Equilibrium Staged Parametric Pumping:

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II. Multiple transfer steps per half-cycle and Reservoir Staging

The limit regimes of equilibrium staged batch parametric pumps are studied. The half-cycle comprises several equilibrations at each temperature, each followed by a discrete transfer of fluid. The concentration distribution of the effluent of each half-cycle is conserved by a cascade of reservoirs. The concepts, methods, and McCabe-Thiele representation are first introduced on the example of the (one-stage, two transfer) pump. The generalization to the (one stage, *n* transfer) pump leads to a limit regime represented by a staircase construction between the two isotherms, the number of steps of the staircase being equal to the number of transfer steps. The limit regime of the general (*N* stage, *n* transfer) pump is then analyzed in terms of the properties of the (one stage, *n* transfer) pump considered above and of the (*N* stage, one transfer) pump discussed in the preceding paper of this series. An analytical solution for the separation factor is given in the case of linear isotherms. The importance of conserving the effluent concentration distribution is illustrated by graphical and numerical comparisons with pumps where this is not done.

SCOPE

The most common form of parametric pumping uses a packed bed of adsorbent, the temperature of which is changed cyclically, and through which a fluid is percolated. The direction of flow is reversed every time the temperature is changed, and the effluent of one half-cycle is reinjected in the opposite direction during the next half-cycle. The variation of adsorptivity with temperature then produces the enrichment of a given component at one end of the bed and its depletion at the other end (Wilhelm et al., 1968).

With respect to most previous work on this subject, the present paper is characterized by the following:

1. The use of a finite number of discrete equilibrium stages, instead of the usual chromatographic column.
2. The use of several discrete transfer steps of discrete fluid fractions, instead of the usual continuous flow.
3. The study of the limit behavior of the pump after many cycles, instead of the transient behavior as a function of number of cycles.
4. The conservation of the concentration distribution of the effluent of each half-cycle, instead of the mixing and the averaging of this distribution.
5. The path from computational results to analytical solutions, through graphical analysis and physical intuition, instead of a pure analytical or pure computational approach.

These characteristics, of course, occur separately in earlier literature, in particular Wakao and al. (1968), Wankat (1973), and the step-go algorithm of Sweed and Wilhelm (1969), for the first two; Camero and Sweed (1976) for the third; and Thompson and Bowen (1972) for the fourth.

With respect to the first paper of this series on staged parametric pumping (Grevillot and Tondeur, 1976), the present paper differs by the second and fourth points. The previous paper was restricted to a single transfer per half-cycle, and thus the effluent of a half-cycle comprised a single fluid fraction. Here, several discrete transfers are considered, and the effluent comprises several fractions (point 2). In normal operation, the fractions are mixed, and this destroys some separation. Here, they are collected separately, in a cascade of reservoirs, and reinjected in reverse order during the next half-cycle (point 4).

The idea of conserving the effluent concentration distribution, although not new, has so far received little attention. Staging reservoirs is a possible application of this concept, to which we hope to give a new impulse by illustrating some of its advantages. Simultaneously, we illustrate the interest of parametric pumps not based on chromatographic columns. This is, of course, most pertinent for systems other than fluid solid, for example, in liquid-liquid extraction (Wankat, 1973).

CONCLUSIONS AND SIGNIFICANCE

The maximal performance of general staged parametric pumps, with *N* equilibrium stages, *n* discrete transfer steps per half-cycle, and staged reservoirs, can be analyzed using the limit regime concept and its graphical representation on a Mc Cabe-Thiele diagram. For the single-stage pump with *n* transfers, the limit pattern is a staircase comprising *n* overhanging steps between the two isotherms, whether these are linear or not. Thus, by increasing *n* and staging reservoirs, it is theoretically possible to obtain an infinite separation even with a single equilibrium stage.

Part I of this paper was published in *AIChE J.*, 22, 1055 (1976).

For the general N staged pump, with linear isotherms, the limit pattern can be viewed as a combination of various limit patterns of elementary pumps; for instance, a combination of N (single stage, n transfer) pumps, or of n (single transfer, N stage) pumps, or of one (N stage, single transfer) pump and one (single stage, n transfer) pump. An analytical expression for the limit separation factor SF of the general pump as a function of the separation factors of the elementary pumps results from this latter configuration:

$$SF\,|N, n|_s = \frac{SF\,|N, 1| \cdot SF\,|1, n|_s}{SF\,|1, 1|}$$

The limit patterns presented here were first obtained by computer calculations, and this, incidentally, shows that valuable qualitative conclusions and analytical solutions may be induced from a proper graphical representation of numerical results, which otherwise bring only poor information. For nonlinear isotherms the rigorous solution is more complicated, but when the isotherms are not far apart and when n is small the linear solution described above is a good qualitative approximation, even with strongly curved isotherms.

For all pumps, including mixed reservoir pumps, the separation increases with the number of stages N. For a given N, when the number of transfers n increases, the separation increases when the reservoirs are staged. When the reservoirs are mixed, the separation is first practically constant and then decreases. In other words, the two types of pumps give a different response to an increase in penetration of the fluid in the cascade. The conservation of the concentration gradients exiting from the cascade of stages at each half-cycle thus appears as fundamental for the performance of the process. Thompson and Bowen (1972) have already shown the effect of this on the speed of the separation; here we show that it brings an increase to the limit separation. This indicates an important direction for experimental and conceptual research, which may be applied to other forms of parametric pumping and in particular to open systems.

In a previous article (Grevillot and Tondeur, 1976), we investigated the operation of a batch parametric pump comprising a finite number of equilibrium stages N and working with a single transfer step per half-cycle. This type of approach was first used by Wakao et al. (1968)[*] with one and two stages. More generally, we showed that such pumps tend toward a limit regime as the number of cycles become large, which is described in a McCabe-Thiele diagram by a staircase pattern with N steps, drawn between the two isotherms. If the equilibrium obeys a simple mass action law, the end concentrations in the two reservoirs are connected by Fenske's equation, and this expresses a striking formal analogy with total reflux binary distillation. In this previous work, the single transfer step per half-cycle means that at each half-cycle, only one liquid fraction is withdrawn at one end of the cascade of stages (and another fraction is injected at the other end). The relative penetration of the mobile phase is then measured by $1/N$ and is therefore not independent of the number of the stages.

In the present paper, the above restriction is removed. Several liquid fractions are withdrawn successively at the end of the cascade at each half-cycle. These fractions may be collected and mixed in a single reservoir, and this is the mode of operation studied in all previous work except one. The fractions may also be collected separately and reinjected in reverse order during the next half-cycle. This second mode of operation is due to Thompson and Bowen (1972). By applying the linear equilibrium theory to a packed-bed parapump, they show that the separation factor is of the order of (constant)$^{2n_c-1}$ after n_c cycles, if mixing in the end compartments is prevented, whereas it is of the order of (constant)^{n_c} if they are mixed.

The mixing of the fractions destroys the concentration gradient coming out of the column or the cascade of stages, and, intuitively, this destruction is the more effective the larger the number of fractions, that is, the larger the relative displacement of the mobile phase during a half-cycle. This result is confirmed by all previous work. Sweed and Wilhelm (1969), using a film diffusion model of the packed bed and the stop-go algorithm, showed that the separation factor decreases when what we call the relative penetration, is increased, that is, the number of interstitial volumes displaced per half-cycle.

They interpreted this result by the fact that a large penetration brings part of the content of one reservoir into the other, resulting in a mixing which reduces the separation. Sweed and Gregory (1971) presented an experimental illustration of this phenomenon, and the remarkable nonlinear equilibrium theory of Camero and Sweed (1976) leads to the same conclusion. The expression for the separation factor established by Aris (1969), using the linear equilibrium model, showed that the increase of the separation factor with number of cycles is slower when the relative penetration becomes larger, and Chen and Hill (1971) obtained the same result.

All these results indicate that when the outcoming fractions are mixed, the quality of the separation becomes poorer as the amount of fluid phase treated becomes larger. In the present paper, we show that this point is worth reconsidering when mixing is avoided.

The approach taken here, as in the previous paper, is based on the analysis of the limit regime of the pump in a McCabe-Thiele diagram. We introduce the method on examples of the simplest parapumps: single equilibrium stage, two transfer steps per half-cycle, and then any number n of transfer steps. The approach is then generalized to (N stages, n transfers) pumps. In each case, we consider both mixed and nonmixed outcoming fractions and linear and nonlinear equilibrium. The conservation of the outcoming fractions is effected here by using a cascade of reservoirs at each end of the cascade of equilibrium stages, and we shall thus speak of staged reservoirs. To simplify the description, we shall designate by $|N, n|_s$ a parapump of N stages and n transfer steps, with staged reservoirs, and by $|N, n|_m$ a similar pump with mixed outcoming fractions.

SINGLE STAGE PARAMETRIC PUMPS, TWO TRANSFER STEPS PER HALF-CYCLE

Staged-Reservoir Pump $|1, 2|_s$

Description (Figure 1). This pump comprises the following elements in series: a top reservoir TR1, a second top

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[*] The paper is in Japanese. We thank P. C. Wankat for drawing our attention to this work while this paper was being written.

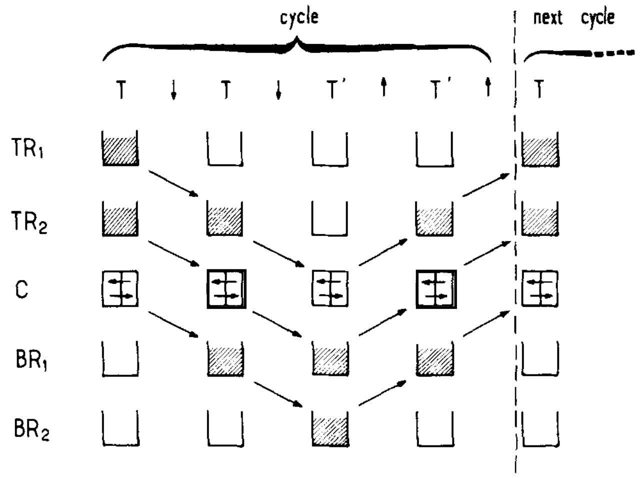

Fig. 1. Description of a (single-stage, two transfer steps per half-cycle) parametric pump with staged reservoirs.

reservoir TR2, a cell C containing the adsorbent or ion exchanger (single stage), a bottom reservoir BR1, and a second bottom reservoir BR2.

The liquid is divided into three equal fractions numbered F1, F2, and F3 from top to bottom of the pump.

One cycle of the operation is defined as follows:

1. First equilibration at *T* (start of cycle). The liquid fractions F1, F2, and F3 are in TR1, TR2, and C, respectively. In cell C, the solid and the liquid are in equilibrium at T.
2. First transfer down. The liquid fractions F1, F2, and F3 are transferred into TR2, C, and BR1, respectively.
3. Second equilibration at *T*. In C, the solid and the liquid fraction F2 are allowed to equilibrate at T.
4. Second transfer down. Liquid fractions F1, F2, and F3 are transferred into C, BR1, and BR2, respectively.
5. First equilibration at *T'*. The temperature of cell C is changed to *T'*, and liquid fraction F1 is allowed to equilibrate with the solid at this temperature.
6. First transfer up.
7. Second equilibration at *T'*.
8. Second transfer up. The liquid fractions are then back in their initial location (end of cycle).

The next cycle will thus begin with a reequilibration of fraction F3 with the solid in C, after the temperature has been brought back to *T*.

McCabe-Thiele Representation. The evolution to the compositions of the solid phase and of the liquid fractions, as cycles proceed, may be represented in the (x, y) diagram in the way described in the preceding article (Grevillot and Tondeur, 1976). The construction uses operating lines representing the material balance equation in cell C:

$$\rho x_i + y_i = \rho x_f + y_f \tag{1}$$

where (x_i, y_i) is the composition of cell C before an equilibration, and (x_f, y_f) is the composition of C after that equilibration. ρ is the stage capacity ratio, given by

$$\rho = \frac{CV}{Q} \tag{2}$$

The operating lines of slope ρ are drawn from points (x_i, y_i) and their intersection with the appropriate isotherm represents the composition (x_f, y_f). There are as many such operating segments per cycle as there are equilibrations, that is, four in the case considered.

For this construction, the isotherms can be drawn using either experimental data or analytical expressions. Here, we describe them by a simple mass action law written for binary ion exchange.

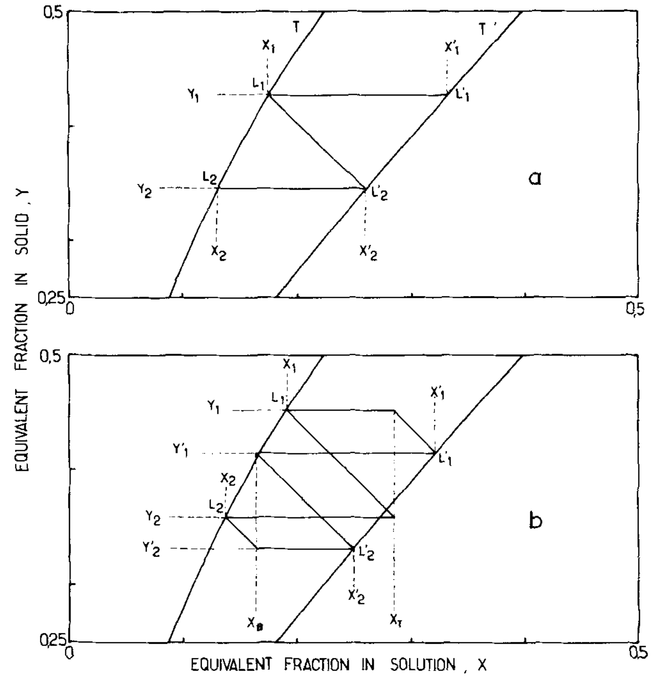

Fig. 2. Limit regime of a (single-stage, two transfer steps per half-cycle) parametric pump.
a—staged reservoir pump (see also Table 1)
b—mixed reservoir pump (see also Table 2)
Parameters values given in Appendix

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \tag{3a}$$

$$y = \frac{\alpha' x}{1 + (\alpha' - 1)x} \tag{3b}$$

where α and α' are the mass law constants or constant separation factors* at the respective temperatures *T* and *T'*. These equations have the same form as the Langmuir isotherm, and the following treatment thus also applies to Langmuir adsorption. In the special case of systems containing only traces of one of the two exchangeables ions, x and y for this ion are very small, and the isotherms may be approximated by their tangents at the origin. The isotherms are then described by

$$y = \alpha x \tag{4a}$$

$$y = \alpha' x \tag{4b}$$

Convergence, Limit regime (Figure 2a). When this construction is made graphically for a few cycles, or by computer calculation for a larger number of cycles, it is observed that two operating segments out of the four per cycle tend to vanish (their length decreases toward zero). One of these two vanishing segments corresponds to the first equilibration at *T* and tends to reduce to a single point on the *T* isotherm, designated by L_2 on Figure 2*a*. Similarly the second vanishing segment corresponds to the first equilibration at *T'* and tends to reduce to L'_1 on the *T'* isotherm. Simultaneously, the two other operating segments tend to merge into a single segment $L_1L'_2$ of slope ρ. Points L_1 and L'_1 are on the same horizontal (same y value). So are L_2 and L'_2.

Thus, the limit regime of the $|1, 2|_s$ pump is represented on a (x, y) graph by an inverted Z. Table 1 indicates the distribution of the concentrations during the cycle in limit

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* Usually employed in ion exchange. Not to be confused with the separation factor measuring the extent of separation in parametric pumping and defined by Wilhelm et al. (1968), which we designate here by SF.

TABLE 1. THE LIMIT REGIME OF A $|1, 2|_s$ PARAMETRIC PUMP (SEE ALSO FIGURE 2a)

	T	↓	T	↓	T'	↑	T'	↑
TR1	x'_1							x'_1
TR2	x'_2	x'_1	x'_1			x'_1	x'_1	x'_2
C	L_2	$x'_2; y_2$	L_1	$x'_1; y_1$	L'_1	$x_1; y_1$	L'_2	$x_2; y_2$
BR1		x_2	x_2	x_1	x_1	x_2	x_2	
BR2				x_2	x_2			

Symbols: T, T' = equilibration of C at T or T', respectively.
↓, ↑ = transfer down, transfer up.

regime, corresponding to Figure 2a. The physical interpretation of this limit regime follows. The solid phase composition (in cell C) does not change from one equilibrium to the next one at a different temperature. On the other hand, this composition changes from one equilibrium to the next at the same temperature; in a cycle, it thus oscillates between two values y_1 and y_2. In other words, when fraction F1 of composition x'_1 (respectively, fraction F3 of composition x_2) is contacted with the solid, and the temperature is changed to T' (respectively, T), the equilibrium is achieved without any mass transfer between phases; the length of the operating segment is zero. The compositions of the two extreme liquid fractions F1 and F3 are constant, x'_1 and x_2; they express the maximal separation obtainable with this pump. The composition of the intermediate liquid fraction F2 oscillates between x_1 and x'_2 at each cycle.

Limit Separation. The separation obtained will be characterized by the ratio of the concentration x'_1 of the enriched fraction F1 to the concentration x_2 of the depleted fraction F3, and we designate this ratio by SF. This separation is limited. It increases with the capacity ratio ρ of the two phases, but for any given finite value of ρ it remains smaller than the separation obtained with the $|2, 1|$ pump described in the preceding article (Grevillot and Tondeur, 1976). This is graphically obvious when one compares Figures 6 of the previous article and Figure 2a here; only when ρ becomes infinite are the two patterns identical.

In the linear case, an analytical expression for SF can be established by using Figure 2a and Equations (4a) and (4b):

$$SF\,|1, 2|_s = \frac{x'_1}{x_2} = \frac{\alpha}{\alpha'}\,\frac{\rho + \alpha'}{\rho + \alpha} \qquad (5)$$

Mixed-Reservoir Pump $|1, 2|_m$

Description. This pump and its operating cycle are obtained from that of Figure 1 by the following changes. Replace TR1 and TR2 by a single reservoir TR able to receive two liquid fractions. Similarly, BR1 and BR2 are replaced by BR. As before, at each transfer step, only one liquid fraction is transferred out of or into C. Thus, the two fractions leaving C during the first half-cycle (respectively, the second) are mixed in BR (respectively, TR). This is the staged version of the usual operating mode of most previous studies on column parapumps.

Limit Regime. The construction on the McCabe-Thiele diagram obeys the same principle as for the staged reservoir pump, except that because of the mixing of the two outcoming fractions, the composition of BR after the second transfer down has to be calculated, and similarly for the composition of TR.

The pump converges toward a limit regime which is best determined by a cycle by cycle computer calculation, until two successive cycles become practically identical. On the (x, y) diagram, the limit regime is represented by a crossed polygonal (Figure 2b), and Table 2 indicates the corresponding distribution of concentrations.

The mixing in the reservoirs is seen to slightly complicate the pattern of the limit regime. In particular, the solid composition is modified at each equilibration; there is no equilibration without mass transfer.

Limit Separation. Let us compare the separation obtained with staged and mixed reservoirs on the examples of Figure 2. These examples are chosen so that the initial composition of the liquid and of the solid are the same, as well as the capacity ratio ρ (namely, $x_o = 0.2$ for the three liquid fractions; $y_o = 0.467$ for the solid, in equilibrium at T with x_o; and $\rho = 1$). The total amount of solute, or of each ionic species in binary ion exchange, is thus the same in both pumps.

The separation obtained with the mixed reservoir pumps can be characterized by the enriched composition x_T obtained in TR and the depleted composition x_B obtained in BR. A comparison of Figures 2a and 2b shows that x_T is smaller than the enriched composition x'_1 of pump $|1, 2|_s$ and that x_B is larger than the depleted composition x_2. The separation factor SF is thus smaller when the reservoirs are mixed.

Figure 2b shows that in the limit regime of pump $|1, 2|_m$, there exist compositions that are better separated than x_T and x_B; these are x'_1 and x_2. Liquid fractions having these compositions can be collected if one avoids mixing the outcoming fractions in BR during the last cycle. This way of ending the operation notably increases the performance of pump $|1, 2|_m$, which, however, remains inferior to that of pump $|1, 2|_s$.

In the case of linear isotherms, it is possible to give an analytical expression for the separation factor of the mixed reservoir pump, defined as the ratio x_T/x_B, as well as the ratio x'_1/x_2. The geometrical structure of Figure 2b, together with the linear isotherm Equations (4a) and (4b), leads to the following expressions:

$$SF\,|1, 2|_m = \frac{x_T}{x_B}$$

TABLE 2. THE LIMIT REGIME OF A $|1, 2|_m$ PARAMETRIC PUMP (SEE ALSO FIGURE 2b)

	T	↓	T	↓	T'	↑	T'	↑
TR	x_T	x_T	x_T			x'_1	x'_1	x_T
C	L_2	$x_T; y_2$	L_1	$x_T; y_1$	L'_1	$x_B; y'_1$	$L'2$	$x_B; y'_2$
BR		x_2	x_2	x_B	x_B	x_B	x_B	

Symbols: T, T' = equilibration of C at T or T', respectively.
↓, ↑ = transfer down, transfer up.

$$x_B = \frac{x_1 + x_2}{2}, \quad x_T = \frac{x'_1 + x'_2}{2}$$

$$= \frac{2(\rho+\alpha)^2(\rho+2\alpha') - \rho(\rho+2\alpha)(\rho+3\alpha')}{\rho(\rho+\alpha)(\rho+2\alpha') + 2\alpha'^2(\rho+2\alpha)} \quad (6)$$

$$\left(\frac{x'_1}{x_2}\right)_m = \frac{\rho(\rho+2\alpha)^2 + 2\alpha\alpha'(\rho+2\alpha) - \alpha\rho(\rho+2\alpha')}{\rho(\rho+\alpha')(\rho+2\alpha') + 2\alpha'^2(\rho+2\alpha)} \quad (7)$$

It can be shown that the following inequalities always hold:

$$SF\,|1,2|_m < (x'_1/x_2)_m < SF\,|1,2|_s \quad (8)$$

SINGLE STAGE PARAMETRIC PUMPS, *n* TRANSFER STEPS PER HALF-CYCLE

Staged-Reservoir Pump $|1, n|_s$

Description. This pump is a generalization of the $|1, 2|_s$ pump. It comprises a single cell C containing the solid, n top reservoirs TR1, TR2, ..., TRn, and n bottom reservoirs BR1, BR2, ..., BRn. The liquid phase is divided into $n + 1$ equal fractions designated by F1, F2, .., F$n + 1$ from top to bottom of the pump. At the start of the cycle, these fractions are located in TR1, ... TRn, and C, respectively. The half-cycle at T is composed of n equilibrations of the solid in C at temperature T, successively with fractions F$n + 1$, Fn, ... F2, each equilibration being followed by a transfer of each fraction one stage down. The next half-cycle is composed of n equilibrations of the solid at T', successively with F1, F2, ... Fn, each followed by a transfer of all fractions one stage up.

Clearly, the number of liquid fractions must exceed by one the number of reservoirs on each side and the number of transfer steps per half-cycle in order for each fraction to contact the solid at least once in a cycle and in order for the solid to be in contact with a fraction at each step.

Limit Regime (Figure 3). On the McCabe-Thiele diagram, the pattern converges after a large number of cycles toward a staircase with overhanging steps drawn between the two isotherms comprising n horizontal segments connected by $n - 1$ operating segments of slope-ρ. The reader will easily build the corresponding algorithm on the model of Table 1.

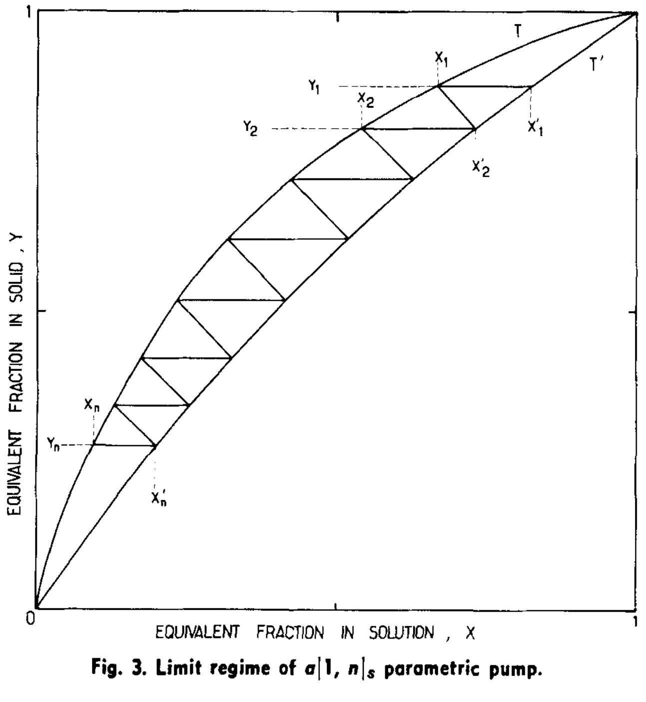

Fig. 3. Limit regime of $a|1, n|_s$ parametric pump.

The physical meaning of this regime follows. The composition of the solid in C changes $2n$ times during a cycle; in the half-cycle at T it is successively $y_n, y_{n-1}, \ldots, y_1$, and in the half cycle at T' it is $y_1, y_2, \ldots y_n$. The compositions x'_1 and x_n of the extreme liquid fractions F1 and F$n + 1$ are constant. The composition of any intermediate fraction F$_i$ oscillates between x_{i-1} and x'_i.

Limit Separation. The extreme concentrations obtained with the $|1, n|_s$ pump are that of fractions F1 and F$n + 1$ in the limit regime, that is, x'_1 and x_n. With nonlinear isotherms, the separation factor can be calculated through the following procedures.

1. Write the relations defining each step of the staircase

$$x'_i = \frac{(\alpha/\alpha')\,x_i}{1 + \left(\frac{\alpha}{\alpha'} - 1\right)x_i} \qquad i = 1, 2, .., n \quad (9)$$

for the horizontal segments, and the material balance equations

$$\rho\,x_i + y_i = \rho\,x'_{i+1} + y_{i+1} \qquad i = 1, 2, \ldots, n-1 \quad (10)$$

for the operating segments. If we express y_i and y_{i+1} with the aid of Equations (3*a*) and (3*b*), respectively, Equation (10) gives

$$x_i = \frac{(\alpha-1)A - (\rho+\alpha) + \{[\rho+\alpha-(\alpha-1)A]^2 + 4A\,\rho(\alpha-1)\}^{1/2}}{2\rho(\alpha-1)} \quad (11)$$

where

$$A = \rho\,x'_{i+1} + \frac{\alpha'\,x'_{i+1}}{1 + (\alpha'-1)x'_{i+1}} \quad (12)$$

2. Utilize recurrence Equations (9) and (11) to calculate x_n starting from x'_1, or x'_1 starting from x_n.

In the case of linear isotherms, the separation factor can be expressed analytically following the same procedure. The recurrence Equations (9) and (11) are to be replaced by

$$x'_i/x_i = \alpha/\alpha' \qquad i = 1, 2, \ldots\ldots\, n \quad (13)$$

$$x_i/x'_{i+1} = \frac{\rho+\alpha'}{\rho+\alpha} \qquad i = 1, 2, \ldots\ldots\, n-1 \quad (14)$$

By successive substitution, eliminate all intermediate x and x' to keep only x'_1 and x_n; this gives

$$\boxed{SF\,|1,n|_s = \frac{x'_1}{x_n} = \left(\frac{\alpha}{\alpha'}\right)^n \left(\frac{\rho+\alpha'}{\rho+\alpha}\right)^{n-1}} \quad (15)$$

The direct calculation of the limit regime from the initial conditions is then possible and will be illustrated further on for the general case of the $|N, n|_s$ pump.

Let us now compare the $|1, n|_s$ pump to that studied in our previous paper (Grevillot and Tondeur, 1976), which was an N stage, one transfer pump $|N, 1|$. In the case where $n = N$, the limit staircases of these two pumps has the same number of steps. But in the N stage pump, the steps are right angled, whereas in the $|1, n|_s$ pump they are overhanging. The staircase is thus more spread out and the separation better in the N stage pump, except when ρ becomes infinite, which implies a very small solid capacity Q relative to the liquid. Clearly, this means that very little mass transfer will occur at each equilibration, and the number of cycles needed to approach the limit regime will become very large in this case.

Effect of Phase Angle. Wilhelm et al. (1968) have shown experimentally the effect of the phase angle between the inversion of flow and the change of temperature on a continuous bed parapump with mixed reservoirs. A numerical study of this phenomenon has been performed by Sweed and Wilhelm (1969) using the stop-go algorithm. It was shown that the maximum separation was obtained for a phase angle 0 or π, and that any deviation from these values decreased separation. In particular, the values $\pi/2$ and $3\pi/2$ of the phase angle result in no separation at all. These results also apply to $|1, n|_s$ parapumps, except that one never obtains rigorously zero separation. In addition, the effect of phase angle is particularly simple to illustrate graphically. In order to do this, we first need to define more accurately the phase angle in the present case.

Let us consider a $|1, n|_s$ pump. We shall say that the phase angle is zero if the cycle is that described so far, that is, each equilibration at T is followed by a transfer down, and each equilibration at T' is followed by a transfer up. We shall say that the phase angle is increased by π/n if all transfer steps are shifted one step toward the beginning of the cycle, with respect to the equilibration steps which remain fixed (that is, there are still n equilibrations at T in the first half-cycle and n equilibrations at T' in the second half-cycle). Therefore, starting from the normal cycle after n such shifts, the phase angle is π. Note that if the phase angle ϕ lies between π and 2π, the operation is identical to the case where the angle is $\phi - \pi$ but looking at the pump head down. There are thus only n different operating regimes.

Figure 4 presents an example (for $n = 4$) illustrating the various shapes of the limit pattern as a function of the phase angle. The properties observed on Figure 4 can be generalized to higher values of n. We merely mention here the simplest rules: the shape of the limit staircase for $\phi \neq 0$ and $\phi \neq \pi$ is obtained from that corresponding to $\phi = 0$ by suppressing some of the extreme horizontal lines and operating segments. The simplest regimes are the following: n even, $\phi = \pi/2$: a single operating segment, and n odd, $\phi = (n + 1)\pi/2n$: a single horizontal segment. In a staged-reservoir pump, any deviation from $\phi = k\pi$ entails a decrease in separation.

Conclusion on pump $|1, n|_s$. Providing the phase angle is zero (or $k\pi$), the separation of this pump can be made as large as one desires by increasing the number of transfer steps and adding the necessary reservoirs. Note that for given n, the limit separation increases with ρ, that is, when the solid capacity decreases. It seems quite remarkable that such a large separation is theoretically possible with very little solid sorbent and a single equilibrium stage. But of course this single stage works a lot, $2n$ equilibrations per cycle, and obviously the time must be available for these equilibria to take place.

The role of the reservoir is to conserve the compositions resulting from the equilibrations and to accumulate the separation. This scheme of parametric pumping is thus a very efficient way of using the equilibrium stage.

Mixed-Reservoir Pump $|1, n|_m$

Description. This pump and its operating cycle are obtained from the $|1, n|_s$ pump just studied by the following modifications. All top reservoirs are replaced by a single reservoir TR able to receive all n outcoming fractions; similarly, there will be a single bottom reservoir BR. At each transfer step, a single liquid fraction is transferred out of C, and another into C, as before. But the n fractions leaving C during one half-cycle are mixed in one of the reservoirs.

Limit Regime. Figure 5*a* shows an example of the limit pattern for $n = 4$. Together with the example of Figure 2*b*, it illustrates how the shape of the construction changes as n increases. The figure is a closed, crossed polygonal, comprising two systems of n steps drawn between a vertical line at the bottom reservoir composition x_B (respectively, top reservoir x_T) and the isotherm at T' (respectively, T). Each operating segment ending on the vertical x_B (respectively, x_T) represents the equilibration of a liquid fraction coming from BR (respectively, TR) with the solid at T' (respectively, T). The extreme operating segments, connecting the two systems of steps, represent the equilibrations which follow the temperature changes. The composition x_B (respectively, x_T) is the average of the compositions x of the four equilibria at T (respectively, T').

The physical meaning of this limit regime is the following. During a half-cycle, the concentration of the fractions entering the cell is constant at x_T at T or x_B at T'. On the other hand, the fractions coming out of the cell during the half-cycle at T have concentrations that result from the equilibrations numbered 1, 2, 3, and 4 on Figure 5*a*, in the order of exit, and similarly 1′, 2′, 3′, and 4′ during the half-cycle at T'. Therefore, they constitute a nonuniform concentration distribution. This distribution is destroyed and becomes uniform as the fractions are mixed in the reservoir. Note that if mixing is prevented in the last cycle, the fraction exiting after the first equilibration of a half-cycle, corresponding to points 1 or 1′ on Figure 5*a*, can be collected. This improves the separation, but the production is reduced to a single fraction.

Limit Separation. Figures 2*b*, 5*a*, and 5*b* show that the separation decreases as n increases (at constant ρ) and tends toward zero when n becomes large (Figure 5*b*). The physical meaning of this evolution is obvious. Increasing n at constant ρ means increasing the amount of liquid that flows through the cell at each half-cycle. After a few equilibrations, at T for example, the solid is in equilibrium with the composition x_T; therefore, the fractions flow

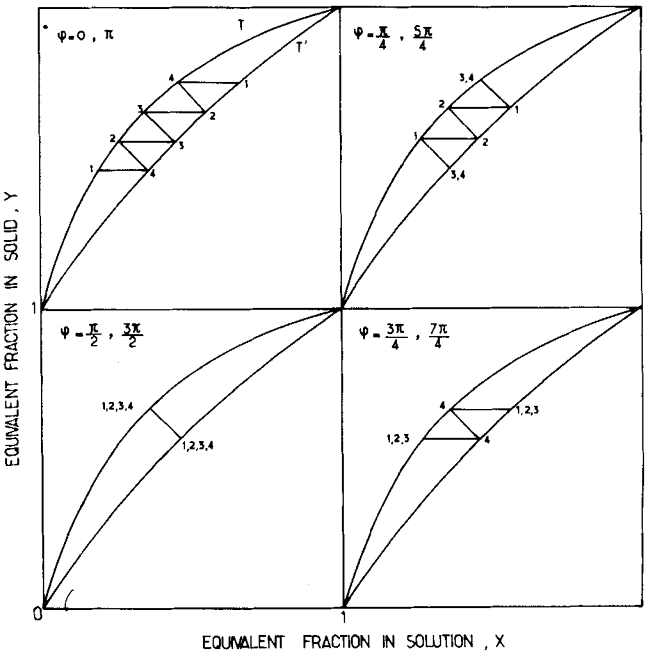

Fig. 4. Effect of phase angle on limit regime of a $|1, 4|_s$ parametric pump. Note: points 1, 2 . . . represent the first, second . . . equilibria of the half-cycle, at T or T'.

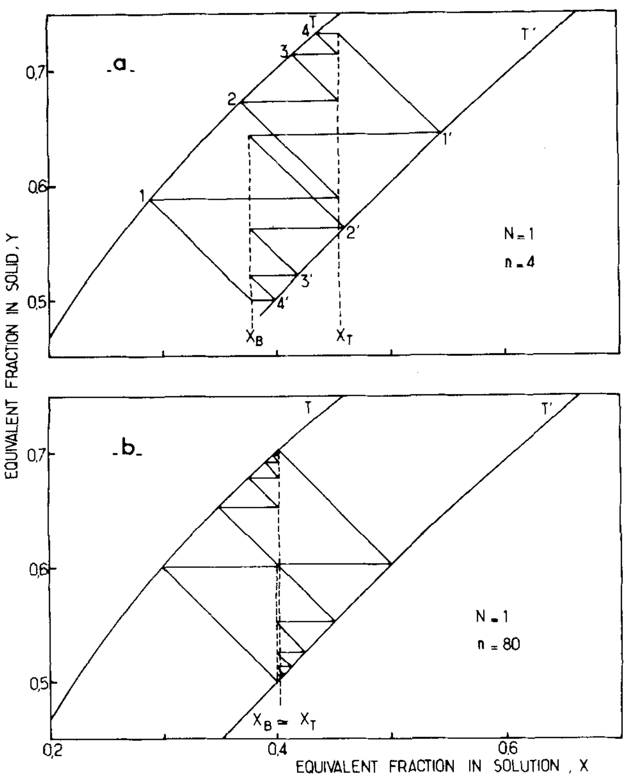

Fig. 5. Limit regime of a $|1, n|_m$ parametric pump: a) $n = 4$ b) $n = 80$.

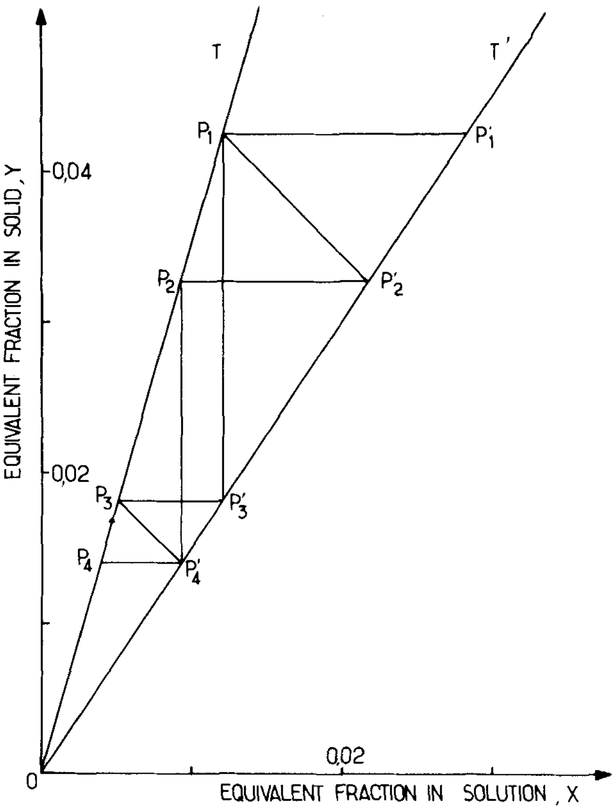

Fig. 6. Limit regime of a $|2, 2|_s$ parametric pump in the case of linear isotherms (see also Table 3).

through the cell without composition change. The reservoir BR thus eventually receives a liquid of composition x_T.

N STAGE PARAMETRIC PUMPS WITH n TRANSFER STEPS PER HALF CYCLE

Staged-Reservoir Pump $|N, n|_s$

Description. This pump generalizes the $|1, n|_s$ pump studied above and the $|N, 1|$ pump of our previous paper. It comprises N identical cells C1, C2, ... CN (equilibrium stages), each containing a capacity Q of solid; n top reservoirs TR1, TR2, ... TRn, and n bottom reservoirs BR1, BR2, ... BRn; $N + n$ equal liquid fractions of volume V.

At the start of the cycle, the fractions are in TR1, TR2, ... TRn, C1, ... CN. A half-cycle comprises n equilibrations at T (respectively, T') of the N cells, each followed by a transfer of each fraction on stage down (respectively, up).

The number of fractions and reservoirs is such that each fraction undergoes at least one equilibration per cycle with the solid and that each cell contains a liquid fraction at each equilibration. Note that n/N measures the penetration in the cascade of cells. It is the discrete analogue of the parameter α used by Camero and Sweed (1976) for packed-bed pumps.

We shall first study the operation of the $|N, n|_s$ pump with linear isotherms, as this facilitates the qualitative understanding of the nonlinear case.

Linear Isotherms, Limit Regime. As in the other pumps studied so far, this pump converges toward a limit regime which can be represented on a McCabe-Thiele diagram. The analysis of the structure of the limit pattern leads to the following proposition, which we illustrate in detail further on: *with linear isotherms, the limit pattern of a $|N, n|_s$ pump can be viewed as an assembly of the limit patterns of N pumps $|1, n|_s$, that is, as many as there are stages, or, alternately, as an assembly of the limit patterns of n pumps $|N, 1|$, that is, as many as there are transfer steps per half-cycle.*

We shall now justify this proposition by analyzing in detail a simple example, the $|2, 2|_s$ pump, and then generalizing from a more complex case, the $|3, 4|_s$ pump.

First example $|2, 2|_s$: the limit regime of this pump is represented on Figure 6, and Table 3 presents the corresponding algorithm. There are two interesting ways of looking at the pattern.

1. The four equilibria that occur in cell C1 during a limit cycle are represented by points P_2, P_1, P'_1, P'_2 in that order. These points are connected by a broken line similar to the limit regime of the $|1, 2|_s$ pump, shown on Figure

TABLE 3. THE LIMIT REGIME OF A $|2, 2|_s$ PUMP (SEE ALSO FIGURE 6)

	T	$\downarrow$	T	$\downarrow$	T'	$\uparrow$	T'	$\uparrow$
TR1	x'_1							x'_1
TR2	x'_2	x'_1	x'_1			x'_1	x'_1	x'_2
C1	P_2	$x'_2; y_2$	P_1	$x'_1; y_1$	P'_1	$x_1; y_1$	P'_2	$x_2; y_2$
C2	P_4	$x_2; y_4$	P_3	$x_1; y_3$	P'_3	$x_3; y_3$	P'_4	$x_4; y_4$
BR1		x_4	x_4	x_3	x_3	x_4	x_4	
BR2				x_4	x_4			
	B		A				B	

$2a$, and, similarly, for points $P_4\ P_3\ P'_3\ P'_4$, representing the equilibria in cell C2. We may thus say that each cell behaves like a pump $|1, 2|_s$.

The two broken lines are connected by two vertical segments. The vertical connection $P_1 P'_3$ expresses the fact that the liquid fraction F2 of pump $|2, 2|_s$ plays at the same time the role of fraction F2 of the $|1, 2|_s$ pump built on C1, and of fraction F1 of the $|1, 2|_s$ pump built on C2. Similarly, the vertical connection $P_2 P'_4$ expresses the double role of fraction F3 of the $|2, 2|_s$ pump.

2. The four equilibria that occur in the cells during the second equilibration at T and the equilibration at T' that follows it are represented by points P_1, P_3, P'_1, P'_3 (Table 3). These points are connected by a straight staircase of two steps $P'_1\ P_1\ P'_3\ P_3$. The four equilibria that occur during the rest of the cycle are connected by a similar staircase $P'_2\ P_2\ P'_4\ P_4$. Each of these two staircases is similar to the limit pattern of a (two cell, one transfer) pump $|2, 1|$ (Grevillot and Tondeur, 1976, Figure 6). The physical meaning of this similitude can be reached as follows. In Table 3, consider the part of the cycle designated by A, comprising the second equilibration step at T and the first at T', together with the two accompanying transfer steps. We thus constitute a pseudo cycle with one transfer per half cycle. Similarly, the second couple of equilibration steps leads to a pseudo cycle B. During pseudo cycle A, the pump $|2, 2|_s$ works as a pump $|2, 1|$ with fractions F1, F2, and F3. During pseudo cycle B, it works as a pump $|2, 1|$ with fractions F2, F3, F4. This is why the limit pattern of pump $|2, 2|_s$ is made of two straight staircases. The connection between the staircases is done through operating segments $P_1\ P'_2$ and $P_3\ P'_4$, which in the real cycle of the $|2, 2|_s$ pump expresses the passage from pseudo cycle A to pseudo cycle B and conversely.

Second example, generalization: we merely give the essential elements of the analysis. Figure 7 shows the limit pattern of pump $|3, 4|_s$. As in the previous example, there are two interesting ways of looking at this pattern.

1. It is made of N overhanging staircase of n steps each (such as $P'_5\ P_5\ P'_6\ P_6\ P'_7\ P_7\ P'_8\ P_8$ on Figure 7).

The connection of these N staircases is by vertical segments. Each staircase concerns one cell; the first staircase (the second, third, respectively) connects points representing the equilibria in C1, (C2, C3, respectively) during the cycle. Each cell thus behaves like a $|1, n|_s$ pump. As there are N cells, there are N staircases. The limit pattern of a $|N, n|_s$ pumps can thus be viewed as an assembly of the limit patterns of N pumps $|1, n|_s$.

2. The figure is made of n straight staircases of N steps each (such as $P'_2\ P_2\ P'_6\ P_6\ P'_{10}\ P_{10}$, for example). The connection of these n staircases is by operating segments. Each staircase represents the limit pattern of a $|N, 1|$ pump. In other words, a $|N, n|_s$ pump works like a $|N, 1|$ pump during pseudo cycles with a single transfer per half-cycle, which are included in the full real cycle in the following way. Take the i^{th} equilibration at T and the $(n - i + 1)^{\text{th}}$ equilibration at T' (they are symmetrical with respect to the middle of the real cycle) and take the transfer step that follows each of these equilibrations. There are n such pseudo cycles in the real cycle; there are thus n straight staircases. The limit pattern of the $|N, n|_s$ pump can thus be viewed as an assembly of the limit patterns of n pumps $|N, 1|$ working on pseudo cycles.

Linear Isotherms, Limit Separation. The interest of the approach explained above lies not only in the physical feeling which it brings, but it also allows an analytical solution of the limit regime. First, we seek an expression for the separation factor SF, defined as the ratio of the concentrations of the most different liquid fractions x'_1 and x_{12} in the example of Figure 7, represented by points P'_1 and P_{12}

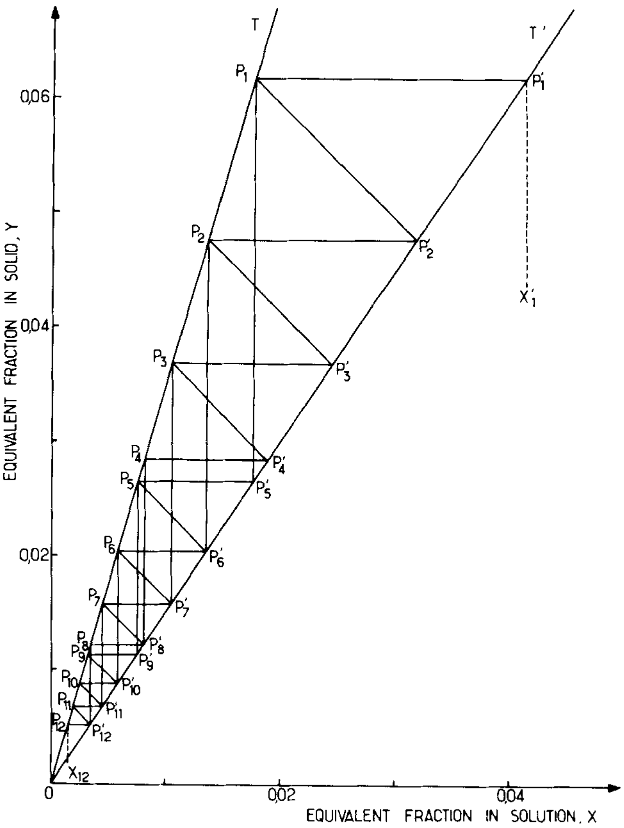

Fig. 7. Limit regime of a $|3, 4|_s$ parametric pump in the case of linear isotherms.

$$SF\ |3, 4|_s \equiv \frac{x'_1}{x_{3,4}} = \frac{x'_1}{x_{12}}$$

and, more generally

$$SF\ |N, n|_s \equiv \frac{x'_1}{x_{Nn}} \tag{16}$$

Points P'_1 and P_{12} are connected by a variety of paths. If we seek all the uninterrupted single line paths, we observe the following property: all paths which simply connect the extreme compositions comprise $N + n - 1$ horizontal segments, $N - 1$ vertical segments, and $n - 1$ operating segments.

Two such paths are of particular interest in that they consist of a straight stair of N steps adjacent to an overhanging stair of n steps (one horizontal step being common). In the present example, these paths are $P'_1\ P_1\ P'_5\ P_5\ P'_9\ P_9\ P'_{10}\ P_{10}\ P'_{11}\ P_{11}\ P'_{12}\ P_{12}$ and $P'_1\ P_1\ P'_2\ P_2\ P'_3\ P_3\ P'_4\ P_4\ P'_8\ P_8\ P'_{12}\ P_{12}$, the second of which is shown in Figure 8. Using this path to express the separation factor, one may write

$$SF\ |3, 4|_s = \frac{x'_1}{x_{12}} = \frac{x'_1}{x_4} \cdot \frac{x_4}{x'_4} \cdot \frac{x'_4}{x_{12}}$$

and, from the definitions of the separation factors

$$SF\ |3, 4|_s = SF\ |1, 4|_s \cdot \frac{1}{SF\ |1, 1|} \cdot SF\ |3, 1|$$

This is easily generalized to

$$\boxed{SF\ |N, n|_s = \frac{SF\ |N, 1| \cdot SF\ |1, n|_s}{SF\ |1, 1|}} \tag{17}$$

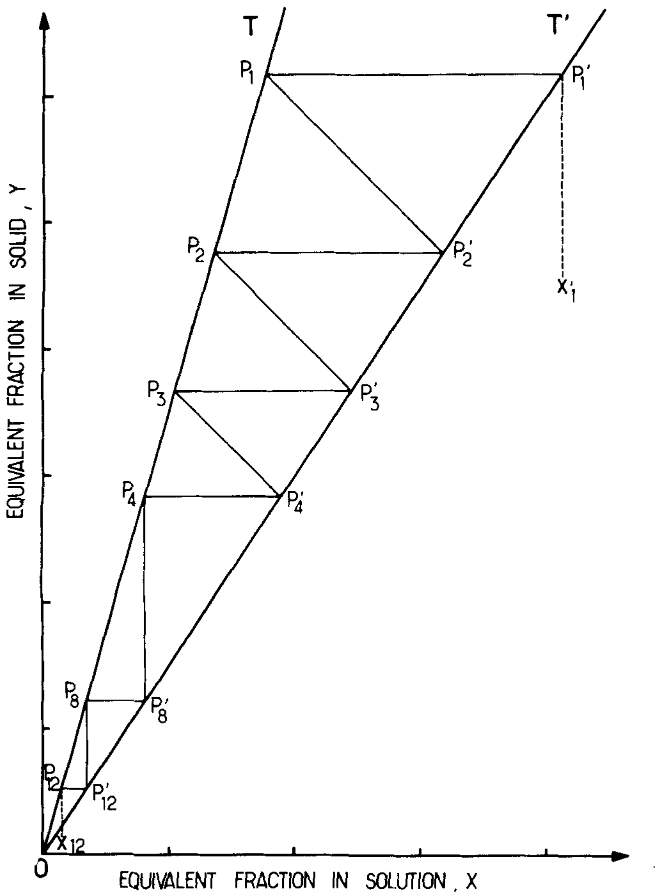

Fig. 8. One of the two distinctive paths between P_1' and P_{12}, leading to Equation (17).

The factor $1/SF\,|1, 1|$ accounts for the horizontal segment common to the two stairs. The limit regime of pump $|N, n|_s$ thus also appears as the juxtaposition of the limit regimes of a pump $|N, 1|$ and a pump $|1, n|_s$.

Equation (17) clearly shows the amplification of separation that results from combining several transfers per half-cycle with staging. It also illustrates algebraically the concept of considering a general pump as a combination of elementary pumps. The separation factor can also be expressed explicitly. In order to do this, $SF\,|N, 1|$ is expressed through a procedure similar to that used for Equation (15) as

$$SF\,|N, 1| = (\alpha/\alpha')^N \tag{18}$$

$SF\,|1, n|_s$ being given by Equation (15).

We then obtain

$$\boxed{SF\,|N, n|_s = \left(\frac{\alpha}{\alpha'}\right)^N \cdot \left(\frac{\alpha}{\alpha'} \cdot \frac{\rho + \alpha'}{\rho + \alpha}\right)^{n-1}} \tag{19}$$

Equation (19) shows that the separation factor increases exponentially with N and n, the contribution of a stage being larger than the contribution of a transfer step, since in the latter case the step is overhanging.

Linear Isotherms, Analytical Calculation of Limit Regime. Let $\overline{x_0}$ and $\overline{y_0}$ be the average initial concentrations of the liquid and solid, respectively, in a $|N, n|_s$ pump. All fractions need not have the same composition. We want to calculate for instance the value of x'_1 in limit regime. The pump being closed with respect to matter, it suffices to write the conservation of the total amount of one species, between the initial and the final state. In the initial state, this amount, expressed in moles or equivalents, is $(N + n)CV\overline{x_0} + NQ\overline{y_0}$. Dividing by the sorption capacity Q of a single solid fraction, we define the nondimensional quantity m_0:

$$m_0 = \rho(N + n)\,\overline{x_0} + N\,\overline{y_0} \tag{20}$$

As final state in the limit regime we choose the end of the first equilibration at T, because this choice leads to the simplest final expressions. In this state, all n top reservoirs contain liquid fractions of respective compositions $x'_1, x'_2, \ldots\ldots x'_n$. All N cells also contain liquid fractions, and their state is represented by points $P_n, P_{2n}, \ldots P_{Nn}$. The conservation of matter then implies

$$m_0 = \rho \sum_{i=1}^{n} x'_i + \sum_{i=1}^{N} (\rho x_{in} + y_{in}) \tag{21}$$

which, if we use Equation (4*a*), becomes

$$m_0 = \rho \sum_{i=1}^{n} x'_i + (\rho + \alpha) \sum_{i=1}^{N} x_{in} \tag{22}$$

But, owing to the structure of Figure 8, x'_i can be expressed as a function of x'_1 using Equations (13) and (15), where $n = i$; one obtains

$$x'_i = \frac{\alpha}{\alpha'} \cdot \frac{x'_1}{SF\,|1, i|_s} \tag{23}$$

For similar reasons, x_{in} can be expressed as a function of x'_1 using Equation (17) with $N = i$, and one obtains

$$x_{in} = \frac{\alpha}{\alpha'} \cdot \frac{x'_1}{SF\,|i, 1|_s \cdot SF\,|1, n|_s} \tag{24}$$

Substituting Equations (23) and (24) into Equation (22), and after some rearranging, one finally obtains

$$x'_1 = m_0 \Bigg/ \frac{\alpha}{\alpha'} \left[\rho \sum_{i=1}^{n} SF^{-1}\,|1, i|_s + (\rho + \alpha)\, SF^{-1}\,|1, n|_s \sum_{i=1}^{N} SF^{-1}\,|i, 1| \right] \tag{25}$$

where $SF^{-1} = 1/SF$, or, more explicitly

$$x'_1 = m_0 \Bigg/ \left[\rho \sum_{i=1}^{n} \left(\frac{\rho + \alpha}{\rho + \alpha'} \cdot \frac{\alpha'}{\alpha}\right)^{i-1} + (\rho + \alpha) \left(\frac{\rho + \alpha}{\rho + \alpha'} \cdot \frac{\alpha'}{\alpha}\right)^{n-1} \sum_{i=1}^{N} \left(\frac{\alpha'}{\alpha}\right)^{i} \right] \tag{26}$$

After the sums of the geometric progressions have been calculated, Equation (26) reduces to

$$x'_1 = \frac{m_0}{\rho} \left[1 - \frac{\alpha'(\rho + \alpha)}{\alpha(\rho + \alpha')} \right] \Bigg/ \left[1 - \left(\frac{\alpha'(\rho + \alpha)}{\alpha(\rho + \alpha')} \right)^n \left(\frac{\alpha'}{\alpha}\right)^N \right] \tag{27}$$

Nonlinear Isotherms, Limit Regime. In this case, the $|N, n|_s$ pump also converges asymptotically towards a limit regime, an example of which is given on Figure 9 for $N = n = 2$. The overall shape is very similar to that of the linear case (compare with Figure 6), but in the detail it is more complicated than the linear case. Points P, representing the equilibria in the cells, are not simply connected by straight or overhanging stairs; for instance, P_1 and P'_3 (and P_2 and P'_4) are not on a same vertical. Points P_2 and P'_2 (and P_3 and P'_3) are not on a same horizontal. The

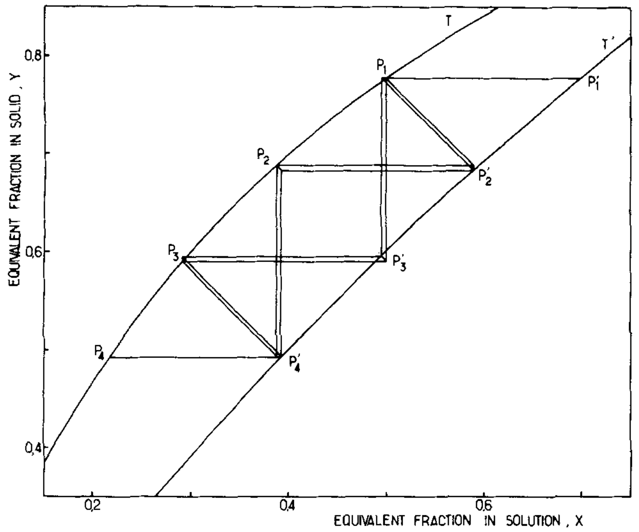

Fig. 9. Limit regime of a $|2, 2|_s$ parametric pump in the case of non-linear isotherms.

equilibria P_2 and P'_3 occur after some mass transfer between phases.

COMPARISON OF THE LIMIT SEPARATION OF STAGED PARAMETRIC PUMPS

We wish to compare the limit separation factors of the various pumps discussed in this paper in the general case of nonlinear isotherms. Because no analytical solutions are available, computer calculations were required. The separation factor depends on several parameters, namely, N, n, ρ, α, α', and also on the average initial composition of the pump (this latter parameter plays no role in the linear case).

The graphical presentation of the results in a plane requires that a limited number of independent variables be chosen. We may, for instance, plot one variable as a function of a second one, at various values of a third, all others being fixed. In addition, several variables may be replaced by as many independent combinations of these variables. There is thus a large variety of possible representations. Here, we consider that the initial composition is given and constant, as well as α and α' (see appendix). Moreover, among the various combinations of the independent variables N, n, and ρ, we have chosen two that are particularly simple and interesting by their physical meaning.

1. The relative penetration n/N, which measures the distance which the fluid penetrates along the cascade of stages. An equivalent quantity has been used previously, for instance, by Sweed and Wilhelm (1969).
2. The output, defined for staged-reservoir pumps by

$$P_S = \rho/N = \frac{CV}{NQ} \tag{28}$$

and for mixed-reservoir pumps by

$$P_m = \frac{n}{N}\rho = \frac{nCV}{NQ} \tag{29}$$

The physical meanings of P_S and P_m are similar to that of the output in batch distillation. They imply the operation of the batch parapump in the following way. The apparatus is loaded with the solution to fractionate; it is then operated in closed system until the limit regime is attained (or approached). Then, part of the solution is withdrawn, and this part represents the output of the system.

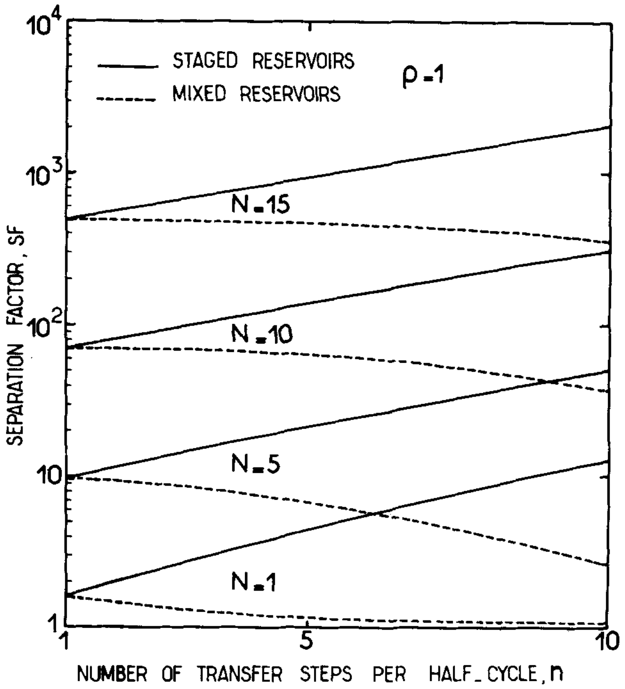

Fig. 10. Comparison of separation factors of staged and mixed reservoir pumps.

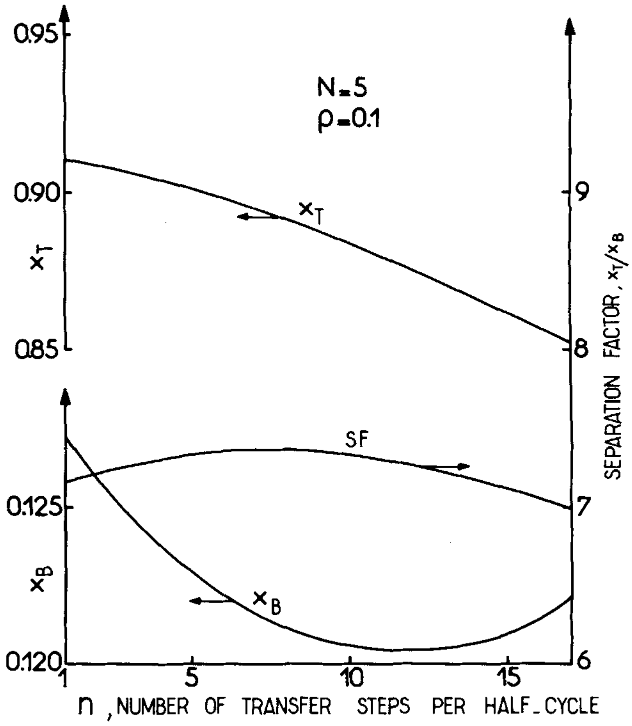

Fig. 11. Illustration of a maximum for the separation factor.

Here the output is taken as one single fraction (the richest or the poorest) in staged-reservoir pumps and as n fractions, that is, the content of a full reservoir, in mixed-reservoir pumps. P_S and P_m have the dimension of equivalents of output per equivalent of ion exchange capacity involved.

Figure 10 shows the separation factor SF as a function of n for different values of N, ρ being fixed and equal to 1. As expected, SF increases with N for all pumps, whether the reservoirs are staged or not. For N given, the separation factor for staged-reservoir pumps increases practically exponentially with n [it is rigorously so with linear isotherms, as Equation (19) shows].

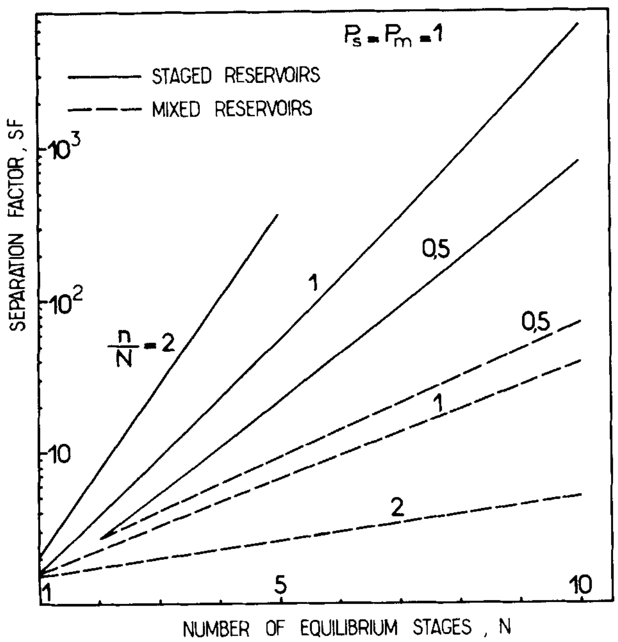

Fig. 12. Effect of penetration on separation of staged and mixed reservoir pumps at equal output.

For mixed-reservoir pumps, the situation is not so simple. For small values of N, SF decreases uniformly when n increases, but for large N (say, $N > 10$), SF shows practically a plateau and then decreases uniformly when n increases. In terms of relative penetration n/N, this means that SF decreases only above a critical penetration, and this result is consistent with the work of Camero and Sweed (1976). (Their continuum equilibrium theory corresponds to $N \to \infty$ in our model.) This critical value of penetration increases when ρ decreases (that is, for instance, when the total concentration of the solution decreases). Figure 11 shows that with $\rho = 0, 1$, SF decreases below its initial value only after $n \simeq 15$, that is, a relative penetration $n/N = 3$.

It might thus seem interesting, for mixed reservoirs, to use small values of ρ in order to allow high values of penetration, and therefore of output P_m, still keeping the separation factor high. In practice, one must keep in mind that the number of cycles needed to approach the limit regime increases rapidly and may become prohibitive as one departs from $\rho = 1$ (see, for instance, Grevillot and Tondeur, 1976, Figure 11, for pumps with a single transfer per half-cycle). The speed of convergence toward the limit regime is thus an important practical parameter, not accounted for here, and which we shall discuss in a forthcoming paper.

Figure 11 also illustrates the detail of the behavior of SF for small values of n. It has a very flat maximum, consistent with the work of Wankat (1973) for the linear case. This is shown to be due to the concentration x_B which presents a minimum, whereas x_T decreases uniformly.

Figure 12 shows SF as a function of number of stages N for different values of penetration, the output being fixed at the same value of 1 for both staged-reservoir and mixed-reservoir pumps. For given n/N, SF increases practically exponentially with N for all pumps. For staged reservoirs, SF increases with the penetration n/N.

APPROXIMATE SOLUTIONS FOR NONLINEAR CASE

Although no rigorous analytical solution is available in the nonlinear case, a detailed inspection of Figure 10 leads us to an approximate expression for SF. As mentioned above, for staged-reservoir pumps, the full straight lines on Figure 10 indicate an exponential dependence of SF on n. In addition, for $N > 1$, these lines are approximately parallel and equally spaced, indicating an exponential dependence on N.

This leads us to the following approximate expression:

$$SF\,|N, n|_s \simeq a\, b^N c^{n-1} \tag{30}$$

where a, b, and c are independent of N and n. In the case of Figure 10, the following values of a, b, and c represent all the results of the figure to within 15%:

$$a = 1.42 \quad b = 1.47 \quad c = 1.17$$

Note the analogy between Equation (30) and the rigorous solution (19) of the linear case.

For the mixed-reservoir pumps, no solution for the separation factor is available, even in the linear isotherm case. However, it is possible to obtain an approximate expression as discussed below. The pumps with one transfer per half-cycle can be considered as mixed-reservoir pumps or staged-reservoir pumps. Therefore, the curves on Figure 10 for the two types of pumps start from the common value $SF\,|N, 1|$, given by relation (30), with $n = 1$:

$$SF\,|N, 1| \simeq a\, b^N \tag{31}$$

Because the separation factor is practically constant below a critical value of penetration (inasmuch as the maximum on Figure 11 is very flat and can be neglected), Equation (31) gives the separation factor of mixed-reservoir pumps within a certain range of penetration.

NOTATION

C = total ionic concentration of the liquid (equivalents/l)
m_o = defined by Equation (20) (dimensionless)
N = number of cells
n = number of transfer steps per half-cycle
P_m = output of mixed-reservoir pumps, defined by Equation (29) (dimensionless)
P_s = output of staged-reservoir pumps, defined by Equation (28) (dimensionless)
Q = total exchange capacity of the solid contained in a cell (equivalents)
$SF\,|N, n|$ = separation factor (in the sense of parametric pumping) of a $|N, n|$ pump in limit regime
T, T' = temperatures
V = volume of a liquid fraction (l)
x, y = equivalent fraction of preferred ion in liquid and solid, respectively (dimensionless)
x_B, x_T = values of x in bottom and top reservoirs, respectively, of a mixed reservoir pump in limit regime
x_o, y_o = initial uniform concentrations of all liquid fractions and all solid fractions, respectively
$\overline{x_o}, \overline{y_o}$ = average values of x and y in the initial state
α, α' = equilibrium separation factors at T and T', respectively (dimensionless)
$\rho = CV/Q$ = stage capacity ratio (dimensionless)
$|N, n|_m$, $|N, n|_s$ = parametric pump with N cells and n transfer steps per half-cycle, with mixed reservoirs and staged reservoirs, respectively

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APPENDIX

The limit regimes of Figures 2 to 9 and the separation factors of Figures 10, 11, and 12 have been calculated cycle by cycle with a computer using extended precision. The nonlinear isotherms are described by Equations (3*a*) and (3*b*) and the linear isotherms by Equation (4*a*) and (4*b*). The parameter values are given below.

	Isotherms					
Figures		α	α'	x_o	y_o	ρ
2	Nonlinear	3.5	1.5	0.2	0.467	1
3, 4, 5	Nonlinear	3.5	1.5	0.4	0.7	1
6, 7, 8	Linear	3.5	1.5	0.01	0.035	1
9, 10	Nonlinear	3.5	1.5	0.4	0.7	1
11	Nonlinear	3.5	1.5	0.4	0.7	0.1
12	Nonlinear	3.5	1.5	0.4	0.7	Varies*

* $\rho = P_S \cdot N = N$ for staged-reservoir pumps, $\rho = P_m \cdot N/n = N/n$ for mixed-reservoir pumps.

Manuscript received March 1, 1977; revision received August 5, and accepted August 8, 1977.

A Solid / Liquid Separation Process Based on Cross Flow and Electrofiltration

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The cross flow/electrifiltration process combines migration of particles in the presence of electrical and shear fields to increase filtration rates. A mathematical model and the experimental data are presented for both a kaolin clay suspension and an oil in water chemically stabilized emulsion. When the filter is operated in a regime above the critical voltage, filtration rate-electric field strength dependence becomes linear, and both electroosmosis in the filtration medium and electrophoresis in the liquid film are the controlling mechanisms of transport. Both experimental data and the mathematical model indicate that the fluid circulation rate tangential to the filtration media does not necessarily increase filtration rate depending on the regime of operation. The model is used in conjunction with the experimental data to separate the liquid film resistance adjacent to the filter cake which is determined by fluid shear and electric field from the cake and filter medium resistances which are influenced by electroosmosis.

SCOPE

The cross flow/electrofilter employs two particle transport mechanisms to minimize accumulation of particles at the filter medium. The process combines particle migration away from the filter due to fluid shear (cross-flow filtration) and electrophoretic migration (electrofiltration). In addition to these two mechanisms, electroosmosis in the filter medium, filter cake, or both can influence the filtration rate. The process offers the potential of both improved filtration rates and steady state operation for filtration of suspensions of micron or submicron sized particles. Most particles in aqueous media are negatively charged. The process should find application in filtration of suspensions where there is relatively low conductivity in the continuous phase. This is true for low ionic strength, aqueous media, and nonaqueous suspending media. The combination of the electrical field with a shear field should be particularly attractive for suspensions of charged, shear sensitive particles. This paper deals entirely with the filtration rate improvement aspects of the cross flow/electrofilter. In principle, this process can be used for particle-particle fractionation of multicomponent particulate suspensions.

The principal objective of this investigation was to experimentally test a mathematical model which permits separation of the effects of the particle concentration polarization in the liquid film on the feed side of the filtration medium, the filter medium resistance including electroosmotic effects, and the filter cake resistance which

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