

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

The Extent of Separation: Close Separations

Peter R. Rony^a

^a CENTRAL RESEARCH DEPARTMENT, MONSANTO COMPANY, ST. LOUIS, MISSOURI

To cite this Article Rony, Peter R.(1970) 'The Extent of Separation: Close Separations', Separation Science and Technology, 5: 2, 121 – 135

To link to this Article: DOI: 10.1080/00372367008057954

URL: <http://dx.doi.org/10.1080/00372367008057954>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Extent of Separation: Close Separations

PETER R. RONY

CENTRAL RESEARCH DEPARTMENT
MONSANTO COMPANY
ST. LOUIS, MISSOURI 63166

Summary

Under the condition of close separations, the equations for the extent of separation have been calculated for twelve different separation techniques, including elution chromatography, multicontact distribution, multistage distribution, and cataphoresis. A method for comparing all separation techniques on an equivalent basis is proposed. It is suggested that the concept of a theoretical plate in chromatographic systems be abandoned.

INTRODUCTION

The goal of this series of articles is to demonstrate how a universal separation index— ξ , *the extent of separation*—can easily and effectively apply to all of the different classes of separation techniques. In previous papers, we have derived equations for the extent of separation for single stage systems (1, 2), elution chromatography (3), cross-current and countercurrent multicontact systems (4), countercurrent multistage systems (5), and cataphoresis (6). In this paper, we would like to propose a new method for comparing these different separation techniques. This method is based upon the choice of a pair of chemical components that differ only slightly in their physical or chemical properties [corresponding to the "close separation case" discussed by Pratt in his book on countercurrent separation processes (7)]. The assumption of close separations not only reduces the complexity of the individual extent-of-separation equations, but also permits a comparison of all separation techniques on an equivalent basis. One of

the dividends of this approach is a new and more realistic definition for the number of theoretical plates in a chromatographic system.

CLOSE SEPARATIONS

The concept of "close separations" can be explained with the aid of the parameter, α , the quotient of the distribution coefficients, K_i , in an equilibrium chemical system (1),

$$\alpha = \frac{K_2}{K_1} \quad (1)$$

If the quantity, ϵ ,

$$\epsilon \equiv \alpha - 1 \quad (2)$$

is sufficiently small,

$$\epsilon < < < 1 \quad (3)$$

the extent-of-separation equation for any separation system can be linearized to the form

$$\lim_{\epsilon \rightarrow 0} \frac{\partial \xi}{\partial \epsilon} = f(\text{physical parameters}) \quad (4)$$

where f is some function of the physical properties of the system. Relationships such as (7)

$$\epsilon \approx \ln \alpha \quad (5)$$

and

$$\alpha \approx e^{(\alpha-1)} = e^\epsilon \quad (6)$$

are frequently employed in the linearization process.

SEPARATION QUOTIENTS

The quantity, α , called the *separation quotient*, need not be restricted to a quotient of distribution coefficients. It can be equal to 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 in a given separation system. For example, in a rate-controlled single equilibrium stage (2), α is equal to the quotient of two rate constants,

$$\alpha = \frac{k_2}{k_1} \quad (7)$$

whereas in a diffusion-controlled single equilibrium stage (2), α represents the quotient of two diffusion coefficients,

$$\alpha = \frac{D_{22}}{D_{12}} \quad (8)$$

An example of a collection of physical properties is the "electrostatic Peclet number," β_i , which is defined as (6)

$$\beta_i = \frac{\left(\frac{c_i^+}{c_i}\right) \frac{\mu_i^+ El}{D_i}}{1 - \left(\frac{c_i^+}{c_i}\right) \left(\frac{D_i - D_i^+}{D_i}\right)} \quad (9)$$

In such a case, the separation quotient is simply

$$\alpha = \frac{\beta_2}{\beta_1} \quad (10)$$

As a final point, the separation quotient is usually not the same as the separation factor, α' , which is defined as (7, 8)

$$\alpha' \equiv \frac{y(1-x)}{x(1-y)} \quad (11)$$

APPLICATION TO INDIVIDUAL SEPARATION TECHNIQUES

A. Single Equilibrium Stage

If we define the separation quotient, α , by Eq. (1), the extent of separation for a single equilibrium stage [Eq. (18) in Ref. 1] becomes

$$\begin{aligned} \xi &= \text{abs} \left[\frac{1}{1+K_1} - \frac{1}{1+K_2} \right] \\ &= \text{abs} \left[\frac{K_2 - K_1}{(1+K_1)(1+K_2)} \right] \\ &= \text{abs} \left[\frac{K_1(\alpha - 1)}{(1+K_1)(1+\alpha K_1)} \right] \\ &= \epsilon \text{abs} \left[\frac{K_1}{(1+K_1)(1+\alpha K_1)} \right] \end{aligned} \quad (12)$$

an equation which has the value

$$\lim_{\epsilon \rightarrow 0} \frac{\partial \xi}{\partial \epsilon} = \frac{K_1}{(1+K_1)^2} \quad (13)$$

in the indicated limit. The maximum value of the extent of separation, for small ϵ , corresponds to

$$\xi_{\max} = \frac{1}{4}\epsilon \quad (14)$$

where $K_{1\text{opt}} = 1$.

B. Rate-Controlled Single Equilibrium Stage

Consider Eq. (38) in Ref. 2,

$$\begin{aligned} \xi &= \zeta_{i2}^{\infty} \text{abs} [e^{-k_1 t} - e^{-k_2 t}] \\ &= \zeta_{i2}^{\infty} e^{-k_1 t} \text{abs} [1 - e^{(k_1 - k_2)t}] \end{aligned} \quad (15)$$

If we define the separation quotient by Eq. (7) and substitute αk_1 for k_2 in Eq. (15), we obtain

$$\xi = \zeta_{i2}^{\infty} e^{-k_1 t} \text{abs} [1 - e^{-\epsilon k_1 t}] \quad (16)$$

For very small ϵ , the relationship,

$$e^{-\epsilon k_1 t} \approx 1 - \epsilon k_1 t \quad (17)$$

holds. Therefore, Eq. (16) becomes

$$\xi = \zeta_{i2}^{\infty} k_1 t e^{-k_1 t} \epsilon \quad (18)$$

or simply

$$\lim_{\epsilon \rightarrow 0} \frac{\partial \xi}{\partial \epsilon} = \zeta_{i2}^{\infty} k_1 t e^{-k_1 t} \quad (19)$$

At the optimum time of separation, t_{opt} (2),

$$t_{\text{opt}} = \frac{\ln k_2/k_1}{k_2 - k_1} \quad (20)$$

the maximum extent of separation becomes

$$\xi_{\max} = \zeta_{i2}^{\infty} e^{-1}\epsilon \quad (21)$$

C. Diffusion-Controlled Single Equilibrium Stage

In this case, the separation quotient is given by Eq. (8). For $\zeta_{i1}^{\infty} = \zeta_{i2}^{\infty} = \zeta_{i1}^{\infty}$, Eq. (49) in Ref. 2,

$$\xi = \zeta_{i1}^{\infty} \text{abs} [\eta_1 - \eta_2] \quad (22)$$

where

$$\eta_i = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left[-\frac{D_{i2}(2n+1)^2 \pi^2 t}{4a^2} \right] \quad (23)$$

leads to

$$\lim_{\epsilon \rightarrow 0} \frac{\partial \xi}{\partial \epsilon} = \frac{2\zeta_{i1}^{\infty} D_{12} t}{a^2} \sum_{n=0}^{\infty} \exp \left[- \frac{D_{12} (2n+1)^2 \pi^2 t}{4a^2} \right] \quad (24)$$

If

$$\frac{D_{12} \pi^2 t}{4a^2} \geq 0.20 \quad (25)$$

Eq. (24) becomes

$$\lim_{\epsilon \rightarrow 0} \frac{\partial \xi}{\partial \epsilon} = \frac{2\zeta_{i1}^{\infty} D_{12} t}{a^2} \exp \left[- \frac{D_{12} \pi^2 t}{4a^2} \right] \quad (26)$$

At the optimum time of separation, t_{opt} (2),

$$t_{\text{opt}} = \frac{4a^2}{\pi^2} \frac{\ln (D_{22}/D_{12})}{D_{22} - D_{12}} \quad (27)$$

the maximum extent of separation corresponding to Eq. (26) is

$$\xi_{\text{max}} = \frac{8}{\pi^2} \zeta_{i1}^{\infty} e^{-1\epsilon} \quad (28)$$

D. Elution Chromatography

If the standard deviation, σ , in Eq. (22) of Ref. 3,

$$\xi_{\text{opt}} = \text{erf} \left\{ \text{abs} \left[\frac{v_m t}{\sigma \sqrt{8}} \left(\frac{1}{1+K_1} - \frac{1}{1+K_2} \right) \right] \right\} \quad (29)$$

is independent of K_i , the value of the function in Eq. (4) is

$$\lim_{\epsilon \rightarrow 0} \frac{\partial \xi_{\text{opt}}}{\partial \epsilon} = \frac{v_m t}{\sigma \sqrt{2\pi}} \frac{K_1}{(1+K_1)^2} \quad (30)$$

For $K_{1\text{opt}} = 1$, Eq. (30) becomes

$$\xi_{\text{max}} = \frac{v_m t}{4\sigma \sqrt{2\pi}} \epsilon \quad (31)$$

If, on the other hand, the standard deviation is given by the equation

$$\sigma = \sqrt{2D_{1\text{eff}} t} = \sqrt{\frac{2D_{12} t}{1+K_1}} \quad (32)$$

the equations corresponding to Eqs. (30) and (31) are, respectively,

$$\lim_{\epsilon \rightarrow 0} \frac{\partial \xi_{\text{opt}}}{\partial \epsilon} = \frac{v_m t}{2\sigma\sqrt{2\pi}} \frac{K_1}{(1 + K_1)^2} \quad (33)$$

$$\xi_{\text{max}} = \frac{v_m t}{9\sigma\sqrt{2\pi}} \epsilon \quad (34)$$

where $K_{1\text{opt}}$ is now equal to two,

$$K_{1\text{opt}} = 2 \quad (35)$$

E. Crosscurrent Distribution with Discrete Equilibrium Contacts

Equation (13) in Ref. 4,

$$\xi = \text{abs} \left[\frac{1}{(1 + K_1)^N} - \frac{1}{(1 + K_2)^N} \right] \quad (36)$$

leads to

$$\lim_{\epsilon \rightarrow 0} \frac{\partial \xi}{\partial \epsilon} = \frac{NK_1}{(1 + K_1)^{N+1}} \quad (37)$$

At the optimum value of K_1 ,

$$K_{1\text{opt}} = \frac{1}{N} \quad (38)$$

Eq. (37) becomes

$$\xi_{\text{max}} = \left(\frac{N}{N+1} \right)^{N+1} \epsilon \quad (39)$$

F. Crosscurrent Distribution with Differential Contact

For a separation quotient of

$$\alpha = \frac{K_2^0}{K_1^0} \quad (40)$$

where

$$K_i^0 = \kappa_{i2} \frac{V_2^0}{V_1^0} \quad (41)$$

κ_{i2} is a partition coefficient, and V_i^0 is the total volume of the contact-phase, Eq. (22) in Ref. 4,

$$\xi = \text{abs} [e^{-K_1^0} - e^{-K_2^0}] \quad (42)$$

yields

$$\lim_{\epsilon \rightarrow 0} \frac{\partial \xi}{\partial \epsilon} = K_1^0 e^{-K_1^0} \quad (43)$$

and

$$\xi_{\max} = e^{-1} \epsilon \quad (44)$$

G. Countercurrent Distribution with Discrete Equilibrium Contacts (Binomial Distribution)

The extent of separation for the Craig countercurrent apparatus is given by Eq. (33) in Ref. 4,

$$\xi_{\text{opt}} = \sum_{r=0}^{r_{\text{opt}}} \frac{N!}{(N-r)!r!} \text{abs} \left[\frac{K_1^r}{(1+K_1)^N} - \frac{K_2^r}{(1+K_2)^N} \right] \quad (45)$$

The function in Eq. (4) is therefore

$$\lim_{\epsilon \rightarrow 0} \frac{\partial \xi_{\text{opt}}}{\partial \epsilon} = \sum_{r=0}^{r_{\text{opt}}} \frac{N!}{(N-r)!r!} \frac{K_1^r}{(1+K_1)^N} (r_{\text{opt}} - r) \quad (46)$$

where

$$r_{\text{opt}} = \frac{K_1 N}{1 + K_1} \quad (47)$$

For $K_{1\text{opt}} = 1$, Eq. (46) simplifies to

$$\xi_{\max} = \epsilon \sum_{r=0}^{N/2} \frac{N!}{2^N (N-r)!r!} \left(\frac{N}{2} - r \right) \quad (48)$$

H. Countercurrent Distribution with Differential Contact (Poisson Distribution)

Equations (40) and (41) also apply to the Poisson distribution. Equation (45) in Ref. 4,

$$\xi_{\text{opt}} = \sum_{r=0}^{r_{\text{opt}}} \frac{1}{r!} \text{abs} [K_1^{0r} e^{-K_1^0} - K_2^{0r} e^{-K_2^0}] \quad (49)$$

leads to

$$\xi_{\max} = \epsilon \sum_{r=0}^{r_{\text{opt}}} \frac{1}{r!} K_1^{0^r} e^{-K_1^0} (r_{\text{opt}} - r) \quad (50)$$

where

$$r_{\text{opt}} = K_1^0 \quad (51)$$

I. Countercurrent Multistage Distribution, No Reflux

For a countercurrent multistage column operated at no reflux, Eq. (15) in Ref. 5,

$$\xi = \text{abs} \left[\frac{\dot{K}_1^m - 1}{\dot{K}_1^{n+m} - 1} - \frac{\dot{K}_2^m - 1}{\dot{K}_2^{n+m} - 1} \right] \quad (52)$$

yields

$$\lim_{\epsilon \rightarrow 0} \frac{\partial \xi}{\partial \epsilon} = \frac{\dot{K}_1^m}{(\dot{K}_1^{n+m} - 1)^2} [n\dot{K}_1^{n+m} - (n+m)\dot{K}_1^n + m] \quad (53)$$

For a symmetrical column ($n = m$), Eq. (53) becomes

$$\lim_{\epsilon \rightarrow 0} \frac{\partial \xi}{\partial \epsilon} = \frac{n\dot{K}_1^n}{(1 + \dot{K}_1^n)^2} \quad (54)$$

and, for $\dot{K}_{1\text{opt}} = 1$,

$$\xi_{\max} = \frac{n}{4} \epsilon \quad (55)$$

J. Countercurrent Multistage Distribution, Total Reflux

The equation for a multistage column operated at total reflux (5),

$$\xi = \text{abs} \left[\frac{1}{\dot{K}_1^{n+m-1} + 1} - \frac{1}{\dot{K}_2^{n+m-1} + 1} \right] \quad (56)$$

gives

$$\lim_{\epsilon \rightarrow 0} \frac{\partial \xi}{\partial \epsilon} = \frac{\dot{K}_1^{n+m-1}}{(1 + \dot{K}_1^{n+m-1})^2} (n + m - 1) \quad (57)$$

and, for $\dot{K}_{1\text{opt}} = 1$,

$$\xi_{\max} = \frac{n + m - 1}{4} \epsilon \quad (58)$$

K. Steady-State Cataphoresis

The extent of separation in a parallel-plate cataphoresis apparatus operated at steady state (θ),

$$\xi = \text{abs} \left[\frac{A_1}{\beta_1} (1 - e^{-\beta_1 \eta_c}) - \frac{A_2}{\beta_2} (1 - e^{-\beta_2 \eta_c}) \right] \quad (59)$$

leads to, for α defined by Eq. (10) and large values of β_i ,

$$\lim_{\epsilon \rightarrow 0} \frac{\partial \xi}{\partial \epsilon} = \beta_1 \eta_c e^{-\beta_1 \eta_c} \quad (60)$$

where

$$A_i = \frac{\beta_i}{1 - e^{-\beta_i}} \quad (61)$$

At the optimum cutpoint, η_{opt} ,

$$\eta_{\text{opt}} = \frac{\ln A_2/A_1}{\beta_2 - \beta_1} \quad (62)$$

Eq. (60) reduces to Eq. (44)

$$\xi_{\text{max}} = e^{-1\epsilon} \quad (44)$$

L. Field-Flow Cataphoresis

The final separation technique that we will theoretically treat is field-flow cataphoresis, one of a family of nonpartitioning techniques that are analogues of elution chromatography (6, 9). For large values of β_i , the optimum extent of separation (θ),

$$\xi_{\text{opt}} = \text{erf} \left\{ \text{abs} \left[\frac{6v_{\text{mt}}}{\sigma\sqrt{8}} \left(\frac{\beta_1 \coth \frac{\beta_1}{2} - 2}{\beta_1^2} - \frac{\beta_2 \coth \frac{\beta_2}{2} - 2}{\beta_2^2} \right) \right] \right\} \quad (63)$$

simplifies to

$$\xi_{\text{opt}} = \text{erf} \left\{ \text{abs} \left[\frac{6v_{\text{mt}}}{\sigma\sqrt{8}} \left(\frac{\beta_1 - 2}{\beta_1^2} - \frac{\beta_2 - 2}{\beta_2^2} \right) \right] \right\} \quad (64)$$

The function in Eq. (4) is therefore

$$\lim_{\epsilon \rightarrow 0} \frac{\partial \xi_{\text{opt}}}{\partial \epsilon} = \frac{6v_{\text{mt}}}{\sigma\sqrt{2\pi}} \frac{\beta_1 - 4}{\beta_1^2} \quad (65)$$

At the optimum value of beta,

$$\beta_{\text{opt}} = 8 \tag{66}$$

Eq. (65) becomes

$$\xi_{\text{max}} = \frac{3v_mt}{8\sigma\sqrt{2\pi}} \epsilon \tag{67}$$

an equation which is similar in form to Eq. (31).

DISCUSSION

In the preceding sections we have calculated the extent of separation, under the condition of close separations, for twelve different separation techniques. In effect, we have linearized the extent-of-separation equation for each separation system to the form

$$\begin{matrix} \text{extent of separation} \\ \text{(dimensionless)} \end{matrix} = \begin{matrix} \text{amplification factor} \\ \text{(dimensionless)} \end{matrix} \times \begin{matrix} \text{difference in} \\ \text{physical properties} \\ \text{(dimensionless)} \end{matrix} \tag{69}$$

TABLE 1
Summary of Equations

Separation technique	Functional form for $\lim_{\epsilon \rightarrow 0} \frac{\partial \xi}{\partial \epsilon}$	Maximum extent of separation for small ϵ
A. Single equilibrium stage	Eq. (13)	Eq. (14)
B. Rate-controlled single equilibrium stage	Eq. (19)	Eq. (21)
C. Diffusion-controlled single equilibrium stage	Eq. (24)	Eq. (28)
D. Elution chromatography	Eq. (30)	Eq. (31)
	Eq. (33)	Eq. (34)
E. Crosscurrent distribution with discrete equilibrium contacts	Eq. (37)	Eq. (39)
F. Crosscurrent distribution with differential contact	Eq. (43)	Eq. (44)
G. Countercurrent distribution with discrete equilibrium contacts (binominal distribution)	Eq. (46)	Eq. (48)
H. Countercurrent distribution with differential contact (Poisson distribution)	—	Eq. (50)
I. Countercurrent multistage distribution, no reflux	Eq. (53)	—
	Eq. (54)	Eq. (55)
J. Countercurrent multistage distribution, total reflux	Eq. (57)	Eq. (58)
K. Steady-state cataphoresis	Eq. (60)	Eq. (44)
L. Field-flow cataphoresis	Eq. (65)	Eq. (67)

TABLE 2

Comparison of the Maximum Extent of Separation that can be Achieved for Different Separation Techniques

Separation technique	Value of ξ_{\max}/ϵ
A. Single equilibrium stage	0.25
B. Rate-controlled single equilibrium stage ^a	0.37
C. Diffusion-controlled single equilibrium stage ^b	0.30
D. Elution chromatography ^c	$0.10(v_m t/\sigma)$
E. Crosscurrent distribution with discrete equilibrium contacts ^d	$0.044 (v_m t/\sigma) \left(\frac{N}{N+1}\right)^{N+1}$
F. Crosscurrent distribution with differential contact	0.37
G. Countercurrent distribution with discrete equilibrium contacts (binominal distribution) ^e	$0.20\sqrt{N}$
H. Countercurrent distribution with differential contact (Poisson distribution) ^f	$0.40\sqrt{K_1^0}$
I. Countercurrent multistage distribution, no reflux ^g	$0.25n$
J. Countercurrent multistage distribution, total reflux	$0.25(n+m-1)$
K. Steady-state cataphoresis	0.37
L. Field-flow cataphoresis	$0.15 (v_m t/\sigma)$

^a For $\zeta_{12}^\infty = 1$ in Eq. (21).

^b For $\zeta_{11}^\infty = 1$ in Eq. (28).

^c Eq. (31).

^d Eq. (34).

^e For large N in Eq. (48).

^f For large K_1^0 in Eq. (50).

^g Eq. (55).

The results of the calculations can therefore be summarized either by

$$\xi = \frac{\text{function of}}{\text{physical parameters}} \times \epsilon \tag{70}$$

(see Table 1) or, if the maximum value of the extent of separation is desired, by

$$\xi_{\max} = \frac{\text{optimized function of}}{\text{physical parameters}} \times \epsilon \tag{71}$$

(see Table 2). Equations (69) through (71) clearly state that the best choice of a separation process is one for which the amplification factor and the difference in physical properties are *both* as large as possible.

Table 2 permits a comparison of all of the separation techniques on a quantitative, and equivalent, basis. For example, if we choose 0.25ϵ as the maximum value of the extent of separation for a single-stage separation process (see A in Table 2) and assume that ϵ has a constant

value for all separation processes, we arrive at the following conclusions:

1. Separation techniques A, B, C, F, and K are all, *at best*, single stage techniques.
2. For large values of N , the number of times the multiple contacting procedure is performed, technique F yields, *at best*, a separation equivalent to four stages.
3. The powerful separation techniques are D, G, H, I, J, and L—the countercurrent, multistage, chromatographic, and field-flow techniques.
4. Countercurrent multistage systems are more efficient than countercurrent distribution systems that rely on discrete equilibrium contacts. In the former, the maximum extent of separation is proportional to n , the number of stages in the extraction or washing sections of the column, whereas in the latter, the maximum extent of separation is proportional to the square root of N , the number of times the multiple contacting procedure is performed.
5. For $n = m$ and $\dot{K}_{\text{opt}} = 1$, countercurrent multistage distribution is about twice as effective at total reflux as at zero reflux.
6. For $N = 100$, technique G yields, *at best*, a separation equivalent to eight stages.
7. For $n = m = 50$, techniques I and J yield, *at best*, separations equivalent to 50 and 99 stages, respectively.
8. Elution chromatography and field-flow cataphoresis readily exhibit their close relationship and lead to comparable separations for identical values of the quantity, v_{mt}/σ .
9. For values of v_{mt}/σ ranging between 10 and 100 and $K_{\text{opt}} = 1$, techniques D and L yield separations equivalent to between 4 and 60 stages.

A formula for calculating the number of stages, $n + m - 1$, in an elution chromatographic system can be obtained by equating Eqs. (31) and (58) to each other to yield (for $K_{\text{opt}} = \dot{K}_{\text{opt}} = 1$)

$$n + m - 1 = \frac{1}{\sqrt{2\pi}} \left(\frac{v_{mt}}{\sigma} \right)^2 \quad (72)$$

This new definition represents the number of stages in a countercurrent multistage column (operated at total reflux) that are required to obtain a separation identical to that achieved in the chromatographic system. Equation (72) can be compared to the commonly used definition for the “number of theoretical plates” in a chromatographic system, n' ,

$$n' = \left(\frac{1}{1 + K_1} \right)^2 \left(\frac{v_m t}{\sigma} \right)^2 \quad (73)$$

(the standard deviation, σ , in Eqs. (72) and (73) has units of length). For $K_{1\text{opt}} = 1$ and $v_m t / \sigma = 100$, Eqs. (72) and (73) yield $n + m - 1 = 40$ stages and $n' = 2500$ theoretical plates, respectively.

We now have the problem of deciding which value—40 stages or 2500 theoretical plates—is a more realistic description for the separating power of the chromatographic system. The answer is quite clear: Only the definition for the number of stages given by Eq. (72) is realistic. Equation (73) has physical significance, however; it is a measure of the relative rates of separation and mixing in the chromatographic system,

$$2n' = \frac{\text{rate of separation}}{\text{rate of mixing}} \quad (74)$$

In the field of chemical engineering, this ratio has been defined for several decades as the Peclet number, Pe ,

$$Pe = \frac{2}{(1 + K_1)^2} \left(\frac{v_m t}{\sigma} \right)^2 = 2n' \quad (75)$$

In view of the above, we have ample justification for suggesting that the old definition for the number of theoretical plates, Eq. (73), be replaced by our new definition for the number of stages, Eq. (72). Rather than doing so, we instead propose that the term, theoretical plate, no matter what form it takes, be abandoned altogether in favor of the approach summarized in this paper. While the concepts of theoretical plates and peak resolution can be extended to any differential migration technique [as Giddings has recently done for electrophoresis and sedimentation (10) and as can be done for mass spectroscopy], such systems are also easily handled by the present approach. The question we must ask ourselves is whether we will live with the scattered theory that presently exists, or whether we will find common denominators in all separation techniques and gradually merge the individual separation theories into a unifying approach. We naturally favor the latter alternative and strongly feel that the consolidation of separation theories will eventually become a reality.

List of Symbols

2a	thickness of membrane (cm)
A	defined by Eq. (61)

c	concentration (moles/cm ³)
c^+	ion concentration (moles/cm ³)
D	diffusion coefficient (cm ² /sec)
D^+	ion diffusion coefficient (cm ² /sec)
E	field strength (V/cm)
k	sum of the forward and reverse pseudo-first-order rate constants (sec ⁻¹)
K	distribution coefficient for a closed system (moles/moles)
\bar{K}	distribution coefficient for an open system (moles/moles)
K^0	distribution coefficient (moles/moles)
l	distance between parallel electrodes (cm)
m	number of stages in the "washing" section
n	number of stages in the "extraction" section
n'	number of theoretical plates (old definition)
N	cycle number
r	tube number
t	time (sec)
v_m	molar velocity of mobile phase (cm/sec)
V	molar velocity (cm/sec)
V^0	total volume of contacting phase (cm ³)
x	mole fraction
y	mole fraction

Greek Letters

α	separation quotient
α'	separation factor
β	electrostatic Peclet number
ζ^∞	extent of segregation at infinite time (equilibrium)
η	dimensionless distance in a steady-state cataphoresis apparatus
η_i	Murphree stage efficiency
κ	partition coefficient (moles/cm ³ :moles/cm ³)
μ^+	mobility of minority ion (cm ² /V-sec)
ξ	extent of separation
σ	standard deviation (cm)

Subscripts

c	cutpoint
i	component i

i_{eff}	effective value for component i
i_j	component i in region j
max	maximum value
opt	optimum value
lopt	optimum value for component 1
1, 2	specific components
i_1, i_2	
22, etc.	specific component-region combinations

REFERENCES

1. P. R. Rony, *Separ. Sci.*, **3**, 239 (1968).
2. P. R. Rony, *ibid.*, **3**, 519 (1968).
3. P. R. Rony, *ibid.*, **3**, 357 (1968).
4. P. R. Rony, *ibid.*, **4**, 493 (1969).
5. P. R. Rony, *ibid.*, **5**, 1 (1969).
6. P. R. Rony and F. H. Shair, *ibid.*, to be submitted.
7. H. R. C. Pratt, *Countercurrent Separation Processes*, Elsevier, New York, 1967, p. 10.
8. M. Benedict and T. H. Pigford, *Nuclear Chemical Engineering*, McGraw-Hill, New York, 1957, p. 492.
9. J. C. Giddings, *Separ. Sci.*, **1**, 123 (1966).
10. J. C. Giddings, *ibid.*, **4**, 181 (1969).

Received by editor November 29, 1969