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THE THEORY OF ISOTOPE SEPARATION BY COUNTERCURRENT CHEMICAL EXCHANGE

AUTHORS:

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THE THEORY OF ISOTOPE SEPARATION BY COUNTERCURRENT CHEMICAL EXCHANGE

W. C. DeMarcus
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A B S T R A C T

The theory of isotope separation by countercurrent chemical exchange is worked out in detail using the continuous transfer concept. A comparison is made with discrete stagewise processes such as gaseous diffusion and with various general concepts of solvent extraction. The effects of a cell structure in the flow system is also worked out. An elementary design procedure is included both for the no-loss case and the case where the losses are small. In addition, a method of estimating stage lengths or transfer rate constants from small scale batch experiments is presented.

THE THEORY OF ISOTOPE SEPARATION BY COUNTERCURRENT CHEMICAL EXCHANGE

INTRODUCTION

Countercurrent cascades for isotope separation are often analyzed by means of the results for processes such as gaseous diffusion, treating a fixed length of plant as equivalent to a stage of a gaseous diffusion plant. This point of view is the one taken by Cohen⁽¹⁾ for example. Although engineers have worked much with continuous extraction problems, a detailed treatment of isotope separation as a continuous process does not seem to be available. For this reason it seems worthwhile to work out a general treatment of the problem for the case of chemical exchange sticking close to the continuous transfer concept. Many of the results can also be obtained by the stagewise treatment although as a general rule modifications of the order of the difference in the separation factor from unity are necessary. Needless to say, for separation factors which differ but infinitesimally from unity the results of the continuous and the stagewise treatment merge completely. Nonetheless one does not operate a plant with such a separation factor and since the correct results of the differential picture are often more readily obtained than the results from the stagewise picture it would seem that the continuous equations could receive more general usage. In this report no consideration is made of the important subject of the behavior of cascades in an unsteady state. This is a flaw which is present in the whole field of cascade theory to a more or less marked degree. However, the kinetic problem can be solved in certain rather special cases and reference in this connection is made to Cohen.⁽¹⁾

(1) Cohen, Karl, The Theory of Isotope Separation, NRES III - 1B, McGraw Hill, New York, (1951), Chapter 3.

I. The Separation Process

1) Chemical Factors

Consider a single chemical element which has two isotopic modifications. Two compounds of this element are respectively components of two immiscible phases. For nomenclature, the two isotopes will be assigned the letters A and B, the two phases the numbers 1 and 2. For the moment it is best to reserve decisions as to which phase will be designated 1. If the two phases are contacted it shall be supposed that the following reactions take place:

The reaction described by equation (I.1) is the transfer of a gram atom of isotope A in phase 1 into phase 2 accompanied by a transfer of a like amount of isotope B in the reverse direction. The reaction specified by equation (I.2) is just the reverse of the one described by (I.1). Let C_{A1} be the concentration of isotope A in phase 1 and let C_{A2} , C_{B1} , and C_{B2} be defined in the same fashion. Then at equilibrium

$$\frac{C_{A1}}{C_{B1}} = \alpha \frac{C_{A2}}{C_{B2}} \quad (I.3)$$

where α is an equilibrium constant. If the phases are numbered arbitrarily, α may be less than, greater than, or equal to unity. The final naming of the phases shall now be done in such a way

that α is greater than unity. The unhappy situation with $\alpha = 1$ is not considered since it will not separate isotopes. When the concentrations do not satisfy the equilibrium relation (I.3), currents of the isotopic species of equal molar magnitudes will flow in opposite senses between the phases until equilibrium is established. As a measure of the departure of the system from equilibrium one may use

$$\alpha C_{A2} C_{B1} - C_{A1} C_{B2} \quad (I.4)$$

The magnitude of the currents flowing to establish equilibrium will, at least for small departures from equilibrium, be proportional to this quantity. For a justification of this statement see Appendix A.

2) Physical Factors

The reactions considered in the preceding section take place at the interface between the two phases. Thus the concentrations at the interface might come close to equilibrium rather quickly while the concentrations away from the interface are still quite different. Once this situation is reached, the rate of the reaction is likely to be determined by the rate at which the various kinds of atoms can diffuse to the interface. Since diffusion rates in static systems are rather slow, the system will often consist of two fluid phases which are individually agitated in order to facilitate the exchange of matter between the interfacial regions and the remainder of the phases. If the agitation of the phases is efficient or unnecessary, the effects of diffusion

in bulk will be negligible except in the region of the fluid boundary layers at the interface. It is customary, and highly convenient, to consider the boundary layers as films of negligible material content. If this last assumption is made, the currents which cross the interface will be constant throughout the film since none of the current need be diverted inside the films for the purpose of changing the local inventories. Schematically one may picture the process as in Figure 1. For clarity the film thicknesses have been exaggerated in comparison with the rest of the phases. The interface has been sketched as a plane surface but it could just as well have been a spherical droplet of one phase immersed in the other phase, for example.

Figure 1

It may happen that the interface between the two phases is not static due to internal agitation. In this case one speaks of an average or effective interface. In this report terminology will be employed which is strictly applicable only for a static interface with the understanding that the property referred to is a suitable average.

The assumption of efficient mixing outside the film regions implies that the concentrations of the various isotopes outside the film regions are uniform. The only other concentrations that matter in the film picture are the concentrations at the interface. This assertion can be shown simply for a plane interface. Let $D(s)$ be the diffusion coefficient applicable for one isotope diffusing through one of the films, s being the distance measured normal to the interface taken positive into the film. The current density of the isotope in question in moles per unit time crossing unit area of a plane parallel to the interface at s is given by

$$J(s) = -D(s) \frac{\partial C(s)}{\partial s} . \quad (I.5)$$

In the equation above, J is the molar current density and $C(s)$ is the concentration of the isotope in question inside the film at distance s from the interface. The negligible amount of material present in the film implies that $J(s)$ is constant across the film. Therefore, one can integrate the above equation across the film at once with the result

$$C(h) - C(0) = -J \int_0^h \frac{ds}{D(s)} \quad (I.6)$$

where h is the total thickness of the film, $C(0)$ is the concentration of the isotope at the interface and $C(h)$ is the concentration at the outer boundary of the film which by the assumption of uniform mixing is the uniform concentration of the bulk of the

phase in question. The constant

$$\int_0^h \frac{ds}{D(s)} \quad (1.7)$$

is called the resistance of the film to diffusion of the isotope in question. Using the superscript 1 to denote quantities evaluated at the interface and the absence of the superscript to denote values in the bulk of the phases, four expressions for the current density J of A particles flowing into phase 1 may be readily written

$$R_{A1} J = C_{A1}^1 - C_{A1} \quad (1.8)$$

$$R_{B1} J = C_{B1} - C_{B1}^1 \quad (1.9)$$

$$R_{A2} J = C_{A2} - C_{A2}^1 \quad (1.10)$$

$$R_{B2} J = C_{B2}^1 - C_{B2} \quad (1.11)$$

wherein R_{A1} is the resistance of the film in phase 1 for passage of particles of isotope A and other resistances are defined in an analogous manner. The sign of the current involving B concentrations has been reversed because J is the current of A particles which is opposite in direction but equal in magnitude to the current of B particles.

3) The Rate of Exchange

The concentrations at the interface are not directly accessible for experimental determination. It is therefore desirable to have an expression for the current involving only the concentrations in the bulk of the phases. Evaluation of Equation (1.4) at

the interface gives

$$J = \gamma \left\{ \alpha C_{A2}^i C_{B1}^i - C_{A1}^i C_{B2}^i \right\} \quad (1.12)$$

where γ is the constant of proportionality mentioned in connection with equation (1.4). Equations (1.8) through (1.10) can be solved for the interfacial concentrations and substituted into (1.12).

There results

$$J = \gamma \left\{ (\alpha C_{A2} C_{B1} - C_{A1} C_{B2}) - J \left[\alpha R_{A2} C_{B1} + \alpha R_{B1} C_{A2} + R_{A1} C_{B2} + R_{B2} C_{A1} \right] + J^2 \left[\alpha R_{A2} R_{B1} - R_{A1} R_{B2} \right] \right\}. \quad (1.13)$$

This relation implicitly gives J as a function of the bulk concentration and the film and chemical constants.

The quantity ψ is defined by the relation

$$\alpha = 1 + \psi. \quad (1.14)$$

With the exception of the hydrogen deuterium mixture, separation factors are generally not much greater than unity, or ψ is generally small. It seems likely that quantities such as the film resistance defined above will also be approximately equal in each film. Consequently, δ_1 and δ_2 are defined by the equations

$$R_{A1} = (1 + \delta_1) R_{B1} \quad (1.15)$$

$$R_{A2} = (1 + \delta_2) R_{B2} \quad (1.16)$$

and one expects that the numerical values of δ_1 and δ_2 will be at most of the same order of magnitude as ψ .

To express the conservation of mass, one defines three inventory parameters I_1 , I_2 and ϕ by the relations

$$I_1 = (C_{A1} + C_{B1}) V_1 = M_1 V_1 \quad (I.17)$$

$$I_2 = (C_{A2} + C_{B2}) V_2 = M_2 V_2 \quad (I.18)$$

$$\phi = C_{A1} V_1 + C_{A2} V_2 \quad (I.19)$$

wherein V_1 and V_2 are the volumes of phase 1 and 2 respectively while M_1 and M_2 are the total molarities.

Finally, mole fractions y and x are introduced via the relations

$$C_{A1} = yM_1 = y(C_{A1} + C_{B1}) \quad (I.20)$$

$$C_{A2} = xM_2 = x(C_{A2} + C_{B2}). \quad (I.21)$$

Equation (I.13) can now be written in terms of quantities introduced in Equations (I.14) through (I.21)

$$\begin{aligned} J = & \gamma \left\{ M_1 M_2 \langle \alpha x(1-y) - y(1-x) \rangle - J \left[R_{B2} M_1 + R_{B1} M_2 + M_2 R_{B1} \right. \right. \\ & \left. \left. \langle \psi x + \delta_1(1-x) \rangle + M_1 R_{B2} \langle \psi + \delta_2 + \psi \delta_2 \rangle (1-y) \right] \right. \\ & \left. + J^2 R_{B1} R_{B2} (\psi + \delta_2 - \delta_1 + \psi \delta_2) \right\}. \quad (I.22) \end{aligned}$$

As a general rule reactions of this type fall rather closely into one or other of two categories. The first category is one in which the actual rate of exchange at the interface is slow enough to offer essentially all the resistance to the isotopic transfer. In

this case the reaction is said to be rate-limited and the current is given by

$$J = \gamma M_1 M_2 [\alpha x(1-y) - y(1-x)] \quad (1.23)$$

The more frequent occurrence is where one or both films offer by far the greater resistance in which case one calls the process film-limited. If only one film, say 1, is limiting then

$$J = \frac{M_1 M_2 [\alpha x(1-y) - y(1-x)]}{R_{B1} M_2 [1 + \psi x + \delta_1 (1-x)]} \quad (1.24)$$

Should $\delta_1 = \psi$ the equation becomes of the same form as before. If $\delta_1 \neq \psi$ we should use for J the form derived above. The analysis is only slightly more complex in the case where the variation of the denominator of (1.24) cannot be neglected and no attempt will be made herein to carry out the treatment in detail except in the section on Batch Experiments. We shall content ourselves otherwise with the case wherein

$$J = K [\alpha x(1-y) - y(1-x)] \quad (1.25)$$

where K may be molarity dependent but not dependent on the isotopic composition.

II. The Separation Plant

1) General

In the simplest case, an isotope separation plant is a system into which feed material of a given mole fraction is introduced and which delivers two streams of altered composition. Often one particular isotope is desired in enriched amounts and when this is

the case it is identified as species A. In case both isotopes are of value one must arbitrarily call one or the other isotope the desired component and assign it the label A.

Schematically, a plant often appears as in Figure 3.

P = rate of product withdrawal

F = feed rate

W = rate of waste discharge

y_f = feed mole fraction of component A

y_p = product mole fraction of component A

x_w = waste mole fraction of component A.

The withdrawal stream which has been enriched in isotope A is the product stream, the other withdrawal stream is called the waste. The portion of the plant between the feed point and the point of product take-off is the enricher, the rest is the stripper.

In a steady state, if there are no losses inside the plant due to leaks, corrosion, evaporation, etc., the amounts of both kinds of isotopes fed per unit time must equal their respective rates of withdrawal in the two exit streams. Thus

$$Fy_f = Py_p + Wx_w \quad (\text{II.1})$$

$$F(1-y_p) = P(1-y_p) + W(1-x_w) . \quad (\text{II.2})$$

The sum of the two equations is

$$F = P + W . \quad (\text{II.3})$$

These three equations are not independent. In general, the most useful pair appears to be (II.1) and (II.3).

2) The Cascade Equations in the Steady State

The differential equations giving the variation of the two mole fractions y and x with distance in the plant are referred to as the cascade or gradient equations.

Distances are measured along the flow path from the feed point, positive when directed toward the product end. The upflow, i.e., toward the product end, is given by $L(s)$. The downflow which is the flow of the alternate phase is $L'(s)$. $L'(s)$ and $L(s)$ must be related by

$$L'(s) = L(s) - P . \quad (\text{II.4})$$

Also $y(s)$ and $x(s)$ must satisfy

$$L(s) y(s) = P y_p + [L(s) - P] x(s) . \quad (\text{II.5})$$

These equations express the fact that the portion of the cascade between s and the product point is not gaining or losing inventory of either isotope. Equation (II.5) may be written in two equivalent forms

$$y(s) = x(s) + \frac{P}{L(s)} [y_p - x(s)] \quad (\text{II.6})$$

$$x(s) = y(s) - \frac{P}{L(s) - P} [y_p - y(s)] . \quad (\text{II.7})$$

Let $T(s)ds$ be the net rate of transfer of isotope A by chemical exchange from the downstream phase into the upstream phase between s and $s+ds$. Also let $-(dL/ds)ds$ moles of the upstream phase be transferred into the downstream phase in the same distance. The net amount of isotope A entering the differential volume of the upstream between s and $s+ds$ per unit time is

$$T(s)ds + L(s) y(s) - L(s+ds) y(s+ds) + y(s) \frac{dL}{ds} ds. \quad (\text{II.8})$$

In the steady state this must vanish. Expansion in a Taylor's Series to the first order in ds and subsequent division by ds yields the cascade equation for y

$$L(s) \frac{dy}{ds} = T(s). \quad (\text{II.9})$$

One notes that the refluxing operation which changes L does not appear explicitly in the equation for y . The differential equation for x can be obtained by differentiating Equation (II.5) with respect to s

$$L(s) \frac{dy}{ds} + y(s) \frac{dL}{ds} = \left[L(s) - P \right] \frac{dx}{ds} + x(s) \frac{dL}{ds} \quad (\text{II.10})$$

and using (II.9) one obtains

$$\left[L(s) - P \right] \frac{dx}{ds} = T(s) + \left[y(s) - x(s) \right] \frac{dL}{ds}. \quad (\text{II.11})$$

The explicit form of the transfer function $T(s)$ can be obtained directly from Equation (I.25) by integrating the current density of that equation over the effective area a of interface per unit height. The result of this integration is the overall transfer

coefficient (K_a) and in terms of it

$$T(s) = (K_a) \left[\alpha x(1-y) - y(1-x) \right]. \quad (\text{II.12})$$

To obtain these cascade equations in a more usable form one may substitute the expression (II.7) for x into (II.12) obtaining

$$L(s) \frac{dy}{ds} = (K_a) \left[\psi y(1-y) - \frac{P(y_p - y)(\alpha - \psi y)}{L(s) - P} \right] \quad (\text{II.13})$$

or eliminate y instead of x by using Equation (II.6), obtaining

$$\left[L(s) - P \right] \frac{dx}{ds} = (K_a) \left[\psi x(1-x) - \frac{P}{L(s)} (y_p - x) \left\{ 1 + \psi x - \frac{1}{(K_a)} \frac{dL}{ds} \right\} \right]. \quad (\text{II.14})$$

The above equations are applicable as they stand to a system with a continuous refluxing process. In case the refluxing is done at discrete points along the cascade one merely holds L constant between two such stations and integrates the equations to obtain the mole fractions at the two ends of the sections. However, care must be taken with the boundary conditions on passing to a new section.

Figure 4

From the figure it is clear that the upstream mole fraction y_{N+1}^B at the bottom of the $N+1$ section is equal to y_N^T , but the downstream

mole fraction x_{N+1}^B at the bottom of the N+1 section is not equal to the corresponding x_N^T at the top of the N section. If the amount of flow cut back is ΔL_N then from Figure 4 it may be seen that

$$(L_N - \Delta L_N - P) x_{N+1}^B + (\Delta L_N) y_N^T = (L_N - P) x_N^T \quad (\text{II.15})$$

or

$$x_{N+1}^B = x_N^T - \frac{(\Delta L_N)}{L_N - P} (y_N^T - x_{N+1}^B) . \quad (\text{II.16})$$

In the stripping section below the feed point the net upward transfer of A is $-Wx_w$ and the net upward transfer of both components is $-W$. Thus from material balance

$$L(s) = L'(s) - W \quad (\text{II.17})$$

and

$$L(s) y(s) = [L(s) + W] x(s) - Wx_w . \quad (\text{II.18})$$

The refluxing now is usually out of the downstream into the upstream so one employs the equation for x

$$\frac{d}{ds} [L'(s) x(s)] = T(s) + x(s) \frac{dL'}{ds} \quad (\text{II.19})$$

which is the analogue of (II.8). Eliminating y from the transfer function

$$[L(s) + W] \frac{dx}{ds} = (Ka) \left[\psi x(1-x) - \frac{W}{L}(x-x_w)(1+\psi x) \right] . \quad (\text{II.20})$$

This is the equation for x in the stripping section. The differential equation for y can be obtained if desired by differentiating (II.18) with respect to s.

3) The Enrichment Equation for Countercurrent Cells

The assumption of internal mixing in each phase only in a direction perpendicular to the isotopic gradient cannot always be approximated in practice. Sometimes it is better to compromise with the tendency to mix along the direction of flow by giving it free rein over limited regions. The flow channel is partitioned into cells. Inside of every cell each phase is mixed thoroughly so that the mole fraction is constant throughout the phase. Schematically, the process then looks something like Figure 5,

Figure 5

but ordinarily the cells are contiguous. In the figure they have been separated so that derivation of the material balance equation can be more readily followed. Let a again be the surface area per unit height of column and let the height of each cell be h . Then considering the steady state and setting the net flow of A atoms into phase 1 of cell N equal to zero there results

$$L_N(y_N - y_{N-1}) = (Kah) \left[\alpha_N(1-y_N) - y_N(1-x_N) \right] \quad (\text{II.21})$$

But the net transport of A toward the top must be $P y_p$ and hence

$$L_N y_N - 1 = (L_N - P) x_N + P y_p \quad (\text{II.22})$$

which can be solved for x_N

$$x_N = y_{N-1} - \frac{P(y_p - y_{N-1})}{L_N - P} \quad (II.23)$$

Let $\Delta = y_N - y_{N-1}$ so that $y_{N-1} = y_N - \Delta$. One may then write

$$x_N = y_N - \frac{P}{L_N - P} (y_p - y_N) - \frac{L_N \Delta}{L_N - P} \quad (II.24)$$

Substituting (II.24) in (II.21)

$$L_N \Delta = (Kah) \left[\psi y_N (1 - y_N) - \frac{P}{L_N - P} (y_p - y_N) (\alpha - \psi y_N) - \frac{\Delta L_N}{L_N - P} (\alpha - \psi y_N) \right] \quad (II.25)$$

and solving for Δ

$$\Delta = \frac{(Kah) \left[\psi y_N (1 - y_N) - \frac{P}{L_N - P} (y_p - y_N) (\alpha - \psi y_N) \right]}{L_N + \frac{L_N}{L_N - P} (Kah) (\alpha - \psi y_N)} \quad (II.26)$$

If the change in y is small from cell to cell the system may be considered continuous and Δ may be approximated by

$$\Delta \approx h \frac{dy}{ds} \quad (II.27)$$

Substitution in Equation (II.26) then gives

$$\frac{dy}{ds} = \frac{(Ka) \left[\psi y (1 - y) - \frac{P}{L - P} (y_p - y) (\alpha - \psi y) \right]}{L + \frac{L}{L - P} (Kah) (\alpha - \psi y)} \quad (II.28)$$

after dropping the subscripts on y . To good approximation when

$P \ll L$ and $\psi \ll 1$ Equation (II.28) may be written

$$\frac{dy}{ds} = \frac{Ka}{L + Kah} \left[\psi y (1 - y) - \frac{P}{L - P} (y_p - y) (\alpha - \psi y) \right] \quad (II.29)$$

By comparing with Equation (II.13) it may be seen that the gradient dy/ds with celling is to the gradient without celling as

$$\frac{K_a}{L + K_a h} \cdot \frac{L}{K_a} = \frac{1}{1 + \frac{K_a h}{L}} \quad (\text{II.30})$$

Below it will be shown that the quantity

$$\frac{L}{K_a} = H \quad (\text{II.31})$$

is a length of column which performs like one stage in a gaseous diffusion process*. Then one may write the ratio of the two gradients as given by (II.30) in the form

$$\frac{1}{1 + \frac{h}{H}} = \frac{H}{H + h} \quad (\text{II.32})$$

The effect of celling is an increase in the height equivalent of a theoretical stage by the length of one cell. For a more exact treatment of the effects of celling the reader is referred to Appendix B.

The derivation of the cascade equations has ignored the effect of material losses within the system. While the inclusion of losses raises no difficulties in principle, the gradient equations are no longer differential equations but become differentio-integral equations. No attempt to deal with the question of losses will be made except from a design standpoint. This question will be taken up in Section V.

*This is not quite correct. It performs like one stage of a gaseous diffusion process only when the gaseous diffusion difference equation can legitimately be approximated by a differential equation.

III. The Stage Concept

1) The Stage Process

In the gaseous diffusion process for the enrichment of uranium isotopes the enriching stage is a clearly defined unit. Each stage separates a feed stream into two fractions, one enriched in the desired isotope - this stream is pumped toward the product end of the cascade - and a fraction depleted in the desired isotope which is pumped down the cascade. Consider the n^{th} stage in a square cascade. A square cascade is one in which all stages

Figure 6

have the same flow.

The concentrations of the two streams leaving the stage are related by the stage enrichment factor ψ . For the n^{th} stage

$$\frac{y_n - x_n}{x_n(1-y_n)} = \psi_n \quad (\text{III.1})$$

A material balance taken about the top of the cascade above the n^{th} stage gives the relationship between x_{n+1} and y_n in terms of the product withdrawal rate P , the product concentration y_p , and

the interstage flow L ,

$$y_n = \left(1 - \frac{P}{L}\right) x_{n+1} + \frac{P}{L} y_p. \quad (\text{III.2})$$

From Equations (III.1) and (III.2) one may obtain

$$x_{n+1} - x_n = \frac{1}{1 - \frac{P}{L}} \left[\psi_n x_n (1 - y_n) - \frac{P}{L} (y_p - x_n) \right]. \quad (\text{III.3})$$

The difference, $x_{n+1} - x_n$, is the enrichment of the downflowing stream afforded by the n^{th} stage. For cascades in which the ψ value is the same for all stages and $\psi \ll 1$ the following approximation can be made:

a) $x_{n+1} - x_n$ may be replaced by dx/dn since the enrichment per stage is small,

b) $1 - y_n = \frac{1 - x_n}{1 + \psi x_n}$ and may be approximated by $1 - x_n$.

Replacing $1 - y_n$ by $1 - x_n$ in Equation (III.3) is equivalent to introducing an error in the value of ψ in that equation, the absolute value of which is not greater than ψ^2 .

Thus Equation (III.3) may be written

$$\frac{dx}{dn} = \frac{1}{1 - \frac{P}{L}} \left[\psi x(1-x) - \frac{P}{L} (y_p - x) \right] \quad (\text{III.4})$$

The number of stages N required to perform a given separation may be obtained by the integration of Equation (III.4)

$$N = \left(1 - \frac{P}{L}\right) \int_{x_B}^{x_T} \frac{dx}{\psi x(1-x) - \frac{P}{L} (y_p - x)} \quad (\text{III.5})$$

2) The Length Equivalent to a Theoretical Stage

Often designers of equipment use the stage concept in countercurrent processes where the concentration gradient is continuous. By analogy with the stagewise enriching cascade, a stage in the continuous process is defined as that length of equipment such that the concentrations of the streams leaving the hypothetical stage are related by a stage separation factor

$$\frac{y_n - x_n}{x_n(1-y_n)} = \Psi. \quad (\text{III.6})$$

The concentrations are defined in Figure 7.

Figure 7

A material balance about the product withdrawal end of the system of Figure 7 taken to the right of the n^{th} stage yields Equation (III.2). Combining Equations (III.2) and (III.6), with $\Psi \ll 1$, an equation similar to (III.4) is obtained

$$\frac{dx}{dn} = \frac{1}{1 - \frac{P}{L}} \left[\Psi x(1-x) - \frac{P}{L}(y_P - x) \right]. \quad (\text{III.7})$$

It has been demonstrated above (Section II) that the transfer of desired component between phases per unit length of equipment is

$$T = K_a \left[\alpha x(1-y) - y(1-x) \right] \quad (\text{II.12})$$

where α is the equilibrium constant for the chemical exchange reaction. Writing $1+\psi$ for α the above equation becomes

$$T = K_a \left[\psi x(1-y) - (y-x) \right]. \quad (\text{III.8})$$

Eliminating y by the material balance, Equation (III.2),

$$T = K_a \left[\psi x(1-x) - \frac{P}{L}(y_p - x)(1 + \psi x) \right] \quad (\text{III.9})$$

thus, for $\psi \ll 1$

$$(L - P)\frac{dx}{ds} = K_a \left[\psi x(1-x) - \frac{P}{L}(y_p - x) \right]. \quad (\text{III.10})$$

Dividing Equation (III.7) by Equation (III.10)

$$\frac{ds}{dn} = \frac{L}{K_a} \frac{\psi x(1-x) - \frac{P}{L}(y_p - x)}{\psi x(1-x) - \frac{P}{L}(y_p - x)}. \quad (\text{III.11})$$

Thus if ψ is chosen equal to ψ a stage length is obtained which is independent of concentration and of reflux ratio and dependent only on the flow and on the transfer coefficient. Setting $\psi = \psi$ in Equation (III.11)

$$\frac{ds}{dn} = \frac{L}{K_a}. \quad (\text{III.12})$$

Integrating over the length of a stage assuming both L and K_a constant we obtain an expression for the stage length H

$$H = \frac{L}{K_a}. \quad (\text{III.13})$$

3) The Height of a Transfer Unit

Consider an enrichment process taking place in a countercurrent apparatus. It is common engineering practice to use as a basis for design equations the two-film theory of Whitman. In general,

it is postulated that there exists in each phase, adjacent to the interface, a film which contains the entire resistance of that phase to mass transfer and that material is transferred between phases through these films by the mechanism of diffusion. Furthermore, it is assumed that equilibrium between the phases exists at the interface (i.e., if a chemical reaction takes place at the interface it is not the mass transfer rate controlling process).

A material balance on the desired isotope taken at steady-state operation about the top of the plant at a height s gives the equation

$$\begin{aligned} L(s) \frac{dy}{ds} - \left[L(s) - P \right] \frac{dx}{ds} &= k_1 a \left[y^1(s) - y(s) \right] = k_2 a \left[x(s) - x^1(s) \right] \\ &= T(s) \end{aligned} \quad (\text{III.14})$$

where k_1 = the enriched phase film mass transfer coefficient
(moles/hr.ft.²)

k_2 = the depleted phase film mass transfer coefficient
(moles/hr.ft.²)

a = ft.² interface/ft.

T = moles of desired isotope transferred (moles/hr.ft.)

$x(s)$ = bulk concentration of the desired isotope in the depleted phase (mole fraction)

$x^1(s)$ = interface concentration of the desired isotope in the depleted phase (mole fraction)

$y(s)$ = bulk concentration of the desired isotope in the enriched phase (mole fraction)

$y^1(s)$ = interface concentration of the desired isotope in the enriched phase (mole fraction).

Since the total inventory of each phase is constant the transfer T takes place by equimolal counter diffusion through the films. Under this circumstance the mass transfer coefficients k_1 and k_2 should be independent of the isotopic concentration⁽¹⁾. From Equation (III.14) one can write

$$y^1(s) - y(s) = \frac{T(s)}{k_2 a} \quad (\text{III.16})$$

By addition

$$y^1(s) - x^1(s) \left[y(s) - x(s) \right] = \frac{T(s)}{K'a} \quad (\text{III.17})$$

where

$$\frac{1}{K'a} = \frac{1}{k_1 a} + \frac{1}{k_2 a}$$

and the concentrations $y^1(s)$ and $x^1(s)$ are in equilibrium. In the usual case the equilibrium relationship is

$$\frac{y - x}{x(1-y)} = \psi \quad (\text{III.18})$$

Thus the gradient equation (the relationship between the concentration and position) is⁽²⁾

$$L(s) \frac{dy}{ds} = \left[L(s) - P \right] \frac{dx}{ds} = K'a \left\{ \psi x^1(s) \left[1 - y^1(s) \right] - \left[y(s) - x(s) \right] \right\} \quad (\text{III.19})$$

Returning to Equation (III.14) one may note the following. If practically the entire resistance of the two films in series lies in the enriched phase film then $K'a \approx k_1 a$ and $x^1 \approx x$. Equation (III.14) can then be written

(1) Sherwood, T. K. and Pigford, R. L., Adsorption and Extraction, p. 7, McGraw-Hill (1952).

Treybal, R. E., Liquid Extraction, p. 98, McGraw-Hill (1952).

(2) Cohen, K., Theory of Isotope Separation, p. 129, McGraw Hill (1951) states that the interface concentrations may be replaced by the bulk concentrations in Equation (III.19) and thus obtain Equation (II.12).

$$T(s) = k_1 a \left[y^*(s) - y(s) \right] \quad (\text{III.20})$$

where $y^*(s)$ is the concentration of the enriched phase which would be in equilibrium with $x(s)$.

Conversely, if practically the entire resistance resides in the depleted phase film $K'a \approx k_2 a$ and $y^i \approx y$. Then

$$T(s) = k_2 a \left[x(s) - x^*(s) \right] \quad (\text{III.21})$$

where $x^*(s)$ is the concentration of the depleted phase which would be in equilibrium with $y(s)$.

In most systems the values of the individual film transfer coefficients are not known. The interfacial concentrations y^i and x^i cannot be evaluated unless the ratio $k_1 a / k_2 a$ has been determined. Therefore, it is common engineering practice to define overall mass transfer coefficients to give equations analogous with Equations (III.20) and (III. 21)

$$T(s) = K_1 a \left[y^*(s) - y(s) \right] = K_2 a \left[x(s) - x^*(s) \right] \quad (\text{III.22})$$

where K_1 is the enriched phase overall mass transfer coefficient and K_2 is the depleted phase overall mass transfer coefficient.

For a linear equilibrium relationship it may be shown that⁽¹⁾

$$\frac{1}{K_1 a} = \frac{1}{k_1 a} + \frac{m}{k_2 a}$$

where $m = \frac{dy}{dx}$

⁽¹⁾ Perry, J. H., Chemical Engineers' Handbook, p. 550, McGraw-Hill (1950).

and

$$\frac{1}{K_2^a} = \frac{1}{k_2^a} + \frac{1}{mk_1^a} . \quad (\text{III.23})$$

In the case under consideration the equilibrium equation, Equation (III.1) is not a linear, but a quadratic relationship, Equation (III.22) may be written

$$\frac{K_2^a}{K_1^a} = \frac{y^*(s) - y(s)}{x(s) - x^*(s)} . \quad (\text{III.24})$$

When ψ is small y will differ only slightly from x at any point in the process, or $y = x + \delta$ where δ is small. Thus Equation (III.24) can be written

$$\frac{K_2^a}{K_1^a} = \frac{(1+\psi)x - x(1+\psi x) - \delta(1+\psi x)}{1 + \psi x} \bigg/ \frac{(1+\psi)x - \psi x^2 - \psi \delta x - x \delta}{1 + \psi - \psi x - \psi \delta} \quad (\text{III.25})$$

in which the position notation has been omitted. Neglecting terms of the order $\psi \delta$

$$\frac{K_2^a}{K_1^a} = \frac{1 + \psi(1-x)}{1 + \psi x} . \quad (\text{III.26})$$

Thus over the entire range of concentrations

$$\frac{1}{1 + \psi} < \frac{K_2^a}{K_1^a} < 1 + \psi . \quad (\text{III.27})$$

Hence, it is apparent that for $\psi \ll 1$

$$K_2^a \simeq K_1^a . \quad (\text{III.28})$$

The gradient equations may be written in terms of the overall

mass transfer coefficients

$$L(s) \frac{dy}{ds} = \left[L(s) - P \right] \frac{dx}{ds} = K_1 a \left[y^*(s) - y(s) \right] = K_2 a \left[x(s) - x^*(s) \right]. \quad (\text{III.29})$$

The number of enriched phase transfer units is defined

$$(\text{NTU})_1 = \int \frac{K_1 a}{L(s)} ds \quad (\text{III.31})$$

and, hence, for a square section in which the flow is constant

$$(\text{NTU})_1 = \frac{K_1 a}{L} S. \quad (\text{III.32})$$

The height of an enriched phase transfer unit is defined as the length of process divided by the number of enriched phase transfer units

$$(\text{HTU})_1 = \frac{S}{(\text{NTU})_1} = \frac{L}{K_1 a}. \quad (\text{III.33})$$

Similarly,

$$(\text{HTU})_2 = \frac{S}{(\text{NTU})_2} = \frac{L - P}{K_2 a}. \quad (\text{III.34})$$

Since for the system in which $\psi \ll 1$, $(L - P)$ is of necessity very nearly equal to L

$$(\text{HTU})_1 \approx (\text{HTU})_2. \quad (\text{III.35})$$

Examination of the definition of the height of a transfer unit indicates that a transfer unit may be considered as the length of system necessary to enrich the phase by a concentration increment equal to the mean driving force in concentration units averaged over that length.

In the circumstance of negligible resistance at the interface the mass transfer at a point in the cascade is given by both

$$Ka \left[\psi x(1-y) - (y-x) \right] \quad (\text{from III.8})$$

and

$$K_1 a \left[y^* - y \right] \quad (\text{from III.22})$$

Making use of the definition of y^*

$$K_1 a \left[y^* - y \right] = K_1 a \left[\frac{x + \psi x}{1 + \psi x} - y \right].$$

Expanding this expression and neglecting terms of the order of ψ^2 since $\psi \ll 1$

$$K_1 a \left[y^* - y \right] \approx K_1 a \left[\psi x(1-x) - (y-x) \right].$$

Thus,

$$Ka \approx K_1 a \approx K_2 a. \quad (\text{III.36})$$

And it follows that, when $\psi \ll 1$

$$H \approx (HTU)_1 \approx (HTU)_2. \quad (\text{III.37})$$

IV. Batch Experiments

1) Theory

It is sometimes possible to determine the transfer coefficient Ka from batch experiments. For a typical batch experiment a cell of some shape which as closely as possible simulates the contemplated countercurrent apparatus is filled to the proper depth with the heavier liquid with the lighter phase floating on top. Let V_1 ,

V_2 be the volumes of the enriching and depleting phase and let M_1 and M_2 be the corresponding molarities. At the start of the experiment let the mole fractions be x_0 and y_0 . The inventory parameters are then readily calculated

$$I_1 = M_1 V_1 \quad (\text{IV.1})$$

$$I_2 = M_2 V_2 \quad (\text{IV.2})$$

$$\phi = I_1 y_0 + I_2 x_0. \quad (\text{IV.3})$$

If the total area of the interface is a , then the total current of A atoms into phase 1 is given by

$$J_{\text{total}} = (Ka) \left[\alpha x(1-y) - y(1-x) \right] \quad (\text{IV.4})$$

to which the relation must be added

$$I_1 y + I_2 x = I_1 y_0 + I_2 x_0 = \phi. \quad (\text{IV.5})$$

Although it is a simple matter to solve for x in terms of y by means of the preceding equation and substitute the result into the expression for the total current, the analysis is much easier if we make the following linear substitution

$$y = \mu + \eta \quad (\text{IV.6})$$

$$x = \lambda + \xi \quad (\text{IV.7})$$

with λ and μ constant but for the moment undetermined. The expression for the current in terms of the new variables becomes

$$J = (Ka) \left[\alpha \lambda (1-\mu) - \mu (1-\lambda) + \alpha \xi - \eta - \psi (\lambda \eta + \mu \xi + \xi \eta) \right] \quad (\text{IV.8})$$

If λ and μ are now determined by the two equations

$$I_1 \mu + I_2 \lambda = 0 \quad (\text{IV.9})$$

$$\frac{\mu}{1-\mu} = \alpha \frac{\lambda}{1-\lambda} \quad (\text{IV.10})$$

then ξ and η must be related by the relation

$$I_1 \eta + I_2 \xi = 0. \quad (\text{IV.11})$$

The quantities λ and μ are the mole fractions at equilibrium or after infinite time. One is now in a position to further simplify the current by eliminating ξ and λ and μ as far as possible

$$J = (K_a) \left[- \left\{ \frac{\alpha I_1 + I_2}{I_2} + \psi \lambda - \frac{\psi I_1}{I_2} \mu \right\} \eta + \psi \frac{I_1}{I_2} \eta^2 \right]. \quad (\text{IV.12})$$

Thus J is composed of a linear and quadratic term in η . The ratio of the absolute values of the quadratic and linear term is

$$\frac{\psi I_1 |\eta|}{\alpha I_1 + I_2 + \psi (I_2 \lambda - I_1 \mu)} \quad (\text{IV.13})$$

which cannot be greater than

$$\frac{\psi |\eta|}{\alpha - \psi \mu} \leq \psi |\eta|. \quad (\text{IV.14})$$

Therefore, under the worst circumstances the quadratic term gives a correction to the linear term which is equivalent to a fractional error of ψ . In general, the correction does not amount to this much and since ψ is restricted to small values

$$J = -(K_a) \left[\frac{\alpha I_1 + I_2 + \psi (I_2 \lambda - I_1 \mu)}{I_2} \right] \eta. \quad (\text{IV.15})$$

The course of η in time can then be determined by the equation

$$\frac{d}{dt} (I_1 \eta) = J = -(K_a) \left[\frac{\alpha I_1 + I_2 + \psi (I_2 \lambda - I_1 \mu)}{I_2} \right] \eta \quad (\text{IV.16})$$

which integrates to

$$\eta = \eta_0 e^{t/T_e} \quad (\text{IV.17})$$

with

$$\frac{1}{T_e} = (K_a) \left[\frac{\alpha I_1 + I_2 + \psi (I_2 \lambda - I_1 \mu)}{I_1 I_2} \right] \quad (\text{IV.18})$$

The quantity T_e is the relaxation time of the batch experiment to a good approximation, even if ψ is not small, after an initial transient period. If ψ is small (IV.18) can be approximated by

$$\frac{1}{T_e} = (K_a) \left[\frac{1}{I_1} + \frac{1}{I_2} \right] \quad (\text{IV.19})$$

The half equilibrium time of the experiment, H.E.T., is defined by the relation

$$(\text{HET}) = (\ln 2) T_e \quad (\text{IV.20})$$

The half equilibrium time is a characteristic of the whole experiment and not of either separate phase. Experimentally, it is determined by plotting the difference in any mole fraction and its equilibrium value on semi-logarithmic paper as a function of time and determining the time for which this quantity falls to half its initial value.

2) Time of transfer Unit

Consider again the countercurrent flow system previously described. The time of a transfer unit will be defined as the period of time required

by a specified phase to flow through a distance equal to one transfer unit. Thus, if we consider the phase being enriched,

$$(\text{TTU})_1 = \frac{(\text{HTU})_1}{\text{phase velocity}} \quad (\text{IV.21})$$

The height of a transfer unit for the phase being enriched is given by

$$\frac{Z}{(\text{HTU})_1} = \int \frac{dy}{y^*-y} \quad (\text{IV.22})$$

where the length is a function of the limits of integration. Differentiating Equation (IV.22) with respect to time, we have

$$\frac{dz/dt}{(\text{HTU})_1} = \frac{dy/dt}{y^*-y} \quad (\text{IV.23})$$

But dz/dt here is the velocity, v_1 , of the phase being enriched.

Substituting this result into Equation (IV.21), we get

$$(\text{TTU})_1 = \frac{y^*-y}{dy/dt} \quad (\text{IV.24})$$

or in the integrated form, assuming the (TTU) constant,

$$\frac{t}{(\text{TTU})_1} = \int \frac{dy}{y^*-y} \quad (\text{IV.25})$$

The time of a transfer unit is seen to be the time required for the material in the phase under consideration to undergo a concentration change equal to the mean concentration driving force $(y^*-y)_m$ for this period. Equation (IV.25) is the same as that presented by Drew and Hixson.⁽¹⁾

⁽¹⁾Perry, J. H., Chemical Engineers' Handbook, p. 557, McGraw-Hill (1950).

Similar equations may be written for the phase being depleted.

This would give

$$\frac{t}{(\text{TTU})_2} = \int \frac{dx}{(x-x^*)} \quad (\text{IV.26})$$

3) The Time of a Transfer Unit in the Batch Experiments

Consideration of the principle of conservation of material in the batch apparatus gives

$$I_1 \frac{dy}{dt} = - I_2 \frac{dx}{dt} = T. \quad (\text{IV.27})$$

In terms of the overall transfer coefficients (see Section III)

$$T = K_1 a (y^* - y) = K_2 a (x - x^*). \quad (\text{IV.28})$$

Thus,

$$y^* - y = \frac{I_1}{K_1 a} \frac{dy}{dt} \quad (\text{IV.29})$$

The time of an enriched phase transfer unit for the batch experiments can now be written

$$\frac{t}{(\text{TTU})_1} = \int \frac{dy}{(y^* - y)} = \int \frac{K_1 a}{I_1} dt \quad (\text{IV.30})$$

$$(\text{TTU})_1 = \frac{I_1}{K_1 a} = \left(1 + \frac{I_1}{I_2}\right) T_e \quad (\text{IV.31})$$

Similarly, for the depleted phase we obtain

$$(\text{TTU})_2 = \frac{I_2}{K_2 a} = \left(1 + \frac{I_2}{I_1}\right) T_e \quad (\text{IV.32})$$

The value of the time of a transfer unit is readily obtained experimentally by plotting

$$\int_{y_0}^y \frac{dy}{y^* - y} \quad \text{vs. } t.$$

The value of (TTU) is then the reciprocal of the slope of the best straight line through the data.

V. Elementary Design Considerations

In building large scale countercurrent plants it is usually of advantage to standardize the equipment as far as possible. Such standardization gives obvious manufacturing and operational simplifications. It is therefore assumed for the present that the cascade is to be built from a series-parallel arrangement of identical pieces of equipment. These will be called separating elements. The reader who is familiar with cascade terminology should be warned at this point that the definition above is somewhat more general than the definition of element commonly employed in cascade literature in that a given element may be more or less than a single equivalent stage in length. Any number of elements in parallel will be termed a section.

Each element must have provision for the two phases to be contacted by countercurrent flow and each element will have a definite area a of contact per unit length. A section will thus have a contact area per unit length which is the single element area per unit length multiplied by the number of elements in parallel. If each element accommodates an upflow of L_0 , the gradient equation within an individual element is

$$L_0 \frac{dy}{ds} = T(s). \quad (V.1)$$

If this is multiplied on both sides by the number of elements m in parallel this becomes the gradient equation across the section

$$m L_0 \frac{dy}{ds} = L \frac{dy}{ds} = m T(s) = (m K_a) [\alpha x(1-y) - y(1-x)] \quad (V.2)$$

Thus, no matter how many identical elements are in parallel, the equation

$$\frac{dy}{ds} = \frac{(K_a)}{L_0} [\alpha x(1-y) - y(1-x)] \quad (V.3)$$

holds.

This constancy of upflow in each element is not the only possibility. One might for instance operate the elements in such a manner that the downflow is kept constant. However, the results do not differ essentially and the case of fixed upflow will be adhered to throughout this report.

The total upflow in the enricher is defined to be the sum of the individual upflows in all the elements. Thus if there is a total of N elements the total flow is $L_0 N$. The contribution to the total flow by a section one element in length with m elements in parallel is given by

$$L = m L_0 \quad (V.4)$$

If ν'_m is the number of sections one element in length with m elements in parallel then the total flow is given by the expression

$$\mathcal{F} = \sum_m m \nu'_m L_0$$

Now the reader may remark with some justice that the simple problem of counting the number of trays in a plant is being excessively complicated by this procedure. A little patience will disclose that it is really

being simplified. One can now write a formula for $\mathcal{N}'_m$ in the following way. Consider an arrangement of the plant in which $\mathcal{N}'_m$ elements in series each with m in parallel raise the upstream mole fraction from y_1 to y_2 . If each element has the common length h then one may calculate

$$\mathcal{N}'_m = \frac{1}{h} \int_{y_1}^{y_2} \frac{dy}{\frac{(Ka)}{L_0} \left[\psi y(1-y) - \frac{P}{mL_0 - P} (y_p - y)(\alpha - \psi y) \right]} \quad (V.5)$$

if the plant is producing at the rate P with mole fraction y_p . This may readily be seen from the statement that the equation

$$\frac{dy}{ds} = \frac{(Ka)}{L_0} \left[\alpha x(1-y) - y(1-x) \right] \quad (V.3)$$

held for any number m of elements in parallel and writing the material balance for the net transport through the paralleled elements

$$m L_0 y - (m L_0 - P)x = P y_p. \quad (V.6)$$

Using this to eliminate x from (V.3) and integrating y between the limits y_1 and y_2 gives the expression (V.5). The number of elements necessary to raise y through the increment $y_2 - y_1$ is thus

$$m \mathcal{N}'_m = \frac{m}{h} \int_{y_1}^{y_2} \frac{dy}{\frac{(Ka)}{L_0} \left[\psi y(1-y) - \frac{P}{m L_0 - P} (y_p - y)(\alpha - \psi y) \right]} \quad (V.7)$$

If the change in y is small we may write (V.7) in the approximate form

$$m \mathcal{N}'_m = \frac{m L_0}{h(Ka)} \int_{y_1}^{y_2} \frac{dy}{\psi y(1-y) - \frac{P}{m L_0 - P} (y_p - y)(\alpha - \psi y)} \quad (V.8)$$

and finally obtain the total number of elements in the enricher

$$R = \sum_m m z'_m$$

in the form

$$R = \frac{L_0}{h(Ka)} \int_{y_f}^{y_p} \frac{m dy}{\psi y(1-y) - \frac{P}{L_0 m - P} (y_p - y)(\alpha - \psi y)} \quad (V.9)$$

which assumes that (Ka) is constant throughout the plant. In principle even if one admits the approximation (V.8) the m values that are used should be integers. This point, although valid, will be deferred until later. The design problem to be solved is then this: for fixed y_p , y_f and P , to choose m as function of y in such a way that the total number of elements R is a minimum. This is not necessarily a realistic design problem from the standpoint of economics and a given situation always dictates special considerations. However, the cascade of minimum size is often a very useful guide. The problem of minimizing (V.9) is a problem in the Calculus of Variations. The basic equations of that discipline⁽¹⁾ state that a necessary condition for a minimum value of (V.9) is

$$\frac{\partial}{\partial m} \left[\frac{m}{\psi y(1-y) - \left(\frac{P}{L_0 m - P}\right)(y_p - y)(\alpha - \psi y)} \right] = 0. \quad (V.10)$$

Carrying out the indicated partial differentiation and equating the derivative to zero results in

(1) Courant, R. and Hilbert, D., Methods of Mathematical Physics I, Interscience Publisher, New York, p. 185 (1953).

$$\psi y(1-y) = \frac{P}{L_0 m - P} (y_p - y)(\alpha - \psi y) \left[1 + \frac{m L_0}{m L_0 - P} \right] \quad (V.11)$$

This equation may be readily solved for the total flow of mL_0 as function of y yielding

$$mL_0 = P + \frac{P(y_p - y)(\alpha - \psi y)}{\psi y(1-y)} \left[1 + \sqrt{1 + \frac{\psi y(1-y)}{(y_p - y)(\alpha - \psi y)}} \right] \quad (V.12)$$

and a second solution which is extraneous. If m could be varied continuously this formula would give its value at each point in the enricher as a function of the value of y at that point. This can be translated into flow as a function of distance by integrating the cascade equation with this flow rate

$$\frac{dy}{ds} = \frac{(Ka)}{L_0} \psi y(1-y) \frac{\sqrt{1 + \frac{\psi y(1-y)}{(y_p - y)(\alpha - \psi y)}}}{1 + \sqrt{1 + \frac{\psi y(1-y)}{(y_p - y)(\alpha - \psi y)}}} \quad (V.13)$$

If length is measured in units of

$$\frac{L_0}{(Ka)}$$

by the substitution

$$n = \frac{(Ka)}{L_0} s$$

(V.13) may be written

$$\frac{dy}{dn} = \frac{\psi y(1-y) \sqrt{1 + \frac{\psi y(1-y)}{(y_p - y)(\alpha - \psi y)}}}{1 + \sqrt{1 + \frac{\psi y(1-y)}{(y_p - y)(\alpha - \psi y)}}} \quad (V.14)$$

For many separation plants the quantity

$$\frac{\psi y(1-y)}{(y_p - y)(\alpha - \psi y)}$$

is small over a good portion of the plant. When this is small (V.12) becomes approximately

$$m L_O = P + \frac{2P(y_p - y)(\alpha - \psi y)}{\psi y(1-y)} \quad (V.15)$$

and (V.14) becomes approximately

$$\frac{dy}{dn} = \frac{\psi}{2} y(1-y) . \quad (V.16)$$

Thus,

$$\frac{y}{1-y} = \frac{y_f}{1-y_f} e^{(\psi/2)n} \quad (V.17)$$

measuring n from the point where $y = y_f$. If this held throughout the enricher, which it obviously cannot, the number of stages N necessary in the enricher would be given by

$$N = \frac{2}{\psi} \ln \frac{\frac{y_p}{1-y_p}}{\frac{y_f}{1-y_f}} \quad (V.18)$$

at total reflux, $P=0$, the gradient equation becomes

$$\frac{dy}{dn} = \psi y(1-y). \quad (V.19)$$

The number of stages necessary in this case to give the same enrichment level at the top is

$$N_{\min} = \frac{1}{\psi} \ln \frac{\frac{y_p}{1-y_p}}{\frac{y_f}{1-y_f}} . \quad (V.20)$$

The notation $N_{\min}$ is employed in conformity with custom to indicate that

this is the minimum number of stages which can enrich material of concentration y_f to the level y_p . Thus for cascades in which the approximation

$$\frac{\Psi y(1-y)}{(y_p-y)(\alpha-\Psi y)} \ll 1$$

holds throughout most of the plant, the minimum number of stages is approximately twice the number required at total reflux.

The practical rules for designing a minimum element plant with constant total upflow can now be stated.

1. Solve the differential equation (V.13) for y as function of s .
2. Calculate the curve of m values as function of distance by inserting the above solution in (V.12). This will be a smooth curve.
3. Approximate the m curve above as closely as possible by a sequence of polygons of integer height. This process is generally called "squaring off".

In general it is possible to find a squared off curve which closely approximates the continuous m curve. The Calculus of Variations may be referred to once more for assurance that the effects of "squaring off" on the number of elements necessary raise that number only by a fraction involving a weighted square of the deviations of the "squared off" curve from the continuous curve. It is therefore advisable to "square off" with slightly more area above the continuous curve than below.

The treatment of the minimum plant problem in the preceding paragraphs took no cognizance of the circumstance that in most countercurrent systems

material is lost through such phenomena as evaporation, splashing, leaks, irreversible chemical processes, and so on. These losses, even when small, significantly affect the shape of the minimum cascade. Below it is shown how such losses may be included in the design calculations.

It is useful to define two auxiliary functions of position in the cascade. The first of these which will be represented by the symbol $\mathcal{L}(s)$ has a numerical value equal to the total amount of both isotopic species which are lost per unit time above the point s in the cascade. The second is given the symbol $\mathcal{L}_1(s)$ and represents the rate of loss of desired component above the point s . Applying material balance to all the cascade above the point s now yields two relations

$$L = L' + P + \mathcal{L}(s)$$

and

$$Ly = L'x + Py_p + \mathcal{L}_1(s) \quad (V.21)$$

the latter of which may be written in the form

$$Ly = \left[L - P - \mathcal{L}(s) \right] x + Py_p + \mathcal{L}_1(s) \quad (V.22)$$

by solving for L' in the former. The derivation of the enrichment equation need not be repeated here since it differs in no way from the previous derivation which led to Equation (II.13). Upon eliminating x from Equation (II.9) by use of the material balance equation (V.22) there results after some algebra

$$\frac{dy}{ds} = \frac{(K\alpha)}{L_0} \left[y(1-y) - \frac{P(y_p - y) + \mathcal{L}_1(s) - y \mathcal{L}(s)}{L - P - \mathcal{L}(s)} (\alpha - y) \right] \quad (V.23)$$

It may be noted that for no losses, $\mathcal{L}(s) = \mathcal{L}_1(s) = 0$, this equation reduces to the cascade equation (II.13) as it should.

It will be assumed that the losses per unit length in the plant are proportional to the total upflow at the point in question. It is not necessary to suppose that the proportionality is the same everywhere in the plant but it must be the same for all parallel elements. The rate of loss in the plant between the points s and $s+ds$ may thus be written in the form

$$\sigma(s) L(s) ds$$

wherein $\sigma(s)$ is the factor of proportionality mentioned above. Consequently, the loss functions may be written

$$\mathcal{L}(s) = \int_s^S \sigma(u) L(u) du \quad (V.24)$$

and

$$\mathcal{L}_1(s) = \int_s^S \sigma(u) y(u) L(u) du \quad (V.25)$$

wherein S is the total length of enricher. To be sure, the above expressions assume implicitly that either all losses are out of the upstream or else that the differences between upstream and downstream flow rates as well as the mole fractions y and x are small. We define two auxiliary functions by the relations

$$\Pi(s) = P + \mathcal{L}(s) \quad (V.26)$$

$$y_\pi(s) = \frac{Py_p + \mathcal{L}_1(s)}{\Pi(s)} \quad (V.27)$$

The gradient equation (V.3) with losses then take the form

$$\frac{dy}{ds} = \frac{(Ka)}{L_0} \left[\psi y(1-y) - \frac{\pi(s) [y_{\pi}(s) - y] (\alpha - \psi y)}{mL_0 - \pi(s)} \right] \quad (V.28)$$

which is exactly of the same form as before. However, the variational problem for determining the minimum area is now much more complicated. We can, however, obtain simple approximate solutions. We introduce a small parameter ϵ into the problem by defining

$$\sigma(s) = \epsilon g(s). \quad (V.29)$$

We then suppose that we may write

$$L(s) = L^{(0)}(s) + \epsilon L^{(1)}(s) + \epsilon^2 L^{(2)}(s) + \dots \quad (V.30)$$

$$y(s) = y^{(0)} + \epsilon y^{(1)}(s) + \epsilon^2 y^{(2)}(s) + \dots \quad (V.31)$$

where $L^{(0)}(s)$ and $y^{(0)}(s)$ are the solutions to the minimum plant problem in the no loss case. We then have

$$\mathcal{L}(s) = \epsilon \int_s^S g(s) L^{(0)}(s) ds + \epsilon^2 \int_s^S g(s) L^{(1)}(s) ds + \dots \quad (V.32)$$

$$\begin{aligned} \mathcal{L}_1(s) = & \epsilon \int_s^S g(s) y^{(0)}(s) L^{(0)}(s) ds + \epsilon^2 \int_s^S g(s) \left[y^{(0)}(s) L^{(1)}(s) \right. \\ & \left. + y^{(1)}(s) L^{(0)}(s) \right] ds + \dots \end{aligned} \quad (V.33)$$

Thus, a first order evaluation of $\mathcal{L}(s)$ and $\mathcal{L}_1(s)$ involves no unknown functions since we assume we can solve the no loss case. The total number

of elements to the first order in ϵ can now be written

$$R = \frac{L_0}{h(Ka)} \int_{y_f}^{y_p} \frac{m \, dy}{\psi y(1-y) - \frac{\Pi(s) [y_\pi(s) - y](\alpha - \psi y)}{m L_0 - \Pi(s)}} \quad (V.34)$$

where $\Pi(s)$ and $y_\pi(s)$ are, to the first order in ϵ , fixed at the outset by solving the no loss problem. Consequently, the variational problem is as before and one finds easily

$$m L_0 = \Pi(s) + \frac{\Pi(y_\pi - y)(\alpha - \psi y)}{\psi y(1-y)} \left\{ 1 + \sqrt{1 + \frac{\psi y(1-y)}{(y_\pi - y)(\alpha - \psi y)}} \right\} \quad (V.35)$$

and the gradient equation

$$\frac{dy}{ds} = \frac{(Ka)}{L_0} \psi y(1-y) \frac{\sqrt{1 + \frac{\psi y(1-y)}{(y_\pi - y)(\alpha - \psi y)}}}{1 + \sqrt{1 + \frac{\psi y(1-y)}{(y_\pi - y)(\alpha - \psi y)}}} \quad (V.36)$$

It is to be emphasized that this solution is only valid as long as the differences predicted from the no loss case are proportionally small. Higher approximations seem to be very messy.

The factor of proportionality for the losses $\sigma(s)$ is in many important cases practically constant. If one decides that the gradient equation

$$\frac{dy}{ds} = \frac{(Ka)}{L_0} \left[\psi y(1-y) - \frac{P(y_p, y)}{L} \right] \quad (V.37)$$

is accurate enough, similar calculations to the above give rise to

equations more susceptible to integration. In this case the upflow of the minimal no loss cascade may be shown to be

$$L^{(0)} = \frac{2P(y_p - y)}{\psi y(1-y)} \quad (V.38)$$

and with losses correct through the first power of the constant loss factor the flow will be

$$L = \frac{2 \left[P(y_p - y) + \alpha_1(y) - y \alpha(y) \right]}{\psi y(1-y)} \quad (V.39)$$

with

$$\alpha(y) = \frac{4P\sigma}{\psi^2} \frac{L_o}{Ka} \left[(2y_p - 1) \ln \left(\frac{R_p}{R} \right) + \frac{(y_p - y)(1 - 2y)}{y(1-y)} \right] \quad (V.40)$$

and

$$\alpha_1(y) = \frac{4P\sigma}{\psi^2} \frac{L_o}{Ka} \left[y_p \ln \frac{R_p}{R} - \frac{y_p - y}{1 - y_p} \right] \quad (V.41)$$

wherein

$$R = \frac{y}{1-y}; \quad R_p = \frac{y_p}{1-y_p}.$$

Thus the correction for losses to this approximation is to increase L by the fraction

$$\frac{\Delta L}{L^{(0)}} = \frac{4\sigma}{\psi^2} \frac{L_o}{Ka} \left[\left(\frac{y_p + y - 2y y_p}{(y_p - y)} \right) \ln \frac{R_p}{R} - 2 \right]. \quad (V.42)$$

The mole fraction y will be the same function of s both with and without losses

$$y = \frac{\frac{(Ka)}{L_o} \frac{\psi}{2} s}{1 - y_f + y_f e^{\frac{(Ka)}{L_o} \frac{\psi}{2} s}} \quad (V.43)$$

in the enriching section.

VI. Summary of Equations

Presented below in outline form are the more important equations which appear in this paper. It is hoped that this listing will facilitate quick reference and also serve as an index to the body of the report.

I. The Separation Process

The separation factor for the isotope enriching process under consideration is defined as the equilibrium constant for the chemical exchange reaction

$$\alpha = \frac{C_{A1}/C_{B1}}{C_{A2}/C_{B2}} \quad (I.3)$$

Expressed in mole fractions the separation factor is given by

$$\alpha = \frac{y/1-y}{x/1-x} \quad .$$

The stage enrichment factor ψ is defined by the relationship

$$\alpha = 1 + \psi \quad (I.14)$$

Thus, in terms of mole fractions

$$\psi = \frac{y-x}{x(1-y)} \quad .$$

The current density of the desired isotope across the phase boundary is given by

$$J = K [\alpha x(1-y) - y(1-x)] \quad (I.25)$$

or, in terms of the stage enrichment factor,

$$J = K [\psi x(1-y) - (y-x)]$$

where

$$\frac{1}{K} = \frac{1}{\gamma M_1 M_2} + \frac{R_{B1}}{M_1} + \frac{R_{B2}}{M_2} \quad .$$

It is apparent from Equation (I.24) that when the chemical reaction at

the interface proceeds very rapidly with respect to the film transfer rates

$$\frac{1}{K} = \frac{R_{B1}}{M_1} + \frac{R_{B2}}{M_2}.$$

On the other hand, when the film resistances are negligible and the chemical reaction is the rate controlling mechanism, the expression for K reduces to

$$K = \gamma M_1 M_2.$$

II. The Separation Plant

The material balance relationship between $x(s)$ and $y(s)$ in the cascade may be written in the form

$$y(s) = x(s) + \frac{P}{L(s)} \left[y_p - x(s) \right] \quad (\text{II.6})$$

or,

$$x(s) = y(s) - \frac{P}{L(s) - P} \left[y_p - y(s) \right]. \quad (\text{II.7})$$

The cascade gradient equation is obtained from a material balance on a differential element of the cascade, the material balance above, and the expression for the current density of desired isotope

$$L(s) \frac{dy}{ds} = (K_a) \left[\psi y(1-y) - \frac{P(y_p - y)(\alpha - \psi y)}{L(s) - P} \right] \quad (\text{II.13})$$

provided the reflux stream is at the concentration $y(s)$ in the desired isotope. Equation (II.13) may be written in terms of the concentration of the depleted phase

$$\left[L(s) - P \right] \frac{dx}{ds} = K_a \left[\psi x(1-x) - \frac{P}{L(s)} (y_p - x) \left\{ 1 + \psi x - \frac{1}{K_a} \frac{dL}{ds} \right\} \right]. \quad (\text{II.14})$$

In the case where the cascade is partitioned into cells of length h in order to reduce the deleterious effect of longitudinal eddy diffusion the gradient equation is

$$\frac{dy}{ds} = \frac{Ka}{L + Kah} \left[\psi y(1-y) - \frac{P}{L-P} (y_p - y)(\alpha - \psi y) \right]. \quad (\text{II.29})$$

This equation, like (II.13), is valid for square sections or for reflux streams at mole fraction $y(s)$. The effect of so partitioning the cascade is to increase the height equivalent to a theoretical stage by the length of one cell.

III. The Stage Concept

If the length of cascade equivalent to a theoretical stage is defined as that length of cascade such that the concentrations of the streams leaving the section are related by the equation

$$\frac{y_n - x_n}{x_n(1-y_n)} = \psi_n, \quad (\text{III.1})$$

one finds that the stage length H is independent of the reflux ratio P/L . For the constant ψ cascade, the number of theoretical stages may be obtained from

$$N = \left(1 - \frac{P}{L}\right) \int_{x_B}^{x_T} \frac{dx}{\psi x(1-x) - \frac{P}{L}(y_p - x)}. \quad (\text{III.5})$$

The length of the theoretical stage is given by

$$H = \frac{L}{Ka}. \quad (\text{III.13})$$

The "number of enriched phase transfer units," $(NTU)_1$ is defined by

the equation

$$(\text{NTU})_1 = \int \frac{dy}{y^*-y} \quad (\text{III.29})$$

It follows that

$$(\text{NTU})_1 = \frac{K_1 a}{L} S \quad (\text{III.32})$$

and that the "height of an enriched phase transfer unit," $(\text{HTU})_1$, is given by

$$(\text{HTU})_1 = \frac{S}{(\text{NTU})_1} = \frac{L}{K_1 a} \quad (\text{III.33})$$

Similar equations exist for the depleted phase and

$$(\text{HTU})_2 = \frac{S}{(\text{NTU})_2} = \frac{L-P}{K_2 a} \quad (\text{III.34})$$

When $\psi \ll 1$

$$H = (\text{HTU})_1 = (\text{HTU})_2 \quad (\text{III.37})$$

IV. Batch Experiments

The relaxation time T of the batch experiment is defined by the equation

$$\eta = \eta_0 e^{-t/T_e} \quad (\text{IV.17})$$

and hence is the time required for the displacement of the system from equilibrium to drop to $1/e$ of its initial value. In terms of the parameters of the batch system a good approximation of the relaxation time in the case of $\psi \ll 1$ may be computed from

$$\frac{1}{T_e} = Ka \left[\frac{1}{I_1} + \frac{1}{I_2} \right] \quad (\text{IV.19})$$

The half equilibrium time of the experiment, or (HET) , is the time required for the displacement of the system to fall to one-half of its initial value.

Thus,

$$(\text{HET}) = (\ln 2) T_e. \quad (\text{IV.20})$$

The time of a transfer unit is defined as the length of time required for the selected phase to undergo a change in concentration equal to the average concentration driving force for that period. The time of an enriched phase transfer unit for the batch experiments can be written

$$(\text{TTU})_1 = \frac{I_1}{K_1 a}. \quad (\text{IV.31})$$

The relationship between the time of the enriched phase transfer unit and the relaxation time is

$$(\text{TTU})_1 = \left[\frac{\alpha I_1 + I_2}{I_2} \right] T_e \approx \left[1 + \frac{I_1}{I_2} \right] T_e.$$

Similarly, for the depleted phase, we have the equations

$$(\text{TTU})_2 = \frac{I_2}{K_2 a} \quad (\text{IV.32})$$

$$(\text{TTU})_2 = \left[\frac{I_1 + \alpha I_2}{I_1} \right] T_e \approx \left[1 + \frac{I_2}{I_1} \right] T_e.$$

V. Elementary Design Considerations

The total number of separating elements in the enricher of a cascade may be obtained from

$$R = \sum_m m \mathcal{J}'_m = \frac{L_0}{(K a) h} \int_{y_f}^{y_p} \frac{m dy}{\psi y(1-y) - \frac{P}{L_0^{m-P}} (y_p - y)(\alpha - \psi y)}. \quad (\text{V.9})$$

In order that the number of elements in the enricher be the minimum necessary to achieve a specified production (P and y_p fixed) the width of the plant must be tapered according to the equation

$$mL_o = P + \frac{P(y_p - y)(\alpha - \psi y)}{\psi y(1-y)} \left[1 + \sqrt{1 + \frac{\psi y(1-y)}{(y_p - y)(\alpha - \psi y)}} \right] \quad (V.12)$$

The width may be calculated as a function of distance by integrating the equation

$$\frac{dy}{dn} = \psi y(1-y) \frac{\sqrt{1 + \frac{\psi y(1-y)}{(y_p - y)(\alpha - \psi y)}}}{1 + \sqrt{1 + \frac{\psi y(1-y)}{(y_p - y)(\alpha - \psi y)}}} \quad (V.14)$$

where the distance is measured in stage lengths, and using the result in conjunction with Equation (V.12).

In general, the quantity

$$\frac{\psi y(1-y)}{(y_p - y)(\alpha - \psi y)}$$

is small with respect to unity throughout the cascade except in the neighborhood of the product withdrawal point. Making this simplification one obtains for the optimum flow or width of plant

$$mL_o = P + \frac{2P(y_p - y)(\alpha - \psi y)}{\psi y(1-y)} \quad (V.15)$$

and Equation (V.14) becomes

$$\frac{dy}{dn} = \frac{\psi}{2} y(1-y). \quad (V.16)$$

Thus, the concentration at any stage n is given by

$$\frac{y}{1-y} = \frac{y_f}{1-y_f} e^{\psi n/2} \quad (V.17)$$

where n is measured from the point $y=y_f$. The number of stages in the enricher as computed from Equation (V.17) is

$$N = \frac{2}{\psi} \ln \left[\frac{y_p}{1-y_p} / \frac{y_f}{1-y_f} \right]. \quad (V.18)$$

At total reflux, $P=0$, the gradient equation becomes

$$\frac{dy}{dn} = \psi y(1-y). \quad (V.19)$$

The number of stages in the enricher for the total reflux case is

$$N_{\min} = \frac{1}{\psi} \ln \left[\frac{y_p}{1-y_p} / \frac{y_f}{1-y_f} \right]. \quad (V.20)$$

The number of stages in the enricher is thus twice the number of stages necessary at total reflux.

In the case of the cascade with losses the gradient equation is

$$\frac{dy}{ds} = \frac{(Ka)}{L_o} \left[\psi y(1-y) - \frac{\overline{\Pi}(s) [y_{\pi}(s) - y] (\alpha - \psi y)}{mL_o - \pi(s)} \right]. \quad (V.28)$$

The area of the cascade will be minimized when the flow or width is chosen in accordance with the equation

$$mL_o = \overline{\Pi} + \frac{\overline{\Pi}(y_{\pi} - y)(\alpha - \psi y)}{\psi y(1-y)} \left[1 + \sqrt{1 + \frac{\psi y(1-y)}{(y_{\pi} - y)(\alpha - \psi y)}} \right]. \quad (V.35)$$

The gradient equation can now be written

$$\frac{dy}{ds} = \frac{Ka}{L_o} \psi y(1-y) \frac{\sqrt{1 + \frac{\psi y(1-y)}{(y_p - y)(\alpha - \psi y)}}}{1 + \sqrt{1 + \frac{\psi y(1-y)}{(y_p - y)(\alpha - \psi y)}}} \quad (V.36)$$

Π and y_p are to be computed from the no loss problem. An approximation for the flow is

$$L = L^o \left(1 + \frac{\Delta L}{L^o}\right)$$

where

$$L^o = \frac{2P(y_p - y)}{\psi y(1-y)} \quad (V.38)$$

and

$$\frac{\Delta L}{L^o} = \frac{4\sigma}{\psi^2} \frac{L_o}{Ka} \left[\left(\frac{y_p + y - 2yy_p}{y_p - y} \right) \ln \frac{R_p}{R} - 2 \right] \quad (V.42)$$

The concentration y is the same function of s both with and without losses

$$y = \frac{y_f e^{\frac{Ka}{L_o} \frac{\psi}{2} s}}{1 - y_f + y_f e^{\frac{Ka}{L_o} \frac{\psi}{2} s}} \quad (V.43)$$

APPENDIX A

At given temperature and pressure the current will be some function of the four concentrations

$$J = f(C_{A1}, C_{A2}, C_{B1}, C_{B2}).$$

Due to the fact that we are dealing with an exchange reaction only one of these is independent, say C_{A1} . Consequently,

$$J = \phi(C_{A1}).$$

The current will vanish at equilibrium when $C_{A1} = C_0$. Let $C_{A1} = C_0 + C'$ and then

$$J = \left(\frac{\partial \phi}{\partial C_{A1}} \right)_{C_0} C' + \dots \text{higher terms in } C'.$$

But $\alpha C_{A2} C_{B1} - C_{A1} C_{B2}$ also vanishes when $C_{A1} = C_0$ and, therefore, to the first order should be linear in C' . Hence, the stated proportionality follows unless C_0 is a repeated root of one of two expressions which seems unlikely.

APPENDIX B

The difference equation for countercurrent cells (II.26) over a region where the interstage flow is constant is

$$y_n - y_{n-1} = \frac{(Kah) \left[\psi y_n(1-y_n) - \frac{P}{L-P} (y_p - y_n)(\alpha - \psi y_n) \right]}{L + \frac{L(Kah)}{L-P} (\alpha - \psi y_n)}.$$

If the dimensionless quantity f is defined by the formula

$$f = \frac{(Kah)}{L}$$

this may be rewritten

$$y_n - y_{n-1} = \frac{f \left[\psi y_n(1-y_n) - \frac{P}{L-P} (y_p - y_n)(\alpha - \psi y_n) \right]}{1 + \frac{fL}{L-P} (\alpha - \psi y_n)}.$$

This difference equation may be solved exactly as follows:

Consider the roots of the quadratic equation

$$\psi y(1-y) - \frac{P}{L-P} (y_p - y)(\alpha - \psi y) = 0.$$

This equation has two roots which in analogy to Shacter and Garrett⁽¹⁾ are denoted by

$$y_0 = \frac{\psi \left(1 + \frac{Py_p}{L-P}\right) + \frac{\alpha P}{L-P} \pm \sqrt{\left[\psi \left(1 + \frac{Py_p}{L-P}\right) + \frac{\alpha P}{L-P}\right]^2 - \frac{4\psi \alpha Py_p L}{(L-P)^2}}}{2\psi \frac{L}{L-P}}$$

and

(1) Garrett, G. A. and Shacter, J., Analogies Between Gaseous Diffusion and Fractional Distillation, AFCD-1940, May 1948.

$$y_1 = \frac{\psi \left(1 + \frac{Py}{L-P}\right) + \frac{\alpha P}{L-P} + \sqrt{\left[\psi \left(1 + \frac{Py}{L-P}\right) + \frac{\alpha P}{L-P}\right]^2 - \frac{4\psi \alpha Py L}{(L-P)^2}}}{2\psi \frac{L}{L-P}}.$$

The subscripts are chosen because at total reflux, $P=0$, $y_0=0$, and $y_1=1$.

In terms of these roots the difference equation may be rewritten in the form

$$y_n - y_{n-1} = \frac{f\psi \frac{L}{L-P} (y_n - y_0)(y_1 - y_n)}{1 + \frac{fL}{L-P}(\alpha - \psi y_n)}.$$

Now let

$$y_n = y_0 + \frac{1}{u_n}.$$

Substituting in the difference equation

$$\frac{1}{u_n} - \frac{1}{u_{n-1}} = \frac{f\psi \frac{L}{L-P} \left(\frac{1}{u_n}\right)(y_1 - y_0 - \frac{1}{u_n})}{1 + \frac{fL}{L-P}(\alpha - \psi y_0 - \frac{\psi}{u_n})}$$

and multiplying both sides by u_n

$$1 - \frac{u_n}{u_{n-1}} = \frac{f\psi \frac{L}{L-P} (y_1 - y_0 - \frac{1}{u_n} + \frac{\alpha}{\psi} - \frac{\alpha}{\psi}) + 1 - 1}{1 + \frac{fL\psi}{L-P} (\frac{\alpha}{\psi} - y_0 - \frac{1}{u_n})}$$

or

$$\frac{u_n}{u_{n-1}} = \frac{1 - \frac{f\psi L}{L-P} (y_1 - \frac{\alpha}{\psi})}{1 + \frac{fL\psi}{L-P} (\frac{\alpha}{\psi} - y_0 - \frac{1}{u_n})}$$

or again

$$u_{n-1} = \frac{u_n \left\{ 1 + \frac{fL\psi}{L-P} (\frac{\alpha}{\psi} - y_0) \right\} - \frac{fL\psi}{L-P}}{1 + \frac{f\psi L}{L-P} (\frac{\alpha}{\psi} - y_1)}.$$

Solving for u_n

$$u_n = \frac{\left\{ 1 + \frac{fL}{L-P} (\alpha - \psi y_1) \right\} u_{n-1} + \frac{fL\psi}{L-P}}{1 + \frac{fL}{L-P} (\alpha - \psi y_0)}$$

Solving this for N cells in series

$$u_N = \left[\frac{1 + \frac{fL}{L-P} (\alpha - \psi y_1)}{1 + \frac{fL}{L-P} (\alpha - \psi y_0)} \right]^N u_B + \frac{1}{y_1 - y_0} \left\{ 1 - \left[\frac{1 + \frac{fL}{L-P} (\alpha - \psi y_1)}{1 + \frac{fL}{L-P} (\alpha - \psi y_0)} \right]^N \right\}$$

where $y_N = y_0 + \frac{1}{u_N}$ and $y_B = y_0 + \frac{1}{u_B}$ with y_N = upstream mole fraction N cells up from cell with mole fraction y_B .

Thus for y_N we obtain

$$y_N = y_0 + \frac{(y_B - y_0) \left[\frac{1 + \frac{fL}{L-P} (\alpha - \psi y_0)}{1 + \frac{fL}{L-P} (\alpha - \psi y_1)} \right]^N (y_1 - y_0)}{y_1 - y_B + (y_B - y_0) \left[\frac{1 + \frac{fL}{L-P} (\alpha - \psi y_0)}{1 + \frac{fL}{L-P} (\alpha - \psi y_1)} \right]^N}$$

This solution is the rigorous solution to a celled countercurrent cascade over an arbitrary length for which L is constant. If now N in the formula above is regarded as a continuous variable rather than discrete one may differentiate with respect to N and obtain a differential equation whose solution is exactly the same at integral values of the argument as the difference equation. Thus it is not difficult to deduce the differential equation

$$\frac{dy}{dN} = \frac{\ln A}{y_1 - y_0} (y - y_0)(y_1 - y)$$

with

$$\ln A = \ln \left[1 + \frac{fL}{L-P} (\alpha - \psi y_0) \right] - \ln \left[1 + \frac{fL}{L-P} (\alpha - \psi y_1) \right].$$

The countercurrent equation with length measured in units of H.E.T.S. if there is no celling is

$$\frac{dy}{ds} = \frac{\psi L}{L-P} (y - y_0)(y_1 - y)$$

in terms of the same roots y_0 and y_1 . Putting $ds = 1$ for one stage we find

$$dN \cdot \frac{\ln A}{(y_1 - y_0)} = \frac{\psi L}{L-P} \cdot 1$$

which can readily be solved for dN , the number of cells equivalent to one H.E.T.S.

$$dN = \frac{\frac{\psi L}{(L-P)} (y_1 - y_0)}{\ln A}.$$

To recapitulate, the exit mole fractions in the upstream phase of a celled countercurrent cascade have the same concentrations as the solutions to the countercurrent cascade without celling at the same points if the H.E.T.S. of the uncelled cascade is equal to the length of dN cells with dN given by the above formula.

It is now possible to examine the validity of the approximate formula for dN

$$dN = \frac{1+f}{f}$$

stated in the main text. Expanding $\ln A$ as a power series

$$\ln A = \frac{\frac{fL}{L-P} \psi (y_1 - y_0)}{1 + \frac{fL}{L-P} (\alpha - \psi y_1)} - \frac{1}{2} \left\{ \frac{\frac{fL}{L-P} \psi (y_1 - y_0)}{1 + \frac{fL}{L-P} (\alpha - \psi y_1)} \right\}^2$$

we find

$$dN = \frac{1 + \frac{fL}{L-P} (\alpha - \psi y_1)}{f} \cdot \frac{1}{1 - \frac{1}{2} \frac{\frac{fL}{L-P} \psi (y_1 - y_0)}{1 + \frac{fL}{L-P} (\alpha - \psi y_1)} + \frac{1}{3} \dots}$$

Thus the formula

$$dN = \frac{1+f}{f}$$

appears highly accurate as long as $P/L \ll 1$, and $\psi \ll 1$. At total reflux we have

$$dN = \frac{1+f}{f} \cdot \frac{1}{1 - \frac{1}{2} \frac{\psi f}{1+f} + \dots}$$

NOMENCLATURE

- A = the desired isotope of a pair of isotopes
 a = interfacial area per foot of cascade (L^2/L)
 a = interfacial area in batch experiments (L^2)
 B = the second of a pair of isotopes
 C = concentration (moles/ L^3)
 D = diffusion coefficient or diffusivity (L^2/T)
 F = rate of feed to the cascade (moles/ T)
 H = stagelength (L)
 h = length of cell in the partitional system (L)
 h = film thickness (L)
 (HET) = half equilibrium time (T)
 (HTU) = height of a transfer unit (L)
 I = inventory of both components in the phase specified (moles)
 J = current density of desired isotope (moles/ L^2T)
 K = material transfer coefficient (moles/ L^2T)
 K' = material transfer coefficient defined by Equation (III.19) (moles/ L^2T)
 k = film material transfer coefficient (moles/ L^2T)
 L = cascade upflow (moles/ T)
 L' = cascade downflow (moles/ T)
 $L^{(0)}$ = cascade upflow in the no-loss cascade (moles/ T)
 L_o = upflow in separating element (moles/ T)
 $\Delta(s)$ = material of both isotopic species lost from the cascade per unit time between s and the product withdrawal point (moles/ T)
 $\Delta_1(s)$ = desired component lost from the cascade per unit time between s and the product withdrawal point (moles/ T)
 M = molarity (moles/ L^3)
 m = number of separating elements in parallel in a cascade section
 N = number of stages
 (NTU) = number of transfer units
 P = rate of product withdrawal (moles/ T)
 R = film resistance (T/L)
 R = number of separating elements in the enricher
 R = abundance ratio, $\frac{y}{1-y}$
 R_p = abundance ratio of product, $\frac{y_p}{1-y_p}$

- r = number of separating elements in series
 S = length of cascade (L)
 s = length (L)
 T = net rate of transfer of desired component (moles/LT)
 T_e = relaxation time (T)
 t = time (T)
 (TTU) = time of a transfer unit (T)
 V = phase volume (L^3)
 W = rate of waste withdrawal (moles/T)
 x = mole fraction of desired isotope in phase being depleted
 x^* = mole fraction of desired isotope in phase being depleted in equilibrium with mole fraction y
 y = mole fraction of desired isotope in phase being enriched
 y^* = mole fraction of desired isotope in phase being enriched in equilibrium with mole fraction x
 z = length of a separating element (L)
 α = equilibrium constant
 γ = constant of proportionality in Equation (I.12) (L^4/MT)
 δ = the fractional difference in the film resistances of two isotopes in a specified phase
 η = the displacement from equilibrium of the mole fraction of the desired isotope in the phase being enriched
 λ = the equilibrium value of the mole fraction of the desired isotope in the phase being depleted
 μ = the equilibrium value of the mole fraction of the desired isotope in the phase being enriched
 ξ = the displacement from equilibrium of the mole fraction of desired isotope in the phase being depleted
 $\Pi(s)$ = net upflow of material (both isotopic species) at point s in the cascade (moles/T)
 $\Pi(s)y_x(s)$ = net upflow of desired component at point s in the cascade
 σ = constant of proportionality between the loss rate and upflow in the cascade
 Φ = total inventory of desired component in both phases of the batch experiments (moles)

- ψ = stage enrichment factor, $\alpha-1$
 $\mathcal{U}$ = stage enrichment factor of hypothetical stage

Subscripts

- A = referring to the desired isotope of the pair of isotopes
 B = referring to the second of a pair of isotopes
 f = referring to feed
 N = designating the Nth square section
 n = referring to the nth stage
 p = referring to product
 w = referring to waste
 1 = referring to phase being enriched in the desired isotope
 2 = referring to the phase being depleted in the desired isotope

Superscripts

- B = referring to the bottom of a square section
 i = referring to the interface
 T = referring to the top of a square section