Smith, K. A., J. H. Meldon, and C. K. Colton, "An Analysis of Carrier—Facilitated Transport," *AIChE J.*, **19**, 102 (1973).

Van Krevelen, D. W. and C. M. E. Baans, "Elimination of Carbon Monoxide from Synthesis Gas by Absorption in Cuprous Salt Solutions," *J. Phys. Coll. Chem.*, **54**, 370 (1950).

Ward, W. J., "Analytical and Experimental Studies of Facilitated Transport," *AIChE J.*, **16**, 405 (1970*a*).

Ward, W. J., "Electrically Induced Carrier Transport," *Nature*, **227**, 162 (1970*b*).

Ward, W. J., and W. L. Robb, "Carbon Dioxide—Oxygen Separation: Facilitated Transport of Carbon Dioxide Across a Liquid Film," *Science*, **156**, 1481 (1967).

Winnick, J., R. D. Marshall, and F. H. Schubert, "An Electrochemical Device for Carbon Dioxide Concentration. 1. System Design and Performance," *Ind. Eng. Chem., Proc. Des. Div.*, **13**, 59 (1974).

Wise, D. L. and G. Houghton, "Diffusion Coefficients of Neon, Krypton, Xenon, Carbon Monoxide, and Nitric Oxide in Water at 10-60°C," *Chem. Eng. Sci.*, **23**, 1211 (1968).

Wittenberg, J. B., "The Molecular Mechanism of Hemoglobin-Facilitated Oxygen Diffusion," *J. Biol. Chem.*, **241**, 115 (1966).

Wittenberg, J. B., "Myoglobin—Facilitated Oxygen Diffusion: Role of Myoglobin in Oxygen Entry into Muscle," *Physiol. Rev.*, **50**, 559 (1970).

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Equilibrium Staged Parametric Pumping:

Part III. Open Systems at Steady-State-McCabe-Thiele Diagrams

The theory of equilibrium staged parametric pumps with discrete fluid transfers has been presented in previous papers for total reflux. Here, it is extended to open, fractionating systems, operating in cyclic steady state. The cases of an enriching section, a stripping section, and a complete fractionating apparatus are successively considered. Providing adequate variables are defined, the result is a diagram which plays the same role as the McCabe-Thiele diagram in distillation. The optimal feed stage location, the minimum reflux, and the separation factor for given operating conditions are determined analytically and graphically in the case of linear equilibrium isotherms. The method is then generalized to non-linear equilibria, particularly of constant relative volatility type.

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SCOPE

In two previous papers of this series, (Grevillot and Tondeur 1976, 1977), parametric pumps were studied in which the usual packed adsorbent bed is replaced by a cascade of discrete equilibrium stages, and the usual continuous flow by discrete transfers of fluid fractions. The study dealt with the steady limit regime (or cyclic steady state) of these pumps at total reflux. Striking analogies *with binary distillation theory are found, in particular with* respect to graphical, McCabe-Thiele-like, constructions. Here, we extend this approach to open pumps at cyclic steady-state, that is pumps with feed introduction, and withdrawal of products. The study is restricted to single-transfer per half-cycle, as was the first article of this series. We present the complete treatment in the case of linear isotherms, as this leads to analytical solutions for the separation factor and the minimum reflux ratio. The treatment is next generalized to Langmuir-type isotherms and to experimental equilibrium data.

CONCLUSIONS AND SIGNIFICANCE

Open equilibrium, staged parametric pumps at cyclic steady state can be analyzed graphically, in a manner analogous to distillation columns. The following concepts must be employed:

1. The fluid fractions of composition x', undergoing transfer upward at temperature T', play the same role as the ascending vapor phase in distillation. The fluid fractions of composition x, undergoing transfer downward at temperature T, play the same role as the descending liquid phase in distillation. Accordingly, a McCabe-Thiele-like diagram will plot x' as a function of x.
2. The linear operating lines relate the compositions that cross each other between stages. They are obtained by a component balance on the end of the enriching or of the stripping section, *over a complete cycle*. The curves relating the compositions x' and x exiting from a given stage are not equilibrium curves as in distillation. They are obtained by component balances on a stage of the enriching section, a stage of the stripping section, and the feed stage, *over a half-cycle*. There are thus three different "partition curves," each depending on the reflux ratio.

Using these concepts, the classical McCabe-Thiele construction of binary distillation in transposed to parametric pumping: stepping off stages between operating and partition lines, optimal location of feed stage, determination of minimum reflux.

For linear equilibrium isotherms, the partitions are also linear. The separation factor may be expressed explicitly as a function of the operating parameters and the number of stages N_e and N_s of each section in the form

$$SF = \frac{x_{\text{top}}}{x_{\text{bottom}}} = \frac{(a_1)^{N_e} a_2 + a_3}{(b_1)^{N_e} b_2 + b_3}$$

The minimum reflux ratio is obtained as the solution of a 4th degree equation.

For arbitrary, non-linear isotherms, (using experimental data for instance) the partition lines are curved, but can still be easily constructed, and the graphical properties still hold. The separation factor and minimum reflux must

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be determined numerically or graphically, by trial and error.

The significance of this approach is, at this stage, mainly conceptual and didactic, and lies precisely in its analogy with the theory of distillation. We believe that parametric pumping has remained so far mysterious to most chemical engineers because it has usually been presented, experimented, and modeled as a complex, transient, batch chromatographic operation. Here, we approach it deliberately as a steady-state, open, staged operation, and thus provide the link with familiar unit operations.

The first description of an open parametric pump, as well as the first experiments (Wilhelm et al. 1968), deal with a recuperative pump without reflux. Shortly after, Gregory and Sweed (1970) use the equilibrium theory developed by Pigford et al. (1969) to model two open systems with top feed, and top and bottom withdrawal. They define a critical reflux ratio, below which the bottom product cannot be perfectly pure. This ratio is analogous to the switching point of Chen and Hill (1971).

These last authors also use the equilibrium theory to study four open systems, with top or bottom feed. Chen and Hill define the notion of penetration distance—that covered by a concentration front during one half-cycle)—and give a very attractive representation of the possibilities of a parametric pump: The diagram of penetration distances, (warm half-cycle vs. cold half-cycle). In particular, the role of column length is illustrated.

All the above systems can be considered as enriching or stripping sections. Complete fractionating systems, involving both enriching and stripping sections, with feed in between, and product withdrawal at both ends, have been studied by Horn and Lin (1969) and Gupta and Sweed (1973). Recently, Camero and Sweed (1976) use the non-linear equilibrium chromatography theory to analyze batch and open para-pumps. Their approach allows prediction of the ideal behavior of a complete fractionation column for binary mixtures. A detailed analysis of the literature concerning open para-pumps is made by Wankat (1974) and Rice (1976).

The approach taken here, as compared to the literature just mentioned, is characterized by the discrete stages and discrete flow model, introduced in two previous publications (Grevillot and Tondeur 1976 and 1977), and by the direct analysis of the limit regime (or cyclic steady-state), by McCabe-Thiele-type methods.

Stage para-pumps have received little attention since Wakao et al. (1968) first introduced the concept. The only experiments have been published by Wankat (1973), together with an extensive numerical study. No work has been done on open-staged systems.

DESCRIPTION OF THE OPEN STAGED PARAMETRIC PUMP (OSPP)

Figure 1 shows the OSPP and its operating cycle. The operating cycle will be described in detail for each of the three sections: enriching, stripping, and feed stage. The system consists of a cascade of N cells, or stages, comprising N_e enriching stages, N_s stripping stages, and one feed stage, so that

$$N = N_e + N_s + 1 \tag{1}$$

Each cell contains the same amount of a solid adsorbent or ion exchanger, with a total capacity per stage Q. The solution is contacted with the solid in the cell, and equilibration occurs at temperature T or T'.

The equilibrium isotherms may be experimental data, or analytical expressions, either linear or non-linear. For the latter case, we use a simple mass-action form, which for binary ion-exchange, writes

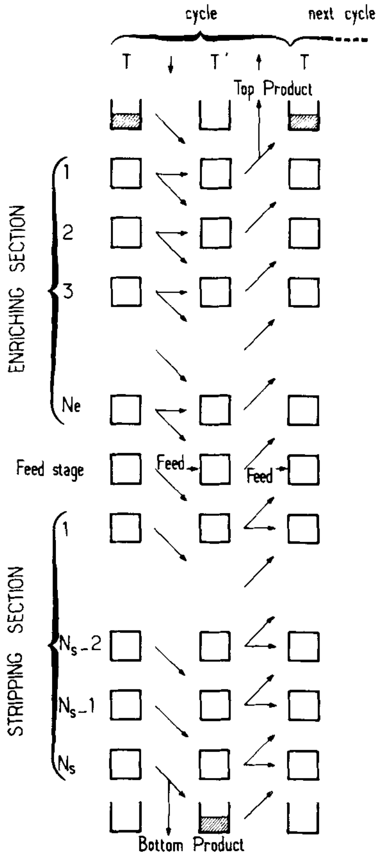

Figure 1. The open para-pump and its operating cycle.

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \tag{2a}$$

$$y' = \frac{\alpha' x'}{1 + (\alpha' - 1)x'} \tag{2b}$$

where α and α' are the equilibrium constants at T and T' respectively. In the following, we always assume that $\alpha > \alpha'$. For trace exchange, these isotherms may be approximated by

$$y = \alpha x \tag{3a}$$

$$y' = \alpha' x' \tag{3b}$$

We shall first present a complete analysis in the case of the linear isotherms (3*a*) and (3*b*), as this leads to analytical solutions for the separation factor and the minimum reflux. We then generalize the treatment to isotherms described by (2*a*) and (2*b*). Finally, we show how arbitrary experimental data may be used.

ENRICHING SECTION

Operating Cycle

One cycle of the operation (Figure 2) is defined as:

1. Equilibration at T (start of cycle): The liquid fractions (each of volume V_e) are in cells 1, . . ., N_e. In each cell, the solid and the liquid are in equilibrium at temperature T. The top reservoir contains a volume $\epsilon_e V_e$.

2. Transfer down: A part $\epsilon_e (0 < \epsilon_e < 1)$ of each liquid fraction V_e is transferred from a cell to the next cell down and the part $1 - \epsilon_e$ remains in the same cell. After this transfer down, each cell contains again a liquid volume V_e, and the top reservoir is empty.

3. Equilibration at T': The temperature is switched to T' and reequilibration is allowed.

4. Transfer up: Each liquid fraction is transferred one stage up. A part $1 - \epsilon_e$ of the liquid contained in cell 1 exits from the cascade as top product. After this transfer up, each cell contains a liquid volume V_e. This ends the cycle: the next cycle will start with a switch to T and reequilibration in each cell of the enriching section.

Operating Line Equation

We proceed to establish a relation between the compositions that cross each other between stages, that is, between compositions x_{n-1} and x'_n flowing between stages $n - 1$ and n (see Figure 2). This relation is obtained by writing a material balance around the top of the enriching section, over a complete cycle, as materialized by the dotted envelope on Figure 2. In the cyclic steady state, this balance is

$$C V_e x'_n = C \epsilon_e V_e x_{n-1} + C(1 - \epsilon_e) V_e x_T \quad (n \geq 1) \tag{4}$$

with $x_o = x_T$. Dividing by CV_e

$$x'_n = \epsilon_e x_{n-1} + (1 - \epsilon_e) x_T \tag{5}$$

Equation (5) is the operating line equation of the enriching section, and shows that in the (x, x') plane, the points (x_{n-1}, x'_n) corresponding to any value of n are on a straight line of slope ϵ_e.

Partition Line Equation

In distillation, the relation between the compositions leaving an equilibrium stage is simply the vapor-liquid equilibrium curve. Here, we need to establish this relation (between x'_n and x_n) by a material balance around a stage over a half-cycle. For stage n, and the half-cycle at T'

$$Q y_n + C(1 - \epsilon_e) V_e x_n + C \epsilon_e V_e x_{n-1} = Q y'_n + C V_e x'_n \tag{6}$$

Eliminating x_{n-1} by use of Equation (5) we obtain

$$y_n + (1 - \epsilon_e) \rho_e (x_n - x_T) = y'_n \tag{7}$$

where

$$\rho_e = \frac{C V_e}{Q} \tag{8}$$

Expressing y_n and y'_n in terms of x by Equation (3), we get finally

$$x'_n = \frac{\alpha + (1 - \epsilon_e)\rho_e}{\alpha'} x_n - \frac{(1 - \epsilon_e)\rho_e}{\alpha'} x_T \tag{9}$$

Equation (9) shows that in the plane (x, x'), all points (x_n, x'_n) are on a straight line of slope $(\alpha + (1 - \epsilon_e)\rho_e)/\alpha'$. We shall call this the *partition line*. It will play the same role as the vapor-liquid equilibrium curve in distillation. However, here, the partition line depends on the reflux ratio as well as the operating line, as can be seen by rewriting Equations (5) and (9)

$$x'_n = \frac{R_T}{R_T + 1} x_{n-1} + \frac{1}{R_T + 1} x_T \tag{10}$$

$$x'_n = \left(\frac{\alpha}{\alpha'} + \frac{1}{R_T + 1} \frac{\rho_e}{\alpha'} \right) x_n - \frac{1}{R_T + 1} \frac{\rho_e}{\alpha'} x_T \tag{11}$$

where

$$R_T = \frac{\epsilon_e}{1 - \epsilon_e} \tag{12}$$

is the top reflux ratio. The dependence of the partition line on the reflux ratio implies that the classical McCabe-Thiele treatment needs some modification. The partition line has to be constructed for each value of the reflux.

McCabe-Thiele Representation

In the (x, x') plane, the operating line represented by Equation (5) cuts the diagonal $(x = x')$ for $x = x_T$ and the x'-axis for $x' = (1 - \epsilon_e) x_T$ (Figure 3). The partition line represented by Equation (9) cuts the vertical $x = x_T$ at $x' = \alpha/\alpha' \, x_T$. A staircase construction between these two straight lines then leads to the compositions x and x' of each stage in the following way. We start with a specified top product x_T, represented by point a on Figure 3 (a is the intersection of the operating line and of the diagonal).

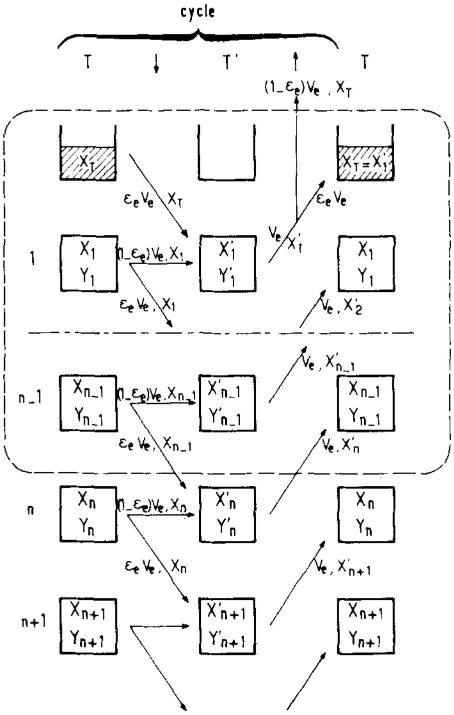

Figure 2. The enriching section and its operating cycle.

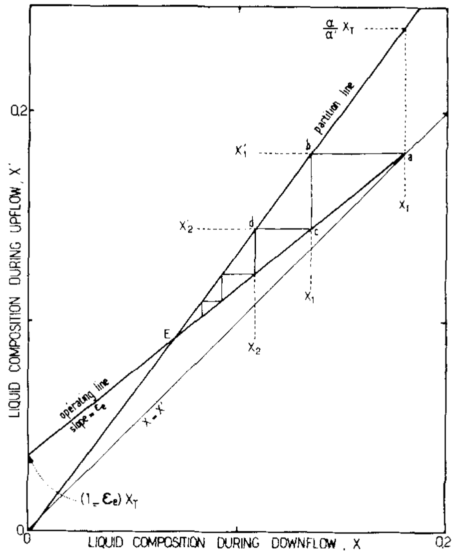

Figure 3. McCabe-Thiele representation for the enriching section.

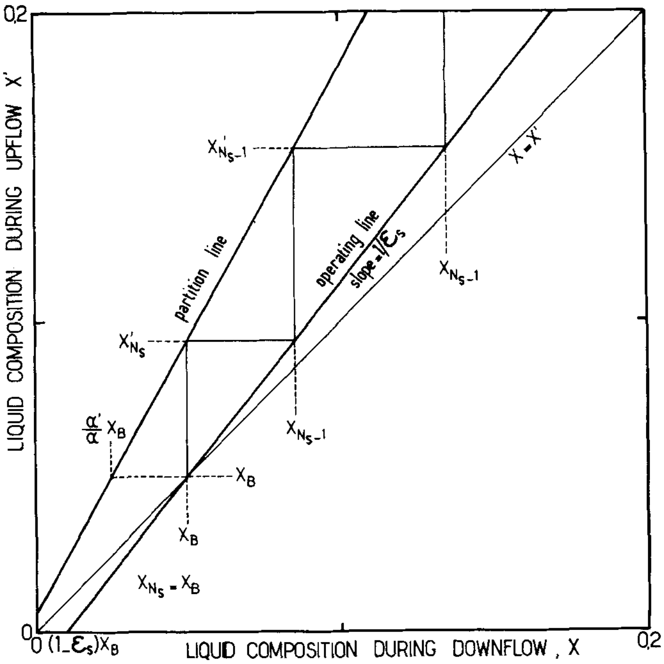

Figure 4. McCabe-Thiele representation for the stripping section.

We also know x'_1, since $x'_1 = x_T$ (see Figure 2). In distillation, this equality would correspond to a total condenser. The composition x_1 in stage 1 in equilibrium at T is then obtained directly as the abscissa of point b of ordinate x'_1, lying on the partition line. The vertical line of abscissa x_1 cuts the operating line at point c of ordinate x'_2, that is the composition in stage 2 at equilibrium at T'. Next the horizontal of ordinate x'_2 cuts the partition line at point d, of abscissa x_2, etc. Thus, the liquid phase composition x and x' of all stages may be determined. We do not need the solid phase composition y, which may, if desired, be calculated using the equilibrium relations.

The coordinates of the point of intersection E of the operating and partition lines of the enriching section are given by

$$x_E = \frac{1 - \epsilon_e}{\eta_e - \epsilon_e} x_T \tag{13}$$

$$x_E' = \eta_e x_T \tag{14}$$

with

$$\eta_e = \frac{\alpha + \rho_e}{\alpha' + \rho_e} \tag{15}$$

E lies on a straight line through the origin and of equation $x' = \eta_e x$. We shall use these properties later on.

Calculation of the Enriching Factor

We define the enriching factor as the ratio of the top product concentration x_T to the bottom product concentration x_{Ne} of the enriching section. This ratio may be calculated by successive use of Equations (5) and (9) between successive stages. More directly, x'_n may be eliminated between these two equations to obtain the first order finite difference equation

$$x_n = b_1 x_{n-1} + b'_1 x_T \tag{16}$$

where

$$b_1 = \frac{\alpha' \epsilon_e}{\alpha + (1 - \epsilon_e)\rho_e} \qquad b'_1 = \frac{(\alpha' + \rho_e)(1 - \epsilon_e)}{\alpha + (1 - \epsilon_e)\rho_e} \tag{17}$$

The solution of Equation (16) is

$$x_n = b_1^{n-1} x_1 + \frac{b_1^{n-1} - 1}{b_1 - 1} b'_1 x_T \tag{18}$$

In addition, Equation (9) allows to express x_1 as a function of x_T (recalling that $x'_1 = x_T$)

$$x_1 = (b_1 + b'_1) x_T \tag{19}$$

which may be substituted into (18). After some rearrangement, Equation (18) may finally be written, with Ne enriching stages

$$\frac{x_T}{x_{Ne}} = \frac{\alpha - \alpha' + (1 - \epsilon_e)(\alpha' + \rho_e)}{(\alpha - \alpha') b_1^{Ne} + (1 - \epsilon_e)(\alpha' + \rho_e)} \tag{20}$$

This equation is comparable to Smoker's equation in distillation, which however applies to non-linear equilibria.

STRIPPING SECTION

Operating Cycle

The cycle is a mirror image of that of the enriching section, as can be seen from Figure 1.

1. Equilibration at T (start of cycle): The liquid fractions of volume V_s are in cells 1, 2, ... N_s, in equilibrium with the solid at T.
2. Transfer down, by one stage, of each liquid fraction: The effluent of cell N_s, of volume $(1 - \epsilon_s)V_s$, is the bottom product of the cascade. After this transfer, each cell contains again a volume V_s of liquid.
3. Equilibration at T'.
4. Transfer up: A part ϵ_s $(0 < \epsilon_s < 1)$ of each liquid fraction is transferred one cell upward, the part $1 - \epsilon_s$ remaining in the same cell. After this, each cell contains again a liquid volume V_s, except cell N_s, which contains $(1 - \epsilon_s)V_s$. This ends the cycle.

Operating Line and Partition Line

We proceed in the same way as for the enriching section. A component balance around the bottom of the stripping section, and over a complete cycle yields

$$x'_{n+1} = \frac{1}{\epsilon_s} x_n - \frac{1 - \epsilon_s}{\epsilon_s} x_B \tag{21}$$

This linear relation shows that in the (x, x') plane, points (x_n, x'_{n+1}) are on a straight line of slope $1/\epsilon_s$, which is the operating line of the stripping section.

The stripping section analogous of Equation (7) is the following

$$y'_n + (1 - \epsilon_s)\rho_s(x'_n - x_B) = y_n \tag{22}$$

where

$$\rho_s = CV_s/Q \tag{23}$$

Eliminating y_n and y'_n by use of Equation (3) we obtain

$$x'_n = \frac{\alpha}{\alpha' + (1 - \epsilon_s)\rho_s} x_n + \frac{(1 - \epsilon_s)\rho_s}{\alpha' + (1 - \epsilon_s)\rho_s} x_B \tag{24}$$

This linear relation shows that points (x_n, x'_n) lie on a straight line of slope $\alpha/(\alpha' + (1 - \epsilon_s)\rho_s)$, which we call the partition line of the stripping section. We also define the bottom reflux ratio R_B as

$$R_B = \frac{\epsilon_s}{1 - \epsilon_s} \tag{25}$$

R_B and ϵ_s vary in the same direction.

McCabe-Thiele Representation

As before, Equations (21) and (24) allow a straightforward representation of the operation of the stripping section (Figure 4). The operating line cuts the diagonal for $x = x_B$ and the x-axis for $x = (1 - \epsilon_s)x_B$. The partition line cuts the horizontal line $x' = x_B$ for $x = \alpha'/\alpha\, x_B$. A staircase construction between the two lines, starting from point (x_B, x_B) yields successively the liquid composition x'_{Ns}, x_{Ns-1}, x'_{Ns-1}, etc. The coordinates of the point S of intersection of the operating and partition line (which we shall use later) are

$$x_S = \frac{1 - \epsilon_s}{1 - \epsilon_s \eta_s} x_B \tag{26}$$

$$x'_S = \eta_s x_S \tag{27}$$

where

$$\eta_s = \frac{\alpha + \rho_s}{\alpha' + \rho_s} \tag{28}$$

Point S lies on a straight line through the origin and of slope η_s.

Calculation of the Stripping Factor

Let us define the stripping factor, in a way similar to the enriching factor, as the ratio x_B/x'_1. Eliminating the x' between Equations (21) and (24), we obtain the first order finite difference equation

$$x_n = \frac{1}{a_1} x_{n-1} - a'_1 x_B \tag{29}$$

where

$$a_1 = \frac{\alpha \epsilon_s}{\alpha' + (1 - \epsilon_s)\rho_s} \quad \text{and} \quad a'_1 = \frac{(\alpha' + \rho_s)(1 - \epsilon_s)}{\alpha \epsilon_s} \tag{30}$$

the solution of which is, for $a_1 \neq 1$

$$x_n = (1/a_1)^{n-1} x_1 - \frac{(1/a_1)^{n-1} - 1}{1/a_1 - 1} a'_1 x_B \tag{31}$$

x_1 is expressed as a function of x'_1 using Equation (24). Equation (31) can be rearranged to make explicit the stripping factor

$$\frac{x_B}{x'_1} = \frac{\alpha - \alpha' - (1 - \epsilon_s)(\alpha + \rho_s)}{(\alpha - \alpha')a_1^{N_s} - (1 - \epsilon_s)(\alpha + \rho_s)} \quad (a_1 \neq 1) \tag{32}$$

Minimum Reflux for Zero Bottom Concentration

When the number of stages N_s becomes infinite, the right hand side of Equation (32) behaves differently according as a_1 is smaller or larger than 1.

for $a_1 < 1$

$$\left(\frac{x_B}{x'_1}\right)_{N_s \to \infty} = 1 - \frac{\alpha - \alpha'}{(1 - \epsilon_s)(\alpha + \rho_s)} \tag{33}$$

for $a_1 > 1$

$$\left(\frac{x_B}{x'_1}\right)_{N_s \to \infty} = 0 \tag{34}$$

To obtain a zero bottom concentration, $x_B = 0$, a_1 must be larger than 1. Graphically, this condition means that the slope of the operating line must be smaller than that of the partition line (this results from Equations 21, 24 and 30). The equality of slopes, for $a_1 = 1$, leads to the minimum reflux $(\epsilon_{sm})_{x_B=0}$ below which it is not possible to obtain $x_B = 0$. This value is

$$(\epsilon_{sm})_{x_B=0} = \frac{\alpha' + \rho_s}{\alpha + \rho_s} \tag{35}$$

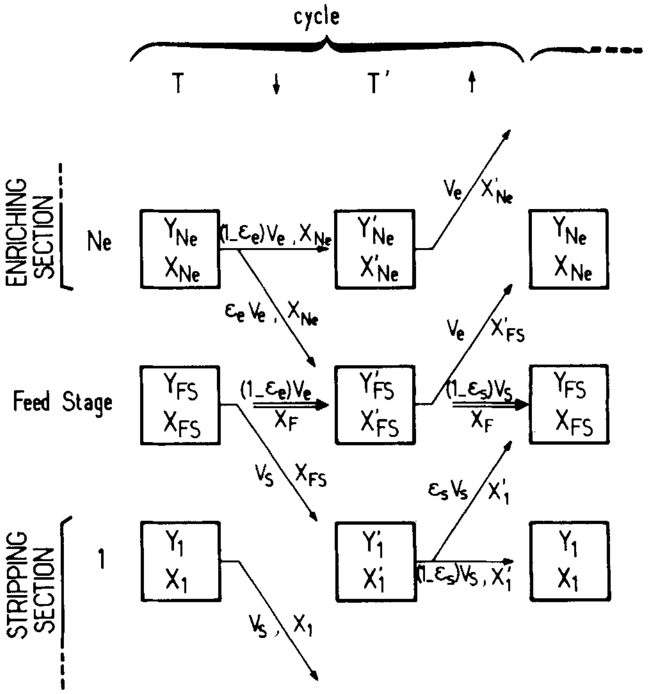

Figure 5. The feed stage and its operating cycle.

which corresponds to the reflux ratio

$$(R_{sm})_{x_B=0} = \frac{\alpha' + \rho_s}{\alpha - \alpha'} \tag{36}$$

This is precisely the value found by Gregory and Sweed (1970) in their Equation (16) for their open pumps with top feed, in particular for the symmetric open system, which is analogous to the stripping section studied here.[*] Although, their approach is completely different, (they use a continuous model, solved by the method of characteristics) this identity is not surprising. When x_B tends toward zero, both operating and partition lines tend to go through the origin. In addition, when the reflux is close to its minimum for $x_B = 0$ (Equation 36), the slopes of operating and partition lines become equal. Therefore, these lines tend to coincide, the number of stairs that can be drawn between them thus becomes infinite, and they are uniformly distributed along the two lines.

Under these conditions, the staged model with an infinite number of stages becomes equivalent to the continuum model, but *only* under these conditions. This equivalence at minimum reflux is lost when the operating and partition lines do not tend to coincide, for instance when $x_B \neq 0$, or when the partition lines are curved.

FEED STAGE

Operating Cycle

The feed of composition x_F is introduced twice per cycle, that is, before each equilibration (Figure 5). One cycle of the operation is defined in accordance with that of the enriching and stripping sections:

1. Equilibration at T (start of cycle): The feed stage contains a liquid fraction of volume V_s and of composition x_{FS}, in equilibrium at T with the solid of composition y_{FS}.

2. Transfer down and feed: The liquid fraction contained in the feed stage is transferred down to stage 1

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[*] The notations are different. Gregory and Sweed's equilibrium parameters A_c and A_h are respectively equal to α/ρ_s and α'/ρ_s.

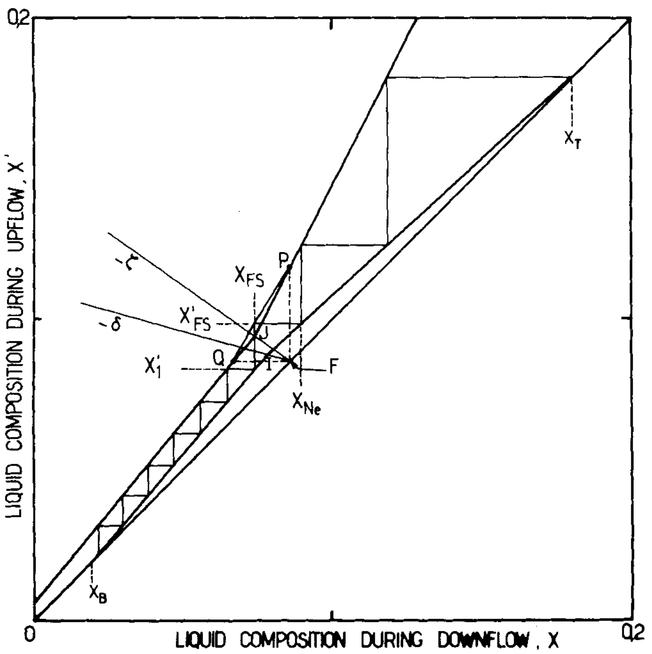

Figure 6. McCabe-Thiele representation for the total open para-pump with linear equilibrium.

of the stripping section. A part ϵ_e of the volume V_e contained in enriching stage N_e is transferred to the feed stage. Then a volume $(1 - \epsilon_e)V_e$ of feed of composition x_F is added into the feed stage and mixed. The feed stage then contains a liquid volume V_e.

3. Equilibration at T': The new solid and liquid compositions are y'_{FS} and x'_{FS} respectively.

4. Transfer up and feed: The liquid of the feed stage is transferred up to enriching stage N_e. Volume $\epsilon_s V_s$ is transferred from stripping stage 1 to the feed stage. Volume $(1 - \epsilon_s)V_s$ of feed of composition x_F is added, to complete the liquid volume at the value V_s. This ends the cycle.

Feed Stage Partition Line

We look for a relation between compositions x_{FS} and x'_{FS} of the downflow and upflow effluents of the feed stage. A component balance around an equilibration at T' is written

$$y_{FS} + (1 - \epsilon_e)\rho_e x_F + \epsilon_e \rho_e x_{N_e} = y'_{FS} + \rho_e x'_{FS} \quad (37)$$

A component balance on the enriching section (excluding the feed stage) over a complete cycle yields

$$x'_{FS} = \epsilon_e x_{N_e} + (1 - \epsilon_e)x_T \quad (38)$$

Using (38), x_{N_e} is eliminated from (37) to give

$$y_{FS} - (1 - \epsilon_e)\rho_e(x_T - x_F) = y'_{FS} \quad (39)$$

Next, y_{FS} and y'_{FS} are expressed in terms of x by the equilibrium relations (3) to give

$$x'_{FS} = \frac{\alpha}{\alpha'} x_{FS} - \frac{(1 - \epsilon_e)\rho_e}{\alpha'}(x_T - x_F) \quad (40)$$

This is the equation of a straight line through the point (x_{FS}, x'_{FS}), and the slope of which is the thermal relative affinity, α/α'. We shall call this the feed stage partition line.

Notice that an equation identical to (40) could have been obtained by writing first a material balance around an equilibration at T, and then a material balance on the stripping section. Instead of (40), one then obtains

$$x'_{FS} = \frac{\alpha}{\alpha'} x_{FS} - \frac{(1 - \epsilon_s)\rho_s}{\alpha'}(x_F - x_B) \quad (41)$$

The second terms on the right-hand side of (40) and (41) can be shown to be equal by a material balance on the complete pump and over a cycle (see later, Equation 44).

COMPLETE OPEN STAGED PARA-PUMP (OSPP)

Properties of the McCabe-Thiele Representation

The McCabe-Thiele diagrams of the enriching and stripping sections, together with the feed stage partition line, leads to the diagram of the complete cascade. The construction is facilitated by the following additional properties, which can be easily verified by examining the corresponding equations.

1. *Feed-stage partition line*: Let P and Q be the intersections of the feed stage partition line with the enriching and stripping sections partition lines respectively (Figure 6). The abscissa of P is x_F and the ordinate of Q is x_F as well. This allows the feed stage partition line to be drawn immediately, knowing x_F and the two other partition lines.

2. *δ-line, or internal feed distribution*: The intersection I of the two operating lines and point $F(x_F, x_F)$ lie on a straight line of slope $-\delta$, with

$$\delta = \frac{V_s - \epsilon_e V_e}{V_e - \epsilon_s V_s} = \frac{\rho_s - \epsilon_e \rho_e}{\rho_e - \epsilon_s \rho_s} \quad (42)$$

This quantity is the ratio of the change in downflow rate to upflow rate across the feed stage. It measures how the feed distributes between the descending and ascending flows *inside* the cascade. The line of slope $-\delta$ is thus the analogous of the feed line, or q-line, in distillation. We shall call it the internal feed distribution line.

3. *ζ-line, or external feed distribution*: The intersection J of the partition lines of the two sections, and point F lie on a straight line of slope $-\zeta$, with

$$\zeta = \frac{(1 - \epsilon_e)V_e}{(1 - \epsilon_s)V_s} = \frac{(1 - \epsilon_e)\rho_e}{(1 - \epsilon_s)\rho_s} \quad (43)$$

This quantity is the ratio of the feed volume introduced during the downflow half-cycle to that introduced during the upflow half-cycle. It measures how the feed is distributed *externally* between the two half-cycles. $\zeta = 1$ if the volumes injected at each half-cycle are equal. We designate by ζ-line or external feed distribution line the line of slope $-\zeta$. Notice that if the feed composition x_F and the products compositions x_B and x_T are specified, ζ is also specified, as can be seen from a material balance over the entire cascade

$$x_F[(1 - \epsilon_s)\rho_s + (1 - \epsilon_e)\rho_e] = (1 - \epsilon_e)\rho_e x_T + (1 - \epsilon_s)\rho_s x_B \quad (44)$$

Combining with Equation (43), one obtains

$$-\zeta = \frac{x_F - x_B}{x_F - x_T} \quad (45)$$

This quantity can also be defined in distillation, but is not currently used. Notice finally that when $V_e = V_s$, we have $\zeta = \delta = (1 - \epsilon_e)/(1 - \epsilon_s)$, the δ-line and the ζ-line coincide, and therefore points F, I and J lie on the same straight line.

Use of the McCabe-Thiele Diagram

Before the McCabe-Thiele diagram can be constructed using these properties, six independent variables must be specified or assumed.* Here, we shall specify x_F, x_T, x_B, the slope of the δ-line, the top reflux ϵ_e, and ρ_e. Clearly, other sets of independent variables are possible. With the present choice, the bottom reflux ϵ_s and ρ_s are not independent. Equations (42) and (43) lead to

$$\epsilon_s = \frac{\epsilon_e(\zeta + 1) + \delta\zeta - 1}{\epsilon_e(\zeta - \delta) + \delta(\zeta + 1)} \tag{46}$$

$$\rho_s = \rho_e \frac{V_s}{V_e} = \frac{\rho_e}{\zeta(1 + \delta)} [\rho_e(\zeta - \delta) + \delta(\zeta + 1)] \tag{47}$$

We then know all the variables necessary to construct the δ-line, the two operating lines and the three partition lines.

Having drawn these different lines, the classical staircase construction between partition lines and operating lines is started, from either x_T or x_B. We shall examine in more detail the construction in the vicinity of the feed stage (Figure 6).

Point (x_{FS}, x'_{FS}) representing the feed stage lies on the feed stage partition line PQ (Equation 40). Point (x_{N_e}, x'_{FS}) representing the passing streams between feed stage and enriching section lies on the enriching operating line. Point (x_{FS}, x'_1) representing the passing streams between feed stage and stripping section lies on the stripping operating line. In other words, above point (x_{FS}, x'_{FS}) the staircase is drawn between the operating and partition lines of the enriching section. Below this point, it is drawn between the stripping lines. There exists an optimal location of point (x_{FS}, x'_{FS}) which minimizes the number of stages. This will be examined in the next section.

In general, this construction will not give an integer number of steps between the specified x_B and x_T. If we want an exact determination of the pump, the construction must be resumed with new, adjusted value of one of the decision variables, usually the reflux ϵ_e. Once the diagram is exact, ϵ_s can be measured on the diagram or calculated by (46); ρ_s is given by (47). The production $(1 - \epsilon_e)V_e$ being specified, V_e is calculated. Knowing ρ_e and the total feed concentration C, one can calculate the capacity Q of solid to be loaded into each stage. The pump is then entirely determined.

Separation Factor

The separation factor SF of the complete cascade is defined as the ratio x_T/x_B of the top and bottom products concentrations of the cascade. To calculate it, an equation similar to (38) is obtained from a component balance around the stripping section, over a complete cycle

$$x_{FS} = \epsilon_s x'_1 + (1 - \epsilon_s)x_B \tag{48}$$

where x'_1 refers to stage 1 of the stripping section. Eliminate x'_1 by using Equation (32). In the same way, eliminate x_{N_e} from Equation (38) by using Equation (20). The two new equations are used to eliminate x'_{FS} and x_{FS} from Equation (40). The relation obtained contains only the concentrations x_F, x_T, x_B. Concentration x_F is next eliminated using Equation (44). After some rearrangement, the separation factor can be expressed as

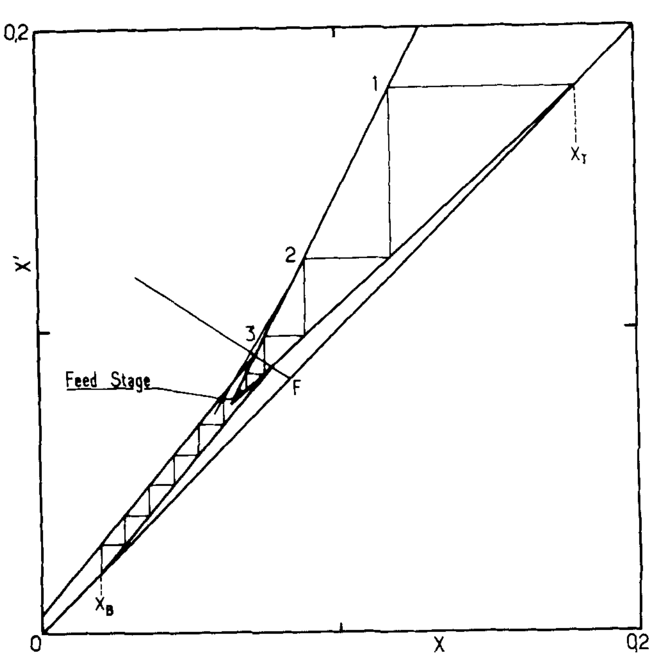

Figure 7. The McCabe-Thiele construction when feed stage is not at the optimum location.

$$\frac{x_T}{x_B} = SF = \frac{a_1^{N_s} a_2 + a_3}{b_1^{N_e} b_2 + b_3} \tag{49}$$

where a_1 and b_1 are given by Equations (30) and (17) respectively, and

$$a_2 = \frac{\alpha\epsilon_s(\alpha - \alpha')}{-(\alpha' + \rho_s) + \epsilon_s(\alpha + \rho_s)} \tag{50}$$

$$b_2 = \frac{\alpha'\epsilon_e(\alpha - \alpha')}{\alpha + \rho_e - \epsilon_e(\alpha' + \rho_e)} \tag{51}$$

$$a_3 = (1 - \epsilon_s)\left[-a_2 \frac{\alpha + \rho_s}{\alpha - \alpha'} + \alpha \right] + a \tag{52}$$

$$b_3 = (1 - \epsilon_e)\left[b_2 \frac{\alpha' + \rho_e}{\alpha - \alpha'} + \alpha' \right] + a \tag{53}$$

$$a = \frac{\rho_e\rho_s(1 - \epsilon_e)(1 - \epsilon_s)}{\rho_e(1 - \epsilon_e) + \rho_s(1 - \epsilon_s)} \tag{54}$$

OPTIMAL FEED STAGE LOCATION

Equation (49) shows that the separation factor depends separately on the number of stages N_s and N_e of each section, and not only on the total number of stages $N = N_e + N_s + 1$.

For a given total number of stages N, there exists an optimal repartition of stages between the two sections, which makes the separation factor maximum. Alternately, for a given separation factor, there exists an optimal repartition of stages leading to a minimum total number N. In other words, there exists an optimal feed stage location, as in distillation. It does not seem possible to determine this location analytically from Equation (49), but a trial and error search is always possible. A graphical solution also exists, presented below.

Suppose the products concentrations x_T and x_B are specified as well as the operating variables such that all the lines of the diagram are known, as shown earlier.

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* This number is obtained by counting the number of variables and the number of equations as is usually done in distillation. If the equilibrium coefficients α and α' are specified, the difference between these numbers is eight. This is the number of degrees of freedom, or the number of variables, that must be specified to design and operate the system. But the McCabe-Thiele diagram is non-dimensional, in the sense that it does not depend on the actual size of the equipment. To draw it, we need not specify the flow-rate to be treated nor the total concentration C of the feed. Therefore, only six independent variables need be specified at this stage.

We look for the staircase with minimum steps, starting say from x_T. As the intersection of the two operating lines is approached, a decision must be made as to when the steps should switch from the enriching lines to the stripping lines, that is also when the feed stage step, utilizing the PQ partition line, should be drawn.

The change should be made so as to obtain the maximum enrichment per stage with as small a number of stages as possible. Inspection of Figure 6 shows that this criterion is met if the switch is made in the vicinity of points I and J. The enrichment per stage is related to the "height" of the steps. Figure 7 shows an example where five steps are drawn in the enriching section. These steps become smaller and smaller as they approach the intersection of the enriching section, and thus contribute less and less to the separation. A similar result would be obtained if the switch is made too early.

MINIMUM REFLUX

Definition

As in distillation, the minimum reflux is that which, if decreased by an infinitesimal amount, will require an infinite number of stages to accomplish a specified separation. Three things should be noted carefully. First, the separation must be specified; second, the number of stages must not be specified; third, it is necessary to specify that the feed be introduced in the optimal location.

It is not as easy as in distillation to see the existence of the minimum reflux on the McCabe-Thiele diagram, because when the reflux is varied, the three partition lines (playing the role of the equilibrium curve in distillation) vary, as well as the operating lines. Therefore, we shall first present the algebraic determination using Equation (49) and then its graphic interpretation.

Calculation of Minimum Reflux for Finite Separation

For $\alpha > \alpha'$, the coefficients of Equation (49) have the following properties $0 < b_1 < 1$; $b_2 > 0$; $b_3 > 0$. This implies that the denominator of (49) decreases when N_e increases, and tends toward b_3 when N_e becomes infinite. Concerning the numerator, there are two cases, depending whether a_1 is smaller or larger than 1. (The latter will be considered further later.) We consider here the case $a_1 < 1$, for which we saw in Equation (33) that a zero bottom concentration ($x_B = 0$) cannot be obtained. It can be shown that, for $\alpha > \alpha'$, $a_1 < 1$ implies that $a_2 < 0$, which in turn implies $a_3 > 0$. The numerator in Equation (49) increases with N_s and tends toward a_3 when N_s becomes infinite. Therefore, when both N_e and N_s become infinite, the separation factor tends toward the limit

$$\lim_{\substack{N_e \to \infty \\ N_s \to \infty}} SF = a_3/b_3 \tag{55}$$

Designating by SF_{sp} the specified separation factor, the problem at hand imposes that

$$a_3/b_3 \geqq SF_{sp} \tag{56}$$

and the equality

$$a_3/b_3 = SF_{sp} \tag{57}$$

corresponds to the minimum reflux. The ratio a_3/b_3 can be expressed in terms of the top reflux ϵ_e (or R_T) only, using Equations (52), (53), (46) and (47). The equality (57) then becomes a fourth degree equation in ϵ_e, the adequate solution of which ($0 < \epsilon_e < 1$) is the minimum top reflux ϵ_{em}, corresponding to the specified separation SF_{sp}. The fourth degree equation is given in detail in the appendix (Equation A1). The minimum reflux ratio R_{Tm} is given by Equation (12) as $\epsilon_{em}/(1 - \epsilon_{em})$.

McCabe-Thiele Interpretation

Figure 8 illustrates the three situations, depending whether the reflux ratio $R = \epsilon/1 - \epsilon$ is larger than, smaller than, or equal to the minimum value R_m. Figure 8c shows the situation where $R < R_m$ and the staircase is drawn starting from x_T, with an infinite number of stages in the enriching section, and approaches point E. But even from point E, it is impossible to draw a step, with the corner on the feed partition line which allows the switch to the stripping section, that is, to point S or to the left of it. Equivalently, we might say that the step going from E to S has its corner (x_S, x'_E) above the feed partition line.

Figure 8a shows the special case where the step from E to S has its corner on the feed partition line. Such a construction implies an infinite number of stages in both enriching and stripping section, and corresponds precisely to the *minimum* reflux. Analytically, this situation is expressed by letting, in Equation (40) $x'_{FS} = x'_E$ and $x_{FS} = x_S$, that is

$$x'_E = \frac{\alpha}{\alpha'} x_S - \frac{(1 - \epsilon_e)\rho_e}{\alpha'} (x_T - x_F) \tag{58}$$

If in this equation, x'_E is eliminated by use of Equation (14), x_S by use of Equation (26), and ϵ_s and ρ_s using Equations (46) and (47), we obtain precisely the fourth degree Equation (A1) of the appendix. The equalities (57) and (58) are thus equivalent.

If the reflux is larger than the minimum, the corner point (x_S, x'_E) lies below the feed stage partition line (Figure 8b). The switch of the staircase from one section to the other is possible without reaching neither E in the enriching section, nor S in the stripping section, that is, with a finite number of stages in each section.

The critical position of the corner point (x_S, x'_E) here is to be compared to the critical position of the intersection of the operating lines, with respect to the equilibrium curve, in distillation.

Minimum Reflux for Infinite Separation ($x_B = 0$)

In the case not considered above where $a_1 > 1$, the numerator of the separation factor (Equation 49) increases indefinitely with N_s. The separation factor may become arbitrarily large. This is due to x_B decreasing toward zero, as Equation (34) shows. The minimum reflux for SF to become infinite corresponds to $a_1 = 1$. It is simply given, in terms of the bottom reflux, as a function of ρ_s, by Equation (35). It may also be expressed in terms of top reflux as a function of ρ_e (see appendix, Equation A3). The proper solution of Equation (A3) is the same as that of Equation (A1), when we let $SF_{sp} \to \infty$. In other words, Equation (A1) always gives the minimum reflux, whatever the value of SF_{sp}, finite or infinite.

TOTAL REFLUX

At total reflux, there is no feed, no withdrawal, and we have

$$\epsilon_e = 1; \quad \epsilon_s = 1 \tag{59}$$

Equations (5) and (21) show that the two operating lines coincide with the diagonal. Equations (9), (24), and (40) show that the three partitions lines coalesce into a single line going through the origin, of slope equal to the relative thermal affinity α/α'

$$x' = \frac{\alpha}{\alpha'} x \tag{60}$$

The McCabe-Thiele construction then consists simply in stepping off stages between this line and the diagonal. The total number of stages N necessary to obtain a specified separation factor SF is minimal. These two quantities are related by

$$SF_{\text{Total reflux}} = \left(\frac{\alpha}{\alpha'}\right)^N \tag{61}$$

REFLUX AND NUMBER OF STAGES

To obtain a specified separation, one will operate between total reflux, necessitating a minimal number of stages, and minimum reflux, necessitating an infinite number of stages. Figure 9, calculated using Equation (49) and an optimal feed stage location, illustrates the dependence of the number of stages on reflux, for different separations. As in distillation, the optimum reflux would result from an economic balance between the equipment costs, mainly a function of the number of stages, and the operating costs, mainly a function of the reflux.

COMPLETE OSPP-MASS-ACTION LAW EQUILIBRIA

In this section, we transpose the treatment presented so far to the case of non-linear liquid-solid equilibria in the cells. We assume that these equilibria are described by a simple mass-action law, represented by Equations (2*a*) and (2*b*), at temperatures T and T' respectively.

Operating and Partition Lines

The operating lines of the enriching and stripping sections are unchanged (Equations 5 and 21). To obtain the enriching partition line, we take Equation (7) and eliminate y_n and y'_n using the equilibrium relations (2*a*) and (2*b*). We obtain the following relation between x'_n and x_n

$$x'_n = \frac{x_n^2(\alpha - 1) + x_n\left[\dfrac{\alpha}{(1-\epsilon_e)\rho_e} + 1 - (\alpha - 1)x_T\right] - x_T}{-x_n^2(\alpha - 1)(\alpha' - 1) + x_n\left[\dfrac{\alpha - \alpha'}{(1-\epsilon_e)\rho_e} - (\alpha' - 1)(1 - (\alpha - 1)x_T)\right] + \dfrac{\alpha'}{(1-\epsilon_e)\rho_e} + (\alpha' - 1)x_T} \tag{62}$$

$$= f(x_n, \alpha, \alpha', x_T, \epsilon_e, \rho_e)$$

This equation replaces Equation (9) of the linear case, and describes a curve in the (x, x') plane which relates the compositions x_n and x'_n leaving stage n during a cycle. It is the *enriching section partition curve,* which plays the same role as the equilibrium curve in distillation, from the point of view of the McCabe-Thiele construction, but depends on the reflux.

A similar calculation leads to the *stripping section partition curve*

$$x_n = f(x'_n, \alpha', \alpha, x_B, \epsilon_s, \rho_s) \tag{63}$$

which has the same form as Equation (62) and is obtained from the latter by changing x'_n to x'_n, α to α' and reciprocally, x_T to x_B, ϵ_e to ϵ_s and ρ_e to ρ_s. This equation replaces Equation (24) of the linear case. For the feed stage, eliminating y_{FS} and y'_{FS} in Equation (39) by use of the equilibrium relations (2*a*) and (2*b*), we get

$$x'_{FS} = \frac{x_{FS}[\alpha - (\alpha - 1)(1-\epsilon_e)\rho_e(x_T - x_F)] - (1-\epsilon_e)\rho_e(x_T - x_F)}{x_{FS}[\alpha - \alpha' + (\alpha - 1)(\alpha' - 1)(1-\epsilon_e)\rho_e(x_T - x_F)] + \alpha' + (\alpha' - 1)(1-\epsilon_e)\rho_e(x_T - x_F)} \tag{64}$$

This replaces Equation (40) of the linear case.

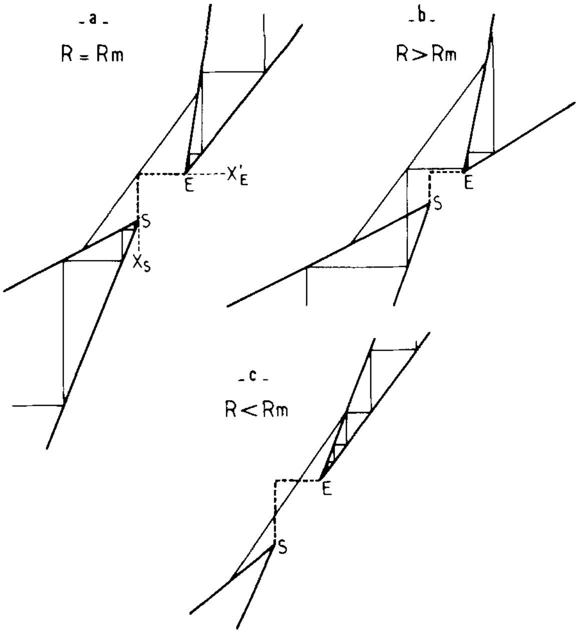

Figure 8. The minimum reflux.

McCabe-Thiele Representation

The McCabe-Thiele diagram with mass-action isotherms differs from that of linear isotherms in that the three partition lines are curved instead of straight, and must be constructed point by point by using Equations (62), (63), and (64). All other geometric properties of the linear diagram are conserved, in particular at minimum reflux, and the slope of the δ-line is still given by Equation (42). Figure 10 shows the detail of the diagram around the feed stage at minimum reflux, with non-linear isotherms.

Total Reflux

At total reflux, that is for $\epsilon_e = \epsilon_s = 1$, the two operating lines coincide with the diagonal. The three partition lines coincide and their Equations (62), (63) and (64) become simply

$$x' = \frac{(\alpha/\alpha')x}{1 + (\alpha/\alpha' - 1)x} \tag{65}$$

This relation replaces Equation (60) of the linear case, and has the same form as the isotherm Equation (2), with a coefficient equal to the thermal relative affinity α/α'. The equivalent of Equation (61), that is the relation between the separation and the number of stages which is minimum, is the following

$$\frac{x_1}{1 - x_1} \Bigg/ \frac{x'_{Ns}}{1 - x'_{Ns}} = \left(\frac{\alpha}{\alpha'}\right)^N \tag{66}$$

which is similar to Fenske's equation in distillation, as established by Grevillot and Tondeur (1976). In that reference, it was also shown that the minimal number

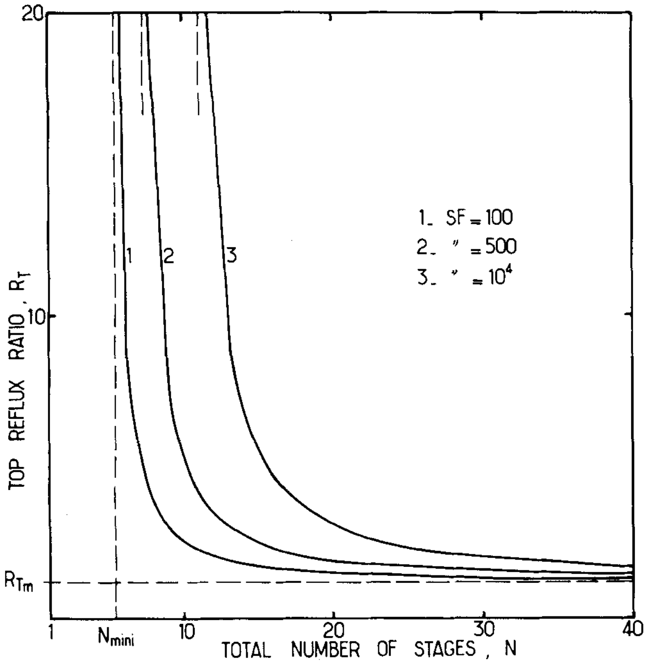

Figure 9. Effect of reflux on number of stages for specified separations, with feed at the optimum location.

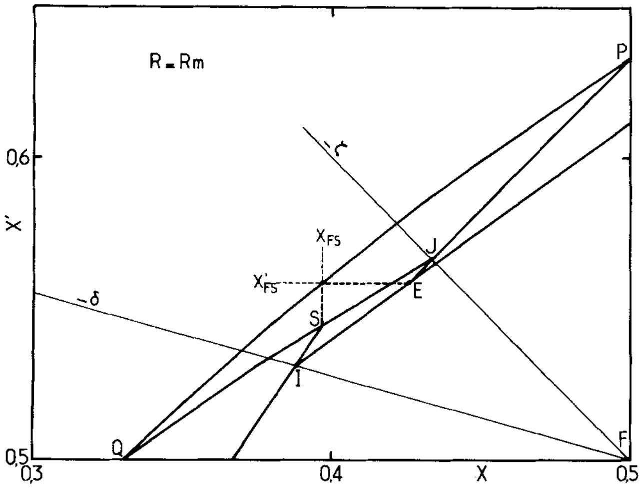

Figure 10. Detail of the McCabe-Thiele diagram at minimum reflux (non-linear isotherms).

of stages could also be determined by stepping off stages between the two isotherms.

At total reflux, the pump studied in this work becomes thus identical to that studied in Part I of this series. The reader is referred to it for more details, for instance, concerning the analogy between parametric pumping and distillation.

COMPLETE OSPP WITH EXPERIMENTAL EQUILIBRIUM DATA

If we have no analytical expression for the equilibrium data, there will obviously be no analytical expression for the partition lines. These lines can nevertheless be easily constructed point by point, if reasonable interpolation between data points is possible. For example, for the enriching section, assuming in Equation (7) a value for x_n, the corresponding y_n is taken from the interpolated equilibrium data at T. The left-hand side of Equation (7) is then calculated and yields y'_n. The equilibrium data at T' then furnish the value x'_n corresponding to y'_n. We have thus constructed the point (x_n, x'_n). The partition line of the stripping section and of the feed stage are obtained similarly by using Equations (22) and (39) respectively. Clearly, these constructions must be repeated for each value of the reflux. The other elements of the McCabe-Thiele diagram do not depend on the equilibrium data and are thus constructed as before.

This method of constructing the partition lines applies equally to the case where the experimental isotherms are represented by implicit functions of x and y. This will be the case in the numerical example presented next.

NUMERICAL EXAMPLE

Here, we illustrate the method and give orders of magnitude based on experimental equilibrium data, for a system of practical interest—the separation of copper and silver. Its purpose is *not* to show that staged para-pumps are superior to packed bed para-pumps.

We propose to treat a solution of silver and copper nitrate at a total concentration 0.5 N. The objective is silver recovery, and we desire a concentrated product containing essentially all the silver, the copper distribution being secondary. The specifications are gathered in Table 1. The values of x and y are relative to silver. The thermally sensitive adsorbent is a strong cation exchange resin, of the sulfonated polystyrene type. The stage capacity ratios ρ_e and ρ_s are chosen as 0.15 in both sections; this implies $V_e = V_s$. With a total exchange capacity of 2 equivalents/L of resin bed, a void fraction of 0.4, and a total solution concentration of 0.5N, the value $\rho = 0.15$ corresponds to a volume of solution per stage, V_e, equal to 150% of the void volume of packed resin. This allows a proper wetting of the solid. The calculations are made on the basis of a feed of one liter of solution per cycle.

Figure 11 shows the experimental exchange isotherms at the two working temperatures, 20°C and 60°C. They have been measured by classical batch equilibration tests. These isotherms are well represented by the following expression

$$a = \frac{y}{x}\left(\frac{1-x}{1-y}\right)^b \tag{67}$$

where $b = 1.43$ (independent of temperature) and $a(20°) = 6.72$; $a(60°) = 4.76$. The curves obtained with these values are shown as discontinuous lines on

TABLE 1. NUMERICAL EXAMPLE

Specifications:

Feed: Cations: Ag^+, Cu^{++}; anion: NO_3^-
Total concentration, $C = 0.5\ N$
Flow rate: one L/cycle
Composition: $x_{F,Ag} = 0.5$

Products: $x_{T,Ag} = 0.9$
$x_{B,Ag} = 0.01$

Stages capacity ratios $\rho_e = \rho_s = 0.15$ $(V_e = V_s = 0.3\ Q)$

Choice of reflux:

Minimum reflux: $R_{Tm} \simeq 6.52$ $(\epsilon_{em} \simeq 0.867)$
Minimum number of stages: 23
Reflux chosen: $R_T = 9$ $(\epsilon_e = 0.9)$

Calculated results:

Bottom reflux: $R_B = 11.2$ $(\epsilon_s = 0.918)$
Number of stages: 39
Feed stage: 17th
Volume of solution/stage: $V_e = V_s = 5.51$
Resin capacity/stage: 18.3 equivalents (about 9 L)

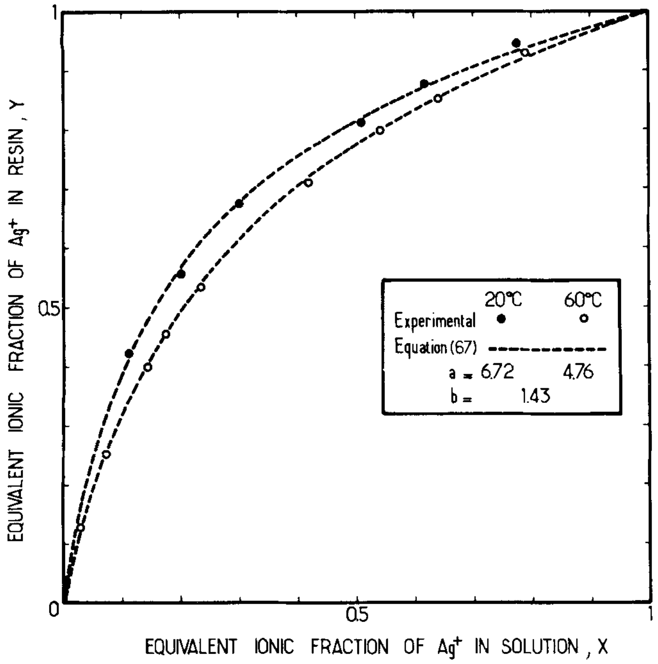

Figure 11. Equilibrium data for the exchange of Ag^+ and Cu^{++} on Duolite C 265 (Anion: NO_3^-; $C = 0.5N$).

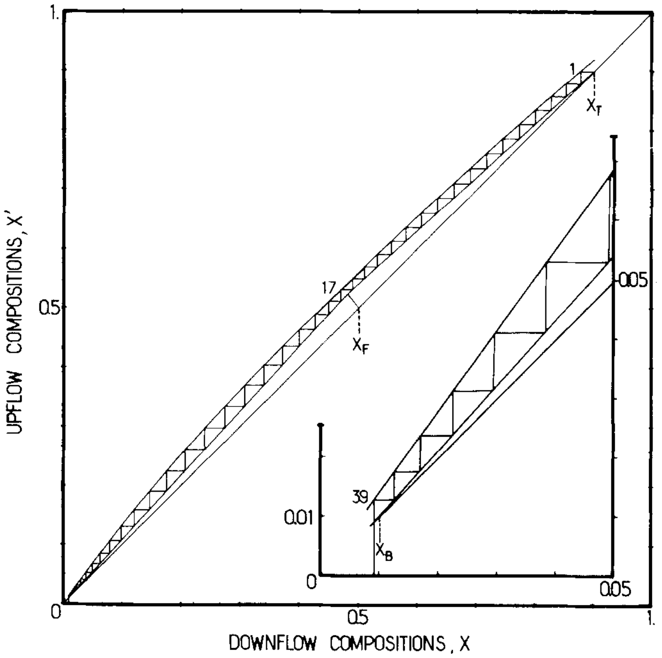

Figure 12. MacCabe-Thiele representation for the open para-pump of the numerical example (top reflux ratio $R_T = 9$).

Figure 11. Equation (67) is used to calculate the present example. Since Equation (67) is an implicit expression in x and y, the partition lines must be constructed point by point, as described in the previous section.

We have seen that six variables needed to be specified to construct the McCabe-Thiele diagram (which is independent of the "dimensional" variables, total concentration C, and feed flow-rate). Five of the six variables needed are already specified: x_F, x_B, x_T, ρ_e, ρ_s. As the sixth, we choose the reflux in the enriching section, ϵ_e. We can choose it arbitrarily, providing it is above the minimum reflux. Let us thus calculate the latter. This is done by the following trial and error:

- Pick a value of ϵ_e.
- Calculate the corresponding ϵ_s from Equation (46), in which $\delta = \zeta$ (since $V_e = V_s$), and ζ is given by Equation (45).
- Calculate the ordinate x'_E of the intersection point of the partition curve and the operating line of the enriching section.
- Calculate x_{FS} corresponding to $x'_{FS} = x'_E$, using the feed stage partition curve.
- Calculate the abscissa x_S of the intersection S for the stripping section.
- Compare x_{FS} and x_S. If $x_{FS} < x_S$, the stepping off from the enriching to the stripping section is possible, and the reflux chosen is above the minimum; if $x_{FS} > x_S$, ϵ_e is below the minimum. A new value of ϵ_e is picked until $x_{FS} = x_S$.

These calculations are somewhat tedious and are best done by computer. In the present example, we find $\epsilon_{em} = 0.867$ or $R_{Tm} = 6.52$. The minimum number of stages (total reflux) is obtained by drawing steps between the two isotherms, from x_T to x_B. We find $N_{\min} = 23$. To proceed, we must now decide on a value of the reflux, knowing that the number of stages increases when reflux decreases. Since we do not know the optimum, we shall take about 1.4 times the minimum reflux ratio, which is current practice in distillation. Thus $R_T = 9$ ($\epsilon_e = 0.9$).

The corresponding value of ϵ_s is obtained as indicated above, as $\epsilon_s = 0.918$ ($R_B = 11.2$). The complete McCabe-Thiele diagram may now be drawn (Figure 12). In this example, the feed partition line practically coincides with the two other partition lines. A total of 39 equilibrium stages are found necessary, with the feed at the 17th stage from the top. The size of each stage is calculated using the specified feed flowrate per cycle: V_e ($=V_s$). This is obtained by writing that the total volume of products per cycle equals one liter, thus

$$V_e = V_s = \frac{1}{2 - \epsilon_e - \epsilon_s} = 5.5\text{L}$$

The resin capacity per stage Q is then obtained using Equation (8), as $Q = 18.3$ equivalents. The cascade is now entirely determined.

The present analysis of open staged para-pumps is restricted to a single transfer of liquid fractions in each half-cycle. The relative penetration in the cascade is thus $1/N$, dependent on the number of stages. Further developments will have to envisage several transfers per half-cycle, as was already done at total reflux (Part II of this series). As in the paper mentioned, two operating modes have to be considered, conserving or not the concentration gradient in the top or bottom effluent.

The analogy with staged distillation developed here suggests that for packed bed para-pumps, an approach based on the transfer unit concept might be valuable, just as for packed bed distillation. However, there is as yet no method other than numerical fitting, for evaluating the HETP or the NTU in a parametric pumping system (see for instance, Nelson et al. 1978).

ACKNOWLEDGMENT

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NOTATION

C = total ionic concentration of the liquid (equivalents/l)
N_e, N_s, N = number of stages in enriching section, stripping section and total pump, respectively
Q = total exchange capacity of the solid contained in a cell (equivalents)
R_B, R_T = bottom and top reflux ratios, defined by Equations (25) and (12) respectively (dimensionless)
SF = separation factor (dimensionless)
T, T' = temperatures
V_e, V_s = volume of a liquid fraction, in enriching section and stripping section, respectively (1)
x, y = equivalent fraction of preferred ion in liquid and solid, respectively (dimensionless)
x_B, x_T = values of x for bottom and top products, respectively
x_F = value of x in feed
α, α' = equilibrium coefficients at T and T' (dimensionless)
δ = slope of feed line, defined by Equation (42) (dimensionless)
ϵ_e, ϵ_s = fraction of liquid fraction "refluxed" in enriching section and stripping section, respectively (dimensionless)
ζ = slope of feed distribution line, defined by Equation (43) (dimensionless)
ρ_e, ρ_s = stage capacity ratio in enriching and stripping section, respectively (dimensionless)

Subscripts

FS = relates to feed stage
m = relates to minimum reflux

Superscripts

prime = relates to T' temperature

APPENDIX: CALCULATION OF MINIMUM REFLUX IN CASE OF LINEAR ISOTHERMS

FINITE SEPARATION FACTOR ($x_B \neq 0$)

We choose here to specify ρ_e and to consider the top reflux ϵ_e as the unknown. Equivalent relations would be obtained with ρ_s specified and ϵ_s the unknown for instance.

Substituting the expressions for ϵ_s and ρ_s given by Equations (46) and (47) into a_3 and b_3 (Equations 52 and 53), and writing that the ratio a_3/b_3 equals the specified separation factor (Equation 57), we obtain the following fourth degree equation with ϵ_e as unknown

$$\epsilon_e^4 j_2 j_5 + \epsilon_e^3 (j_4 j_5 + j_2(\alpha - j_7)) + \epsilon_e^2 [j_3 j_5 - j_4 j_7 + j_2(j_6 - \eta_e \alpha) + \alpha j_1] + \epsilon_e [j_4 j_6 - j_3 j_7 + \alpha(j_0 - \eta_e j_1)] + j_3 j_6 - \eta_e \alpha j_0 = 0 \quad \text{(A1)}$$

with

$$j_0 = \alpha' \zeta + \rho_e \delta + \zeta\delta(\alpha' + \rho_e)$$
$$j_1 = (\zeta - \delta)(\alpha'\zeta + \rho_e) - (\zeta + 1)(\alpha'\zeta + \rho_e \delta)$$
$$j_2 = -\rho_e (\zeta - \delta)$$
$$j_3 = j_0 + \zeta(1 - \delta\zeta)(\alpha - \alpha')$$
$$j_4 = j_1 - \zeta(\zeta + 1)(\alpha - \alpha')$$
$$j_5 = \rho_e (SF_{sp} - 1)/(1 + \zeta)$$
$$j_6 = \left[\alpha' SF_{sp} + \rho_e \frac{SF_{sp} - 1}{1 + \zeta} \right] \eta_e \quad \text{and} \quad j_7 = j_5 + j_6 \quad \text{(A2)}$$

The suitable solution ϵ_{em} must be comprised between 0 and 1 and this facilitates the numerical search. In the numerous examples calculated, there was always a unique solution in the suitable interval, but we have not established the generality of this property.

INFINITE SEPARATION FACTOR ($x_B = 0$)

As above, specify ρ_e and calculate ϵ_e. Substituting the expressions for ϵ_s and ρ_s given by Equations (46) and (47) into Equation (35), one obtains

$$\epsilon_e^2 h_1 + \epsilon_e h_2 + h_3 = 0 \quad \text{(A3)}$$

with

$$h_1 = \rho_e (\zeta - \delta)(1 + \delta)$$
$$h_2 = (1 + \delta)[\zeta[\alpha(\zeta + 1) - \alpha'(\zeta - \delta)] - \rho_e [\zeta(1 - \delta) - 2\delta]] \quad \text{(A4)}$$
$$h_3 = -(\zeta + 1)\delta [\alpha'\zeta(1 + \delta) + \rho_e \delta(\zeta + 1)] + (\delta\zeta - 1)[\alpha\zeta(1 + \delta) + \rho_e \delta(\zeta + 1)]$$

In terms of ϵ_s, with ρ_s specified, Equation (35) is

$$\epsilon_s = \frac{\alpha' + \rho_s}{\alpha + \rho_s}$$

LITERATURE CITED

Camero, A. A., and N. H. Sweed, "Separation of Nonlinearly Sorbing Solutes by Parametric Pumping," *AIChE J.*, **22**, 369 (1976).

Chen, H. T., and F. B. Hill, "Characteristics of Batch, Semicontinuous, and Continuous Equilibrium Parametric Pumps," *Separ. Sci.*, 6, 411 (1971).

Gregory, R. A., and N. H. Sweed, "Parametric Pumping: Behavior of Open Systems. Part I: Analytical Solutions," *Chem. Eng. J.*, 1, 207 (1970).

Grevillot, Georges, and Daniel Tondeur, "Equilibrium Staged Parametric Pumping: Part I—Single Transfer Step Per Half-cycle and Total Reflux: the Analogy with Distillation," *AIChE J.*, 22, 1055 (1976). Part II—Multiple Transfer Steps Per Half-cycle and Reservoir Staging," *AIChE J.*, 23, 840 (1977).

Gupta, Ramesh, and N. H. Sweed, "Modeling of Nonequilibrium Effects in Parametric Pumping," *Ind. Eng. Chem. Fundam.*, 12, 335 (1973).

Horn, F. J. M., and C. H. Lin, "On Parametric Pumping in Linear Columns under Conditions of Equilibrium and Nondispersive Flow," *Ber. Bunsenges. Phys. Chem.*, 73, 575 (1969).

Mc Cabe, W. L., and E. W. Thiele, "Graphical Design of Fractionating Columns," *Ind. Eng. Chem.*, 17, 605 (1925).

Nelson, W. C., D. F. Silarski, and P. C. Wankat, "Continuous Flow Equilibrium Staged Model for Cycling Zone Adsorption," *Ind. Eng. Chem. Fundam.*, 17, 32 (1978).

Pigford, R. L., B. Baker, and D. E. Blum, "An Equilibrium Theory of the Parametric Pump," *Ind. Eng. Chem. Fundam.*, 8, 144 (1969).

Rice, R. G., "Progress in Parametric Pumping," *Sep. Purification Methods*, 5, 139 (1976).

Wakao, N., H. Matsumoto, K. Suzuki, A. Kawahara, "Adsorption Separation of Liquids by Means of Parametric Pumping," *Kagaku Kogaku*, 32, 169 (1968).

Wankat, P. C., "Cyclic Separation Processes," *Sépar. Sci.*, 9, 85 (1974).

Wankat, P. C., "Liquid-Liquid Extraction Parametric Pumping," *Ind. Eng. Chem. Fundam.*, 12, 372 (1973).

Wilhelm, R .H., A. W. Rice, R. W. Rolke, and N. H. Sweed, "Parametric Pumping: A Dynamic Principle for Separating Fluid Mixtures," *Ind. Eng. Chem. Fundam.*, 7, 337 (1968).

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