Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

A Critical Approach to Separations Theory through the "Contaminant Ratio" Concept, with a Note on Optimum Separation

T. R. C. Boyde[a]
[a] DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF HONG KONG, HONG KONG

To cite this Article Boyde, T. R. C.(1979) 'A Critical Approach to Separations Theory through the "Contaminant Ratio" Concept, with a Note on Optimum Separation', Separation Science and Technology, 14: 2, 79 — 106
To link to this Article: DOI: 10.1080/01496397908062549
URL: http://dx.doi.org/10.1080/01496397908062549

SEPARATION SCIENCE AND TECHNOLOGY, 14(2), pp. 79–106, 1979

A Critical Approach to Separations Theory through the "Contaminant Ratio" Concept, with a Note on Optimum Separation

---

T. R. C. BOYDE

DEPARTMENT OF BIOCHEMISTRY
UNIVERSITY OF HONG KONG
HONG KONG

Abstract

Separation parameters may be classified primarily as predictive (Class 1), descriptive (Class 2), or indicative (Class 3). To predict fully the results of a separation process requires at least four independent statements of the value of appropriate Class 1 parameters or equivalent statements: similarly, to describe fully the results of a separation process requires at least four parameters of Class 2. In either case, where less than four statements are given the deficiency is made good by implicit assumptions, which may restrict the generality of any conclusions or invalidate them completely. Indicative parameters incorporate both predictive and descriptive information: there are comparable limitations upon the use of this class also.

When describing results, uncertainty may be avoided by using indices of both composition and yield, which have the further advantage of applicability to any separation method. If they are to be exploited to the full, it is necessary to know how theoretical values may be derived from knowledge of operating conditions (i.e., from Class 1 parameters), and this is now set out for idealized single-step, multistage, and chromatographic procedures.

The conditions for optimum separation vary with the choice of criterion for defining "optimum." In a single-step separation of two components into two product regions, and if a symmetrical distribution of components is required, the condition is that the product of distribution ratios shall be unity, but this does not apply generally.

INTRODUCTION

Except in certain special cases a definition of separative resolution can only be firmly based on the composition of the product. Moreover, since separations may not be mutually good, a rigorous treatment can only deal with the separation of one component from one contaminant at any given time. Measures of separation intended for general use should reflect these requirements, but most do not do so. The "contaminant ratio," η, may be used as a fundamental expression of separation actually achieved (*1*), preferably in association with an indication of yield, such as "fractional yield," Y.

It is desirable to know how values of η and Y, or related parameters, can be derived from the theory of various separation processes, and this is done in the present paper, which attempts to show how these parameters can be applied universally to express predicted separation as well as that actually achieved, and thus facilitate comparison between the two. Before embarking on this, however, it is necessary to define the terms and symbols to be used, examine the varieties of separations parameter which will be needed, and determine the number of parameters required to predict or describe the results of a separation process.

TERMINOLOGY

A mixture is regarded as being composed of a finite number of components, each consisting of particles either identical or having some property in common sufficient to permit their distinction from the particles of other components. Thus, no assumption is made that we wish to deal only with separations of molecules. In many cases, perhaps the majority, separation processes are examples of physical chemistry in action, but this is not necessarily the case and there is no need to limit ourselves in this way. A separation is viewed simply as a process in which at least one component is enriched in at least one product region, relative to another component. That is, its contaminant ratio declines.

By "region" is meant the portion of space into which one product of a separation process is segregated. Rony, who introduced the term, restricted himself to separations of molecular species and his definition refers to products only (*2*): we have no appropriate word to refer to the distinguishable portions of space (whether separate phases or not) between which a component may distribute or redistribute itself during the course of a separation process. These we will call "domains." Examples are the two phases in distillation, solvent extraction, partition chromatography, and crystallization, or distinct portions of space which are not necessarily recognizable as phases, such as the spaces inside and outside "molecular sieves," solution and surface in the case of adsorption, and the spaces on either side of a sieve, filter, or membrane. In the case of a single-step separation process, the concepts of region and domain may merge, but in multistep processes the distinction is plain and seems worthy of recognition by an appropriate choice of terminology. "Product" means the totality of particles of components of the original mixture which at the end of the process are found in a chosen region. "Product region" is synonymous with "region," and is used occasionally to avoid any possible ambiguity.

"Contaminant ratio," when unqualified, refers to the ratio of a contaminant (say, B) to the component of greatest interest (say, A) in any region or domain to be defined (*1*). It is often convenient to employ the "equalized contaminant ratio." The latter is written ${}^{e}\eta_{\mathrm{A,B}}$ and the former, "unequalized," ratio is written ${}^{u}\eta_{\mathrm{A,B}}$. By definition,

$${}^{e}\eta_{\mathrm{A,B}} = {}^{u}\eta_{\mathrm{A,B}}\frac{(Q_{\mathrm{A}})_0}{(Q_{\mathrm{B}})_0}$$

But very often the distinction between ${}^{u}\eta$ and ${}^{e}\eta$ will be obvious or unnecessary; often, also, the components under discussion will be too obvious to mention, and in such cases the superior and inferior characters may be omitted.

It is now recommended that the identifiers ^{e} and ^{u} appear in the top left position to avoid confusion with the mathematical convention for "to the power of. . . ." Another new recommendation is that the identifier ${}_{p}$ be used in the lower left position when it is necessary to indicate that the η value under discussion is predicted from theory and not experimentally determined. In the latter case, ${}_{x}$ may be used instead if thought necessary for emphasis. Additional information may be given outside parentheses, such as units of measurement or definition of region under consideration. In the present paper, only the latter is required.

The symbol θ is used for "contaminant complement" ($\equiv 1 - \eta$), this verbal form being advised in preference to the misleading "enrichment ratio" (*1*). "Purity ratio," ζ, is defined as $1/\eta$. The identifiers described above may be used with either of these symbols, retaining the same significance as before. All three parameters, η, ζ, and θ, may be referred to collectively as of "Type η."

There appears to be no objection to the use of the unequalized indices in respect of any mixtures whatever, whether concerned in a separation process or not, but equalized indices imply that such a process is being considered. Normally, equalized indices would refer to a product region or, conceivably, to a domain. Application to any other mixture, including one which is to be separated, results in the trivial values $\eta = \zeta = 1, \theta = 0$.

"Type-η" parameters describe the results of a real or abstract separations process. It may be valuable to extend the "Type- " nomenclature somewhat so that all parameters which have common features may be referred to collectively, thus emphasizing their common features without denying the differences which may also exist. This suggestion does not conflict with the classification scheme proposed in the next section. In describing the behavior of components of a mixture undergoing separation, three types of parameters are much used. They are not commonly all used together, and are not always sufficient.

(1) Type χ. The essential property upon which a separation is to be based and which permits a distinction to be made between the particles of different components. Examples are thermodynamic distribution coefficient, molecular weight or dimensions, and electrophoretic mobility.

(2) Type ψ. The property of Type χ as modified by the experimental conditions chosen, such as distribution ratio or actual migration velocity.

(3) Type ω. The ratio of Type-ψ parameters in respect to two components, such as the ratio of distribution coefficients, and relative volatility. These parameters are, of course, dimensionless.

In defining a parameter of Type ψ it is often necessary to make an arbitrary choice over whether to write (say) a distribution ratio in a certain way or its inverse. Thus one may choose to so define the parameter that it has a larger value for components which are more mobile, or which more greatly favor the less dense or more volatile phase. But the opposite convention is at least equally common, and is accepted, for example, in chromatography. It is proposed to use the symbol ψ in the first instance and the inverted symbol $\rotatebox[origin=c]{180}{\ensuremath{\psi}}$ ($\equiv 1/\psi$), with the verbal equivalent "ips," in the second. Similar problems of convention might in principle occur with Type-χ and Type-ω parameters. In the latter case confusion has apparently been avoided by tacit universal agreement that ω should be always so defined as to be greater than 1. The choice of Type-ψ parameter ought to determine practice in respect of the corresponding Type-χ parameter.

As implied in the preceding paragraph, the symbols χ, ψ, $\rotatebox[origin=c]{180}{\ensuremath{\psi}}$, and ω may be used to stand for quantities deemed to fall within the corresponding type. This is not a necessary feature of the "type" nomenclature system; appropriate conventional symbols could certainly be used instead, but it may prove helpful when one is trying, as now, to emphasize the basic unity of separation processes and bring them under one theoretical umbrella.

As indicated, further types of predictive parameters may be needed in addition to types χ, ψ, and ω. This applies particularly to zonal separations involving the action of a force field when processes leading to remixing of zones or to zone imperfections must be considered explicitly.

Finally, the word "parameter" is used to include quantities which stand as variables in an equation. This is somewhat unusual these days, but not without precedent. A "statement" is a definite piece of information, whether or not in explicitly algebraic form. Thus we may have an "equation" indicating the value of a particular parameter, or we may have some other equivalent expression, particularly in the case of describing the boundaries of regions or domains which may be difficult to express in purely mathematical terms (though presumably possible in principle). The special meanings of some other words will become clear as they are introduced.

CLASSES OF SEPARATION PARAMETER

In order to predict the results of a separations process, we are required to make certain statements about the properties of the components and the selected conditions. The number of statements required is discussed in the next section, but the first step is to recognize that all can be grouped together as a broad class of separation parameters which will be called "predictive" (or Class 1). Similarly, parameters describing the product regions and indicating their contents may be grouped together under the label "descriptive" (or Class 2). Of the parameters so far discussed, obviously those of Type χ, Type ψ, and Type ω are predictive, whereas η and its congeners are essentially descriptive. These "classes" may be subdivided into "groups" (1A, 1B, etc.), and a third class must be added to cover the case where information from predictive and descriptive statements is pooled (Class 3, "indicative").

Among predictive parameters we may immediately distinguish qualities of the apparatus and of such aspects of the working conditions as are within the operator's control, in principle—Group 1A—from those relating to the properties of the separands (and of the mixture where these are nonadditive)—Group 1B. Specification or delimitation of the product region boundaries falls within Group 1A: this point is amplified below. Clearly, Type-χ parameters are of Group 1B, but Type-ψ parameters could incorporate information or quantities properly belonging to Group 1A. Such hybrid parameters will be called "pooled predictive" or Group 1C. Type-ω parameters should probably be placed under Group 1C, but it is worth noting that in two classical cases, relative volatility (α) and the ratio of distribution coefficients in liquid–liquid partition (β), the Type-ω parameter is invariant over a wide range of experimental conditions; that is, changes in the Group 1A parameter are without effect. These and other examples combine to suggest that although the groups of predictive parameter can be quite clearly differentiated, it is of less importance to do so than in the case of the descriptive parameters (see below).

In Class 2, we may recognize parameters showing composition of product (Group 2A) and yield of product (Group 2B). In a third group, information about product composition and yield is combined into a single index, explicitly or otherwise; these we will call "pooled descriptive" (Group 2C).

In the case of zonal separation methods, the selection of product region boundaries may take place after the principal part of the separations process is complete. This gives rise to the question of whether the definition of boundaries should be placed under Class 1 (predictive) or Class 2 (descriptive), but the argument leads also to the recognition of the third class of parameters (indicative). Consider, for example, the results of a zonal chromatography experiment, expressed in terms of a recorder trace relating the concentrations of two components to volume of eluate. One way of looking at the matter is that we may now manipulate the boundaries of the product zones, that is, the range of fractions to be pooled, so that we achieve whatever particular result we desire—purity of one component at the expense of recovery, or *vice versa*. This manipulation takes place after the experiment proper; how then can it be regarded as predictive? But until a decision on boundaries has been taken, no statement whatever can be made concerning the yield or purity of either product, and an additional way of expressing the same conclusion is that no value for a pooled descriptive parameter (such as Rony's ξ) can be calculated until the "cut-point" between the peaks is chosen (*3*). Strictly speaking, the separation process is not complete until the choice has been made.

The recorder trace does, however, provide us with a very considerable amount of information which might also be expressed by means of the indices R or ξ_{opt} (*3*). The latter is the value of ξ when the cut-point has been suitably selected so as to yield a maximum value. It thus incorporates information on the product region boundaries and is an index which pools information from both the predictive and descriptive classes of parameter. R gives no more and no less information than ξ_{opt} so that, in spite of the difference in origins and the other limitations on the validity of R, it seems reasonable to place R and ξ_{opt} together in a special third class of separation parameter for which the name "indicative" may be suitable.

It may be argued that such parameters are more powerful than those of Classes 1 and 2, and it is certainly true that they can be extremely useful, especially in theoretical work. But one must not overlook the inherent weaknesses which spring precisely from the attempt to combine several pieces of information in a single index. A statement of the value of ξ_{opt} cannot give as much information as is contained in separate statements of the values of the individual parameters which go to make it up. In addition, use of this index in practice would involve relinquishing free choice over cut-point, and the choice thus forced upon the experimenter might or might not be correct for his purpose. Use of ξ_{opt} may prove misleading unless the separation happens to be symmetrical (*1*). When using R it is not sufficient even that separation is symmetrical; individual distribution profiles must be of ideal form if the index is to have any meaning at all. The note below on optimum separation is relevant here, and the matter of implicit definition of product region boundaries finds expression in other ways in single-step distribution processes and multistage processes.

How Many Statements Are Required?

Consider the simplest possible case, in which a mixture of two components, of known composition, is fractionated so as to give two products:

$$\begin{array}{ccccc} \text{Original mixture} & \rightarrow & \text{Product 1} & + & \text{Product 2} \\ [(Q_A)_0 + (Q_B)_0] & \rightarrow & [(Q_A)_1 + (Q_B)_1] & + & [(Q_A)_2 + (Q_B)_2] \end{array}$$

Product 1 is completely specified by two quantities and two further quantities are listed for Product 2—but these are trivial since the assumption is incorporated above that $(Q_A)_0 = (Q_A)_1 + (Q_A)_2$ and $(Q_B)_0 = (Q_B)_1 + (Q_B)_2$. This might lead us to suppose that two statements, two descriptive parameters, suffice to describe the results of this separation process, and hence, from the theory of equations, that two predictive parameters would suffice to forecast the result.

Complete recovery is a very substantial assumption, however, and if it were dropped, all four Q values would be required to describe the results of the process. Arguing as before from the theory of equations, this demands the specification of four parameters from Class 1 before the result could be predicted. A surprising conclusion, but it appears to be borne out in practice as is discussed later with regard to several key methods. In some of these it may appear at first that two or three parameters are enough, but in such cases a close examination reveals that values are assumed or allotted implicitly for the remainder, bringing the total up to at least four. The "missing" parameters will generally be found to specify the product region boundaries: in the above example we may presumably regard specification of boundaries as determining recoveries—if the regions are sufficiently large, recovery is complete.

THEORY OF ARCHETYPAL PROCESSES

Discussion is limited to a few methods of central theoretical importance (single-step distribution, multistage distribution, chromatography) and uses models involving equilibrium distribution between two phases or domains. The intention is to give a general, comparative picture of the manner in which various methods operate, and it is not pretended that any actual process will behave exactly according to the equations given here. Other processes are covered insofar as they can reasonably be modeled after these three.

For present purposes, ψ refers to the *distribution ratio* of a component between two regions or domains, i.e.,

$$\psi_A = (Q_A)_1/(Q_A)_2$$

For any two defined components, $\omega = \psi_A/\psi_B$, and numeration of components, domains, and regions is chosen so that $\omega > 1$.

The (proportional or fractional) yield is defined thus, taking as an example the yield of Component A in Region 2:

$$(Y_A)_2 = (Q_A)_2/(Q_A)_0$$

Ideal behavior is assumed, that is, Type-ψ parameters are taken as constant. It was shown in the last section that, even so, at least four predictive parameters are required if the results of the process are to be deduced in full. The analysis of each process opens with a statement of a suitable set of parameters or boundary conditions. This is followed by the equations predicting η and, where necessary, Y, and then a discussion of any points which may give difficulty. The discussion is in terms of total overall recovery.

1. A Single Step Distribution between Two Domains

Examples

Solvent extraction, flash distillation, classification, filtration, crystallization. It is acknowledged that the first may often be operated close to ideality, but that this applies to the last only very rarely: the principles remain the same, however. The discussion is in terms of solvent extraction and might require modification for other methods.

Predictive Parameters

i and ii) Distribution ratios for each of the two species assumed to be concerned. For any single species, the distribution ratio is the product of the partition coefficient and the volume ratio of phases, that is,

$$\psi = K \times \frac{\text{vol. Phase 1}}{\text{vol. Phase 2}}, \quad \text{where } K \text{ is defined as } \frac{\text{concentration in Phase 1}}{\text{concentration in Phase 2}}$$

iii and iv) As shown in the last section, we have in reality to define product region boundaries even for the simple case of an assumed complete recovery and constant ψ. In practice this means enclosing the phases in a container so that none may escape, and making the cut between phases with absolute precision (no loss, no carry-over, etc.). Besides, we have to set the multiplicity of operation as unity—as immediately appears from a comparison with multistage operation.

Theory

An initial quantity of each component—say $(Q_A)_0$ for Component A—is divided between the two phases, i.e., between the two product regions, thus

$$\begin{tikzcd} & (Q_A)_1 \\ (Q_A)_0 \arrow[ur] \arrow[dr] & \\ & (Q_A)_2 \end{tikzcd}$$

$$\begin{tikzcd} & (Q_B)_1 \\ (Q_B)_0 \arrow[ur] \arrow[dr] & \\ & (Q_B)_2 \end{tikzcd}$$

So that

$$\left.\begin{aligned} (Q_A)_1 &= (Q_A)_0 - (Q_A)_2 \\ (Q_B)_1 &= (Q_B)_0 - (Q_B)_2 \end{aligned}\right\} \tag{1}$$

$$\left.\begin{aligned}
\psi_A &= \frac{(Q_A)_1}{(Q_A)_2} = \frac{(Q_A)_1}{(Q_A)_0 - (Q_A)_1} = \frac{(Q_A)_0 - (Q_A)_2}{(Q_A)_2}\\
\psi_B &= \frac{(Q_B)_1}{(Q_B)_2} = \frac{(Q_B)_1}{(Q_B)_0 - (Q_B)_1} = \frac{(Q_B)_0 - (Q_B)_2}{(Q_B)_2}
\end{aligned}\right\} \tag{2}$$

$$\left.\begin{aligned}
({}^{u}\eta_{A,B})_1 &= \frac{(Q_B)_1}{(Q_A)_1} = \frac{\psi_B (Q_B)_0 (1 + \psi_A)}{(1 + \psi_B)\psi_A (Q_A)_0}\\
({}^{u}\eta_{A,B})_2 &= \frac{(Q_B)_2}{(Q_A)_2} = \frac{(Q_B)_0 (1 + \psi_A)}{(1 + \psi_B)(Q_A)_0}\\
({}^{u}\eta_{B,A})_1 &= \frac{(Q_A)_1}{(Q_B)_1} = \frac{\psi_A (Q_A)_0 (1 + \psi_B)}{(1 + \psi_A)\psi_B (Q_B)_0}\\
({}^{u}\eta_{B,A})_2 &= \frac{(Q_A)_2}{(Q_B)_2} = \frac{(Q_A)_0 (1 + \psi_B)}{(1 + \psi_A)(Q_B)_0}
\end{aligned}\right\} \tag{3}$$

And from these sets of defining equations and identities, the following relationships may very readily be deduced for equalized contaminant ratios (or actual equal initial amounts of components if that happens to be the case—by chance or choice).

Separation of Component A from B. Conditions in Region 1:

$$({}^{e}\eta_{A,B})_1 = \frac{\psi_B(1 + \psi_A)}{\psi_A(1 + \psi_B)}, \qquad (Y_A)_1 = \frac{\psi_A}{1 + \psi_A} \tag{4a}$$

Conditions in Region 2:

$$({}^{e}\eta_{A,B})_2 = \frac{1 + \psi_A}{1 + \psi_B}, \qquad (Y_A)_2 = \frac{1}{1 + \psi_A} \tag{4b}$$

Separation of Component B from A. Conditions in Region 1:

$$({}^{e}\eta_{B,A})_1 = \frac{\psi_A(1 + \psi_B)}{\psi_B(1 + \psi_A)}, \qquad (Y_B)_1 = \frac{\psi_B}{1 + \psi_B} \tag{4c}$$

Conditions in Region 2:

$$({}^{e}\eta_{B,A})_2 = \frac{1 + \psi_B}{1 + \psi_A}, \qquad (Y_B)_2 = \frac{1}{1 + \psi_B} \tag{4d}$$

It may be perfectly reasonable to concentrate for practical purposes on one domain and on the separation of one component from another (indeed, that is exactly what the parameter η is intended for), but to understand the process as a whole requires us to look at both product regions and from both points of view—the separation of A from B and *vice versa*. These elementary equations defining the operation of a single equilibrium distribution underlie much of separations theory, and are given here in full because of that central role and to emphasize their asymmetry. The equations are also used below in a discussion of the meaning of "optimum separation."

2. Multistage Countercurrent Systems

Examples

Fractional distillation (rectification), which may be continuous or batch-operated, absorption towers, countercurrent solvent extraction systems, Craig-type "countercurrent distribution" (CCD) operated in the continuous mode. The term CCD is well-established in describing the admirable and effective systems developed by Craig and his associates (*4*). But the word "countercurrent" is objectionable here since in none of the systems is there actual flow of two opposing streams, and only in the continuous mode referred to above is there even transfer of phases in opposing directions. Also, the same term, CCD, is used for this process, the performance of which resembles that of true multistage countercurrent systems, and for processes which closely resemble elution chromatography in performance.

Reflux

Practical systems exist operating with or without (terminal) reflux. In the case of distillation of a 2-component mixture, it is commonly stated that to operate without reflux is equivalent to simple or flash distillation, a single-stage process, but in view of the quite high performance of multistage extraction processes without terminal reflux this seems unlikely. In many cases, perhaps, reflux occurs even when not specifically provided for. Generally, however, efficient rectification is done with a high reflux ratio—that is, most of the product is condensed and returned to the column; for continuous distillation, most of the bottom product is reboiled.

Solvent extraction procedures can also be operated at high reflux ratio, but this is much more complex and expensive than in the case of distillation, hence less common in either commercial or laboratory practice.

Predictive Parameters

i) Number of ideal stages. If our mental construct is a distillation column consisting of perfect plates, then one ideal stage consists of one such plate and the space between it and the next one. That is, a column containing **n** structures which behave as perfect plates (including the kettle), operates as only **n** − 1 stages if the top product is taken off at the top plate or **n** stages if the top product is the vapor above the top plate. Analogous rules are applied for processes other than distillation. Only by defining and counting stages in this way can we avoid confusing alternative formulations of several of the theoretical equations. For generality, and with an inevitable increase in complexity of equations, it is necessary to introduce the concept of separate extraction and washing sections of the train (different words are used in distillation practice). Feed is considered to be at a stage which counts both as one of n stages in the extraction section and of m stages in the washing section of the train. Thus the actual number of ideal stages physically present in the train is $n + m - 1$. If feed is at one end of the train, $m = 1$ and the total number of stages is equal to n. In this paper, **n** may be used to replace $n + m - 1$, i.e., **n** always represents the total number of ideal stages in the system whether or not a washing section is present.

ii) and iii) Volatility or distribution ratio for each component. (For total reflux, it appears to be sufficient to know ω. This paradox is discussed below.)

iv) Boundaries of product regions: In the case of batch distillation we must choose very carefully the column-head temperature at which the collecting receptacle is changed; this clearly is a definition of product region boundaries. In continuous distillation the take-off point of each product stream determines its composition. If there are only two such streams, e.g., top and bottom products, we have apparently self-defining product regions, but in reality the whole process has been designed to yield specific predetermined product purities (determining in turn the number of ideal stages required, and the reflux ratios). This can be accepted as equivalent to defining product boundaries.

Theory

It is not intended to repeat well-known derivations which may be found in the literature. There are, however, some errors and misinterpretations to be corrected, and to facilitate this the conventional order of presentation is reversed so that we deal with partial reflux first.

2a) *Partial Reflux.* The general case, where portions only of the end products emerging from the train are returned to the train (in the other phase), was first successfully analyzed by Klinkenberg (*5*), but his key equation (Ref. *5*, Eq. 25), as printed, unfortunately contains an error (*6*) in that the coefficient of E^m in the denominator should be 1 and not $(r_w + 1)$. Rony (*7*) followed Klinkenberg's development and derived an expression for the net fractional yield of a solute emerging from the train in Phase 1 which may be rewritten in present symbols, thus (from Ref. *7*, Eq. 33):

$$(Y)_1 = \frac{r_w + \dfrac{\hslash^m - 1}{\hslash - 1}}{r_w + r_e\hslash^{n+m-1} + \dfrac{\hslash^{n+m} - 1}{\hslash - 1}} \qquad (5)$$

Here r_e and r_w are reflux ratios for the extraction and washing sections of the train, defined for present purposes as

$$\frac{\text{total outflow of solute in Phase 2}}{\text{solute returned (at same end) in Phase 1}} = \frac{r_w + 1}{r_w}$$

$$\frac{\text{total outflow of solute in Phase 1}}{\text{solute returned (at same end) in Phase 2}} = \frac{r_e + 1}{r_e}$$

The composition of products may readily be calculated from the values of Y; thus $({}^e\zeta_{A,B})_1 = (Y_A)_1/(Y_B)_1$, and so on.

2b) *Zero (Terminal) Reflux.* Where solute emerging from the ends of an extraction train is not returned to the system, the fractional yield for each component in Phase 1 is (from Eq. 5):

$$(Y)_1 = \frac{\hslash^m - 1}{\hslash^{n+m} - 1} \qquad (6)$$

This is a version of the Kremser (*8*) equation for solvent entering the system in a pure condition rather than already contaminated with some of the solute to be extracted, and allowing for a washing section. Again, values for Type-η parameters are readily calculated from fractional yields.

2c) *Total Reflux.* The result of Fenske (*9*) may be rewritten in the simplest possible form for a system of n stages:

$${}^e\zeta = \omega^n = (\hslash_B/\hslash_A)^n \qquad (7)$$

(or, of course, $\log {}^{e}\zeta = n \log \omega$, $\log {}^{e}\eta = -n \log \omega$, etc.). From what follows, however, it will appear that this could be misleading, unless perhaps one distinguishes the ${}^{e}\zeta$ value obtained in this way as the *maximal* purity ratio, say $({}^{e}\zeta)_{\max}$.

Because of a different presentation, it has apparently been overlooked that the equations of Klinkenberg (*5*) and Rony (*7*) express a result quite different from that of Fenske. Rony's equation for fractional yield at total reflux is (Ref. *7*, Eq. 25)

$$(Y)_1 = 1/(1 + \mathscr{p}^n)$$

corresponding to a purity ratio of

$${}^{e}\zeta_{\mathrm{A,B}} = (Y_{\mathrm{A}})_1/(Y_{\mathrm{B}})_1 = (1 + \mathscr{p}_{\mathrm{B}}{}^n)/(1 + \mathscr{p}_{\mathrm{A}}{}^n) \tag{8a}$$

It is shown elsewhere (*6*) that Rony's equation, and Klinkenberg's equivalent, are valid only for the case where the reflux ratios at the two ends of the extraction train are equal as they approach infinity. The generally-valid expression is

$$(Y)_1 = \frac{1}{1 + \dfrac{r_e}{r_w}\mathscr{p}^n} \tag{8b}$$

From this we obtain for the purity ratio

$${}^{e}\zeta_{\mathrm{A,B}} = \frac{(Y_{\mathrm{A}})_1}{(Y_{\mathrm{B}})_1} = \frac{1 + \dfrac{r_e}{r_w}\mathscr{p}_{\mathrm{B}}{}^n}{1 + \dfrac{r_e}{r_w}\mathscr{p}_{\mathrm{A}}{}^n} \tag{8c}$$

If the ratio r_e/r_w is now allowed to approach infinity, Eq. (8c) reduces to Eq. (7), so that the Fenske equation is confirmed, and its range of application is extended in an interesting manner. (For the relationship of the Klinkenberg and Rony equations, see Ref. 6.)

There may be some difficulty over the above conclusions since physically there cannot be any yield of a process operating at total reflux and because we are asked to accept first that r_w may approach infinity while r_e/r_w retains a finite value, and then separately that the ratio r_e/r_w may itself approach infinity. A simple numerical example will show what is involved.

We postulate an extraction system consisting of two ideal stages which are operated so that equilibrium is reached before phases are transferred. Total reflux is achieved by taking solute which emerges from each end of the train and returning it dissolved in the other solvent. That is, in the case of solute emerging at the top of the train, dissolved in Solvent 1, this latter is removed (say, by evaporation) and the solute dissolved in the appropriate volume of Solvent 2 before being returned to the same end of the train for the next equilibration step. Figure 1 shows the buildup to steady state for a single solute (A) of $\psi = 2$. In each equilibration unit, Solvent 1 is shown on the left and Solvent 2 on the right: Solvent 1 moves upward in the train and Solvent 2 downward. ψ is defined so as to be larger for a solute favoring Solvent 1, and the initial quantity of solute is 100 units.

Figure 2 summarizes the steady state for two components having ψ values of 2(A) and 0.5(B).

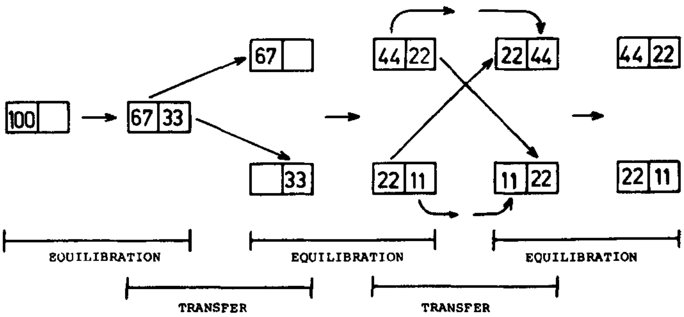

Fig. 1. Two-stage extraction train with total reflux, showing the steady state and how it is approached. For details, see text. To save space, equilibration and transfer operations are shown overlapping; thus the conditions at the end of an equilibration process are shown above the right-hand end of the corresponding line. The phases thus obtained are then transferred as shown by oblique arrows, or removed, and the solutes reintroduced in the opposite solvent as shown by curved arrows.

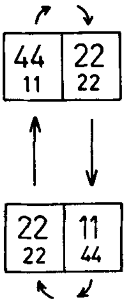

Fig. 2. Two-stage extraction train with total reflux in the steady state. Distributions are shown for two solutes. For details, see text.

$\omega = (\psi_A/\psi_B) = 4$, and from Eq. (7) we expect ${}^e\zeta_{A,B} = 4^2 = 16$. This appears to be borne out. Solute entering the bottom of the column in Solvent 1 has the composition ${}^u\zeta = 0.25$; that leaving the top of the column has the composition ${}^u\zeta = 4.0$. Thus we have achieved 16-fold purification, exactly as expressed by ${}^e\zeta = 16$.

But looking at apparent yields, we find that at the top of the column the fractional yield of Component A is 0.44 and of Component B is 0.11. That is, $[(Y_A)_1/(Y_B)_1] = ({}^e\zeta_{A,B})_1 = (0.44/0.11) = 4$. This is the same result as is given by direct application of Rony's formula, discussed above, so that we are faced with a paradox.

To solve it, note that there is no actual product of the system as described so far. We should look instead at what happens when we introduce an infinitesimal amount of feed—not sufficient to bring about a detectable change in the solute content of either equilibration unit. To maintain the steady state, an amount of each solute equal to the amounts added as feed must be removed from the system in the form of top and bottom products, and it follows from the condition laid down above that the composition of these products will not alter, i.e., the values of ${}^u\zeta$ for each outflow will be unchanged. But the total amounts taken from top and bottom *are* open to being varied; in fact, they must necessarily be adjusted so that the total amounts of Solutes A and B removed from the system are equal to the amounts added in the feed mixture. For if this is not done, the composition of solutions in the train will change and the system will not remain in steady state. Varying the amounts of top and bottom products independently of each other amounts, of course, to varying the reflux ratios independently.

It follows, further, that the composition of the feed can be varied at will within the limits set by the compositions of the top and bottom outflows from the column. The values of ${}^e\zeta$ would depend on what was the actual composition of the true net feed. In our numerical example, if the infinitesimal feed to the lower plate were of the composition ${}^u\zeta_{A,B} = 1/4$, i.e., $[A]/[B] = 1/4$, it would be necessary to remove as product an equal amount of substance of the same overall composition in order to preserve the steady state. This would necessarily all be as bottom product and the net top product would actually be zero (infinite reflux ratio at top, $r_e = \infty$). Only if the ratio of $[A]/[B]$ in the feed were very slightly greater than 1/4 would it be possible to take a minute amount of top product of composition $[A]/[B] = 4/1$. This makes plain the significance of $({}^e\zeta)_{max}$, introduced above. It is an ideal, unattainable in practice even for the tiniest actual net yield of products. To approach it requires in our example that the bottom reflux ratio (r_w) should be very large and the top reflux ratio (r_e) much larger still, and that the feed composition should approximate that of the bottom reflux input. It may be approached only in the most extreme favorable circumstances.

If the feed composition lies, in our example, outside the limits $4 \geqslant {}^u\zeta_{A,B} \geqslant 0.25$, then no product of either of the compositions indicated above can be obtained. This particular steady state cannot be maintained in the face of such a feed composition.

Equations (8a) and (8c) naturally give very different figures for predicted maximal performance of a multistage separations system. For the special case of $\hslash_A = 1/\hslash_B = \hslash$, say, Eq. (8c) yields ${}^e\zeta = \hslash^{2n}$ whereas Eq. (8a) yields the square root of this. Plainly, comparative discussions of theoretical maximal performance should be reviewed in this light.

3. Chromatographic and Zonal Pseudochromatographic Systems

Examples

Elution chromatography, thin-layer or paper chromatography, zone electrophoresis in supporting media such as paper or gel, centrifugation in a density gradient.

The image which springs most easily to mind is of a distribution profile for each component along a time, distance, or volume axis, of at least approximately Gaussian form, and our task is envisaged to be the description of the degree of overlap of two such adjacent profiles. This indeed is generally applicable to all the examples listed immediately above, and will be the model used here, for generality and simplicity. But we have endeavored to use examples based upon true equilibrium distribution, and in that case it would seem more appropriate to employ as a model the Craig-type "countercurrent distribution" apparatus in the fundamental mode, which is actually expected to give profiles following the binomial rather than the Gaussian distribution. The choice of Gaussian forms is simply because of their generality, and in any case the binomial distribution approaches the Gaussian as the number of transfers becomes sufficiently large.

Predictive Parameters

Even assuming theoretically perfect distribution profiles, so that these need not be more precisely described, in order to predict the result of such a process we require at least the following:

Type-ψ parameters defining mobilities of the "peaks" in the separation dimension or the ratio (ω) of two such plus the actual value of one of them

A measure of dispersion

Definition of the product region boundaries

3a) *Chromatography.* i and ii) $\not{h}_A$ and $\not{h}_B$, or ω and one value of $\not{h}$ which is obviously exactly equivalent.

iii) Number of theoretical plates in the column.

iv) Boundaries of product regions—implicitly or otherwise we must select a cut-point between the two product regions and also nominate where we begin collecting and where we finish. Type-ψ parameters are clearly very relevant here also, and we might define product regions in terms proportionate to these parameters.

3b) *Zonal Pseudochromatographic Systems.* i) and ii) ψ_A and ψ_B.

iii) The use of a parameter equivalent to the number of theoretical plates, as a measure of dispersion, is here highly artificial, of value only in preserving a comparison with chromatography proper. $N \equiv z^2/\sigma^2$, where z is the displacement of the peak of a zone along the separation dimension, and σ is the standard deviation of the distribution profile, expressed in the same units.

iv) As for 3a.

Theory

Martin and Synge (*10*) made clear that for a given peak separation and defined product region boundaries, the contamination of one product by the undesired component was open to computation from the properties of the distribution profile, in their case by making use of tabulated values of the area under the Gaussian normal curve of error. Inevitably, we here adopt a model based on theirs, and examine the overlap between two Gaussian profiles of equal width and height.

We choose to make the division between two product regions at the midpoint between the two profiles (considered independently). There is no minimum here if the two distributions are close to each other, but if far enough apart to allow the formation of a col between these peaks, then our cut is at the minimum of the col if the two peaks are equal. This is the obvious cut-point; it was chosen by Martin and Synge (*10*) and is the cut-point yielding the maximum or optimum value for Rony's extent of separation—ξ_{opt} (*3*). This choice defines the common boundary of the two product regions. The other boundaries are chosen to be so far distant from the cut-point that the amount of each component lying outside the two product regions may be neglected.

The amount of Component A in Region B, or *vice versa*, is given by

$$(Q_A)_2 = (Q_A)_0 - (Q_A)_1 = (Q_B)_1 = (Q_B)_0 - (Q_B)_2 \tag{9}$$

From Eqs. (9) and the definitions of η and Y,

$$1 - (Y_A)_1 = (Y_B)_1 = \frac{(Q_B)_1}{(Q_A)_1}\frac{(Q_A)_1}{(Q_A)_0} = (\eta_{A,B})_1(Y_A)_1 \tag{10}$$

Hence

$$(Y_A)_1 = \frac{1}{\eta + 1} \tag{11}$$

From the definition of ξ,

$$\xi_{opt} = (Y_A)_1 - (Y_B)_1 = 2(Y_A)_1 - 1 = \frac{1 - \eta}{1 + \eta} \tag{12}$$

In Eqs. (11) and (12), η has been substituted for the fuller form $(\eta_{A,B})_1$. Note further than the initial assumptions of equal peaks and a cut at the mid-point mean that in this case $\xi = \xi_{opt}$. More generally, Eqs. (11) and (12) hold for ${}^e\eta$ but not for ${}^u\eta$ [unless, of course, $(Q_A)_0 = (Q_B)_0$, when ${}^u\eta$ and ${}^e\eta$ are identical].

In the case of chromatography, we can relate purity ratios directly to ω, $\mathscr{k}$, and N. The resulting equation does not apply exactly to other cases but will be a close approximation where peak separation is small relative to displacement along the separation dimension. For chromatography, the predicted resolution is

$$R = \frac{\omega - 1}{4}\frac{\mathscr{k}_A}{1 + \mathscr{k}_A}\sqrt{N}$$

[see Note below] and Rony (*3*) has further shown that for sufficiently closely spaced peaks (separation less than one-half of the standard deviation of either peak)

$$\xi_{opt} = R\sqrt{8/\pi} \tag{13a}$$

If we define $N'' = N(\mathscr{k}/(1 + \mathscr{k}))^2$, the resolution equation simplifies to

$$R = \frac{\omega - 1}{4}\sqrt{N''} \tag{13b}$$

From Eqs. (12) and (13) we may now write

$$\frac{1-\eta}{1+\eta} = \frac{\omega - 1}{4}\sqrt{\frac{8N''}{\pi}} \tag{14}$$

whence

$$\frac{1}{\eta} = ({}^{e}\zeta)_{\xi_{\rm opt}} = \frac{1 + (\omega - 1)\sqrt{N''/2\pi}}{1 - (\omega - 1)\sqrt{N''/2\pi}} \tag{15}$$

As may be expected from the mode of derivation, this equation is valid only for close separations, becoming absurd for large ω (easy separation) and/or large N'' (highly efficient apparatus with low dispersion).

Note. For a discussion of alternative forms of the "resolution equation," see Karger (*11*). That given above is the simplest, and is therefore the most appropriate for present purposes.

DISCUSSION

One difficulty in this work was to find appropriate new symbols. In many cases, existing usage could have been followed but only at the risk of confusion or lack of balance because either the one type of parameter has been associated with several symbols in the past, or one symbol with several parameters. For example, α has been used for relative volatility in discussing distillation and β for the ratio of distribution coefficients in solvent extraction. The two fill identical roles; both are of Type ω. But the symbols have also been used for parameters of Type ψ or Type χ. The solution attempted has been to find coherent sets of symbols to fill the roles required, but trying to avoid those which have previously been used for other purposes in the field of separations. It is difficult and unnecessary to find new symbols for every case. "Resolution," for example, has been defined by an international body and there seems little point in avoiding use of some symbol based on the upper-case italic letter R, even though this has actually been used for several different, though related, parameters (*1*). But "capacity factor," k', although also defined authoritatively, is not adopted, partly because it cannot be fitted into a coherent set and partly because both the symbol and the verbal equivalent seem rather unfortunate choices.

The symbol for contaminant ratio, η, was taken from the work of Glueckauf (*12*) in recognition of his stimulating contributions (which have been unjustly criticized). However, he used no less than four verbal equivalents, some of which are open to misinterpretation and should therefore be avoided. Furthermore, Glueckauf's use of η was circumscribed in a number of significant ways: proposals to eliminate these restrictions appeared only recently (*1*, *13*). Parameters related to contaminant ratio have been used before, but apparently not as a coherent set of equalized and unequalized quantities. Marques' "enrichissement" corresponds to ${}^{e}\zeta$ (*14*). Sandell's separation factor, S, is numerically identical to ${}^{e}\eta$ and has been used in an extensive theoretical study (*15*), but Sandell's S is hedged about with assumptions and restrictions which made it difficult to adopt for development in the manner desired.

Such a fundamental approach as that of De Clerk and Cloete (*13*) commands great interest and respect. They propose the use of specific entropy of mixing as a separation index; as a measure, in fact, of the extent of contamination of the principal component in a given region. For a binary separation of A from B and for low contamination, they arrive at the following expression (in the symbols of this paper), and writing j for any unspecified region,

$$(\eta_{\mathrm{A,B}})_j \to 0, \qquad (S')_j \to -(\eta_{\mathrm{A,B}})_j \ln (\eta_{\mathrm{A,B}})_j$$

Recognizing that $(S')_j$ is too cumbersome for routine use, they select $-\log \eta$ as their everyday resolution function, named the "purity index," $(I)_j$. Clearly the equations derived here could be rewritten in terms of their purity index, and the coincidence of two such different approaches appears to reinforce the case for working in terms of η, or related quantities, wherever possible.

De Clerk and Cloete attempt to extend the concepts of $(S')_j$ and $(I)_j$ to the whole system, defining $I \equiv \sum_j (I)_j$. Unfortunately, I as thus defined is a Class 3 (indicative) parameter, subject to the same limitations as any other member of this class and therefore unsuitable for work in which it is desired to avoid very substantial assumptions about symmetry.

Since some of the pooled types of parameter are plainly very useful, it may seem unreasonable to advance such criticisms as these. But the limitations on their validity can be expressed in a very general way by means of the analogy of simultaneous equations. If $x = 1$ and $y = 2$, then $3x + 2y = 7$, $2x + 7y = 16$, and so forth. Two such statements will normally suffice to allow us to determine both x and y. No single statement will permit the evaluation of either x or y, unless one of the coefficients happens to be zero; in every other case the values remain indeterminate. We wish to suggest that this is really rather more than an analogy, and that the theory of equations will prove to be directly and exactly applicable to the theory of separations.

If the result of a separation is expressed in terms of a pooled descriptive parameter, we cannot calculate the actual result (yield and composition) for any region without introducing new information (additional statements, boundary conditions, or equations). The result, in fact, is indeterminate. The new information is likely to consist of assumptions concerning symmetry of separation, or ideality of distribution curves, or "sensible" choices of product region boundaries. Insofar as these assumptions are correct, then so also the result of the separation can be calculated correctly.

The consequences of using pooled predictive parameters (Group 1C) appear to be less serious. Such parameters can carry no more information than the fundamental parameters from which they were derived, but if used only for the predictive function, this is unimportant because they do not carry any less information either, provided that the total number of independent Class 1 parameters is sufficient. Difficulties of the kind described in the preceding paragraph can and do arise, however, when measurements of fundamental molecular properties are made from separations experiments. It often happens that the results are indeterminate, and in consequence some manifestly secondary kind of measurement has perforce to be accepted as a "working" molecular constant.

Optimum Separation

It is perfectly reasonable in many cases to assume that the separation of two components ought to be symmetrical. But in practice it is not always so, and, as has been remarked elsewhere, the assumption of symmetry carries with it as a corollary that equal importance is attached to the two components. This or any other general "weighting" of the components must be arbitrary, and may mislead (*1*). When considering any real separations process, yield and purity of product are considered separately and the final selection of process conditions is based on external factors, which in the case of industry will often be economic. The indicative parameters used in laboratory and theoretical work offer the tempting prospect of an overall measure of separation efficiency, which can be optimized. This brief note attempts to explore the limits and the consequences of such an approach.

It is commonly stated that in single-step distribution (e.g., solvent extraction) the condition for optimum separation is $\psi_A = 1/\psi_B$. Although aware that product purity and yield should be considered separately, Rogers (*16*) gives the relationship nevertheless. Stene (*17*, p. 57) most clearly recognized that the meaning of "optimum separation" must vary with the objective of the separation. "But this is no definite concept. In some cases we may want to get one compound as pure as possible, not being interested in the purity of the second compound, and being willing to loose (sic) some of the first compound in the interest of purity."

More recently, Rony made a fresh approach to the problem of determining the conditions for optimum separation (*2*, *3*, *7*, *18*). Basing himself, naturally, on his "extent of separation," ξ, he sought the relationship of ψ_A to ψ_B which would give optimal or maximal values of ξ. In the case of single-step distribution, and many others, but, significantly enough, not in every case, the answer is that first given, $\psi_A = 1/\psi_B$. The exceptions, apparently, are processes in which this condition cannot give symmetrical distribution of components.

Using the example of single-step distribution, let us first examine the consequences of putting $\psi_A\psi_B = 1$. To the inverse relationships between certain of the ${}^e\eta$, obvious from Eqs. (4a)–(4d), this step adds relationships of identity, as follows,

$$({}^e\eta_{A,B})_1 = ({}^e\eta_{B,A})_2 = \psi_B \tag{16a}$$

and related inversely to these,

$$({}^e\eta_{A,B})_2 = ({}^e\eta_{B,A})_1 = \psi_A \quad (= 1/\psi_B) \tag{16b}$$

Also,

$$(Y_A)_1 = (Y_B)_2 = \frac{1}{1 + \psi_B} = \frac{\psi_A}{1 + \psi_A} \tag{17a}$$

$$(Y_A)_2 = (Y_B)_1 = \frac{\psi_B}{1 + \psi_B} = \frac{1}{1 + \psi_A} \tag{17b}$$

Plainly, then, the condition of $\psi_A = 1/\psi_B$ does carry as a corollary that the separation will be symmetrical, by which we mean that it will be truly symmetrical if the initial quantities of Components A and B are equal and that algebraically the same must hold if the results are expressed in terms of ${}^e\eta$ (and provided always that ψ values are invariant). What we are really seeking is proof that *only* an implicit prerequisite of symmetry can lead to the stated optimum condition. It is doubtful whether strict proof of this is obtainable, but we can offer at least strong inference by these further steps:

Examination of the numerical examples offered by others in support of the condition $\psi_A = 1/\psi_B$ (i).

Examination of the consequences of optimizing other indices of separation than ξ; namely, η (ii) and decrease of entropy (iii).

i) Table 1 shows the values of $^u\eta$ and Y for each component for each phase using a theoretical example resembling those of Rogers (*16*) and Sandell (*2*, *19*). Cases *a* and *b* refer to equal initial amounts of the components, an assumption which is dropped for Cases *c* and *d*; Case *e* examines the case where *both* components favor the more dense phase. Note that the ratio of distribution coefficients, ω, is always equal to 4.0, but that the value of $\psi_A\psi_B$ varies widely. The figures are grouped so that each η value is found adjacent to the relevant Y.

The figures as presented in Table 1 are rather overwhelming: it may be of assistance therefore to abstract a few for consideration. We are asked to believe that Case *a* is a "better" separation (from all points of view) than Case *b*. But if our objective is to get a small yield of Component B in reasonable purity, then Case *b* is actually superior (Column 5) since we can get a one-sixth yield, $(Y_B)_2 = 0.167$, of Component B containing little more than a quarter of its own weight (or whatever other units are employed) of component A, $(^u\eta_{B,A})_2 = 0.286$. This may seem unimpressive, but if we turn to the comparison of Cases *c* and *d* we find that the latter enables us to obtain a yield again of one-sixth (3.3 units) contaminated by only 0.24 units of Component A, $(^u\eta_{B,A})_2 = 0.071$, this in a single operation of the process. True enough, by employing the conditions of Case *c* and reextracting the first lot of Phase 2 with fresh Phase 1 we could obtain both a better yield and better purity, but this would be doubling the work involved and might for various reasons be impractical or undesirable. For a laboratory separation then, especially for analytical purposes, the conditions of Cases *a* and *c* would be employed. In other circumstances, where the objectives might be different and economic considerations paramount, different conditions may be preferred.

ii) If ζ is differentiated with respect to $\psi_A\psi_B$, no maximum is obtained except for conditions which imply complete retention of one component in one phase, i.e., absolute purity, infinite ζ, in a single step. Superficially, the case may appear trivial, but it serves to emphasize that the relationship of ψ_A to ψ_B for optimum separation may depend upon the choice of separation index.

iii) Joy and Payne (*20*) express the quality of a separation as the ratio of the negative entropy of separation achieved to the ideal negative

TABLE 1

Distribution of Two Solutes in a Single Extraction Operation for Various Absolute Values of Distribution Ratios (ψ) but a Fixed Relationship between Them ($\omega = \psi_1/\psi_2 = 4$)[a]

Case	$(Q_A)_0$ (arbitrary units)	$(Q_B)_0$	ψ_A	ψ_B	ω	$\psi_A\psi_B$	$({}^u\eta_{A,B})_1$	$(Y_A)_1$	$({}^u\eta_{A,B})_2$	$(Y_A)_2$	$({}^u\eta_{B,A})_2$	$(Y_B)_2$	$({}^u\eta_{B,A})_1$	$(Y_B)_1$
a	1	1	2.0	0.5	4.0	1.0	0.5	0.67	2.0	0.33	0.5	0.67	2.0	0.33
b	1	1	20	5	4.0	100	0.875	0.952	3.5	0.048	0.286	0.167	1.14	0.83
c	5	20	2.0	0.5	4.0	1.0	2.0	0.67	8	0.33	0.125	0.67	0.50	0.33
d	5	20	20	5	4.0	100	3.5	0.952	14	0.048	0.071	0.167	0.286	0.83
e	1	1	0.4	0.1	4.0	0.04	0.385	0.286	1.27	0.714	0.786	0.91	3.14	0.91
Column No.	1		2				3		4		5		6	

[a] For explanation of symbols, see text. Notes: Wherever $(Q_A)_0 = (Q_B)_0$, ${}^u\eta = {}^e\eta$ and the figures given would be valid for ${}^e\eta$ for all actual values of $(Q)_0$. Where ${}^e\eta > 1$, the process has made things worse instead of better, but only for the component indicated as for the time being of greatest interest, and only for the phase concerned.

entropy of complete separation of the components into their pure (standard) states. They then employ the differential calculus to determine at what fractional yield of the desired component this ratio is maximal. The corresponding values of ψ (distribution ratio) can be calculated from their figures and hence $\psi_A\psi_B$, which over the range considered by them takes values from about 0.1 to about 13. Thus, if this definition of optimum separation is employed, $\psi_A\psi_B = 1$ proves to be not a general requirement for optimum separation, and indeed is valid only for one value of ω.

Symmetry of separation may or may not necessarily lead to the condition $\psi_A = 1/\psi_B$ for optimum separation. Proof is lacking, and in any case the conclusion may vary with the separations method employed. But it is quite clear from the above that the condition cannot be generally valid, the actual ideal relationship varying with the chosen criterion of optimum performance. In laboratory work, $\psi_A = 1/\psi_B$ may be widely useful; in other fields it cannot be applied without fuller consideration.

SYMBOLS

A, B	specified components of a mixture	
j	any (unspecified) region	
I	purity index as defined in Ref. *13*	
n	extraction section	number of ideal stages in a distillation or other multistage system
m	washing section	
$\mathbf{n}$	total, $= n + m - 1$	
N	"number of theoretical plates" in a chromatographic or other zonal separation method, defined as z^2/σ^2	
N''	$N(\psi/(1 + \psi))^2$ (chromatography only)	
Q	quantity of substance, in any convenient units to be defined	
R	resolution, defined as peak separation ÷ mean peak width (where peak width = 4 × standard deviation of a Gaussian distribution profile)	
S	separation factor as defined in Ref. *15*	
S'	specific entropy as defined in Ref. *13*	
z	distance of a distribution profile along a separation dimension	

Superscripts and Subscripts

e	equalized	identifiers for use with η, ζ, or θ
u	unequalized	

0	indicates initial (unseparated) state	
p	predicted	identifiers for use with η, ζ, or θ
x	experimental	

Note that A, B, and j also appear as inferior characters

Greek Letters

α, β	in discussion only	
η	contaminant ratio	defined in text $({}^e\eta_{\mathrm{A,B}})_j = \frac{(Q_\mathrm{B})_j}{(Q_\mathrm{A})_j} \times \frac{\text{total A}}{\text{total B}}$
ζ	"purity ratio" ($= 1/\eta$)	
θ	"contaminant complement" ($= 1 - \eta$)	
ξ, ξ_{opt}	extent of separation and optimum extent of separation, as defined in Ref. *2*	
σ	standard deviation (of a distribution profile)	
χ, ψ, $\pitchfork$, ω	see text. $\pitchfork = 1/\psi$, so that $\omega = \psi_\mathrm{A}/\psi_\mathrm{B} = \pitchfork_\mathrm{B}/\pitchfork_\mathrm{A}$	

Other Symbols

( )	used with η, ζ, and θ. Identifiers appearing within parentheses indicate the components considered and whether the parameter is equalized or unequalized, predicted or experimental. Identifiers outside the parentheses indicate the region concerned, boundaries, recovery, etc.
ln	logarithm to base e
log	logarithm to base 10

REFERENCES

1. T. R. C. Boyde, *Sep. Sci.*, *6*, 771 (1971).
2. P. R. Rony, *Ibid.*, *3*, 239 (1968).
3. P. R. Rony, *Ibid.*, *3*, 357 (1968).
4. T. D. King and L. C. Craig, in *Methods of Biochemical Analysis*, Vol. 10 (D. Glick, ed.), Interscience, New York, 1962, p. 201.
5. A. Klinkenberg, *Chem. Eng. Sci.*, *1*, 86 (1951).
6. T. R. C. Boyde and C. B. Spencer, *Sep. Sci. Technol.*, *14*, 163 (1979).
7. P. R. Rony, *Sep. Sci.*, *5*, 1 (1970).
8. A. Kremser, *Natl. Pet. News*, *22*, 43 (May 31, 1930).
9. M. R. Fenske, *Ind. Eng. Chem.*, *24*, 482 (1932).
10. A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, *35*, 1358 (1941).
11. B. L. Karger, *J. Gas Chromatogr.*, *5*, 161 (1967).

12. E. Glueckauf, *Trans. Faraday Soc.*, *51,* 34 (1955).

13. K. De Clerk and C. Cloete, *Sep. Sci.*, *6*, 627 (1971).

14. B. E. Marques, *C. R. Acad. Sci.*, *196,* 1309 (1933).

15. E. B. Sandell, *Anal. Chim. Acta*, *4,* 504 (1950).

16. L. B. Rogers, in *Treatise on Analytical Chemistry*, Part I, Vol. 2 (I. M. Kolthoff and P. J. Elving, eds.), Interscience, New York, 1961, p. 917.

17. S. Stene, *Ark. Kemi, Mineral. Geol.*, *18A*(*18*), 1–121 (1944).

18. P. R. Rony, *Sep. Sci.*, *4*, 493 (1969).

19. E. B. Sandell, *Anal. Chem.*, *40*, 834 (1968).

20. E. F. Joy and J. H. Payne, *Ind. Eng. Chem.*, *47*, 2157 (1955).

Received by editor June 29, 1978