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General Theory of Separation and Chromatography

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The fundamental characteristics of the operation of chromatographic columns have been discussed from the standpoints of the general theory of separation; relations applicable in principle to any method of the chromatographic separation of binary mixtures, regardless of the nature and magnitude of the elementary separation step on which it is based, are presented. The bibliography includes 34 references.

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I. INTRODUCTION

In connection with the elaboration[1] and development[2-5] of the circulation chromatographic method whereby it is possible to employ repeatedly the same stationary sorbent bed for the separation of a binary mixture, there arose the necessity to compare it with other processes involving the separation of binary mixtures in columns (distillation, thermal diffusion, centrifuging, etc.). At first sight, the concept of theoretical plates developed in a number of studies[6-8] might serve for this purpose. However, in chromatography the theoretical plate bears no relation[9] to the concept of the theoretical separation stage in the general theory of separation[10].

Comparatively recently the concept of an ideal cascade in chromatography was developed[11]. This involved the introduction of the idea of the height equivalent to the theoretical stage (HETS), which is equivalent to the analogous idea employed earlier for a chromatographic column with complete (special) phase reversal at the ends of the separation zone[12,13]. However, when formulating a specific problem—the comparison of various versions of the continuous circulation-type separation of binary mixtures—the relation between the general theory of separation and chromatography was inadequately elucidated and was limited essentially to the discovery of an analogy between partition in terms of relative concentrations in the chromatographic column and in an ideal fine-separation cascade.

In order to reflect more completely the existing relation, a parallelism is drawn here between chromatographic separation processes and liquid extraction processes, on the basis of which a clearer definition of HETS in chromatography is given together with its relation to the height equivalent to a theoretical plate (HETP) and the optimum conditions for chromatographic separation are discussed. An analogy is also drawn between the operation of a chromatographic column with full phase reversal and a rectangular fine-separation cascade and certain new methods of gas-chromatographic separation are discussed.

II. ANALOGY BETWEEN LIQUID EXTRACTION AND CHROMATOGRAPHY IN THE LIGHT OF THE GENERAL THEORY OF SEPARATION

In the study of chromatographic separation processes an analogy is often drawn between them and liquid extraction processes. This analogy has in fact led to the development of the concept of the theoretical plate in chromatography. The chromatographic column is regarded as consisting of individual elements (plates). Equilibrium must be attained in each such element, i.e. the process takes place as follows: initially the substance enters the first element where equilibrium is established, then the same thing occurs in the second element and in the next, etc., i.e. the real process is imagined to take place on the pattern of the processes occurring in Craig apparatuses[14-16].

In the present section the analogy between liquid extraction and chromatography will also be employed for the further development of the concept of the ideal cascade in chromatography.

1. Ideal Liquid-Extraction Cascade

We shall analyse the operation of a separation apparatus the three stages of which are shown in Fig. 1. The apparatus is a cascade consisting of N series-connected theoretical separation stages. Here the theoretical or ideal stage is understood, as usual[17], as a stage in which the duration of the interaction between the phases is sufficient for the attainment of equilibrium characterised by the elementary separation step. Thus the extract and the material leaving the theoretical stage are solutions in thermodynamic equilibrium with one another.

We shall restrict the treatment to the case of immiscible extractants and to extraction with independent partition of the components (which is frequently observed for dilute solutions, particularly when the partitioned components are undissociated substances or substances which do not react

with any components of the extractant[17]). One of the separation stages in this cascade is shown in Fig. 2 with an indication of the streams and the corresponding concentrations. The separation stage has the following characteristics: a feed flux L at a concentration x enters it with two fluxes emerging at the other end—one partially enriched in the component extracted (L', x') and the other partially depleted in the component (L'', x''). In the case of extraction

$$L' = \varkappa u c_1 + \varkappa u c_2 = \varkappa u c_0 , \quad (1)$$

$$L'' = \varkappa_1 v a_1 + \varkappa_1 v a_2 = \varkappa_1 v a_0 . \quad (2)$$

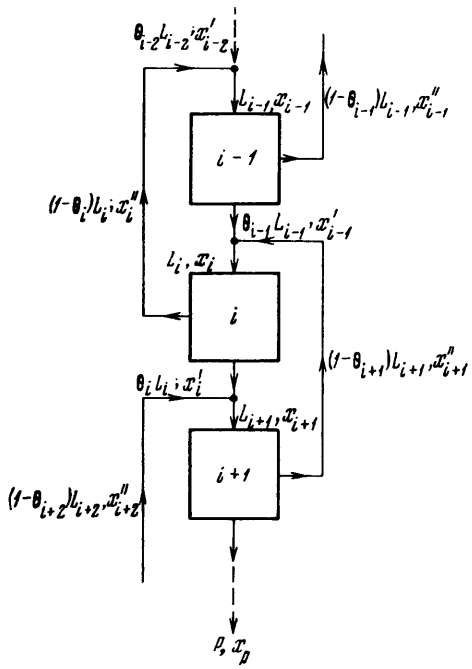


Figure 1. The cascade.

Here u and v are the linear velocities of the extractants, κ and κ_1 are the fractions of the cross-section of the stage occupied by the extractants, c_1 and c_2 are the amounts of the first and second components of the mixture to be separated in the first extractant, and a_1 and a_2 are the amounts of the first and second components in the second extractant.

Bearing in mind that

$$L = L' + L'' , \quad (3)$$

we obtain

$$L = \varkappa u (c_0 + \lambda a_0) , \quad (4)$$

where

$$\lambda = \frac{\varkappa_1 v}{\varkappa u} \quad (5)$$

is the ratio of the extractant fluxes.

Then

$$x' = \frac{c_1}{c_1 + c_2} = \frac{c_1}{c_0} , \quad (6)$$

$$x'' = \frac{a_1}{a_1 + a_2} = \frac{a_1}{a_0} . \quad (7)$$

Since

$$Lx = L'x' + L''x'' \quad (8)$$

by substituting Eqns. (1), (2), (4), (6) and (7) in Eqn. (8), we obtain

$$x = \frac{c_1 + \lambda a_1}{c_0 + \lambda a_0} . \quad (9)$$

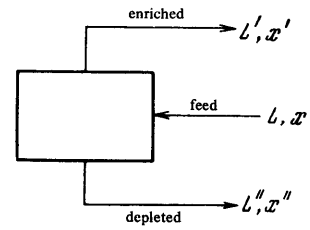


Figure 2. A stage in the cascade.

The relative concentrations[18] will be correspondingly defined by the following equations:

$$\xi' = \frac{x'}{1 - x'} = \frac{c_1}{c_2} , \quad (10)$$

$$\xi'' = \frac{x''}{1 - x''} = \frac{a_1}{a_2} , \quad (11)$$

$$\xi = \frac{x}{1 - x} = \frac{c_1 + \lambda a_1}{c_2 + \lambda a_2} . \quad (12)$$

Introducing the ratio of the enriched fraction to the feed flux (the degree of separation[18]), we obtain

$$\theta = \frac{L'}{L} = \frac{c_0}{c_0 + \lambda a_0} . \quad (13)$$

The degree of separation attained in one stage is called[18] the separation factor α. The latter is defined as the ratio of the relative concentration in the enriched fraction to the relevant concentration in the depleted flux:

$$\alpha = \frac{\xi'}{\xi''} = \frac{a_2}{a_1} \cdot \frac{c_1}{c_2} = \frac{k_2}{k_1} , \quad (14)$$

where k_1 and k_2 are partition coefficients.

Another measure of the degree of separation achieved in the stage is the effective separation factor[18] β:

$$\beta = \frac{\xi'}{\xi} = \frac{1 + \lambda k_2}{1 + \lambda k_1} . \quad (15)$$

Hence

$$\lambda = \frac{\beta - 1}{k_2 - \beta k_1} . \quad (16)$$

It is known[17] that in the separation of components by liquid extraction best results are achieved when the volume ratio of the phases corresponds to symmetrical separation:

$$\lambda_0 = \frac{1}{\sqrt{k_2 k_1}} . \quad (17)$$

We shall attempt to explain this result from the standpoint of the general theory of separation. For this purpose, the principle of the rationality of the cascade formulated previously[19,20] will be employed.

In principle, the role of each stage and of the entire separation cascade consists in the separation of the mixture components. In terms of thermodynamics, this means that under all conditions the operation of the cascade and all its elements consists in a decrease of the entropy (of mixing) of the system. Hence a cascade operating without mixing in any of its units fractions with different concentrations of the component to be extracted must evidently be regarded as thermodynamically the most effective (ideal).

Fig. 1 shows that each stage of the cascade is fed by two fluxes: by the enriched flux from the upper adjacent stage and by the depleted fraction from the lower stage. Only in these units is there a possibility of the mixing of fractions and consequently it is in fact here that particular care should be taken to avoid an increase of entropy.

Thus according to the principle of the ideality of the cascade,

$$\ldots\ ;\ x''_{i+2} = x'_i;\ x''_{i+1} = x'_{i-1};\ x''_i = x'_{i-2};\ \ldots \tag{18}$$

and consequently

$$\ldots\ ;\ x_{i+1} = x'_i;\ x_i = x'_{i-1};\ x_{i-1} = x'_{i-2};\ \ldots \tag{19}$$

Conditions (18) and (19) can also be expressed in terms of relative concentrations:

$$\xi''_{i+1} = \xi'_{i-1} = \xi_i\ . \tag{20}$$

By definition of the effective separation factor,

$$\xi'_i = \beta\xi_i\ . \tag{21}$$

According to Eqn. (20), for an ideal cascade,

$$\xi'_i = \beta\xi''_{i+1} \tag{22}$$

and

$$\xi'_{i+1} = \beta\xi'_i\ . \tag{23}$$

Multiplying together the last two equations, we obtain

$$\xi'_{i+1} = \beta^2\xi''_{i+1}\ , \tag{24}$$

but, by definition of the separation factor,

$$\xi'_{i+1} = \alpha\xi''_{i+1}\ , \tag{25}$$

so that

$$\beta = \sqrt{\alpha}\ . \tag{26}$$

This relation between the effective and thermodynamic separation factors is[10,18-20] the fundamental property of the ideal cascade.

Using Eqns. (14), (15) and (26), it is easy to show that condition (17) is identical with the fundamental property of the ideal cascade and is thus a necessary and sufficient condition for its determination.

For the practically important case of fine separation[10,18-20] where $\alpha - 1 \ll 1$, the geometrical mean may be replaced by the arithmetical mean. Then

$$\lambda_0 \simeq \frac{2}{k_1 + k_2}\ . \tag{27}$$

The resulting equation is identical with the equation derived previously[21] in the calculation of the optimum ratio of the carrier fluxes in a countercurrent chromatographic column and can thus serve as additional confirmation of the validity of the concept of the ideal cascade in chromatography.

It is useful to note that so far in the general theory of separation only one type of ideal cascade has been considered—the continuous-operation ideal cascade characterised by a maximum[10,18,19] on the overall flux distribution curve, the positions of which coincides with the feed point. However, according to the literature data[17], condition (17) is valid not only for a liquid extraction cascade with continuous feed but also for fractional extraction in a Craig apparatus[17], where the distribution of the component fluxes is Gaussian[17,22]. On this basis, one may consider two types of ideal cascade differing in the specific distribution of the component fluxes.

It is possible to show that the overall degree of separation q_0 achieved by the ideal cascade is defined[10] by an equation of the following form:

$$q_0 = \frac{\xi_N}{\xi_0} = \alpha^{N/2}\ . \tag{28}$$

For the case of fine separation we have correspondingly

$$\xi_N = \xi_0\ e^{N/2\cdot(\alpha-1)}\ , \tag{29}$$

where ξ_0 is the relative concentration at the feed point.

On the basis of the above equations, one can imagine how the transition from the second type of ideal cascade to the first may occur. Indeed, we can find the changes which will occur when, during the separation of a binary mixture, the latter is continuously introduced at the feed point. If the condition of extraction with independent partition of components is not thereby violated, the relative concentration partition law should hold, so that continuous introduction of the mixture may be regarded as an infinite number of pulse injections of the mixture at the feed point, which leads to a superposition of a large number of Gaussian distribution curves[11].

2. HETS in Chromatography

HETS in chromatography may be determined from a consideration of the chromatographic zone for a binary mixture. Fig. 3 shows that

$$A'_1 = A_{\max_1}\exp\left[-\frac{(s'_1)^2}{4D^*_1 t}\right]\ , \tag{30}$$

$$A_{0,1} = A_{\max_1}\exp\left[-\frac{(s^0_1)^2}{4D^*_2 t}\right]\ , \tag{31}$$

where

$$s'_1 = \pm\,(l - s^0_1)\ , \tag{32}$$

$$D^*_1 = \frac{D_{\mathrm{eff}_1}\varkappa}{\Gamma_1}\ , \tag{33}$$

$$A_1 = c_1\Gamma_1\ , \tag{34}$$

$$\Gamma_1 = \varkappa\left(1 + \frac{\varkappa_1}{\varkappa}k\right) = \varkappa(1 + k'_1)\ , \tag{35}$$

and D_{eff_1} is the effective diffusion coefficient[22,23].

After dividing Eqn. (30) by Eqn. (31) and using Eqn. (32), we obtain

$$\ln\frac{A'_1}{A_{0,1}} = \frac{l}{4D^*_1 t}[2s^0_1 - l]\ . \tag{36}$$

For the second component

$$A'_2 = A_{\max_2}\exp\left[-\frac{(s'_2)^2}{4D^*_2 t}\right]\ , \tag{37}$$

$$A_{0,2} = A_{\max 2}\exp\left[-\frac{(s_2^0)^2}{4D_2^* t}\right], \quad (38)$$

where

$$s_2^l = s_2^0 + l . \quad (39)$$

Having divided Eqn. (37) by Eqn. (38) and using Eqn. (39), we have

$$\ln\frac{A_2^l}{A_{0,2}} = -\frac{l}{4D_2^* t}[2s_2^0 + l] . \quad (40)$$

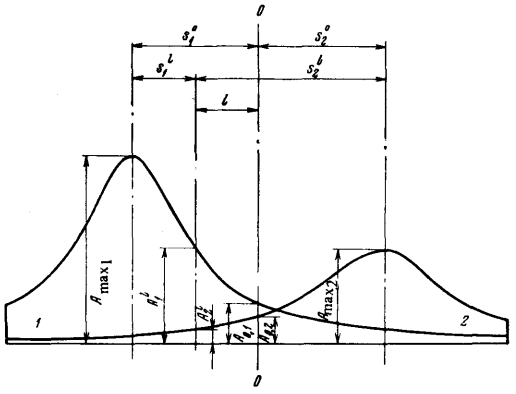


Figure 3. A chromatographic band.

By combining Eqns. (36) and (40) and putting $D_1^* = D_2^*$, we obtain

$$\ln q_0 = \frac{l(s_1^0 + s_2^0)}{2D^* t} . \quad (41)$$

The values of s_1^0 and s_2^0 may be found using the equation derived previously[11,21] for the calculation of the velocities of the chromatographic zones in a system of coordinates linked to the feed cross-section of the chromatographic band:

$$v_{s_1} = \frac{s_1^0}{t} = \frac{u(1-\lambda_0 k_1)}{1+k_1'} , \quad (42)$$

$$v_{s_2} = \frac{s_2^0}{t} = \frac{u(1-\lambda_0 k_2)}{1+k_2'} . \quad (43)$$

From the condition

$$v_{s_2} = -v_{s_1} , \quad (44)$$

we obtain

$$\lambda_0 = \frac{\tilde{\alpha}+1}{k_2 + \tilde{\alpha}k_1} , \quad (45)$$

where

$$\tilde{\alpha} = \frac{\Gamma_2}{\Gamma_1} . \quad (46)$$

On substituting Eqn. (45) in Eqns. (42) and (43), we obtain

$$|s_1^0| = |s_2^0| = \frac{\varkappa u}{\Gamma_1}\frac{\alpha-1}{\alpha+\tilde{\alpha}} \cdot t , \quad (47)$$

whence

$$\ln q_0 = \frac{l}{\frac{D_{\text{eff}_1}}{u}} \cdot \frac{\alpha-1}{\alpha+\tilde{\alpha}} . \quad (48)$$

The application of the concept of HETS to columns is known[10,17] to be useful only in the separation of isotopes where $\alpha - 1 \ll 1$. In the separation of the usual mixtures, the best characteristic is the height per unit transfer[10,17] (HET), since with a correct choice of the determining phase, HET is independent of α, in contrast to HETS.

Taking this into account, we can transform Eqn. (48) for the case of $\alpha - 1 \ll 1$, obtaining

$$\ln q_0 \simeq \frac{l}{\frac{D_{\text{eff}}}{u}} \cdot \frac{\alpha-1}{2} . \quad (49)$$

We may note that under these conditions Eqn. (45) becomes identical with Eqn. (27), which makes it possible to compare Eqn. (49) with Eqn. (29) and thus obtain

$$\text{HETS} = \frac{D_{\text{eff}}}{u} . \quad (50)$$

The resulting value of HETS differs significantly from the concept of HETP widely used at the present time in chromatography[22,23]:

$$\text{HETP} = \frac{2D_{\text{eff}}}{u_0} , \quad (51)$$

where u_0 is the velocity of the developer in a system of coordinates linked to the column. It is evidently of interest to compare these two concepts.

In the separation of a mixture on a stationary sorbent in a system of coordinates linked to the feed cross-section[11,21], there is a countercurrent of the eluent and the sorbent and the following equation applies:

$$u_0 = u + v . \quad (52)$$

Using Eqn. (27), it is possible to show that

$$u = u_0 \cdot \frac{k'}{1+k'} . \quad (53)$$

On substituting the value of u from Eqn. (53) in Eqn. (50), we obtain after some rearrangement the expression

$$\text{HETS} = \text{HETP} \cdot \frac{1+k'}{2k'} , \quad (54)$$

from which it follows that the values of HETS and HETP are identical only when $k' = 1$. When $k' \ll 1$, HETS differs significantly from HETP. We may note that, when $k' = 0$ (no sorption of the components to be separated), the concept of HETS loses significance, since this quantity tends to infinity, which is physically understandable because the absence of sorption of the components separated implies also the absence of chromatographic separation.

Eqns. (28) and (48) are used to determine HET in chromatography. Under conditions where $\tilde{\alpha} = \sqrt{\alpha}$, Eqn. (45) is transformed into Eqn. (17). On this basis (for any value of α), one can write

$$\text{HETS} = \frac{D_{\text{eff}_1}}{u} \cdot \frac{(\alpha+\sqrt{\alpha})\ln\alpha}{2(\alpha-1)} \cdot \frac{\frac{\sqrt{\alpha}-1}{\sqrt{\alpha}}}{\frac{\sqrt{\alpha}-1}{\sqrt{\alpha}}} = \frac{D_{\text{eff}_1}}{u} \cdot \frac{\frac{1}{2}\ln\alpha}{1-\frac{1}{\sqrt{\alpha}}} . \quad (55)$$

According to the literature data[17],

$$\text{HETS} = \text{HET} \cdot \frac{\ln\varepsilon}{1-\frac{1}{\varepsilon}} , \quad (56)$$

where

$$\varepsilon = k_2\lambda_0 = \sqrt{\alpha} . \quad (57)$$

Comparison of Eqns. (55) and (56) shows that

$$\mathrm{HET} = \frac{D_{\mathrm{eff}1}}{u} \ . \qquad (58)$$

3. The Validity of the Assumption that $D_1^* = D_2^*$

Eqn. (49) may be transformed into a formula analogous to the formulae for the calculation of the number of theoretical plates n in the chromatographic column[2,23,24]. Indeed, if it is assumed that $l = s_1^0$, then

$$2\ln q_0 = 2\ln\left[\frac{A_1 \cdot A_{\max 2}}{A_2 \cdot A_{\max 1}}\right] = 2\ln\left[\frac{A_{\max 2}}{A_2}\right] = \sigma^2_{\max} \ , \qquad (59)$$

where $\sigma_{\max_2}$ is the number of standard deviations at a specified peak height. According to Eqns. (49) and (54),

$$\sigma^2_{\max 2} = \frac{s_1^0}{\mathrm{HETP}} \cdot \frac{2k'}{1+k'}(\alpha - 1) \ . \qquad (60)$$

From Eqns. (47) and (53), we have

$$s_1^0 = \frac{u_0}{1+k'} \frac{k'}{1+k'} \cdot \frac{\alpha - 1}{2} \cdot t \ . \qquad (61)$$

On substituting Eqn. (61) in Eqn. (60), we obtain

$$t = \frac{\mathrm{HETP}}{u_0} \cdot \frac{\sigma^2_{\max 2}}{(\alpha-1)^2} \frac{(1+k')^2}{(k')^2} \ . \qquad (62)$$

Since

$$t = \frac{H}{u_0}(1+k') \ , \qquad (63)$$

where H is the height of the chromatographic column, it follows that

$$n = \frac{\sigma^2_{\max}}{(\alpha-1)^2}\left(\frac{1+k'}{k'}\right)^2 . \qquad (64)$$

According to Purnell[24],

$$n = \frac{36}{(\alpha-1)^2} \cdot \left(\frac{1+k'}{k'}\right)^2 , \qquad (65)$$

while according to Zhukhovitskii[23],

$$n = \frac{32K_1}{(\alpha-1)^2} = \frac{32K_1}{(\alpha-1)^2} \cdot \left(\frac{1+k'}{k'}\right)^2 , \qquad (66)$$

where K_1 is the separation criterion.

According to Martin[2],

$$n = \frac{16\sigma}{(\alpha-1)^2} = \frac{16\sigma}{(\alpha-1)^2} \cdot \left(\frac{1+k'}{k'}\right)^2 . \qquad (67)$$

Eqn. (64) is identical with Eqns. (65), (66), and (67). The conclusions based on the equations formulated (see, for example, Purnell and Quinn[24]) are satisfactorily confirmed in practical chromatographic analysis despite the assumption of the equality of D_1^* and D_2^*. Therefore Eqn. (49) derived here should also hold in practice both by analogy and as a result of its relation to the equations already available. Indeed, on the basis of Eqn. (49), one can imagine the way in which the transition from the periodic version of development-type circulation chromatography to its continuous separation version with periodic additional feed and take off may be achieved[5,11]. Without resorting to the above assumption, it is difficult to account for the real existence of continuous-operation chromatography such as the method proposed for gas chromatography by Pichler and Schulz[25].

4. Optimum Conditions for Chromatographic Separation

If the role of the chromatographic column consists only in the separation of the binary mixture to the required degree of purity (sufficient, for example, for analysis), then in principle it is possible to ensure conditions of chromatographic separation such that the work of separation is a minimum. The study of the optimum separation conditions in the general theory of separation leads to the conclusion that cascades with reduction of the fluxes from one separation element to another (and in the case of low separation factors cascades with a continuous variation of the fluxes) are most convenient. When certain laws governing the distribution of the fluxes and the relative concentrations (corresponding to the distribution in an ideal cascade) operate, the work of separation in such cascades is a minimum[10]. Bearing in mind the analogy found between a chromatographic column and an ideal cascade, it is therefore of interest to elucidate under what conditions the chromatographic column most closely approaches the ideal cascade.

According to Eqn. (45), when

$$\tilde{\alpha} = \sqrt{\alpha} \qquad (68)$$

the volume ratio of the phase fluxes in the chromatographic column becomes equal to the analogous ratio in the ideal cascade [see Eqn. (17)]. Thus condition (68) may be called the optimum condition for chromatographic separation. From it and from the fundamental equation of the ideal cascade, it follows directly that under optimum conditions

$$\tilde{\alpha} = \beta \ . \qquad (69)$$

On substituting the values of $\tilde{\alpha}$ and β from Eqns. (15) and (46) in Eqn. (69) and using Eqn. (35), it is easy to show that condition (69) corresponds to the equality $u = v$. Consequently, judging from Eqns. (5) and (17), the equality

$$\frac{\varkappa_1}{\varkappa}\sqrt{k_2 k_1} = k'_{\mathrm{av}} = 1 \ , \qquad (70)$$

also constitutes a condition identical with the optimum condition.

It is remarkable that the limiting value of k', determined[24] from the condition for the minimum duration of analysis and corresponding to the complete absence of resistance to mass transfer in the stationery phase, is about 0.9, which is close to unity.

III. THE RELATIVE CONCENTRATION PARTITION LAW IN THE CHROMATOGRAPHIC CONCENTRATION OF ISOTOPES

Spedding et al.[1] succeeded for the first time in showing experimentally that, by observing the conditions[26] for the sharpening of the fronts of the chromatographic zone of a binary isotope mixture, it is possible to transfer the zone across a length of the sorbent bed exceeding by a factor of 50–100 the intrinsic length of the zone without the slightest spreading. An analogous result can evidently be arrived at with the aid of the thermal factor in chromatography[3,4]; the chromatographic enrichment method then becomes more economical[4], since the consumption of expensive chemical reagents is replaced by the consumption of low-potential heat.

Fig. 4 shows the stationary chromatographic zone of a binary isotope mixture moving down the bed of a stationary sorbent. In a system of coordinates linked to the zone, there exists[12,13] a countercurrent of the sorbent and the

solution and the flux of the mixture with the sorbent is equal to the flux of the mixture with the solution:

$$L' = \varkappa_1 v a_0 = \varkappa_2 c_0 \qquad (71)$$

and

$$\frac{a_1}{a_2} = \text{const} \cdot \frac{c_1}{c_2} \ . \qquad (72)$$

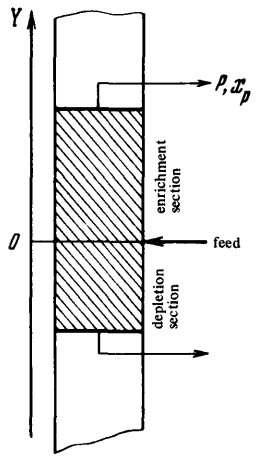


Figure 4. A stationary chromatographic zone.

The latter equation is valid when the sorbent is in thermodynamic equilibrium with the solution. Using Eqn. (71), one can also write[12,13]

$$\text{div}\, I = \frac{\partial x'}{\partial s} - \frac{\partial x''}{\partial s} - \frac{D_{\text{eff}}}{u} \frac{\partial^2 x'}{\partial s^2} \ . \qquad (73)$$

At the instant of attainment of equilibrium div $I = 0$ and

$$\Delta x = x' - x'' = \frac{D_{\text{eff}}}{u} \cdot \frac{\partial x'}{\partial s} \ , \qquad (74)$$

i.e. a concentration gradient is established in the zone such that the reverse diffusion flux will fully balance the entire flux of the first (extracted) component.

For substances with similar physicochemical characteristics ($\alpha - 1 \ll 1$), Eqn. (14) may be approximated[18] in the following way:

$$\Delta x = (\alpha - 1)\, x'\,(1 - x') \ . \qquad (75)$$

On substituting Eqn. (75) in Eqn. (74), we obtain after integration

$$\xi_l = \xi_0 e^{lu/D_{\text{eff}}(\alpha-1)} \ . \qquad (76)$$

Hence, according to Eqn. (50)

$$N_{\min} = \frac{\ln q_0}{\alpha - 1} \ . \qquad (77)$$

The resulting expression is the familiar Fenske equation[10] for the calculation of the number of theoretical separation stages in a rectangular cascade with total phase reversal. We may note that, for the chromatographic column under consideration, this equation could be formulated immediately, since Eqns. (71) and (72) in no way differ from the familiar equations[10] for mass transfer in a column with total phase reversal.

In the presence of take off[13] the expression for the flux of the first component through a cross-section in the enrichment section of the zone must be written in the following way:

$$I = L' \left[(\alpha - 1)\, x'\,(1 - x') - \frac{D_{\text{eff}}}{u} \frac{dx'}{ds} \right] + Px' \ , \qquad (78)$$

where P is the take-off flux. At equilibrium a concentration gradient is established in the zone such that the reverse diffusion flux will balance the entire flux of the first component with the exception of the take-off flux:

$$L' \left[(\alpha - 1)\, x'\,(1 - x') - \frac{D_{\text{eff}}}{u} \cdot \frac{dx'}{ds} \right] + Px' = Px_p \ ,$$
$$\frac{dx'}{ds} = \frac{u}{D_{\text{eff}}} (\alpha - 1)\, x'\,(1 - x') - \frac{u}{D_{\text{eff}}} \frac{P}{L'} (x_p - x') \ . \qquad (79)$$

Using Eqn. (50), it is easy to find that

$$\frac{dx'}{dN} = (\alpha - 1)\, x'\,(1 - x') - \frac{P}{L'} (x_p - x') \ , \qquad (80)$$

i.e. the familiar mass-exchange equation[10] widely employed in the theory of isotope separation.

From the general theory of separation, it is known that[10] Eqn. (80) describes also the cascade in which the flux L' is a continuous function of the number of the stage with a maximum at the feed point. The overall flux is then

$$\Sigma L' = \int L'\, dN = \int L'\, dx' \frac{dN}{dx'} = \int \frac{dx'}{\frac{1}{L'} \cdot \frac{dx'}{dN}} \ . \qquad (81)$$

In the ideal cascade the overall flux is a minimum[10,18,19]. According to Eqn. (81), the overall flux is a minimum when the integrand $x'(dN/dx')$ is a minimum for all x', i.e. when the reciprocal is a maximum:

$$\frac{1}{L'} \frac{dx'}{dN} = \frac{(\alpha - 1)\, x'\,(1 - x')}{L'} - \frac{P}{L'} \ . \qquad (82)$$

From the condition for the maximum, i.e. by differentiating Eqn. (82) with respect to L' and putting $(\partial/\partial L')[(1/L')(\partial x'/\partial N)] = 0$, one can find[10]

$$L'_{\text{id}} = \frac{2P}{\alpha - 1} \cdot \frac{x_p - x'}{x'\,(1 - x')} \ . \qquad (83)$$

On substituting Eqn. (83) in Eqn. (80) and integrating, we obtain Eqn. (29).

The expression for the flux at any stage in the cascade for any value of the separation factor has been obtained by the method of finite differences[27,28].

IV. NEW METHODS OF GAS CHROMATOGRAPHIC SEPARATION

Adsorption may be regarded[29] as a result of the attraction of gas molecules to adsorbent molecules. In consequence of this attraction, a potential force field is established above the adsorbent. If this field is regarded as constant at a certain distance h, then

$$a = ShC_0 e^{-\Delta v/kT} \ , \qquad (84)$$

where Δv is the difference between the energy of the molecule near the adsorbent and in the gas phase and S is the surface area of the adsorbent.

We may note that an equation analogous to Eqn. (84) describes[29] also the distribution of molecules in the gravitational force field. In this connection a new method of gas-chromatographic separation of heavy element isotopes in the artificial gravitational field of a gas centrifuge (gas–gas chromatography) has been proposed recently[30]; it differs from the familiar method (in a countercurrent gas centrifuge[10]) to the same extent that gas–liquid chromatography differs from distillation.

The centrifuge[30] is a cylinder *1* rotating at a high angular velocity (Fig. 5). The internal wall of the cylinder is a porous partition *2* firmly bound to the cylinder. The partition has narrow channels, positioned at right angles to the axis of the apparatus, in which the molecules of the components separated can pass freely. Along the axis of the centrifuge, the carrier gas moves in a continuous stream. The channels in the partition are then also filled by the carrier gas and play a role analogous to that of adsorption centres in gas-adsorption chromatography. When the apparatus rotates, a gravitational field identical with the field of sorption forces is established.

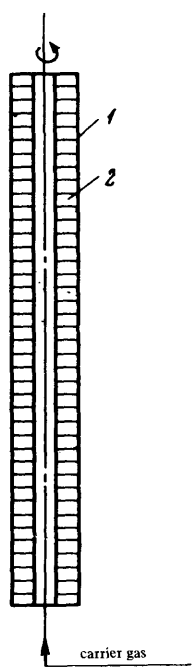


Figure 5. Gas centrifuge: *1*) cylinder; *2*) porous partition.

When a sample of the mixture to be separated is introduced into the stream of the carrier gas, zones corresponding to individual components may be obtained at the outlet from the apparatus by virtue of the repeated partitioning of the molecules of these components between the moving gas phase and the stationary phase and also by virtue of the difference in the partition of the components caused by the difference between their molecular weights Δm. In this case the separation factor is defined by the following equation[10]:

$$\alpha = e^{\Delta m\, \omega^2 \cdot \Delta r / kT}, \qquad (85)$$

where ω is the angular velocity of the gas centrifuge and r is the radius.

Large separation factors can be obtained only at relatively high angular velocities and correspondingly high rates of rotation (above 60 000 rev min^{-1}). Thus in the separation of uranium isotopes[10] in a countercurrent centrifuge with $\Delta r = 6$ cm for $\Delta m = 3$ g $mole^{-1}$, $k = 8.315 \times 10^7$ erg $mole^{-1}$ and $T = 300°K$, we would have $\alpha = 1.085$. Calculation[31] for a mixture of UF_6 containing uranium isotopes, carried out on the assumption that the difference in absorbability is determined by the difference between the zero-point energies, gives $(\Gamma_2 - \Gamma_1)/(\Gamma_2 + \Gamma_1) = 10^{-5}$.

To obtain small amounts of the isotopes of light and intermediate elements, thermal diffusion columns[10]—the simplest laboratory apparatus for isotope separation—are now widely employed. However, separation on thermal diffusion columns (as in the case of fractional distillation) requires comparatively large amounts of the initial mixture. In this connection the chromatographic method in a thermogravitational field is also of interest[21]. The separation factor in the thermal diffusion of a binary mixture is determined[10] by an equation of the following form:

$$\alpha = 1 + \delta \frac{\Delta T}{\bar{T}}, \qquad (86)$$

where

$$\delta = \frac{105}{108} \cdot \frac{\Delta m}{2m} \cdot R_T = \delta_0 R_T \qquad (87)$$

and R_T is a correction coefficient taking into account the nature of the intermolecular forces.

When the gravitational field of the gas centrifuge is brought into coincidence with the thermal field, it is evidently possible to achieve a method of gas-chromatographic separation which in many cases is not inferior to chromatography in a sorption field.

The analogy may be drawn further by considering other known methods of separation in countercurrent columns[10]. As usual, the choice of the method[10] will determine the value of the separation factor, the thermodynamic efficiency (characterising the energy consumption), the nature of the apparatus, and finally the conditions of the analysis or the scale of the process. In this connection it is useful to recall that the concept of the ideal cascade developed here leads to the introduction in chromatography of concepts such as the work of separation, the separating power, and the separating potential[10,18,19,32–34]. By calculating the cost of all things consumed in the operation of the separating column per hour, it is possible to calculate the cost per unit separating power when a particular technological procedure is employed. Clearly the best technological procedure is one which ensures the minimum cost per unit separating power. The calculation of the cost of one kilogram-separating unit per hour[32] is analogous to a comparison of separating apparatus in terms of the efficiency in real technological processes.

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