1} \qquad (k = l, l+1, \ldots, h-1)$$

then these roots satisfy also the characteristic bottom equation and they provide thus precisely $h - l$ *independent linear equations*[1])

$$L_b = \sum_{i=l}^{J} s_{bi} F_i/(1 - \alpha_i \Omega_k) \qquad (k = l, l+1, \ldots, h-1)$$

in the $h - l + 2$ *unknowns* $L_b, s_{bl}, s_{bl+1}, \ldots, s_{bh}$.[2])

The number of unknowns exceeds the number of equations by two. Hence, to define a solution (= separation) one must prescribe the values of two variables, for which can be chosen any pair of separation ratios, or both reflux ratios R_B and R_D or still an other pair of variables.

In distillation practice it is customary to prescribe the separation of two *key components*. Although one usually takes the lightest and heaviest distributed component for the keys, it should be stressed that from the mathematical point of view the distributed components are completely equivalent, so that any two of them can serve as keys. The selection of the separation ratios of the keys is known as *specification*.

MURDOCH and HOLLAND, as well as ACRIVOS and AMUNDSON, have derived explicite solutions, expressing the product rates of the distributed components in the key product rates. The present author, however, prefers to pertain to the original set of linear equations. The reader should bear in mind that the coefficients $F_i/(1 - \alpha_i \Omega_k)$, occurring in the linear equations, are the fractions of the right hand member of UNDERWOOD's equation and hence are automatically obtained during the calculation of the roots Ω_k. In computer programs, therefore, it seems imperative to stick to the set of linear equations and to utilize the computation of the roots Ω_k in the construction of these linear equations, rather than to introduce the more sophisticated formulae of the authors mentioned above.

3.5. SPECIFICATION

It follows from UNDERWOOD's method that the number of linear equations, as well as the number of unknowns, is determined by the values of l and h, i.e. by the extension of the separation band.

In this thesis it will be shown that the separation band is completely and uniquely determined by the specification of the separation ratios $s_{b\mu}$ and $s_{b\nu}$, $\mu < \nu$ say, of two arbitrarily chosen distributed components (key components). By implication l and h are *additional unknowns* depending on $s_{b\mu}$ and $s_{b\nu}$, but a simple relation between l and h on the one hand and $s_{b\mu}$ and $s_{b\nu}$ on the other hand does not exist.

[1]) The mutual independence of these equations is proved in appendix IV.

[2]) Apparently one has for the separation ratios of the volatile non-distributed components $s_{b1} = s_{b2} = \ldots = s_{bl-1} = 0$ and for those of the less volatile non-distributed components $s_{bh+1} = s_{bh+2} = \ldots = s_{bJ} = 1$.

Current distillation literature apparently ignores this problem. As far as is known to the present author, only ACRIVOS and AMUNDSON briefly mention the subject [2, page 71]

"...Of course, it must be understood that h and l are not known a priori, and so, in general, there are more unknowns than there are equations. However, it turns out, in all the cases which have been investigated so far, that the system of equations ... and ... has only one solution which satisfies the additional requirement

$$0 < s_{bi} < 1 \qquad \text{for } l < i < h \qquad (+)$$

(our notation!)

In practice it is best to assume h and l first, and then to solve equation... This process is repeated until (+) is obeyed. ..."

In this quotation the uniqueness of a solution, determined by $s_{b\mu}$ and $s_{b\nu}$, is presumed. We shall give a proof for this uniqueness in chapter 4. ACRIVOS and AMUNDSON recognize the risk of false solutions due to the use of incorrect values for l and h. We shall demonstrate in chapter 5, however, that their condition (+), meant to single out the unique *consistent* solution, is not adequate, and we shall replace this condition by a necessary and sufficient criterion.

It must be realized that an arbitrary combination of values for $s_{b\mu}$ and $s_{b\nu}$ does not necessarily correspond to a physically possible state (consistent solution). In the specification one has to make allowance for the monotonic increase of the ratios s_{bi} with respect to the component index i, (first monotony theorem). So if $\mu < \nu$, then $s_{b\mu}$ belongs to the more volatile component and, hence, $s_{b\mu} < s_{b\nu}$. That this condition is not sufficient can be seen, by way of example, from Fig. 6, where the shaded part indicates the forbidden combinations of s_{b4} and s_{b7} for the ten component system. Here $q = 0.6$. In the white area of consistent combinations values of l and h occur ranging from 1 to 4 and from 7 to 10 respectively.

We conclude that, having fixed q in advance, the specification of the keys requires a knowledge of

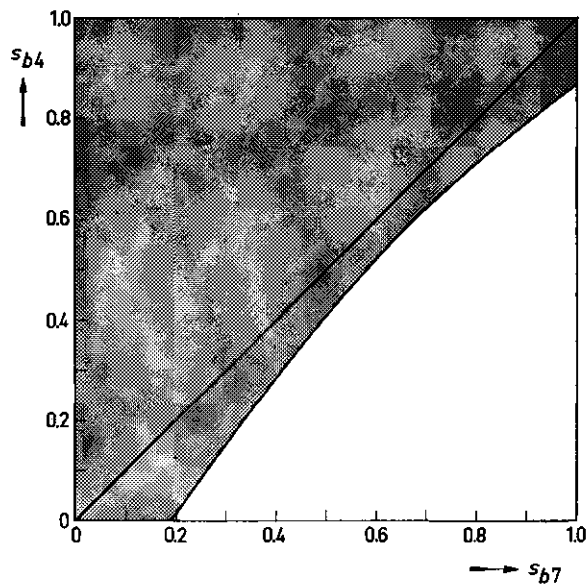

FIG. 6. Forbidden combinations (shaded part) of s_{b4} and s_{b7} for the ten component system ($q = 0.6$).

a) *the domain of consistent combinations of* s_{bu} *and* s_{bv}.
b) *the appropriate values of* l *and* h *conjugate to these combinations.*

Later on we shall see that there exist exactly $\frac{1}{2}J(J-1)$ borderline cases in which this information is a priori available, (*vertex-separations*, vide chapter 4).

Similar difficulties arise if one specifies both reflux ratios R_B and R_D instead of two keys.

3.6. PINCH PARAMETERS

We introduce as independent variables the smallest roots Φ_{bl}^{-1} and Φ_{th}^{-1} of the characteristic equations for the bottom and the top section respectively. It must be understood that the indices l and h are to be considered as variables themselves, so that Φ_{bl}^{-1} and Φ_{th}^{-1} can be made to coincide with the smallest roots of the characteristic equations corresponding to *any* separation of the multicomponent system.

The roots Φ_{bl}^{-1} and Φ_{th}^{-1} are the respective reciprocal values of the absorption factor at the bottom pinch and the stripping factor at the top pinch of the reference component (with $\alpha = 1$, vide chapter 6).

$$\begin{aligned} \Phi_{bl} &= A_{b\text{pinch}} \\ \Phi_{th} &= S_{t\text{pinch}} \end{aligned} \tag{3,14}$$

Therefore, they will be termed the *pinch* parameters to distinguish them conveniently from the *terminal* parameters q, R_B and R_D.

Specification of the pinch parameters adjusts the number of equations to the number of unknowns instead of decreasing the latter number as happens in ordinary specification.

Indeed, to the linear equations which occur in UNDERWOOD's method and which obviously may be written [1])

$$L_b - \sum_{i=l}^{h} s_{bi}F_i/(1-\alpha_i\Omega_k) = \sum_{j=h+1}^{J} F_j/(1-\alpha_j\Omega_k) \tag{3,15}$$

$$k = l,\ l+1,\ \ldots,\ h-1.$$

are added the equations

$$L_b - \sum_{i=l}^{h} s_{bi}F_i/(1-\alpha_i\Phi_{bl}^{-1}) = \sum_{j=h+1}^{J} F_j/(1-\alpha_j\Phi_{bl}^{-1}) \tag{3,16}$$

and

$$L_b - \sum_{i=l}^{h} s_{bi}F_i/(1-\alpha_i\Phi_{th}) = q - \sum_{j=1}^{h} F_j/(1-\alpha_j\Phi_{th}) \tag{3,17}$$

Thus we have precisely $h-l+2$ linear equations in the $h-l+2$ unknowns L_b, s_{bl}, s_{bl+1}, ..., s_{bh}. Equation (3,16) is essentially the characteristic bottom equation (3,1)[1]), rewritten in terms of the separation ratios s_{bi}.

Equation (3,17) is a modification of the characteristic top equation (3,2). Substituting Eq. (3,8) into (3,2) we find

$$-L_t = \sum_{i=1}^{h} D_i/(1-\alpha_i\Phi_{th}) \tag{3,18}$$

[1]) Recalling $s_{bh+1} = s_{bh+2} = \ldots = s_{bJ} = 1$, the unknowns have been concentrated in the left hand member.

Substitution of Eq. (3,18) into the defining equation of q

$$q = L_b - L_t$$

yields

$$L_b = q - \sum_{i=1}^{h} D_i/(1 - \alpha_i \Phi_{ih})$$

Recalling $D_i = F_i - B_i = F_i - s_{bi}F_i$ and recalling $s_{b1} = s_{b2} = \ldots = s_{bl-1} = 0$, we can write

$$L_b = q - \sum_{i=1}^{h} F_i/(1 - \alpha_i \Phi_{ih}) + \sum_{i=l}^{h} s_{ib}F_i/(1 - \alpha_i \Phi_{ih})$$

which is Eq. (3,17).

The matrix of coefficients of the system (3,15), (3,16) and (3,17) is non-singular.

The proof is given in appendix IV.

As tools for the systematic detection of consistent solutions the pinch parameters Φ_{bl}^{-1} and Φ_{ih}^{-1} are superior over the separation ratios $s_{b\mu}$ and $s_{b\nu}$ of two key components, as the pinch parameters have the great advantage of possessing a priori computable intervals of consistent values *with known values l and h, conjugate to these intervals.*

In fact we have the theorem

Φ_{bl}^{-1} has J disjunct intervals along the s-axis, corresponding to the integral values from 1 to J inclusive for l. These intervals are closed to the left and open to the right.

$$\Omega_{l-1} \leqslant \Phi_{bl}^{-1} < \alpha_l^{-1} \qquad \text{for any } q \text{ if } 2 \leqslant l \leqslant J \qquad (3,19)$$

$$0 \leqslant \Phi_{b1}^{-1} < \alpha_1^{-1} \qquad \text{for } q \leqslant 1 \text{ if } l = 1 \qquad (3,20)$$

$$0 < \Omega_0 \leqslant \Phi_{b1}^{-1} < \alpha_1^{-1} \qquad \text{for } q > 1 \text{ if } l = 1 \qquad (3,21)$$

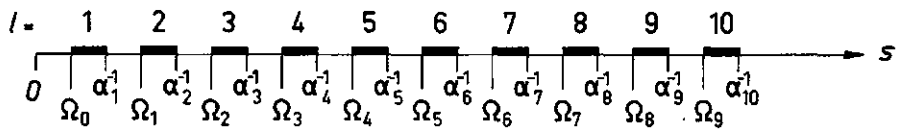

FIG. 7. Consistent intervals (heavy bars) of Φ_{bl}^{-1} on s-axis. Conjugate values of l are indicated (schematical) ($q > 1$).

Proof. Suppose l has the value λ and, hence, that $\Phi_{bl}^{-1} = \Phi_{b\lambda}^{-1}$ is situated somewhere between $\alpha_{\lambda-1}^{-1}$ and α_λ^{-1} (vide Figs. 9A and 9B). Then λ is the lightest distributed component. When $s_{b\lambda}$ is very small, the term $s_{b\lambda}F_\lambda/(1 - \alpha_\lambda s)$ can become large only if s nearly equals α_λ^{-1}. Hence when $s_{b\lambda} \to 0$ the graph of the characteristic bottom function will be pressed against the vertical asymptote at $s = \alpha_\lambda^{-1}$ and the root $\Phi_{b\lambda}^{-1}$ will approach α_λ^{-1}. Therefore, it can be assumed that $\Phi_{b\lambda}^{-1}$ is situated in the *right hand* part of its interval if $s_{b\lambda}$ is sufficiently small, i.e.

$$\Omega_{\lambda-1} < \Phi_{b\lambda}^{-1} < \alpha_\lambda^{-1}$$

Let now $\Phi_{b\lambda}^{-1}$ move to the left, towards $\Omega_{\lambda-1}$. Then $\Phi_{b\lambda}^{-1}$ becomes "inside root"

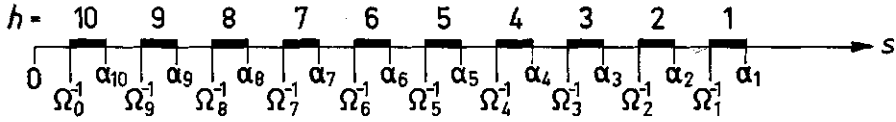

FIG. 8. Consistent intervals (heavy bars) of Φ_{ih}^{-1} on s-axis. Conjugate values of h are indicated (schematical) ($q < 0$).

at the instant it reaches the point $s = \Omega_{\lambda-1}$, that is when $s_{b\lambda-1}$ starts to differ from zero, i.e. when component $\lambda - 1$ starts to join the bottom product. At the same instant, however, if the variation of the separation ratios, causing the shift of $\Phi_{b\lambda}^{-1}$, is continued the root $\Phi_{b\lambda-1}^{-1}$ comes into existence. Hence Φ_{bl}^{-1} jumps from the point $s = \Omega_{\lambda-1}$ to the consecutive interval at the left. Thus it is seen that Φ_{bl}^{-1} cannot reach the left hand part of the interval beyond $\Phi_{\lambda-1}$.

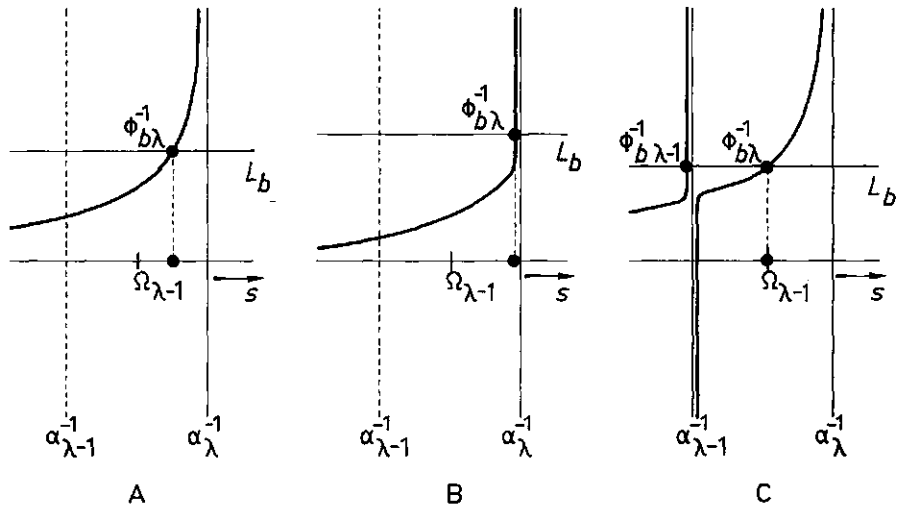

FIG. 9. Extinction and genesis of distributed components. If pinch parameter $\Phi_{b\lambda}^{-1} \to \alpha_\lambda^{-1}$ then $s_{b\lambda} \to 0$.
If $\Phi_{b\lambda}^{-1} \to \Omega_{\lambda-1}$ then a new root $\Phi_{b\lambda-1}^{-1}$ corresponding to a new distributed component $s_{b\lambda-1}$ appears.

The left hand terminal point Ω_{l-1} of (3,19) can be actually reached because the coefficients in the equations stay finite when Φ_{bl}^{-1} takes the value Ω_{l-1}. Therefore the intervals are closed at the left sides. When Φ_{bl}^{-1} approaches α_l^{-1}, the ratio s_{bl} must vanish in order to suppress its indefinitely increasing coefficient $F_l/(1 - \alpha_l \Phi_{bl}^{-1})$, since inspection of the system of equations (3,15), (3,16) and (3,17) shows the other terms to be bounded. The fraction $s_{bl}F_l/(1 - \alpha_l \Phi_{bl}^{-1})$ itself does not vanish but yields a limiting value (see below). The intervals are hence open at their right hand sides. The analogous inequalities (3,20) and (3,21) are considered in section 4.3.

Similarly one can prove the theorem

Φ_{ih}^{-1} has J disjunct intervals along the s-axis, corresponding to the integral values from 1 to J inclusive for h. These intervals are closed to the left and open to the right.

$$\Omega_h^{-1} \leqslant \Phi_{th}^{-1} < \alpha_h \qquad \text{for any } q \quad \text{if } 1 \leqslant h \leqslant J-1 \tag{3,22}$$

$$0 \leqslant \Phi_{tJ}^{-1} < \alpha_J \qquad \text{for } q \geqslant 0 \quad \text{if } h = J \tag{3,23}$$

$$0 < \Omega_0^{-1} \leqslant \Phi_{tJ}^{-1} < \alpha_J \qquad \text{for } q < 0 \quad \text{if } h = J \tag{3,24}$$

Next we formulate the *second monotony theorem*, (the first monotony theorem will be found in appendix I).

On lines of constant Φ_{th}^{-1} *the reboil ratio* R_B, *the total liquid rate* L_b, *the total bottom product B and the ratios* s_{bi} *are continuous and monotonic functions of* Φ_{bl}^{-1} *in the intervals* (3,19) *and* (3,20) *or* (3,21). *On lines of constant* Φ_{bl}^{-1} *the reflux ratio* R_D, *the total liquid rate* L_b, *the total top product D and the ratios* s_{bi} *are continuous and monotonic functions of* Φ_{th}^{-1} *in the intervals* (3,22) *and* (3,23) *or* (3,24). *One has (for constant q)*

$$\frac{\partial R_B}{\partial(\Phi_{bl}^{-1})} > 0; \quad \frac{\partial B}{\partial(\Phi_{bl}^{-1})} < 0; \quad \frac{\partial L_b}{\partial(\Phi_{bl}^{-1})} > 0; \quad \frac{\partial s_{bi}}{\partial(\Phi_{bl}^{-1})} < 0 \tag{3,25}$$

and

$$\frac{\partial R_D}{\partial(\Phi_{th}^{-1})} > 0; \quad \frac{\partial D}{\partial(\Phi_{th}^{-1})} < 0; \quad \frac{\partial L_b}{\partial(\Phi_{th}^{-1})} > 0; \quad \frac{\partial s_{bi}}{\partial(\Phi_{th}^{-1})} > 0 \tag{3,26}$$

The tedious but essential elementary algebraic proof is given in appendix II. We shall now prove the *first theorem of continuation:*

If Φ_{th}^{-1} *is kept constant and if* Φ_{bl}^{-1} *approaches the right hand terminating point* α_l^{-1} *of any interval*

$$\Omega_{l-1} \leqslant \Phi_{bl}^{-1} < \alpha_l^{-1}$$

then R_B, L_b, *B and the ratios* s_{bi} $(l \leqslant i \leqslant h)$ *approach the values corresponding to the left hand terminating point* Ω_l *of the consecutive interval*

$$\Omega_l \leqslant \Phi_{bl}^{-1} < \alpha_{l+1}^{-1}$$

Proof. We know that $s_{bl} \to 0$ when $\Phi_{bl}^{-1} \to \alpha_l^{-1}$. Therefore, s_{bl} will be eliminated from the equations (3,15), (3,16) and (3,17). This is easily done by solving s_{bl} from equation (3,16), yielding

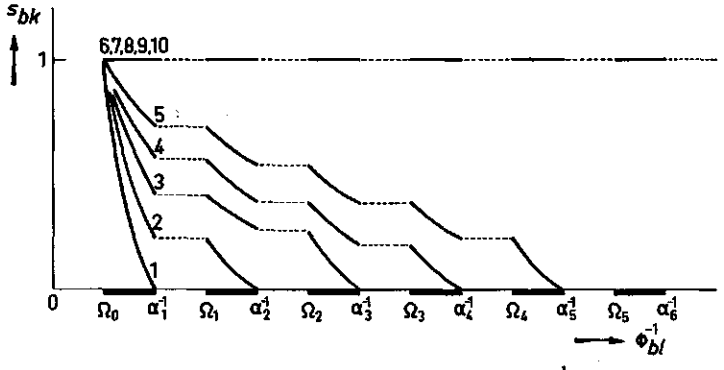

FIG. 10. Monotonic behaviour of the ratios on line of constant Φ_{th}^{-1}. $(q > 1$, hence $0 < \Omega_0 \leqslant \leqslant \Phi_{bl}^{-1} < \alpha_1^{-1})$ (schematical).

$$s_{bl} = \frac{1 - \alpha_l \Phi_{bl}^{-1}}{F_l} \cdot \left[L_b - \sum_{i=l+1}^{h} s_{bi} F_i / (1 - \alpha_i \Phi_{bl}^{-1}) - \sum_{j=h+1}^{J} F_j / (1 - \alpha_j \Phi_{bl}^{-1}) \right]$$

which we abbreviate as

$$s_{bl} = \frac{1 - \alpha_l \Phi_{bl}^{-1}}{F_l} \cdot [\ldots] \tag{3,27}$$

Substitution of (3,27) into Eqs. (3,15) and (3,17) yields

$$L_b - \sum_{i=l+1}^{h} s_{bi} F_i / (1 - \alpha_i \Omega_k) = \sum_{j=h+1}^{J} F_j / (1 - \alpha_j \Omega_k) + \frac{1 - \alpha_l \Phi_{bl}^{-1}}{1 - \alpha_l \Omega_k} \cdot [\ldots] \tag{3,28}$$

with $k = l,\ l+1,\ \ldots,\ h-1$, and

$$L_b - \sum_{i=l+1}^{h} s_{bi} F_i / (1 - \alpha_i \Phi_{th}) = q - \sum_{j=1}^{h} F_j / (1 - \alpha_j \Phi_{th}) + \frac{1 - \alpha_l \Phi_{bl}^{-1}}{1 - \alpha_l \Phi_{th}} \cdot [\ldots] \tag{3,29}$$

When Φ_{bl}^{-1} approaches α_l^{-1} the coefficients of the bracket expressions vanish and the equations (3,28) and (3,29) are seen to reduce exactly to the system which may be obtained from the equations (3,15), (3,16) and (3,17) by replacing l by $l+1$ and by putting Φ_{bl}^{-1} equal to Ω_l. And this settles the theorem.

Without proof we state the *second theorem of continuation*

If Φ_{bl}^{-1} is kept constant and if Φ_{th}^{-1} approaches the right hand terminating point α_h of any interval

$$\Omega_h^{-1} \leqslant \Phi_{th}^{-1} < \alpha_h$$

then R_D, L_b, B and the ratios s_{bi} $(l \leqslant i \leqslant h)$ approach the values corresponding to the left hand terminating point Ω_{h-1}^{-1} of the consecutive interval

$$\Omega_{h-1}^{-1} \leqslant \Phi_{th}^{-1} < \alpha_{h-1}$$

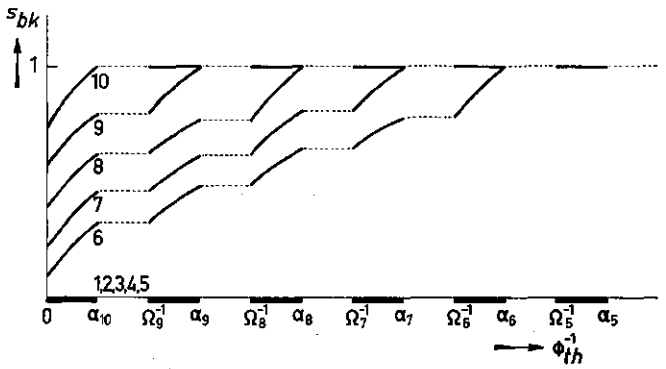

FIG. 11. Monotonic behaviour of the ratios on line of constant Φ_{bl}^{-1}. $(0 < q < 1$, hence $\Omega_0 < 0 \leqslant \Phi_{t0}^{-1} < \alpha_{t0})$. (schematical).

Both theorems of continuation are qualitatively illustrated by Figs. 10 and 11. The proof of the second theorem is omitted as it obviously runs along the same lines as the proof given for the first theorem. It may suffice to point out a difference between Eqs. (3,16) and (3,17). In Eq. (3,17) two terms instead of one tend to increase indefinitely when Φ_{th}^{-1} approaches α_h. Inspection of Eq.

(3,17) reveals that s_{bh} must approach 1 to force both terms to cancel. This is clearly demonstrated by Fig. 11, where the curves bend upwards instead of downwards, as is the case in Fig. 10.

3.7. CLASSIFICATION

The dominant role, played by the separation band, suggests the use of the latter as a base for classification. Therefore, two separations P and Q are defined to be equivalent ($P \sim Q$) if both have identical distributed components[1]), that is the same value of l and h. Evidently this relation satisfies the requirements of a true equivalence (reflexivity, commutativity and transitivity) and, therefore, induces a classification of separations.

The classes will be denoted with regard to number and identity of the distributed components as "class of multiplet separations ($l.h$)", which may conveniently be abbreviated by "multiplet ($l.h$)". For the ten component system we can distinguish

1	decuplet	(1.10)
2	nonuplets	(1.9) and (2.10)
3	octuplets	(1.8), (2.9) and (3.10)
4	septuplets	(1.7), (2.8), ..., (4.10)
5	sextuplets	(1.6), (2.7), ..., (5.10)
6	quintuplets	(1.5), (2.6), ..., (6.10)
7	quadruplets	(1.4), (2.5), ..., (7.10)
8	triplets	(1.3), (2.4), ..., (8.10)
9	doublets	(1.2), (2.3), ..., (9.10)
10	singlets	(1), (2), ..., (10)

To these classes must be appended

9 classes of absolute separations (2.1), (3.2), (4.3), ..., (10.9)

which have no distributed components at all! The latter classes have the common characteristic of $l = h + 1$, where l and h now have the meaning of lightest component in the bottom product and heaviest component in the top product respectively.

Obviously the total number of classes amounts

$$\tfrac{1}{2}J(J+1) + (J-1) = \tfrac{1}{2}J(J+3) - 1 \qquad (3,30)$$

which comes to 64 classes for the ten component system.

The classes are completely determined by the values of l and h, as are the permissible intervals for Φ_{bl}^{-1} and Φ_{ih}^{-1} respectively. Hence we are able to indicate at once the domain of combinations $(\Phi_{bl}^{-1}, \Phi_{ih}^{-1})$ pertaining to the separations of any one of the classes. These domains are shown in Fig. 12.

For clearness' sake the diagram again has been drawn purely schematically. The real values of the roots Ω_k of Eq. (3,12) computed for the ten component system for various values of the feed condition parameter q are collected in appendix V.

The small straight lines along the diagonal of Fig. 12 represent symbolically the classes of absolute separations. If distributed components are absent, the

[1]) P and Q are not meant to have identical separation ratios for the distributed components!

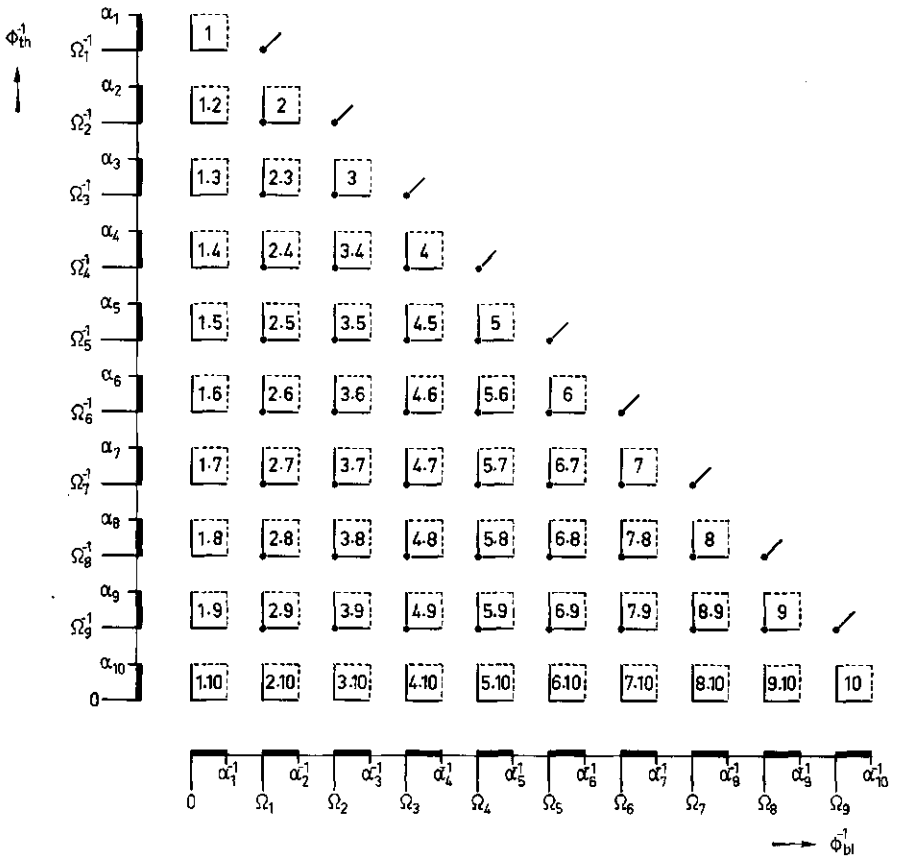

FIG. 12. Classification of separations of ten component system, (schematical). Numbers in squares indicate values of l and h respectively. ($0 < q^* < 1$, hence $\Omega_0 < 0$).

absolute separations are determined by Eqs. (3,16) and (3,17) only. The separation ratios s_{bl}, however, are now simultaneously known in advance.

$$(s_{b1} = s_{b2} = \ldots = s_{bl-1} = 0 \text{ and } s_{bl} = s_{bl+1} = \ldots = s_{bJ} = 1)$$

The only remaining unknown is L_b. The summations in the left hand members of Eqs. (3,16) and (3,17) apply to distributed components and, hence, are to be ignored. Recalling that in this case $h = l - 1$, the equations become respectively

$$L_b = \sum_{i=l}^{J} F_i/(1 - \alpha_i \Phi_{bl}^{-1}) \tag{3,31}$$

and

$$L_b = q - \sum_{i=1}^{l-1} F_i/(1 - \alpha_i \Phi_{tl-1}) \tag{3,32}$$

Subtraction yields

$$q = \sum_{i=1}^{l-1} F_i/(1 - \alpha_i \Phi_{tl-1}) + \sum_{j=l}^{J} F_j/(1 - \alpha_j \Phi_{bl}^{-1}) \tag{3,33}$$

From Eq. (3,33) it is seen that Φ_{th}^{-1} and Φ_{bl}^{-1} are no longer independent. Hence

the classes of absolute separations must be represented by curves instead of rectangles. As the exact shape of these curves is irrelevant for the present consideration, we have not cared to compute the curves. The marked terminating points, however, are exact, as comparison of Eq. (3,33) with UNDERWOOD's equation shows that $\Phi_{tl-1} = \Phi_{bl}^{-1} = \Omega_{l-1}$ is a solution of (3,33)!

The squares, representing the classes, are open along their northern and eastern boundaries (dotted lines) and closed along their southern and western boundaries, (compare the intervals (3,19) to (3,24) inclusive). The distributed squares must be put together like the pieces of a jigsaw puzzle. The first and second theorem of continuation govern the fitting together of the pieces. Adjacent eastern and western and adjacent northern and southern boundaries are to be identified, to obtain a pattern which is continuous in all directions.

The diagram provides a guide to consistent solutions, i.e. solutions compatible with the underlying basic equations of the present model.[1]) In this sense Fig. 12 affords a complete survey of the multitude of separations, but the survey is purely analytical. The diagram concerns the systems of equations, not the solutions. Therefore, we have now to solve the equations and to convert this implicit representation into an explicit one. This will be carried out in the next chapter, where the entire assemblage of separations will be pictured into three dimensional (q, R_B, R_D)-space.

CHAPTER 4

MULTIPLET REPRESENTATION

4.1. (q, R_B, R_D)-SPACE

In the present model the three dimensionless terminal parameters q, R_B and R_D command the column performance. Therefore, it is logical to represent the separations by the points of the space in which q, R_B and R_D are taken as orthogonal Cartesian coordinates.

4.2. PENCIL OF LINES OF CONSTANT B IN PLANE OF CONSTANT q

From our definition of the feed condition parameter q

$$q = L_b - L_t \tag{4,1}$$

if

$$F = B + D = 1 \tag{4,2}$$

and from the well known relations [2])

$$L_b = (R_B + 1)B \tag{4,3}$$

and

$$L_t = R_D D \tag{4,4}$$

we can obtain by simple algebra the relation

[1]) Vide chapter 6.
[2]) Vide chapter 4.

$$R_D = \frac{B}{1-B} R_B + \frac{B-q}{1-B} \tag{4,5}$$

In a plane of constant q, ($q = q^*$), Eq. (4,5) takes for constant B, ($B = B^*$), the form

$$R_D = \frac{B^*}{1-B^*} R_B + \frac{B^*-q^*}{1-B^*} \tag{4,6}$$

which is a linear equation in R_B and R_D. The substitutions $R_B = q^* - 1$ and $R_D = -q^*$ satisfy Eq. (4,6) independently of the value of B^*. Hence, Eq. (4,6) represents a plane pencil of straight lines radiating from the centre C with coordinates

$$(R_B, R_D) = (q^* - 1, -q^*) \tag{4,7}$$

This is shown in Fig. 13 for the plane $q = 0.6$.

From (4,7) it follows that the centre C is situated on the straight line

$$R_B + R_D = -1 \tag{4,8}$$

Note that Eq. (4,8) is independent of the value q^*.

Differentiation of Eq. (4,6) with respect to R_B yields

$$\frac{\partial R_D}{\partial R_B} = \frac{B^*}{1-B^*} \tag{4,9}$$

Differentiation of Eq. (4,9) with respect to B^* results in

$$\frac{\partial^2 R_D}{\partial B^* \partial R_B} = \frac{1}{(1-B^*)^2} > 0 \tag{4,10}$$

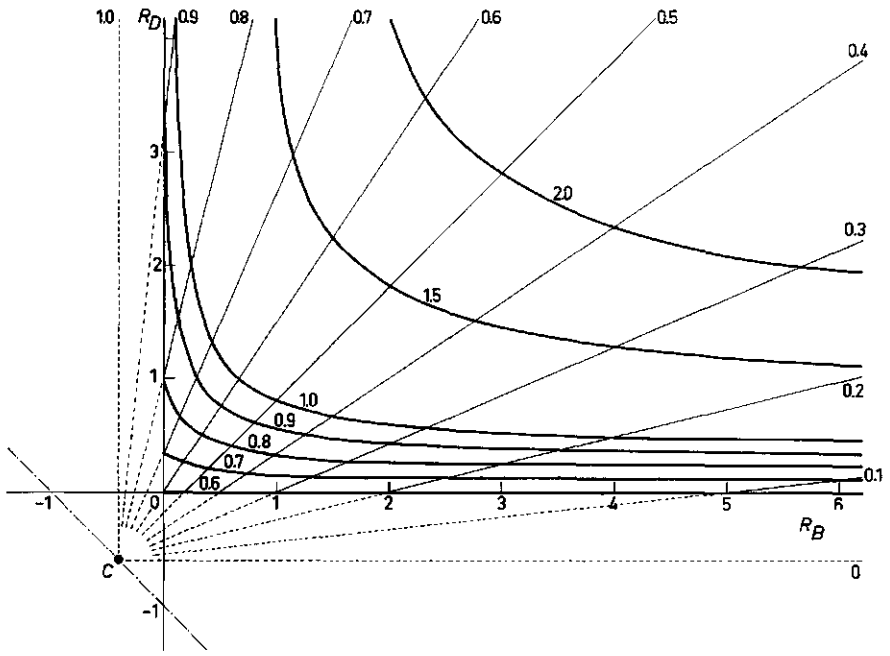

FIG. 13. Plane $q = 0.6$ with first quadrant of pencil of lines $B = B^*$ and with curves $L_b = L_b^*$. The positive R_B-axis is the line $L_b = 0.6$.

Hence the slope of the straight line (4,6) is a monotonic increasing function of B^* only. We find

The pencils in all the planes of constant q are congruent.

Of course only the lines of a pencil corresponding to values of B^*, ranging from 0 to 1, are of interest.[1]) From (4,9) it is seen that the line $B = 0$ runs parallel to the R_B-axis and the line $B = 1$ parallel to the R_D-axis.

The right angle, bounded by $B = 0$ and by $B = 1$, is said to be the *first quadrant* of the pencil.

4.3. Empty zones and interpretation of Ω_0

Clearly[2]) the points of a plane $q = q^*$ represent separations only if they coincide with lines $B = B^*$ and

$$0 \leqslant B^* \leqslant 1 \tag{4,11}$$

Hence only the part of the positive quadrant of the (R_B, R_D)-plane, which is *covered* by the first quadrant of the pencil, contains the separations.

In Fig. 14 the line (4,8) is divided into three parts, laying in the second, third and fourth quadrant of the (R_B, R_D)-plane. From (4,7) it is seen that $q^* < 0$ corresponds to the part in the second quadrant, $0 < q^* < 1$ to the part in the

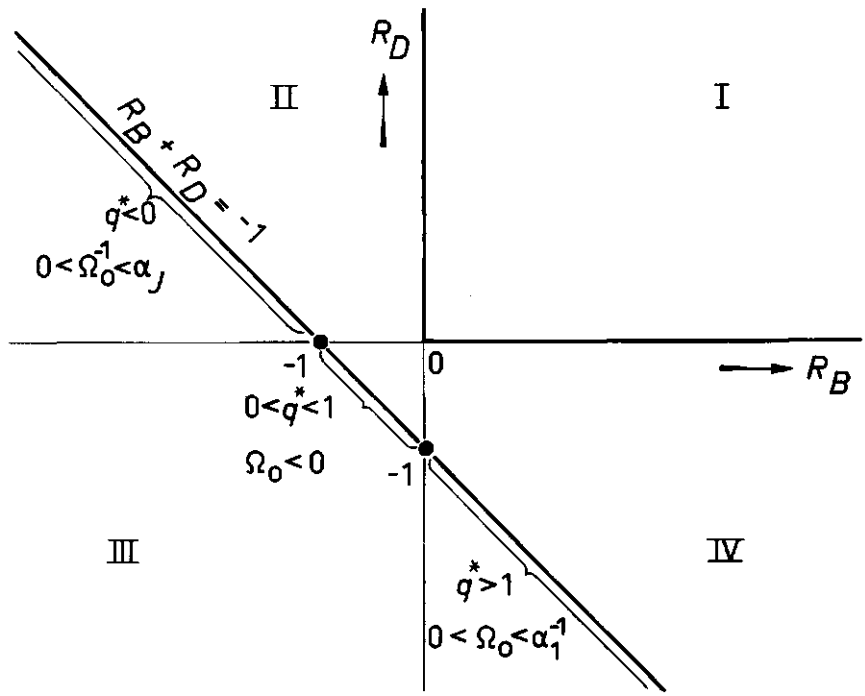

FIG. 14. Values of q^* and Ω_0 pertaining to various positions of centre C of pencil of lines $B = B^*$.

[1]) Since $B \leqslant F = 1$.
[2]) The total feed rate $F = 1$!

third quadrant and $q^* > 1$ to the part in the fourth quadrant. In section 3.3 it was found that

$$\begin{array}{lll} 0 < \Omega_0^{-1} < \alpha_J & \text{when } q^* < 0 & \\ \Omega_0 < 0 & \text{when } 0 < q^* < 1 & (4,12) \\ 0 < \Omega_0 < \alpha_1^{-1} & \text{when } q^* > 1 & \end{array}$$

We consider now the case of $q^* > 1$. (Fig. 15).

It is seen that the positive quadrant is not entirely covered by the positive quadrant of the pencil. An *empty zone* occurs between the R_D-axis and the boundary of the domain of separations, i.e. the line $B = 1$.

From (4,7) again it follows that the abscis of the point of intersection P of $B = 1$ with the R_B-axis equals $q^* - 1$.

Hence for the separation P (and also for any separation of the boundary line $B = 1$) we have

$$\begin{cases} q = q^* > 1 \\ R_B = q^* - 1 \\ B = 1 \end{cases} \tag{4,13}$$

Writing out the characteristic bottom equation for the root Φ_{b1}^{-1} for this case [1]) we get, recalling $L_b = (R_B + 1)B = q^*$

$$q^* = \sum_{i=1}^{J} B_i/(1 - \alpha_i \Phi_{b1}^{-1}) \tag{4,14}$$

Obviously one has

$$B_i \leqslant F_i \tag{4,15}$$

Subtracting

$$\Sigma B_i = 1 \tag{4,16}$$

from

$$\Sigma F_i = 1 \tag{4,17}$$

yields

$$\Sigma (F_i - B_i) = 0 \tag{4,18}$$

With regard to (4,15) all the terms of the summation in (4,18) are non-negative. Therefore, the terms must vanish simultaneously. Hence

$$B_i = F_i \qquad i = 1, \ldots, J \tag{4,19}$$

in this case and Eq. (4,14) can be written

$$q^* = \sum_{i=1}^{J} F_i/(1 - \alpha_i \Phi_{b1}^{-1}) \tag{4,20}$$

We conclude that Φ_{b1}^{-1} satisfies UNDERWOOD's equation and hence must be identified with one of the roots Ω_k. Comparing intervals, it is found that both Φ_{b1}^{-1} and Ω_0 are situated between 0 and α_1^{-1}, hence

$$\Phi_{b1}^{-1} = \Omega_0 \tag{4,21}$$

Here the meaning of Ω_0 becomes clear

When $q^* > 1$, there exists an empty zone along the R_D-axis in the planes $q = q^*$. The boundary between the empty zone and the domain of separations is the line $B = 1$, parallel to the R_D-axis. The minimum value of R_B equals $q^* - 1$. One has then

[1]) As $B = 1$ the ratio $s_{b1} \neq 0$ and hence $l = 1$.

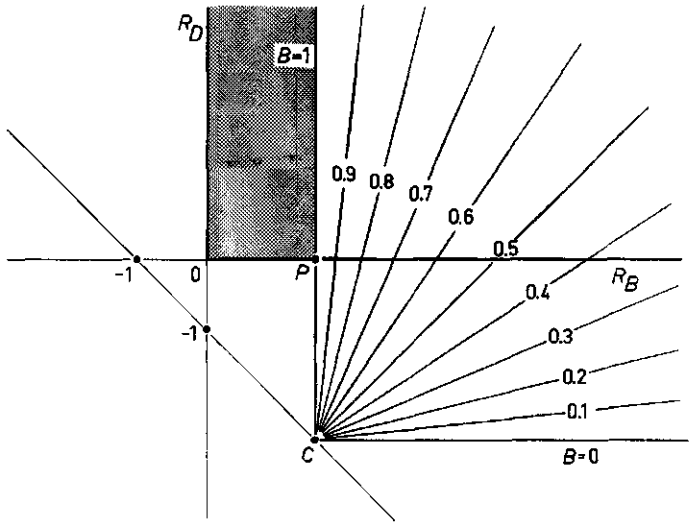

FIG. 15. Empty zone along R_D-axis in plane $q = q^*$ if $q^* > 1$ and hence $0 < \Omega_0 < \alpha_1^{-1}$.

$$0 < \Omega_0 < \alpha_1^{-1} \tag{4,22}$$

and

$$\Omega_0 \leqslant \Phi_{bl}^{-1} < \alpha_1^{-1}$$

To the separations of the boundary corresponds the value Ω_0 for the pinch parameter Φ_{bl}^{-1}. For the separations on the R_B-axis the pinch parameter $\Phi_{th}^{-1} = 0$.

Quite analogously one can show

When $q^* < 0$ there exists an empty zone along the R_B-axis in the planes $q = q^*$. The boundary between the empty zone and the domain of separations is the line $B = 0$, parallel to the R_B-axis. The minimum value of R_D equals $-q^*$. One has then

$$0 < \Omega_0^{-1} < \alpha_J \tag{4,23}$$

$$\Omega_0^{-1} < \Phi_{tj}^{-1} < \alpha_J$$

To the separations of the boundary corresponds the value Ω_0^{-1} for the pinch parameter Φ_{th}^{-1}. For the separations on the R_D-axis the pinch parameter $\Phi_{bl}^{-1} = 0$.

When $0 < q^* < 1$ the entire positive quadrant of the plane $q = q^*$ consists of points representing separations. One has

$$\Omega_0 < 0$$

$$0 \leqslant \Phi_{bl}^{-1} < \alpha_1^{-1} \tag{4,24}$$

$$0 \leqslant \Phi_{tj}^{-1} < \alpha_J$$

For the separations on the R_B-axis $\Phi_{th}^{-1} = 0$ and for those on the R_D-axis $\Phi_{bl}^{-1} = 0$.

4.4 MULTIPLETS IN PLANE OF CONSTANT q

The diagram of multiplets in the $(\Phi_{bl}^{-1}, \Phi_{th}^{-1})$-plane of Fig. 12, $(q = q^*)$, will

now be mapped onto the intersection of the positive quadrant of the (R_B, R_D)-plane (with same value of q^*) and the first quadrant of the pencil of lines $B = B^*$ in the latter plane.

Obviously each point (R_B, R_D) of this intersection represents one and only one separation. Hence it follows that the multiplets fill the intersection without gaps and overlaps.

The construction of the net of multiplets has been carried out quantitatively for the ten component system in the plane $q = 0.6$ (Fig. 16). As $0 < q^* < 1$ in this case, no empty zone occurs.

In the process of mapping, the squares are distorted and condensed into a continuous pattern. The theorems of continuation guarantee that their order is preserved. The second monotony theorem determines the orientation of the pattern. Qualitatively one may say that the Φ_{bl}^{-1}-axis becomes R_B-axis and the Φ_{lk}^{-1}-axis becomes R_D-axis. In the treated case this can be verified easily as follows

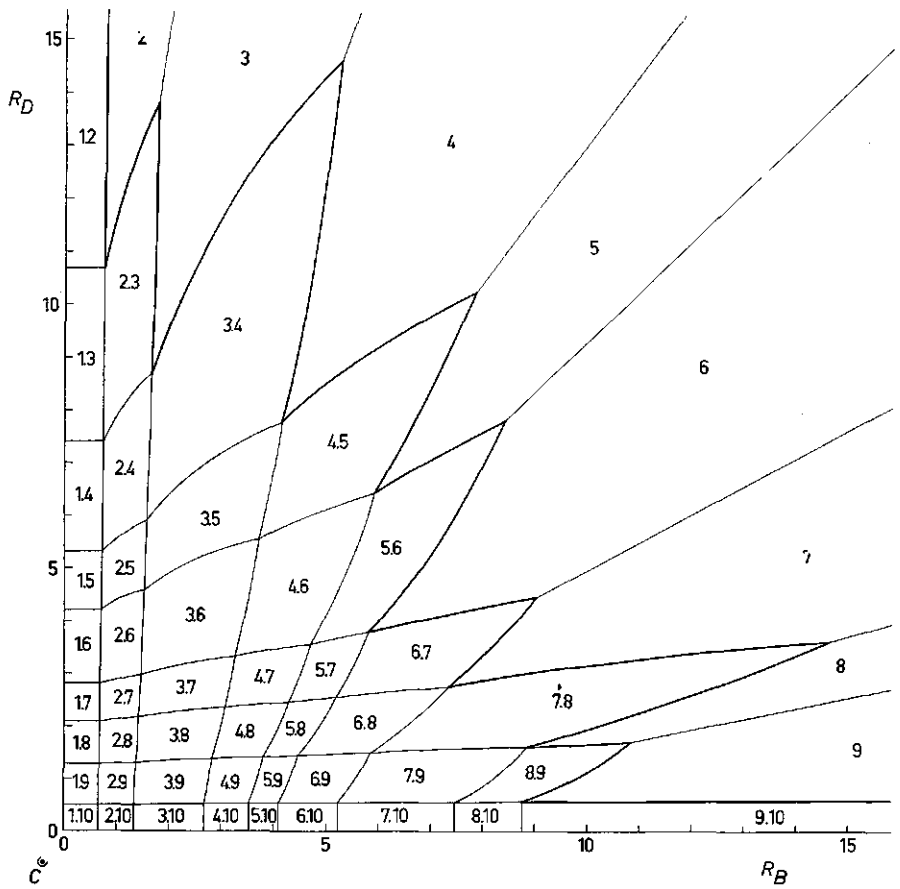

FIG. 16. Multiplets in plane $q = 0.6$. Values (l. h) are indicated. The R_D-axis points to the north and the R_B-axis to the east.

For the points of the R_B-axis one has $R_D = 0$. Hence $V_i = (0 + 1)D = D$ and the characteristic top equation (3,2) becomes

$$D = \sum_{i=1}^{h} D_i/(1 - \alpha_i^{-1}s) \tag{4,25}$$

The smallest root of Eq. (4,25) is $s = \Phi_{ih}^{-1} = 0$ and this is the equation of the Φ_{bl}^{-1}-axis. The second monotony theorem states

$$\frac{\partial R_B}{\partial (\Phi_{bl}^{-1})} > 0$$

and hence both the Φ_{bl}^{-1}-axis and the R_B-axis have the same direction with respect to the pattern of multiplets. A similar argument is valid for the Φ_{ih}^{-1}-axis and the R_D-axis.

4.4.1. *Interior multiplets*

The multiplets $(\lambda.\ \eta)$ with

$$2 \leqslant \lambda < \eta \leqslant J - 1 \tag{4,26}$$

are called *interior multiplets*. They are surrounded by a chain of peripheral multiplets, i.e. the multiplets alongside the R_B-axis and the R_D-axis and the multiplets of infinite extension. As $\lambda < \eta$ at least two distributed components are present in the interior multiplets.

The construction starts with the computation of the coordinates (R_B, R_D) of the interior vertices of the net. These vertices correspond to the marked southwest corners of Fig. 12. They stand out by the specific values of the pinch parameters [1])

$$\begin{aligned} \Phi_{bl}^{-1} &= \Omega_j \qquad & 1 \leqslant j \leqslant k \\ \Phi_{ih}^{-1} &= \Omega_k^{-1} \qquad & 1 \leqslant k \leqslant J - 1 \end{aligned} \tag{4,27}$$

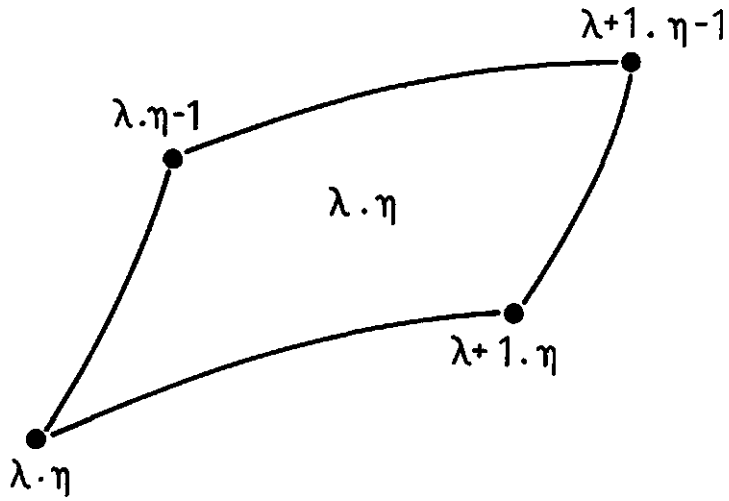

FIG. 17. Designation of vertices.

[1]) The cases $j = k$ will be discussed in the section on peripheral multiplets (vide singlet separations).

Hence there exist $1 + 2 + \ldots + (J-1) = \frac{1}{2} J(J-1)$ such vertices, which will be labelled after the lightest (λ) and heaviest (η) distributed component occurring in the separation presented by the vertex (vide Fig. 17). It should be remembered that the squares are closed along their southern and western boundaries so that the southwest corner really belongs to the square, i.e. really *has the same distributed components* as the interior points of the square. The other three corners of a square, on the contrary, represent limiting cases in which either the separation ratio of the lightest distributed component vanishes or (and) the separation ratio of the heaviest distributed component becomes unity (vide the theorems of continuation).

Because the multiplets and the squares are similarly oriented in their coordinate systems a southwest corner of a square becomes a southwest corner of the corresponding multiplet. For convenience the dominant features of the construction are comprised into the following lemmas:

Lemma 1.

The separation in the vertex (λ, η) *with* $2 \leqslant \lambda < \eta \leqslant J-1$ *is specified by the values* $\Omega_{\lambda-1}$ *and* Ω_{η}^{-1} *of the pinch parameters* Φ_{bl}^{-1} *and* Φ_{ih}^{-1} *respectively and is determined by the linear equations*

$$L_b - \sum_{i=\lambda}^{\eta} s_{bi} F_i/(1-\alpha_i\Omega_k) = \sum_{j=\eta+1}^{J} F_j/(1-\alpha_j\Omega_k) \tag{4,28}$$

with $k = \lambda - 1, \lambda, \ldots, \eta$.

$\eta - \lambda + 2$ *unknowns* $s_{b\lambda}, s_{b\lambda+1}, \ldots, s_{b\eta}$ *and* L_b

$\eta - \lambda + 2$ *equations*

Proof. The lemma is a direct application of the equations (3,15), (3,16) and (3,17).

Lemma 2.

On any line $s_{b\nu}$ = *constant in multiplet* $(\lambda.\ \eta)$, $(\lambda \leqslant \nu \leqslant \eta$ *and* $\lambda < \eta)$ *the separation ratios* s_{bi} *are either constant or they are linear functions of an arbitrarily selected ("distributed") ratio* $s_{b\mu}$. $(\lambda \leqslant \mu \leqslant \eta;\ \mu \neq \nu)$. *One has*

$$\begin{aligned} s_{bi} &= 0 && i < \lambda \\ s_{bi} &= T_{i,\mu}^{(\lambda,\eta,\nu)}\, s_{b\mu} + U_{i,\mu}^{(\lambda,\eta,\nu)} && \begin{cases} \lambda \leqslant i \leqslant \eta \\ i \neq \nu,\ i \neq \mu \end{cases} \\ s_{bi} &= 1 && i > \eta \end{aligned} \tag{4,29}$$

The constants $T_{i,\mu}^{(\lambda,\eta,\nu)}$ *and* $U_{i,\mu}^{(\lambda,\eta,\nu)}$ *depend on the identity* $(\lambda.\ \eta)$ *of the multiplet and on the choice of the components* i, μ *and* ν. *The constants U depend also on the value of the constant ratio* $s_{b\nu}$. *The total liquid rate* L_b *depends also linearly on* $s_{b\mu}$

$$L_b = T_{\mu}^{(\lambda,\eta,\nu)}\, s_{b\mu} + U_{\mu}^{(\lambda,\eta,\nu)}$$

Consequently the same holds for L_i, B *and* D.

Proof. According to UNDERWOOD's method L_b and the ratios s_{bi} $(i \neq \nu$ and $\neq \mu)$ satisfy the linear equations

$$\begin{aligned} L_b - \sum_{i=\lambda}^{\eta}{}'' s_{bi} F_i/(1-a_i\Omega_k) = \sum_{j=\eta+1}^{J} F_j/(1-\alpha_j\Omega_k) + s_{b\mu} F_\mu/(1-\alpha_\mu\Omega_k) + \\ + s_{b\nu} F_\nu/(1-\alpha_\nu\Omega_k) \end{aligned} \tag{4,30}$$

The primes '' indicate that the values μ and ν for i are to be skipped in the summation. The index k takes the values $\lambda, \lambda+1, \ldots, \eta-1$, ($\eta-\lambda$ equations, $\eta-\lambda$ unknowns). Hence every unknown ("distributed") ratio s_{bi} can be expressed into the coefficients and the known terms in the right hand members, yielding Eqs. (4,29). (Compare also appendix III where Eqs (4,29) are written as $s_{bi} = T_i s_{b\mu} + U_i$ for simplicity.) L_t, B and D depend linearly on $s_{b\mu}$ because they are linear functions of L_b or the ratios s_{bi}.

Lemma 3.

The northern boundary of multiplet $(\lambda.\eta)$ *can be interpreted as the line* $s_{b\eta} = 1$ *of this multiplet, or, alternatively, as the line* $\Phi_{ih}^{-1} = \Omega_{\eta-1}^{-1}$. *Hence to the points of this boundary the equations*

$$L_b - \sum_{i=\lambda}^{\eta-1}{}'' s_{bi}F_i/(1-a_i\Omega_k) = \sum_{j=\eta}^{J}{}'' F_j/(1-\alpha_j\Omega_k) \qquad (4,31)$$

apply with the same set of UNDERWOOD*-roots* $\Omega_\lambda, \Omega_{\lambda+1}, \ldots, \Omega_{\eta-1}$ *as occurs in the equations concerning any interior point of multiplet* $(\lambda.\eta)$. *There are* $\eta-\lambda$ *equations for the* $\eta-\lambda+1$ *unknowns* $L_b, s_{b\lambda}, \ldots, s_{b\eta-1}$. *Hence one of the ratios can be used to label the points of the northern boundary.*

Proof. Lemma 3 is an immediate consequence of the second theorem of continuation. Any point of the northern boundary can be interpreted as the (limiting) terminating point of a line $\Phi_{b\lambda}^{-1} =$ constant (vide Fig. 12). If a point travels along this line in the northern direction then $\Phi_{i\eta}^{-1} \to \alpha_\eta$ and $s_{b\eta} \to 1$.

The theorem of continuation then states that in the limit Φ_{ih}^{-1} must be taken in the first point $\Omega_{\eta-1}^{-1}$ of the interval $(\Omega_{\eta-1}^{-1}, \alpha_{\eta-1})$, i.e. the equations (3,15), (3,16) and (3,17) apply with the particular values λ and $\eta-1$ for l and h respectively and the value 1 for $s_{b\eta}$. One has

$$(3,15) \to L_b - \sum_{i=\lambda}^{\eta-1}{}'' s_{bi}F_i/(1-\alpha_i\Omega_k) = \sum_{j=\eta}^{J}{}'' F_j(1-\alpha_j\Omega_k)$$
$$(k = \lambda, \lambda+1, \ldots, \eta-2)$$

$$(3,16) \to L_b - \sum_{i=\lambda}^{\eta-1}{}'' s_{bi}F_i/(1-\alpha_i\Phi_{b\lambda}^{-1}) = \sum_{j=\eta}^{J}{}'' F_j(1-\alpha_j\Phi_{b\lambda}^{-1})$$

$$(3,17) \to L_b - \sum_{i=\lambda}^{\eta-1}{}'' s_{bi}F_i/(1-\alpha_i\Omega_{\eta-1}) = \sum_{j=\eta}^{J}{}'' F_j(1-\alpha_j\Omega_{\eta-1})$$

(3,15) and (3,17) yield the equations (4,31). Equation (3,16) can be neglected to make the number of unknowns one more than the number of equations.

Lemma 4.

The separation ratios (and L_b*) in any point of the northern boundary of multiplet* $(\lambda.\eta)$ *can be obtained by linear interpolation between their values in the terminating points of this boundary, i.e. the vertices* $(\lambda, \eta-1)$ *and* $(\lambda+1, \eta-1)$. *The same holds for* L_t, B *and* D.

Proof. Lemma 4 is the direct application of lemmas 2 and 3. Quite similarly to lemma 3 and lemma 4 one can prove the lemmas 5 and 6.

Lemma 5.

The eastern boundary of multiplet $(\lambda.\ \eta)$ *can be interpreted as the line* $s_{b\lambda} = 0$ *of this multiplet, or, alternatively as the line* $\Phi_{bl}^{-1} = \Omega_\lambda$. *To the points of this boundary the equations*

$$L_b - \sum_{i=\lambda+1}^{\eta} s_{bi}F_i/(1-\alpha_i\Omega_k) = \sum_{j=\eta+1}^{J} F_j/(1-\alpha_j\Omega_k) \tag{4,32}$$

apply with the same set of UNDERWOOD*-roots* $\Omega_\lambda, \Omega_{\lambda+1}, \ldots, \Omega_{\eta-1}$ *as occurs in the equations concerning any interior point of multiplet* $(\lambda.\ \eta)$. *There are* $\eta - \lambda$ *equations of the* $\eta - \lambda + 1$ *unknowns* $L_b, s_{b\lambda+1}, s_{b\lambda+2}, \ldots, s_{b\eta}$. *Hence one of the ratios can be used to label the points of the eastern boundary.*

Lemma 6.

The separation ratios (and L_b*) in any point of the eastern boundary of multiplet* $(\lambda.\eta)$ *can be obtained by linear interpolation between their values in the terminating points of this boundary, i.e. the vertices* $(\lambda+1, \eta)$ *and* $(\lambda+1, \eta-1)$ *The same holds for* L_t, B *and* D.

Applying lemma 1 one can compute L_b and the ratios s_{bi} in any vertex. One finds B from

$$B = \sum_{i=\lambda}^{J} s_{bi}F_i \tag{4,33}$$

D from

$$D = 1 - B \tag{4,34}$$

L_t from

$$L_t = L_b - q^* \tag{4,35}$$

and hence R_B and R_D from

$$R_B = (L_b - B)/B \tag{4,36}$$

$$R_D = L_t/D \tag{4,37}$$

In this way the coordinates (R_B, R_D) of all the vertices of the net of multiplets can be computed. Applying lemmas 4 and 6 one can find next the values of L_b, B, L_t and D on the boundaries by linear interpolation between appropriate vertices. With Eqs. (4,36) and (4,37) the coordinates of the interpolated points can be obtained.

4.4.2. *Peripheral multiplets*

We consider first the *peripheral multiplets alongside the coordinate axes*, i.e. the multiplets $(1.\ \eta)$ with $2 \leqslant \eta$ and $(\lambda.\ J)$ with $\lambda \leqslant J-1$. All that has been said for the interior multiplets is valid also for these multiplets $(1.\ \eta)$ and $(\lambda.\ J)$ as far as concerns their northern or eastern boundaries.

Additionally one has:

Lemma 7.

The eastern boundaries of the multiplets $(\lambda.\ J)$ *with* $\lambda \leqslant J-1$ *are perpendicular to the* R_B*-axis.*

Proof. The equations (4,32) can be written for this case

$$L_b - \sum_{i=\lambda+1}^{J}{}' s_{bi}F_i/(1-\alpha_i\Omega_k) = s_{b\mu}F_\mu/(1-\alpha_\mu\Omega_k) \tag{4,38}$$

(The prime ′ indicates that i skips the value μ). Writing in accordance with Cramer's rule $s_{bi} = D^{(i)}/D$, it can be proved that $D^{(i)}/D = T^{(\lambda)}_{i\mu}.\, s_{b\mu}$[1]). Similarly one can write $L_b = T^{(\lambda)}_{\mu}\, s_{b\mu}$.

Hence one has

$$B = \sum_{i=\lambda+1}^{J}{}' s_{bi}F_i = s_{b\mu} \sum_{i=\lambda+1}^{J} T^{(\lambda)}_{i\mu}F_i \tag{4,39}$$

and

$$R_B = \frac{L_b - B}{B} = \frac{T^{(\lambda)}_{\mu} - \sum_{i=\lambda+1}^{J}{}' T^{(\lambda)}_{i\mu}F_i}{\sum_{i=\lambda+1}^{J} T^{(\lambda)}_{i\mu}F_i} = \text{constant}, \tag{4,40}$$

which means that the boundary is a straight line perpendicular to the R_B-axis.

Quite similarly one can prove:

Lemma 8.

The northern boundaries of the multiplets (1. η) *with* $2 \leqslant \eta$ *are perpendicular to the* R_D*-axis.*

The peripheral multiplets of infinite extension represent singlet separations. In these singlets $\lambda = \eta$ so that they may be denoted by a single number λ. In Fig. 16 the singlets (1) and (10) are not represented because the large values of R_D or R_B, associated with them, would have reduced the scale of the figure too much.

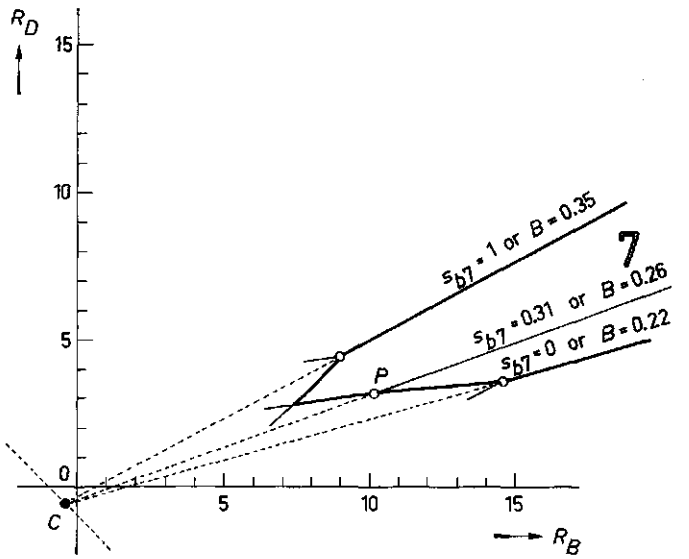

FIG. 18. Singlet (7) in plane $q = 0.6$. Lines of constant s_{b7} are identical with lines of constant B.

[1]) Compare appendix III, formula (III, 16). Putting $\nu = \lambda$ and $s_{b\lambda} = 0$, the determinants in the right hand member vanish simultaneously except the one containing $s_{b\mu}$.

In singlet (λ) one has

$$s_{bi} = \begin{cases} 0 & \text{for } i < \lambda \\ s_{b\lambda} & i = \lambda \\ 1 & i > \lambda \end{cases} \tag{4,41}$$

Hence

$$B = s_{b\lambda} F_\lambda + \sum_{j=\lambda+1}^{\bar{j}} F_j \tag{4,42}$$

in which the sum is a constant.

Hence it follows:

Lemma 9.

In singlet (λ) *the lines* $s_{b\lambda}$ = *constant are identical with the straight lines* $B = B^*$ *filling the singlet.*

From Eqs. (4,41), lemma 9 and the positive sign of (4,9) it follows:

Lemma 10.

The separations (i.e. the sets of s_{bi}*), represented by the points of a line* $s_{b\lambda}$ = *constant, are mere repetitions of the separation, represented by the point of intersection P on the boundary with the adjacent doublet. The separation P, however, can be performed with the smallest values of* R_B *and* R_D.

Because λ is the only distributed component in singlet (λ), one obviously has:

Lemma 11.

The singlet (λ) *is separated from singlet* (λ + 1) *by the line* $s_{b\lambda} = 0$ *and from singlet* (λ − 1) *by the line* $s_{b\lambda} = 1$. (*The line* $s_{b\lambda} = 0$ *of singlet* (λ) *is identical with the line* $s_{b\lambda+1} = 1$ *of singlet* $s_{b\lambda+1}$).

From lemma 11 it is clear that the separations belonging to the straight boundaries between the singlets contain no distributed components at all! These separations may be termed *absolute separations.*

4.5. Separations at minimum reflux

We have obtained in Fig. 16 a complete survey of all possible separations of the ten component system, performed by an infinite column operated at $q = 0.6$. Lemma 10 states that the separations represented by the points of the singlets can be found again with lower values of R_B and R_D on the outer boundary of the chain of doublets.

The separations represented by the points of the singlets can hence be regarded as superfluous and the singlets must be cut out of the (R_B, R_D)-plane. The remaining part, bounded by the axes (or eventually by one of the axes and an empty zone alongside the other one) and by the northern and eastern (limiting) boundaries of the doublets, must be identified with the assemblage of all possible minimum reflux separations of the multicomponent system at a feed condition q^*.

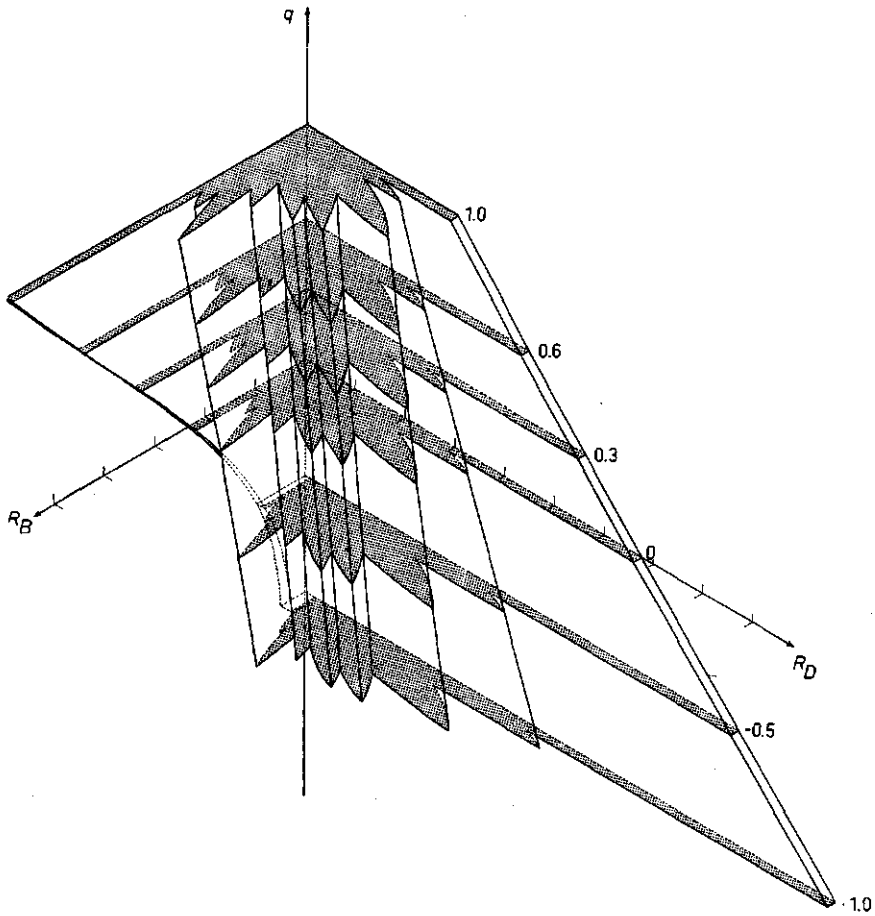

FIG. 19. Solid of minimum reflux between planes $q = +1$ and $q = -1$. Distances of 5 units are indicated on horizontal axes.

4.6. SOLID OF MINIMUM REFLUX

The multiplet patterns in the planes $q = q^*$ constitute a solid in (q, R_B, R_D)-space. This *solid of minimum reflux* is composed of *multiplet tubes* which are associated with the various separation bands of the multicomponent system. The part of the solid between the planes $q = -1$ and $q = +1$ has been drawn quantitatively in Fig. 19. From the mathematical point of view the solid is of infinite extension in the direction of the q-axis; for the use in distillation practice of course only the part corresponding to "not too large" values of $|q|$ is of importance.

4.7. LINES OF CONSTANT s_{bi} IN PLANE OF CONSTANT q

In Fig. 20 lines $s_{b7} = s^*_{b7}$ (s^*_{b7} is a constant) have been drawn for the ten component system ($q = 0.6$). The lines corresponding to values $0 < s^*_{b7} < 1$ are lying in a strip of the (R_B, R_D)-plane, consisting of the multiplets in which

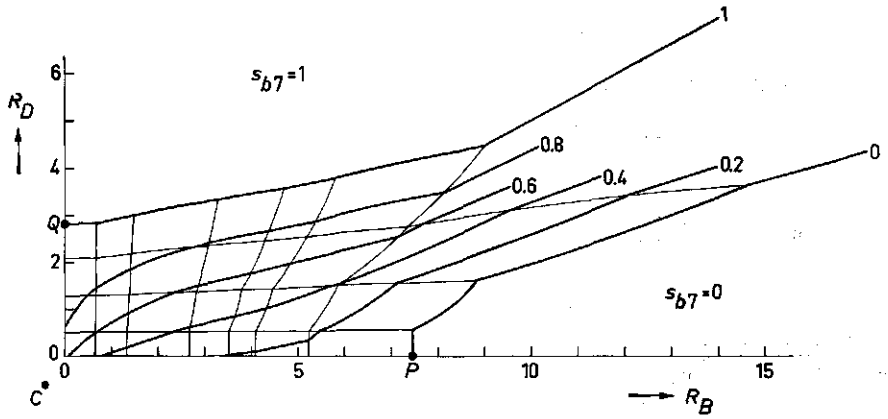

FIG. 20. Zones of $s_{b7} = 0$ and of $s_{b7} = 1$ and strip of lines of constant s_{b7} in plane $q = 0.6$.

component 7 occurs as distributed component. The strip is bounded by the northern boundaries of the multiplets $(\lambda,7)$ and singlet (7), (lemma 3), and by the eastern boundaries of the multiplets $(7,\eta)$ and singlet (7), (lemma 5). In the entire zone beneath the strip the ratio s_{b7} vanishes and in the zone north of the strip the ratio s_{b7} equals unity.

The east boundary of the strip intersects the R_B-axis in point P in which $s_{b7} = 0$. According to the second monotony theorem this ratio increases steadily along the R_B-axis (on which $\Phi_{ih}^{-1} = 0 =$ constant!) in the direction to the origin, and this ratio continues to increase steadily along the R_D-axis ($\Phi_{bl}^{-1} = 0$) towards the point of intersection Q with the strip's north boundary, on which $s_{b7} = 1$. Hence any value of s_{b7} between 0 and 1 can be found once and only once on the coordinate axes and hence any curve $s_{b7} = s_{b7}^*$ with $0 < s_{b7}^* < 1$ has *one* terminating point on either the R_B-axis or the R_D-axis.

Repeating the argument for the south and the west boundary of singlet (7), (which correspond respectively to $\Phi_{ih}^{-1} = \Omega_7^{-1}$ and $\Phi_{bl}^{-1} = \Omega_6$) it follows from the second monotony theorem that any value s_{b7}^* between 0 and 1 occurs once only on these boundaries. And hence any curve $s_{b7} = s_{b7}^*$, with $0 < s_{b7}^* < 1$, has *one* terminating point on either the south or the west boundary of singlet 7. In this way it can be shown:

Any curve $s_{bi} = s_{bi}^*$ with $0 < s_{bi}^* < 1$ runs from a point on one of the coordinate axes towards singlet (i), where it becomes a straight $B = B^*$-line.

In Fig. 21 the families of lines of constant s_{b4} and of constant s_{b7} are represented. In this figure the combinations (s_{b4}, s_{b7}), suitable for specification, can be read from the points of intersection of s_{b4}-lines with s_{b7}-lines.

In Fig. 22, finally, the lines $s_{bi} = 0.5$ have been drawn for $i = 1, 2, \ldots, 9$. The line $s_{b10} = 0.5$ corresponds to values of R_B larger then 15 and hence does not occur in the picture.

For the lines $s_{bi} =$ constant one can prove the

third monotony theorem:

Let μ, ν and i denote different, arbitrarily selected, distributed components in multiplet $(\lambda.\ \eta)$ with $\lambda < \eta$. Then on a line $s_{b\nu} =$ constant

$$\frac{\partial s_{bi}}{\partial s_{b\mu}} > 0 \qquad \begin{cases} \text{if } \mu \text{ and } i > \nu \\ \text{or if } \mu \text{ and } i < \nu \end{cases} \tag{4.43}$$

that is if μ *and* i *are at one side of* ν *and*

$$\frac{\partial s_{bi}}{\partial s_{b\mu}} < 0 \qquad \begin{cases} \text{if } \mu < \nu < i \\ \text{or if } i < \nu < \mu \end{cases} \tag{4,44}$$

that is if μ *and* i *are at either side of* ν.

The proof of this theorem is given in appendix III (vide also Fig. 24).

4.8. Uniqueness theorem

From the properties of the lines $s_{b\nu} = s^*_{b\nu}$ and from the second and the third monotony theorem the uniqueness of the solutions can be derived.

4.8.1. *Orientation of the boundaries*

The collective north boundary of the multiplets $(l.\eta)$, $l = 1, 2, \ldots, \eta - 1$,

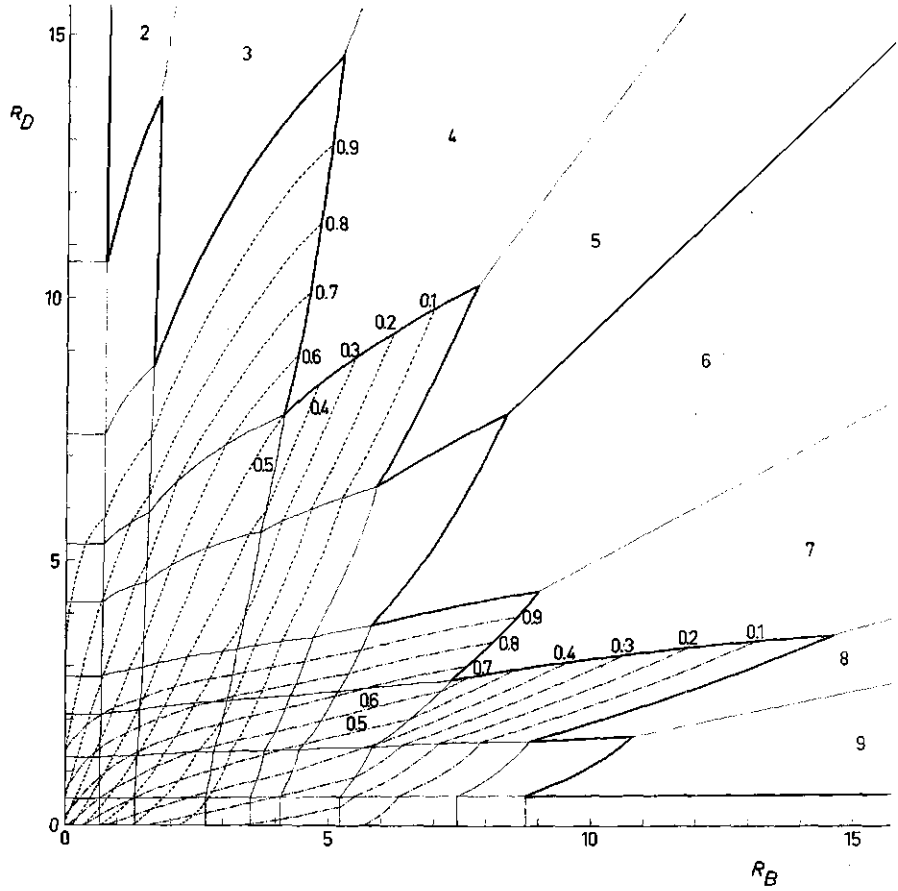

FIG. 21. Families of lines of constant s_{b4} and constant s_{b7} in plane $q = 0.6$.

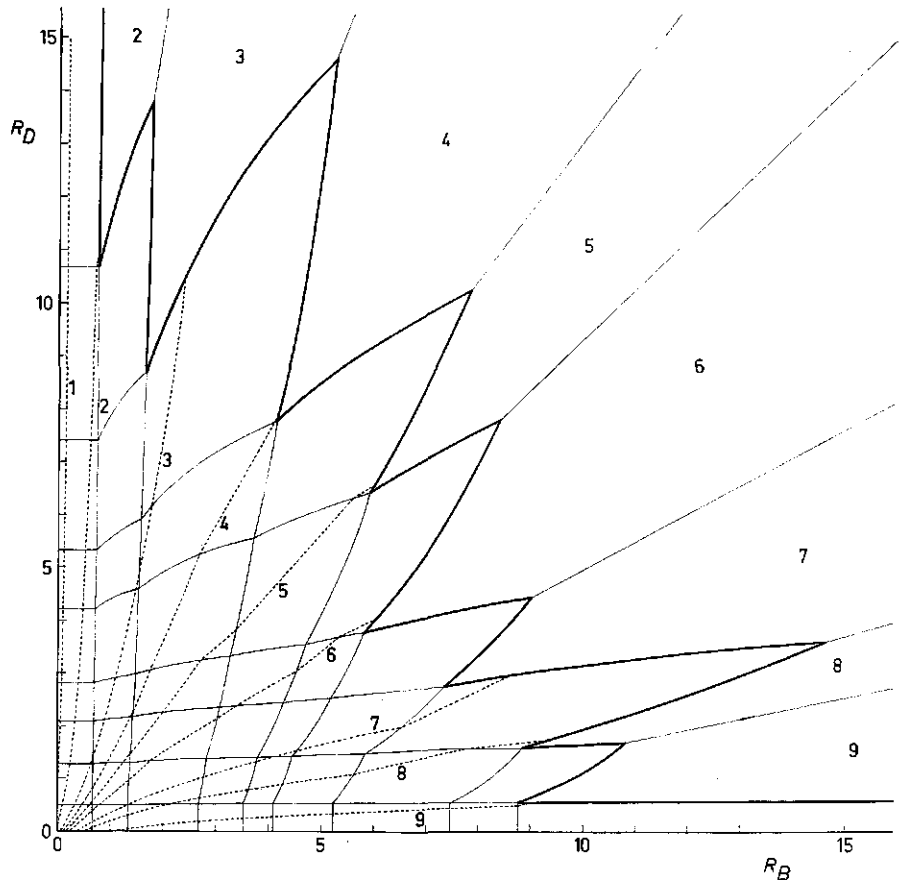

FIG. 22. Lines $s_{bk} = 0.5$ in plane $q = 0.6$. Values of k are indicated.

(η fixed), is the line $\Phi_{ih}^{-1} = \Omega_{\eta-1}^{-1}$ (lemma 3) and the collective east boundary of the multiplets (λ. h), λ fixed and $h = \lambda + 1, \lambda + 2, \ldots, J$, is the line $\Phi_{bl}^{-1} = \Omega_{\lambda}$. According to the second monotony theorem the (distributed) ratios s_{bi} increase steadily and simultaneously when Φ_{bl}^{-1} (or R_B) decreases along a line of constant Φ_{ih}^{-1}. Similarly the (distributed) ratios s_{bi} increase steadily and simultaneously when Φ_{ih}^{-1} (or R_D) increases along a line of constant Φ_{bl}^{-1}.

The monotonic behaviour of the ratios s_{bi} on the boundaries allows an orientation of the boundaries; the direction in which the ratios increase is chosen as the positive one. Arrows can be drawn anti-parallel to the positive R_B-axis in each north boundary and parallel to the positive R_D-axis in each east boundary. The ratios are known to increase in the directions of these arrows.

4.8.2. *Orientation of the lines* $s_{bv} = s_{bv}^*$

It has been shown in the preceding section that the lines $s_{bv} = s_{bv}^*$ are spun between the axes and the outer doublet boundaries. Therefore, these lines are orientable, i.e. a positive direction can be introduced pointing away from the axes and towards the doublet boundaries. This orientation will be termed the

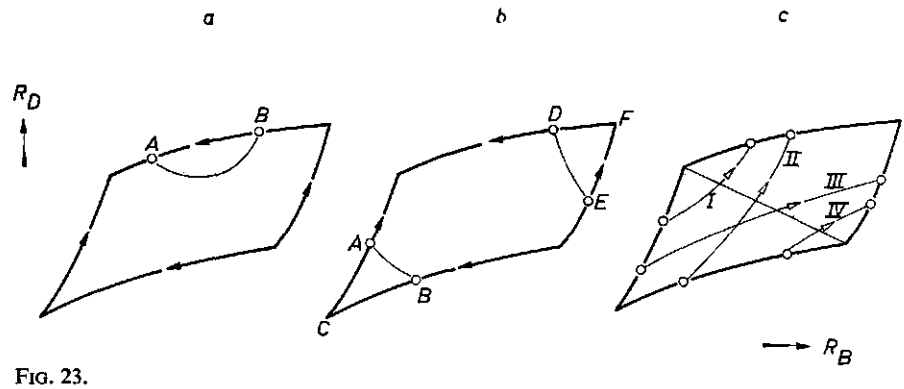

FIG. 23.

macro-orientation, because an arrow in an arbitrary point of a line $s_{bv} = s^*_{bv}$ can be drawn only if one of the two terminating points is given.

The difficulty at this stage is that we still know nothing of the direction in which the ratios s_{bi} increase or decrease along this line. A further complication results from the "mixed monotony" along $s_{bv} = s^*_{bv}$, i.e. part of the ratios increase and part of the ratios decrease in a certain direction. Therefore, we have to fix an orientation of these lines first and then to link the behaviour of the ratios with this orientation. But in accordance with the peculiar character of the mathematics involved, (the mathematics of many sets of equations, each set being valid in its particular multiplet and "neighbouring" sets being connected along common boundaries), the third monotony theorem has been formulated *per* multiplet and hence the monotonic behaviour of the ratios cannot be made to depend on the terminating points of $s_{bv} = s^*_{bv}$ but must be related to the orientation of the *segment* of this line within a multiplet. Therefore, we have to derive a *micro-orientation*, i.e. a precept to find the direction of a segment $s_{bv} = s^*_{bv}$, exclusively using elements of the multiplet which contains the segment.

Corollary 1.

A segment $s_{bv} = s^*_{bv}$ cannot have both its terminating points A and B on one same multiplet boundary.

Proof. The case of both A and B on the north boundary is presented in Fig. 23*a* and implies that the value s^*_{bv} occurs twice on this boundary, which contradicts the simultaneous monotonic increase of the ratios in the direction of the arrow.

Corollary 2.

A segment $s_{bv} = s^*_{bv}$ cannot be spun between a west and a south boundary (Fig. 23*b*, segment *AB*) *or between a north and an east boundary* (Fig. 23*b*, segment *DE*).

Proof. In Fig. 23*b* the ratios increase steadily over the path *BCA* and hence $(s_{bv})_A \neq (s_{bv})_B$. Similarly $(s_{bv})_E \neq (s_{bv})_D$.

From these corollaries follows evidently

Corollary 3.

A segment $s_{bv} = s^*_{bv}$ surpasses the northwest-southeast diagonal.

The remaining possibilities are represented in Fig. 23*c*.

We choose as the positive direction on the segments the direction from the southwest part towards the northeast part.

We consider next each of the four possibilities for the segment $s_{b\nu} = s^*_{b\nu}$. Of course $\lambda \leqslant \nu \leqslant \eta$. Suppose first $\nu \neq \lambda$ and $\nu \neq \eta$.

Case I (Fig. 23*c*, $s_{b\eta}$ is the guide-ratio)

Among the ratios s_{bi} with $i > \nu$ occurs the ratio $s_{b\eta}$ which yields its maximum value $s_{b\eta} = 1$ in the terminating point on the north boundary. Hence, according to the third monotony theorem (vide (4,43)) the ratios s_{bi} with $i > \nu$ increase simultaneously with $s_{b\eta}$ and hence the ratios s_{bi} with $i > \nu$ increase in the positive direction. Then, with regard to (4,44), the ratios s_{bi} with $i < \nu$ decrease in the positive direction.

Case II (Fig. 23*c*, $s_{b\eta}$ is the guide-ratio)

Repeating the argument we arrive at the same conclusion as in case I.

Case III (Fig. 23*c*, $s_{b\lambda}$ is the guide-ratio)

Among the ratios s_{bi} with $i < \nu$ occurs the ratio $s_{b\lambda}$ which yields its minimum value $s_{b\lambda} = 0$ in the terminating point on the east boundary. And hence the ratios s_{bi} with $i < \nu$ decrease simultaneously in the positive direction and consequently the ratios s_{bi} with $i > \nu$ increase in the positive direction.

Case IV is similar to case III.

If $\nu = \lambda$ and hence if the segment is $s_{b\lambda} = s^*_{b\lambda}$, $(s^*_{b\lambda} > 0)$, then the segment cannot reach the east boundary where $s_{b\lambda} = 0$ and hence it must have a terminating point on the north boundary. But then again $s_{b\eta}$ is known to yield the value 1 and hence all the ratios s_{bi} with $i > \nu \equiv \lambda$ increase simultaneously.

If $\nu = \eta$, then the segment must terminate on the east boundary and the ratios s_{bi} $(i < \nu \equiv \eta)$ decrease simultaneously in positive direction.

So in any case we find:

If $\lambda \leqslant i < \nu$, *then* s_{bi} *decreases in positive direction*

If $\nu < i \leqslant \eta$, *then* s_{bi} *increases in positive direction*

Next we have to show that the micro-orientation agrees with the macro-orientation. Consider the segment of $s_{b\nu} = s^*_{b\nu}$ in multiplet $(\lambda.\ \eta)$. Following the segment's positive direction we cross either the multiplet's north boundary and enter the southwest part of multiplet $(\lambda.\ \eta - 1)$ or we cross the east boundary and enter the southwest part of multiplet $(\lambda + 1.\ \eta)$. In both cases the difference $\eta - \lambda$ has been decreased by 1. Proceeding in this way we finally enter a multiplet with $\eta - \lambda = 1$, i.e. a doublet.

Following the negative direction either λ decreases by 1 or η increases by 1 each time an adjacent multiplet is being entered. Hence in the end we arrive either in a multiplet (1. *h*), adjacent to the R_D-axis or in a multiplet (*l. J*), adjacent to the R_B-axis. And hence the positive directions of the micro-orientation agree with the positive direction of the macro-orientation. Both orientations may be interchanged and the monotonic properties can hence be related to the macro-orientation, turning the micro-monotony into a macro-monotony. We conclude:

In the positive direction of the *line* $s_{b\nu} = s^*_{b\nu}$ the local "distributed" ratios s_{bi} with $i < \nu$ decrease and the local "distributed" ratios s_{bi} with $i > \nu$ increase in the positive direction.

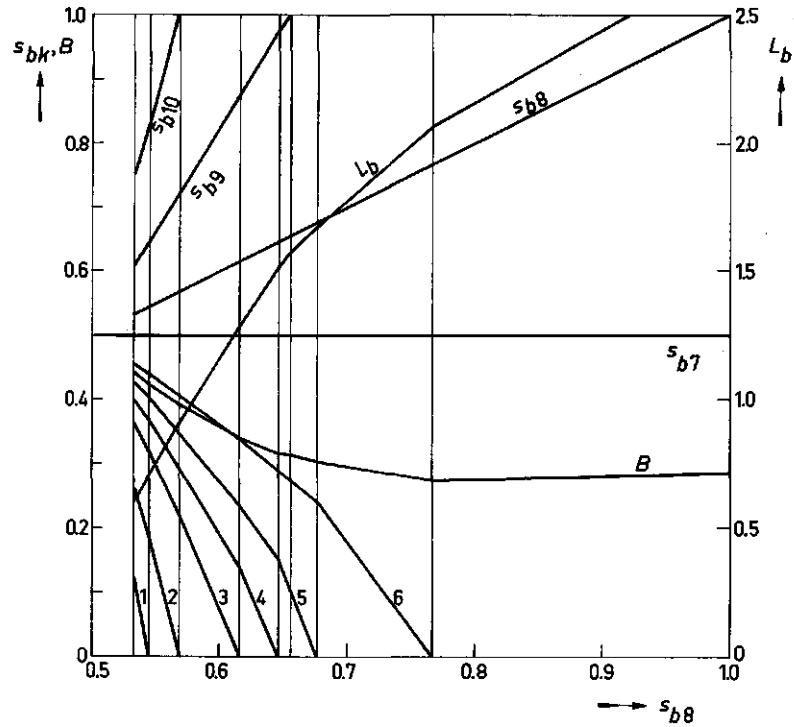

FIG. 24. Monotonic behaviour of L_b and the ratios s_{bi} against s_{b8} on line $s_{b7} = 0.5$ in plane $q = 0.6$. Note that B is not monotonic. Verticals represent points of intersection of $s_{b7} = 0.5$ with R_B-axis, (1.10)E, (2.10)NE, (3.9)E, (4.9)E, (5.9)N, (5.8)E, (6.8)E, (7.8)N respectively.
On north boundaries (N) the ratio of the heaviest distributed component becomes 1, on east boundaries (E) the ratio of the lightest distributed component vanishes. (NE denotes northeast vertex).

This is clearly demonstrated by the families of curves $s_{b4} = s^*_{b4}$ and $s_{b7} = s^*_{b7}$ in Fig. 21 and by Fig. 24.

4.8.3. *Uniqueness theorem*

The uniqueness of the solutions can now be derived easily. Given a line $s_{b\nu} = s^*_{b\nu}$, then any occurring „distributed" ratio $s_{b\mu}$, $(\mu \neq \nu)$, varies steadily along this line either until it becomes 0 or 1 and hence ceases to be a "distributed" ratio, or until it reaches an end point value. Hence any "distributed" value $s_{b\mu}$ occurs once and only once on this line, *or not at all.* This means that any possible, ("consistent"), combination $(s_{b\mu}, s_{b\nu})$ occurs once and only once, or:

If the feed condition q is prescribed, a consistent combination $(s_{b\mu}, s_{b\nu})$ *specifies one and only one separation.*

CHAPTER 5

SPECIFICATION OF CONSISTENT SOLUTIONS

5.1. GENERAL

In this chapter a rigorous, straightforward, procedure on the basis of the model of constant relative volatilities and constant molal overflows is presented to disclose the limits and possibilities of specification of the minimum reflux separations, which approach the requirements of the designer.

Usually the separation must satisfy more conditions than there exist degrees of freedom in specification. To find a suitable compromise, the effects of small tolerances in the initially proposed specification must be examined.

Hence specification of a separation (at minimum reflux) of a multicomponent feed involves both the element of preparative computation and the element of personal judgment. We do not go into details concerning the latter aspect of specification, the subject of designing lying beyond the scope of this thesis. After the developments in the preceding chapters, however, the first aspect, the preliminary analysis, can be carefully dealt with.

Introducing a *specification diagram*, the inevitable numerical labour has been reduced to the minimum without sacrificing accuracy.

Before discussing this diagram, a few critical remarks will be made concerning the present state of specification theory, and its principal need, an adequate criterion of consistency, will be supplied.

5.2. PSEUDO-SOLUTIONS

In distillation theory little has been said concerning the problem of specification. The current point of view is expressed in the following quotations from an article by MURDOCH and HOLLAND, [3, page 288]:

"CONDITIONS AT MINIMUM REFLUX

The minimum reflux ratio at which specified separations of two key components can be carried out is the reflux ratio for which an infinity of plates in each section of the column is required. When the reflux is at this value, there is in each section a region (called the pinch) extending over an infinity of plates, within which the composition change from plate to plate is infinitesimal. *At minimum reflux, no components heavier than the heavy key appear in the top product, and no components lighter than the light key appear in the bottom product...*" [1])

and once more (same page):

"Suppose, initially, that the keys are adjacent components. ... *Since at minimum reflux the components lighter and heavier than the keys go entirely into either the top or bottom product*, the amounts and compositions of these products are completely known... However, when the system contains any number of components *between the keys*, the problem is more difficult since neither D nor the distribution of the components between the keys is known in advance..." [1])

The cardinal point in these quotations is the suggestion that, in the limit, the light key becomes the lightest distributed component l and that the heavy key becomes the heaviest distributed component h. If, with a finite number of trays, the bottom product rates lighter than the keys and the top product rates heavier

[1]) Author's italics.

than the keys are "sufficiently small" and hence if, by implication, the separation of the keys is "sufficiently sharp", the quotations may contain a correct description of the column performance at minimum reflux. But this observation merely shifts the problem from minimum reflux specification to finite column specification. When we specify a priori two keys, will then the appropriate outside product rates really become negligible with a finite number of trays?

MURDOCH and HOLLAND present a numerical example in which the specification reads:

$$s_{b4} = 0.125\,000 \qquad (5,1)$$
$$s_{b7} = 0.833\,333$$

Their solution, in which the feed condition q has been taken 0.6, is correct and consequently the specification (5,1) is "sufficiently sharp". The sharpness, how-

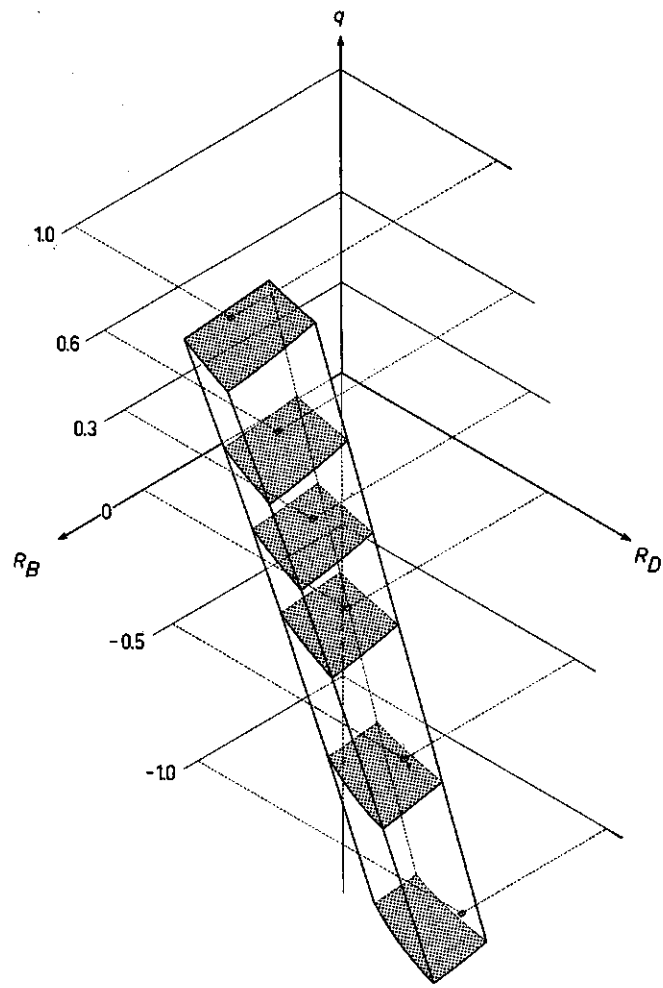

FIG. 25. Quadruplet-tube (4.7).

ever, turns out to depend on the feed condition q. The specification (5,1) is sharp enough at $q = 0.6$, but it need not be so for other values of q.

This is clearly demonstrated by Fig. 25, which shows the quadruplet-tube (4.7) of the solid of minimum reflux for $-1 \leqslant q \leqslant +1$. Plane cross sections are drawn, showing the quadruplets (4.7) at $q = -1.0, -0.5, 0, +0.3, +0.6$ and $+1.0$. In each of them the point is indicated which represents the separation specified by (5,1). It is seen that for $q = -1.0$ the point has slipped over the west boundary and is situated in the adjacent quintuplet (3.7), where $l = 3$ instead of 4. (Compare Fig. 16). For $q = +1.0$ the point is about to cross the south boundary with quintuplet (4.8). Hence if specification (5,1) is made for values of q a little larger than 1, h must be taken 8 instead of 7. Sticking to the values $l = 4$ and $h = 7$ in the latter cases causes false solutions („pseudo-solutions").

In the quotation of ACRIVOS and AMUNDSON on page 16 this problem is clearly stated and a criterion is proposed to test the consistency of the solutions obtained by imposing various separation bands upon an a priori specification q, $s_{b\mu}$, $s_{b\nu}$. It is advised to check the solutions with the condition

$$0 < s_{bi} < 1 \quad \text{for} \quad l \leqslant i \leqslant h \tag{5,2}$$

Of course the condition (5,2) is *necessary*, it being a direct consequence of the law of conservation of matter. It is, however, *not sufficient*, as it permits the construction of pseudo-multiplets containing (among others) an infinity of false solutions.

Let us seek all the solutions pertaining to the separation band (λ. η) and to a fixed value of q and obeying condition (5,2). These solutions are represented by the points of a pseudo-multiplet. Condition (5,2) requires that $s_{b\eta} \leqslant 1$ and $s_{b\lambda} \geqslant 0$; hence the north and the east boundary of the pseudo-multiplet coincide (partially) with the corresponding boundaries of the proper multiplet (λ. η), (lemmas 3 and 5). There are, however, no conditions defining the west and the south boundary. Instead of extending the pseudo-multiplet in these directions as far as (5,2) allows, it seems reasonable to introduce the condition

$$s_{b\lambda} \leqslant s_{b\lambda+1} \leqslant \ldots \leqslant s_{b\eta} \tag{5,3}$$

to cut off trivial nonsensical solutions contradicting the first monotony theorem.

This has been carried out quantitatively for the pseudo-doublet (5.6) for $q = 0.6$. The result is presented in Fig. 26. The pseudo-doublet is seen to contain the doublet (5.6) and parts of the multiplets (4.6), (4.7), (4.8), (4.9), (5.7) and (5.8). Families of pseudo-lines of constant s_{b5} and constant s_{b6} can be constructed, which coincide only within the proper doublet (5.6) with the real lines of constant s_{b5} and s_{b6}. Only the pseudo-lines $s_{b5} = 0.1$ and $s_{b6} = 0.2$ have been drawn.

Suppose it is required to keep the heavy components 7, 8, 9 and 10 out of the top product. This can be realized by an absolute separation with $R_B = 9.003$ and $R_D = 4.463$ (Fig. 16), if $q = 0.6$.

Suppose we want to lower the reflux ratios by tolerating the ratios s_{b5} and s_{b6} to be 0.1 and 0.2 respectively. Then the point of intersection of the pseudo-lines 0.1 and 0.2 suggests the solution

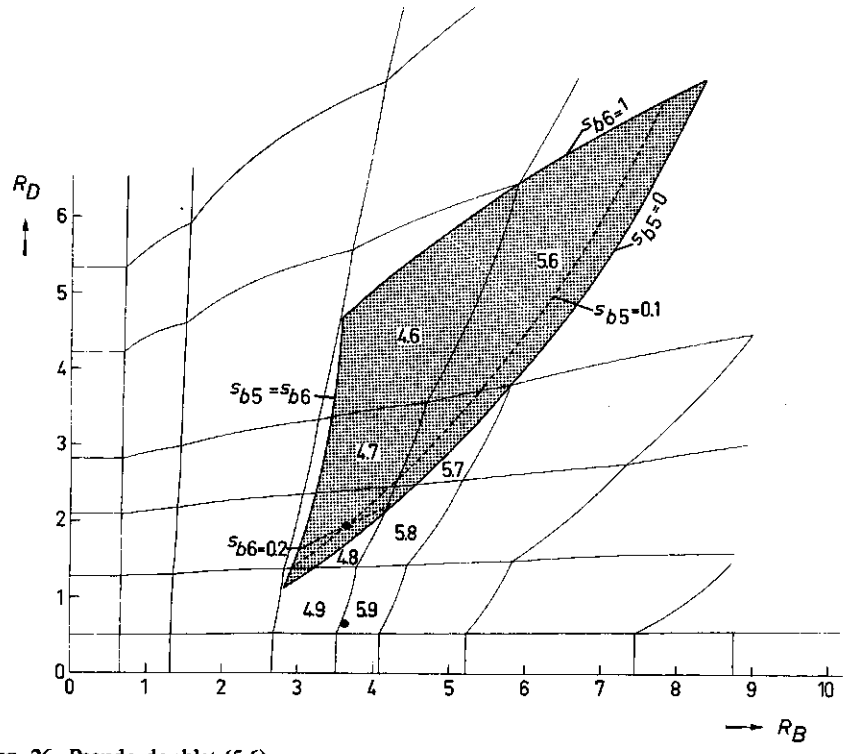

FIG. 26. Pseudo-doublet (5.6).

$$\begin{array}{llll} R_B = 3.637\,03 & L_b = 1.789\,89 & s_{bi} = 0 & i < 5 \\ R_D = 1.937\,94 & B = 0.386\,00 & s_{b5} = 0.1 & \\ & q = 0.6 & s_{b6} = 0.2 & \\ & & s_{bi} = 1 & i > 6 \end{array} \qquad (5,4)$$

The solution (5,4) satisfies condition (5,2) perfectly and so far nothing indicates the solution to be false. However, discrepancies arise if we try to compute the feed tray conditions.

The correct solution, specified by $s_{b5} = 0.1$, $s_{b6} = 0.2$ and $q = 0.6$ is represented by the dot in quintuplet (5.9). One finds

$$\begin{array}{llll} R_B = 3.610\,28 & L_b = 1.078\,86 & s_{bi} = 0 & i < 5 \\ R_D = 0.625\,16 & B = 0.234\,01 & s_{b5} = 0.1 & \\ & q = 0.6 & s_{b6} = 0.2 & \\ & & s_{b7} = 0.345\,97 & \\ & & s_{b8} = 0.447\,97 & \\ & & s_{b9} = 0.671\,98 & \\ & & s_{b10} = 1 & \end{array} \qquad (5,5)$$

Finally the correct solution in the point (R_B, R_D) of the pseudo-solution (5,4) has been computed. B and L_b have the same values as in case (5,4), be-

cause B depends only on R_B, R_D and q, according to Eq. (4,5) and $L_b = (R_B + 1)B$. Hence

$$R_B = 3.637\,03 \qquad L_b = 1.789\,89$$
$$R_D = 1.937\,94 \qquad B = 0.386\,00$$
$$q = 0.6$$

The ratios $s_{b4}, s_{b5}, \ldots, s_{b8}$ are found from the equations (3,15), which read in this case

$$-\sum_{i=4}^{8} s_{bi}F_i/(1-\alpha_i\Omega_k) = \sum_{j=9}^{10} F_j/(1-\alpha_j\Omega_k) - 1.789\,89 \qquad (5,6)$$

with $k = 4$, 5, 6 and 7.

The set of equations is completed by

$$\sum_{i=4}^{10} s_{bi}F_i = B = 0.386.\,00 \qquad (5,7)$$

One finds

$$s_{b1} = s_{b2} = s_{b3} = 0 \qquad s_{b7} = 0.660\,50$$
$$s_{b4} = 0.070\,33 \qquad s_{b8} = 0.856\,10$$
$$s_{b5} = 0.243\,01 \qquad s_{b9} = s_{b10} = 1 \qquad (5,8)$$
$$s_{b6} = 0.404\,55$$

which is entirely different from (5,4)!

5.3. Criterion of consistency

The criterion results immediately from the one-to-one correspondence, established in chapter 3, between the points of the $(\Phi_{bl}^{-1}, \Phi_{th}^{-1})$-plane and the separations:

A solution is consistent if and only if

$$\Omega_{l-1} \leqslant \Phi_{bl}^{-1} < \alpha_l^{-1} \qquad (5,9)$$
$$\text{and } \Omega_h^{-1} \leqslant \Phi_{th}^{-1} < \alpha_h$$

Checking the solutions of the preceding section with (5,9), one finds:

Pseudo-solution (5,4); $l = 5$, $h = 6$.

$$\Omega_4 = 0.7758 < \Phi_{b5}^{-1} = 0.7838 < \alpha_5^{-1} = 0.8 \qquad (5,10)$$
$$\Phi_{t6}^{-1} = 0.8966 < \Omega_6^{-1} = 1.0504 < \alpha_6 = 1.15$$

Φ_{th}^{-1} is seen to occur outside the proper interval.

Correct solution (5,5); $l = 5$, $h = 9$.

$$\Omega_4 = 0.7758 < \Phi_{b5}^{-1} = 0.7777 < \alpha_5^{-1} = 0.8 \qquad (5,11)$$
$$\Omega_9^{-1} = 0.4176 < \Phi_{t9}^{-1} = 0.4642 < \alpha_9 = 0.7$$

Both pinch parameters occur in the proper intervals.

Correct solution in point of pseudo-solution, (5,8); $l = 4$, $h = 8$

$$\Omega_3 = 0.6919 < \Phi_{b4}^{-1} = 0.7240 < \alpha_4^{-1} = 0.7407 \qquad (5,12)$$
$$\Omega_8^{-1} = 0.7472 < \Phi_{t8}^{-1} = 0.8411 < \alpha_8 = 0.9$$

Again both pinch parameters satisfy condition (5,9).

The precept, given by ACRIVOS and AMUNDSON, might be corrected in the following way:

"*Assume h and l first and solve the equations. Repeat the process until* (5,9) *is obeyed.*"

This advice is of value only if one can make a "good guess" for s_{bl}, s_{bh}, l and h. If little is known about the multicomponent system it is better to proceed in a manner set forth in section 5.4.

5.4. SPECIFICATION DIAGRAM

The construction of the diagram of multiplets of Fig. 16 is a laborious task. The complete diagram has been constructed to gain a better understanding of the complex interdependence of the many variables occuring in minimum reflux calculations.

In distillation practice, however, where usually the feed condition q and the approximate extension (l, h) of the separation band ("overlap") are prescribed in advance, it is sufficient to construct at most a few central multiplets. This has been done by way of example in Fig. 27. Conclusions can be drawn from this partial diagram concerning variations in the reflux ratios R_B and R_D resulting from certain tolerances in the sharpness of the specification.

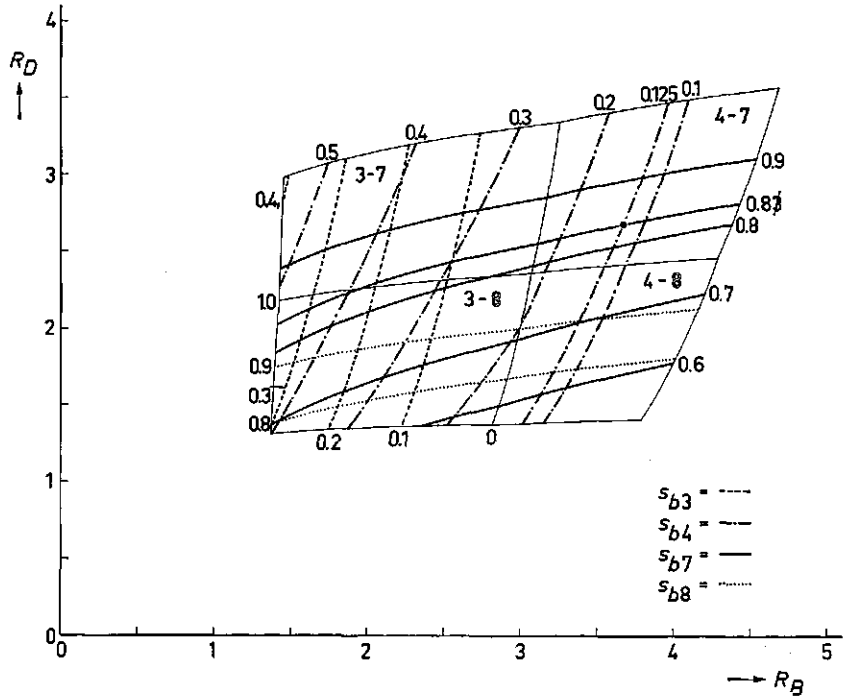

FIG. 27. Four central multiplets with line segments of constant s_{b3}, s_{b4}, s_{b7} and s_{b8}. North boundary of (3.7) and (4.7) pertains to $s_{b7} = 1$; north boundary of (3.8) and (4.8) to $s_{b8} = 1$; east boundary of (3.7) and (3.8) to $s_{b3} = 0$ and east boundary of (4.7) and (4.8) to $s_{b4} = 0$.
Example of Murdoch and Holland ($s_{b4} = 0.125$; $s_{b7} = 0.83$) is indicated. ($q^* = 0.6$).

To utilize fully the linear relations, which exist between the variables L_b, B, s_{bl}, ..., s_{bh} and which are laid down in lemmas 2, 4 and 6 of chapter 4, the values of each variable *in the four vertices* of multiplet (l. h) are plotted against one arbitrarily selected ratio $s_{b\mu}$, ($l \leqslant \mu \leqslant h$), (vide Fig. 28). In this process, one vertex generates ($h - l + 2$) corner points, situated on the vertical which corresponds to the value of $s_{b\mu}$ *in* the vertex. The original multiplet is split into ($h - l + 2$) quadrangles. According to lemmas 4 and 6 the *curved* multiplet boundaries become *straight* quadrangle sides. The quadrangles represent the domains of the variables L_b, B and s_{bk} ($k \neq \mu$) over the multiplet (l. h).

By way of example, the specification diagram has been constructed quantitatively (Fig. 28) for the values

$$q = 0.6;\ l = 4;\ h = 7 \tag{5,13}$$

and, hence, concerns the quadruplet (4.7). The construction requires the calculation of

1. the roots Ω_{l-1}, ..., Ω_h of UNDERWOOD's equation (3,12)
2. the values of L_b, B, s_{bl}, ..., s_{bh} of the vertex separations (l. h), ($l + 1$. h), ($l + 1$. $h - 1$) and (l. $h - 1$) with the equations (4,28) of lemma 1.

(5,14)

These calculations are rather time consuming but can be readily performed by a digital computer.

5.5 Specification and solution by ruler construction

Let the points of the diagram, representing a set of values of L_b, B, s_{bl}, ..., s_{bh} pertaining to one same separation, be termed *conjugate*. Then the following statements hold:

1) *Conjugate points are situated on the same vertical.*

(The values in the conjugate points pertain simultaneously to the *same* value $s_{b\mu}$ of the separation which is represented by the set of conjugate points).

2) *Quadrangle corner points on the same vertical are conjugate and correspond to the same vertex-solution.*

(In Fig. 28 the multiplet vertices corresponding to the verticals through sets of conjugate corner points are indicated. In Fig. 29 conjugate corner points are conveniently designated *a*, *b*, *c* or *d*).

Straight line segments are called conjugate if the points of intersection of the segments with any arbitrarily erected vertical are conjugate. One has then:

3) *Sides between conjugate corner points are conjugate.*

(Conjugate sides correspond simultaneously to the multiplet boundary between the vertices which are the originals of the conjugate corner points. A vertical at $s_{b\mu} = s^*_{b\mu}$ generates a set of points of intersection pertaining to the separation of the boundary at $s_{b\mu} = s^*_{b\mu}$).

4) *All segments of one conjugate set lie between two verticals.*

Through an arbitrary interior point of multiplet (l. h) pass ($h - l + 1$) curved line segments $s_{b\nu} = s^*_{b\nu}$, ($\nu = l, l + 1, \ldots, h$). As on these line segments,

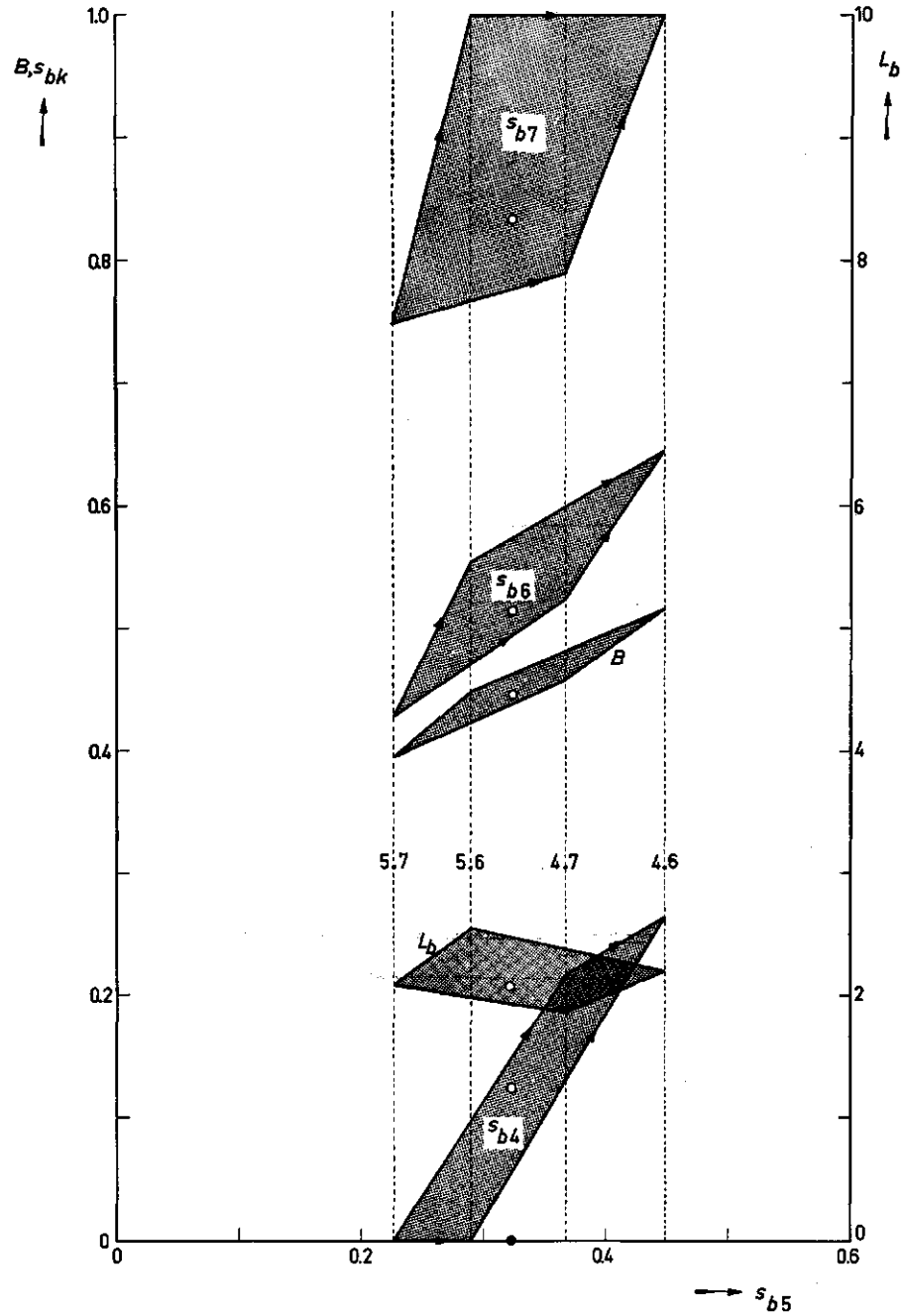

FIG. 28. Specification diagram showing domains of s_{b4}, s_{b6}, s_{b7}, B and L_b corresponding to quadruplet separations (4.7). ($q^* = 0.6$). Set of conjugate points pertains to separation of section (7,14).

by virtue of lemma 2, linear relationships hold between L_b, B and the ratios $s_{b1}, \ldots, s_{bh}$, each curved line segment generates a set of conjugate straight line segments in the specification diagram. Fig. 28 shows a set of conjugate points pertaining to a separation of quadruplet (4. 7). In quadruplet (4. 7) lines of constant s_{b4}, s_{b5}, s_{b6} and s_{b7} pass through the point representing this separation. The ratio s_{b5} has been taken as independent variable along the horizontal axes of Figs. 28 and 29. Fig. 29 shows three sets of conjugate segments corresponding to the curved segments of constant s_{b4}, s_{b6} and s_{b7} respectively. The set of segments corresponding to constant s_{bk} is distinguished by the occurrence of a horizontal segment in the quadrangle representing the domain of s_{bk}. The segments corresponding to $s_{b5} = s^*_{b5}$ are the *vertical* segments cut out by the quadrangles on the vertical at $s_{b5} = s^*_{b5}$, ("vertical set").

Fig. 29 clearly demonstrates that the set of conjugate points, representing the separation, are the points of intersection of the vertical set with any of the other sets.

Regarding the statements 1, 2, 3 and 4, the segments of one set are closely interconnected. A set of conjugate segments is completely determined by the selection of the horizontal segment of the set.

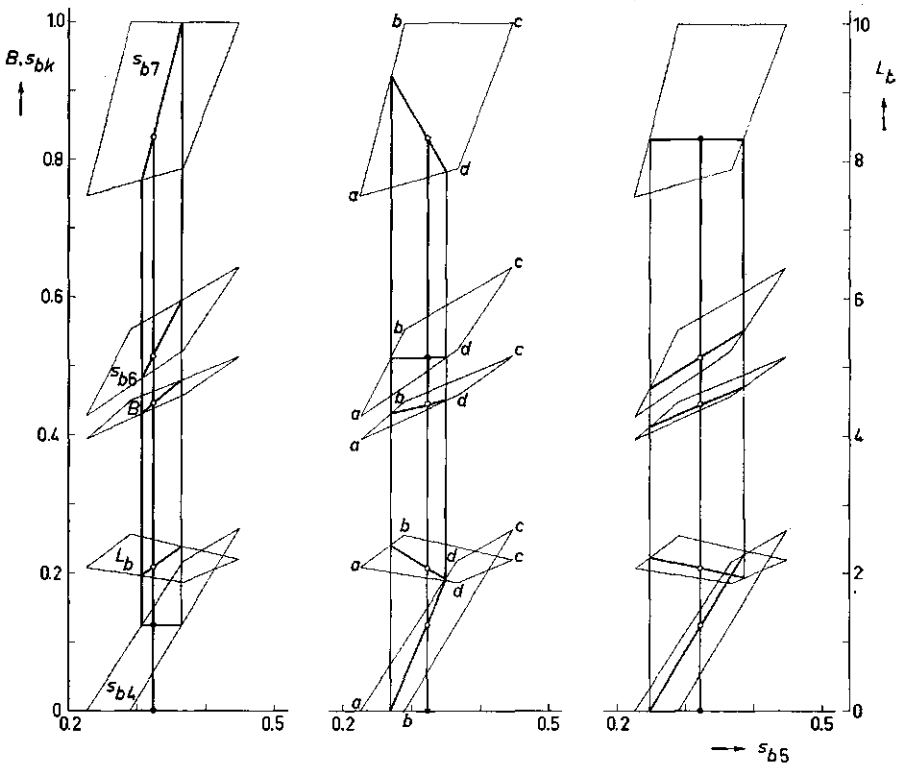

FIG. 29. Ruler constructions of solution pertaining to specified combinations (s_{b4}, s_{b5}), (s_{b5}, s_{b6}) and (s_{b5}, s_{b7}) respectively.
Specified values are indicated by heavy dots. Sets of conjugate corner points are denoted *a*, *b*, *c* and *d* respectively. (Each construction starts with specification, i.e. selection of central vertical and of horizontal segment).

Hence specification and solution are now united into one ruler construction. Specification consists in the selection of one horizontal segment and of the vertical on which the vertical set is situated. Solution consists in the completion of the set pertaining to the horizontal segment. Both sets intersect in a set of points L_b, B and s_{bi}, representing the solution pertaining to the specification made. These variables can be readily read from the graph in three significant digits. The reflux ratios are obtained without effort from $R_B = (L_b - B)/B$ and $R_D = L_t/D = (L_b - q)/(1 - B)$.

Hence, once the electronic computer has put out the vertex solution (5,14), corresponding to an a priori selected feed condition q and overlap (l. h), the minimum reflux separation of even a giant multicomponent system can be rigorously specified and rigorously solved (on the basis of the model of constant relative volatilities and constant molal overflow) with the greatest of ease.

CHAPTER 6

MATHEMATICS OF MULTICOMPONENT DISTILLATION

6.1. EXTENSION OF VAN WIJK'S FORMULATION

The previous chapters concerned primarily the computation of the product streams. To this purpose, using UNDERWOOD's method, only a handful of formulae suffice.

To derive the necessary formulae for the computation of the compositions and equilibrium constants throughout the column, however, the complex mathematics of multicomponent distillation in its entirety is indispensable.

The formulation of distillation mathematics, set forth in sections 1, 2, 3, 4 and 5 of this chapter, has been developed by W. R. VAN WIJK during the second world war [8, 9].

The distinctive feature of VAN WIJK's formulation is the dominant function of the absorption factor product $Ap_b(m)$ in the bottom section and of the stripping factor product $Sp_t(n)$ in the top section (vide sections 6.2 and 6.3).

All physical variables pertaining to the bottom section can be expressed in the absorption factor product $Ap_b(m)$, the reboil ratio R_B and the bottom yields B_i. Likewise the variables of the top section can be expressed in the stripping factor product $Sp_t(n)$, the reflux ratio R_D and the top yields D_i.

Both the absorption factor product and the stripping factor product and hence the compositions and equilibrium constants can be written as functions of the poles and residues of typical "generating" functions. The poles are the roots of algebraic equations, (characteristic equations), of a degree which, in the case of finite columns, equals the number of components present in the feed.

Inherent in this formulation are the difficulties, encountered in computing the central functions $Ap_b(m)$ and $Sp_t(n)$ in the vicinity of the feed tray, (compare section 6.2).

Consequently, even in the case of minimum reflux, iterative procedures could hitherto not be avoided.

Duplicating VAN WIJK's formulation by the simultaneous introduction of a complementary "mirror-formulation" (section 6.6) the author has found a *direct*

solution to the problem of the computation of the physical conditions throughout infinite columns. It is felt that the logical coherence of the theory has been increased considerably.

The basic formulae of the extended formulation are derived in the present chapter. The definitive theory of infinite columns is given in chapter 7.

6.2. Basic formulae for the bottom section[1])

Application of the *law of conservation of matter* to the closed surface I in Fig. 1 yields

$$L_{bi,\,m+1} = V_{bi,\,m} + B_i \tag{6,1}$$

for the flow rates of an arbitrary component i.

The *assumption of constant molal overflow* reads

$$\sum_{i=1}^{J} L_{bi,\,m} = L_b = \text{constant} \tag{6,2}$$

which expresses that the total liquid rate L_b in the stripping section is independent of the tray number m. From Eqs. (6,1) and (6,2) it follows

$$L_b = V_b + B \tag{6,3}$$

and

$$\sum_{i=1}^{J} V_{bi,\,m} = V_b = \text{constant} \tag{6,4}$$

Assuming that the reboil vapour has the same composition as the residue

$$V_{bi,\,0} = R_B B_i \tag{6,5}$$

(in which the constant R_B is called the reboil ratio), one has in view of Eqs. (6,4) and (6,3)

$$V_b = R_B B \tag{6,6}$$

and

$$L_b = (R_B + 1)B \tag{6,7}$$

The *equilibrium condition*, expressing that vapour and liquid leaving the same (ideal!) tray are in perfect equilibrium, can be written

$$L_{bi,\,m} = A_{bi,\,m} V_{bi,\,m} = V_{bi,\,m}/S_{bi,\,m} \tag{6,8}$$

$A_{bi,\,m}$ and $S_{bi,\,m} = 1/A_{bi,\,m}$ are called absorption factor and stripping factor respectively of component i on tray m. Clearly

$$A_{bi,\,m} = L_{bi,\,m}/V_{bi,\,m} = x_{bi,\,m} L_b / y_{bi,\,m} V_b \tag{6,9}$$

Hence, in accordance with the current definition of equilibrium constant $K_{bi,\,m}$

$$K_{bi,\,m} = y_{bi,\,m}/x_{bi,\,m} \tag{6,10}$$

one has

$$A_{bi,\,m} = L_b/K_{bi,\,m} V_b \quad (m > 1) \tag{6,11}$$

The definition of (constant!) relative volatility α_i reads

$$\alpha_i = K_{bi,\,m}/K_{bm} \tag{6,12}$$

K_{bm} is the equilibrium constant on tray m of an arbitrary component r, called the reference component.[2])

[1]) A list of notations is given in appendix VII.

[2]) For convenience the component index r is usually omitted in the subscripts.

From Eqs. (6,11) and (6,12) it follows

$$A_{bi,\,m} = A_{bm}/\alpha_i \tag{6,13}$$

At this stage VAN WIJK introduces the absorption factor product $Ap_b(m)$, i.e. the product of the absorption factors of the reference component on the first m trays of the stripping section

$$Ap_b(m) = A_{b1}A_{b2}A_{b3} \ldots A_{bm} \tag{6,14}$$

By definition

$$Ap_b(0) = 1 \tag{6,15}$$

From Eqs. (6,1), (6,8) and (6,13) it can be derived by repeated substitutions

$$L_{bi,\,m+1} = \frac{B_i}{Ap_b(m)} \left[R_B\alpha_i^m + \sum_{k=0}^{m} Ap_b(k)\alpha_i^{m-k}\right] \tag{6,16}$$

Substitution of (6,16) into (6,2) yields

$$L_b = \frac{1}{Ap_b(m)} \sum_{i=1}^{J} B_i \left[R_B\alpha_i^m + \sum_{k=0}^{m} Ap_b(k)\alpha_i^{m-k}\right] \tag{6,17}$$

Once the function $Ap_b(m)$ is known, one can compute from Eq. (6,16) the individual liquid rates and hence the liquid composition on each tray of the stripping section. With Eq. (6,1) the vapour rates (and the vapour composition) on each tray can be calculated. Finally the equilibrium constant of the reference component throughout the stripping section is found from Eq. (6,10). Hence the problem has been reduced to the task of solving the central function $Ap_b(m)$. This can be done step by step from $Ap_b(1)$ on with Eq. (6,17), *provided R_B and the bottom product rates B_i are simultaneously known in advance.* As has been shown in the preceding chapters, this situation occurs in the case of minimum reflux. At minimum reflux, however, the bottom products B_1 to B_{l-1} inclusive are non existent and drop out of Eq. (6,17). Hence the components, lighter than component l, do not contribute to $Ap_b(m)$, which consequently applies only to the part of the stripping section below the bottom pinch.

Introducing the function

$$u_b(k) = \sum_{i=1}^{J} B_i\alpha_i^k \tag{6,18}$$

equation (6,17) can be rewritten

$$L_b = \frac{1}{Ap_b(m)} \left[R_B u_b(m) + \sum_{k=0}^{m} Ap_b(k)u_b(m-k)\right] \tag{6,19}$$

A peculiar feature of Eq. (6,19) is the occurrence of the function $u_b(m)$ instead of the individual bottom products B_i. VAN WIJK [9, 12] has made this property a base for the reduction of multicomponent systems to systems with a smaller number of components. This subject, however, will not be dealt with in this thesis.

6.3. BASIC FORMULAE FOR THE TOP SECTION

The basic formulae for the stripping section and those for the top section result from exactly the same assumptions (conservation of matter, ideal trays, constant reflux and constant relativities). Consequently, between the formulae

of both sections a parallelism exists, which is expressed by the following list of "corresponding variables":

bottom section	top section
L	V
V	L
B	D
R_B	R_D
A	S
S	A
m	n
M	N

Therefore, the formulae for the top section are summarized below without comment.

$$V_{ti,\,n+1} = L_{ti,\,n} + D_i \tag{6,1a}$$

$$\sum_i V_{ti,\,n} = V_t = \text{constant} \tag{6,2a}$$

$$V_t = L_t + D \tag{6,3a}$$

$$\sum_i L_{ti,\,n} = L_t = \text{constant} \tag{6,4a}$$

$$L_{ti,\,0} = R_D D_i \tag{6,5a}$$

$$L_t = R_D D \tag{6,6a}$$

$$V_t = (R_D + 1)D \tag{6,7a}$$

$$V_{ti,\,n} = S_{ti,\,n} L_{ti,\,n} = L_{ti,\,n}/A_{ti,\,n} \tag{6,8a}$$

$$S_{ti,\,n} = K_{ti,\,n} V_b/L_b \tag{6,11a}$$

$$\alpha_i = K_{ti,\,n}/K_{tn} \tag{6,12a}$$

$$S_{ti,\,n} = \alpha_i S_{tn} \tag{6,13a}$$

$$Sp_t(n) = S_{t1} S_{t2} S_{t3} \ldots S_{tn} \tag{6,14a}$$

$$Sp_t(0) = 1 \tag{6,15a}$$

$$V_{ti,\,n+1} = \frac{D_i}{Sp_t(n)} \left[R_D \alpha_i^{-n} + \sum_{k=0}^{n} Sp_t(k) \alpha_i^{k-n}\right] \tag{6,16a}$$

$$V_t = \frac{1}{Sp_t(n)} \sum_{i=1}^{J} D_i \left[R_D \alpha_i^{-n} + \sum_{k=0}^{n} Sp_t(k) \alpha_i^{k-n}\right] \tag{6,17a}$$

$$u_t(k) = \sum_{i=1}^{J} D_i \alpha_i^{-k} \tag{6,18a}$$

$$V_t = \frac{1}{Sp_t(n)} \left[R_D u_t(n) + \sum_{k=0}^{n} Sp_t(k) u_t\,(n-k)\right] \tag{6,19a}$$

6.4. Analytical solutions and characteristic equation for the bottom section

In this section the central function $Ap_b(m)$, (and hence all the flow rates and equilibrium constants), will be expressed in the roots of the characteristic bottom equation (3,1). To this purpose equation (6,17) must be solved analytically. Van Wijk's elegant method employing generating functions [8[is followed.

We introduce the *generating functions:*

$$\mathbf{U}_b(s) = \sum_{k=0}^{\infty} u_b(k)s^k \tag{6,20}$$

and

$$\mathbf{A}_b(s) = \sum_{k=0}^{\infty} Ap_b(k)s^k \tag{6,21}$$

The functions are power series of a mathematical auxiliary variable s which is defined in the interval

$$0 \leqslant s < \varepsilon \tag{6,22}$$

ε is assumed to be "sufficiently small" to guarantee the convergence of the power series.

According to the product rule for power series one has

$$\mathbf{A}_b(s)\mathbf{U}_b(s) = \sum_{m=0}^{\infty} \sum_{k=0}^{\infty} Ap_b(k)u_b(m-k)s^m \tag{6,23}$$

Multiplication of Eq. (6,19) with $Ap_b(m)$ and with s^m and summation over m yields

$$L_b \sum_{m=0}^{\infty} Ap_b(m)s^m = R_B \sum_{m=0}^{\infty} u_b(m)s^m + \sum_{m=0}^{\infty} \sum_{k=0}^{m} Ap_b(k)u_b(m-k)s^m \tag{6,24}$$

Apparently Eq. (6,24) can be rewritten

$$L_b\mathbf{A}_b(s) = R_B\mathbf{U}_b(s) + \mathbf{A}_b(s)\mathbf{U}_b(s) \tag{6,25}$$

from which it follows

$$\mathbf{A}_b(s) = R_B\mathbf{U}_b(s)/[L_b - \mathbf{U}_b(s)] \tag{6,26}$$

The function $\mathbf{U}_b(s)$ can be summed

$$\mathbf{U}_b(s) = \sum_{m=0}^{\infty} \left[\sum_{i=1}^{J} B_i\alpha_i^m \right] s^m = \sum_{i=1}^{J} B_i \sum_{m=0}^{\infty} (\alpha_i s)^m = \sum_{i=1}^{J} \frac{B_i}{1-\alpha_i s} \tag{6,27}$$

Hence

$$\mathbf{A}_b(s) = \frac{R_B \sum_{i=1}^{J} B_i/(1-\alpha_i s)}{L_b - \sum_{i=1}^{J} B_i/(1-\alpha_i s)} \tag{6,28}$$

The function $\mathbf{A}_b(s)$ will now be examined. The variable s may take any positive value. It should be noted, however, that only if s is in the interval (6,22) the function $\mathbf{A}_b(s)$ can be expanded into the power series (6,21). Both numerator and denominator contain the characteristic bottom function (6,27). This function is qualitatively represented in Fig. 3 for the case $B_1 = B_2 = \ldots = B_{l-1} = 0$, as occurs at minimum reflux. The (complete) characteristic bottom function possesses J poles $s = \alpha_i^{-1}$. The values $s = \alpha_i^{-1}$, however, are not poles of the function $\mathbf{A}_b(s)$ as obviously

$$\mathbf{A}_b(\alpha_i^{-1}) = \frac{R_B B_i}{0 - B_i} = -R_B \tag{6,29}$$

The J distinct and positive poles of $\mathbf{A}_b(s)$ are the zeros of the denominator

$$L_b - \sum_{i=1}^{J} B_i/(1-\alpha_i s) = 0 \tag{6,30}$$

Eq. (6,30) is the (complete) characteristic bottom equation (3,1), which has J distinct and positive roots Φ_{bi}^{-1} satisfying

$$\left.\begin{aligned} \alpha_{i-1}^{-1} < \Phi_{bi}^{-1} < \alpha_i^{-1} \qquad & i > 1 \\ 0 < \Phi_{b1}^{-1} < \alpha_1^{-1} \qquad & i = 1 \end{aligned}\right\} \tag{6,31}$$

The poles of $\mathbf{A}_b(s)$ are of the first order. Their residues

$$c_{bi} = \lim_{s \to \Phi_{bi}^{-1}} (1 - \Phi_{bi}s)\mathbf{A}_b(s)$$

can be easily computed with l'Hopital's rule, yielding

$$c_{bi} = \frac{R_B\Phi_{bi} \sum_{k=1}^{J} B_k/(1 - \alpha_k\Phi_{bi}^{-1})}{\sum_{k=1}^{J} B_k\alpha_k/(1 - \alpha_k\Phi_{bi}^{-1})^2} = \frac{R_B\Phi_{bi}L_b}{\sum_{k=1}^{J} B_k\alpha_k/(1 - \alpha_k\Phi_{bi}^{-1})^2} \tag{6,32}$$

From Eq. (6,28) it follows

$$\lim_{s \to \infty} \mathbf{A}_b(s) = 0 \tag{6,33}$$

Hence $\mathbf{A}_b(s)$ can be written as a sum of J elementary fractions only:

$$\mathbf{A}_b(s) = \sum_{i=1}^{J} c_{bi}/(1 - \Phi_{bi}s) \tag{6,34}$$

From Eqs. (6,29) and (6,34) it follows

$$\sum_{k=1}^{J} c_{bk}/(1 - \Phi_{bk}\alpha_i^{-1}) = -R_B \qquad (i = 1, 2, \ldots, J) \tag{6,35}$$

The set of linear equations in the c_{bk} (6,35) presents an alternative way to compute the residues.

From Eq. (6,28) it follows with regard to Eq. (6,7)

$$\mathbf{A}_b(0) = R_B B/(L_b - B) = 1 \tag{6,36}$$

Hence substitution of $s = 0$ into Eq. (6,34) yields

$$\sum_{i=1}^{J} c_{bi} = 1 \tag{6,37}$$

And hence from Eqs. (6,32) and (6,37) it follows that the residues c_{bi} are positive numbers smaller than unity

$$0 \leqslant c_{bi} < 1 \tag{6,38}$$

From (6,32) and again from (6,35) it follows

$$\lim_{\Phi_{bi} \to \alpha_i} c_{bi} = 0 \tag{6,39}$$

If $0 < s < \Phi_{b1}^{-1}$, (Φ_{b1}^{-1} is the smallest root of Eq. (6,30)), then $\mathbf{A}_b(s)$ can be expanded as follows

$$\mathbf{A}_b(s) = \sum_{i=1}^{J} c_{bi} \left[\sum_{k=0}^{\infty} (\Phi_{bi}s)^k\right] = \sum_{k=0}^{\infty} \left[\sum_{i=1}^{J} c_{bi}\Phi_{bi}^k\right] s^k \tag{6,40}$$

Identification of Eqs. (6,21) and (6,40) yields

$$Ap_b(k) = \sum_{i=1}^{J} c_{bi}\Phi_{bi}^k \tag{6,41}$$

Substitution of (6,41) into Eq. (6,16) yields the analytical expression for the individual liquid rates:

$$L_{bi,\,m+1} = \frac{B_i}{Ap_b(m)} \cdot [R_B \alpha_i^m + \sum_{k=0}^{m} \sum_{j=1}^{J} c_{bj} \Phi_{bj}^k \alpha_i^{m-k}] \tag{6,42}$$

Summing the geometrical series occurring in Eq. (6,42) and recalling Eq. (6,35), one obtains

$$L_{bi,\,m+1} = \frac{B_i}{Ap_b(m)} \sum_{j=1}^{J} c_{bj} \Phi_{bj}^{m+1} / (\Phi_{bj} - \alpha_i) \tag{6,43}$$

Finally we prove the monotony of the absorption factor A_{bm}: [1])

$$A_{bm} > A_{bm-1} \qquad (m \geqslant 2) \tag{6,44}$$

As

$$A_{bm} = Ap_b(m)/Ap_b(m-1)$$

we have to show that

$$Ap_b(m) Ap_b(m-2) - Ap_b(m-1) Ap_b(m-1) > 0 \tag{6,45}$$

The first term can be written

$$\sum_{i,j} c_{bi} c_{bj} \Phi_{bi}^m \Phi_{bj}^{m-2} = \tfrac{1}{2} \sum_{i,j} [c_{bi} c_{bj} \Phi_{bi}^m \Phi_{bj}^{m-2} + c_{bj} c_{bi} \Phi_{bj}^m \Phi_{bi}^{m-2}] =$$

$$= \tfrac{1}{2} \sum_{i,j} c_{bi} c_{bj} \Phi_{bi}^{m-2} \Phi_{bj}^{m-2} [\Phi_{bi}^2 + \Phi_{bj}^2] \tag{6,46}$$

Here both i and j take the values 1, 2, ..., J.

The second term of (6,45) can be written

$$\sum_{i,j} c_{bi} c_{bj} \Phi_{bi}^{m-1} \Phi_{bj}^{m-1} = \tfrac{1}{2} \sum_{i,j} c_{bi} c_{bj} \Phi_{bi}^{m-2} \Phi_{bj}^{m-2} \cdot [2 \Phi_{bi} \Phi_{bj}] \tag{6,47}$$

Obviously

$$\tfrac{1}{2} \sum_{i,j} c_{bi} c_{bj} \Phi_{bi}^{m-2} \Phi_{bj}^{m-2} [\Phi_{bi}^2 - 2 \Phi_{bi} \Phi_{bj} + \Phi_{bj}^2] > 0$$

which proves the inequality (6,45).

6.5. Analytical solutions and characteristic equation for the top section

Because of the formal parallelism between stripping and rectifying section, the formulae corresponding to those of the preceding section will be briefly summarized.

$$\mathbf{U}_t(s) = \sum_{k=0}^{\infty} u_t(k) s^k \tag{6,20a}$$

$$\mathbf{S}_t(s) = \sum_{k=0}^{\infty} Sp_t(k) s^k \tag{6,21a}$$

$$\mathbf{S}_t(s) = R_D \mathbf{U}_t(s) / [V_t - \mathbf{U}_t(s)] \tag{6,26a}$$

$$\mathbf{S}_t(s) = \frac{R_D \sum_{i=1}^{J} D_i/(1 - \alpha_i^{-1} s)}{V_t - \sum_{i=1}^{J} D_i/(1 - \alpha_i^{-1} s)} \tag{6,28a}$$

[1]) Proof by W. R. van Wijk, private communication.

$$S_t(\alpha_i) = -R_D \tag{6,29a}$$

$$V_t - \sum_{i=1}^{J} D_i/(1-\alpha_i^{-1}s) = 0 \tag{6,30a}$$

$$\left.\begin{array}{ll} \alpha_{i+1} < \Phi_{ti}^{-1} < \alpha_i & i < J \\ 0 < \Phi_{tJ}^{-1} < \alpha_J & i = J \end{array}\right\} \tag{6,31a}$$

$$c_{ti} = \frac{R_D\Phi_{ti}\sum_{k=1}^{J} D_k/(1-\alpha_k^{-1}\Phi_{ti}^{-1})}{\sum_{k=1}^{J} D_k\alpha_k^{-1}/(1-\alpha_k^{-1}\Phi_{ti}^{-1})^2} = \frac{R_D\Phi_{ti}V_t}{\sum_{k=1}^{J} D_k\alpha_k^{-1}/(1-\alpha_k^{-1}\Phi_{ti}^{-1})^2} \tag{6,32a}$$

$$S_t(s) = \sum_{i=1}^{J} c_{ti}/(1-\Phi_{ti}s) \tag{6,34a}$$

$$\sum_{k=1}^{J} c_{tk}/(1-\Phi_{tk}\alpha_i) = -R_D \qquad 1 \leqslant i \leqslant J \tag{6,35a}$$

$$\sum_{i=1}^{J} c_{ti} = 1 \tag{6,37a}$$

$$0 \leqslant c_{ti} < 1 \tag{6,38a}$$

$$\lim_{\Phi_{ti}\to\alpha_i^{-1}} c_{ti} = 0 \tag{6,39a}$$

$$Sp_t(k) = \sum_{i=1}^{J} c_{ti}\Phi_{ti}^{k} \tag{6,41a}$$

$$V_{ti,\,n+1} = \frac{D_i}{Sp_t(n)} \cdot \sum_{j=1}^{J} c_{tj}\Phi_{ij}^{n+1}/(\Phi_{tj}-\alpha_i^{-1}) \tag{6,43a}$$

$$S_{tn} > S_{tn-1} \qquad (n \geqslant 2) \tag{6,44a}$$

6.6. Complementary formulation for bottom section

The limit (6,39) is the root of the difficulties arising in actual distillation computations employing analytical expressions.

It will be shown that at minimum reflux the terms $c_{bi}\Phi_{bi}^{m}$ with $i < l$ drop out of expression (6,41) for $Ap_b(m)$. This collapse of the light residues c_{bi} confines the range of $Ap_b(m)$ as expressed by Eq. (6,41) to the region between reboiler and bottom pinch. This is in accordance with the observation that the light components i ($<l$) do not occur below the bottom pinch and hence do not contribute to the function $Ap_b(m)$.

Calculations of absorption factors and compositions on trays below the bottom pinch can be perfectly based on Eq. (6,41) for $Ap_b(m)$. For calculations concerning the region between feed tray and bottom pinch, however, a "complementary" expression for $Ap_b(m)$ will be derived, capable of reaching "beyond the pinch". To this purpose we introduce a *complementary formulation* for the bottom section, i.e. a "top-section-like" treatment of the bottom section. The trays of the bottom section are renumbered from the feed tray downwards. (Fig. 30). In this system of numbering an arbitrary tray will be indicated by the

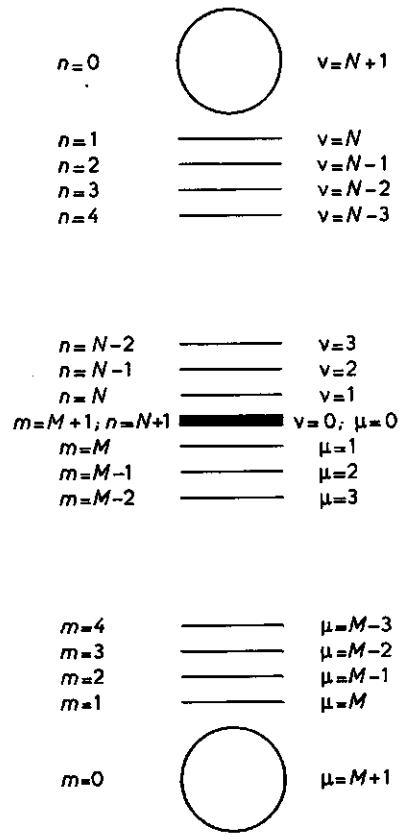

FIG. 30. Ordinary (m and n) and complementary system (μ and ν) of tray numbering.

greek index μ. If again M is the number of trays between reboiler and feed tray then the reboiler receives the number $\mu = M + 1$. One has

$$m + \mu = M + 1 \tag{6,48}$$

The product of the stripping factors of the reference component on the first μ trays below the feed tray will be denoted $Sp_{Fb}(\mu)$.[1]) One clearly has

$$Sp_{Fb}(\mu) = \frac{1}{A_{bM}} \cdot \frac{1}{A_{bM-1}} \cdots \frac{1}{A_{bM+1-\mu}} = \frac{Ap_b(M-\mu)}{Ap_b(M)} \tag{6,49}$$

and

$$Sp_{Fb}(M) = 1/Ap_b(M) \tag{6,50}$$

Also

$$Sp_{Fb}(0) = 1 \tag{6,51}$$

The law of conservation of matter and the equilibrium condition are now written:

$$V_{Fbt,\,\mu+1} = L_{Fbt,\,\mu} - B_t \tag{6,52}$$

[1]) An index F preceding the index b indicates either that the quantity belongs essentially to the complementary formulation or that the tray number refers to the complementary system of numbering.

and

$$V_{Fbi,\,\mu} = S_{Fbi,\,\mu}\, L_{Fbi,\,\mu} \tag{6,53}$$

From Eqs. (6,52) and (6,53) it follows by repeated mutual substitution [1])

$$V_{Fbi,\,\mu+1} = \frac{1}{Sp_{Fb}(\mu)} \left[L_{Fbi,\,0}\alpha_i^{-\mu} - B_i \sum_{k=0}^{\mu} Sp_{Fb}(k)\alpha_i^{k-\mu}\right] \tag{6,54}$$

Summation over i yields

$$V_b = \frac{1}{Sp_{Fb}(\mu)} \sum_{i=1}^{J} \left[L_{Fbi,\,0}\alpha_i^{-\mu} - B_i \sum_{k=0}^{\mu} Sp_{Fb}(k)\alpha_i^{k-\mu}\right] \tag{6,55}$$

Introducing the function

$$\mathbf{S}_{Fb}(s) = \sum_{k=0}^{\infty} Sp_{Fb}(k)s^k \tag{6,56}$$

it can be derived that

$$\mathbf{S}_{Fb}(s) = \frac{\sum_{i=1}^{J} L_{Fbi,\,0}/(1-\alpha_i^{-1}s)}{V_b + \sum_{i=1}^{J} B_i/(1-\alpha_i^{-1}s)} \tag{6,57}$$

Hence the complementary characteristic bottom equation reads

$$V_b + \sum_{i=1}^{J} B_i/(1-\alpha_i^{-1}s) = 0 \tag{6,58}$$

If the roots of Eq. (6,58) are denoted Φ_{Fbi}^{-1} it can be shown that

$$\Phi_{Fbi}^{-1} = \Phi_{bi} \tag{6,59}$$

i.e. *the roots of Eq.* (6,58) *are the reciprocals of the roots of the characteristic bottom equation.*

The substitutions $s = w^{-1}$ and $V_b = L_b - B$ turn Eq. (6,58) after some obvious simplifications into

$$L_b = \sum_{i=1}^{J} B_i/(1-\alpha_i^{-1}w) \tag{6,60}$$

which is indeed the characteristic bottom equation having roots $w = \Phi_{bi}^{-1}$.

The roots Φ_{Fbi}^{-1} are poles of the first order of $\mathbf{S}_{Fb}(s)$, which can be written

$$\mathbf{S}_{Fb}(s) = \sum_{i=1}^{J} c_{Fbi}/(1-\Phi_{Fbi}s) \tag{6,61}$$

The residues

$$c_{Fbi} = \lim_{s \to \Phi_{Fbi}^{-1}} (1-\Phi_{Fbi}s)\,\mathbf{S}_{Fb}(s)$$

can be computed from

$$c_{Fbi} = \frac{\sum_{k=1}^{J} L_{Fbk,\,0}\alpha_k/(1-\alpha_k\Phi_{bi}^{-1})}{\sum_{k=1}^{J} B_k\alpha_k/(1-\alpha_k\Phi_{bi}^{-1})^2} \tag{6,62}$$

in which $\Phi_{Fbi} = \Phi_{bi}^{-1}$ has been substituted.

[1]) $L_{Fbi,\,0} \equiv L_{bi,\,M+1}$ are the liquid rates leaving the feed tray.

One has

$$Sp_{Fb}(\mu) = \sum_{i=1}^{J} c_{Fbi}\Phi_{Fbi}^{\mu} = \sum_{i=1}^{J} c_{Fbi}\Phi_{bi}^{-\mu} \tag{6,63}$$

From Eqs. (6,57) and (6,61) it follows

$$Sp_{Fb}(0) = \sum_{i=1}^{J} c_{Fbi} = S_{Fb}(0) = L_b/(V_b + B) = 1 \tag{6,64}$$

By virtue of Eq. (6,49) one can write

$$Sp_{Fb}(\mu) = [\sum_{i=1}^{J} c_{bi}\Phi_{bi}^{M-\mu}]/Ap_b(M)$$

or

$$Sp_{Fb}(\mu) = \sum_{i=1}^{J} [c_{bi}\Phi_{bi}^{M}/Ap_b(M)]\Phi_{bi}^{-\mu} \tag{6,65}$$

Identification of formulae (6,63) and (6,65) yields

$$c_{Fbi} = c_{bi}\Phi_{bi}^{M}/Ap_b(M) \tag{6,66}$$

The analytical expression of Eq. (6.54) reads

$$V_{Fbi,\,\mu+1} = \frac{-B_i}{Sp_{Fb}(\mu)} \cdot \sum_{j=1}^{J} c_{Fbj}\Phi_{bj}^{-(\mu+1)}/(\Phi_{bj}^{-1} - \alpha_i^{-1}) \tag{6,67}$$

And hence

$$L_{Fbi,\,\mu} = V_{Fbi,\,\mu+1} + B_i = \frac{B_i}{Sp_{Fb}(\mu)} \cdot \sum_{j=1}^{J} c_{Fbj}\Phi_{bj}^{-\mu}/(1 - \alpha_i\Phi_{bj}^{-1}) \tag{6,68}$$

6.7. Complementary formulation for top section

To the stripping factor product $Sp_t(n)$ in the top section is appended the absorption factor product $Ap_{Ft}(\nu)$, running from feed tray towards condenser.[1]) The adhering system of numbering is indicated in Fig. 30. Again the principal formulae of the complementary formulation for the top section, corresponding to those for the bottom section, are briefly summarized.

$$n + \nu = N + 1 \tag{6,48a}$$

$$Ap_{Ft}(\nu) = \frac{1}{S_{tN}} \cdot \frac{1}{S_{tN-1}} \cdots \frac{1}{S_{tN+1-\nu}} = \frac{Sp_t(N-\nu)}{Sp_t(N)} \tag{6,49a}$$

$$Ap_{Ft}(N) = 1/Sp_t(N) \tag{6,50a}$$

$$Ap_{Ft}(0) = 1 \tag{6,51a}$$

$$L_{Fti,\,\nu+1} = V_{Fti,\,\nu} - D_i \tag{6,52a}$$

$$L_{Fti,\,\nu} = A_{Fti,\,\nu}V_{Fti,\,\nu} \tag{6,53a}$$

$$L_{Fti,\,\nu+1} = \frac{1}{Ap_{Ft}(\nu)} [V_{Fti,\,0}\alpha_i^{\nu} - D_i \sum_{k=0}^{\nu} Ap_{Ft}(k)\alpha_i^{\nu-k}] \tag{6,54a}$$

[1]) An index F preceding the index t indicates either that the quantity belongs essentially to the complementary formulation or that the tray number refers to the complementary system of numbering.

$$L_t = \frac{1}{Ap_{Ft}(\nu)} \sum_{i=1}^{J} [V_{Fti,\,0}\alpha_i^{\nu} - D_i \sum_{k=0}^{\nu} Ap_{Ft}(k)\alpha_i^{\nu-k}] \tag{6,55a}$$

$$\mathbf{A}_{Ft}(s) = \sum_{k=0}^{\infty} Ap_{Ft}(k)s^k \tag{6,56a}$$

$$\mathbf{A}_{Ft}(s) = \frac{\sum_{i=1}^{J} V_{Fti,\,0}/(1-\alpha_i s)}{L_t + \sum_{i=1}^{J} D_i/(1-\alpha_i s)} \tag{6,57a}$$

Complementary characteristic top equation:

$$L_t + \sum_{i=1}^{J} D_i/(1-\alpha_i s) = 0 \tag{6,58a}$$

The roots are:

$$\Phi_{Fti}^{-1} = \Phi_{ti} \tag{6,59a}$$

i.e. *the reciprocals of the roots of the characteristic top equation.*

$$\mathbf{A}_{Ft}(s) = \sum_{i=1}^{J} c_{Fti}/(1-\Phi_{Fti}s) \tag{6,61a}$$

$$c_{Fti} = \frac{\Phi_{ti}^{-1} \sum_{k=1}^{J} V_{Ftk,\,0}/(1-\alpha_k\Phi_{ti})}{\sum_{k=1}^{J} -D_k\alpha_k/(1-\alpha_k\Phi_{ti})^2} \tag{6,62a}$$

$$Ap_{Ft}(\nu) = \sum_{i=1}^{J} c_{Fti}\Phi_{Fti}^{\nu} = \sum_{i=1}^{J} c_{Fti}\Phi_{ti}^{-\nu} \tag{6,63a}$$

$$Ap_{Ft}(0) = \sum_{i=1}^{J} c_{Fti} = \mathbf{A}_{Ft}(0) = V_t/(L_t + D) = 1 \tag{6,64a}$$

$$c_{Fti} = c_{ti}\Phi_{ti}^{N}/Sp_t(N) \tag{6,66a}$$

$$L_{Fti,\,\nu+1} = \frac{-D_i}{Ap_{Ft}(\nu)} \cdot \sum_{j=1}^{J} c_{Ftj}\Phi_{tj}^{-(\nu+1)}/(\Phi_{tj}^{-1} - \alpha_i) \tag{6,67a}$$

$$V_{Fti,\,\nu} = L_{Fti,\,\nu+1} + D_i = \frac{D_i}{Ap_{Ft}(\nu)} \cdot \sum_{j=1}^{J} c_{Ftj}\Phi_{tj}^{-\nu}/(1-\alpha_i^{-1}\Phi_{tj}^{-1}) \tag{6,68a}$$

CHAPTER 7

THEORY OF INFINITE COLUMNS

7.1. PINCHES

Infinite columns permit the indices m, μ, n and ν to increase indefinitely. Therefore, the analytical expressions of liquid rates, vapour rates, absorption factors and stripping factors approach limiting values.

In the limit these quantities have become constant, i.e. independent of the tray index. Hence, *due to their infinite extension*, in both top and bottom section a region develops in which all physical parameters are uniform. These regions are termed *pinches*.

In the course of the present analysis it will become clear that *one and only one* pinch, the *bottom pinch*, occurs below the feed tray and simultaneously *one and only one* pinch, the *top pinch*, occurs over the feed tray.

Exhaustion zones, consisting of infinite numbers of trays, may separate the pinches from the feed tray.

In an exhaustion zone between feed tray and bottom pinch, (zone III in Fig. 2), one or more of the lightest components are eliminated from the total liquid rate.

Such components start flowing downward from the feed tray with finite amounts but their concentrations decrease asymptotically with increasing distance from the feed tray. Likewise, in an exhaustion zone over the feed tray, (zone IV in Fig. 2), one or more of the heaviest components are eliminated from the total vapour rate.

A transition zone, again consisting of an infinity of trays, may occur between reboiler and bottom pinch (zone I in Fig. 2), and (or) between top pinch and condenser, (zone VI in Fig. 2).

With respect to the occurrence of zone I, III, IV and VI one has the following rules:

absence of	means
I	$B = B_J$ only, no stripping near reboiler
III	$B = B_1$ to B_J incl., no elimination below feed tray
IV	$D = D_1$ to D_J incl., no elimination over feed tray
VI	$D = D_1$ only, no absorption near condenser.

Obviously the simultaneous absence of both I and III implies the degeneration of the bottom section to one bottom pinch in which no stripping takes place.

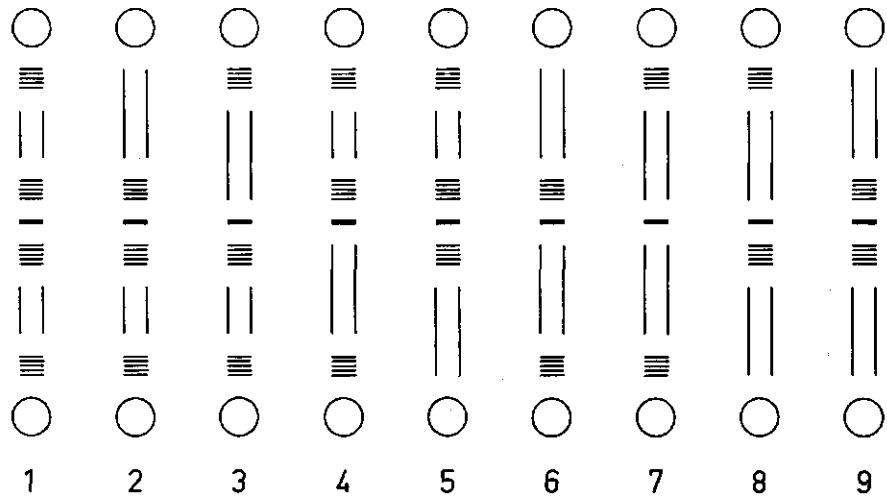

FIG. 31. Types of pinch location in infinite columns. (Compare Fig. 2).

Discarding trivial arrays of this kind, there remain 3 possibilities for the bottom section (I absent, III absent, neither I nor III absent), and likewise 3 possibilities for the top section (IV absent, VI absent, neither IV nor VI absent). Hence $3 \times 3 = 9$ types of pinch spacing are to be distinguished. (Fig. 31). Some particulars of the separations connected with the types are listed in the following table, in which l denotes the lightest component present in the bottom product and h denotes the heaviest component of the top product.

type	separation	remarks
1	$1 < l \leqslant h < J$	–
2	$l = 2; h = 1$	absolute
3	$1 < l; l < h = J$	–
4	$l = 1; l < h < J$	–
5	$l = J; h = J - 1$	absolute
6	$l = h = 1$	comp. 1 distr.
7	$l = 1; h = J$	all comp. distr.
8	$l = h = J$	comp. J distr.
9	$l = 2; h = 1$	abs. (binary systems only)

7.2. Absorption factor in bottom pinch

In the bottom pinch liquid rates, vapour rates and compositions are uniform. Therefore, the (constant) index p will be substituted for the tray index m (or μ) when the quantity pertains to the bottom pinch.

Evidently Eqs. (6,1) and (6,8), expressing conservation of matter and equilibrium condition respectively, become

$$L_{bi,\,p} = V_{bi,\,p} + B_i \tag{7,1}$$

and

$$L_{bi,\,p} = A_{bi,\,p} V_{bi,\,p} = A_{bp} V_{bi,\,p}/\alpha_i \tag{7,2}$$

Substitution of Eq. (7,2) into Eq. (7,1) yields

$$L_{bi,\,p} = B_i/(1 - \alpha_i A_{bp}^{-1}) \tag{7,3}$$

Some important conclusions can be drawn from Eq. (7,3). As obviously the liquid rates $L_{bi,\,p}$ cannot be negative, one has

$$A_{bp}^{-1} \leqslant \alpha_i^{-1} \tag{7,4}$$

Let us assume that the magnitude of A_{bp}^{-1} is intermediate between α_{l-1}^{-1} and α_l^{-1}. Then clearly

$$\alpha_l^{-1} > A_{bp}^{-1} > \alpha_{l-1}^{-1} > \alpha_{l-2}^{-1} > \ldots > \alpha_1^{-1} \tag{7,5}$$

and we conclude with regard to (7,4)

$$B_1 = B_2 = \ldots = B_{l-1} = 0 \tag{7,6}$$

and

$$L_{b1,\,p} = L_{b2,\,p} = \ldots = L_{bl-1,\,p} = 0 \tag{7,7}$$

Hence, the first $l - 1$ components do not occur in the bottom pinch and, consequently, do not occur in zone I below the bottom pinch either.

And hence component l is the lightest component in the bottom product.

In zone I the equations (6,1), (6,2) and (6,8), representing conservation of matter, constancy of molal overflow and ideality of trays respectively, are valid

with respect to the components l, $l+1$, ..., J. Repeating the arguments of chapter 6 it can be found that a (reduced) characteristic bottom equation

$$L_b = \sum_{k=l}^{J} B_k/(1-\alpha_k s) \tag{7,8}$$

with roots Φ_{bk}^{-1} satisfying

$$\Phi_{bl}^{-1} < \alpha_l^{-1} < \Phi_{bl+1}^{-1} < \alpha_{l+1}^{-1} < \ldots < \Phi_{bJ}^{-1} < \alpha_J^{-1} \tag{7,9}$$

and a (reduced) absorption factor product

$$Ap_b(m) = \sum_{k=l}^{J} c_{bk}\Phi_{bk}^{m} \tag{7,10}$$

apply to zone I.

The pinch absorption factor A_{bp} can be easily connected with the pinch parameter (chapter 3) Φ_{bl}^{-1}, as summation of Eq. (7,3) over all components occurring in the pinch yields

$$L_b = \sum_{k=l}^{J} B_k/(1-\alpha_k A_{bp}^{-1}) \tag{7,11}$$

Comparison of Eqs. (7,8) and (7,11) shows that A_{bp}^{-1} is a root of Eq. (7,8). In view of assumption (7,5) and enumeration convention (7,9) we conclude

$$A_{bp} = \Phi_{bl} \tag{7,12}$$

This result can also be reached in the following way. From Eq. (7,10) it follows

$$A_{bm} = \Big(\sum_{k=l}^{J} c_{bk}\Phi_{bk}^{m}\Big)/\Big(\sum_{k=l}^{J} c_{bk}\Phi_{bk}^{m-1}\Big) \tag{7,13}$$

Hence

$$A_{bp} = \lim_{m \to \infty} A_{bm} = \Phi_{bl}$$

as Φ_{bl} is the largest of the Φ_{bk}.

7.3. Stripping factor in top pinch

In a quite analogous way it can be shown that

$$V_{ti,\,p} = D_i/(1-\alpha_i^{-1}S_{ip}^{-1}) \tag{7,3a}$$

are the vapour rates in the top pinch. As the denominators must be positive again one has

$$S_{ip}^{-1} \leqslant \alpha_i \tag{7,4a}$$

Assuming

$$\alpha_{h+1} < S_{ip}^{-1} < \alpha_h < \alpha_{h-1} < \ldots < \alpha_1 \tag{7,5a}$$

it follows

$$D_{h+1} = D_{h+2} = \ldots = D_J = 0 \tag{7,6a}$$

and

$$V_{th+1,\,p} = V_{th+2,\,p} = \ldots = V_{tJ,\,p} = 0 \tag{7,7a}$$

Hence component h is the heaviest component occurring in the top product.

A reduced characteristic top equation

$$V_t = \sum_{k=1}^{h} D_k/(1-\alpha_k^{-1}s) \tag{7,8a}$$

with roots Φ_{tk}^{-1} satisfying

$$\Phi_{th}^{-1} < \alpha_h < \Phi_{th-1}^{-1} < \alpha_{h-1} < \ldots < \Phi_{t1}^{-1} < \alpha_1 \tag{7,9a}$$

and a reduced stripping factor product

$$Sp_t(n) = \sum_{k=1}^{h} c_{bk} \Phi_{tk}^{n} \tag{7,10a}$$

apply to zone VI.

One also has

$$S_{tp} = \lim_{n \to \infty} S_{tn} = \Phi_{th} \tag{7,12a}$$

7.4. Zero residues c_{Fbk} and c_{Ftk}

For clearness' sake the uniqueness of both top and bottom pinch is taken for granted in this section. (The proof will be given in section 7.15).

If only one bottom pinch exists, then the stripping factor in the bottom pinch

$$S_{bp} = A_{bp}^{-1} \tag{7,14}$$

must be the limiting value of the stripping factor $S_{Fb\mu}$ of the complementary formulation, i.e.

$$\lim_{\mu \to \infty} S_{Fb\mu} = S_{Fbp} \equiv S_{bp} \tag{7,15}$$

(The uniqueness of the bottom pinch implies the identity of S_{Fbp} and S_{bp}).

Hence, with regard to Eq. (7,12) and recalling

$$\Phi_{Fbk} = \Phi_{bk}^{-1}$$

it follows

$$\lim_{\mu \to \infty} S_{Fb\mu} = \Phi_{bl}^{-1} \equiv \Phi_{Fbl} \tag{7,16}$$

or

$$\lim_{\mu \to \infty} \left(\sum_{i=1}^{J} c_{Fbi} \Phi_{Fbi}^{\mu} \right) / \left(\sum_{i=1}^{J} c_{Fbi} \Phi_{Fbi}^{\mu-1} \right) \equiv \Phi_{Fbl} \tag{7,17}$$

The residues c_{Fbi} being constants (i.e. independent of μ) smaller than unity, only the largest of the Φ_{Fbi} survives in the limit.

As

$$\Phi_{Fbl} < \Phi_{Fbl+1} < \ldots < \Phi_{FbJ}$$

it follows that the terms with $i > l$ do not occur in Eq. (7,17).

Hence

$$c_{Fbl+1} = c_{Fbl+2} = \ldots = c_{FbJ} = 0 \tag{7,18}$$

In a quite analogous way, assuming the uniqueness of the top pinch, it can be shown that

$$c_{Ft1} = c_{Ft2} = \ldots = c_{Fth-1} = 0 \tag{7,19}$$

The results (7,18) and (7,19) are important as they involve Underwood's theorem as well as the key to a direct computation of the compositions and equilibrium constants throughout the (infinite) column.

7.5. UNDERWOOD'S THEOREM

Applying the explicit analytical expressions (6,62) of the residues c_{Fbi}, the equations (7,18) can be written

$$\sum_{k=1}^{J} L_{Fbk,\,0}\alpha_k/(1-\alpha_k\Phi_{bi}^{-1}) = 0 \qquad (7{,}20)$$

$$(i = l+1,\ l+2,\ \ldots,\ J)$$

as the denominators in Eqs. (6,62) are non-zero.

With the conditions of equilibrium at the feed tray [1])

$$L_{Fbk,\,0} = A_F V_{Ftk,\,0}/\alpha_k \qquad (7{,}21)$$

in which A_F is the absorption factor of the reference component at the feed tray, the liquid rates $L_{Fbk,\,0}$ are eliminated from Eqs. (7,20). Dropping the constant factor A_F from the resulting equations, one finds

$$\sum_{k=1}^{J} V_{Ftk,\,0}/(1-\alpha_k\Phi_{bi}^{-1}) = 0 \qquad (7{,}22)$$

$$(i = l+1,\ l+2,\ \ldots,\ J)$$

Applying the analytical expressions (6,62a) of the residues c_{Fti}, the equations (7,19) yield

$$\sum_{k=1}^{J} V_{Ftk,\,0}/(1-\alpha_k\Phi_{ti}) = 0 \qquad (7{,}23)$$

$$(i = 1,\ 2,\ \ldots,\ h-1)$$

Comparison of Eqs. (7,22) and (7,23) shows that the roots Φ_{bi}^{-1} (with $i > l$) and Φ_{ti} (with $i < h$) satisfy the *same equation*

$$\sum_{k=1}^{J} V_{Ftk,\,0}/(1-\alpha_k s) = 0 \qquad (7{,}24)$$

which has exactly the structure of the (complete) characteristic bottom equation and, hence, possesses $J-1$ distinct and positive roots s_k (1 root is infinite) obeying the conditions

$$\alpha_1^{-1} < s_2 < \alpha_2^{-1} < \ldots. < s_J < \alpha_J^{-1} \qquad (7{,}25)$$

i.e. one and only one root s_{k+1} is situated between consecutive reciprocal relative volatilities α_k^{-1} and α_{k+1}^{-1}.

Clearly, if a root Φ_{bi}^{-1} and a root Φ_{ti}, simultaneously satisfying Eq. (7,24), are both situated in the same interval $(\alpha_k^{-1}, \alpha_{k+1}^{-1})$, they must be identical. Comparing intervals (7,9) and (7,9a) it follows the relations

$$\left.\begin{aligned} \Phi_{bl+1}^{-1} &= \Phi_{tl} \\ \Phi_{bl+2}^{-1} &= \Phi_{tl+1} \\ &\vdots \\ \Phi_{bh}^{-1} &= \Phi_{th-1} \end{aligned}\right\} \qquad (7{,}26)$$

which constitute UNDERWOOD's theorem. (In chapter 3 these roots have been denoted Ω_l, Ω_{l+1}, ..., Ω_{h-1}, respectively).

It has been shown that UNDERWOOD's theorem (7,26) is a direct consequence

[1]) Complete mixing at feed tray assumed!

of Eqs. (7,18) and (7,19), and hence a direct consequence of the uniqueness of both top and bottom pinch.

7.6. NON-ZERO RESIDUES c_{Fbi} AND c_{Fti}

The reduced characteristic bottom equation (7,8) is the limiting case ($M \to \infty$) of the complete characteristic bottom equation (6,30).

Let us consider the case of "very large" M and, hence, "very small" values of $B_1, B_2, \ldots, B_i, \ldots, B_{l-1}$. Substituting the root Φ_{bi}^{-1}, $(i < l)$, the (still complete) characteristic bottom equation can be written [1])

$$B_i/(1 - \alpha_i \Phi_{bi}^{-1}) = L_b - \sum_{k=1}^{l-1}{}' B_k/(1 - \alpha_k \Phi_{bi}^{-1}) - \sum_{j=l}^{J} B_j/(1 - \alpha_j \Phi_{bi}^{-1}) \qquad (7,27)$$

In the limit $M \to \infty$, the products B_k with $k < l$ vanish simultaneously and the roots Φ_{bk}^{-1} are pressed against the vertical asymptotes at α_k^{-1} (compare Fig. 9B). Hence both numerator and denominator of the left hand member of Eq. (7,27) vanish. The quotient, however, stays finite, as one clearly has

$$\lim_{\Phi_{bi}^{-1} \to \alpha_i^{-1}} \frac{B_i}{1 - \alpha_i \Phi_{bi}^{-1}} = L_b - \sum_{j=l}^{J} B_j/(1 - \alpha_j \alpha_i^{-1}) \qquad (i < l) \qquad (7,28)$$

In the complementary stripping factor product $Sp_{Fb}(\mu)$, the non-zero residues c_{Fbk}, $(k = 1, 2, \ldots, l-1)$, are associated with the $\Phi_{Fbk} = \Phi_{bk}^{-1}$, having the limiting values α_k^{-1}, and the remaining non-zero residue c_{Fbl} is associated with $\Phi_{Fbl} = \Phi_{bl}^{-1}$. Hence, we have to compute the limit $\Phi_{bi}^{-1} \to \alpha_i^{-1}$ of Eq. (6,62).

Multiplying both numerator and denominator of (6,62) with $(1 - \alpha_i \Phi_{bi}^{-1})$, we get [1])

$$\frac{L_{Fbi,\,0}\alpha_i + \sum_{k=1}^{J}{}' L_{Fbk,\,0}\alpha_k(1 - \alpha_i \Phi_{bi}^{-1})/(1 - \alpha_k \Phi_{bi}^{-1})}{B_i \alpha_i/(1 - \alpha_i \Phi_{bi}^{-1}) + \sum_{k=1}^{J}{}' B_k \alpha_k (1 - \alpha_i \Phi_{bi}^{-1})/(1 - \alpha_k \Phi_{bi}^{-1})^2} \qquad (7,29)$$

In the limit the terms in the summations vanish simultaneously. Applying the limit (7,28) and dropping the factor α_i we find

$$c_{Fbi} = \frac{L_{Fbi,\,0}}{L_b - \sum_{j=l}^{J} B_j/(1 - \alpha_j \alpha_i^{-1})} \qquad (i < l) \qquad (7,30)$$

From Eq. (6,64) it follows

$$c_{Fbl} = 1 - \sum_{i=1}^{l-1} c_{Fbi} \qquad (7,31)$$

In a quite analogous way it can be shown:

$$\lim_{\Phi_{ti}^{-1} \to \alpha_i} \frac{D_i}{1 - \alpha_i^{-1} \Phi_{ti}^{-1}} = V_t - \sum_{j=1}^{h} D_j/(1 - \alpha_j^{-1} \alpha_i) \qquad (i > h) \qquad (7,28a)$$

[1]) The prime $'$ indicates that k must skip the value i.

$$c_{Fti} = \frac{V_{Fti,\,0}}{V_t - \sum_{j=1}^{h} D_j/(1-\alpha_j^{-1}\alpha_i)} \qquad (i < h) \tag{7,30a}$$

and

$$c_{Fth} = 1 - \sum_{i=h+1}^{J} c_{Fti} \tag{7,31a}$$

7.7. Computation of liquid rates $L_{Fbi,\,0}$ and of vapour rates $V_{Fti,\,0}$ (feed tray conditions)

Given a specification of two bottom products, then, applying Underwood's method, the unknown product rates, the total liquid rate L_b, the total vapour rate V_t and hence all roots Φ_{bj}^{-1} and Φ_{tk}^{-1} can be computed.

Substitution of the roots

$$\Phi_{t1}, \ldots, \Phi_{tl-1};\ \Omega_l, \ldots, \Omega_{h-1};\ \Phi_{bh+1}^{-1}, \ldots, \Phi_{bJ}^{-1} \tag{7,33}$$

into Eq. (7,24)

$$\left.\begin{aligned} &\sum_{k=1}^{J} V_{Ftk,\,0}/(1-\alpha_k s) = 0 \\ &\sum_{k=1}^{J} V_{Ftk,\,0} = V_t \end{aligned}\right\} \tag{7,34}$$

yields with

$(l-1) + (h-l) + (J-h) + 1 = J$ linear equations from which the J vapour rates $V_{Ftk,\,0}$ can be solved.[1])

Next the absorption factor A_F can be computed.[2]) Summation of Eq. (7,21) over all components yields

$$L_b = A_F \sum_{k=1}^{J} V_{Ftk,\,0}\alpha_k^{-1} \tag{7,35}$$

in which L_b is known and in which the $V_{Ftk,\,0}$ have been found from Eqs. (7,34).

Thereafter the individual liquid rates $L_{Fbk,\,0}$ can be obtained applying Eqs. (7,21).

7.8. Computation of equilibrium constant K_F of reference component at feed tray

A_F has been found from Eq. (7,35). Applying Eq. (6,11) to the reference component at the feed tray (and hence replacing V_b by V_t), one has

$$K_F = L_b/A_F V_t \tag{7,36}$$

7.9. Computation of non-zero residues c_{Fbi} and c_{Fti}

Once the liquid rates $L_{Fbk,\,0}$ and the vapour rates $V_{Ftk,\,0}$ have been computed according to section 7.7, the non-zero residues c_{Fbi} and c_{Fti} can be obtained from Eqs. (7,30), (7,31), (7,30a) and (7,31a) respectively.

[1]) The independence of the equations follows from appendix IV.

[2]) Complete mixing at feed tray assumed!

7.10. Computation of compositions and equilibrium constants between feed tray and bottom pinch

The complementary stripping factor product for infinite columns reads

$$Sp_{Fb}(\mu) = \sum_{k=1}^{l-1} c_{Fbk}\alpha_k^{-\mu} + c_{Fbl}\Phi_{bl}^{-\mu} \tag{7,37}$$

The equilibrium constant $K_{Fb\mu}$ (with $\mu \geqslant 1$) of the reference component can be computed from

$$K_{Fb\mu} = S_{Fb\mu}L_b/V_b = Sp_{Fb}(\mu)L_b/Sp_{Fb}(\mu-1)V_b \tag{7,38}$$

(compare Eq. (6,11a)).

From Eq. (6,68) it follows

$$L_{Fbi,\,\mu} = \frac{B_i}{Sp_{Fb}(\mu)} \cdot \left[\sum_{j=1}^{l-1} \frac{c_{Fbj}\alpha_j^{-\mu}}{1-\alpha_i\alpha_j^{-1}} + \frac{c_{Fbl}\Phi_{bl}^{-\mu}}{1-\alpha_i\Phi_{bl}^{-1}}\right] \quad (i \geqslant l) \tag{7,39}$$

Eq. (7,39), constituting the limit ($M \to \infty$) of Eq. (6,68), is valid only for the liquid rates of the components $i \geqslant l$.

For a component k with $k < l$, the bottom product B_k vanishes and hence all terms of the right hand member of Eq. (7,39) vanish, except the k^{th} term in the summation, which yields a zero denominator $(1-\alpha_k\alpha_k^{-1})$. Application of the limit (7,28) yields [1])

$$L_{Fbk,\,\mu} = \frac{c_{Fbk}\alpha_k^{-\mu}}{Sp_{Fb}(\mu)} \cdot \left[L_b - \sum_{j=l}^{J} B_j/(1-\alpha_j\alpha_k^{-1})\right] \quad (k < l) \tag{7,40}$$

Next the composition of the liquid on tray μ ($\geqslant 1$)

$$\left.\begin{aligned} x_{Fbi,\,\mu} &= L_{Fbi,\,\mu}/L_b \qquad i \geqslant l \\ x_{Fbk,\,\mu} &= L_{Fbk,\,\mu}/L_b \qquad k < l \end{aligned}\right\} \tag{7,41}$$

can be computed from Eqs. (7,39) and (7,40) respectively.

7.11. Computation of compositions and equilibrium constants between feed tray and top pinch

The complementary absorption factor product for infinite columns reads

$$Ap_{Ft}(\nu) = c_{Fth}\Phi_{th}^{-\nu} + \sum_{k=h+1}^{J} c_{Ftk}\alpha_k^{\nu} \tag{7,37a}$$

The equilibrium constant $K_{Ft\nu}$ ($\nu \geqslant 1$) of the reference component can be computed from

$$K_{Ft\nu} = L_t/A_{Ft\nu}V_t = Ap_{Ft}(\nu-1)\,L_t/Ap_{Ft}(\nu)V_t \tag{7,38a}$$

(compare Eq. (6, 11)).

From Eq. (6,68a) it follows

$$V_{Fti,\,\nu} = \frac{D_i}{Ap_{Ft}(\nu)} \cdot \left[\frac{c_{Fth}\Phi_{th}^{-\nu}}{1-\alpha_i^{-1}\Phi_{th}^{-1}} + \sum_{j=h+1}^{J} \frac{c_{Ftj}\alpha_j^{\nu}}{1-\alpha_i^{-1}\alpha_j}\right] \quad (i \leqslant h) \tag{7,39a}$$

[1]) Note that $\lim_{\mu\to\infty} L_{Fbi,\,\mu} = B_i/(1-\alpha_i\Phi_{bl}^{-1})$ if $i \geqslant l$, (in accordance with (7,3) and (7,12), and that $\lim_{\mu\to\infty} L_{Fbi,\,\mu} = 0$ if $i \leqslant l-1$, as $\Phi_{bl}^{-1} > \alpha_j^{-1}$ if $j \leqslant l-1$.

and, with regard to (7,28a)

$$V_{Ftk,\,\nu} = \frac{c_{Ftk}\alpha_k^{\nu}}{Ap_{Ft}(\nu)} \cdot [V_t - \sum_{j=1}^{h} D_j/(1-\alpha_j^{-1}\alpha_k] \qquad (k > h) \qquad (7,40a)$$

The liquid compositions on tray ν ($\nu \geqslant 1$) can be computed from

$$\left.\begin{aligned} x_{Fti,\,\nu} &= L_{Fti,\,\nu}/L_t = A_{Ft\nu}\alpha_i^{-1}V_{Fti,\,\nu}/L_t \qquad (i \leqslant h) \\ x_{Ftk,\,\nu} &= L_{Ftk,\,\nu}/L_t = A_{Ft\nu}\alpha_k^{-1}V_{Ftk,\,\nu}/L_t \qquad (k > h) \end{aligned}\right\} \qquad (7,41a)$$

7.12. Computation of compositions and equilibrium constants between reboiler and bottom pinch

From

$$Ap_b(m) = \sum_{k=l}^{j} c_{bk}\Phi_{bk}^{m}$$

and

$$K_{bm} = L_b/A_{bm}V_b = Ap_b(m-1)L_b/Ap_b(m)V_b \qquad (7,42)$$

the equilibrium constant K_{bm} can be computed.
From [1])

$$L_{bi,\,m+1} = \frac{B_i}{Ap_b(m)} \sum_{j=l}^{j} c_{bj}\Phi_{bj}^{m}/(1-\alpha_i\Phi_{bj}^{-1}) \qquad (7,43)$$

and

$$x_{bi,\,m+1} = L_{bi,\,m+1}/L_b \qquad (7,44)$$

the liquid compositions $x_{bi,\,m+1}$ can be obtained.

7.13. Computation of compositions and equilibrium constants between top pinch and condenser

The equilibrium constant K_{tn} follows from

$$Sp_t(n) = \sum_{k=1}^{h} c_{tk}\Phi_{tk}^{n}$$

and

$$K_{tn} = S_{tn}L_t/V_t = Sp_t(n)L_t/Sp_t(n-1)V_t \qquad (7,42a)$$

The liquid compositions follow from [2])

$$V_{ti,\,n+1} = \frac{D_i}{Sp_t(n)} \cdot \sum_{j=1}^{h} c_{tj}\Phi_{tj}^{n}/(1-\alpha_i^{-1}\Phi_{tj}^{-1}) \qquad (7,43a)$$

and

$$x_{ti,\,n+1} = L_{ti,\,n+1}/L_t = V_{ti,\,n+1}/S_{tn+1}\alpha_i L_t \qquad (7,44a)$$

[1]) Clearly $\lim_{m\to\infty} L_{bi,\,m+1} = B_i/(1-\alpha_i\Phi_{bl}^{-1})$, in accordance with (7,3) and (7,12), as $\Phi_{bl} > \Phi_{bj}$ if $j > l$.

[2]) $\lim_{n\to\infty} V_{ti,\,n+1} = D_i/(1-\alpha_i^{-1}\Phi_{th}^{-1})$ in accordance with (7,3a) and (7,12a).

7.14. NUMERICAL EXAMPLE

The liquid compositions and equilibrium constants throughout the infinite column have been evaluated numerically for the separation specified by

$$q = 0.6;\ s_{b4} = 0.125\,000;\ s_{b7} = 0.833\,333$$

The separation is situated in quadruplet (4.7), as is shown in Fig. 27.
UNDERWOOD's method yields

$$s_{b5} = 0.323\,063 \qquad L_b = 2.082\,790$$
$$s_{b6} = 0.514\,701 \qquad V_t = 2.036\,553$$

The product rates B_i and D_i and the roots of the characteristic top and bottom equation are collected in Table 2.

TABLE 2.

i	B_i	D_i	Φ_{bi}^{-1}	Φ_{ti}^{-1}
1	0	0.050 000	0.333 333	2.941 540
2	0	0.080 000	0.500 000	1.944 880
3	0	0.140 000	0.666 667	1.449 865
4	0.020 000	0.140 000	0.715 910	1.289 029
5	0.025 845	0.054 155	0.775 778	1.201 578
6	0.072 058	0.067 942	0.832 239	1.050 375
7	0.108 333	0.021 667	0.952 041	0.942 352
8	0.050 000	0	1.092 856	0.900 000
9	0.120 000	0	1.364 513	0.700 000
10	0.050 000	0	2.448 519	0.400 000
Σ	0.446 236	0.553 764	-	-

Note that $\Phi_{bi}^{-1} = \alpha_i^{-1}$ if $i \leqslant 3$ and $\Phi_{ti}^{-1} = \alpha_i$ if $i \geqslant 8$. In addition, $\Phi_{b5}^{-1} = \Omega_4$, $\Phi_{b6}^{-1} = \Omega_5$, $\Phi_{b7}^{-1} = \Omega_6$, $\Phi_{t4}^{-1} = \Omega_4^{-1}$, $\Phi_{t5}^{-1} = \Omega_5^{-1}$ and $\Phi_{t6}^{-1} = \Omega_6^{-1}$. (The roots Ω_k are collected in appendix V).

Subsequently the liquid and vapour rates, leaving the feed tray, are computed according to section 7.7. The results are collected in Table 3.

TABLE 3.

i	$V_{Fti,0}$	$L_{Fbi,0}$	
1	0.071 112	0.028 870	
2	0.144 676	0.088 103	
3	0.349 373	0.283 675	
4	0.421 722	0.380 476	
5	0.196 044	0.191 012	
6	0.324 147	0.343 306	$A_F = 1.217\,932$
7	0.280 374	0.341 475	
8	0.095 388	0.129 084	
9	0.131 226	0.228 320	
10	0.022 492	0.068 483	
Σ	2.036 554	2.082 804	

The non-zero residues c_{Fbi} and c_{Ftj} are collected in Table 4.

TABLE 4.

i	c_{Fbi}	j	c_{Ftj}
1	0.020 089	7	0.548 916
2	0.071 740	8	0.291 654
3	0.419 813	9	0.141 704
4	0.488 356	10	0.017 723
Σ	0.999 998	Σ	0.999 997

To test the accuracy, the residues c_{Fb4} and c_{Ft7} have been calculated from Eqs. (6,62) and (6,62a) respectively, instead of Eqs. (7,31) and (7,31a).

The liquid rates in the bottom pinch can be calculated from Eq. (7,3), substituting Φ_{i4}^{-1} for A_{ip}^{-1}. Analogously the vapour rates in the top pinch follow from Eq. (7,3a), taking $S_{ip}^{-1} = \Phi_{i7}^{-1}$. The results are collected in Table 5.

TABLE 5.

i	$L_{bi,p}$	$V_{ti,p}$
1	–	0.072 899
2	–	0.151 279
3	–	0.376 582
4	0.596 623	0.463 636
5	0.245 878	0.220 037
6	0.407 789	0.376 276
7	0.381 333	0.375 850
8	0.140 575	–
9	0.240 547	–
10	0.070 064	–
	2.082 809	2.036 559

Finally all remaining liquid and vapour rates, absorption and stripping factors, compositions and equilibrium constants have been calculated according to sections 8, 10, 11, 12, and 13 of this chapter. The resulting liquid compositions x_i and the equilibrium constant of the reference component, throughout the infinite column, are graphically represented in Fig. 32.

7.15. UNIQUENESS OF PINCHES

The uniqueness of the pinches, which was postulated in the preceding sections, will now be proved.

The bottom pinch is unique if and only if S_{bm} and $S_{Fb\mu}$ yield identical limiting values.

Let now c_{bl} be the „lightest" non-zero ordinary residue, i.e.

$$c_{b1} = c_{b2} = \ldots = c_{bl-1} = 0 \tag{7,45}$$

Then, by implication,

$$\Phi_{bk}^{-1} = \alpha_k^{-1} \quad \text{if} \quad k \leqslant l - 1 \tag{7,46}$$

Hence, the complementary residues c_{Fbk} with $k \leqslant l - 1$ have the limiting values (7,30) and, therefore, are non-zero as obviously $L_{Fbk,0} \neq 0$ for any value of k.

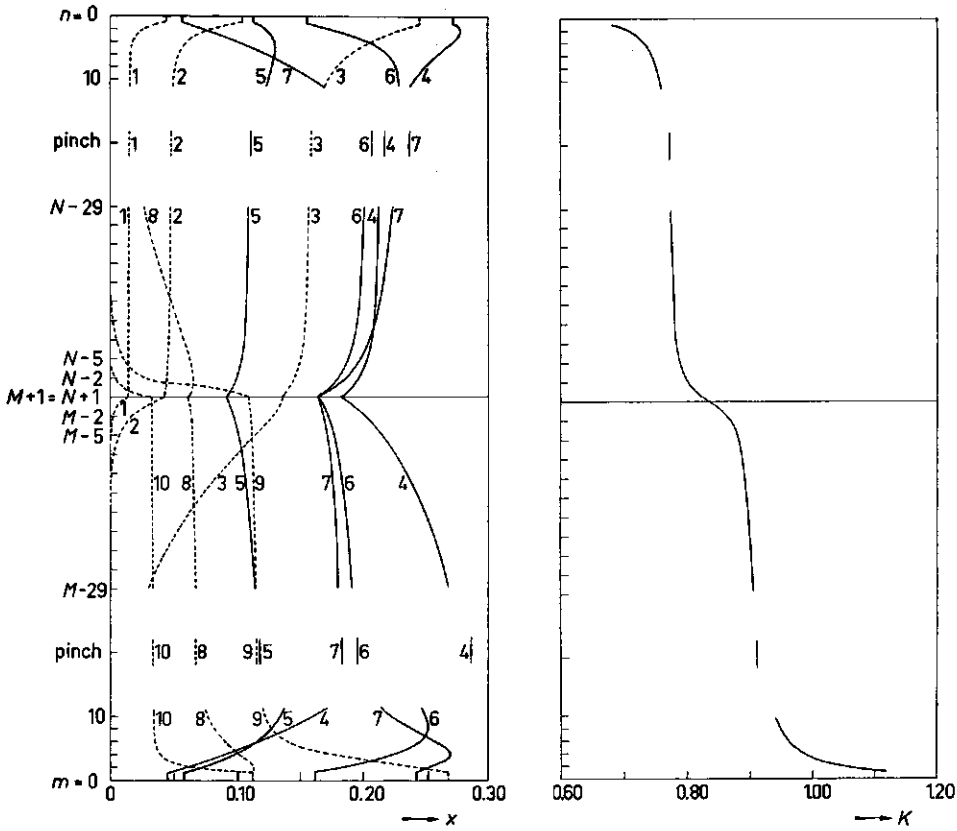

FIG. 32. Liquid composition and equilibrium constant K of reference component throughout infinite column.

Thus

$$c_{Fbk} \neq 0 \quad \text{if} \quad k \leqslant l-1 \tag{7,47}$$

It follows that if

$$Ap_b(m) = c_{bl}\Phi^m_{bl} + c_{bl+1}\Phi^m_{bl+1} + \ldots + c_{bJ}\Phi^m_{bJ} \tag{7,48}$$

then

$$Sp_{Fb}(\mu) = c_{Fb1}\Phi^\mu_{Fb1} + c_{Fb2}\Phi^\mu_{Fb2} + \ldots + c_{Fb\lambda}\Phi^\mu_{Fb\lambda} \tag{7,49}$$

and, (with regard to (7,47))

$$\lambda \geqslant l-1 \tag{7,50}$$

For large values of m the decisive term in $Ap_b(m)$ is $c_{bl}\Phi^m_{bl}$ and for large values of μ the decisive term in $Sp_{Fb}(\mu)$ is $c_{Fb\lambda}\Phi^\mu_{Fb\lambda}$, as

$$\Phi_{bl} > \Phi_{bl+1} > \ldots > \Phi_{bJ}$$

and

$$\Phi_{Fb\lambda} > \Phi_{Fb\lambda-1} > \ldots > \Phi_{Fb1}$$

Hence

$$\lim_{m\to\infty} S_{bm} = [\lim_{m\to\infty} A_{bm}]^{-1} = \Phi^{-1}_{bl}$$

and

$$\lim_{\mu \to \infty} S_{Fb\mu} = \Phi_{Fb\lambda} = \Phi_{b\lambda}^{-1}$$

It follows that the bottom pinch is unique if and only if

$$\lambda = l \tag{7,51}$$

For finite columns, Eqs. (6,66) constitute links between the ordinary residues c_{bk} and the complementary residues c_{Fbk}. These equations contain the absorption factor product

$$Ap_b(M) = \sum_{k=1}^{J} c_{bk} \Phi_{bk}^{M} \tag{7,52}$$

In the limit $M \to \infty$, however, the residues c_{bk} with $k \leqslant l-1$ vanish. Therefore, they are eliminated from (7,52) by substitution of the first $(l-1)$ expressions (6,66) yielding

$$Ap_b(M) = \sum_{j=1}^{l-1} c_{Fbj} Ap_b(M) + \sum_{k=l}^{J} c_{bk} \Phi_{bk}^{M} \tag{7,53}$$

from which it follows

$$Ap_b(M) = [\sum_{k=l}^{J} c_{bk} \Phi_{bk}^{M}] / [1 - \sum_{j=1}^{l-1} c_{Fbj}] \tag{7,54}$$

Now $Ap_b(M)$ depends only on non-vanishing residues c_{bk} and c_{Fbj} as is shown by comparison with (7,45) and (7,47).

By virtue of Eqs. (6,66) and (7,54) the residue $c_{Fb\lambda}$ can be written

$$c_{Fb\lambda} = c_{b\lambda} [1 - \sum_{j=1}^{l-1} c_{Fbj}] / [\sum_{k=l}^{J} c_{bk} (\Phi_{bk} \Phi_{b\lambda}^{-1})^{M}] \tag{7,55}$$

If $\lambda > l$, then $\Phi_{b\lambda} < \Phi_{bl}$ or $(\Phi_{bl} \Phi_{b\lambda}^{-1}) > 1$ and hence, for $M \to \infty$, the first term of the summation in the denominator increases indefinitely. We conclude

$$c_{Fb\lambda} = 0 \qquad \text{if } \lambda > l \tag{7,56}$$

If $\lambda = l$, then $\Phi_{b\lambda} > \Phi_{bk}$ or $(\Phi_{bk} \Phi_{b\lambda}^{-1}) < 1$ if $k > l$.
Hence, in the limit $M \to \infty$, all terms of the summation vanish except the first term which is c_{bl}.

And hence

$$c_{Fb\lambda} \to c_{bl} [1 - \sum_{j=1}^{l-1} c_{Fbj}] / c_{bl} \qquad \text{if } \lambda = l$$

or

$$c_{Fbl} = 1 - \sum_{j=1}^{l-1} c_{Fbj} \tag{7,57}$$

which is non-zero as long as $\Phi_{bl}^{-1} > \Omega_{l-1}$, regarding (7,18) and (7,26).[1])

We conclude: $\lambda = l$ in expression (7,49), which settles the uniqueness of the bottom pinch.

The uniqueness of the top pinch can be proved in a quite analogous way.

7.16. Pinch paradox

A striking feature of the diagram of classes (Fig. 12) is the discontinuity of

[1]) For $\Phi_{bl}^{-1} = \Omega_{l-1}$ compare section 7.16, formulae (7,65) and (7,66) and below.

the pinch parameter $\Phi_{bl}^{-1} = A_{bp}^{-1}$ at east boundaries and of the pinch parameter $\Phi_{th}^{-1} = S_{tp}^{-1}$ at north boundaries.

Now let us consider two separations P and Q at infinitesimal distance on either side of an arbitrary east boundary in the diagram of multiplets in a plane of constant q, (Fig. 33). Then P and Q have identical values for q and have only infinitesimal differences in R_B and R_D. As q, R_B and R_D command the column performance, it is to be expected that the physical conditions in the column, performing separation P, approximate tray for tray the physical conditions in the column which performs separation Q. Moreover, π being an arbitrary path joining P and Q and T being its point of intersection with the east boundary, it is to be expected that the *physical systems* P and Q become identical, i.e. both attain the limiting system T, if we let P and Q travel to T along π. The latter argument,[1]) however, contradicts the above observation concerning the discontinuity of the pinch parameters. This contradiction is termed the *pinch paradox*.

Apparently the paradox concerns the conditions at (and hence the equations of) the boundaries, i.e. the very basis of the diagram of multiplets. Therefore, it is worth while to examine this paradox in some detail. It will be shown that T represents two column states which differ with respect to pinch conditions only.

To understand the twofold nature of T we consider the question: "What is

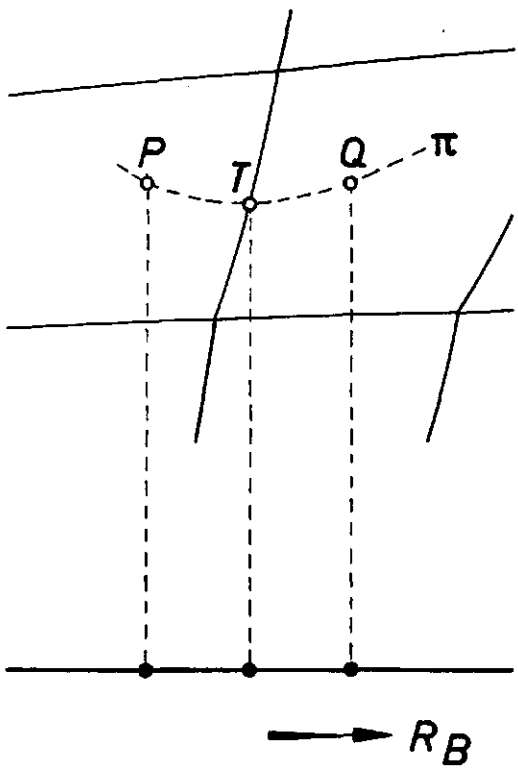

FIG. 33.

[1]) A similar argument can be constructed for north boundaries.

the meaning of $B_i = 0$?" For an interior point of a multiplet (P or Q) the answer is simply that component i does not occur in the bottom product and neither will do so if the point is subjected to an arbitrary displacement not traversing a multiplet boundary. For a point T at an east boundary, however, the answer depends on the history of the column. Either component i has been driven out of the bottom product by an increase of R_B (case a, say), or component i is at the verge of being admitted to the bottom product after decrease of R_B (case b). In case a component i is still leaking out of the bottom pinch but its liquid rate fails to survive the descend through the infinity of trays below the bottom pinch. In case b component i is reflected at the top of the bottom pinch. Hence there exist two states T, denoted $\vec{T}$ in case a and $\overleftarrow{T}$ in case b, which differ with respect to the number of non-zero (bottom) pinch rates.

Let the lightest distributed component in P's multiplet by λ and hence $\lambda + 1$ in Q's multiplet. Then $A_{bp} = \Phi_{b\lambda}$ in P's multiplet and $A_{bp} = \Phi_{b\lambda+1}$ in Q's multiplet. Hence the absorption factor of the reference component in the bottom pinch becomes α_λ for $\vec{T}$ and Ω_λ^{-1} for $\overleftarrow{T}$. And hence, according to Eq. (7,3), one has [1])

$$\vec{L}_{bi,\,p} = B_i/(1 - \alpha_i\alpha_\lambda^{-1}) \qquad (i \geqslant \lambda + 1) \tag{7,58}$$

and, by virtue of the limit (7,28)

$$\vec{L}_{b\lambda,\,p} = L_b - \sum_{j=\lambda+1}^{J} B_j/(1 - \alpha_j\alpha_\lambda^{-1}) \qquad (i = \lambda) \tag{7,59}$$

for $\vec{T}$, and for $\overleftarrow{T}$ we find

$$\overleftarrow{L}_{bi,\,p} = B_i/(1 - \alpha_i\Omega_\lambda) \qquad (i \geqslant \lambda + 1) \tag{7,60}$$

Eqs. (7,58), (7,59) and (7,60) show clearly the distinct differences which exist between the pinch conditions of $\vec{T}$ and $\overleftarrow{T}$.

If we let π in the immediate vicinity of T approximate the line of constant Φ_{th}^{-1} through T, then it follows from the first theorem of continuation (section 3.6) that $\vec{T}$ and $\overleftarrow{T}$ have identical values for R_B, L_b, B, $B_{\lambda+1}$, ..., B_J and also for R_D, V_t, D, D_1, ..., D_h. Hence $\vec{T}$ and $\overleftarrow{T}$ have identical characteristic bottom and top equations and hence identical sets of roots $\Phi_{b\lambda+1}^{-1}$, $\Phi_{b\lambda+2}^{-1}$, ..., Φ_{bJ}^{-1} and Φ_{t1}^{-1}, Φ_{t2}^{-1}, ..., Φ_{th}^{-1}. It follows that $\vec{T}$ and $\overleftarrow{T}$ have the same set of roots (7,33) and hence the same set of equations (7,34) and hence identical feed tray vapour rates $V_{Ftk,\,0}$. Next, from Eq. (7,35) follows the same value of A_F and from Eq. (7,36) the same value of K_F for $\vec{T}$ and $\overleftarrow{T}$. Finally, application of Eqs. (7,21) yields the same set of feed tray liquid rates $L_{Fbk,\,0}$ for $\vec{T}$ and $\overleftarrow{T}$. We conclude:

$\vec{T}$ and $\overleftarrow{T}$ have identical feed tray conditions. (7,61)

According to Eqs. (7,30) one has also:

$\vec{T}$ and $\overleftarrow{T}$ have identical complementary residues $c_{Fbi} \neq 0$ with $i = 1, 2, \ldots, \lambda$. (7,62)

The non-zero residues c_{bk}, $(k = \lambda + 1, \lambda + 2, \ldots, J)$ of $\vec{T}$ and of $\overleftarrow{T}$ are the solutions of the same set of linear equations

[1]) Quantities pertaining to $\vec{T}$ or $\overleftarrow{T}$ are distinguished by $^{\rightarrow}$ and $^{\leftarrow}$ respectively.

$$\sum_{k=\lambda+1}^{J} c_{bk}/(1-\Phi_{bk}\alpha_i^{-1}) = -R_B \qquad (i=\lambda+1,\ \lambda+2,\ \ldots,\ J) \tag{7,63}$$

as the roots Φ_{bk} and R_B are the same for $\vec{T}$ and $\overleftarrow{T}$. Hence

$\vec{T}$ and $\overleftarrow{T}$ have identical residues $c_{bk} \neq 0$ with
$k = \lambda+1,\ \lambda+2,\ \ldots,\ J.$ (7,64)

Having the same roots and residues, it follows that $\vec{T}$ and $\overleftarrow{T}$ have the same absorption factor product $Ap_b(m)$ and stripping factor product $Sp_{Fb}(\mu)$

$$\vec{Ap}_b(m) = \overleftarrow{Ap}_b(m) = \sum_{k=\lambda+1}^{J} c_{bk}\Phi_{bk}^{m} \tag{7,65}$$

and

$$\vec{Sp}_{Fb}(\mu) = \overleftarrow{Sp}_{Fb}(\mu) = \sum_{k=1}^{\lambda} c_{Fbk}\alpha_k^{-\mu} \tag{7,66}$$

Note that $\Phi_{b\lambda+1} = \Omega_\lambda^{-1}$ in Eq. (7,65). A peculiarity of Eqs. (7,65) and (7,66) is the absence of a common root. Hence

$$\lim_{m\to\infty} Ap_b(m)/Ap_b(m-1) \neq \lim_{\mu\to\infty} Sp_{Fb}(\mu-1)/Sp_{Fb}(\mu) \tag{7,67}$$

for both $\vec{T}$ and $\overleftarrow{T}$. It must be borne in mind, however, that the pinch conditions of $\vec{T}$ (and mutatis mutandis the same holds for $\overleftarrow{T}$) are the results of two limit procedures. For the absorption factor A_{bp} of $\vec{T}$, for instance, the limits are

$$\lim_{P\to T}\ [\lim_{m\to\infty} \{Ap_b(m)/Ap_b(m-1)\}_P] = \alpha_\lambda \tag{7,68}$$

as we interpret $\vec{T}$ as the limiting case of P and hence the bottom pinch of $\vec{T}$ as the limiting case *of the bottom pinch of P!*

The limits in (7,67) imply an interchange of both procedures, i.e.

$$\lim_{m\to\infty}\ [\lim_{P\to T} \{Ap_b(m)/Ap_b(m-1)\}_P] = \Omega_\lambda^{-1} \tag{7,69}$$

Apparently (7,68) and (7,69) do not yield the same result, and we conclude that (7,68) does and (7,69) does not meet the general requirements of continuity for the multiplet diagram, expressing that macro-physical states be continuous functions of the independent parameters. Therefore, Eq. (7,67), which contradicts the uniqueness of the bottom pinch, must be rejected!

For finite values of m and μ Eqs. (7,65) and (7,66) apply. Now $A_{b1} = Ap_b(1)/Ap_b(0) = Ap_b(1)$ and likewise $S_{Fb1} = Sp_{Fb}(1)$. As $\Omega_\lambda^{-1} \geqslant \Phi_{bk}$ if $k \geqslant \lambda+1$ and as $\alpha_\lambda^{-1} \geqslant \alpha_k^{-1}$ if $k \leqslant \lambda$, it follows from Eq. (7,65)

$$\vec{A}_{b1} = \overleftarrow{A}_{b1} = \sum_{k=\lambda+1}^{J} c_{bk}\Phi_{bk} < \Omega_\lambda^{-1}\{\sum_{k=\lambda+1}^{J} c_{bk}\} = \Omega_\lambda^{-1} = \overleftarrow{A}_{bp} \tag{7,70}$$

and from Eq. (7,66)

$$\vec{A}_{Fb1} = \overleftarrow{A}_{Fb1} = 1/[\sum_{k=1}^{\lambda} c_{Fbk}\alpha_k^{-1}] > 1/[\alpha_\lambda^{-1}\{\sum_{k=1}^{\lambda} c_{Fbk}\}] = \alpha_\lambda = \vec{A}_{bp} \tag{7,71}$$

Hence we find:

$$\vec{A}_{b1} = \overleftarrow{A}_{b1} < \overleftarrow{A}_{bp} < \vec{A}_{bp} < \vec{A}_{Fb1} = \overleftarrow{A}_{Fb1} \tag{7,72}$$

The inequalities (7,72) constitute the key to the solution of the pinch paradox.

With regard to the monotony of A_{bm} (vide (6,44)), we conclude from (7,72) that the bottom pinch of $\overleftarrow{T}$ lies lower than the bottom pinch of $\overrightarrow{T}$.

Moreover, recalling the limits

$$\lim_{P \to T} c_{b\lambda} = 0 \tag{7,73}$$

and

$$\lim_{Q \to T} c_{Fb\lambda+1} = 0 \tag{7,74}$$

it can be read from (7,72) that when P is "very close" to T, a region exists below P's bottom pinch in which the absorption factor is "nearly" constant and "nearly" equals the absorption factor $\overleftarrow{A}_{bp}$. Similarly, when Q is "very close" to T, a region exists over Q's bottom pinch in which the absorption factor is "nearly" constant and "nearly" equals the absorption factor $\overrightarrow{A}_{bp}$.

Summing up:

If (Fig. 33) the ratios R_B and R_D of the separations P and Q differ by an *infinitesimal* amount and if the points P and Q are separated by an east boundary, then the bottom pinch absorption factors of P and Q show a *finite* difference approximately equal to $\alpha_\lambda - \Omega_\lambda^{-1}$. The bottom pinches of P and Q, however, are not directly comparable, as the bottom pinch of P lies higher than the bottom pinch of Q. Only corresponding trays, i.e. trays with the same tray index, are to be compared. For corresponding trays it is true that the physical conditions of P and Q differ only infinitesimally.

SAMENVATTING

Dit proefschrift bevat een analyse van de *theorie van de minimum reflux*, uitsluitend vanuit het standpunt van het model van constante relatieve vluchtigheden en constante molaire refluxen.

De analyse heeft een theoretisch karakter. Er is niet gepoogd om verkorte rekenwijzen voor praktische toepassingen te ontwikkelen. Evenmin is de bruikbaarheid van dit (veel toegepaste) model besproken. Het doel van het onderzoek is het opruimen van enkele vage en foutieve interpretaties, die in de destillatieliteratuur bestaan ten opzichte van het probleem van de specificatie van een minimum-reflux-scheiding.

Een uitvoerig mathematisch onderzoek van een nauwkeurig omschreven model heeft verschillende voordelen. Een volledig en exact model

1. veroorlooft kwalitatieve gevolgtrekkingen van heuristische waarde;
2. levert ons de middelen om benaderingsmethoden na te rekenen, die op dezelfde fundamentele onderstellingen steunen;
3. levert een gedegen grondslag voor uitbreiding van het model door verzwakking of veralgemening van de onderstellingen die het model bepalen.

In 1946 publiceerde A. J. V. UNDERWOOD [4, 5] een theorema, waardoor (binnen genoemd model) de eerste rechtstreekse berekeningen mogelijk werden

in de theorie van de destillatie van systemen bestaande uit een groot aantal componenten. Verschillende auteurs [1, 3] leverden strenge bewijzen voor deze stelling. In dit stadium was het mogelijk om de productsamenstellingen en de minimale refluxverhouding R_{Dmin} uit te rekenen indien de verdeling van twee sleutelcomponenten en een (thermische) voedingstoestandparameter q à priori gegeven waren. Een moeilijkheid hierbij is echter, dat de aantallen lichte en zware, niet verdeelde, componenten geraden moeten worden. Bovendien voert niet iedere keuze van de verdelingen der sleutelcomponenten tot een fysisch bestaanbare oplossing. Een criterium ter beoordeling van deze bestaanbaarheid (consistentie) was niet voorhanden. De methode ontbeerde derhalve wiskundige strengheid en kon gemakkelijk aanleiding geven tot schijnoplossingen.

Men neemt algemeen aan, dat een (consistente) specificatie van q en de beide sleutelcomponenten slechts één (consistente) oplossing toelaat (éénduidigheidstheorema). De schrijver heeft echter in de destillatieliteratuur geen bewijs voor deze stelling kunnen vinden.

Ook een rechtstreekse berekening van de toestand bij de voedingsplaat (voor "oneindige kolommen" en op basis van genoemd model) is niet bekend. Wel hebben W. R. VAN WIJK en medewerkers een iteratiemethode ontwikkeld voor het geval van scheidingen met twee naast elkaar liggende sleutelcomponenten [10, 11, 12].

De inhoud van dit proefschrift valt in twee delen uiteen. Het eerste deel, (de hoofdstukken 2 tot en met 5), behandelt het onderwerp van de *specificatie*. Enkele hoofdpunten zijn:

Klassificatie

In hoofdstuk 3 wordt de geldigheid van de stelling van UNDERWOOD gepostuleerd en daarna worden enkele wiskundige hulpmiddelen ontwikkeld. Aangetoond wordt, dat de kleinste wortels van twee karakteristieke algebraïsche hogeremachtsvergelijkingen geschikte onafhankelijke parameters ("pinch-parameters") vormen voor het aanwijzen van scheidingen bij minimum reflux. De scheidingen in oneindige kolommen worden geklassificeerd naar aantallen verdeelde componenten en de relatie tussen klassen en discrete intervallen van de pinch-parameters wordt vastgesteld.

Meetkundige voorstelling

In hoofdstuk 4 wordt een meetkundige voorstelling ontwikkeld om een overzicht te verkrijgen over het gehele complex van scheidingen, die bij alle mogelijke voedingstoestanden q met een oneindige kolom verkregen kunnen worden. De scheidingen worden daartoe voorgesteld door de punten van een ruimte met de voedingstoestand q, de opkookverhouding R_B en de refluxverhouding R_D als coördinaten. De minimum-reflux-scheidingen liggen dan in de punten van een eigenaardig gevormd deel van de (q, R_B, R_D)-ruimte (minimum-refluxlichaam, Fig. 19). Scheidingen, die bij een vaste waarde van q behoren, worden voorgesteld door de punten van een "*multiplettendiagram*" (Fig. 16), d.w.z., een verdeling van het (R_B, R_D)-vlak in vakken ("multipletten"), die met de bovengenoemde klassen corresponderen. Naar de aantallen verdeelde componenten van de klassen worden deze vakken doubletten, tripletten, quadrupletten, etc. genoemd. De scheidingen in de punten van zo'n multiplet zijn oplossingen van een voor dat multiplet karakteristiek stel lineaire vergelijkingen. Het minimum-

refluxlichaam is dan opgebouwd uit multipletbuizen; zo'n buis bevat alle scheidingen met een vast stel verdeelde componenten (echter met verschillende mate van verdeling) en met verschillende voedingstoestand q.

Vertex-scheidingen kunnen à priori worden gespecificeerd

Specificatie van een scheiding is de keuze van de parameter q en van de scheidingsverhoudingen $s_{b\mu}$ en $s_{b\nu}$ van twee willekeurige verdeelde componenten, die dan sleutelcomponenten worden genoemd. (De scheidingsverhouding s_{bi} van component i is het quotient van de stroom B_i in het bodemproduct en de voedingsstroom F_i; $s_{bi} = B_i/F_i$). Om de scheiding te berekenen moet men echter reeds een deel van de oplossing van tevoren kennen, nl. de identiteit van de niet-verdeelde componenten en de mogelijkheid (consistentie) van de specificatie. De knooppunten (vertices) van het multiplettendiagram vormen uitzonderingen op deze regel. Een "vertex-scheiding" is volkomen gedefinieerd, d.w.z. zijn vergelijkingen zijn volkomen bepaald, door het kiezen van de niet-verdeelde componenten alleen. De vertices vormen daarom een hecht uitgangspunt voor het berekenen van het multiplettendiagram.

Lineaire interpolatie

Lineaire vergelijkingen vormen een belangrijk bestanddeel van de theorie. De scheidingen in punten van de randen kunnen daardoor worden verkregen door lineaire interpolatie tussen vertex-scheidingen; scheidingen in inwendige punten kunnen worden verkregen door lineaire interpolatie tussen geschikte punten van de randen.

Consistentiecriterium

Een afdoend consistentiecriterium volgt rechtstreeks uit de één-één-correspondentie tussen scheidingen en paren pinch-parameters.

Monotonie en eenduidigheidsstelling

De ordening van de componenten naar afnemende vluchtigheid induceert monotonie-eigenschappen van de scheidingsverhoudingen s_{bi} over de multipletranden en over de lijnen van constante s_{bk}. Bewijzen voor deze eigenschappen zijn in de appendices gegeven. Uit deze monotoniestellingen wordt in hoofdstuk 4 de één-éénduidigheid van de scheiding, behorend bij een consistente specificatie bewezen.

Specificatiediagram

In hoofdstuk 5 wordt een definitieve discussie van het specificatievraagstuk gegeven. Een diagram wordt ingevoerd, waarin een multiplet door een aantal afzonderlijke vierhoeken wordt vertegenwoordigd. Iedere vierhoek bevat het waardengebied van òf een scheidingsverhouding, òf de totale vloeistofstroom beneden de voedingsschotel, òf het totale bodemproduct, over het gehele multiplet. Specificatie en oplossing zijn daar teruggebracht tot een (exacte!) lineaalconstructie, die gebaseerd is op de lineariteit van de betreffende vergelijkingen.

De aan deze constructie noodzakelijk voorafgaande berekeningen bestaan uit het bepalen van de vier vertex-scheidingen van het multiplet. Wegens de à priori specificeerbaarheid van vertex-scheidingen kunnen deze berekeningen gemakkelijk door een digitale rekenmachine worden uitgevoerd.

Het tweede deel, (de hoofdstukken 6 en 7) betreft de berekening van de vloeistofsamenstelling en van de evenwichtsconstanten door de gehele oneindige kolom. Hoofdpunten van dit deel zijn:

Formulering van de theorie

De gebezigde formulering van de theorie is een uitbreiding van de door W. R. VAN WIJK gegeven formulering. Deze auteur publiceerde een aantal jaren eerder dan ACRIVOS en AMUNDSON analytische oplossingen van de fundamentele vergelijkingen voor de destillatie van discrete mengsels van veel componenten. (Zie [8] en [1]). Om de typische moeilijkheden in de berekening van de toestand bij de voedingsschotel op te heffen is in hoofdstuk 6 de oorspronkelijke formulering van VAN WIJK aangevuld met een complementaire "spiegelbeeldformulering". Daardoor kon in hoofdstuk 7 een strenge theorie van oneindige kolommen worden opgebouwd.

Eénduidigheid van de pinches

De "pinches" van de kolom zijn gebieden, bestaande uit een oneindig aantal opeenvolgende schotels, waarin de vloeistofsamenstelling en de evenwichtsconstanten uniform zijn. In hoofdstuk 7 wordt bewezen, dat zowel boven als beneden de voedingsplaat één en slechts één pinch optreedt.

Typen van pinch-combinaties

De aangrenzende schotels van de condensor, de voedingsplaat en de reboiler kunnen al of niet tot een pinch behoren. In verband hiermee kan men 9 typen van pinch-combinaties onderscheiden (Fig. 31). Hiervan kan type 9 uitsluitend voorkomen bij de scheiding van binaire mengsels.

Theorema van UNDERWOOD

Aangetoond wordt, dat het theorema van UNDERWOOD een rechtstreeks gevolg is van de éénduidigheid der pinches.

Lineaire vergelijkingen voor de toestand op de voedingsplaat van oneindige kolommen

Tot nu toe kon men de toestand bij de voedingsschotel hoogstens berekenen met iteratiemethoden. In hoofdstuk 7 is een stel lineaire vergelijkingen afgeleid, waaruit rechtstreeks de samenstelling van damp en vloeistof van de voedingsplaat (en dus de evenwichtsconstanten) exact kunnen worden berekend.

Pinch-paradox

De pinch-parameters zijn discontinu op de randen van het multiplettendiagram. Hieruit volgt een schijnbare tegenspraak, de pinch-paradox. Deze paradox wordt geanalyseerd en opgelost in paragraaf 7.16.

Alle ontwikkelingen zijn toegelicht met een aantal diagrammen en numerieke voorbeelden, die betrekking hebben op een representatief systeem, bestaande uit tien componenten.

APPENDIX I

PROOF OF THE FIRST MONOTONY THEOREM

If the feed rates $F_1, F_2, \ldots, F_J$ are ordered with respect to decreasing volatility, then

$$s_{bi} < s_{bj} \quad \text{if } l \leqslant i < j \leqslant h$$

Proof. The liquid rates of the distributed components, leaving the feed tray, are

$$L_{Fbk,\,0} = B_k \sum_{j=1}^{l} c_{Fbj}/(1-\alpha_k\Phi_{bj}^{-1}) \qquad l \leqslant k \leqslant h \tag{I,1}$$

and the vapour rates of the distributed components, leaving the feed tray, are

$$V_{Ftk,\,0} = D_k \sum_{j=h}^{J} c_{Ftj}/(1-\alpha_k^{-1}\Phi_{ij}^{-1}) \qquad l \leqslant k \leqslant h \tag{I,2}$$

according to Eqs. (7,39) and (7,39a) respectively. Applying the conditions of perfect equilibrium at the feed tray

$$L_{Fbk,\,0} = A_F\alpha_k^{-1}V_{Ftk,\,0} \tag{I,3}$$

we find

$$\frac{B_k}{D_k} = \frac{A_F\alpha_k^{-1}\sum_{j=h}^{J} c_{Ftj}/(1-\alpha_k^{-1}\Phi_{ij}^{-1})}{\sum_{j=1}^{l} c_{Fbj}/(1-\alpha_k\Phi_{bj}^{-1})} \quad \text{with } l \leqslant k \leqslant h \tag{I,4}$$

Recalling $\Phi_{ij}^{-1} = \alpha_j$ if $j > h$ and $\Phi_{bj}^{-1} = \alpha_j^{-1}$ if $j < l$, it follows from Figs. 3 and 4 that all denominators in the right hand member of (I,4) are positive. Because of the mentioned ordering, increase of the index k implies decrease of α_k and increase of α_k^{-1} and hence a simultaneous increase of the fractions in the numerator of (I,4) and a simultaneous decrease of the fractions in the denominator of (I,4). Hence the right hand member of (I,4) is a monotonic function of the index k.

But $B_k/D_k = B_k/(F_k - B_k) = s_{bk}/(1-s_{bk})$ is a monotonic function of s_{bk} and vice versa. And hence s_{bk} is a monotonic function of k.

APPENDIX II

PROOF OF THE SECOND MONOTONY THEOREM

From the equations (3,15), (3,16) and (3,17), which are linear in the unknowns L_b, s_{bl}, s_{bl+1}, ..., s_{bh}, we solve an arbitrary separation ratio s_{bi}, $(l \leqslant i \leqslant h)$.

Using Cramer's rule, application of elementary algebra (expansion of the occurring determinants and simplification of the fraction) yields:

$$s_{bi} = \frac{(1-\alpha_i\Phi_{th})\,(1-\alpha_i\Phi_{bl}^{-1})}{(\Phi_{bl}^{-1}-\Phi_{th})} \cdot X_i \cdot \left[\sum_{j=1}^{h} \frac{(1-\alpha_h\Phi_{th})}{(1-\alpha_j\Phi_{th})} \cdot Y_{ij} + \right.$$

$$\left. + \sum_{j=h+1}^{J} \frac{(1-\alpha_h\Phi_{bl}^{-1})}{(1-\alpha_j\Phi_{bl}^{-1})} \cdot Y_{ij}\right] \tag{II,1}$$

in which

$$X_l = -\left[\prod_{p=l}^{h-1}(1-\alpha_l\Omega_p)\right] / \left[F_l\alpha_l \prod_{p=l}^{h}{}'(\alpha_l-\alpha_p)\right] \qquad \text{(II,2)}$$

and

$$Y_{lj} = \left[F_j\alpha_j \prod_{p=l}^{h-1}{}'(\alpha_j-\alpha_p)\right] / \left[\prod_{p=l}^{h-1}(1-\alpha_j\Omega_p)\right] \qquad \text{(II,3)}$$

(the primes ′ exclude the value i, that is the component index of s_{bi}, from the domain of the running index p).

The quantities X_l and Y_{ij} are not depending on either Φ_{bl}^{-1} or Φ_{th}. Partial differentiation with respect to Φ_{bl}^{-1} yields

$$\frac{\partial s_{bi}}{\partial(\Phi_{bl}^{-1})} = \frac{-(1-\alpha_i\Phi_{th})s_{bi}}{(\Phi_{bl}^{-1}-\Phi_{th})(1-\alpha_i\Phi_{bl}^{-1})} + \\ + \frac{(1-\alpha_i\Phi_{th})(1-\alpha_i\Phi_{bl}^{-1})}{(\Phi_{bl}^{-1}-\Phi_{th})} \cdot X_i \sum_{j=h+1}^{J} \frac{(\alpha_j-\alpha_h)Y_{ij}}{(1-\alpha_j\Phi_{bl}^{-1})^2} \qquad \text{(II,4)}$$

The monotonic behaviour of the separation ratio s_{bi}, that is the permanence of the sign of its partial derivative, stems from the order-relations between the relative volatilities α_k, the roots Ω_k and the parameters Φ_{bl}^{-1} and Φ_{th}^{-1}. Consulting Figs. 7 and 8 and recalling $l \leqslant i \leqslant h$, it is seen that [1])

$$\text{sign}\,(X_l) = (-1)\,.\,(-1)^{h-i}/(-1)^{i-l} = (-1)^{h+l+1} \qquad \text{(II,5)}$$

$$\text{sign}\,(Y_{ij}) = (-1)^{h-l-1}/(+1) = (-1)^{h+l+1} \qquad \text{(II,6)}$$

The coefficient of s_{bi} has the sign (-1). $\dfrac{(-1)}{(-1)(+1)} = (-1)$ and the remaining terms have the sign

$$\frac{(-1)(+1)}{(-1)} \cdot (-1)^{h+l+1} \cdot \frac{(-1)}{(+1)} \cdot (-1)^{h+l+1} = (-1)$$

Hence the terms of (II, 4) are simultaneously negative, and hence

$$\frac{\partial s_{bi}}{\partial(\Phi_{bl}^{-1})} < 0 \qquad l \leqslant i \leqslant h \qquad \text{(II,7)}$$

As the order-relations hold in the entire intervals (3,19) to (3,24) inclusive, the inequality (II,7) holds in any point of these intervals.

From

$$B = \sum_{i=l}^{J} F_i s_{bi}$$

it follows

$$\frac{\partial B}{\partial(\Phi_{bl}^{-1})} = \sum_{i=l}^{h} F_i \frac{\partial s_{bi}}{\partial(\Phi_{bl}^{-1})} < 0 \qquad \text{(II,8)}$$

as $s_{bi} = 1 = \text{constant}$ for $i > h$.

From Eq. (3,17) we find

$$\frac{\partial L_b}{\partial(\Phi_{bl}^{-1})} = \sum_{i=l}^{h} \frac{F_i}{1-\alpha_i\Phi_{th}} \cdot \frac{\partial s_{bi}}{\partial(\Phi_{bl}^{-1})} > 0 \qquad \text{(II,9)}$$

as $1-\alpha_i\Phi_{th} < 0$

[1]) The exponents can be computed modulo 2.

From $L_b = (R_B + 1)B$ we find

$$\frac{\partial R_B}{\partial(\Phi_{bl}^{-1})} = [B \frac{\partial L_b}{\partial(\Phi_{bl}^{-1})} - L_b \frac{\partial B}{\partial(\Phi_{bl}^{-1})}] / B^2 > 0 \qquad \text{(II,10)}$$

because of (II,8) and (II,9).

Because of the formal dualisme between top and bottom a similar proof can be given for the signs of the partial derivatives with respect to Φ_{th}^{-1}.

In chapters 2 to 5 inclusive we have concentrated on the s_{bk}, the bottom ratios, and hence the formal symmetry has been lost. One can rewrite, however, Eqs. (3,15), (3,16) and (3,17) in terms of the top ratios $s_{tk} = 1 - s_{bk}$ instead of s_{bk}, V_t instead of L_b, α_k^{-1} instead of α_k, Ω_k^{-1} instead of Ω_k etc. etc. and repeat the argument. In this way it is found

$$\frac{\partial s_{tt}}{\partial(\Phi_{th}^{-1})} < 0 \qquad \text{or} \qquad \frac{\partial s_{bi}}{\partial(\Phi_{th}^{-1})} > 0 \qquad \text{(II,11)}$$

Hence

$$\frac{\partial D}{\partial(\Phi_{th}^{-1})} = \frac{\partial}{\partial(\Phi_{th}^{-1})} \sum_i F_i s_{ti} < 0 \qquad \text{(II,12)}$$

Partial differentiation of Eq. (3,16) yields

$$\frac{\partial L_b}{\partial(\Phi_{th}^{-1})} = \sum_{i=l}^{h} \frac{F_i}{1 - \alpha_t \Phi_{bl}^{-1}} \cdot \frac{\partial s_{bi}}{\partial(\Phi_{th}^{-1})} > 0 \qquad \text{(II,13)}$$

in view of (II,11)

From

$$L_b - q = L_t = R_D D > 0 \qquad \text{(II,14)}$$

it is found

$$\frac{\partial R_D}{\partial(\Phi_{th}^{-1})} = [D \frac{\partial L_b}{\partial(\Phi_{th}^{-1})} - (L_b - q) \frac{\partial D}{\partial(\Phi_{th}^{-1})}] / D^2 > 0 \qquad \text{(II,15)}$$

with regard to (II,12) and (II,13).

APPENDIX III

Proof of the third monotony theorem

Consider a line $s_{b\nu}$ = constant in the multiplet (l. h) and choose $s_{b\mu}$ as independent variable labeling the points of this line. ($l \leqslant \mu \leqslant h$, $l \leqslant \nu \leqslant h$, $\mu \neq \nu$). As the ratios s_{bi} are solutions of a set of linear equations, one can write

$$s_{bi} = T_i s_{b\mu} + U_i \qquad l \leqslant i \leqslant h,\ i \neq \mu \qquad \text{(III,1)}$$

Let first be $i < \nu$ and $\mu < \nu$.

T_i and U_i are not depending on $s_{b\mu}$ but contain only constants α_k, Ω_k and F_k and the ratio $s_{b\nu}$ which has been assumed constant either. Hence

$$\frac{\partial s_{bi}}{\partial s_{b\mu}} = T_i \qquad \text{(III,2)}$$

We have to show that $T_i > 0$.

Putting

$$[^{i}_{k}] = \frac{1}{1 - \alpha_i \Omega_k} \tag{III,3}$$

one can rewrite the set of equations (3,15)

$$L_b - \sum_{i=l}^{h}{}'' [^{i}_{k}] F_i s_{bi} = \sum_{j=h+1}^{J} [^{j}_{k}] F_j + [^{\mu}_{k}] F_\mu s_{b\mu} + [^{\nu}_{k}] F_\nu s_{b\nu}$$

with $k = l, l+1, \ldots, h-1$.

Application of Cramer's rule yields (after obvious simplification)

$$s_{bi} = \frac{D^{(i)}}{D} \tag{III,5}$$

in which D stands for the determinant

$$\begin{vmatrix} 1 & [^{l}_{k}] & [^{l+1}_{k}] & \ldots & -[^{i}_{k}] F_i & \ldots & [^{h-1}_{k}] & [^{h}_{k}] \end{vmatrix} \tag{III,6}$$

and $D^{(i)}$ for the determinant

$$\begin{vmatrix} 1 & [^{l}_{k}] & [^{l+1}_{k}] & \ldots & \{k\} & \ldots & [^{h-1}_{k}] & [^{h}_{k}] \end{vmatrix} \tag{III,7}$$

The primes remind us that the columns $[^{\mu}_{k}]$ and $[^{\nu}_{k}]$ are missing. The symbol $\{k\}$ denotes

$$\{k\} = \sum_{j=h+1}^{J} [^{j}_{k}] F_j + [^{\mu}_{k}] F_\mu s_{b\mu} + [^{\nu}_{k}] F_\nu s_{b\nu} \tag{III,8}$$

Both determinants are of degree $h - l$ and hence have $h - l$ rows corresponding to the values $l, l+1, \ldots, h-1$ for k.

Next we consider a determinant Δ of degree n and of the type

$$\Delta = \begin{vmatrix} 1 & \frac{1}{1-\beta_1\Upsilon_k} & \frac{1}{1-\beta_2\Upsilon_k} & \cdots & \frac{1}{1-\beta_{n-1}\Upsilon_k} \end{vmatrix} \tag{III,9}$$

with n rows corresponding to the values $1, 2, \ldots, n$ for k. By complete induction with respect to the degree n it can be shown that Δ may be expanded into

$$\Delta = \frac{(-1)^{n-1} \cdot \prod_{i=1}^{n-1} \beta_i \cdot \prod_{j<k} (\beta_j - \beta_k) \cdot \prod_{s<t} (\Upsilon_s - \Upsilon_t)}{\prod_{j,k} (1 - \beta_j \Upsilon_k)} \tag{III,10}$$

Let now the quantities β_j and Υ_k obey the respective conditions

$$\beta_1 > \beta_2 > \ldots > \beta_{n-1} \tag{III,11}$$

and

$$\Upsilon_1 < \Upsilon_2 < \ldots < \Upsilon_n \tag{III,12}$$

Then inspection of (III,10) shows that the differences $\beta_j - \beta_k$ with $j < k$ are simultaneously positive and the differences $\Upsilon_s - \Upsilon_t$ with $s < t$ are simultaneously negative. The number of the differences $\Upsilon_s - \Upsilon_t$ amounts to $1 + 2 + \ldots + (n-1) = \frac{1}{2}n(n-1)$.

Hence the sign of the numerator of (III,10) becomes

$$(-1)^{n-1} \cdot (-1)^{\frac{1}{2}n(n-1)} = (-1)^{\frac{1}{2}n(n+1)-1}$$

We consider next the series of inequalities

$$0 < \beta^{-1}_{(1)} < \Upsilon_{(1)} < \beta^{-1}_{(2)} < \Upsilon_{(2)} < \ldots < \beta^{-1}_{(n)} < \Upsilon_{(n)} < \beta^{-1}_{(n+1)} \tag{III,13}$$

Obviously the quantities $\beta_{(j)}$ and $\Upsilon_{(k)}$ still satisfy the conditions (III,11) and (III,12). We strike out two arbitrarily chosen quantities $\beta_{(j)}$, say $\beta_{(\mu)}$ and $\beta_{(\nu)}$.

The number of the remaining $\beta_{(j)}$ thereafter equals $(n-1)$. We now renumber the $(n-1)$ quantities $\beta_{(j)}$, preserving their order and hence conditions (III,11) and (III,12), and omit the brackets of the indices, yielding $\beta_1, \beta_2, \ldots, \beta_{n-1}$. These are the quantities occurring in the determinant (III,10). We compute now the sign of the denominator. A factor in the denominator is negative if $1 < \beta_j \Upsilon_k$ or $\beta_j^{-1} < \Upsilon_k$, hence, with regard to (III,13) if $(j) \leqslant (k)$. The number of negative factors is most easily determined with the help of a scheme, drawn here by way of example for the case $n = 5$. The signs of all the terms $1 - \beta_j \Upsilon_k$ are indicated, μ and ν have been taken 3 and 5 respectively.

One has:

Total number of negative factors in complete scheme with $(n) = 5$ amounts $1 + 2 + \ldots + n = \frac{1}{2}n(n+1)$.

Number of negative factors in column μ amounts $n - \mu + 1$ and similarly in column ν this number is $n - \nu + 1$. Hence after striking out two $\beta_{(k)}$ from (III,13) the total number of negative factors in the denominator amounts

$$\tfrac{1}{2}n(n+1) - n + \mu - 1 - n + \nu - 1 = \tfrac{1}{2}n(n-3) + \mu + \nu - 2$$

index of		β 1	2	3	4	5	6
	1	−	+	+	+	+	+
	2	−	−	+	+	+	+
Υ	3	−	−	−	+	+	+
	4	−	−	−	−	+	+
	5	−	−	−	−	−	+

Calling the determinant (III,9) a determinant of the Δ-type, we find: [1])

$$\text{sign } (\Delta) = \frac{(-1)^{\frac{1}{2}n(n+1)} - 1}{(-1)^{\frac{1}{2}n(n-3) + \mu + \nu - 2}} = (-1)^{\mu+\nu+1} \qquad \text{(III,14)}$$

If we take a factor $-F_i$ out of D, it is seen that D is of the Δ-type with degree $h - l$. Hence we conclude

$$\text{sign } (D) = \text{sign } (-F_i \Delta) = (-1) \cdot (-1)^{\mu+\nu+1} = (-1)^{\mu+\nu} \qquad \text{(III,15)}$$

We expand the determinant $D^{(i)}$ by splitting up the column $\{k\}$

$$\begin{aligned} D^{(i)} = \sum_{j=h+1}^{J} & \left| 1 \quad [_k^1] \quad \ldots \quad [_k^j] F_j \quad \ldots \quad [_k^h] \right| + \\ + & \left| 1 \quad [_k^1] \quad \ldots \quad [_k^\mu] F_\mu s_{b\mu} \quad \ldots \quad [_k^h] \right| + \\ + & \left| 1 \quad [_k^1] \quad \ldots \quad [_k^\nu] F_\nu s_{b\nu} \quad \ldots \quad [_k^h] \right| \end{aligned} \qquad \text{(III,16)}$$

Identification of (III,1) with (III,5) shows with regard to (III,16)

$$T_i = \frac{F_\mu}{D} \left| 1 \quad [_k^1] \quad \ldots \quad [_k^\mu] \quad \ldots \quad [_k^h] \right| \qquad \text{(III,17)}$$

The quantities $[_k^\mu]$ fill column i. They can be shifted to the position of the missing (!) column μ by $|i - \mu| - 1$ successive column interchanges, introducing

[1]) Exponents can be calculated modulo 2.

in this way an interchange-sign-factor $(-1)^{|i-\mu|-1}$. Now again a Δ-type determinant is obtained with "missing columns" i and ν and hence in view of (III,14) with a sign $(-1)^{i+\nu+1}$. We conclude:

$$\text{sign } (T_i) = \frac{(-1)^{|i-\mu|-1} \cdot (-1)^{i+\nu+1}}{(-1)^{\mu+\nu}} = +1 \qquad \text{(III,18)}$$

It does not make any difference wether $\mu < i$ or $\mu > i$ and nothing changes if μ and i are *both* $> \nu$.

Finally we consider the case in which μ and i occur on either side of ν. The proof can be repeated without change until the development of $D^{(i)}$. Formula (III,17) becomes

$$T_i = \frac{F_\mu}{D} \cdot \begin{vmatrix} 1 & [^{i}_{k}] & \cdots & [^{\mu}_{k}] & \cdots & [^{\nu}_{k}] \end{vmatrix} \qquad \text{(III,19)}$$

Here the first prime denotes the missing column μ and the second prime the missing column ν. The shift of column $[^{\mu}_{k}]$ to the position of the (missing) column μ can now be performed by a number of column interchanges

$$|\, i - \mu \,| - 2 \qquad \text{(III,20)}$$

which is one less than in the former case, because $[^{\mu}_{k}]$ must pass the column ν, which is absent, and hence does not need to be interchanged with $[^{\mu}_{k}]$. So for μ and i on either side of ν one has

$$\text{sign } (T_i) = -1 \qquad \text{(III,21)}$$

APPENDIX IV

Independence of linear equations

Disregarding the sign and positive factors F_k, (eventually positive factors $V_{Ftk,\,0}$), the determinant of the matrix of coefficients of the system of linear equations is of the Δ-type (III,9), (vide appendix III). It can be read at once from the expansion of Δ given by Eq. (III,10) that the matrix is singular if and only if at least either two β's or two γ's are identical, which obviously is not the case.

APPENDIX V

ROOTS Ω_i OF UNDERWOOD'S EQUATION

$$\sum_{k=1}^{10} \frac{F_k}{1 - \alpha_k \Omega_i} = q$$

FOR SOME VALUES OF q.

i \ q	−1	−0.5	0
1	0.339 546	0.340 947	0.343 143
2	0.512 482	0.514 677	0.517 738
3	0.685 530	0.687 240	0.689 189
4	0.768 836	0.770 961	0.773 151
5	0.823 390	0.825 991	0.828 777
6	0.930 295	0.937 420	0.944 393
7	1.076 656	1.082 616	1.087 309
8	1.232 997	1.272 899	1.308 141
9	1.781 498	2.069 048	2.302 725

i \ q	+0.3	+0.6	+1
1	0.345 167	0.348 180	0.355 332
2	0.520 207	0.523 368	0.529 133
3	0.690 482	0.691 869	0.693 863
4	0.774 470	0.775 778	0.777 477
5	0.830 501	0.832 239	0.834 536
6	0.948 342	0.952 041	0.956 532
7	1.089 589	1.091 535	1.093 702
8	1.324 865	1.338 396	1.352 424
9	2.361 732	2.394 842	2.420 750

APPENDIX VI

COEFFICIENTS $\frac{F_k}{1 - \alpha_k \Omega_i}$ OF LINEAR EQUATIONS PERTAINING TO PLANE $q = 0.6$

k	Ω_1	Ω_2	Ω_3	Ω_4	Ω_5
1	−1.122 601	−0.087 703	−0.046 485	−0.037 669	−0.033 406
2	0.263 470	−1.711 749	−0.208 474	−0.145 044	−0.120 395
3	0.293 052	0.651 320	−3.703 213	−0.855 395	−0.563 701
4	0.301 911	0.545 232	2.425 142	−3.382 664	−1.295 309
5	0.141 649	0.231 354	0.591 880	2.642 226	−1.985 173
6	0.233 492	0.351 647	0.685 101	1.298 035	3.261 491
7	0.199 442	0.272 747	0.421 900	0.579 783	0.774 912
8	0.072 819	0.094 524	0.132 515	0.165 673	0.199 215
9	0.158 673	0.189 384	0.232 697	0.262 608	0.287 471
10	0.058 090	0.063 239	0.069 132	0.072 496	0.074 951

k	Ω_6	Ω_7	Ω_8	Ω_9
1	–0.026 938	–0.021 982	–0.016 583	–0.008 085
2	–0.088 488	–0.067 621	–0.047 710	–0.021 110
3	–0.327 056	–0.219 676	–0.138 945	–0.054 007
4	–0.560 901	–0.337 858	–0.198 306	–0.071 651
5	–0.420 939	–0.219 528	–0.118 872	–0.040 129
6	–1.476 059	–0.548 450	–0.259 665	–0.079 814
7	2.710 649	–1.420 221	–0.384 165	–0.093 201
8	0.349 252	2.837 926	–0.244 431	–0.043 277
9	0.359 743	0.508 635	1.901 065	–0.177 413
10	0.080 751	0.088 749	0.107 610	1.188 687

APPENDIX VII

NOTATION

Components are arranged with respect to decreasing volatility.

Sometimes an * is used to denote a constant value of a variable.

Symbols pertaining to bottom section are distinguished by a first subindex b. Sometimes, however, index b is preceded by an index F, indicating either that the symbol belongs essentially to the complementary formulation, or that the tray number refers to the complementary system of numbering. (Fig. 30).

If the symbol depends on the component index, b is immediately followed by this index. The component index is separated by a comma from the tray number, which comes last.

Similar rules apply to symbols pertaining to top section, where b is replaced by t.

$\mathbf{A}_b$; $\mathbf{A}_{Ft}$	generating functions of absorption factor products.
A_F	absorption factor of reference component at feed tray.
A_{bm}; $A_{Ft\nu}$	absorption factors of reference component.
$A_{bi,\,m}$; $A_{Fti,\,\nu}$	absorption factors of component i.
$Ap_b(m)$	absorption factor product $A_{b1}\ A_{b2} \ldots A_{bm}$ of reference component.
$Ap_{Ft}(\nu)$	absorption factor product $A_{Ft1}\ A_{Ft2} \ldots A_{Ft\nu}$ of reference component.
B	total residue rate.
B_k	residue rate of component k.
c_{bi}; c_{Fbi}; c_{ti}; c_{Fti}	residues of poles of generating functions.
D	total distillate rate.
D_k	distillate rate of component k.
F	total feed rate; by convention $F=1$ throughout this thesis.
F_k	feed rate of component k.
h	index of heaviest distributed component or heaviest component in distillate rate.
i	component index.
J or $\mathfrak{J}$	total number of feed rates F_k.
j	component index.
K_F	equilibrium constant of reference component at feed tray.
K_{bm}; $K_{Fb\mu}$	equilibrium constant of reference component at tray m (or μ) of bottom section.
K_{tn}; $K_{Ft\nu}$	equilibrium constant of reference component at tray n (or ν) of top section.
$K_{bi,\,m}$; $K_{Fbi,\,\mu}$	equilibrium constant of component i at tray m (or μ) of bottom section.
$K_{ti,\,n}$; $K_{Fti,\,\nu}$	equilibrium constant of component i at tray n (or ν) of top section.
k	component index.
L_b	total liquid rate (= total molal overflow) in bottom section; throughout this thesis L_b is assumed independent of tray number.
$L_{bk,\,m+1}$; $L_{Fbk,\,\mu+1}$	liquid rate of component k leaving tray $m+1$ (or $\mu+1$) of bottom section.

L_t	total liquid rate (= total molal overflow) in top section; throughout this thesis L_t is assumed independent of tray number.
$L_{tk,\ n+1}$; $L_{Ftk,\ \nu+1}$	liquid rate of component k leaving tray $n+1$ (or $\nu+1$) of top section.
l	index of lightest distributed component or lightest component in residue rate.
M	total number of trays *between* reboiler and feed tray of finite columns.
m	tray number index (bottom section).
N	total number of trays *between* feed tray and condenser of finite columns.
n	tray number index (top section).
p	tray index denoting pinch.
$q = L_b - L_t$	thermal feed condition parameter, (total feed rate $F=1$!).
$R_B = V_b/B$	reboil ratio.
$R_D = L_t/D$	reflux ratio.
$\mathbf{S}_{Fb}$; $\mathbf{S}_t$	generating functions of stripping factor products.
S_F	stripping factor of reference component at feed tray.
$S_{Fb\mu}$; S_{tn}	stripping factors of reference component.
$S_{Fbi,\ \mu}$; $S_{ti,\ n}$	stripping factors of component i.
$Sp_t(n)$	stripping factor product $S_{t1}\ S_{t2} \ldots\ S_{tn}$ of reference component.
$Sp_{Fb}(\mu)$	stripping factor product $S_{Fb1}\ S_{Fb2} \ldots\ S_{Fb\mu}$ of reference component.
$s_{bk} = B_k/F_k$	separation ratio of component k.
$s_{tk} = D_k/F_k$	(top) separation ratio of component k.
$\mathbf{U}_b$; $\mathbf{U}_t$	generating functions.
$u_b(k)$	auxilliary function (6,18).
$u_t(k)$	auxilliary function (6,18a).
x	mole fraction in liquid.
y	mole fraction in vapour.
α_i	relative volatility of component i with respect to reference component $= K_{bm,\ i}/K_{bm} = K_{tn,\ i}/K_{tn}$; in this thesis assumed constant throughout column.
η	particular value of index h.
λ	particular value of index l.
μ	tray number for bottom section in complementary system of numbering (Fig. 30); sometimes used as component index.
ν	tray number for top section in complementary system of numbering (Fig. 30); sometimes used as component index.
Φ_{bk}^{-1}	k' th root of characteristic bottom equation (3,1).
Φ_{tk}^{-1}	k' th root of characteristic top equation (3,2).
$\Phi_{Fbk}^{-1} = \Phi_{bk}$	k' th root of complementary characteristic bottom equation (6,58).
$\Phi_{Ftk}^{-1} = \Phi_{tk}$	k' th root of complementary characteristic top equation (6,58a).
Ω_k	k' th root of UNDERWOOD's equation (3,12).

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