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ESTIMATION OF ISOTOPE SEPARATION POWER OF CHROMATOGRAPHY

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ABSTRACT

A mathematical model for the distribution of isotopic concentration in a displacement chromatogram is derived starting from a simple concept that the chromatographic movement of species can be expressed as the sum of the movement caused by the external forces and the movement caused by the internal concentration gradient. The theoretical equation is combined with appropriate material balance to develop a set of equations which relate the size, production, and start-up time of the chromatographic separation equipment to the degree of isotope enrichment. These equations are easy to use and require a minimum of empirical data.

The model incorporates a series of simplifying assumptions which are valid for displacement chromatography where the isotopic separation coefficient is small and the degree of enrichment accomplished in a single column is not very high. The model is applied to estimate isotope separation power for the cases of boron and uranium isotope separation.

INTRODUCTION

Although theoretical aspects of chromatographic separation have received considerable attention, many problems remain. Even for the limiting case involving the chromatographic separation of isotopes, several theoretical approaches have been made to predict the maximum isotope separation which can be obtained at one end of the chromatographic column. However, while this parameter is of primary interest in the operation of continuous separation devices, chromatographic columns or ionic-migration equipment is usually operated batchwise. In this case the concentration profile within the column is of interest; models which describe only the degree of isotope separation at a single point are inadequate.

We shall develop the model sought on the basis of fundamental considerations and make only those simplifying assumptions which can be expected to hold reasonably well in isotope separation systems. In this way we derive a comprehensive expression which can describe the concentration profile in any kind of chromatography; the result can be applied not only to ion exchange and gas chromatography, but to ionic migration proceses as well.

We have previously derived the general expression which describes the transport of any chemical species *i* in a chromatographic column (1):

$$\frac{\partial C_i(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[-v_i(x,t)C_i(x,t) + D_i(x,t)\frac{\partial C_i(x,t)}{\partial x}\right]. \qquad (1)$$

This expression relates the time rate of change of the concentration of species *i*, $\partial C_i(x,t)/\partial t$, to the velocity $v_i(x,t)$ of species *i* which results from the application of an external force along the x-axis, and to the chromatographic diffusion coefficient $D_i(x,t)$ characteristic of species *i* in the particular system. If v_i and D_i are independent of position, then Eq. (1) reduces to

$$\frac{\partial C_i(x,t)}{\partial t} = D_i\frac{\partial^2 C_i(x,t)}{\partial x^2} - v_i\frac{\partial C_i(x,t)}{\partial x}. \qquad (2)$$

For the case of a two-isotope system (the element whose isotopes are to be separated consists of two isotopes, A and B), under the restriction that the sum of the concentrations of the two isotopes is kept constant at any point in the column, Eq. (2) yields (1)

$$R_A(x,t) + K = A(t)\exp(kx), \qquad (3)$$

where $R_A(x,t)$ denotes the mole fraction of isotope A at the distance x at time t, the parameters k and K are constants, and A(t) is an additional constant which may, however, be time-dependent.

These equations permit us to perform numerical calculations associated with the separation of uranium isotopes and of isotopes of boron, and allow us to expand on discussions presented in previous papers (1,2). The results for uranium isotope separation by ion exchange chromatography are presently of particular interest. The results presented here can be used to determine the theoretical efficiency of the existing process and what must be done to improve upon the present separation power. The results also form the basis for an economic comparison between chromatographic and other isotope separation methods, such as gaseous diffusion.

THEORY

The brief treatment given below is confined to a description of band displacement chromatography involving two isotopes; the band is assumed to be sharply defined and the total concentration of isotopes in the band is assumed constant.

At the beginning of the operation, the chromatographic column contains none of the species whose isotopes (A and B) are to be separated. A solution containing this species [with the isotopic mole fraction $R_A^o(\ell)$ of A] is fed continuously to the column at a constant rate until a certain bandwidth of the species is formed. At this stage, the isotopic distribution in the band is nearly uniform. The band is then developed by an adequate eluent, and sharp boundaries are maintained at both ends of the band. As band development proceeds, the front part of the band is enriched in one isotope (A) and the rear part of the band is depleted in that isotope. There will of course be a plateau region between the front and the rear of the band. After a certain period of development, the isotopic mole fraction of A at the front of the band increases, to attain the value required for product (and the value of the isotopic mole fraction of A at the rear of the band decreases). This condition is shown schematically in Fig. 1. Once the isotopic mole fraction of A at the front of the band reaches the value required for product, material can be withdrawn continuously or semi-continuously from this end as product of the desired degree of enrichment ("production stage"). At the same time, material may be withdrawn from the other end of the band as waste. The time elapsed between initiation of the operation and the beginning of the production stage is termed the "start-up" time (t_s); this period is designated as the "preliminary stage."

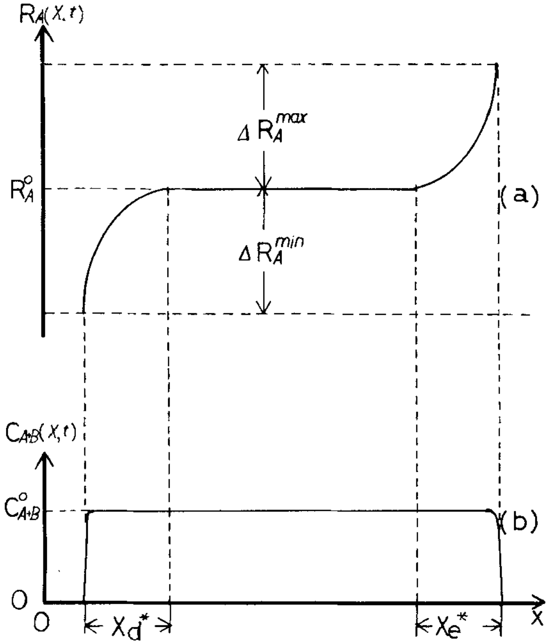

FIGURE 1. Mole fraction (a) and concentration (b) profiles in a band chromatographic separation.

We write the isotopic mole fraction of A in the band in equilibrium with the feed solution as R_A^o and the one required for product as R_A^*, and we define $R_A^{max} = R_A^* - R_A^o$. Other quantities which are employed in an estimation of the rate of isotope separation, the isotope separation power, etc. are given by the following equations (1,2):

For the start-up time t_s,

$$t_s = \frac{1 + \varepsilon[1 - R_A^o(\ell)]}{\eta\varepsilon\bar{v}k_e} \{\Delta R_A^{max} - A_e' \ln (\frac{\Delta R_A^{max}}{A_e'} + 1)\}, \qquad (4)$$

where ε is dependent upon the difference in distribution coefficients of the two isotopes,

$$\varepsilon = (d_B/d_A) - 1, \qquad (5)$$

$$d_i = \frac{C_i(s)(1 - \alpha)}{C_i(\ell)}, \qquad (6)$$

α is the void fraction of the chromatographic column, and $C_i(s)$ and $C_i(\ell)$ denote the concentrations of isotope i in the solid and liquid phases, respectively. The parameter η is defined by the expression

$$\eta = \frac{R_A^o(\ell)[1 - R_A(\ell)]}{1 + (\alpha/d)}, \qquad (7)$$

where $R_A(\ell)$ represents the mole fraction of isotope A in the liquid phase at the point x in the column at time t, i.e.,

$$R_A(\ell) = \frac{C_A(\ell)}{C_A(\ell) + C_B(\ell)}, \qquad (8)$$

and

$$d = [\frac{C_A(s) + C_B(s)}{C_A(\ell) + C_B(\ell)}] (1 - \alpha). \qquad (9)$$

The band velocity $\bar{v}$ is related to the superficial velocity of the feed solution $v^{\ell'}$ through the expression

$$\bar{v} = \frac{v^{\ell'}}{\alpha + d} \, . \tag{10}$$

The parameter in Eq. (4) is termed the "slope coefficient"; it is related to the velocities v_i and the diffusion coefficients D_i of the two isotopes A and B through the expression

$$k_e = \frac{V_A - V_B}{D_A - D_B} = \frac{V_B \varepsilon_v}{D_B \varepsilon_D} \, , \tag{11}$$

where

$$\varepsilon_v = (V_A/V_B) - 1, \tag{12}$$

and

$$\varepsilon_D = (D_A/D_B) - 1. \tag{13}$$

The "enrichment coefficient" A'_e is given by

$$A'_e = c[\exp(k_e \kappa_e t)\exp(k_e x_p)], \tag{14}$$

where c is an experimentally determined constant, x_p is the distance from the origin (x = 0) at which $R_A(x,t)$ begins to deviate from the value R^o_A, and

$$\kappa_e = \frac{v_A D_B - v_B D_A}{D_A - D_B} \, . \tag{15}$$

The width of the enriched zone x^*_e is given by

$$x^*_e = \frac{1}{k_e} \ln \left[\frac{\Delta R^{max}_A}{A'_e} + 1\right], \tag{16}$$

and the rate of growth of the enriched zone (dx^*_e/dt) is given by

$$\frac{dx^*_e}{dt} = \frac{\eta \varepsilon \bar{v}}{\Delta R^{max}_A \{1 + \varepsilon[1 - R^o_A(\ell)]\}} \, . \tag{17}$$

Provided the product is withdrawn continuously in the production stage, then U^{max}_P, the maximum amount of product withdrawn per unit time per unit band volume is

$$U^{max}_P = \frac{C^o_{A+B}(dx^*_e/dt)}{x^*_e + x^*_d} \, , \tag{18}$$

where

$$C^o_{A+B} = C^o_A + C^o_B, \tag{19}$$

and x^*_e and x^*_d are the width of the enriched zone and the width of the depleted zone, respectively. The parameter U^{max}_p is the most significant quantity in estimating the isotope separation power of chromatography. For example, if we choose (3% uranium-235) $kg \cdot m^{-3} \cdot y^{-1}$ as the unit for the case of 3% uranium-235 enrichment, it is to be compared with the amount of product of the same degree of enrichment per unit time and per unit barrier area produced by the gaseous diffusion method [(3% uranium-235) $kg \cdot m^{-2} \cdot y^{-1}$], though this comparison is not, of course, a rigorous one between the two methods.*

CALCULATED RESULTS

We performed numerical calculations of the essential factors of ion exchange chromatographic separations of boron and uranium isotopes with the equations presented above. Ranges of parameter values include those actually obtained in practice. In order to simplify the calculations, we assumed

$$R^o_A = R^o_A(\ell),$$
$$1 + \varepsilon[1 - R^o_A(\ell)] = 1,$$
$$1 + (\alpha/d_A) = 1,$$

and

$$C^o_{A+B} = 1 \text{ mole/L}.$$

Separation of Boron-10 and Boron-11

In this case we selected

$$R^o_A(\ell) = 0.198$$
$$R^*_A = 0.5,$$

---

*The total cost required to produce the unit amount of product of the same degree of enrichment should be used for the rigorous comparison of the isotope separation power between chromatography and other methods.

that is, the desired isotopic composition of boron-10 in the product was taken to be 50%. The results of the calculations are presented graphically in Figs. 2-5.

Separation of Uranium-235 and Uranium-238

For this separation we chose

$$R_A^o(\ell) = 0.0072$$

and

$$R_A^* = 0.03;$$

this conforms to the enrichment commonly required in present

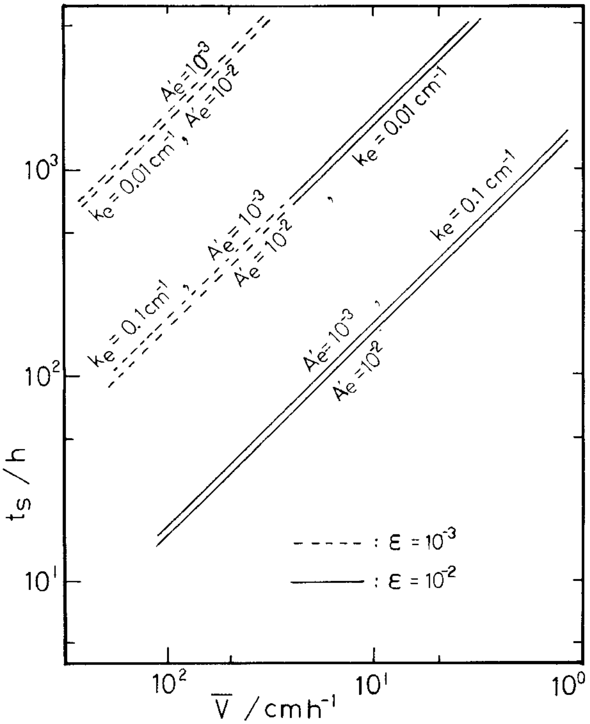

FIGURE 2. Effects of ε, k_e, A'_e, and $\overline{v}$ on t_s (50% boron-10 enrichment).

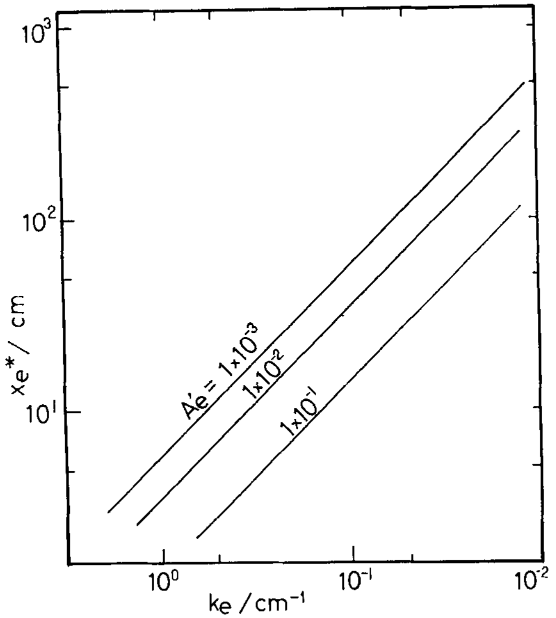

FIGURE 3. Effects of k_e and A_e' on x_e^* (50% boron-10 enrichment).

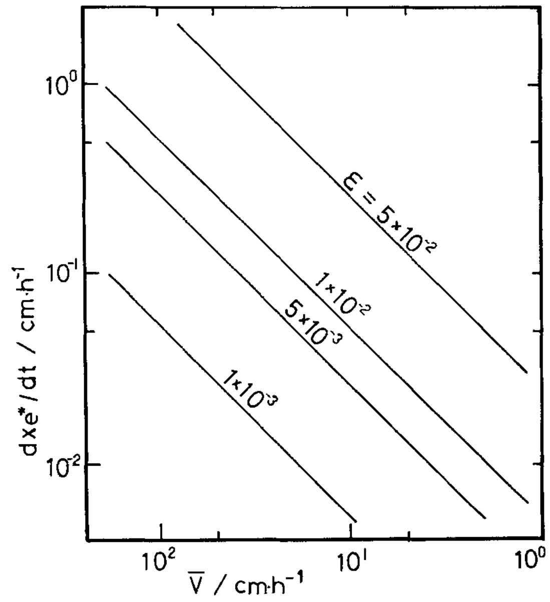

FIGURE 4. Effects of ε and $\overline{v}$ on dx_e^*/dt (50% boron-10 enrichment).

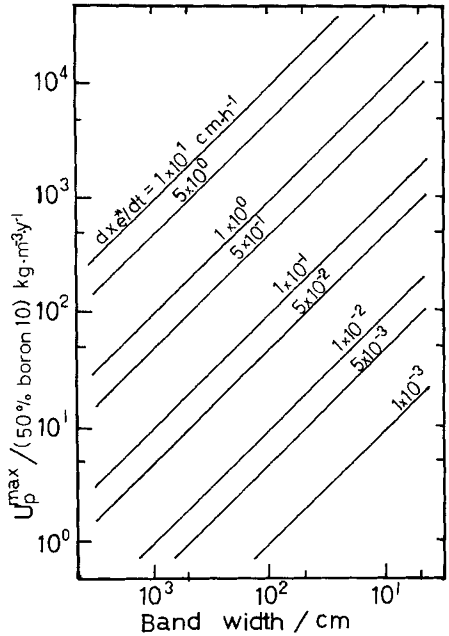

FIGURE 5. Effects of dx_e^*/dt and band width on U_p^{max} (50% boron-10 enrichment).

nuclear reactors. The results for this separation are presented in Figs. 6-9.

DISCUSSION

Since the main purpose of a previous paper (2) was the derivation of a set of equations necessary for analysis of displacement chromatography, these were only briefly presented in this paper. Now we wish to consider the equations in greater detail, and then to supplement the remarks given in the previous paper (2).

Start-up Time (t_s)(Figs. 2 and 6)

The start-up time t_s is the time spent during the preliminary stage; once production has commenced, it has no significant meaning.

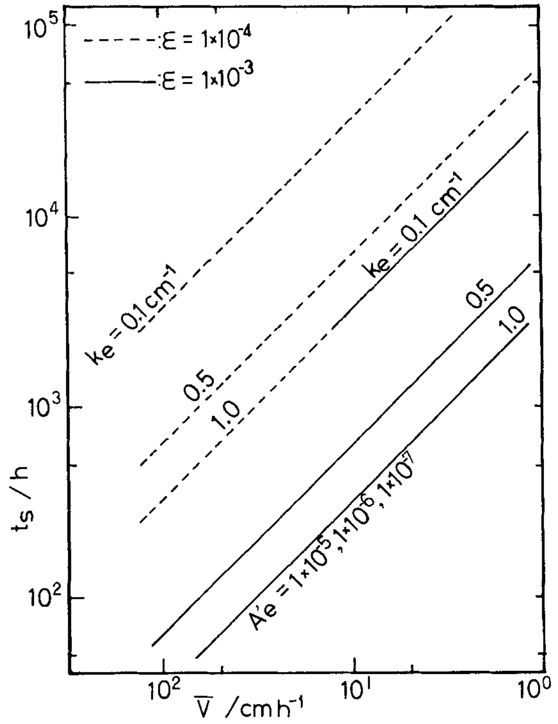

FIGURE 6. Effects of ε, k_e, A'_e and $\bar{v}$ on t_s (3% uranium-235 enrichment).

The more the value of the isotopic mole fraction required for product deviates from the value of the feed, the longer t_s becomes. In practice, the start-up time should of course be minimized. Since t_s is a function of ε, $\bar{v}$, k_e and A'_e, it can be controlled through these parameters. The effect of A'_e is relatively small, especially when A'_e is much smaller than ΔR_A^{max}. For example, in the case of uranium isotopes in Fig. 6, t_s remains nearly unchanged in the range of $7.2 \times 10^2 \leq (\Delta R_A^{max}/A'_e) \leq 7.2 \times 10^4$ (three straight lines for $A'_e = 1 \times 10^{-5}$, 1×10^{-6}, and 1×10^{-7} were superposed into one line), provided that the other parameters are constant. This means that we can omit the second term in the

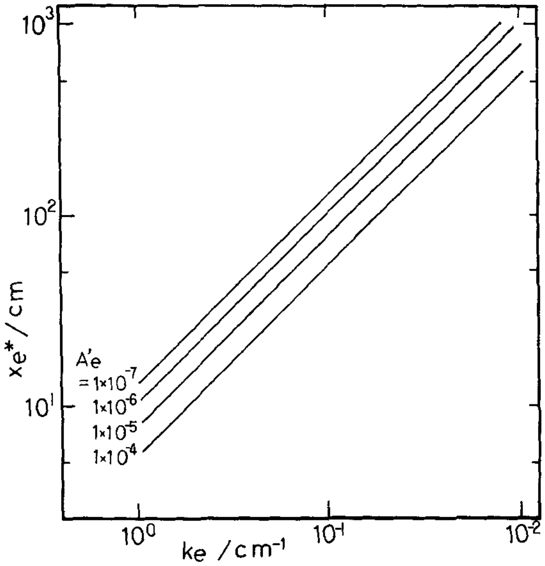

FIGURE 7. Effects of k_e and A'_e on x_e^* (3% uranium-235 enrichment).

bracket of Eq. (4) if $\Delta R_A^{max} >> A'_e$, and rewrite Eq. (4) in the simplified form

$$t_s = \frac{1 + \varepsilon[1 - R_A^o(\ell)]}{\eta\varepsilon\bar{v}\, k_e}\,\Delta R_A^{max}. \tag{20}$$

On the other hand, the effects of ε, $\bar{v}$ and k_e are large; t_s is influenced by each of these parameters by the same degree, and is inversely proportional to each if the other two and A'_e are kept constant.

The Width of the Enriched Zone x_e^* (Figs. 3 and 7)

The width of the enriched zone affects that of the band, and consequently the scale of the apparatus. The narrower the

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*The distance between two adjacent lines in Figs. 3 and 7 becomes smaller as A'_e becomes smaller.

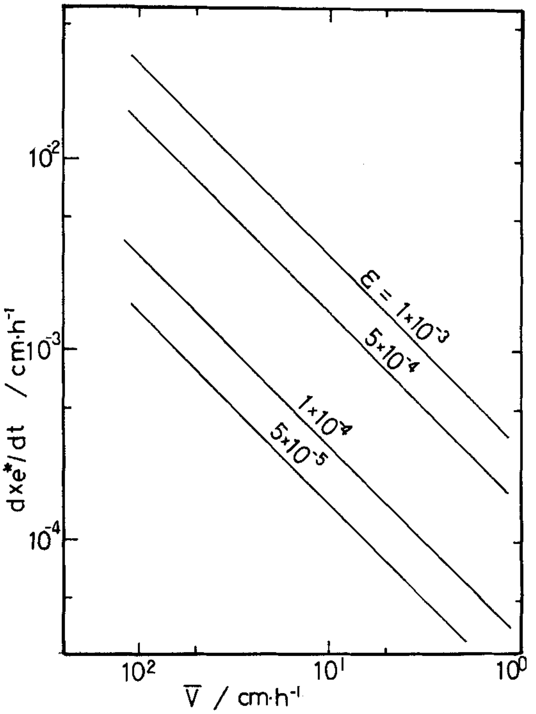

FIGURE 8. Effects of ε and $\bar{v}$ on dx_e^*/dt (3% uranium-235 enrichment).

enriched zone, the smaller the size of the apparatus. As can be easily ascertained from an examination of Eq. (16), x_e^* is a function of k_e and A_e' for a given value of ΔR_A^{max}. Although the width of the enriched zone is not directly influenced by ε and $\bar{v}$, there is an implicit dependence through k_e and A_e'. The effect of A_e' on x_e^* becomes smaller for a constant value of k_e as the ratio $\Delta R_A^{max}/A_e'$ increases*. In cases where A_e' is much smaller than ΔR_A^{max}, Eq. (16) can be rewritten to a good approximation in the form

$$x_e^* = \frac{1}{k_e} \ln \left(\frac{R_A^{max}}{A_e'}\right). \tag{21}$$

Since the width of the enriched zone is inversely proportional to k_e at constant A_e', and moreover depends more sensitively on

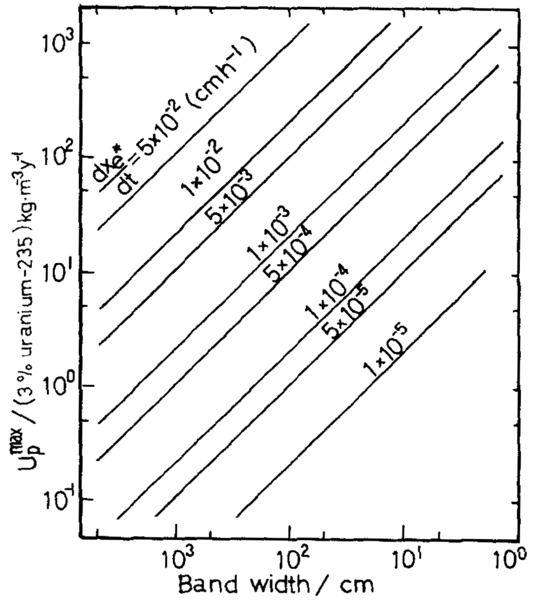

FIGURE 9. Effects of dx_e^*/dt and bandwidth on U_p^{max} (3% uranium-235 enrichment).

this parameter, it is important to maximize k_e in order to minimize x_e^*. Furthermore, as is described in the Appendix, k_e can be shown to be inversely proportional to HETP (Height Equivalent to a Theoretical Plate). Hence making k_e large is equivalent to making HETP small.

The Rate of Growth of the Enriched Zone (dx_e^*/dt)(Figs. 4 and 8)

The rate of growth of the enriched zone directly affects the amount of product obtained, since dx_e^*/dt multiplied by the cross-sectional area of the column and the total concentration of isotopes in the band is the amount of product obtained per unit time. More significantly stated, the value of dx_e^*/dt determines whether or not a chromatographic process can be put into practical use for isotope separation. For a given ΔR_A^{max}, dx_e^*/dt is a function of ε and $\bar{v}$, but does not depend on k_e and A_e' directly. In order to make dx_e^*/dt larger, it is most important to choose the system where the value of ε is larger. But once the system is chosen, ε cannot be varied to a great extent, and it becomes necessary to make the band velocity as high as possible. It is a matter of course that the higher ΔR_A^{max} becomes, the smaller dx_e^*/dt becomes.

The Maximum Amount of Product per Unit Time per Unit Band Volume (U_p^{max})(Figs. 5 and 9)

The maximum amount of product per unit time per unit band volume is the most important parameter for estimating the isotope separation power of the process. The larger the value of U_p^{max}, the higher the power of the process. In order to make U_p^{max} as large as possible, it is necessary to maximize dx_e^*/dt and to minimize $x_e^* + x_d^*$.

In the following, we estimate the power for uranium isotope separation by ion exchange chromatography. This method is currently being considered as a practical means for uranium isotope separation. As an example, if we select

$\varepsilon = 1 \times 10^{-3}$,

$k_e = 0.1\ cm^{-1}$,

$\bar{v} = 50\ cm/h$,

and

$A'_e = 1 \times 10^{-6}$;

then, from Fig. 6,

$t_s \approx 650\ h$;

from Fig. 7,

$x_e^* \approx 100\ cm$;

and from Fig. 8,

$(dx_e^*/dt) \approx 1.5 \times 10^{-2}\ cm/h$

for 3% uranium-235 enrichment. If it is further assumed that the slope coefficient k_d and the enrichment coefficient A'_d in the depleted zone are identical to the corresponding values (k_e and A'_e) in the enriched zone, and that the maximum degree of depletion in the depleted zone $R_A^{min} = 0.0062$, we obtain, from Fig. 9,

$U_p^{max} = 160\ kg\cdot m^{-3}\cdot y^{-1}$.

In practice, a plateau region in which $R_A = R_A^o$ is necessary between the enriched and the depleted zones to keep them separate, hence a bandwidth approximately three times x_e^* is required. Moreover, the band should be displaced by a zone of about 200 cm, so that a chromatographic column about 500 cm in length is actually required for the example considered.

If $\varepsilon = 7 \times 10^{-4}$ and $C_{A+B} = 0.7$ mole/L, then

$U_p^{max} \approx 30\ kg \cdot m^{-3} \cdot y^{-1}$,

or, alternately, if the process were characterized by $\varepsilon = 2 \times 10^{-4}$ and $k_e = 0.2\ cm^{-1}$,

$U_p^{max} \approx 8\ kg \cdot m^{-3} \cdot y^{-1}$.

These parameters appear to be physically realistic; thus it appears that ion exchange chromatography may offer a practical approach to uranium isotope separation.

By way of comparison, we calculate from the data given by Higashi (3) that the amount of product obtained per unit time per unit area of barrier is about 1 $kg \cdot m^{-2} \cdot y^{-1}$ by gaseous diffusion if 3% enrichment is produced. A direct comparison of this result with U_p^{max} is of course midleading, since other factors, such as energy demand, hold-up, capital cost, etc. must be considered.

CONCLUSION

Numerical calculations were presented to demonstrate the use of band chromatography to achieve isotope separations in boron and uranium systems. The results for uranium isotope separation indicate that ion exchange chromatography can be developed into a practical process for this system.

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APPENDIX

Relationship Between Slope Coefficient (k) and HETP

In accordance with Glueckauf's* concept of a chromatographic plate we first derive a fundamental equation for heterogeneous chromatography. Consider a chromatographic column which is oriented along the x axis and is of cross-sectional area $\Delta y \Delta z$. The column is divided into theoretical plates with height H as shown in Fig. A-1. We write c_i and v^ℓ for the overall concentration of solute in the column and the velocity of solute in mobile phase, respectively. The concentration of solute in the mobile phase, c_i^ℓ, is related to c_i by the equation $c_i^\ell = c_i/(\alpha + d_i)$, where d_i is the distribution coefficient and α is the void fraction. The net gain (Δ) of solute in a plate under consideration (the shaded plate in Fig. A-1) in a very small time interval Δt is

$$\begin{aligned} \Delta &= \alpha\{c_i^\ell(x - H) - c_i^\ell(x)\}v^\ell \Delta y \Delta z \Delta t, \\ &= \frac{\alpha v^\ell}{\alpha + d_i}\{c_i(x - H) - c_i(x)\}\Delta y \Delta z \Delta t. \qquad \text{(A-1)} \end{aligned}$$

Using the concentrations at times t and t + Δt, $c_i(t)$ and $c_i(t + \Delta t)$, Δ is also expressed as

$$\Delta = H\{c_i(t + \Delta t) - c_i(t)\}\ \Delta y \Delta z. \qquad \text{(A-2)}$$

Expanding $c_i(x - H)$ and $c_i(t + \Delta t)$ in Taylor's series about x and t and neglecting terms higher than the third term with respect

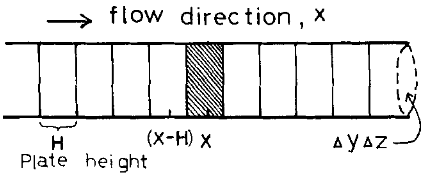

FIGURE A-1. Chromatographic column divided into theoretical plates.

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*E. Glueckauf, Trans. Faraday Soc. 51, 34 (1955).

to $c_i(x - H)$ and the second term with respect to $c_i(t + \Delta t)$, Eqs. (A-1) and (A-2) become

$$\Delta = \frac{\alpha v^{\ell}}{\alpha + d_i} \{- (\frac{\partial c_i}{\partial x}) + \frac{H}{2} (\frac{\partial^2 c_i}{\partial x^2})\} \Delta t \Delta y \Delta z H, \tag{A-3}$$

and

$$\Delta = (\frac{\partial c_i}{\partial t}) \Delta t \Delta y \Delta z H, \tag{A-4}$$

respectively. From these two equations, we obtain

$$\frac{\partial c_i}{\partial t} = \frac{\alpha v^{\ell} H}{2(\alpha + d_i)} \frac{\partial^2 c_i}{\partial x^2} - \frac{\alpha v^{\ell}}{\alpha + d_i} \frac{\partial c_i}{\partial x} . \tag{A-5}$$

Equation (A-5) is the fundamental equation for chromatography based on the concept of theoretical plates.

Comparing this equation with Eq. (2) in the text,

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} - v_i \frac{\partial c_i}{\partial x} , \tag{A-6}$$

we obtain the following two identities:

$$D_1 = \frac{\alpha v^{\ell} H}{2(\alpha + d_i)} , \tag{A-7}$$

and

$$v_i = \frac{\alpha v^{\ell}}{\alpha + d_i} . \tag{A-8}$$

Using Eqs. (A-7) and (A-8), we can derive the relation between k and HETP. According to Glueckauf's assumption that isotopes A and B have the same value of HETP*, k is expressed in terms of H as

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*This assumption is not a good one. It is clear that the HETP of each isotope should be different if there is to be an isotope effect.

$$k = \frac{v_A - v_B}{D_A - D_B} = \frac{2}{H} . \qquad \text{(A-9)}$$

But the fundamental equation derived by our theory is not necessarily equivalent to that derived by plate theory. Therefore, it is more reasonable to indicate instead that

$$k \propto \frac{1}{H}. \qquad \text{(A-10)}$$