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Separation of Close Species by Displacement Development on Ion Exchangers. I. A Theoretical Equation of Steady-State Permutation Front. Experimental Verification in the Case of the Separation of Boron Isotopes

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Abstract

The chromatographic plate theory is applied to the displacement development on ion exchangers of a band containing a mixture of two very closely related species. When the number of plates of the band P is small and the separation factor $\alpha = 1 + \epsilon$ is close to unity so that $P\epsilon \ll 1$, and if one of the species of the mixture is of a small percentage, then a linear distribution of the concentrations in the band is obtained. In a more general case the distribution's equation is given. The band is symmetrical only if its initial composition is 50–50. In every other case the plate corresponding to the initial mixture is not the median plate of the band. We have derived a mathematical expression which gives the place of the median in the band. A practical determination of the distribution of species in a steady-state band, when P, ϵ, and the composition of the mixture are known, is given. A limited experimental verification is given for the case of the separation of boron isotopes.

INTRODUCTION

When one seeks to separate closely related species by means of an exchange reaction between a solution and an ion-exchange resin, the most efficient chromatographic technique is that of the development by displacement conceived by Tiselius (*1*) and Claesson (*2*) and effectively utilized in practice for certain difficult separations such as of rare earths, amino acids, nitrogen isotopes, and boron isotopes.

In the case of a mixture of two species B and C, this technique consists in displacing a band of the mixture fixed on a column of ion exchanger initially in the A form by a solution of a specie D, called the developer, under conditions of the following order of affinity: $D > C > B > A$ (assuming that C has a greater affinity for the resin than has B).

The band keeps a constant length during the displacement and is enriched in B at the front and in C at the rear. If the exchange constant $K_B{}^C$ is superior to, say 1.2, we get, after a displacement of the band (of length l_0):

$$L = l_0 \frac{K_B{}^C}{K_B{}^C - 1}$$

a state of equilibrium in which the permutation front between B and C is bilogarithmic, and for which the equation is

$$\log \frac{|B|}{|C|} = \frac{l}{h} \log K_B{}^C$$

where h is the height equivalent to one theoretical plate (HETP) and l is the abscissa measured along the column, the origin being the point where $|B| = |C|$ (*3*).

Figure 1a shows the variations of the concentrations of different species in a steady-state band in the case of an exchange constant sufficiently large and of a band sufficiently long to obtain pure B and C separated by a zone of permutation where the concentrations vary according to the preceeding bilogarithmic law.

The problem is different when the affinity of species B and C for the exchanger are close ($K_B{}^C \sim 1$). There is again a stationary distribution of the concentration in the band, but pure B and C are not obtained.

In the case of a constant differing little from 1 (1.001) of a short band (50 plates), and for a mixture containing two species in greatly differing percentages (0.72% for one, 99.28% for the other), Persoz (*4*) has shown, in calculating the distribution of concentrations plate by plate by means of a computer, that the distribution of the concentrations along a steady-state band are linear (Fig. 1b).

For a greater equilibrium constant, to the order of 1.01, Urgell et al. (*5*), by studying boron isotopes separation (^{10}B of 20%; ^{11}B of 80%,

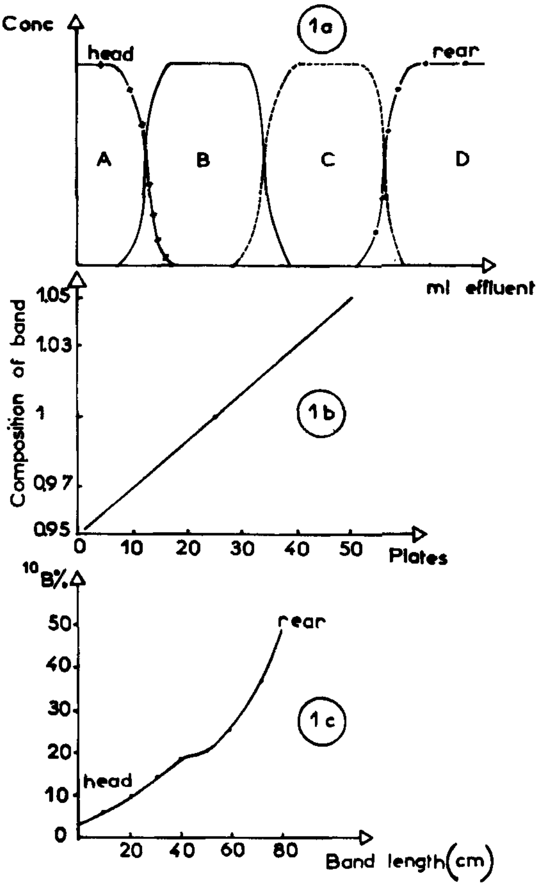

FIG. 1. Different forms of distribution in a steady-state band. (a) Exchange constant $K_B^C > 1.2$; long band, bilogarithmic front. (b) $K = 1.001$, band of 50 plates. Linear distribution. As an ordinate the composition of the band is expressed in relation to that of the median plate of the band (Plate No. 25) taken as a unit. (c) $K = 1.01$, band length 80 cm, separation of boron isotopes, nonlinear distribution [Urgell et al. (*5*)].

approx) by displacement development of a 80-cm band of boric acid on a column length of 25 m (i.e., 31 times the band length), obtained the ^{10}B distribution along the band which is shown in Fig. 1c. This distribution is neither linear nor bilogarithmic.

In other words, in a steady-state distribution we can have, according to the conditions of separation (value of the exchange constant, number of plates in the band, composition of the mixture to be separated), a distribution going from linear distribution to bilogarithmic distribution. These are evidently the two limit distributions ($K \sim 1$ and $K \gg 1$).

We propose to establish the general equation of the steady-state permutation front when the constant is very close to 1 and to state precisely what conditions must be fulfilled for a linear distribution.

THEORETICAL

Diagram of a Band Displacement

Let us consider a column of ion-exchange resin in the form of an ion U (concentration of U in the resin C_R meq/ml of resin phase), bathed by a solution of U to the concentration C_S meq/ml of solution. In a column of volume v the solution occupies a fraction x (interstitial volume of the column, generally to the order of 35% of the total volume) and the resin a fraction $1 - x$. We will designate by m the ratio of U quantities to the resin and solution phases.

$$m = \frac{\mathrm{U}_R}{\mathrm{U}_S} = \frac{v(1-x)C_R}{vxC_S} = \frac{1-x}{x}\frac{C_R}{S_S}$$

when $x = 0.35$, $m = 1.85C_R/C_S$. If the concentration in the resin is generally very much higher than the concentration in the solution, m is large; e.g., if $C_R = 3$, $C_S = 0.1$ and $m = 55$.

We will show that in order to advance a band of 1 plate, it is necessary to effect $m + 1$ transfers, that is to say, to send to the top of the column $m + 1$ plate volumes of solution. We shall reason in the simple case where $m = 1$ (equal amounts of element U in the two phases) and we shall suppose that the band contains only the element U and fills 3 plates. Each plate will be represented diagrammatically in the following manner:

SOLUTION
RESIN

The species initially present in the resin and displaced by U is an ion A;

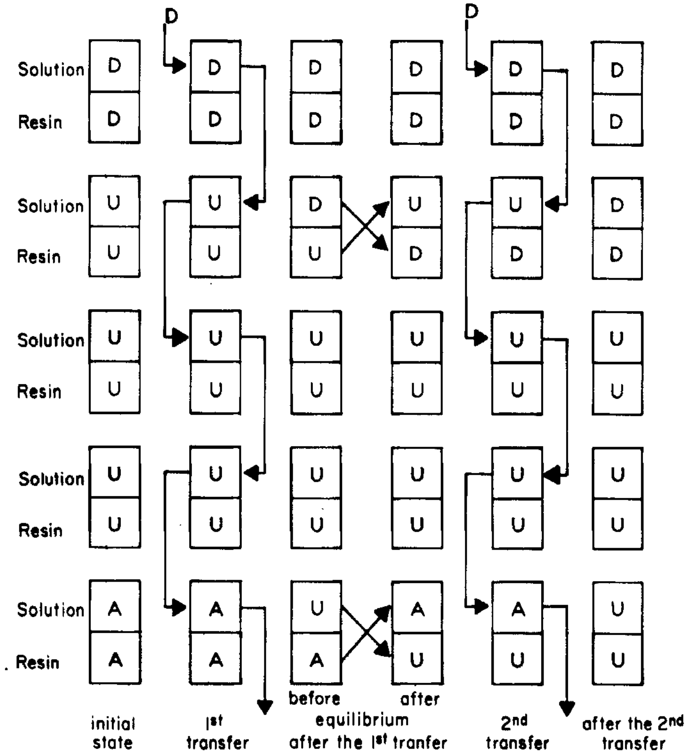

FIG. 2. Schematic representation of the migration of a 3-plates band of a specie U displaced by developer D.

D is the developer. Figure 2 represents the operations required to advance the band of 1 plate. It can be seen that 2 transfers, i.e., $m + 1$ since $m = 1$, are necessary to advance from 1 plate. It is simple to generalize this reasoning when $m \neq 1$; in conclusion, $m + 1$ transfers and therefore $m + 1$ equilibrations are necessary to advance from 1 plate.

Displacement Development of a Short Band Consisting of the Mixture of Two Very Close Elements, One of Which Is Present in a Much Weaker Concentration Than the Other

Let A and B be the two elements of the mixture, and x and y their respective molar fractions. The equilibrium process is

$$A_S + B_R \rightleftharpoons A_R + B_S$$

which corresponds to the constant of the mass action law

$$x_R y_S / x_S y_R = 1 + \epsilon \qquad \text{with } \epsilon \ll 1$$

since we are supposing that the elements A and B possess a very close affinity for the resin.

In the same phase the sum of the molar fractions of different components is equal to 1 and we can write

$$x_R(1 - x_S)/x_S(1 - x_R) = 1 + \epsilon$$

or again

$$x_R/x_S = 1 + \epsilon(1 - x_R)$$

If A is present in a weak amount relative to B, that is $x_R \ll 1$, then

$$x_R/x_S = 1 + \epsilon \tag{1}$$

In order that Eq. (1) be valid during all the displacement of the band from the initial state to the steady-state, the two following conditions must be fulfilled: (a) the enrichment process to each transfer should be of little importance, corresponding to $\epsilon \ll 1$, and (b) the band should be short enough so that the compositional difference between the extreme plates of the band is weak; that is to say, P is small, where P represents the total number of plates in the band.

Note: (1) Further on we will show that the mathematical condition which must be put into effect in order to validate Eq. (1) is $P\epsilon \ll 1$. (2) We assume that the element with the greatest affinity for resin A was present in the smallest proportion. The reverse case does not present any difficulty. In practice this corresponds to the displacement of short bands of uranium consisting of 0.72% of ^{235}U and 92.8% of ^{238}U, ^{235}U being more fixed that ^{238}U on sulfonate resin in a complexing media with an exchange constant between 1.00006 and 1.0006 (*6–11*).

Steady-State Distribution. Let x be the average molar fraction of A in a plate (comprising resin and solution phase). Then

$$x = \frac{mx_R + x_S}{m + 1} \tag{2}$$

from Eqs. (1) and (2):

$$x_R = \frac{(m + 1)(1 + \epsilon)x}{1 + m + m\epsilon} = \frac{(m + 1)(1 + \epsilon)x}{\delta} \tag{3}$$

$$x_S = \frac{(m + 1)x}{1 + m + m\epsilon} = \frac{(m + 1)x}{\delta} \tag{4}$$

where $1 + m + m\epsilon = \delta$.

We have just indicated that once the conditions $\epsilon \ll 1$, small P, and $x_R \ll 1$ were set, computer simulation of the phenomenon of band displacement gave a linear steady-state distribution of the concentrations in the band. Suppose then, that this is so and let us call Z the factor by which one must, in a steady-state band, multiply the molar fractions to pass from one plate to the following one. Notice that as A is the most fixed element on the resin, its molar fraction will decrease as the front of the band is neared, and then $Z < 1$.

Let us now consider two successive plates (Fig. 3), the first of average molar fraction x_0 and the second of average molar fraction x_0Z. During

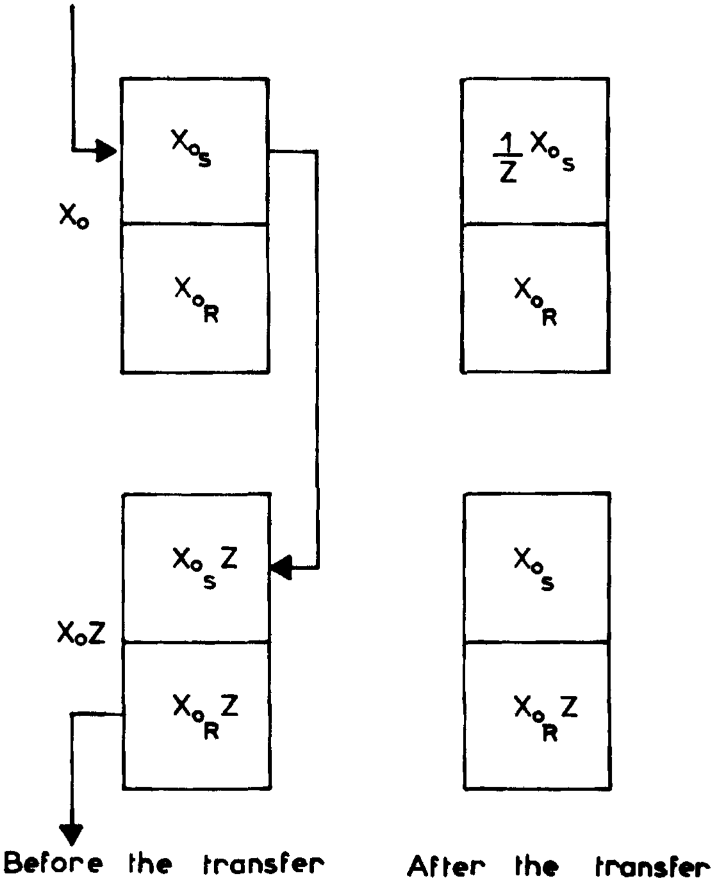

FIG. 3. Diagram of a transfer.

transfer, the solution contained in the first plate (x_{0_S}) comes into contact with the resin in the second plate ($x_{0_R}Z$); in this second plate, the average molar fraction is thus

$$x = \frac{mx_{0_R}Z + x_{0_S}}{m + 1}$$

Replacing x_{0_R} and x_{0_S} by their expressions as functions of x_0 as given in Eqs. (3) and (4), the above equation becomes

$$x = \frac{m(1 + \epsilon) + (1/Z)}{\delta} Zx_0$$

The average molar fraction in the second plate was x_0Z before this transfer. Thus, to pass from the distribution at the transfer t to the distribution at the transfer $t + 1$ in a plate, one has only to multiply the molar fraction of A by

$$y = \frac{m(1 + \epsilon) + (1/Z)}{\delta}$$

Therefore, as we have previously demonstrated, in order to advance the band of 1 plate, one must perform $m + 1$ transfers. After these transfers the initial molar fraction of A will subsequently be multiplied by y^{m+1}.

Once these $m + 1$ transfers have been executed, the concentration of the plate $N + 1$ should be equal to the concentration of the plate N before the $m + 1$ transfers since the band is in equilibrium according to the equation which will allow us to determine Z:

$$y^{m+1}Zx_0 = x_0$$

Letting $1/Z = \mathrm{U}^{m+1}$ and replacing δ by its value, the equation then becomes

$$\mathrm{U}^{m+1} - (1 + m + m\epsilon)\mathrm{U} + m(1 + \epsilon) = 0 \qquad (5)$$

Equation (5) takes $\mathrm{U} = 1$ as its root, which corresponds to a uniform distribution ($Z = 1$) in the band. This particular solution, which actually corresponds to a steady-state, is obviously of no practical interest.

Dividing Eq. (5) by U − 1:

$$U^m + U^{m-1} + \cdots + U - m - m\epsilon = 0 \qquad (6)$$

We made the supposition that the compositional difference between the farthest plates of the band was weak; Z should thus be close to 1 and U equally so. We can then write $U = 1 + \gamma$ and develop $(1 + \gamma)^n$, limiting it to the first term, that is to say, $U^n \sim 1 + n\gamma$.

Equation (6) now becomes

$$1 + m\gamma + 1 + (m - 1)\gamma + \cdots + 1 + \gamma - m - m\epsilon = 0 \qquad (7)$$

the terms $m\gamma$, $(m - 1)\gamma, \ldots$ are those of an arithmetical progression of m terms, which amounts to

$$\frac{m(m + 1)\gamma}{2}$$

and is present m times the number 1; Eq. (7) is thus written

$$m + \frac{m(m - 1)\gamma}{2} - m - m\epsilon = 0$$

Therefore

$$\gamma = 2\epsilon/(m + 1)$$

The very small value of γ is concordant with the set hypothesis. This can now be expressed as

$$U = 1 + \frac{2\epsilon}{m + 1}$$

and $Z = U^{-(m+1)}$, therefore

$$Z = 1 - 2\epsilon$$

The value of Z is shown to be less than 1. If one were to number the plates from front to rear, in other words, in the direction of an increasing amount of A, then

$$Z' = 1/Z \sim 1 + 2\epsilon$$

The distribution along the band in equilibrium is then given by

$$x = x_0(1 + 2\epsilon)^p \qquad (8)$$

where x_0 being the molar fraction of A in the initial mixture and p the number of the plates, taking as origin the plate whose composition is the same as that of the initial mixture ($x = x_0$).

If p is small with respect to $1/2\epsilon$, then $(1 + 2\epsilon)^p$ and $1 + 2p\epsilon$ can be confused. This means that at the time of the displacement of a short band extending over a total number of plates P, such that $P\epsilon \ll 1$, small p leads towards a linear distribution of the concentrations of the two species which is independant of the value of m.

Figure 4 represents the composition of a band if $x_0 = 0.72\%$ and $\epsilon = 0.001$ (separation of uranium isotopes). The full-line curve represents the straight line of the equation $x = x_0(1 + 2p\epsilon)$; the dotted curve corresponds to the equation $x = x_0(1 + 2\epsilon)^p$. For $p = 50$ (end of a band of 100 plates) the linear distribution gives $x = 1.1x_0$ and the other $x = 1.105x_0$; the difference between the two distributions is only 5% when $P\epsilon = 0.1$.

In conclusion, we have shown that if the conditions of the separation

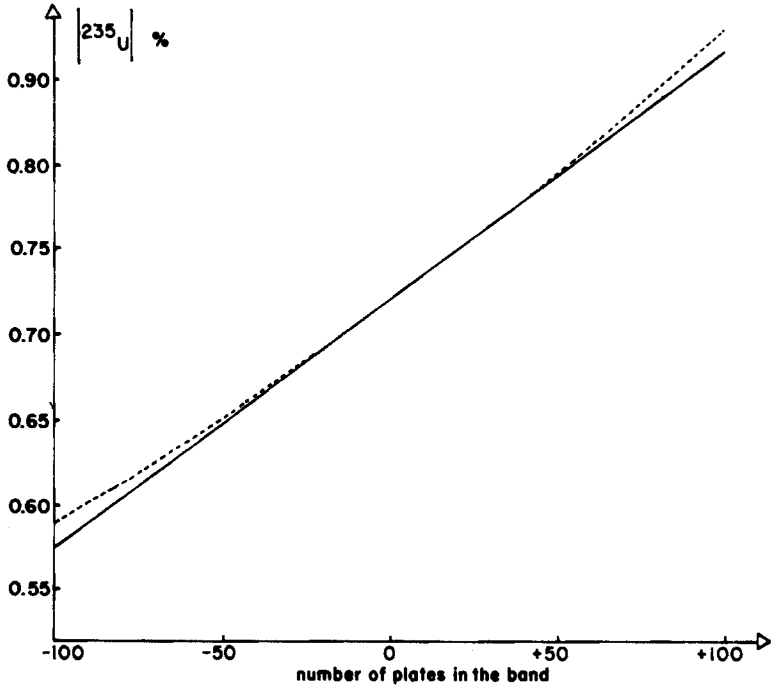

FIG. 4. Limit of the validity of relationship $x = x_0(1 + 2p\epsilon)$ for $x_0 = 0.72\%$ and $\epsilon = 0.001$ as a function of the number of plates in the band. Solid curve: $x = x_0(1 + 2p\epsilon)$. Dashed curve: $x = x_0(1 + 2\epsilon)^p$.

and the length of the displaced band are such that $P\epsilon \ll 1$ in the steady state, and if one of the species of the mixture to be separated is of a small percentage, then a linear distribution of the concentrations in the band is obtained.

We now discuss the case in which the composition of the mixture and the band length are indeterminate.

Development by Displacement of a Band of Any Length Consisting of the Mixture of Two Very Close Elements in Any Proportion

If A and B are the two elements of the mixture, and if x_S and x_R are the molar fractions of A in the solution and the resin, we established in the first part of this study the general relationship

$$x_R/x_S = 1 + \epsilon(1 - x_R)$$

which reduces to

$$x_R/x_S = 1 + \epsilon \qquad \text{if } x_R \ll 1$$

If x_R is indeterminate, one can still write

$$x_R/x_S = 1 + \epsilon'$$

assuming

$$\epsilon' = \epsilon(1 - x_R)$$

In other words, in a range where there is little variation of x_R, it is possible to use the general Eq. (1) established when $x_R \ll 1$, but only if ϵ is replaced by ϵ'.

On the other hand, with ϵ' being small, x_R and x_S are not very different, and m is still more than 20 in practice; and x_R and x, the average molar fraction of A in a plate, can be confused. In effect:

$$x = \frac{mx_R + x_S}{m + 1}$$

if $x_S = x_R + \eta$, and

$$x = x_R + \frac{\eta}{m + 1} \sim x_R$$

if η is small and $m + 1$ is large.

Steady-State Distribution. Let us consider in the stationary band a short zone of p plates in which the percentage in A increases from x to $x + \Delta x$; p being small, $p\epsilon \ll 1$, and, in this zone, one can consider that the distribution of the concentration is linear and one can apply the

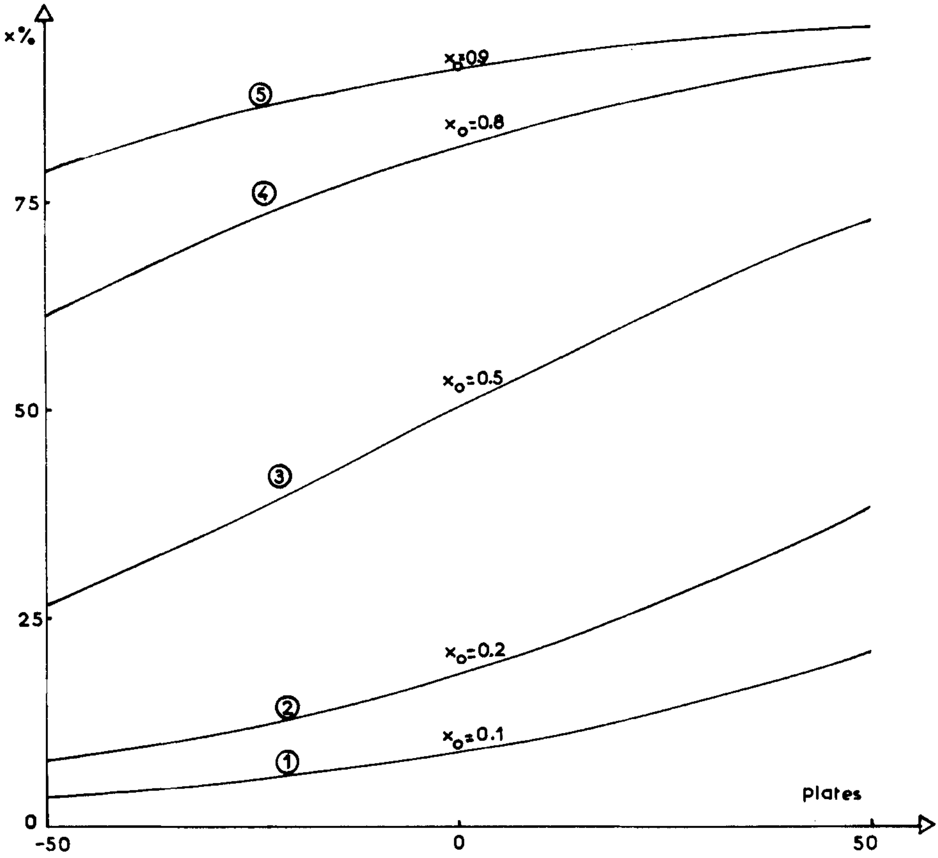

FIG. 5. Distribution of species in a steady-state band of 100 plates ($\epsilon = 0.01$) for different values of x_0: 0.1 (1), 0.2 (2), 0.5 (3), 0.8 (4), and 0.9 (5).

relationship previously established provided that in the meantime ϵ is replaced by ϵ', taking into account that x can be any number and not $\ll 1$. Therefore

$$x + \Delta x = x(1 + 2p\epsilon')$$

$$p = \Delta x / 2\epsilon' x$$

If Δx is infinitely small, the number of plates should be formulated as dp and in replacing ϵ' by its value as a function of x, one finds

$$dp = dx/2\epsilon x(1 - x) \qquad (9)$$

By integrating Eq. (9) starting from the plate for which the percentage in A is equal to its percentage in the initial mixture ($x = x_0$) (this plate would be fixed as the origin), then we find

$$p = \frac{1}{2\epsilon}\left(\ln\frac{x}{1-x} - \ln\frac{x_0}{1-x_0}\right) \tag{10}$$

or

$$x = \frac{1}{1 + \dfrac{1-x_0}{x_0}\exp(-2p\epsilon)} \tag{11}$$

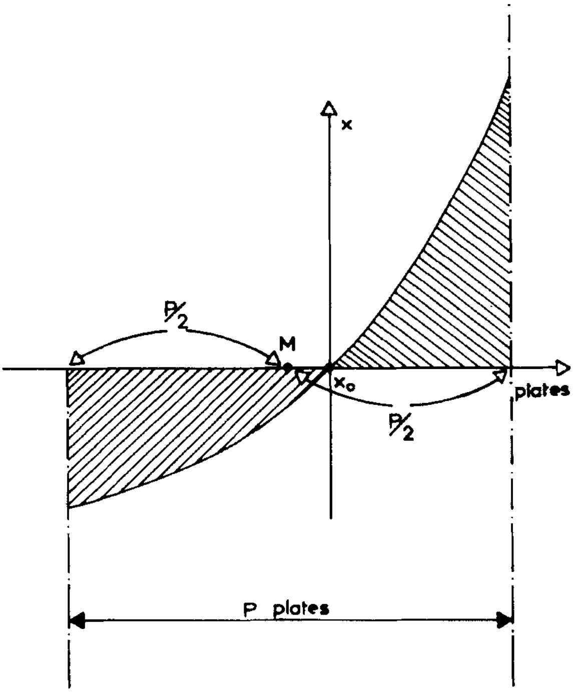

Fig. 6. Position of the medium of the band. The hatched areas are equal. In general the band medium does not coincide with the plate of initial composition x_0 (exept when $x_0 = 0.5$).

The distribution of the species is no longer linear; Fig. 5 shows several distributions for different values of x_0 and $\epsilon = 0.01$ when a band has 100 plates.

Place of the Medium in the Band. To establish Eq. (11) we have taken as the origin the plate which has the same composition as that of the initial mixture: x_0. But the band is symmetrical only if $x_0 = 0.5$. In every other case the plate origin ($x = x_0$) is not the median plate of the band, and it is interesting to locate this median plate which will be determined by its abscissa M measured relative to the plate of composition x_0 (Fig. 6).

According to the law of the conservation of matter, the mixture obtained by assembling all the species contained in the different plates must have the initial composition x_0. Let P be the total number of plates in the band. This will extend from $M - (P/2)$ to $M + (P/2)$. If the abscissa y is measured in relation to the median plate ($y = p - M$), then Eq. (11) is written

$$x = \frac{[x_0/(1 - x_0)] \exp 2\epsilon(y + M)}{1 + [x_0/(1 - x_0)] \exp 2\epsilon(y + M)}$$

Let

$$\beta = \frac{x_0}{1 - x_0} \exp 2\epsilon M$$

Then

$$x = \frac{\beta \exp 2\epsilon y}{1 + \beta \exp 2\epsilon y}$$

and one should have

$$\int_{-P/2}^{+P/2} x(y)\, dy = Px_0$$

Integration yields

$$\ln \frac{1 + \beta \exp \epsilon P}{1 + \beta \exp -\epsilon P} = 2\epsilon P x_0$$

from which is derived

$$\beta = \frac{\exp(2\epsilon P x_0) - 1}{\exp \epsilon P - \exp \epsilon P(2x_0 - 1)}$$

or

$$\boxed{M = \frac{1}{2\epsilon}\ln\left[\frac{1-x_0}{x_0}\,\frac{\exp\,(2\epsilon Px_0)-1}{\exp\,\epsilon P - \exp\left(\dfrac{\epsilon P}{2x_0-1}\right)}\right]} \tag{12}$$

Practical Determination of the Distribution of Species in a Stationary Band. Experimental conditions fix the values of x_0, ϵ, and P (and m, which is not involved at the equilibrium). One has only to place upon the representative curve of Eq. (10) (dependent on ϵ alone)

$$p = \frac{1}{2\epsilon}\ln\frac{x}{1-x}$$

the plate for which $x = x_0$ (molar fraction of initial mixture in the specie

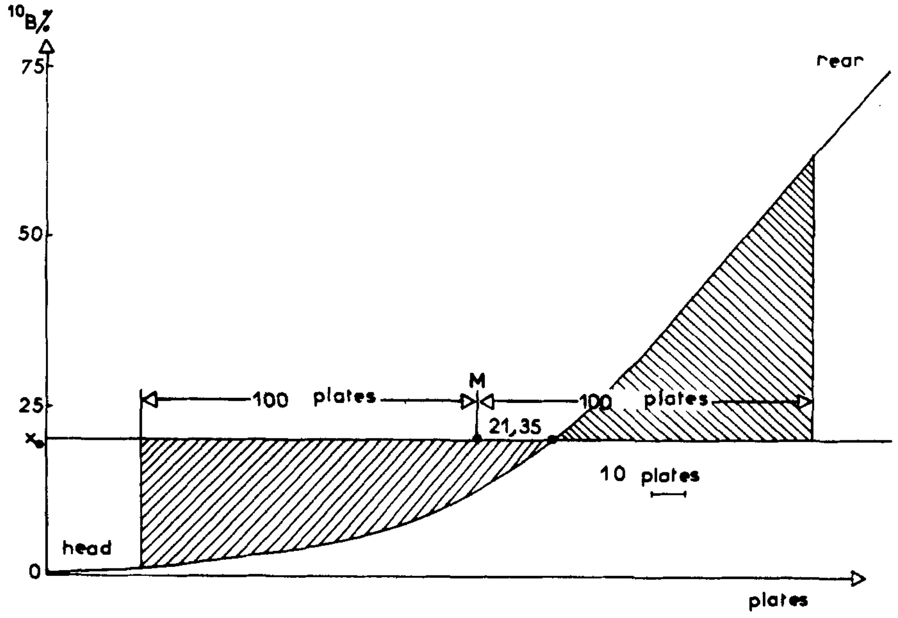

FIG. 7. Theoretical distribution of species in a natural boron band of 200 stationary plates (ϵ = 0.012, x_0 = 0.2014).

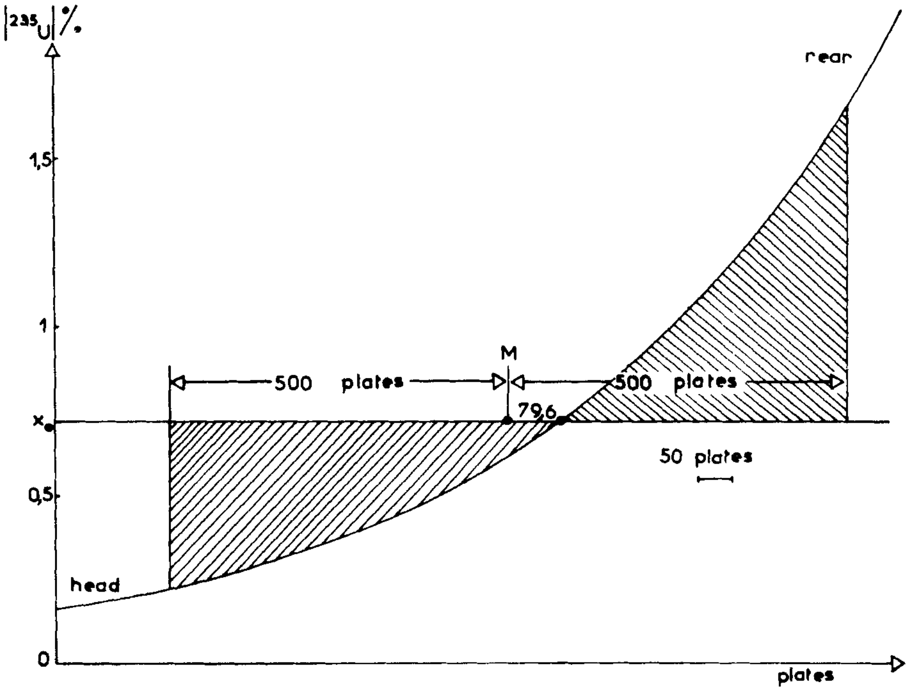

FIG. 8. Theoretical equilibrium distribution of species in a natural uranium band of 1000 plates ($\epsilon = 0.001$, $x_0 = 0.0072$).

having the greater affinity for the resin). Starting from this plate, one places the median plate M determined by Eq. (12) and, finally, one considers $P/2$ plates on both sides of M.

Figure 7 represents this construction when $\epsilon = 0.012$, $x_0 = 0.2014$, and $P = 200$, which would correspond to the displacement up to the steady state of a band of natural boron of 200 plates (when the most fixed isotope is isotope 10, which is 20.14% in natural boron). Equation (12) thereby gives $M = -21.35$.

Figure 8 corresponds to a band of 1000 plates with $\epsilon = 0.001$ and $x_0 = 0.0072$ (uranium isotopes). We find, therefore, that $M = -79.6$.

In conclusion, when exchange constants are close to 1 ($\epsilon \ll 1$), the shape of the distribution front can vary, according to the conditions, from the linear front (an extremely limited case corresponding to $P\epsilon \ll 1$ and to a weak proportion of one of the elements in the mixture) to the bilogarithmic front (long band, initial molar fraction close to 50%) going through parts of bilogarithmic curves, e.g., the curves in Figs. 7 and 8.

Note: When the bands are very long (P very large), the numerator and denominator of Eq. (12) are divided by exp $2\epsilon P x_0$, and exp $-2\epsilon P x_0$ is permitted to approach zero, then

$$M \to (x_0 - \tfrac{1}{2})P$$

It is possible to obtain this result directly. Indeed, if the band is very

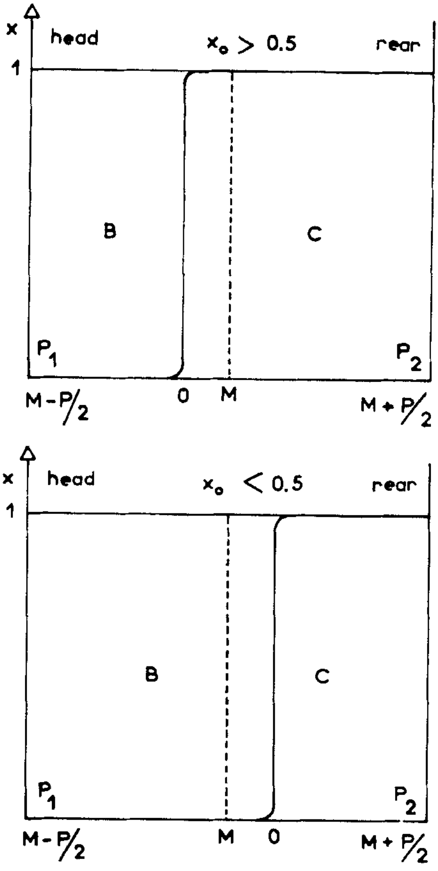

FIG. 9. A band of extremely long length.

long, pure C will be obtained at the rear, pure B at the front, and the distribution between the two species will only take up a small number of plates in comparison with the total number of plates in the column (Fig. 9). One can thus think of the stationary band as being made up of P_1 plates containing pure B and P_2 plates containing pure C, with

$$P_1 + P_2 = P$$

and the band extending from $M - P/2(-P_1)$ to $M + P/2(+P_2)$. The average composition of the band in A is equal to P_2/P, or $(M + P/2)/P$, and must be equal to the composition of the initial mixture x_0. Then

$$\frac{M + P/2}{P} = x_0$$

$$M = (x_0 - \tfrac{1}{2})P$$

which confirms the result deduced from Eq. (12).

Experimental Verification for the Separation of Boron Isotopes

The separation of boron isotopes on anion exchange resin according to Eq. (12) allows confirmation of the validity of Eqs. (11). The separa-

TABLE 1

Separation Conditions

Nature of the resin	Dowex 2 × 10 (100–200 mesh)
Concentration of injected boric acid	0.100 *M*
Concentration of developer (HCl)	0.05 *M*
m	100
Length of the band of boric acid	29 cm
Quantity of displaced boron (in meq)	115
Length covered	1163 cm
Ratio $\frac{\text{length covered}}{\text{band length}}$	39
Displacement rate	1.28 cm/hr
HETP (mm)	10
Exchange constant *K*	1.012
Isotopic concentration of natural boron (in atomic fraction of ^{10}B)	20.14%

tion is based on the exchange reaction

$$H^{10}BO_{2S} + {}^{11}BO_{2R} \rightleftarrows H^{11}BO_{2S} + {}^{10}BO_{2R}^{-}$$

with an exchange constant

$$K = \frac{|\,{}^{10}B\,|\,r\,|\,{}^{11}B\,|\,s}{|\,{}^{10}B\,|\,s\,|\,{}^{11}B\,|\,r}$$

equal to 1.012 under the conditions of the experiment. What is presented here is only a succinct experimental verification in the case of a 29-plate band. Then $P\epsilon = 0.35$ and the distribution is no longer linear but must correspond to that given by Eq. (11).

Table 1 lists the separation conditions.

EXPERIMENTAL

We used the resin Dowex 2 × 10, 100–200 mesh, carefully washed beforehand so that the finest beads were eliminated and had undergone 10 complete exchanges of Cl^-/HO^- (0.5 *M* HCl solution and noncarbonated sodium hydroxide 2*M*).

Operational Technique

We utilized 5 Pyrex-glass columns, each with a 1-cm^2 area and a length of 105 cm, joined together by a capillary tube of 5 mm o.d. and 1 mm i.d. These columns were filled with resin and packed by 10 exchanges of Cl^-/HO^-. By means of a peristaltic pump Sigmamotor Type AL 2E, a 0.1-*M* solution of boric acid was injected at the top of the first column at a flow rate of 40 ml/cm^2/hr. The boric acid solution was prepared with deionized water degassed by bubbling pure nitrogen, and it was preserved under nitrogen. A band of boric acid of given length was thus fixed. It was then displaced by injecting a 0.05-*M* solution of hydrochloric acid with a flow of 40 ml/cm^2/hr.

We obtained a continuous functioning by adding regenerated columns after the column which closes the band and removing the columns which are not in use.

The resin is regenerated in the form of HO^- by the passage of a 2-*M* solution of decarbonated sodium hydroxide. The effluent is split into 12 ml portions by a Lecourt Minimatic-type fraction collector.

Note. Commercial sodium hydroxide always contains notable quantities of carbonates, and it is essential to avoid any preferential fixation of these carbonates on the resin. In effect, when the band is displaced by HCl, CO_2 is degassed and disturbs the progression of the band. To avoid this disturbance, we used a 50% Baker No. 7067 sodium hydroxide containing less than 0.05% carbonate. The dilutions were made with desionized water collected directly at the end of a column of mixed bed resin and degassed for 2 hr by bubbling nitrogen. The 2-*M* sodium hydroxide solution thus prepared was preserved in a polyethylene carboy under permanent bubbling of nitrogen and was passed through a column of quaternary ammonium anion exchanger resin Dowex 21K before being injected into the columns to be regenerated. Despite all these precautions, some traces of carbonates subsist in the sodium hydroxide solution, and this results in the formation of a small band of CO_2 between the rear of the band of boric acid and the Cl^- ions.

Isotopic Analyses

The isotopic analyses were performed with a Thomson-CSF 204 mass spectrometer equipped with a single filament thermoionic emission source. To accomplish the deposit, the sample of boric acid was neutralized with sodium hydroxide up to about pH 8 and the solution thus obtained was concentrated in a platinum crucible until it started to crystallize. A few microliters of this saturated solution were then deposited on the Nichrome filament. The beam of ions thus obtained was stable for several hours. The results were determined with a standard relative deviation of 0.3% with a confidence of 95%.

RESULTS

Figure 10 shows the percentage variations ^{10}B in the band of boric acid displaced up to a steady state (dashed curve); the solid curve represents the theoretical profile of a 29-plate band in the steady state as well as allowing the calculation of Eq. (11).

There is full agreement between the theoretical front and the experimental front except in the first plates of the band. This lack can be explained by the fact that the isotopic exchange constant and the plate height are not necessarily constant at the front of the band because of the spread of the chemical front (*12*).

Also, there is a shift of the plate origin ($x = x_0 = 20.14\%$ ^{10}B) but it

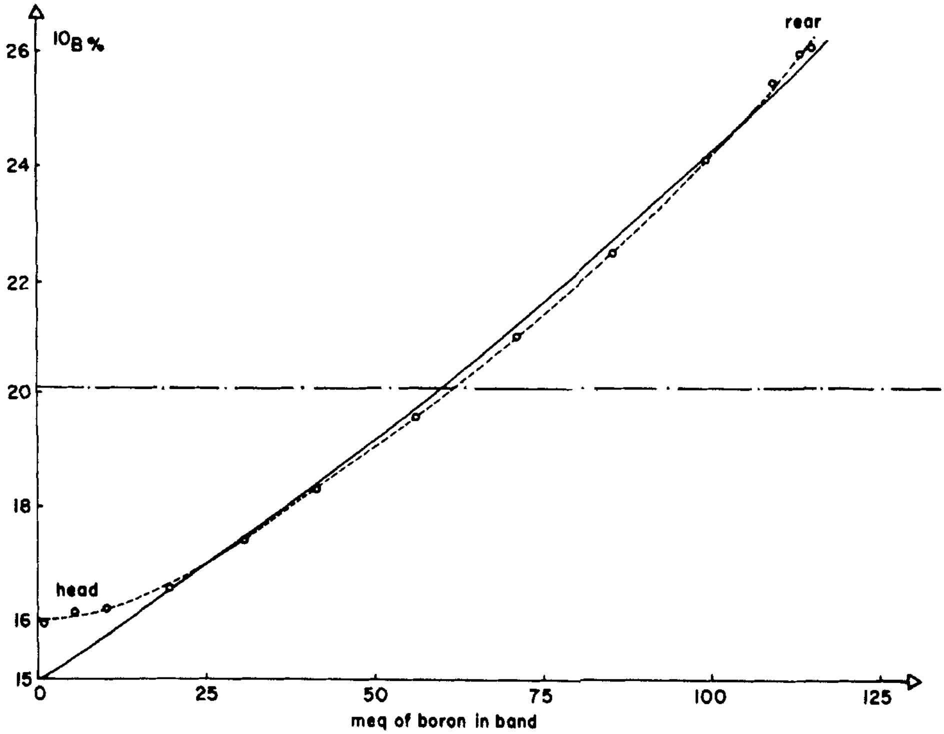

Fig. 10. Theoretical profile of a 29-plate band in the steady state (solid curve) and percentage variations ^{10}B in a band of boric acid (length 29 cm) displaced up to steady state (dashed curve).

is too weak (0.5 plate) to permit a precise verification of Eq. (12). This will be the subject of a later publication.

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