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The Extent of Separation: A Universal Separation Index

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Summary

A universal separation index, the extent of separation, is proposed and mathematically described. This index is easily calculated, normalized, invariant to a permutation in indices, and conceptually similar to the De Donder extent of reaction. It applies to any type of separation system, any initial or final level of component purity, any concentration profile (if one exists), any initial amount of components, multicomponent systems, and both separation and mixing processes. The index is employed to characterize one of the simplest of all separation systems—the single equilibrium stage.

INTRODUCTION

In a keynote article in the first issue of *Separation Science,* Pfann discussed common concepts and features of separation and purification techniques and then noted that two of the major goals for a science of purification are "to seek out and define the underlying unity of the various classes of materials and methods involved and to express this underlying unity in basic, elementary theoretical form, much as thermodynamics underlies the various sciences today" (*1*). One reason for the absence of unity in the field of chemical separations is the lack of a universal mathematical expression, applicable to any type of separation process, that permits the evaluation of how well a pair of chemical components are separated. Sandell has recently pointed out why α, the quotient of the distribution coefficients,

$$\alpha = \frac{K_2}{K_1} \tag{1}$$

is inadequate as a separation factor and has discussed an alternative definition for such a factor,

$$\text{Separation factor} = S_{2/1} = \frac{Y_{21}}{Y_{11}} \tag{2}$$

(Y_{11} and Y_{21} will be defined shortly) (*2*). Although numerous investigators in the field of chromatography have developed equations to express the separation of a pair of components in terms of experimental or theoretical chromatographic parameters (*3–12*), only one of these expressions—Said's recovery index (*7*)—is not restricted to elution chromatographic systems (Gaussian peaks). None of these chromatographic expressions has been universally accepted, not even the internationally recommended form of the resolution equation (*3*),

$$R = 2\,\frac{t_{R_2} - t_{R_1}}{w_1 + w_2} \tag{3}$$

Furthermore, these expressions are generally not applicable to peaks of more irregular shape, as was recently pointed out by Littlewood, who stated: "It proved impossible to define precisely what was acceptable as a degree of separation of incompletely separated peaks unless the peaks could be assumed to be Gaussian or skew-Gaussian" (*12*).

When we ask how well have a pair of chemical components been separated, we are posing a mathematical question, one that is independent of the chemical, physical, and engineering aspects of the separation process itself. There is no need to know what the separation process is, what chemical components are being separated, how long the process takes, or how much equipment is required. Accordingly, if we could develop a universal separation index, we would expect it to apply to any type of separation system, any initial or final level of component purity, any type of concentration profile (if one exists), and to pairs of chemical components selected from a multicomponent mixture. Above all, the universal separation index would be physically meaningful and easily calculable from experimental data.

We would like to propose a new separation index, ξ, called the extent of separation, which meets all these criteria. In this article we shall mathematically define this index; verbally describe the auxiliary concepts of regions, binary separation systems, and segregation fractions; and apply these concepts to the theoretical characterization of one of the simplest of all separation systems—the single equilibrium stage. Subsequent papers in this series will probe the application of the extent of separation to chromatographic, multistage, and multicomponent separation systems.

REGIONS

The mathematical expression for ξ is based upon the following definition for the concept of separation: Separation is the hypothetical condition where there is complete isolation, by m separate macroscopic regions, of each of the m chemical components which comprise a mixture. In other words, the goal of any separation process is to isolate the m chemical components, in their pure forms, into m separate vessels, such as glass vials or polyethylene bottles. Each vessel or container is then considered as the *region* for its respective component.

A *binary separation system* contains only two components (designated by the indices $i = 1, 2$) and only two regions (designated by the indices $j = 1, 2$). If many fractions are obtained, they are consolidated into only two fractions, one containing a preponderance of component 1 and the other containing a preponderance of component 2.

In many separation processes, we never actually isolate the separated components into individual containers or fractions, but instead depend upon recorder chart paper (gas–liquid chromatography) or spots on filter paper (paper chromatography) to indicate how well we have separated our components. Figure 1 indicates how we treat such situations for binary separation systems: A dotted line drawn between the two spots or chromatographic peaks is sufficient to define the boundaries of the two regions. In distillation columns, the term *regions* refers to the gas or liquid streams emanating from the column. In these special cases, the use of the word region is generally preferable to the use of the words vessel, container, or fraction.

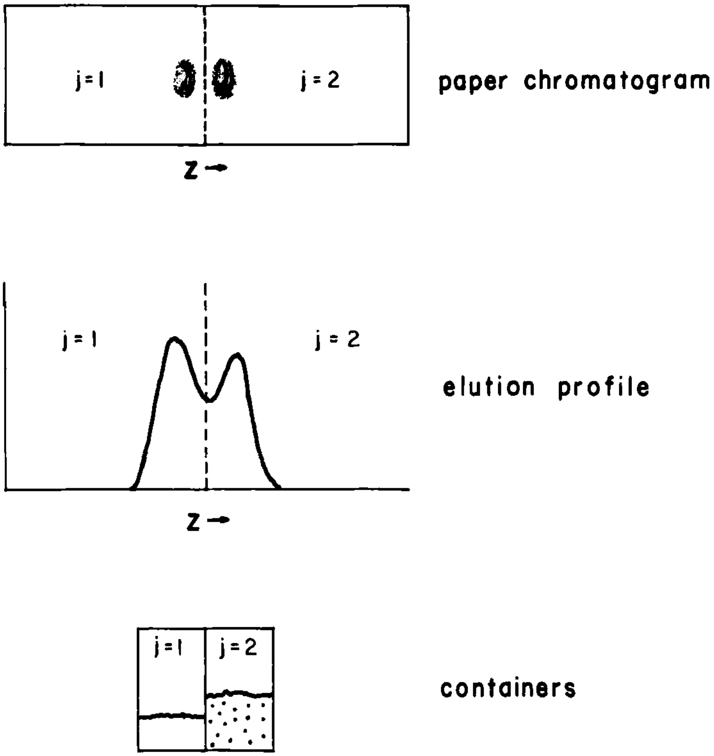

FIG. 1. Schematic diagrams of some typical "regions" in separation systems.

MOLE AND SEGREGATION FRACTIONS

Before the mathematical expression for ξ can be given, the following quantities must first be defined: (a) n_{ij}, the number of moles of component i in region j; (b) n_i^0, the total number of moles of component i initially present in the system,

$$n_i^0 \equiv \sum_j^m n_{ij} \tag{4}$$

(c) X_{ij}, the mole fraction of component i in region j,

$$X_{ij} \equiv \frac{n_{ij}}{\sum_i^m n_{ij}} \tag{5}$$

(d) Y_{ij}, the segregation fraction of component i in region j,

$$Y_{ij} \equiv \frac{n_{ij}}{\sum_{j}^{m} n_{ij}} \equiv \frac{n_{ij}}{n_i^0} \tag{6}$$

and (e) X_i^0, the initial mole fraction of component i in any region,

$$X_i^0 \equiv \frac{n_i^0}{\sum_{i}^{m} n_i^0} \tag{7}$$

Three identity relationships exist for the X_{ij}'s, Y_{ij}'s, and X_i^0's:

$$\sum_{i}^{m} X_{ij} \equiv 1 \tag{8}$$

$$\sum_{j}^{m} Y_{ij} \equiv 1 \tag{9}$$

$$\sum_{i}^{m} X_i^0 \equiv 1 \tag{10}$$

The discussion in this article will be restricted to binary separation systems ($m = 2$). The meanings of the mole and segregation fractions are quite evident from their mathematical definitions and will not be discussed further. It is interesting to note that these two quantities represent the only two simple ways of formulating fractional quantities from a set of n_{ij}.

EXTENT OF SEPARATION

For a binary separation system, the extent of separation is defined as the absolute value of the determinant of a binary separation matrix (**T**) that is written in terms of the four segregation fractions,

$$\xi \equiv \text{abs det } \mathbf{T} \equiv \text{abs det} \begin{vmatrix} Y_{11} & Y_{12} \\ Y_{21} & Y_{22} \end{vmatrix} \tag{11}$$

Table 1 lists alternative forms for ξ that are based upon Eq. (11); they are valid only for binary separation systems. Other mathematical definitions for ξ have been considered [the most notable ones being (a) Eq. (2) and (b) a matrix equation analogous to Eq. (11) but

TABLE 1

Alternative Forms for the Extent of Separation, ξ, for a Binary Separation System

In terms of Y_{ij}	In terms of n_{ij} and n_i^0
$\mathrm{abs}[Y_{11}Y_{22} - Y_{12}Y_{21}]$	$\frac{1}{n_1^0 n_2^0}\,\mathrm{abs}[n_{11}n_{22} - n_{12}n_{21}]$
$\mathrm{abs}[Y_{11} + Y_{22} - 1]$	$\mathrm{abs}\left[\frac{n_{11}}{n_1^0} + \frac{n_{22}}{n_2^0} - 1\right]$
$\mathrm{abs}[1 - Y_{12} - Y_{21}]$	$\mathrm{abs}\left[1 - \frac{n_{12}}{n_1^0} - \frac{n_{21}}{n_2^0}\right]$
$\mathrm{abs}[Y_{11} - Y_{21}]$	$\mathrm{abs}\left[\frac{n_{11}}{n_1^0} - \frac{n_{21}}{n_2^0}\right]$
$\mathrm{abs}[Y_{22} - Y_{12}]$	$\mathrm{abs}\left[\frac{n_{22}}{n_2^0} - \frac{n_{12}}{n_1^0}\right]$

in terms of the four mole fractions], but all of them have been found to be far inferior to Eq. (11).

The extent of separation possesses all the desirable characteristics of a broadly applicable separation index. For example, it is

a. Normalized, $0 \leqq \xi \leqq 1$ (Fig. 2)

b. Invariant to a permutation of the component indices i or the region indices j,

c. Independent of the units in which Y_{ij} is calculated

d. Easily calculated

e. Conceptually similar to the normalized De Donder extent of reaction, ξ_D *(13)*

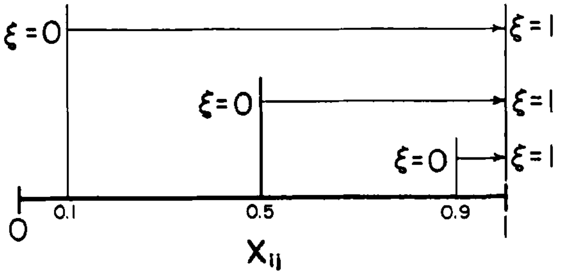

FIG. 2. Schematic diagram showing the normalization characteristic of the extent of separation. For simplicity of representation, it is assumed here that $n_{21} = 0$ and therefore $X_{ij} = X_{22}$.

and it applies to

f. Any type of separation system
g. Any initial level of component purity
h. Any initial amount of components
i. Any final level of component purification
j. Any concentration profile (if one exists)
k. Both separation and mixing processes
l. Pairs of chemical components
m. Time normalization and minimum time analysis
n. Other forms of optimization.

When high component purity is obtained and ξ has a value near unity, it is convenient to define another index, the complementary extent of separation, ψ,

$$\psi \equiv 1 - \xi \qquad (12)$$

Where applicable (to non-steady-state systems), the *rate of separation*, r^S, can be defined as

$$r^S \equiv \frac{d\xi}{dt} \qquad (\mathrm{sec}^{-1}) \qquad (13)$$

which is conceptually similar to the definition for the normalized *rate of reaction*, r^R,

$$r^R \equiv \frac{d\xi_D}{dt} \qquad (\mathrm{moles\ sec}^{-1}) \qquad (14)$$

given by Prigogine and Defay (*13*). The object of much of the research work in the fields of chemical kinetics and chemical separations is to selectively maximize these two quantities for specific chemical systems. From the above equations, it is clear that there is a close correspondence between these two fields.

The extent of separation is conceptually similar to the recovery index (*7*). Although not stated by Said, the latter index, like ξ, has one significant advantage over previously defined chromatographic separation indices: It is not dependent upon the characteristics of Gaussian peaks and thus can apply to other types of separation profiles and systems. The only basic difference between the two indices is that the extent of separation always has a definite value, while the recovery index never has one.

EXAMPLE: SINGLE EQUILIBRIUM STAGE

To illustrate the use of the extent of separation, let us consider a single equilibrium stage in which two components ($i = 1, 2$) each distribute between two regions ($j = 1, 2$). The stage is operated batchwise and is in thermodynamic equilibrium; one example of such a system is a laboratory separatory funnel containing two components which distribute between two immiscible liquid phases. The extent of separation can be calculated according to an equation given in Table 1,

$$\xi_{SS} = \text{abs}\left[\frac{n_{11}}{n_1^0} - \frac{n_{21}}{n_2^0}\right] \tag{15}$$

From the definition of the distribution coefficient, K_i,

$$K_i = \frac{n_{i2}}{n_{i1}} \tag{16}$$

Equation (15) can be simplified to

$$\xi_{SS} = \text{abs}\left[\frac{n_{11}}{n_{11} + n_{12}} - \frac{n_{21}}{n_{21} + n_{22}}\right] \tag{17}$$

$$= \text{abs}\left[\frac{1}{1 + K_1} - \frac{1}{1 + K_2}\right] \tag{18}$$

which, from the definition of the quotient of the distribution coefficients given in Eq. (1), can be further simplified to

$$\xi_{SS} = \text{abs}\left[\frac{1}{1 + K_1} - \frac{1}{1 + \alpha K_1}\right] \tag{19}$$

For a given value of α, Eq. (19) can be differentiated with respect to K_1 and the result set equal to zero to yield the optimum value of K_1,

$$K_1\bigg|_{\text{opt}} = \alpha^{-1/2} \tag{20}$$

the optimum value of K_2,

$$K_2\bigg|_{\text{opt}} = \alpha^{1/2} \tag{21}$$

and the maximum value of the extent of separation, $\xi_{\max}$, for these optimum values of K_i,

$$\xi_{\max} = \text{abs}\left[\frac{\alpha^{1/2} - 1}{\alpha^{1/2} + 1}\right] \tag{22}$$

These equations are quite important, since the volume ratio of the two regions can frequently be adjusted to make K_1 and K_2 approach their optimum values.

We can employ Sandell's two examples to demonstrate that ξ_{SS} is "a quantity that will allow separability to be formulated and to be calculated when the necessary experimental variables are specified." As can be seen from Eq. (19), under no conditions, for the same value of K_1, does $\alpha = 5$ represent a better separation than $\alpha = 10$, but $\alpha = 10/0.1 = 100$ does indeed represent a far better separation than $\alpha = 1000/10 = 100$.

OTHER APPLICATIONS

The extent of separation can be readily applied to mixing processes as well as to chromatographic, multistage, and other types of separation processes; such applications are partially treated elsewhere and will be the subject of subsequent articles in this series (*14*). By extending the 2 × 2 matrix given in Eq. (11) into an $m \times m$ matrix, the use of the extent of separation can be extended to multicomponent separation systems. This application will be discussed in a forthcoming publication.

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