R_{loop} = reliability of a coolant loop
R_{pipe} = reliability of the coolant piping
R_{pumps} = reliability of the pump(s) in a loop
R_{sgs} = reliability of the steam generator(s) in a loop
θ = uniform random number between zero and one

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Manuscript received June 11, and accepted July 29, 1976.

Equilibrium Staged Parametric Pumping

I. Single Transfer Step per Half-cycle and Total Reflux—the Analogy with Distillation

Equilibrium staged batch parametric pumps are studied with nonlinear isotherms. The half cycle is composed of one single equilibration step and one discrete transfer. The limiting regime (for infinite number of cycles) is shown to correspond to a staircase construction between the two isotherms, the number of steps being equal to the number of stages. The reservoir concentrations are then connected by Fenske's equation. Several analogies with binary total reflux distillation are suggested.

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SCOPE

Parametric pumping is a separation technique based on the periodic movement of a fluid phase over a solid adsorbent bed and a coupled energy input into the system to effect the separation. The most common form of parametric pumping is one in which a packed bed of adsorbent, undergoing a cyclic temperature change, is subjected to a synchronous, alternating, axial flow. The variation of adsorptivity with temperature and the synchronized relative motion of the fluid over the fixed phase makes possible the enrichment of a given component at one end of the column and its depletion at the other end. In this form, parametric pumping was first described by Wilhelm et al. (1966). Since this paper, several similar processes have been described and studied, including continuous, semicontinuous, and nonthermal processes.

The scope of the present paper may be explained by the following key words, in addition to parametric pumping:

1. Finite staging. The continuous column of Wilhelm's scheme is here replaced by a cascade of discrete stages; the number of these stages is finite and in some examples small.

2. Discrete transfer. The continuous flow of Wilhelm's

scheme is replaced by discrete transfer of given volumes of fluid from each stage to the next.

3. Equilibrium. Equilibrium is allowed on each stage after the fluid transfer.

4. Batch. After the initial load, no feed nor withdrawal occur.

5. Direct mode. The temperature change is simultaneous in all stages.

6. Single transfer per half cycle. In other words, only one equilibration occurs in any stage at each temperature. This is a limiting case.

7. Nonlinear isotherms. Described either analytically, or by an experimental curve. (The case of linear isotherms appears then as a particular case.)

This voluntarily restricted scope is justified by the mainly didactic and qualitative objectives of this paper, which are twofold. First, improve the understanding of parametric pumping by offering a visualization of the mechanism of separation, by tying it with familiar concepts of chemical engineering (equilibrium stage, operating line, reflux) and by showing the analogy with distillation. Second, open up new areas of research by illustrating the possibility of carrying out parametric pumping other than in a chromatographic column.

The article starts from the discrete transfer equilibrium stage model of Wankat (1973) in its simplest version, the single-stage model. This allows a graphical visualization of how the separation builds up in time and converges toward a limit regime (maximum separation) and shows that a single stage already achieves some separation. This approach is then extended to two and more stages.

The example of binary ion exchange is discussed in which the temperature dependent isotherms are described by constant separation factors (simple mass action law). In this case, an analytical solution for the limit regime is given for N stages.

CONCLUSIONS AND SIGNIFICANCE

A simple equilibrium model of stage batch parametric pumping with nonlinear isotherms is presented for the case of a single transfer per half cycle. Using the single-stage and the two-stage models, we show by graphical construction on the equilibrium diagram how the separation builds up. In the general case of N stages, a simple limit regime is found when the number of cycles becomes large. In this limit regime, all concentrations of the different liquid and solid fractions are constant. These concentrations are connected by a staircase construction between the two isotherms, each step corresponding to one stage. This result also applies to linear isotherms. For isotherms described by a constant separation factor, the limit concentrations of the top and bottom reservoirs are connected by Equation (11), which is identical to Fenske's equation in distillation.

Several analogies between this particular mode of parametric pumping and total reflux distillation are then suggested for binary systems. In particular, the temperature on a distillation plate is analogous to the solid phase concentration in a stage of the parametric pump, and the relative volatility is analogous to the ratio of the equilibrium constants at the two temperatures. The meaning of the notion of reflux used in parametric pumping is thus clarified. An analytical solution of the limit regime and thus of the limit separation is given as a function of the number of stages and of the initial conditions. It is shown that the existence of a dead volume in the reservoirs does not modify the form of the limit regime. Finally, calculated examples indicate that the speed of convergence toward the limit regime decreases as the number of stages and the dead volume increase, that this speed is practically independent of the initial conditions, and that it goes through a maximum when the capacity ratio ρ is close to 1.

The significance of this approach lies in particular in its simplicity and in the further developments that is suggests. The simple concepts on which it is based allow, we believe, a better understanding of the mechanism of separation than other published models and furnish a didactic tool for explaining parametric pumping. In addition, this approach provides a model for real, physically staged parametric pumps (such as a plate column or a cascade of tanks). As presented here, it does not constitute a suitable model for packed-bed operation because of the restriction of a single transfer per half cycle.

It should thus not be compared to a packed-bed model. This restriction has been imposed here as it greatly simplifies the calculation and the graphical construction and leads to a straightforward analogy with distillation.

In a forthcoming paper, we shall consider several transfers per half cycle; some of the simplicity of the present paper will then be lost, in particular, the simple analogy with distillation. However, a variety of modes of contact of the two phases appears which opens up new areas for investigation.

The first theoretical analysis of parametric pumping was developed by Wilhelm et al. (1968) with a sophisticated model which rather obscured the reasons of the separation. The next advance was the linear local equilibrium theory developed by Pigford et al. (1969) and generalized by Aris (1969). Axial dispersion was neglected in this model. The hyperbolic partial differential equation was solved analytically by the method of characteristics. The characteristic lines can be used to show graphically the development of the separation. An equation was obtained giving the separation factor vs. the number of cycles. Simultaneously with Pigfords equilibrium theory, Sweed and Wilhelm (1969) developed the stop-go algorithm: flow without interphase transfer and then transfer of solute between phases without flow. The isotherms do not have to be linear, and the two phases are not assumed to be in equilibrium. The resolution required numerical computer calculations. Rhee and Amundson (1970) succintly analyzed the effect of the nonlinearity of the isotherms and suggested that the separation is limited in this case. They showed graphically on the equilibrium diagram how the separation occurs. Patrick et al. (1972) also utilized the equilibrium diagram for a qualitative understanding of the separation. Wankat (1973) utilized two equilibrium staged theories for a continuous flow parametric pump and for a parametric pump with discrete transfer and equilibrium steps. This latter technique is similar to the stop-go algorithm. Wankat assumed linear equilibrium and solved the material balances from cycle to cycle by direct computer substitution. While this article was being written, Camero and Sweed (1976) presented a quite general nonlinear equilibrium theory for column parapumps (equivalent to an infinite number of stages).

The objective of the present paper is in part didactic:

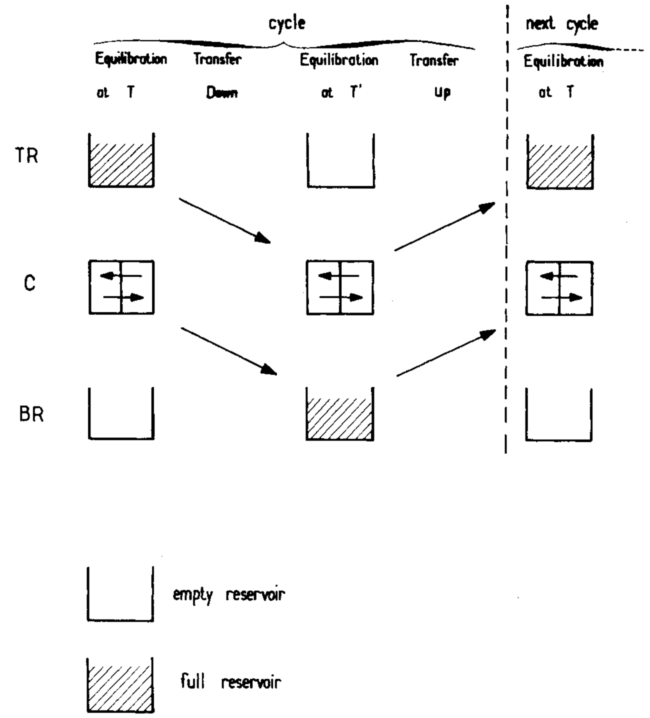

Fig. 1. Description of a single-stage parametric pump and of its operating cycle.

to bring a better understanding and a visualization of the mechanism of separation in parametric pumping by the use of familiar concepts of chemical engineering. We believe that the approach presented here, although it provides a model for staged systems only and not for the classical column type of operation, does give much insight into the mechanism of separation, even in the latter case. In addition, it allows us to incorporate isotherm nonlinearity without further complication. The approach presented here starts from Wankat's discrete transfer equilibrium stage model, but we include nonlinear isotherms, either experimental or analytically described. However, instead of aiming at computational results, we search for simple graphical and analytical solutions. To do this, we start with the simplest version of Wankat's model: the single-stage model.

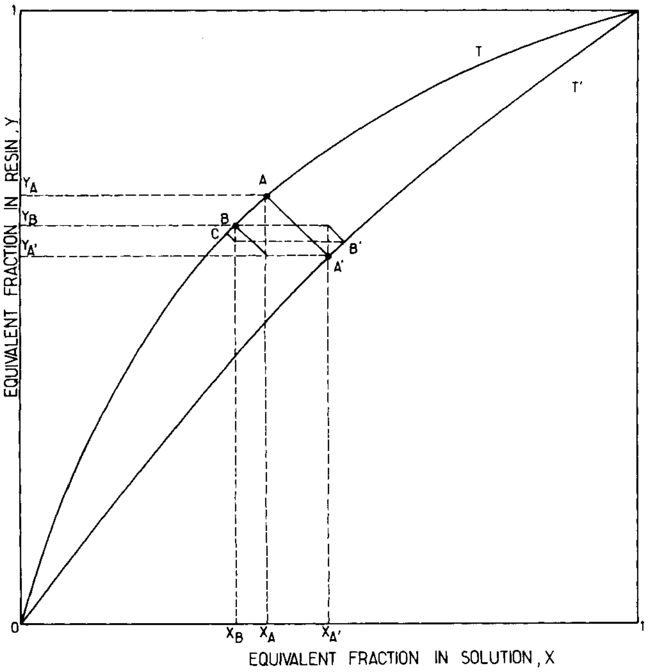

Fig. 2. McCabe-Thiele representation of the first cycles of a single-stage parametric pump.

SINGLE-STAGE PARAMETRIC PUMP

Description

This pump comprises one cell (or stage) *C*, containing the ion exchange resin, a top reservoir *TR*, and a bottom reservoir *BR* (Figure 1). The liquid is divided into two equal fractions. One cycle of the operation is defined as follows:

1. Equilibration at *T* (start of cycle). The liquid fractions are in *TR* and in cell *C*; in *C*, the solid and the liquid are in equilibrium at temperature *T*.
2. Transfer down. The liquid fraction contained in *C* is transferred into *BR*; the fraction contained in *TR* is transferred into *C*.
3. Equilibration at *T'*. The temperature of the cell is changed to *T'*, and the two phases are allowed to equilibrate at this new temperature.
4. Transfer up. The liquid fractions are brought back to their initial position (end of cycle).

The next cycle will thus begin with a reequilibration in *C* at temperature *T*.

McCabe-Thiele Representation

Let x and y be the liquid and solid phase mole fractions or equivalent fractions, respectively, of the preferred ion. The process described above may then be represented in an (x, y) diagram. We first draw equilibrium isotherms at the two temperatures T and T' (Figure 2), using either experimental data or analytical expressions of the general form

$$y = f_T(x) \qquad y = f_{T'}(x) \qquad (1, 2)$$

At the start of the first cycle, we suppose that the two liquid fractions have the same concentration x_A and that the cell is in equilibrium at T, the resin concentration being y_A (Table 1). The cell composition is thus represented by point A on Figure 2.

The transfer down brings the fraction x_A from *TR* in contact with the resin at y_A. The switch from T to T' and the reequilibration then leads to a new composition in the cell $(x_{A'}; y_{A'})$, represented by point A'. This point A' is located at the intersection of the T' isotherm and of the operating segment representing the mass balance constraint

$$\rho x_A + y_A = \rho x_{A'} + y_{A'} \qquad (3)$$

with

$$\rho = CV/Q \qquad (4)$$

The operating segment connects points A and A', and its slope is $-\rho$. The composition $(x_{A'}; y_{A'})$ can also be determined analytically by solving the system of Equations (2) and (3), if the equation of the isotherm is available.

The next step is the transfer up of the liquid fractions, which brings fraction x_A from *BR* in contact with the resin at $y_{A'}$. The composition of the cell is represented by the point $(x_A; y_{A'})$ (not in equilibrium). The first cycle is completed.

The first step of the second cycle (Table 1) is the equilibration at T. The cell composition is represented by point B, intersection of the T isotherm and of the operating segment through $(x_A; y_{A'})$ and of slope $-\rho$. The top reservoir *TR* contains a fraction at $x_{A'}$.

A certain separation is already observed, as the two liquid fractions originally both at x_A are now $x_{A'}$ and x_B, respectively, such that $x_B < x_A < x_{A'}$. Notice the change of the resin composition from y_A to y_B, indicating that the enrichment of one liquid fraction is not simply opposite to the depletion of the other.

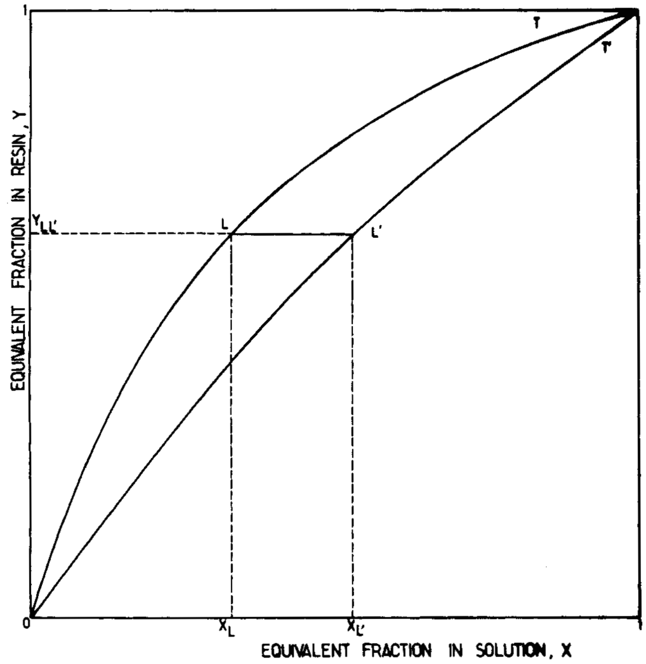

Fig. 3. The limit regime of a single-stage parametric pump.

Convergence of the Single-Stage Model Limit Regime

The reader may now easily construct the following cycles on the McCabe-Thiele diagram, as shown on Figure 2. It can be seen that the open quadrilateral representing each cycle (that is, the path going from B to B', and then C) tends to flatten out; it converges asymptotically toward a *simple horizontal* segment LL' as the number of cycles becomes infinite (Figure 3).

The physical meaning of this limiting regime is the following. The solid has a constant composition at any time of the cycle; this composition is the y value $y_{LL'}$ of the horizontal segment LL'. The compositions of the solutions in TR at T and in BR at T' are represented by the values $x_{L'}$ and x_L, respectively.

In this way, when the fraction of composition $x_{L'}$ (respectively x_L) is brought in contact with the resin, and the temperature brought to T' (respectively T), the equilibrium is reached without any mass transfer between the two phases. The length of the operating segments is zero.

Separation

It is clear that the separation obtained with the single-stage pump is limited and small. The amount of resin used and the concentration and volume of solution used have little effect on the limiting concentrations x_L and $x_{L'}$ (inasmuch as these factors do not affect the isotherms). However, the speed of convergence toward the limiting regime strongly depends on ρ.

The separation varies with $y_{LL'}$ and depends on the spacing between the two isotherms. Here it goes through a maximum at some intermediate value of $y_{LL'}$. The final composition $y_{LL'}$ depends on the overall material content of the system and may be obtained through a material balance between the initial and final states, as the system is closed to matter. This is obtained quantitatively further on in this paper.

TWO-STAGE PARAMETRIC PUMP

Description (Figure 4)

This model comprises two cells C_1 and C_2 containing the same amount of resin and three equal fractions of liquid. A top reservoir TR and a bottom reservoir BR collect alternately the fraction which leaves one of the cells at each half cycle.

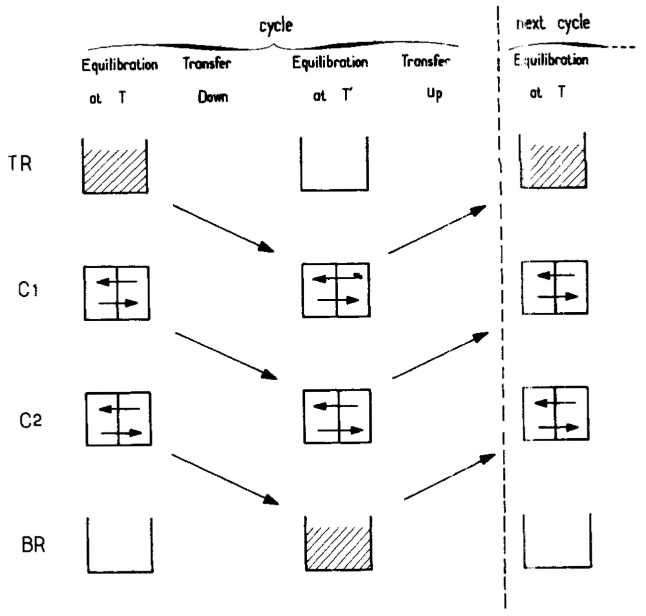

Fig. 4. Description of a two-stage parametric pump and of its operating cycle.

A cycle is described as follows:

1. Equilibrium at T (start of cycle). The liquid fractions are contained in TR, C_1, and C_2. Equilibrium is established in each cell at T.
2. Transfer down. The content of C_2 goes to BR. The content of C_1 goes to C_2. The content of TR goes to C_1.
3. Equilibrium at T'. The temperature is switched to T', and reequilibration is allowed.
4. Transfer up. Symmetrically to the transfer down, this brings the fractions back to their initial position. This ends the first cycle. The next one will start with a switch to T and reequilibration of C_1 and C_2.

McCabe-Thiele Representation

The history of the concentrations in the various parts of the system can be represented in the (x, y) plane through a construction similar to that described for the single-stage model. Figure 5 shows the graphical construction for the three first cycles. We leave to the reader the establishment of the corresponding algorithm, on the model of Table 1 but with two cells.

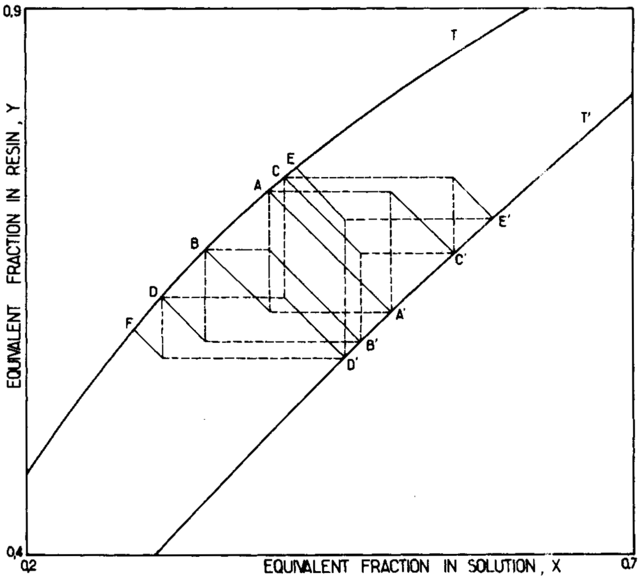

Fig. 5. McCabe-Thiele representation of the three first cycles of a two-stage parametric pump.

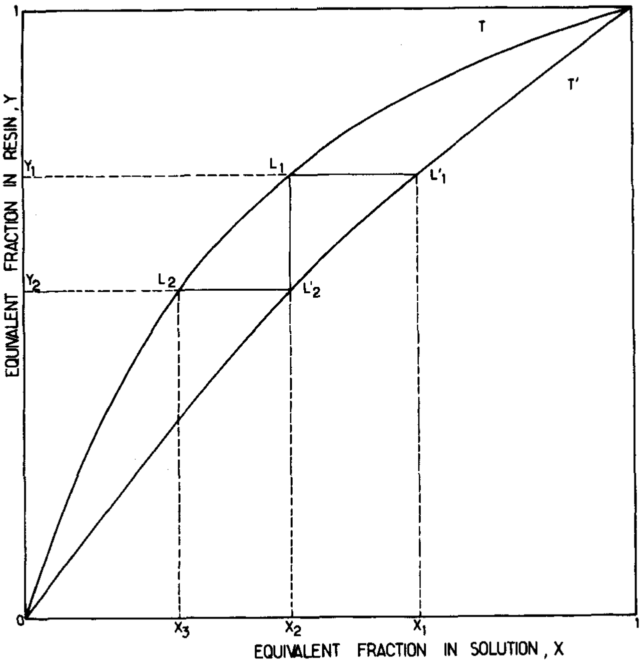

Fig. 6. The limit regime of a two-stage parametric pump.

The initial state has been chosen uniform; both cells have the same composition (x_A; y_A), represented by point A on the T isotherm, and the fraction contained in TR has the concentration x_A.

As an example, let us construct point D. The equilibirum in cell C_2 at T' in the second cycle is represented by point B', the transfer up brings the fraction at x_B (previously in BR) in contact with the resin at $y_{B'}$, the operating segment through point (x_B; $y_{B'}$) and of slope $-\rho$ is now drawn, and point D is at its intersection with the T isotherm.

Convergence of the Two-Stage Model Limit Regime

When this same construction is done for several cycles, it appears that the operating segments shorten more and more, and their length tends toward zero; correspondingly, the points representing the two equilibrium states of a cell in a cycle tend to be on a same horizontal (same value of y), for example, in C_2, A and A', B and B', D and D'. Moreover, couples of points such as A' and A, B' and C, D' and E, etc . . ., tend to be on a same vertical (same value of x).

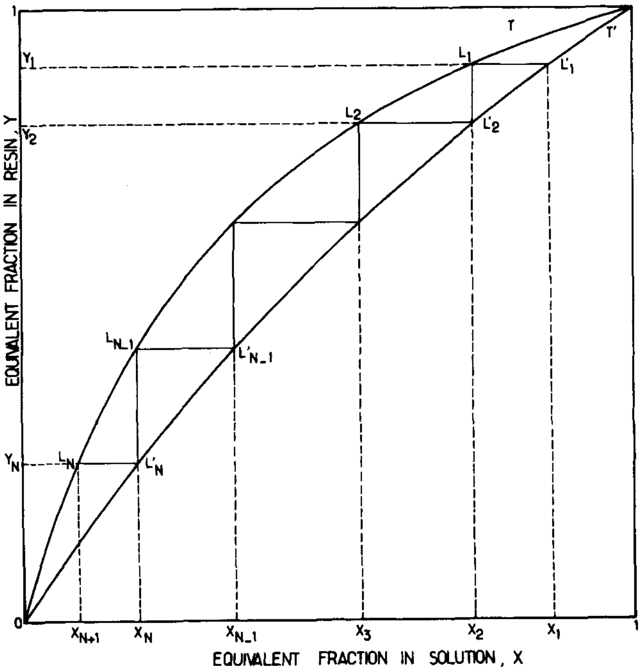

Fig. 7. The limit regime of an N-stage parametric pump.

Table 1. Algorithmic Representation for the Single-Stage Parametric Pump, First Cycle

	Cycle 1				Cycle 2
Operation →	Equilibration at T	Transfer down	Equilibration at T'	Transfer up	Equilibration at T
Symbol →	T	$\downarrow$	T'	$\uparrow$	T
TR	x_A			x_A'	x_A'
C	x_A; y_A	x_A; y_A	x_A'; y_A'	x_A; y_A'	x_B; y_B
BR		x_A	x_A		

After a large number of cycles, the construction converges toward a staircase with two steps between the isotherms (Figure 6). Point L_1 results from the convergence of points A, C, E . . .; similarly we have the series C', E', . . . $\rightarrow L'_1$; A', B', D', . . . $\rightarrow L'_2$; B, D, F, . . . $\rightarrow L_2$.

The successive cycles now become identical; the pump has reached its limiting regime.

The physical meaning of this limit cycle is the following. The concentration of the solid phase in each cell is invariant in this regime (that is, y_1 in C_1, y_2 in C_2). The concentration of each liquid fraction is also invariant (that is, x_1 for the top fraction, x_2 for the intermediate, x_3 for the bottom fraction).

Thus, no mass transfer occurs between solid and liquid in the limit cycle at any time in the cycle. For example, after a transfer up, the concentrations in contact in a cell, say (x_2; y_1) in C_1, are such that they will be in equilibrium at the new temperature T. The concentration x_2 of the intermediate fraction is such that it is in equilibrium with the solid in C_1 at T and with the solid in C_2 at T'.

The operating segments are of zero length.

Separation

Figure 6 shows clearly that the separation obtained with the two-stage pump results from the juxtaposition of the separations of each stage, as in distillation for example. The separation is thus larger than for the single-stage pump; nevertheless, it is limited. It depends on the position of the staircase between the two isotherms and is maximum when the staircase is roughly in the region of largest spacing between the isotherms. The analytical study of the separation is presented further on in this paper for the general case of N stages.

N-STAGE PARAMETRIC PUMP

Description

The N-stage pump is a generalization of the two-stage pump. It comprises N cells, C_1, C_2, . . ., C_N, each containing the same amount of resin. There are two reservoirs, TR and BR, and the liquid phase is divided into $N + 1$ equal fractions. The cycle is identical to the previous cases: equilibration of all cells at T, transfer of all liquid fractions one stage down, equilibration of the cells at T', and transfer of all liquid fractions one stage up.

Convergence-Limit Regime

The McCabe-Thiele construction is made in the same way as described for the one- and two-stage models. After a certain number of cycles, the construction converges toward a limit, represented by an N-step staircase between the two isotherms (Figure 7). If N is large, the graphical construction obviously becomes impractical and highly unprecise as it converges toward the limit cycle. However,

TABLE 2. THE LIMIT CYCLE OF AN N-STAGE PARAMETRIC PUMP

	T	$\downarrow$	T'	$\uparrow$
TR	x_1			x_1
C_1	L_1	$x_1; y_1$	L'_1	$x_2; y_1$
C_2	L_2	$x_2; y_2$	L'_2	$x_3; y_2$
C_{N-1}	L_{N-1}	$x_{N-1}; y_{N-1}$	L'_{N-1}	$x_N; y_{N-1}$
C_N	L_N	$x_N; y_N$	L'_N	$x_{N+1}; y_N$
BR		x_{N+1}	x_{N+1}	

Note: The composition in an equilibrated cell is replaced by the letter representing the corresponding point on Figure 7 (for example, x_2, y_1 is simply replaced by L_1).

the numerical iteration corresponding to this construction presents no difficulty, and we used it to construct the figures of this paper (see Appendix). Table 2 shows the algorithm in limiting regime. The graphical staircase connects the compositions $L_1, L_2, \ldots, L_N$ of the cells in equilibrium at T to the compositions $L'_1, L'_2, \ldots, L'_N$ of the cells in equilibrium at T'.

In the limiting regime, the concentration of the resin in each cell is invariant (and represented by the y value of the segment LL' corresponding to the cell considered; y_1 for C_1, y_2 for C_2, etc ...). The concentration of each liquid fraction is also invariant: $x_1, x_2, \ldots x_{N+1}$.

The operating segments have zero length; no mass transfer occurs between phases at any time in the limit cycle.

Separation

The extreme concentrations obtained with the N-stage parapump are the concentrations of the top and bottom fractions, namely, x_1 and x_{N+1}. Clearly, the limiting separation increases with the number N of stages. The separation obtained with a parapump is thus not limited by equilibrium, even with nonlinear isotherms.[*] A perfect separation clearly requires an infinite number of stages.

Let us now examine analytically the limit separation of an N-stage parapump. (We are not able to do it in the transient operation with our model.) We describe the isotherms by a simple mass action law (constant separation factors). Equations (1) and (2) are thus

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \tag{5}$$

$$y = \frac{\alpha' x}{1 + (\alpha' - 1)x} \tag{6}$$

where α and α' are the separation factors at the respective temperatures T and T'. The isotherms in the figures of this paper correspond to $\alpha = 3.5$ and $\alpha' = 1.5$.

We want to establish an algebraic relationship between the extreme concentrations x_1 and x_{N+1} in limit cycle (Figure 7). To do this, consider the solid phase concentration y of a particular cell, say C_1. To this value y_1 correspond two equilibrium states L_1 and L'_1; the liquid phase concentrations are, respectively, x_2 and x_1, related to each other and to y_1 by Equations (5) and (6) which may be rewritten as

$$y_1 = \frac{\alpha x_2}{1 + (\alpha - 1)x_2} = \frac{\alpha' x_1}{1 + (\alpha' - 1)x_1} \tag{7}$$

from which one obtains

$$x_1 = \frac{(\alpha/\alpha')x_2}{1 + \left(\frac{\alpha}{\alpha'} - 1\right)x_2} \tag{8}$$

This equation shows that the liquid concentrations x_1 and x_2, in equilibrium with the same solid concentration y_1, respectively, at T' and T, are related by an equation of the same form as Equations (5) or (6). x_1 and x_2 play the same role as y and x, respectively, and the ratio α/α' plays the role of the separation factor.

Following the same procedure for cell C_2 at y_2, we obtain

$$x_2 = \frac{(\alpha/\alpha')x_3}{1 + \left(\frac{\alpha}{\alpha'} - 1\right)x_3} \tag{9}$$

Eliminating x_2 between (8) and (9), one obtains

$$x_1 = \frac{(\alpha/\alpha')^2 x_3}{1 + \left[\left(\frac{\alpha}{\alpha'}\right)^2 - 1\right]x_3} \tag{10}$$

a relation between the extreme concentrations of the two first stages, still of the same form, but with $(\alpha/\alpha')^2$ as the separation factor. We proceed to establish a relation such as (9) between x_3 and x_4; x_3 is next eliminated between this relation and (10) to obtain an equation of the same form relating x_1 to x_4, with the separation factor $(\alpha/\alpha')^3$. Proceeding on to the N^{th} stage, we finally obtain

$$x_1 = \frac{(\alpha/\alpha')^N x_{N+1}}{1 + [(\alpha/\alpha')^N - 1]\, x_{N+1}} \tag{11a}$$

or alternately

$$\frac{x_1}{1 - x_1} \quad \frac{x_{N+1}}{1 - x_{N+1}} = \left(\frac{\alpha}{\alpha'}\right)^N \tag{11b}$$

This equation shows that the separation depends only on the ratio α/α' of the separation factors and on the number of stages. Equation (11) may be rewritten to give explicitly the number of stages N required to obtain the desired compositions x_1 and x_{N+1} in the top and bottom reservoir, respectively

$$N = \frac{\ln \frac{x_1}{1 - x_1} - \ln \frac{x_{N+1}}{1 - x_{N+1}}}{\ln \alpha/\alpha'} \tag{12}$$

Analogy With Total Reflux Binary Distillation

Equation (12) is identical to Fenske's equation in which α/α' would represent the relative volatility,[†] x_1 the composition of the distillate (top product), x_{N+1} the composition of the bottoms, N the number of stages (reboiler included), the condenser being total. Similar equations are also obtained in the ideal cascade theory (for instance, Pratt, 1967).

Fenske's equation applies to total reflux binary distillation, and in that case, the McCabe-Thiele construction consists in drawing steps between the vapor-liquid equilibrium curve (described by the constant relative volatility) and the diagonal. We show below that an identical representation may be found in parametric pumping.

We have seen that Equations (8) or (9) are relations between the two x values in equilibrium with a same y at the two temperatures. More generally, we shall write these equations in the form

$$x(T') = \frac{(\alpha/\alpha')x(T)}{1 + \left(\frac{\alpha}{\alpha'} - 1\right)x(T)} \tag{13}$$

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[*] Inasmuch as the isotherms do not cross each other. This result has been controversial for a time (Rhee and Amundson, 1970).

[†] Sweed (1972) already calls volatility the ratio of the slopes of the isotherms, in the linear case.

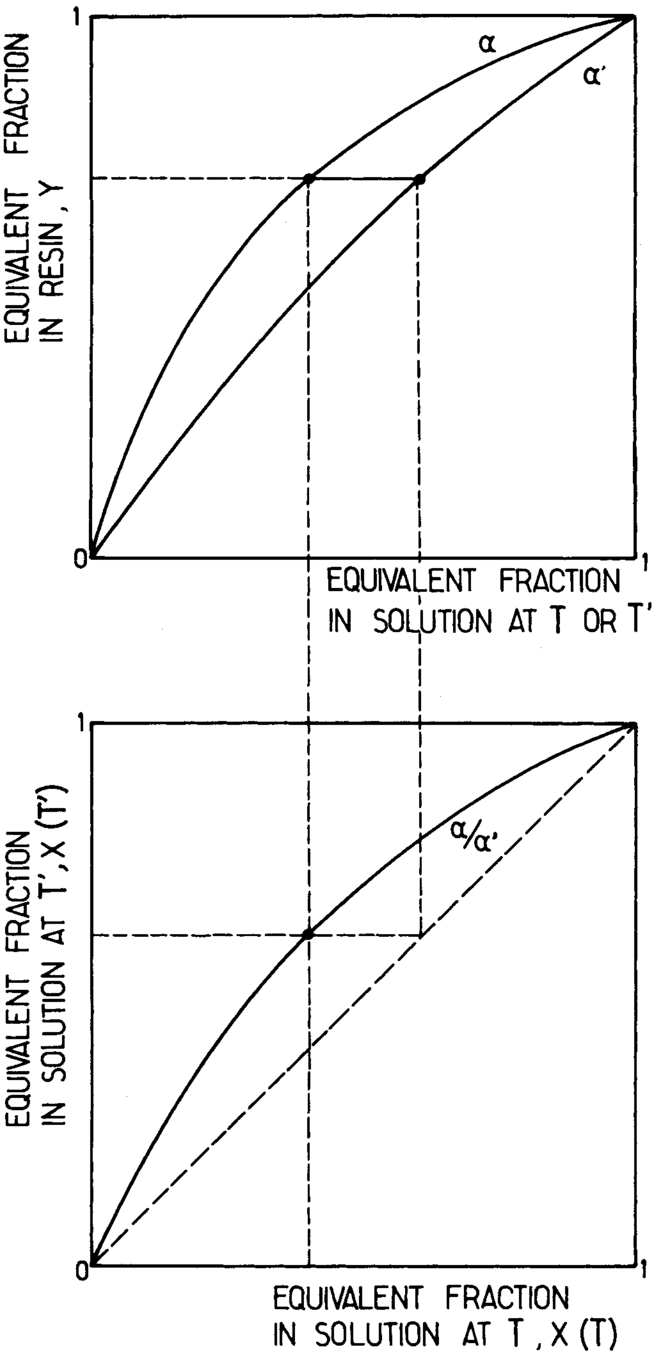

Fig. 8. Representation of the isotherms in the $[x(T), x(T')]$ plane.

Figure 8 shows the curve representing this equation and its relation to the isotherms. The staircase constructions of Figure 7 may now be transposed in the $x(T)$, $x(T')$ plane. The result is shown on Figure 9. The correspondence is established in the following way:

1. The two equilibrium states represented by points L_1 and L'_1 (having the same $y = y_1$) become, on Figure 9, the unique point 1 whose coordinates are $x(T) = x_2$ and $x(T') = x_1$.

2. Similarly, points L_2 and L'_2 of Figure 7 merge into point 2 of Figure 9.

3. In addition, the fact that L_1 and L'_2 on Figure 7 have the same $x = x_2$ entails that $x(T)$ for point 1 equals $x(T')$ for point 2 on Figure 9; point 2 is thus graphically related to point 1 by a single step drawn between the α/α' curve and the diagonal. This is easily generalized, and the construction in the $x(T')$, $x(T)$ plane, corresponding to that of Figure 7, is obtained by drawing steps between the curve of separation factor α/α' and the diagonal in the same way as in distillation.

We can push the analogy a little further by examining the following correspondence:

Batch parametric pump (limit regime)	Total reflux distillation (steady state)
1. Liquid phase at temperature T	— Liquid phase
2. Liquid phase at temperature T'	— Vapor phase
3. Ratio α/α' of separation factors	— Relative volatility
4. $x(T')$ vs. $x(T)$ curve on Figure 8	— Vapor-liquid equilibrium curve (composition of vapor vs. composition of liquid)
5. Solid phase concentration y in a stage	— Temperature T_d on a stage
6. Isotherms α and α' in (x, y) plane	— Boiling curve and dew curve in (composition of liquid or vapor, T_d) plane
7. Reflux: liquid phase withdrawn from top of column at T' and reinjected at T	— Vapor phase withdrawn from top of column and reinjected as liquid phase
8. Reboiling: liquid phase withdrawn from bottom at T and reinjected at T'	— Liquid phase withdrawn from bottom and reinjected as vapor

Let us comment on this analogy. The $x(T')$ vs. $x(T)$ curve is an equilibrium curve in the following sense. The points of this curve represent the compositions $x(T')$ and $x(T)$ of two liquid fractions that are in equilibrium with a given y on a given stage, in the same way as the vapor-liquid equilibrium curve represents the compositions of two phases that are in equilibrium at a given temperature on a given stage. The $x(T')$ vs. $x(T)$ curve may be scaled in terms of y in the same way as the vapor liquid equilibrium may be scaled in terms of T_d. In the parapump, y plays the same role as T_d in distillation. Each stage of the

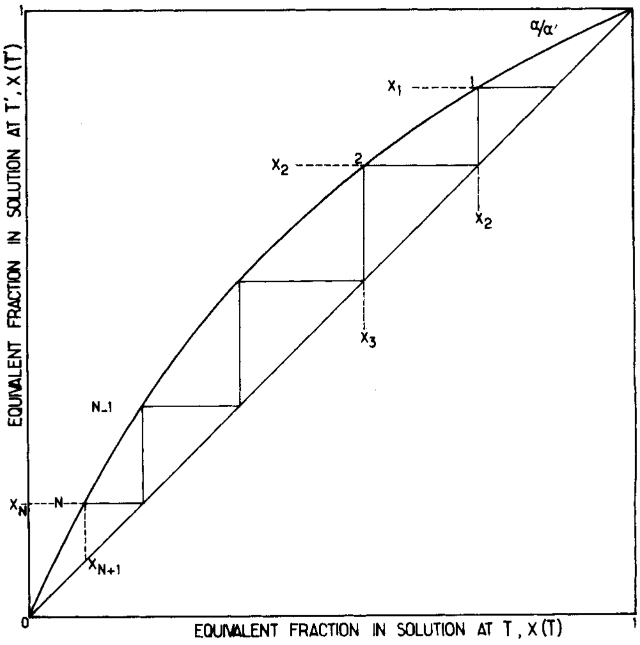

Fig. 9. Representation of Figure 7 in the $[x(T), x(T')]$ plane, illustrating the analogy with the McCabe-Thiele construction for binary total reflux distillation.

column is characterized by a constant value of y (respectively T_d in distillation). In this way, $x(T')$ appears to play the role of the vapor phase composition and $x(T)$ that of the liquid phase. Stated differently, changing the temperature in the parapump is similar to going from vapor to liquid (or reciprocally) in distillation. Note, however, that in the parapump, the liquid fractions of composition $x(T')$ and $x(T)$ related by the equilibrium curve are never in contact with each other, whereas in distillation, the analogous vapor and liquid phases are actually in contact.

The $y \leftrightarrow T_d$ analogy entails the analogy between the (x, y) curves in the parapump (isotherms) and the composition vs. T_d curves in distillation (boiling curve and dew curve). In fact, the correspondence between the two diagrams in Figure 8 also exists for vapor-liquid equilibrium (see, for instance, Treybal, 1955).

The notion of reflux (or reboiling) may then be analyzed in the following way. In distillation take the fluid exiting at one end of the column, add or substract heat to effect a change of phase (not necessarily a change of temperature), and reinject it (in part or in totality) at the same end of column but in opposite direction. In parametric pumping the description is identical, except that the addition or substraction of heat results in a change of temperature without a change of phase. We may thus speak of a generalized reflux.

Analytical Calculation of Limit Regime

The search for the limit regime amounts to locating the staircase between the two isotherms as depending on the initial state of the parapump. More precisely, let us consider an N-stage, $N + 1$ fraction pump, whose average initial composition is represented by $\overline{x}_o$ (in liquid) and $\overline{y}_o$ (in the solid). The composition of all stages and fractions is not necessarily the same. We look for the values of x_1 and x_{N+1} obtained in the limit regime.

Note first that only one of these concentrations is necessary, the second being then obtained from Equation (11). The pump being closed with respect to matter, it suffices to write the conservation of the total amount of one ionic species between the initial and the final state. We choose here the species whose affinity for the resin is highest. In the initial state we may express this amount as

$$(N + 1)CV\overline{x}_o + NQ\overline{y}_o \tag{14}$$

or

$$(N + 1)\rho\overline{x}_0 + N\overline{y}_o \equiv m_o \tag{15}$$

In the limit regime, let $x_1, x_2, \ldots x_{N+1}$ be the liquid fraction compositions and $y_1, y_2, \ldots y_N$ the solid compositions in the cells. The material balance is then

$$m_o = \rho \sum_{i=1}^{N+1} x_i + \sum_{i=1}^{N} y_i \tag{16}$$

The y_i's may be expressed in terms of x_i's by Equations (5) or (6) and then the x_i's as functions of x_1 or x_{N+1} by use of Equations (9) or (10), for instance, which express that the x_i's are related by a staircase between the isotherms. In terms of x_1, the result may be written as

$$m_o = \rho \sum_{i=0}^{N} \frac{x_1/\beta^i}{1 + (1/\beta^i - 1)x_1} + \sum_{i=0}^{N-1} \frac{x_1\alpha'/\beta^i}{1 + (\alpha'/\beta^i - 1)x_1} \tag{17}$$

with

$$\beta = \alpha/\alpha' \tag{18}$$

As discussed below, Equation (17) has only one solution in x_1 comprised between 0 and 1. This solution is therefore easy to calculate numerically, and the limit cycle is then entirely determined from the initial conditions and the operating parameters.

Existence and Uniqueness of Solution

This is easily shown by analyzing the second member of Equation (17), which we designate by $m(x_1)$. Each term of this sum has a pole (value of x_1 for which it becomes infinity) and is continuously increasing outside its pole. None of these $2N$ poles lies in the interval (0, 1). Therefore, in this interval, the sum $m(x_1)$ is continuously increasing and goes at most once through any given value m_o. This shows the uniqueness of the solution of Equation (17). Furthermore, the limiting values of $m(x_1)$ in this interval are

$$m(x_1 = 0) = 0 \quad \text{and} \quad m(x_1 = 1) = N + \rho + N_\rho$$

but from the definition of m_o [Equation (15)]

$$0 \leq m_o \leq N + \rho + N_\rho$$

Thus, $m(x_1)$ goes necessarily through the value m_o in the interval, and there exists a solution.

N-STAGE PARAMETRIC PUMP WITH DEAD VOLUME IN RESERVOIRS

Description (Figure 10)

Consider the N-stage pump described earlier but with the following modification. During the equilibration at T (respectively T'), TR contains a volume $(1 + k)V$ (respectively kV) and BR a volume kV [respectively $(1 + k)V$]. The dead volume in reservoirs are thus kV $(k \geq 0)$. All cells contain a volume V, and all transfers are of volume V as earlier. When $k = 0$, this model reduces to the model described earlier. Notice that k influences the total amount of material present in the system.

Convergence—Limit regime

The construction on the operating diagram is similar to that described except that the composition of BR (respectively TR) at each cycle must be calculated from the mixing of the dead volume kV and volume V coming from C_N (respectively C_1). For more than two or three stages,

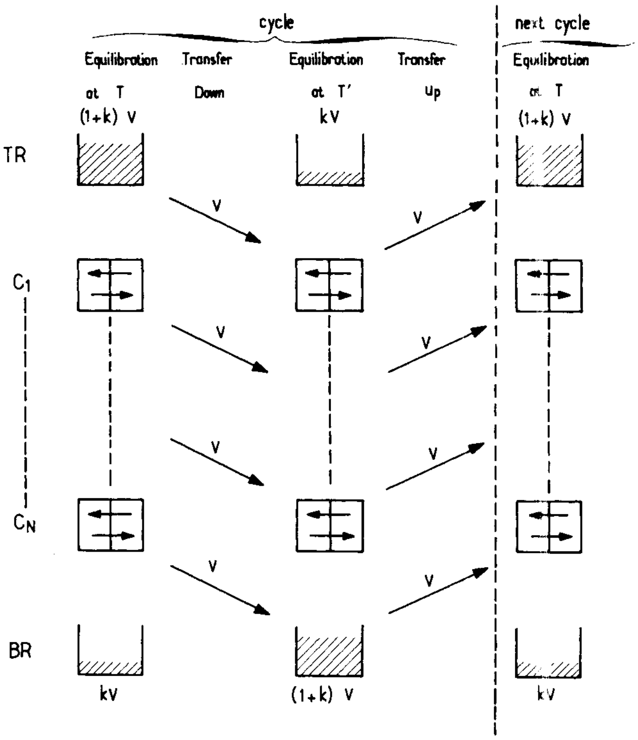

Fig. 10. Description of a staged parametric pump with dead volume.

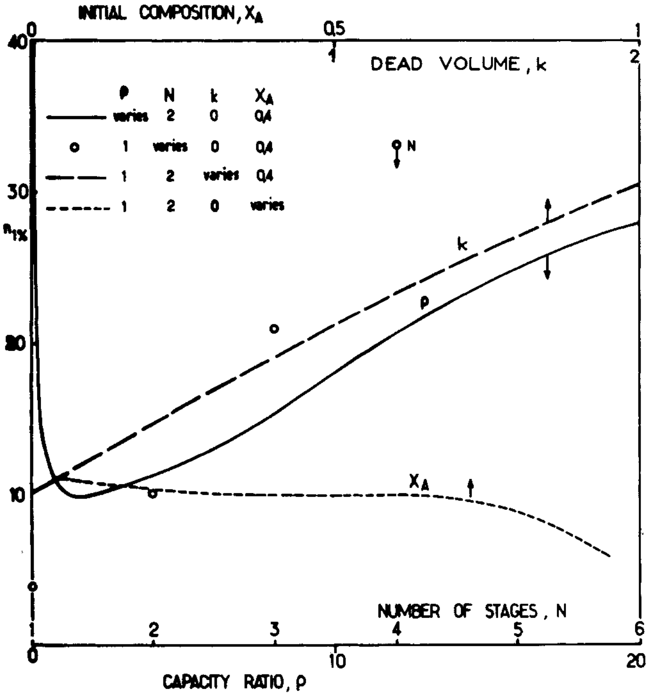

Fig. 11. Number of cycles necessary to attain the limit regime to within 1% as a function of the operating parameters of the pump.

the behavior of the system is more conveniently studied numerically, cell by cell and cycle by cycle, and the following conclusion is reached.

The N-stage pump with dead volume kV converges toward a limiting regime similar to that of the N-stage pump without dead volume ($k = 0$).

That means that the operating diagram, in the limiting regime, is a staircase construction with N steps, such as that of Figure 7. The solution in BR during the equilibration at T (dead volume) has the same composition x_{N+1} as that in C_N, and the solution in TR during the equilibration at T' has the same composition x_1 as that in C_1. Therefore, the mixing in the reservoirs occurs between solutions of the same compositions and has thus no more effect on composition in limit regime. The location of the staircase depends on k because k influences the total amount of exchangeable ions in the system and increases the weight of the x_1 and x_{N+1} compositions in the overall mass balance with respect to $x_2, x_3, \ldots, x_N$ compositions.

SPEED OF CONVERGENCE

We give here a very succinct view of the effect of various parameters on the speed of convergence of the system toward its limit regime. More conveniently, we measure the slowness of convergence by the number of cycles necessary to attain the limit concentrations to within 1% in both reservoirs and designate this number $n_{1\%}$. The parameters considered are the number of stages N, the capacity ratio ρ, the dead volume k, and the initial composition x_A.

The initial state is taken as uniform; that is, all liquid fractions have initially the composition x_A and, on all stages, the solid has a composition in equilibrium with x_A at T. We do not consider the effect of an initial concentration profile in the stages.

Some typical results (for few stages) are gathered on Figure 11, which shows the tendencies. The slowness $n_{1\%}$ is not much affected by the initial composition; it increases roughly linearly with the number of stages and with the dead volume. More remarkably, it presents a minimum as a function of ρ in the vicinity of $\rho = 1$. (Recall that the value $\rho = 1$ corresponds to the equality between the exchange capacity of a solid fraction and the total amount of exchangeable ions of a liquid fraction.) We have not elucidated the exact meaning of this minimum, but its existence is clearly interesting, since ρ can be optimized by choosing the size of the fractions.

NOTATION

C = total ionic concentration of the liquid, (equivalents/liter)
k = dead volume expressed as number of volumes V
N = number of stages, that is, of cells
$n_{1\%}$ = number of cycles necessary to reach the limit concentrations to within 1% in both reservoirs
m_o = defined by Equation (15) (dimensionless)
Q = total exchange capacity of the solid contained in a cell (equivalents)
T, T' = temperatures
T_d = temperature in distillation
V = volume of a liquid fraction (liters)
x, y = equivalent fraction of preferred ion in liquid and solid, respectively (dimensionless)
$\bar{x}_o, \bar{y}_o$ = average values of x and y in the initial state
α, α' = separation factors at T and T', respectively (dimensionless)
$\beta = \alpha/\alpha'$ = thermal relative affinity (dimensionless)
$\rho = CV/Q$ = capacity ratio (dimensionless)

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APPENDIX

All graphical constructions on McCabe-Thiele diagrams presented in this article have been done with the following numerical values:

$$\alpha = 3.5 \qquad \alpha' = 1.5 \qquad \rho = 1$$

In the initial state, all liquid fractions have the composition $x_A = 0.4$. All solid fractions are in equilibrium at T with this composition (their composition is then $y_A = 0.7$).

Numerical calculations, cycle by cycle, have been performed by computer to verify that the system converges toward the limit regime described. Once the form of this limit regime is known, it can be calculated directly through Equation (17).

Manuscript received April 28, 1976; revision received July 20 and accepted August 9, 1976.