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

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To cite this Article Sirkar, Kamalesh K.(1977) 'On the Composite Nature of the Extent of Separation', Separation Science and Technology, 12: 3, 211 — 229

To link to this Article: DOI: 10.1080/00372367708058073

URL: http://dx.doi.org/10.1080/00372367708058073

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SEPARATION SCIENCE. 12(3), pp. 211–229, 1977

On the Composite Nature of the Extent of Separation

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Abstract

The fundamental expression for Rony's extent of separation in a 2-component system has been reexamined for any separation stage with respect to its relation with the traditional stage separation factor for a wide variety of separation processes. It has been shown that for a single entry or double entry rate governed barrier separation stage, the extent of separation is a composite index consisting of a stage capacity factor proportional to the barrier area and a stage enrichment factor $(\alpha - 1)$ or $(\beta_1 - 1)$. The latter need not be close to zero. For a reverse osmosis and a gaseous diffusion stage, the extent of separation has been expressed in terms commonly used for these processes. The composite nature of the extent of separation has been also determined for batch dialysis, batch thermal diffusion, as well as for a single equilibrium stage, and related to known features of these separation processes in terms of stage capacity and stage enrichment.

INTRODUCTION

In a series of pioneering articles admirably summarized in Ref. *1*, Rony had introduced the universal separation index, ξ, the extent of separation, and demonstrated its superiority over other available separation indices including the commonly used separation factor, α. The extent of separation, ξ, was defined by Rony (*1*) in terms of various segregation fractions, Y_{ij}, for a binary system of two components $i = 1, 2$ distributed between two regions $j = 1, 2$. Determination of Y_{ij} for any separation process

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followed by calculation of ξ allowed Rony to develop, in addition, a methodology for classifying and comparing separation processes, a procedure for determining optimum conditions for maximum separation, and concepts like the rate of separation and the amplification function.

In the paper dealing with the extent of separation for close separations (*2*), Rony has claimed that the extent of separation equation for all separation processes can be linearized to the form

$$\xi = [\text{function of physical variables}]\varepsilon' \qquad (1)$$

where $\varepsilon' = \alpha' - 1$ for $\varepsilon' \ll 1$. Here α' is the separation quotient defined by Rony (*2*) to be the ratio of any pair of physical properties or collection of physical properties whose values are critical in determining the degree of separation that can be achieved via a given separation process. The function of physical variables in Relation (1) has been called an amplification function by Rony (*1*) so that

$$\text{amplification function} = \lim_{\varepsilon' \to 0} \frac{\partial \xi}{\partial \varepsilon'} \qquad (2)$$

In Ref. *2*, Rony has termed this dimensionless function the amplification factor. The maximum amplification factor has also been defined by Rony (*1*) to be

$$\text{maximum amplification factor} = \lim_{\varepsilon' \to 0} \frac{\partial \xi_{\max}}{\partial \varepsilon'} \qquad (3)$$

The amplification functions and the maximum amplification factors were determined by Rony (*1*) for 12 different separation processes: single equilibrium stage, elution chromatography, steady-state and field flow cataphoresis, crosscurrent or countercurrent equilibrium distribution with discrete equilibrium or differential equilibrium contact, and countercurrent multistage distribution with total reflux or without reflux.

It is known (*1*) that Rony's separation quotient α' need not be equal to the traditional separation factor α. In fact, α' is different from α for the separation processes of gaseous diffusion, thermal diffusion, sweep diffusion, mass diffusion, gas centrifugation, reverse osmosis, etc. (*1*). In this paper we would like to explore in greater detail expressions of Type (1) for the extent of separation. Specifically we would like to demonstrate that for a single separation stage or element in many separation processes, the extent of separation, ξ, may be represented by an equation of the following type:

$$\xi = \{\text{function of physical variables}\}(\alpha - 1) \text{ or } (\beta_1 - 1) \qquad (4)$$

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where α is the stage separation factor and β_1 is the heads separation factor (*3*). The value of α or β_1 need not be close to 1 for such a relation to be valid. Further, it will be shown that the so-called "function of physical variables" often has a simple meaning in that it indicates the stage capacity in some manner whereas the factors $(\alpha - 1)$ or $(\beta_1 - 1)$ quantify the composition changes undergone by various streams in the stage. Thus the composite nature of the separation index, extent of separation, will be the subject of this paper.

SOME DEFINITIONS

The definitions adopted here have been mostly introduced earlier by Rony (*1*). The quantity n_{ij} is the total number of moles of component i in the region j in a closed system containing n_i^0 moles of component i. The segregation fraction Y_{ij} of ith component in the jth region of a closed system is defined as

$$Y_{ij} = n_{ij}/\textstyle\sum_{j=1}^{2} n_{ij} = n_{ij}/n_i^0 \tag{5}$$

if $j = 1, 2$ only. The extent of separation ξ for a closed system of two components $i = 1, 2$ distributed between two regions $j = 1, 2$ is defined to be

$$\xi = |Y_{11} - Y_{21}| = |Y_{22} - Y_{12}| = \begin{vmatrix} Y_{11} & Y_{12} \\ Y_{21} & Y_{22} \end{vmatrix} \tag{6}$$

The mole fraction x_{ij} of component i in region j is defined by the relation

$$x_{ij} = n_{ij}/\textstyle\sum_{i=1}^{2} n_{ij} \tag{7}$$

The traditional separation factor α for a binary system of two components $i = 1, 2$, is defined in terms of mole fractions as

$$\alpha = x_{11}x_{22}/x_{12}x_{21} \tag{8}$$

For a closed system, a distribution ratio K_i for the component i is defined as

$$K_i = n_{i2}/n_{i1} \tag{9}$$

The distribution coefficient of component i between the two regions in a closed system is given by

$$m_i = C_{i2}/C_{i1} \tag{10}$$

where C_{ij} is the molar concentration of the ith species in the region j. For an open system, $\dot{n}_{ij}(k)$ is the molar flow rate of component i in the jth

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stream coming out of the stage k. Let the total molar feed flow rate to the stage k be denoted by $\dot{F}_k$. Let f_{ik} represent the mole fraction of the ith component in the total feed to stage k. The segregation fractions for an open system are defined thus:

$$\dot{Y}_{ij}(k) = \dot{n}_{ij}(k)/\dot{F}_k f_{ik} \tag{11}$$

For a single entry separating element or stage, $\dot{F}_k$ is the actual molar feed flow rate whereas for a double entry separating element or stage, $\dot{F}_k$ is the sum of the molar flow rates of the two feed streams entering the element or the stage and $\dot{F}_k f_{ik}$ is the sum of the molar inflow rates of component i through the two feed streams. In an open system with two product streams, the light fraction will be denoted by $j = 1$ and the heavy fraction by $j = 2$, just as the light component will be denoted by $i = 1$ and the heavy component by $i = 2$. The same will hold true for a closed system. Further, as is evident, we will restrict ourselves to a binary system ($i = 1, 2$) only.

EXTENT OF SEPARATION FOR VARIOUS SEPARATION PROCESSES

Separation processes may be broadly classified into rate-governed and equilibrium separation processes. The rate-governed separation processes may in turn be classified into barrier separation processes and field separation processes (*4*). Barrier separation processes are usually carried out in single entry separating elements. We will consider first the expression for the extent of separation in any single entry separation stage of any rate-governed barrier separation process operating continuously. We will then determine the extent of separation for a few such individual barrier separation processes of considerable industrial interest, e.g., reverse osmosis desalination and gaseous diffusion. This will be followed by the determination of the expressions for the extent of separation of the barrier separation process of dialysis when it is operated in the batch mode. The batch thermal diffusion process in a 2-bulb cell will be dealt with next as an example of a field separation process. At the very end, we will consider the extent of separation for a batch single equilibrium stage.

Consider a single entry separation stage k with a barrier as shown in Fig. 1A. The extent of separation for this process may be written following Rony (*5*) as

$$\xi = \text{abs}|\dot{Y}_{11} - \dot{Y}_{21}| \tag{12}$$

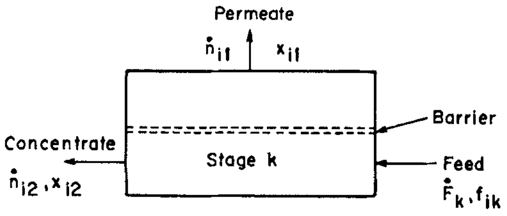

FIG. 1A. Single entry barrier separation stage.

The relevant segregation fractions are

$$\dot{Y}_{11} = \frac{\dot{n}_{11}}{(\dot{n}_{11} + \dot{n}_{12})} = \frac{\dot{n}_{11}}{\dot{F}_k f_{1k}} = \frac{(\dot{n}_{11} + \dot{n}_{21})x_{11}}{\dot{F}_k f_{1k}} \tag{13}$$

and

$$\dot{Y}_{21} = \frac{\dot{n}_{21}}{(\dot{n}_{21} + \dot{n}_{22})} = \frac{\dot{n}_{21}}{\dot{F}_k f_{2k}} = \frac{(\dot{n}_{11} + \dot{n}_{21})x_{21}}{\dot{F}_k f_{2k}} \tag{14}$$

where $f_{2k} = (1 - f_{1k})$ and $x_{21} = (1 - x_{11})$.

Therefore

$$\xi = \frac{(\dot{n}_{11} + \dot{n}_{21})}{\dot{F}_k} \operatorname{abs} \left| \frac{x_{11}}{f_{1k}} - \frac{x_{21}}{(1 - f_{1k})} \right| \tag{15}$$

where the cut for the stage k, θ_k, is defined by Ref. *6* as

$$\theta_k = \frac{(\dot{n}_{11} + \dot{n}_{21})}{\dot{F}_k} \tag{16}$$

It is obvious from Expressions (15) and (16) that θ_k is some sort of a stage capacity factor whereas the second term is a function of compositions of various streams only. This aspect of ξ will get amplified further if we notice that Expression (15) may also be written as

$$\xi = \left[\frac{(\dot{n}_{11} + \dot{n}_{21})x_{21}}{\dot{F}_k(1 - f_{1k})} \right] \operatorname{abs} \left| \frac{x_{11}(1 - f_{1k})}{(1 - x_{11})f_{1k}} - 1 \right| \tag{17}$$

$$= \begin{bmatrix} \text{(Fraction of heavy species 2 originally} \\ \text{present in the feed and transferred} \\ \text{through the barrier in stage } k) \end{bmatrix} \operatorname{abs}|\beta_1 - 1| \tag{18}$$

where β_1 is the heads separation factor for stage k [as per the definition of Benedict and Pigford (*3*)]. The extent of separation ξ for a single entry

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separating element for any rate-governed barrier separation process operating continuously is then a product of two quantities: the first quantity (similar to the amplification factor of Rony) is the fraction of heavy species 2 originally present in the feed and transferred through the stage barrier; the second quantity is the heads separation factor $\beta_1 - 1$ indicating in some manner the enrichment of the light fraction with respect to the feed stream composition. The first quantity, as we shall soon see, will be proportional to the total barrier area available in the stage for a given barrier (or to the total stage length) while the second quantity is ideally independent of the stage area or stage length and depends on the intrinsic separating ability of the barrier, i.e., the barrier separation factor. The first quantity in Expression (17) or (18) indicates the stage capacity in some way whereas the second quantity indicates the degree of enrichment of the light fraction in the light component with respect to that in the feed stream. It may be mentioned here that for a stage of infinitesimal length, the heads separation factor β_1 reduces to α, the stage separation factor of Definition (8) since β_1 becomes the barrier separation factor which is in this case equal to the stage separation factor since the feed stream composition will hardly change in a differential length of the barrier.

The Relations (15), (16), (17), and (18) are valid for any barrier separation process with a single entry separation stage. We will now show how these terms are related to some commonly used terms in reverse osmosis desalination.

Reverse Osmosis

Reverse osmosis is preferred for systems with a high separation factor as is valid for, say, desalination of brackish water or seawater with polymeric semipermeable membranes. For sufficiently dilute feed solutions (as is true for brackish water or seawater), the various quantities indicating mole fractions of water in various streams may be modified in the following manner if water is component 1 and salt is component 2:

$$\frac{x_{11}}{f_{1k}} = \frac{\left[\dfrac{\text{moles of water/volume}}{\text{total moles/volume}}\right] \text{in permeate}}{\left[\dfrac{\text{moles of water/volume}}{\text{total moles/volume}}\right] \text{in feed}} \cong \frac{C_{11}}{C_{1f}} \tag{19}$$

where C_{1f} is the molar concentration of water in the feed to stage k.

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Similarly

$$\left(\frac{x_{21}}{1 - f_{1k}}\right) \cong \frac{C_{21}}{C_{2f}} \tag{20}$$

The extent of separation Expression (15) may now be changed to

$$\begin{aligned} \xi &= \theta_k \operatorname{abs}\left|\frac{C_{11}}{C_{1f}} - \frac{C_{21}}{C_{2f}}\right| \\ &= \theta_k\left(\frac{C_{21}}{C_{2f}}\right) \operatorname{abs}\left|\frac{C_{11}C_{2f}}{C_{1f}C_{21}} - 1\right| \end{aligned} \tag{21}$$

Further, since the solutions are dilute, $C_{11} \cong C_{1f}$ so that the heads separation factor for the reverse osmosis stage is

$$\beta_1 = \frac{x_{11}(1 - f_{1k})}{x_{21}f_{1k}} \cong \frac{C_{11}C_{2f}}{C_{1f}C_{21}} \cong \frac{C_{2f}}{C_{21}} \tag{22}$$

and the extent of separation is

$$\xi = \frac{\theta_k}{\beta_1} \operatorname{abs} |\beta_1 - 1| \tag{23}$$

Expression (23) may also be written as

$$\xi = \theta_k \operatorname{abs}\left|1 - \frac{C_{21}}{C_{2f}}\right| = \theta_k \operatorname{abs}\left|1 - \frac{1}{\beta_1}\right| \tag{24}$$

Both the factors on the right-hand side of Expression (24) are familiar quantities in the literature on desalination by reverse osmosis (*7*). The quantity θ_k represents essentially the fraction of water removed from the dilute feed brine in stage k, whereas the quantity $(C_{2f} - C_{21}/C_{2f}) \times 100$, known as the percent rejection of salt by the membrane, is the most common measure of the membrane's semipermeability or solute rejection characteristics. Both the quantities are of great importance in the process design of any reverse osmosis desalination stage.

It is known (*7*) that the heads separation factor β_1 at any point in the reverse osmosis desalination stage is given by

$$\beta_1 \cong \frac{C_{2f}}{C_{21}} = \frac{D_{1M}m_1\bar{V}_1(\Delta P - \Delta\pi)}{D_{2M}m_2RT} \tag{25}$$

where $\bar{V}_1$ is the partial molar volume of water in solution; D_{1M} is the Fickian diffusion coefficient for water transport in membrane subject to a pressure difference of ΔP; D_{2M} is the Fickian diffusion coefficient of salt in the membrane; m_1 and m_2 are the distribution coefficients of water and salt, respectively, between the membrane and the interfacial solution; and $\Delta\pi$ is the osmotic pressure difference between the solutions on two sides of the membrane. The flux of water through the membrane is given by (7)

$$N_1 = \frac{D_{1M}C_{1M}\overline{V}_1}{RTl}(\Delta P - \Delta\pi) \tag{25a}$$

so that neglecting salt flux through the membrane for determining θ_k, we get

$$\theta_k = \frac{D_{1M}C_{1M}\overline{V}_1(\Delta P - \Delta\pi)(\text{membrane area})}{RT\dot{F}_k l} \tag{26}$$

where l is the membrane thickness and C_{1M} is the concentration of water in the membrane. This last quantity C_{1M} is essentially constant for a given membrane and operating conditions. In the expression for θ_k, we have assumed negligible variation in feed concentration and concentration polarization along the membrane length. By means of Expressions (25), (25a), and (26), the Expression (23) for the extent of separation becomes

$$\xi = \left[\frac{(\text{membrane area})C_{1M}D_{2M}m_2}{l\dot{F}_k}\right] \text{abs}\,|\beta_1 - 1| \tag{27}$$

$$= \left[\frac{C_{1M}}{\dot{F}_k}(\text{membrane area})\frac{(\text{salt flux})}{(C_{2f} - C_{21})}\right] \text{abs}\,|\beta_1 - 1| \tag{28}$$

since salt flux is given by (7)

$$N_2 = \frac{D_{2M}m_2(C_{2f} - C_{21})}{l} \tag{28a}$$

For $C_{21} \ll C_{2f}$, as is normally valid in reverse osmosis desalination, the first quantity within brackets in Eq. (28) for ξ is proportional to membrane area for a given system and operating conditions. Further, for a given low salt concentration C_{21} in the permeate, this quantity is directly proportional to the total water removal rate through the barrier in the stage whereas the second quantity only indicates compostional changes for a given membrane under given operating conditions. Due to the nonidealities in the system, θ_k and β_1 are somewhat mutually dependent for a given membrane and operating conditions. However, the composite nature of the separation index, the extent of separation, is quite clear. Further, the present β_1 is different from that of Rony's (*1*) α' which in this

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case would simply be $(m_1D_{11}/D_{22}m_2)$ and β_1 can have very high values compared to 1.

Gaseous Diffusion

The governing expression for the extent of separation for any gaseous diffusion stage continues to be (15) and (17) deduced earlier. Considering the present Relation (17) for close separation gaseous diffusion as given in Ref. *6*, we find that for stage k, $x_{21} \cong f_{2k} = (1 - f_{1k})$ so that

$$\xi = \theta_k \operatorname{abs} |\beta_1 - 1| \tag{29}$$

For an ideal cascade of close separation gaseous diffusion stages used commonly for isotope enrichments, it is known from Pratt (*6*) that $(\beta_1 - 1) \cong \frac{1}{2}(\alpha - 1)$ since $\beta_1 = \alpha^{1/2}$. The extent of separation for such a stage then becomes

$$\xi = \frac{\theta_k}{2} \operatorname{abs} |\alpha - 1| \tag{30}$$

Further, for a close separation ideal cascade, from Pratt (*6*) it is known that $\theta_k \cong \frac{1}{2}$ so that

$$\xi = \varepsilon/4 \tag{31}$$

for any stage in a close separation ideal gaseous diffusion cascade. This result is valid for any barrier separation process operated as an ideal cascade of close separation single entry separating elements. It may be recalled that Rony (*2*) had obtained a similar result $\xi_{\max} = \varepsilon'/4$ for an entirely different situation, namely, the maximum value of the extent of separation for a close separation single equilibrium stage.

If we now consider an ideal crossflow gaseous diffusion stage such that the Murphree stage efficiency is 1, then from Pratt (*6*) we know that the stage separation factor is equal to the ideal barrier separation factor which for a binary system of $i = 1, 2$ is

$$\alpha = \sqrt{M_2/M_1} \tag{32}$$

Therefore the expression for the extent of separation for a close separation gaseous diffusion stage with ideal cross-flow and Murphree efficiency equal to 1 is

$$\xi = \frac{\theta_k}{2}\left[\sqrt{\frac{M_2}{M_1}} - 1\right] \tag{33}$$

In this manner, any other barrier separation process with a single feed

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stream entering the stage can be dealt with to provide an expression for the extent of separation. Regardless of whether $(\alpha - 1) \ll 1$ or $\alpha \gg 1$, the conclusions arrived at earlier regarding the composite nature of the separation index, extent of separation, will hold. We will illustrate these aspects further when we consider next the extent of separation for a double entry barrier separation stage. Examples of such processes are continuous dialysis, electrodialysis, and gas permeation with purge gas on the permeate side.

Double Entry Barrier Separation Stage

The extent of separation for such a separation stage k with countercurrent flow shown schematically in Fig. 1B is

$$\xi = \text{abs}|\dot{Y}_{11}(k) - \dot{Y}_{21}(k)| \tag{34}$$

Following Rony (*1*), this may be alternatively written as

$$\xi = \text{abs}|\dot{Y}_{11}(k)\dot{Y}_{22}(k) - \dot{Y}_{12}(k)\dot{Y}_{21}(k)| \tag{35}$$

which may be modified thus:

$$\xi = \dot{Y}_{12}(k)\dot{Y}_{21}(k)\,\text{abs}\left|\frac{\dot{Y}_{11}(k)\dot{Y}_{22}(k)}{\dot{Y}_{12}(k)\dot{Y}_{21}(k)} - 1\right| \tag{36}$$

$$= \dot{Y}_{12}(k)\dot{Y}_{21}(k)\,\text{abs}\left|\frac{\dot{n}_{11}(k)\dot{n}_{22}(k)}{\dot{n}_{12}(k)\dot{n}_{21}(k)} - 1\right|$$

$$= \dot{Y}_{12}(k)\dot{Y}_{21}(k)\,\text{abs}\left|\frac{x_{11}(k)x_{22}(k)}{x_{12}(k)x_{21}(k)} - 1\right|$$

$$= \dot{Y}_{12}(k)\dot{Y}_{21}(k)\,\text{abs}\,|\alpha - 1| \tag{37}$$

since $\dot{n}_{11}(k) = x_{11}(k)[\dot{n}_{11}(k) + \dot{n}_{21}(k)]$ and $\dot{n}_{21}(k) = x_{21}(k)[\dot{n}_{11}(k) + \dot{n}_{21}(k)]$, etc. A closer consideration of the two quantities $\dot{Y}_{12}(k)$ and $\dot{Y}_{21}(k)$ reveals that

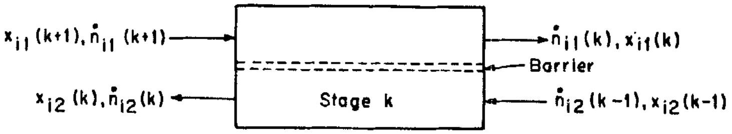

FIG. 1B. Double entry barrier separation stage.

$$\dot{Y}_{21}(k) = \frac{\dot{n}_{21}(k)}{\dot{n}_{21}(k) + \dot{n}_{22}(k)} = \frac{\dot{n}_{21}(k)}{\dot{n}_{21}(k+1) + \dot{n}_{22}(k-1)} = \frac{\dot{n}_{21}(k)}{\dot{n}_2^0(k)}$$

$$1 - \dot{Y}_{21}(k) = -\frac{-\dot{n}_{21}(k+1) + \dot{n}_{21}(k)}{\dot{n}_2^0(k)} + \frac{\dot{n}_{22}(k-1)}{\dot{n}_2^0(k)} \tag{38}$$

Here

$$\dot{n}_2^0(k) = \dot{F}_k f_{2k} \tag{39}$$

The first term on the right-hand side of Relation (38) is the fraction of species 2 present in the feed to stage k that is transferred through the barrier. For a given type of barrier and given operating conditions (like concentrations, etc.), this quantity will be proportional to the barrier area and is therefore related to the stage capacity. The second term on the right-hand side of (38) is merely the fraction of species 2 entering the stage k from the stage $(k - 1)$ below it and this will be dependent on the composition levels of the streams entering stage k. Thus we notice that for a given separation factor α and operating conditions, the term $\dot{Y}_{21}(k)$ indicates the stage capacity in a particular way. Similar interpretation may be offered for the term $\dot{Y}_{12}(k)$ so that the composite constitution of ξ as a product of terms reflecting stage capacity and stage enrichment separately is quite clear for a double entry barrier separation stage with countercurrent flow. Further, α in Relation (37) need not be close to 1. We consider next the extent of separation for dialysis operated in the batch mode.

Batch Dialysis

Consideration of batch dialysis is facilitated if we determine the general expression for the extent of separation in a closed system with Regions 1 and 2 having volumes V_1 and V_2, respectively, separated by a barrier. In such a case, for a binary system, the extent of separation may be written following Rony (*1*) as

$$\xi = |Y_{11}Y_{22} - Y_{12}Y_{21}| = Y_{12}Y_{21}\left|\frac{Y_{11}Y_{22}}{Y_{12}Y_{21}} - 1\right| \tag{40}$$

$$= Y_{12}Y_{21}\left|\frac{n_{11}n_{22}}{n_{12}n_{21}} - 1\right| = Y_{12}Y_{21}\left|\frac{x_{11}x_{22}}{x_{12}x_{21}} - 1\right|$$

$$\xi(t) = Y_{12}Y_{21}|\alpha - 1| = Y_{12}(t)Y_{21}(t)|\alpha(t) - 1| \tag{41}$$

where $\alpha(t)$ may have any value greater than or equal to 1. For batch

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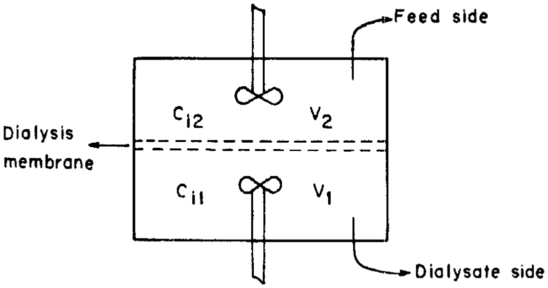

FIG. 2A. Batch dialysis stage.

dialysis stage shown in Fig. 2A, Region 1 is the dialysate getting richer in light Component 1 with time whereas Region 2 is the feed side getting richer in the heavy Component 2 with time. However, since this rate-governed process is being operated in the batch mode, ultimately the concentration of each species on both sides of the barrier will be equal. Let the initial concentrations of ith species in the feed side and the dialysate side be C_{i2}^0 and 0, respectively. The concentrations of the ith species in the feed chamber and the dialysate chamber at any time t may be obtained following the procedure in Ref. *8* as

$$\frac{C_{i2}(t)}{C_{i2}^0} = \left(\frac{V_2}{V_2 + V_1}\right) + \left(\frac{V_1}{V_2 + V_1}\right) \exp\left[\left(-\frac{A_M D_{iM}}{l}\right)\left(\frac{1}{V_2} + \frac{1}{V_1}\right)t\right] \tag{42}$$

and

$$\frac{C_{i1}(t)}{C_{i2}^0} = \left(\frac{V_2}{V_2 + V_1}\right)\left[1 - \exp\left(-\frac{A_M D_{iM}}{l}\right)\left(\frac{1}{V_2} + \frac{1}{V_1}\right)t\right] \tag{43}$$

The separation factor $\alpha(t)$ in Expression (41) is

$$\alpha(t) = \left[\frac{x_{11}(t)x_{22}(t)}{x_{21}(t)x_{12}(t)}\right] = \left[\frac{C_{11}(t)C_{22}(t)}{C_{21}(t)C_{12}(t)}\right] \tag{44}$$

On substituting Expressions (42) and (43) in the above expression, we will get, after simplifications,

$$\alpha(t) = \frac{[1 - \exp(-a_1 t)][V_2 + V_1 \exp(-a_2 t)]}{[1 - \exp(-a_2 t)][V_2 + V_1 \exp(-a_1 t)]} \tag{45}$$

where

$$a_i = \frac{A_M D_{iM}}{l}\left(\frac{1}{V_2} + \frac{1}{V_1}\right) \tag{46}$$

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For small time,

$$\alpha(t) = \frac{D_{1M}}{D_{2M}}\left[\frac{1 - (A_M D_{2M}/lV_2)t}{1 - (A_M D_{1M}/lV_2)t}\right] \tag{47}$$

so that

$$\alpha(t) = \alpha = D_{1M}/D_{2M} = \alpha' \tag{48}$$

only at time $t = 0$. The extent of separation ξ for batch dialysis may be obtained from Expression (41) as

$$\xi(t) = \left[\frac{n_{12}(t)}{n_{12}(t) + n_{11}(t)}\right]\left[\frac{n_{21}(t)}{n_{21}(t) + n_{22}(t)}\right]|\alpha(t) - 1| \tag{49}$$

$$= \left[\frac{C_{12}(t)V_2}{C_{12}{}^0 V_2}\right]\left[\frac{C_{21}(t)V_1}{C_{22}{}^0 V_2}\right]|\alpha(t) - 1|$$

$$= \left(\frac{V_1}{V_1 + V_2}\right)[V_2 + V_1 \exp(-a_1 t)]\left[\frac{1 - \exp(-a_2 t)}{V_1 + V_2}\right]|\alpha(t) - 1| \tag{50}$$

For small time, this reduces to

$$\xi(t) = \left[1 - \frac{A_M D_{1M} t}{lV_2}\right]\left[\frac{A_M D_{2M} t}{lV_2}\right]|\alpha(t) - 1| \tag{51}$$

It is to be noted that the first two terms on the right-hand side of (51) are stage capacity terms and for a given solute-solvent-membrane system are dependent on the membrane area A_M, the time t, and the feed volume V_2. While we can easily interpret these two terms in terms of fraction of certain species transferred in a given time from the feed chamber, it is more fruitful to simplify the whole Expression (51) using Expression (47) and note that for small time t,

$$\xi(t) = \frac{A_M D_{2M} t}{lV_2}\left[\frac{D_{1M}}{D_{2M}} - 1\right] = \frac{A_M D_{2M} t}{lV_2}[\alpha' - 1] \tag{52}$$

The composite nature of ξ is clearer in this relation. Further, here neither α nor α' have to be close to 1. The general expression for $\xi(t)$ is being given below to complete our treatment of the batch dialysis separation stage:

$$\xi(t) = \frac{V_1}{(V_1 + V_2)}[\exp(-a_2 t) - \exp(-a_1 t)] \tag{53}$$

This is similar to the expressions derived by Rony (9) for $\xi(t)$ for the rate-governed equilibrium stage.

Thermal Diffusion

The rate-governed separation processes dealt with so far were dependent for separation on varying transmission rates of individual species through a suitable barrier. Rate-governed separation processes operating without barrier but in a specific field, e.g., temperature gradient, pressure gradient, and electrical potential gradient, are also of some importance. A 2-bulb cell connected by means of a capillary as shown in Fig. 2B is a standard device for measuring the amount of separation due to thermal diffusion when Bulb 1 having volume V_1 is kept at a temperature T_1 which is greater than T_2 the temperature of Bulb 2 having volume V_2. It is known from Ref. *6* that the amount of separation one can obtain by thermal diffusion is quite small even when $T_1 \gg T_2$ so that close separation approximations are routinely used for thermal diffusion. Further, if we are dealing with a binary gas mixture of initial mole fraction Z_1 (of light species), the separation factor α is given in Ref. *6* as

$$\alpha \cong 1 + \gamma \ln\left(-\frac{T_1}{T_2}\right) \tag{54}$$

where

$$\alpha - 1 = \varepsilon \cong \frac{x_{11} - x_{12}}{Z_1(1 - Z_1)} \tag{55}$$

and γ is the thermal diffusion constant for the system. Here Bulb 1 has more of the light component 1. The extent of separation for this closed system is

$$\xi = \text{abs}\,|Y_{11} - Y_{21}| \tag{56}$$

Assuming the ideal gas law to be valid, we note that

$$n_{11} = \frac{PV_1}{RT_1}x_{11}; \qquad n_{22} = \frac{PV_2}{RT_2}x_{22}; \qquad \text{etc.} \tag{57}$$

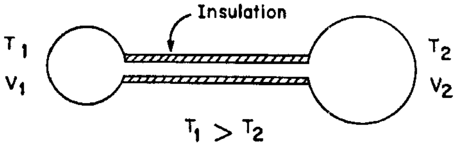

FIG. 2B. Batch thermal diffusion in a two-bulb apparatus.

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so that

$$\xi = \text{abs}\left| \frac{\dfrac{x_{11}V_1}{T_1}}{\dfrac{x_{11}V_1}{T_1} + \dfrac{x_{12}V_2}{T_2}} - \frac{\dfrac{x_{21}V_1}{T_1}}{\dfrac{x_{21}V_1}{T_1} + \dfrac{x_{22}V_2}{T_2}} \right| \tag{58}$$

Now

$$Z_1 = \frac{n_{11} + n_{12}}{(n_{11} + n_{21}) + (n_{12} + n_{22})} = \frac{\dfrac{V_1x_{11}}{T_1} + \dfrac{V_2x_{12}}{T_2}}{\dfrac{V_1}{T_1} + \dfrac{V_2}{T_2}} \tag{59}$$

and

$$\xi = \frac{V_1V_2}{\left(\dfrac{V_1}{T_1} + \dfrac{V_2}{T_2}\right)T_1T_2\left(\dfrac{V_1}{T_1} + \dfrac{V_2}{T_2}\right)} \text{abs}\left|\frac{x_{11} - x_{12}}{Z_1(1 - Z_1)}\right|$$

$$= \frac{1}{\left[\dfrac{V_1}{T_1}\dfrac{T_2}{V_2} + \dfrac{V_2}{T_2}\dfrac{T_1}{V_1} + 2\right]}\varepsilon \tag{60}$$

$$= \frac{1}{\left[\dfrac{n_{T1}}{n_{T2}} + \dfrac{n_{T2}}{n_{T1}} + 2\right]}\varepsilon \tag{60a}$$

Also

$$\xi = \frac{1}{\left[\dfrac{V_1}{V_2}e^{-(\varepsilon/\gamma)} + \dfrac{V_2}{V_1}e^{(\varepsilon/\gamma)} + 2\right]}\varepsilon \tag{61}$$

where n_{T_1} and n_{T_2} are the total number of moles in Bulbs 1 and 2, respectively. Both of the Expressions (60a) and (61) clearly show the composite nature of the separation index, extent of separation, for the batch field separation process of thermal diffusion. Expression (61) demonstrates that for a given gas mixture and operating conditions, the first factor on the right-hand side is a function of (V_1/V_2) or of the volumetric capacity ratio of the system whereas ε indicates the amount of enrichment possible in this separation process for a given gas mixture subjected to two different temperatures T_1 and T_2.

It is possible to determine the maximum extent of separation in a 2-

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bulb thermal diffusion cell by differentiating Expression (60) for the extent of separation with respect to the ratio (V_2/V_1) and equating it to zero. One finds that $(\partial\xi/\partial(V_2/V_1)]$ becomes zero when

$$V_2/V_1 = T_2/T_1 \tag{61a}$$

For such a condition, the extent of separation Eq. (60) becomes

$$\xi_{\max} = \varepsilon/4 \tag{61b}$$

which was obtained by Rony (*2*) for the maximum extent of separation in a single equilibrium stage for close separations.

Single Equilibrium Stage

We will now consider the extent of separation for any single equilibrium stage:

$$\xi = \text{abs}|Y_{11}Y_{22} - Y_{12}Y_{21}| = Y_{12}Y_{21}\,\text{abs}\left|\frac{Y_{11}Y_{22}}{Y_{12}Y_{21}} - 1\right| \tag{62}$$

$$= \left(\frac{n_{12}}{n_1{}^0}\right)\left(\frac{n_{21}}{n_2{}^0}\right)\text{abs}\left|\frac{n_{11}n_{22}}{n_{12}n_{21}} - 1\right|$$

$$= \left[\frac{n_{12}}{n_1{}^0}\right]\left[\frac{n_{21}}{n_2{}^0}\right]\text{abs}\left|\frac{x_{11}x_{22}}{x_{12}x_{21}} - 1\right|$$

$$= \left[\frac{C_{12}V_2}{n_1{}^0}\right]\left[\frac{n_{21}}{n_2{}^0}\right]\text{abs}\,|\alpha - 1|$$

$$= \left[\frac{m_1 n_{11}V_2}{n_1{}^0 V_1}\right]\left[\frac{n_{21}}{n_2{}^0}\right]\text{abs}\,|\alpha - 1|$$

$$= \left[\frac{m_1}{n_1{}^0 n_2{}^0}\right]\left[\frac{V_2}{V_1}\right]n_{11}n_{21}\,\text{abs}\,|\alpha - 1| \tag{63}$$

Here for a given α, $n_1{}^0$, $n_2{}^0$, and a range of concentrations in the two regions, m_1 is essentially constant, and n_{11} etc. are dependent on V_1 and V_2. Thus the first term is a function of the capacities of the various regions of the stage under consideration whereas the second term indicates stage enrichment. Further, such a relation is possible at all levels of α and not necessarily only for close separations. Rony (*2*) had earlier obtained a relation similar to Relation (63), without attaching the significance indicated here for the capacity factor.

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DISCUSSION

The foregoing calculations have allowed us to determine the extent of separation for a number of separation processes not considered previously. The results of these calculations indicate that the extent of separation equation for almost all separation processes carried out in a single stage have the following form:

$$\xi = (\text{extent of separation}) = (\text{capacity factor}) \times (\text{enrichment factor}) \tag{64}$$

Further, the enrichment factor can be either $(\alpha - 1)$ or $(\beta_1 - 1)$, whereas for a given separation factor (α or β_1) the capacity factor will be proportional to the barrier area for barrier separation processes. For other separation processes considered, the capacity factor is a function of the volumes of the two regions when other quantities are held constant. Also, the enrichment factor in (64) can be large and the separation processes need not be of the close separation type in order that a relation like (64) may be valid for the separation index, the extent of separation. If we recall Rony's (*1*) claim that the extent of separation is superior to the commonly used separation factor α, the reasons for such a claim are clearer now. The separation factor α merely indicates the compositional differences between various regions of the stage but ignores the total amount of material transferred between the regions or present in a given region. The capacity factor component of the extent of separation seems to eliminate this shortcoming.

SYMBOLS

a_i	defined by Eq. (46)
A_M	membrane surface area (cm^2)
C_{1M}	concentration of water in the membrane
C_{if}	concentration of species i in the feed to a stage (moles/cm^3)
C_{ij}	concentration of species i in region j or stream j
D_{iM}	diffusion coefficient of species i in membrane (cm^2/sec)
f_{ik}	mole fraction of species i in the feed to kth stage
$\dot{F}_k$	molar feed flow rate to stage k (moles/sec)
K_i	distribution ratio of species i in a closed system (moles/moles), Eq. (9)
l	membrane thickness (cm)

m_i	distribution coefficient of species i in a closed system (moles/cm^3: moles/cm^3), Eq. (10)
M_i	molecular weight of species i
n_{ij}	number of moles of species i in region j in a closed system
n_i^0	total number of moles of species i present in a closed system
$\dot{n}_{ij}^0(k)$	molar flow rate of species i in the jth stream coming out of stage k (moles/sec)
P	total pressure (kg/cm^2)
ΔP	pressure difference between the two sides of a barrier (kg/cm^2)
R	universal gas constant (1.987 Gibbs/mole)
t	time (sec)
T_j	temperature of region j (°K)
$\bar{V}_i$	partial molar volume of species i
V_j	volume of region j (cm^3)
x_{ij}	mole fraction of species i in region j, Eq. (7)
Y_{ij}	segregation fraction of species i in region j, Eq. (5)
$\dot{Y}_{ij}$	segregation fraction of species i in stream j leaving a stage, Eq. (11)
Z_i	mole fraction of i present initially in a mixture to be separated, Eq. (59)

Greek Letters

α	separation factor
α'	separation quotient
β_1	heads separation factor, $[x_{11}(1 - f_{1k})/f_{1k}(1 - x_{11})]$
γ	thermal diffusion constant
ε	enrichment factor, equal to $\alpha - 1$
ε'	defined by $\alpha' - 1$
θ_k	cut for stage k, Eq. (16)
$\Delta\pi$	difference in osmotic pressures of feed solution and permeated solution in reverse osmosis (kg/cm^2)
ξ	extent of separation
$\xi_{\max}$	maximum extent of separation

Subscripts

f	feed stream
i	component i
j	region j or stream j

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M	membrane
1, 2	specific components
$i1$, $1j$, ij, 12, etc.	specific component-region or component-stream combinations

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Received by editor August 28, 1976

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