Recent Developments in Separation Science

Volume III
Part A

Editor

Norman N. Li, Sc.D.

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Exxon Research and Engineering Company
Linden, New Jersey

PREFACE

It was about 5 years ago that we published our first two volumes. At that time, we did not have plans to publish additional volumes. Volumes I and II, which contain a total of 22 chapters, were therefore designed to cover practically all the important aspects of separation science and technology. Our readers' favorable responses in the past years have convinced us to make the book a multivolume series so that additional volumes can be published from time to time. This two-part volume is the first of several volumes that we plan to publish in the next few years.

We are very proud to note that in this volume (Parts A and B) we are able to present 15 chapters written by the leading authorities in separation science and technology. These chapters present discourses on unifying theories for separation processes, on the theories describing the interactions of fluid dynamics, interfacial phenomena, and mass transfer, and on a variety of separation methods and processes. The last category includes dynamically formed membranes, electrolytical purification, facilitated transport through membranes, gas absorption, ion exchange process, liquid clathrates, liquid membranes, supercritical extraction, ultrafiltration, and waste water treatment for fermentation processes.

The materials discussed in each chapter are, in general, the author's own research work and his critical review of the current state of art. The authors had complete freedom in choosing certain important areas for emphasis. As a result, some chapters treat the related chemistry or mathematics in more detail than others, and some deal more with the engineering and economics aspects of a separation process. Each chapter, consequently, possesses its own special feature and appealing points.

All the chapters were reviewed by Dr. E. W. Funk of Exxon and myself, with two chapters reviewed also by Professor R. W. Rousseau of North Carolina State University of Raleigh. I wish to thank both of them for their help. I would like to express my sincere appreciation also to the authors and the Staff of CRC Press for their effort in making Volume III possible. Special thanks are due to Ms. M. Magee and Ms. T. Weintraub of CRC Press for their editorial assistance.

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Norman N. Li
Linden, New Jersey

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THE EDITOR

Norman N. Li, Sc.D., heads the Separation Science Group at the Corporate Research Laboratories of Exxon Research and Engineering Company. He has numerous scientific publications and patents on topics of crystallization, extraction, blood oxygenation, enzyme membranes, water treatment, liquid membranes, and polymeric membranes. Of the many patents he holds, 21 alone deal with the basic invention and various applications of liquid surfactant membranes. He was a consultant on gas diffusion for the Apollo project and has given lectures at many universities and industrial research laboratories. Dr. Li teaches two short courses for the American Institute of Chemical Engineers, "New Separation Processes" and "Surface Chemistry and Emulsion Technology." He served as chairman of two Gordon Research Conferences, "Separation and Purification" and "Transport Phenomena in Synthetic and Biological Membranes," and of several symposia on separations for the American Chemical Society and the American Institute of Chemical Engineers.

CONTRIBUTORS

Jerry L. Atwood, Ph.D.
Department of Chemistry
University of Alabama
University, Alabama

Alan R. Berens, Ph.D.
B.F. Goodrich Co.
Research and Development Center
Brecksville, Ohio

Dibakar Bhattacharyya, Ph.D.
Department of Chemical Engineering
University of Lexington
Lexington, Kentucky

Heinz-Günter Blaschke, Ph.D.
Farbenfabrik Bayer AG
Leverkusen, West Germany

Ulf Brunke, D.Sc.
Henkel AG
Düsseldorf, West Germany

Enrico Drioli, Ph.D.
Facolta di Ingegneria
Istituto di Principi di Ingegneria Chimica
Universita degli Studi di Napoli
Naples, Italy

John W. Frankenfeld, Ph.D.
Exxon Reearch and Engineering Co.
Linden, New Jersey

Edward W. Funk, Ph.D.
Exxon Research and Engineering Co.
Linden, New Jersey

R. B. Grieves, Ph.D.
Department of Chemical Engineering
University of Kentucky
Lexington, Kentucky

Harold B. Hopfenberg, Sc.D.
Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina

Cyrus Irani, Ph.D.
Exxon Research and Engineering Co.
Linden, New Jersey

Isao Karube, D. Eng.
Research Laboratory of Resources Utilization
Tokyo Institute of Technology
Tokyo, Japan

Takashi Koike, B.S.
Kyowa Hakko Kogyo Co. Ltd.
Tokyo, Japan

Russel J. Lander, M.S.
Department of Chemical and Biochemical
Engineering
University of Pennsylvania
Philadelphia, Pennsylvania

Ho-Lun Lee, Ph.D.
Department of Chemical Engineering
University of Wisconsin
Madison, Wisconsin

Norman N. Li, Sc.D.
Exxon Research and Engineering Co.
Linden, New Jersey

Edwin N. Lightfoot, Jr., Ph.D.
Department of Chemical Engineering
University of Wisconsin
Madison, Wisconsin

R. N. Maddox, Ph.D.
School of Chemical Engineering
Oklahoam State University
Stillwater, Oklahoma

William S. Miller, B.S.
The Permutit Company
Research and Development Center
Princeton, New Jersey

Albert B. Mindler, B.S.
The Permutit Company
Research and Development Center
Princeton, New Jersey

Minoru Nagashima, M.S.
Kyowa Hakko Kogyo Co. Ltd.
Tokyo, Japan

Sadao Noguchi, B.S.
Kyowa Hakko Kogyo Co. Ltd.
Tokyo, Japan

Robert L. Pigford, Ph.D.
Department of Chemical Engineering
University of Delaware
Newark, Delaware

John A. Quinn, Ph.D.
Department of Chemical and Biochemical
  Engineering
University of Pennsylvania
Philadelphia, Pennsylvania

Joachim F. G. Reis, Ph.D.
Department of Chemical Engineering
University of Wisconsin
Madison, Wisconsin

Hirotoshi Samejima, Ph.D.
Tokyo Research Laboratory
Kyowa Hakko Kogyo Co. Ltd.
Tokyo, Japan

Karl Schügerl, Ph.D.
Institute for Technical Chemistry
Technical University of Hanover
Hanover, West Germany

Jerome S. Schultz, Ph.D.
Department of Chemical Engineering
University of Michigan
Ann Arbor, Michigan

T. Thomas Shih, Ph.D.
Chemical Research Laboratory
Allied Chemical Company
Morristown, New Jersey

Douglas R. Smith, M.S.
Department of Chemical and Biochemical
  Engineering
University of Pennsylvania
Philadelphia, Pennsylvania

Rolf Streicher, D.Sc.
Lurgi Mineralöltechnik GmbH
Frankfurt am Main, West Germany

Shuichi Suzuki, D.Sc.
Research Laboratory of Resources Utilization
Tokyo Institute of Technology
Tokyo, Japan

Mario S. Waissbluth, Ph.D.
Department of Biotechnology and Bioengineering
Center for Advanced Studies
National Polytechnic Institute
Mexico City, Mexico

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THE SYSTEMATIC DESCRIPTION AND DEVELOPMENT OF SEPARATIONS PROCESSES

H. L. Lee, E. N. Lightfoot, J. F. G. Reis, and M. D. Waissbluth

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INTRODUCTION

During the last decade there has been an enormous increase in the specific needs for physical separations, in the technology available for producing them, and also in the number of processes available in fully developed form.

The development of new processes has been especially impressive in the general areas of synthetic polymers, biological macromolecules, and colloidal particles. To mention just a few new or rapidly evolving processes we cite parametric pumping,[108,111,119] affinity chromatography,[26,39] polarization chromatography,[48,68] continuous chromatography[37,107] high-speed liquid chromatography,[33,80] zonal centrifugation,[3,19] continuous electrophoresis,[49,50,64,66] isotachophoresis,[25] dielectrophoresis,[62] separation by flow,[31] and spreading,[85] and a variety of membrane separations.[81,88,91]

We can also refer the reader to a number of relatively new journals and periodic reviews devoted entirely to separations, for example *Progress in Separation and Purification, Separation Science,* and *Separation and Purification Methods.*

The bulk of newly developed separations are still primarily confined to analytical and small-scale preparative applications. It is a major challenge to scale these operations up, particularly to meet the challenges of increasing energy and raw materials costs. Moreover, since the available number of possibilities is already very large, and since there are doubtless many processes yet to be discovered, even the systematic listing of possibilities becomes a major task. For example, it is suggested by Pauschmann that the number of potentially useful and qualitatively distinct separations is on the order of 10^4.

The organization and rationalization of all this material have proven to be a difficult task, and the available frameworks appear inadequate. An opportunity therefore exists for a long overdue restructuring of this classic field, and such a reorganization should take full advantage of recent advances in transport theory, the strategy of process design,[96,97] and the more ambiguous area of existing technology. The challenge is clearly to combine these hitherto largely unrelated areas in such a way as to facilitate the solution of important separations problems: the invention and development of new processes, the selection among existing processes, and the systematic study of separations as a scholarly discipline. Meeting this challenge is our major goal.

Substantial efforts have already been made in these directions, notably by Karger et al.,[59] Rony,[93] Giddings,[43] Pauschmann,[82] and De Clerk et al.[28] It is, however, our belief that a more powerful organization can be provided by the conservation and rate laws of transport phenomena, and we outline such an approach below. The rationale for this is of course that all separations are almost by definition transport processes and therefore described in detail by the equations of change.

This rationalization is, however, only partially correct. First, the very generality of the transport equations makes them unsuitable for distinguishing between individual processes; these distinctions lie primarily in the boundary conditions (including system geometry) and equations of state. Second, the essentially descriptive nature of transport phenomena makes this discipline a weak point of departure for any creative activity: invention, development, or design.

We must therefore build our transport-based description into a synthesis-oriented strategic framework flexible enough to accommodate a great deal of poorly organized information: chemical or physical, financial, and political. Our approach to this problem is fourfold. We begin by developing an essentially heuristic classification scheme which facilitates the listing of possibilities and choosing between alternatives. This is the primary concern of the present discussion. Second, we are beginning to devise a synthesis scheme for generating promising processes from our fundamental classification. Third, we are seeking efficient means for comparison of alternate schemes. Since the synthesis and comparison must encompass a very large number of possibilities, it will be most efficient to combine these two operations into a staged series or hierarchy of successively more accurate, and expensive, computational or experimental procedures. Finally we shall be interested in the implementation of the above ideas, by way of concrete examples, to test the utility of our ideas.

All of these activities must of course be based on a solid understanding of separation as a basic concept. In this paper we start with the definition of separation as a basic concept and then present a general morphological description. We next provide a detailed framework for the quantitative

description of separations and suggest how one may use this framework and understanding of separations morphology for classification and synthesis.

THE STRUCTURE OF SEPARATIONS PROCESSES

Definitions of Separation and Separative Work

We begin here by considering the rather general separation process of Figure 1 in which a feed stream or sample is converted into an unspecified number of products. We first define separation qualitatively in terms of scaled feed and product compositions, and then go on to present two methods of characterizing separation quantitatively: purity, or separation indices, and effort, or separative power. Purity is of paramount interest to the user of separations processes, particularly in analytical applications, and considerations of purity have dominated the separations literature. The effort required to achieve a given separation is clearly also an important consideration, however, particularly to engineers, and greater attention to this aspect of our field seems overdue.

Separation in Terms of Scaled Composition Changes

We define a separations process as one in which a feed mixture F is converted to M product mixtures, as suggested in Figure 1. These product mixtures may be readily identifiable streams, as in a distillation process, or arbitrarily selected regions, for example effluent fractions from a gas or liquid chromatograph or two-dimensional zones in paper chromatography.

In general, separation can be expressed in terms of composition changes, and we shall use here two measures of composition:*

$$x_i = \text{mole fraction of species i at any position and time} \tag{1}$$

and

$$x_i = x_i/x_{iF} = \text{relative molar fraction} \tag{2}$$

where x_{iF} is the mole fraction of species i in the feed. For a system of N species the compositions may then be expressed as the vectors

$$\underline{x} = (x_1, x_2, \cdots x_N) \tag{3}$$

$$\underline{x} = (x_1, x_2, \cdots x_N) \tag{4}$$

$$\underline{x}_F = 1 \tag{5}$$

Note that these are local or point compositions.

We next define average compositions of the M product streams as

$$\pi_{ij} = \text{the mole fraction of species i in product stream j taken as a whole} \tag{6}$$
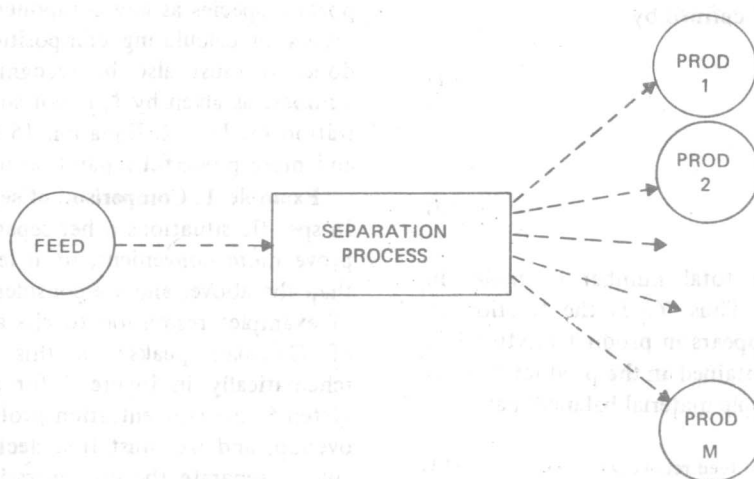
and

$$\Pi_{ij} = \pi_{ij}/x_{iF} \tag{7}$$

FIGURE 1. The nature of separation.

*It may on occasion be preferable to use mass or volume fractions.

We may therefore express product compositions as an N by M matrix, e.g.,

$$\underline{\pi} = \begin{pmatrix} \pi_{11}, & ---- & \pi_{1M} \\ & & \\ \pi_{N1} & ---- & \pi_{NM} \end{pmatrix} \qquad (8)$$

Note that the π_{ij} are averaged compositions, e.g., cup-mixing averages in flow systems, or volume averages in batch ones.

It is now clear that separation will occur whenever there is one element of Π for which

$$\Pi_{ij} \neq 1 \qquad (9)$$

and that species k and ℓ will be separated to some extent whenever there is a product, for which

$$\Pi_{kj} \neq \Pi_{\ell j} \qquad (10)$$

Equations 9 and 10 are sufficiently broad to include all measures of separation known to the authors, and they may clearly be written in other terms, for example, on a solvent-free basis or in mass or volume fractions. They are, in fact, too broad in that they are inherently qualitative, and we now turn our attention to quantitative measures of purity.

Separation Indices: Measures of Product Purity

We therefore now look at more specialized measures of separation, of which a great many have been proposed.[46,59,61,92,93]

One particularly useful example is the degree of segregation matrix $\underline{Y}$ defined by

$$Y_{ij} \equiv r_j \Pi_{ij} / \sum_{\ell=1}^{M} r_\ell \Pi_{i\ell} \qquad (11)$$

where

$$r_j = m_j / \sum_{\ell=1}^{M} m_\ell \qquad (12)$$

and m_j equals the total number of moles in product mixture j. Thus Y_{ij} is the fraction of recovered i which appears in product mixture j. If all of the feed is contained in the product streams it follows from a simple material balance that

$$\sum_{\ell=1}^{M} r_\ell \Pi_{i\ell} = 1 \qquad \text{(total feed recovery)} \qquad (13)$$

and

$$Y_{ij} = r_j \Pi_{ij} \qquad \text{(total feed recovery)} \qquad (14)$$

Equations 13 and 14 will not be valid if there is chemical degradation or other product loss, or for transient situations. The degree of separation has proven a useful index, but it does not give a direct measure of relative segregation, which is often desired.

A more far-reaching index which does this is Rony's extent of separation ξ, defined as the magnitude of the determinant of $\underline{Y}$:

$$\xi = |\det \underline{Y}| \qquad (15)$$

The physical significance of ξ may be seen most easily for a binary system where

$$\xi = |Y_{11} Y_{22} - Y_{12} Y_{21}| \qquad (16)$$

Furthermore, for a binary system

$$Y_{11} = r_1 \Pi_{11} / (r_1 \Pi_{11} + r_2 \Pi_{12}) \qquad (17)$$

$$= 1 - Y_{12} \qquad (18)$$

$$\xi = |Y_{11} - Y_{21}| = |Y_{22} - Y_{12}| \qquad (19)$$

In this simple situation, then, ξ is just the difference in degrees of segregation into either of the two product mixtures.

This index has proven useful for comparing such dissimilar processes as stagewise distillation and zone melting. It is, however, only applicable where the number of components N to be separated is equal to the number of product streams M. If $N > M$ one may choose M particularly important species as key components and ignore the others in calculating composition. This is often done. It must also be recognized that a single number, as given by ξ, is not sufficient characterization for $N > 2$. Equation 15 is inadequate here and more powerful separation indices are needed.

Example 1: Comparison of separation indices — In specific situations other separation indices may prove more convenient, or at least more popular, than the above, and we consider one here by way of example: resolution to characterize separation of Gaussian peaks. In this situation, shown schematically in Figure 2 for a one-dimensional system*, the concentration profiles of two species overlap, and we must first decide upon a line of cut to separate the concentration field into two product mixtures. The proper positioning of this line may present a difficult decision in some cases,

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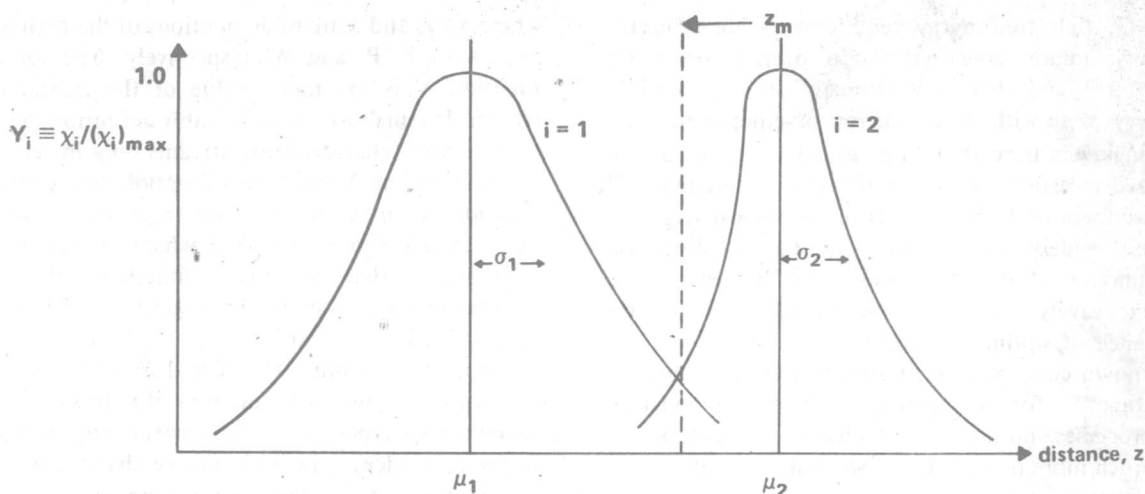*A three-dimensional Gaussian distribution is discussed in Example 2.

FIGURE 2. A simple one-dimensional separation.

but it is frequently satisfactory to separate at the point of equal fractional loss of major constituent, i.e., at the intersection of the normalized concentration distributions. This point is designated as z_m in Figure 2. Separation in such a system is frequently characterized in terms of the resolution R, usually defined[59] by

$$R \equiv \frac{1}{2} \cdot \frac{|\mu_1 - \mu_2|}{\sigma_1 + \sigma_2} \qquad (20)$$

where μ_1, μ_2 are the positions of the concentration maxima of solutes 1 and 2 and σ_1, σ_2 are the standard deviations about these two means. The fraction of the major constituent which is contained in the respective product mixtures is* then $P(R)$ where

$$P(R) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{R} e^{-z^2/2} dz \qquad (21)$$

is the normal probability integral.

It follows from Equations 11 and 19 that

$$Y_{ii} = 1 - Y_{ij} = P(R) \qquad (i = 1, 2; j \neq i) \qquad (22)$$

and

$$\xi = 2P - 1 \qquad (23)$$

A few representative comparisons of these indices are given in Table 1.

*See for example Reference 1, Section 26.2.8.

TABLE 1

Comparison of Separation Indices for Symmetrical One-dimensional Gaussian Separations*

R	P	Y_{ii}	ξ
0	0.5	0.5	0
0.25	0.691	0.691	0.383
0.5	0.841	0.841	0.683
0.75	0.933	0.933	0.866
1.0	0.977	0.977	0.954
1.25	0.994	0.994	0.988

*Note that

$$P_3 < P(x) < P_1$$

$$P_1 = \frac{1}{2}\left[1 + \sqrt{1 - \exp(-2x^2/\pi)}\,\right]$$

$$P_3 = \frac{1}{2}\left[1 + \sqrt{1 - \exp(-2x^2/\pi) - \frac{2(\pi-3)}{3\pi^2} x^4 e^{-x^2/2}}\,\right]$$

Separative Power and the Value Function: Measures of Effort

One frequently needs a mechanism-independent measure of separator performance which combines the requirements of purity and productivity, and which is independent of product and feed compositions. No one such measure is best in all circumstances, and as a result quite a variety has evolved. The most general and unambiguous is minimum requirement of thermodynamic free energy, and this is normally also the most useful in the early stages of process design, for providing estimates of feasibility. Experience shows, how-

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ever, that free-energy requirements are typically very minor contributors to overall separation effort* and that they normally do not correlate very well with either energy or equipment cost. Engineers have therefore turned to more specialized measures, and the most common are required numbers of transfer units or theoretical stages. A less widely used measure is the amplification function of Rony.[93] These tend, however, to be excessively specialized and to ignore the importance of optimizing productivity. The less widely known concept of separative power, developed by Dirac** for comparing isotope fractionation processes during the Manhattan Project, seems much more powerful, and we shall concentrate our attention on it here.

Discussions of separative power are made here in connection with the simple binary splitter of Figure 3 and confined to systems of only one valuable component (binary or pseudo-binary systems). The apparatus pictured splits a feed stream F into "product" and "waste" streams P and W, respectively; F, P, and W refer to molar stream rates for a continuous process or molar amounts for a batch process. This figure can be adapted to stagewise countercurrent apparatus by considering F as the combined input streams to any stage, and to continuous countercurrent processes by considering the splitter to represent a differential section of the apparatus.

Referring to this figure we define the separative power of this basic unit as

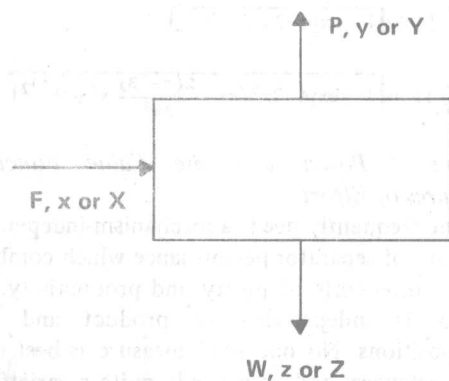$$\delta U = PV(y) + WV(z) - FV(x) \qquad (24)$$

FIGURE 3. A simple binary splitter.

where x, y, and z are mole fractions of the desired species in F, P, and W, respectively. The value function V is the molar value of the indicated stream. It remains to complete this definition, but, since we are characterizing streams only in terms of composition, V must be a function only of the appropriate mole fraction. We must now determine an expression for $V(x)$ which satisfies the requirement that δU be a function only of equipment and system characteristics, and not feed or product compositions.

To do this we must write P and W in terms of F and replace y and z by functions of x; this in turn requires two types of relations: overall and species material balances, and performance characteristics of the process unit. Those chosen here are

$$P = \theta F \qquad (24a)$$
$$W = (1 - \theta)F \qquad (24b)$$
and
$$x = y\theta + z(1 - \theta) \qquad (25)$$
with
$$Y = \gamma X \qquad (26)$$
$$Z = \beta X \qquad (27)$$
where
$$X = x/(1 - x) \qquad (28)$$
$$Y = y/(1 - y) \qquad (29)$$
$$Z = z/(1 - z) \qquad (30)$$

Here θ is known as the cut while γ and β are called enrichment ratios. Use of mole ratios rather than mole fractions introduces some mathematical difficulty, and the form of Equations 26 and 27 specializes our discussion considerably. However, there are a great many systems for which the enrichment ratios may be considered composition independent, and it is important to provide useful specific examples. It should be possible to parallel the discussion below for other performance characteristics.

We now wish to use the above relations to eliminate P, W, y, and z from Equation 23, and it may be seen immediately that our system is overdetermined. We may thus eliminate*** the cut θ by noting that

*As a specific example less than $2 \times 10^{-3}\%$ of the power consumption of a typical uranium-enrichment centrifuge is needed to supply the free energy of separation.[58]

**Usually referenced simply as "P.A.M. Dirac, British MS, 1941." Separative work and the associated concept of the value function are, however, discussed in a number of more easily available works. These include Cohen,[20] Olander,[78] and Shachter et al.[100]

***The cut θ is introduced primarily because of its importance in later discussions.

$$y = \frac{Y}{1+Y} = \frac{\gamma X}{1+\gamma X} \tag{31}$$

etc., and therefore that

$$\frac{X}{1+X} = \left(\frac{\gamma X}{1+\gamma X}\right)\theta + \left(\frac{\beta X}{1+\beta X}\right)(1-\theta) \tag{32}$$

and

$$\theta = \left(\frac{1-\beta}{\gamma-\beta}\right)\left(\frac{1+\gamma X}{1+X}\right) \tag{33}$$

$$(1-\theta) = \left(\frac{1-\gamma}{\beta-\gamma}\right)\left(\frac{1+\beta X}{1+X}\right) \tag{34}$$

It follows that

$$\delta U/F = \left(\frac{1-\beta}{\gamma-\beta}\right)\left(\frac{1+\gamma X}{1+X}\right)V\left(\frac{\gamma X}{1+\gamma X}\right) + \left(\frac{1-\gamma}{\beta-\gamma}\right)\left(\frac{1+\beta X}{1+X}\right)$$

$$V\left(\frac{\beta X}{1+\beta X}\right) - V(x) \tag{35}$$

which is our desired result. It only remains to find an expression for $V(x)$ making δU independent of composition.

Careful inspection of Equation 35 will show that the form of $V(x)$ depends on the ratio of β to γ, and that obtaining a general solution is a formidable problem; it does not appear to have been solved at the time of writing. Fortunately, however, essentially equivalent solutions exist for two very important special cases, and we shall confine discussion to these:

1. Antisymmetric enrichment: $\beta = 1/\gamma$ so that

$$Y = \alpha Z \tag{36}$$

with

$$\alpha = \gamma^2 \tag{37}$$

and

$$\theta = (1+\sqrt{\alpha}X)/(1+\sqrt{\alpha})(1+X) \tag{38}$$

2. Small enrichment ratios:

$$\gamma - 1 << 1$$

$$\beta - 1 << 1$$

so that

$$Y = \alpha Z \tag{39}$$

with

$$\alpha - 1 << 1 \tag{40}$$

and θ is arbitrary.

The antisymmetric case is of particular importance in cascades, and we shall have more to say about it in the third section of this chapter. We note here only that the local reflux in any cascade can be set to meet the requirements of Equations 36 to 38 and that such a cascade (known as ideal) is the most efficient possible by the criteria normally used. Our first special case thus provides a performance standard for any linear cascade. The small-enrichment limit is similarly important in continuum contactors since differential segments of such a contractor always provide small enrichment ratios. We return to this point immediately after giving expressions for $V(x)$ for these two limiting situations.

The antisymmetric case is treated by Cohen* who shows that

$$V(x) = C\left(\frac{\sqrt{\alpha}+1}{\sqrt{\alpha}-1}\right)\frac{(2x-1)\ln\left[\left(\frac{x}{1-x}\right)\bigg/\left(\frac{x_0}{1-x_0}\right)\right]}{\ln\sqrt{\alpha}}$$

$$+ A\left(\frac{1-x_0}{x_0}\right) + B(1-x) \tag{41}$$

where A and B are arbitrary constants, C is $\delta U/F$, and x_0 is an arbitrary reference concentration. The simplest and most symmetric choice is to set x_0 equal to one half, B equal to zero, and

$$V = (2x-1)\ln[x/(1-x)] \tag{42}$$

Then

$$\delta U/F = \frac{(\sqrt{\alpha}-1)\ln\alpha}{2(1+\sqrt{\alpha})} \tag{43}$$

Cohen suggests, however, that for any specific separation problem it may prove more convenient to set x_0 equal to the feed concentration and to define both feed and waste streams to have zero value. This last definition requires establishing a

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*Cohen defines his enrichment ratio α as Y/X, but this choice is inconvenient because it is ordinarily strongly dependent on θ. The ratio Y/Z used in Equation 41 is often independent of θ, at least in the first approximation. For the antisymmetric situation consider here

$$Y/Z = (Y/X)^2$$

but this simple relation holds only when θ is given by Equation 38.

waste composition in advance, but in any event the specific choices made are clearly matters of taste, hence inarguable.

The value function is important in relating engineering effort to changes in composition. Thus, for a cascade of constant α, separative work δU is proportional to the sums of stage overflows and an ideal cascade is that which minimizes this sum. The value function is particularly useful for estimating the effect of changing feed or product specifications, but it also facilitates comparison between alternate processing procedures. It is most helpful in the intermediate stages of design, before accurate economic estimates are feasible, for concentrating attention on "reasonable" configurations.

The results for small enrichment may be obtained from Equation 35 by* using the truncated series expressions:

$$\ell n \gamma \doteq \epsilon - \frac{\epsilon^2}{2} \qquad (44)$$

$$\epsilon = (\gamma - 1) \qquad (45)$$

and

$$\ell n \beta \doteq \epsilon - \frac{\epsilon^2}{2} \qquad (46)$$

$$\epsilon = (\beta - 1) \qquad (47)$$

which yield:

$$V = (2x - 1) \, \ell n \, [x/(1 - x)] \qquad (48)$$

$$\delta U/F = \frac{1}{2} \theta \, (1 - \theta)(\alpha - 1)^2 \qquad (49)$$

It may be seen that Equation 48 is identical with Equation 42 and that Equation 49 is consistent with Equation 43. Now, however, α and θ are mathematically independent.** We find then that the choice made for $V(x)$ is a surprisingly useful one, and we shall have several occasions to make use of it below. We shall find the concepts of separative power and value useful from many standpoints in comparing alternate processes, and also for estimating the maximum separation potential of a given type of equipment. It will be helpful for this type of estimation to establish one further concept, that of volumetric value production rate, and we conclude our discussion by doing

this. (This discussion is taken with only minor modifications from Olander.[78])

The value as defined by Equations 42 or 48 is a property of the fluid in a thermodynamic sense, and, just as for any other property it is possible to write a conservation statement for the value in the moving fluid. The "value transport equation" so obtained is very similar to the entropy transport equation which plays a fundamental role in non-equilibrium thermodynamics; it may be written as

$$\frac{\partial (cV)}{\partial t} + \nabla \cdot N_V = R_V \qquad (50)$$

In Equation 50, c is the total concentration of the fluid, V is the value of a unit amount of fluid, and N_V is the vector flux of value. The rate of production of value per unit volume of fluid is denoted by R_V. This quantity is related to the separative power of a unit of volume τ by

$$\delta U = \int_\tau R_V \, d\tau \qquad (51)$$

Just as in the transport of matter, the transport of value can be broken up into a diffusive term J_V^* and a convective term:***

$$N_V = J_V^* + cv^* V \qquad (52)$$

Inserting the above equation into Equation 50 yields

$$c \frac{\partial V}{\partial t} + cv^* \cdot \nabla V + \nabla \cdot J_V^* = R_V \qquad (53)$$

where the overall mass continuity equation

$$\frac{\partial c}{\partial t} + \nabla \cdot (cv^*) = 0 \qquad (54)$$

has been used (we have assumed that the average molecular weight of the fluid is everywhere uniform).

We now need to develop an expression for the diffusive component of the value flux, J_V^*. The property called value does not "diffuse" in the same sense that molecules or heat diffuse. Rather, value is transported due to the interdiffusion of the two species in the mixture which are denoted by A and B. The value flux due to molecular transport by diffusion may be expressed by

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*Alternate derivations which are simpler if one considers only the small enrichment case are given by Olander[78] and by Shachter et al.[100]

**In any actual separator the observed value of α will generally depend on θ, however.

***See Reference 11, Chapter 16. Here v* is the molar average mixture velocity, N_V is the flux of value relative to the coordinate system, and J_V^* is the corresponding flux relative to v*.

$$J_v^\star = J_A^\star \overline{V}_A + J_B^\star \overline{V}_B \tag{55}$$

where $J_A^\star$ and $J_B^\star$ are the diffusive fluxes of A and B, i.e. fluxes relative to $v^\star$. By analogy to energy transport by interdiffusion in multicomponent systems[11] and entropy transport in a moving fluid, the quantities $\overline{V}_A$ and $\overline{V}_B$ are identified with partial molal values. The partial molal value is defined as follows: Consider a volume of fluid containing n_A moles of A and n_B moles of B. The total value of this region of fluid, V_{tot}, is

$$V_{tot} = (n_A + n_B)V(x_A) \tag{56}$$

where V is the value function and x_A is the mole fraction of component A. The partial molal value of components A and B are then given by

$$\overline{V}_A = (\partial V_{tot}/\partial n_A)_{n_B} \tag{57}$$

and

$$\overline{V}_B = (\partial V_{tot}/\partial n_B)_{n_A} \tag{58}$$

It follows that

$$\overline{V}_A = V(x_A) + (1 - x_A)(dV/dx_A) \tag{59}$$

$$\overline{V}_B = V(x_A) - x_A(dV/dx_A) \tag{60}$$

Substituting Equations 59 and 60 into Equation 55 results in

$$J_v^\star = J_A^\star (dV/dx_A) \tag{61}$$

where we have used the fact that $J_A^\star + J_B^\star = 0$.[11] The divergence of $J_V^\star$ is

$$\nabla \cdot J_v^\star = \nabla \cdot \left[J_A \left(\frac{dV}{dx_A} \right) \right] = \left(\frac{dV}{dx_A} \right) \nabla \cdot J_A + J_A \cdot \nabla \left(\frac{dV}{dx_A} \right) \tag{62}$$

Since the value function depends only upon composition x_A, the gradient of V or its derivative may be expressed by

$$\nabla V = \left(\frac{dV}{dx_A} \right) \nabla x_A \tag{63}$$

$$\nabla \left(\frac{dV}{dx_A} \right) = \left(\frac{d^2 V}{dx_A^2} \right) \nabla x_A \tag{64}$$

Substituting Equations 62 to 64 into Equation 53 yields

$$R_v = J_A^\star \cdot \nabla x_A \left(\frac{d^2 V}{dx_A^2} \right) + \left[c \frac{\partial x_A}{\partial t} + cv^\star \cdot \nabla x_A + \nabla \cdot J_A^\star \right]$$

$$\left(\frac{dV}{dx_A} \right) \tag{65}$$

Now the bracketed term in Equation 65 is identically zero by virtue of the species continuity equation, and

$$R_v = (J_A^\star \cdot \nabla x) \frac{d^2 V}{dx^2} \tag{66}$$

Note that we have so far made no assumption as to the concentration dependence of the value function, and therefore we are not limited by the above expressions. If we now put Equation 48 into Equation 65 we obtain the specific result

$$R_v = (J_A^\star \cdot \nabla x)/[x(1-x)]^2 \tag{67}$$

which is the expression normally used. It is shown in Example 10 that this simple result is extremely powerful for estimating maximum separation potentials of proposed processes.

Characterization of Concentration Distributions

Determination of species concentration distributions is one of the primary problems facing us, and there is no one most effective approach to solving it. Rather there are four levels of organization on which we can proceed and which we designate here as:

1. Molecular
2. Continuum
3. Pseudo-continuum
4. Discrete

Description at each of these levels is obtained from its immediate predecessor by a process of contraction, and as a result this listing is in decreasing order of amount of information provided. However, since obtaining information about diffusing systems often requires considerable effort, it is desirable in practice to settle for the least amount needed to solve the problem at hand. Each of these levels thus has its merits.

The Molecular Level

On the molecular level, the physical system is characterized not by species concentration distributions, but by a set of particle position vectors, $\{x_1, x_2, \ldots x_N\}$, where N is the total number of molecules. One must then calculate the trajectories of individual molecules by describing their interactions with each other and any confining sur-