

Aktivierungsenergie, wie dies auch experimentell gefunden wurde. Neben der Aktivierungsenergie kann jedoch auch die Aktivierungsentropie der Diffusion für die isotopen Moleküle unterschiedlich sein. Isotopie-Effekte isobarer Moleküle wurden auch bei Thermo-Diffusionsmessungen gefunden<sup>24</sup>. Eine vollständige theoretische Behandlung solcher Effekte, wie

sie kürzlich BIGEISEN<sup>25</sup> für Gleichgewichtseigenschaften (Dampfdrucke) durchgeführt hat, steht für Transportvorgänge noch aus.

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<sup>25</sup> J. BIGEISEN, J. Chim. Phys. **59**, 35 [1962].

## The Separative Power of Short Countercurrent Columns

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*Dedicated to Prof. Dr. W. GROTH on his sixtieth birthday*

For separating isotopes on a large scale, the separative power of a unit is its most important feature. For a countercurrent device it is commonly assumed that its separative power is a maximum throughout the column. A detailed treatment of the equation of a square cascade, which is formally equal to the column equation, shows that it depends on the way how the square cascade is operated. In most cases the column is operated as a closed unit, under which circumstances the separative power is reduced to 80% of its maximum value.

In most cases, the partial differential equation which describes the concentration field in a countercurrent column, like for example a mass diffusion column, can in the stationary state be transformed to an ordinary differential equation, giving the axial concentration gradient. This transformation is permitted, if the variation of the axial component of the concentration gradient in radial direction is small as compared to the variation of the other relevant parameters in radial direction.

For the most general case, the column equation for the stationary state has been derived by COHEN<sup>1</sup>.

$$P(N_p - N) = c_1 N(1 - N) - c_5 (dN/dz). \quad (1)$$

The molar concentration is denoted by  $N$ , the concentration at the top of the column by  $N_p$ . Of the column parameters, the productstream is given by  $P$ , while  $c_1$  and  $c_5$  are defined by:

$$c_1 = -2\pi \int_{r_1}^{r_2} 2\alpha dr \int_{r_1}^r \varrho w r' dr',$$

$$c_2 = 2\pi \int_{r_1}^{r_2} \varrho D r dr,$$

$$c_3 = 2\pi \int_{r_1}^{r_2} \frac{dr}{\varrho D r} \left( \int_{r_1}^r \varrho w r' dr' \right)^2, \quad (2)$$

$$c_5 = c_2 + c_3, \quad P = 2\pi \int_{r_1}^{r_2} \varrho w r dr.$$

The radial boundaries of the column are given by  $r_1$  and  $r_2$  respectively;  $\varrho$  is the density,  $D$  the binary diffusion coefficient, while  $w$  is the axial velocity in the column. The separation mechanism is without further specification given by  $2\alpha$ ,  $2\alpha$  being the dynamic equilibrium gradient of the logarithm of the abundance ratio  $R$ ;  $R = N/(1 - N)$ .

When the column equation is given in this way, it is formally equivalent to the equation of a square cascade. The connection between the parameters  $\varepsilon$  and  $G$  of a square cascade and the column parameters  $c_1$  and  $c_5$  is given by the equations

$$c_1 = \varepsilon G, \quad c_5 = G/2. \quad (3)$$

In contravention of the notation used by COHEN, we call  $G/2$  the interstage feed flow between two

<sup>1</sup> K. COHEN, Proceedings of the Symposium on Isotope Separation, North Holland Publ. Cy., Amsterdam 1958, S. 3.

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successive stages of the square cascade; the effective simple-process factor is denoted by  $\alpha_{el}$ , while  $\varepsilon = \alpha_{el} - 1$ .

As to the behaviour of a square cascade, or of a blocked-off or squared-off cascade, this problem has been treated by COHEN<sup>2</sup>. He also considers the case of a squared-off cascade, consisting of identical small square cascades, showing that the separative work done by this cascade is not diminished by the squaring-off; in other words, the separative power of a square sub-cascade per unit stage is given by

$$\delta U = \frac{c_1^2}{4 c_5} = \frac{G \varepsilon^2}{2} \quad (4)$$

which is equivalent to the separative power of the elements composing the square sub-cascade.

For a cascade composed of countercurrent columns, this means that the separative work, done by the cascade is equal to the separative power of 1 cm length of a column, multiplied by the total length of the columns; this under optimal operating conditions.

However, in the treatment of COHEN, it is supposed that the total flow of the square subcascade is fed into and drawn off the square subcascade. So the flow of the square subcascade is part of the total flow of the cascade. This operating condition is illustrated in Fig. 1 a. In some cases, countercurrent

columns are actually operated in this way. For example in the countercurrent centrifuges of BEAMS et al.<sup>3</sup> the countercurrent is fed into and drawn off the centrifuges at both ends, the difference between the two countercurrent flows giving the production rate of the centrifuge.

In most cases however, the countercurrent columns are operated quite differently. The countercurrent flow is short-circuited at both ends of the column; the feeding is done somewhere in the middle of the column, while product and waste are withdrawn at the opposite ends of the column.

A column of this type, as shown in Fig. 1 b, can be thought to consist of a rectifying part and a stripping part, added together at the feed point. For example the countercurrent centrifuge of GROTH<sup>4</sup> and the mass diffusion column of GVERDTSITELLI<sup>5</sup> are operated in this way.

The behaviour of the two types is quite different and the maximum separative power of the second type is decreased by 20% compared with the first type. Nevertheless, the advantages of an internal countercurrent are so obvious that it outweighs the loss of separative power.

### Column Type I

Although this type has been extensively treated in Chapter II of reference<sup>2</sup>, separative power and optimal operating conditions will be derived in slightly another way. Although mathematically less rigorous, the method followed leads to the same conclusions and provides physically a better understanding.

When the square subcascade or the countercurrent column is one out of  $n_s$  parallel identical units which compose stage  $s$  of the cascade, the product-stream per unit is  $P/n_s$ , where  $P$  is the total product-stream of the cascade. When no remixing occurs, the concentrations at top and bottom of the column are then the stage concentrations  $N_{s+1}$  and  $N_s$  respectively. The column equation for this case is given by

$$\frac{P}{n_s} (N_p - N) = c_1 N(1 - N) - c_5 \frac{dN}{dz}. \quad (5)$$

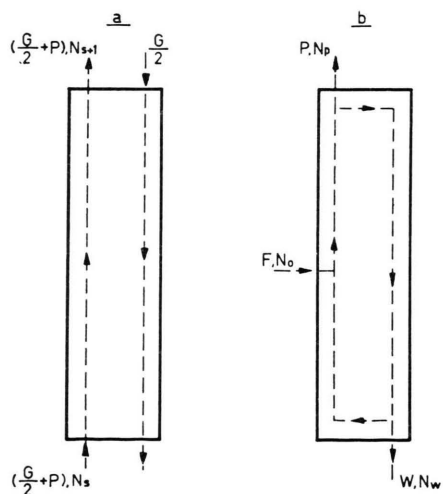


Fig. 1. Schematic drawing of the two column types.

<sup>2</sup> K. COHEN, *The Theory of Isotope Separation as Applied to the Large-Scale Production of U<sup>235</sup>*, McGraw-Hill Book Co., Inc., New York 1951.

<sup>3</sup> J. W. BEAMS, A. C. HEGG, and E. V. MURPHREE, TID-5230, U.S. Atomic Energy Commission [1951].

<sup>4</sup> W. GROTH u. K. H. WELGE, *Z. Phys. Chem.*, N.F. **19**, 1 [1959].

<sup>5</sup> L. G. GVERDTSITELLI, R. Y. KUCHEROV, and V. K. TSKHAKAYA, U.N. Peaceful Uses of Atomic Energy, Second International Conference [1958].

The internal column coordinate is  $z$ , where the total length of a column is  $L$ .

As is well known the solution of this equation gives an implicit relation between the production rate and the separation factor

$$\varepsilon l \Delta(\Phi_s) = \tanh^{-1} \frac{(N_{s+1} - N_s) \Delta(\Phi_s)}{(N_{s+1} - 2N_{s+1}N_s + N_s) - (2N_p - N_{s+1} - N_s) \Phi_s} \quad (6)$$

where  $\Phi_s = P/(n_s c_1)$ ,

$$\Delta(\Phi_s) = [1 + 2\Phi_s(1 - 2N_p) + \Phi_s^2]^{1/2}. \quad (7)$$

Because the argument of the arctanh is small, development to the argument can be broken off after the linear term. The resulting equation is very similar to the general cascade equation

$$\frac{dN_s}{ds} = \varepsilon l (N_{s+1} - 2N_{s+1}N_s + N_s) - \varepsilon l \Phi_s (2N_p - N_{s+1} - N_s).$$

When the column is sufficiently small as compared to the cascade as a whole that is when  $N_{s+1} \rightarrow N_s$ , for every stage, except the topstage, the above expression can be replaced by the cascade equation

$$dN/ds = 2\varepsilon l N(1 - N) - 2\varepsilon l \Phi(N_p - N). \quad (8)$$

This equation has been extensively treated<sup>2</sup> and conclusions will be drawn without further proof.

Maximum separative power is obtained when throughout the cascade the concentration gradient is half the gradient at total reflux

$$dN/ds = \varepsilon l N(1 - N). \quad (9)$$

For this case the separative power per stage is given by

$$(dU)_{\text{stage}} = \frac{n c_1^2}{4 c_5} l. \quad (10)$$

For the individual column this means that it has to be operated in such a way that the separation factor and separative power are

$$\frac{R(l)}{R(0)} = \frac{R_{s+1}}{R_s} = e^{\varepsilon l}, \quad \delta U = \frac{c_1^2}{4 c_5} l \quad (11), (12)$$

which is obtained for a production rate per column,

$$\frac{P}{n c_1} = \frac{N(1 - N)}{2(N_p - N)} \quad (13)$$

which production rate is clearly depending on the concentration and consequently on the place of the column in the cascade.

So every column has to be operated according to the square root law, while the columns have to

be arranged in such a way as to give maximum separative power per stage, in which case the separative power of the square subcascade or countercurrent column is a maximum.

Because the concentration of every stage in the cascade is determined by equation (11), substitution of these values in equation (6) then gives  $\Phi_s$  for a certain stage. Then from equation (7) the number of parallel columns is found.

As already mentioned, the conclusions we arrive at are the same as drawn from the more rigorous treatment of COHEN<sup>2</sup>. The above approximations remain valid for a separation factor per column of about 2.

## Column Type II

For the column, where the countercurrent is internally closed, the separative power will be less than for type I. This immediately follows from the column equation (1). At the top of the column, the concentration approaches  $N_p$  and the net material transport  $P(N_p - N)$  tends to zero. So the top of the column will contribute less to the separative power than under optimal conditions. The same applies for the bottom of the column.

With the internally closed countercurrent the column can be treated as the combination of a rectifying part, from feed point to top with length  $l_p$ , and a stripping part, from feed point to bottom with length  $l_w$ . The rectifying part is described by column equation (1), while the stripping part is described by the analogous equation for a stripper

$$-W(N_w - N) = c_1 N(1 - N) - c_5 (dN/dz) \quad (14)$$

the solution of which is easily found to be analogous to the solution for the rectifier.

So the equations which describe the behaviour of the column are

$$\varepsilon l_p \Delta_p(\Phi_p) = \tanh^{-1} \frac{(N_p - N_0) \Delta_p(\psi_p)}{(N_p - 2N_p N_0 + N_0) - (N_p - N_0) \psi_p} \quad (15)$$

$$\varepsilon l_w \Delta_w(\psi_w) = \tanh^{-1} \frac{(N_0 - N_w) \Delta_w(\psi_w)}{(N_0 - 2N_0 N_w + N_w) - (N_0 - N_w) \psi_w} \quad (16)$$

$$l_p + l_w = l, \quad (17)$$

$$(N_p - N_0) \psi_p = (N_0 - N_w) \psi_w, \quad (18)$$

$$R_p/R_0 = R_0/R_w = q \quad (19)$$

with  $\psi_p = P/c_1$ ,  $\psi_w = W/c_1$ ,

$$A_p(\psi_p) = [1 + 2(1 - 2N_p)\psi_p + \psi_p^2]^{1/2}, \quad (20)$$

$$A_w(\psi_w) = [1 - 2(1 - 2N_w)\psi_w + \psi_w^2]^{1/2}.$$

Equations (15) and (16) are the solutions of the column equations for the rectifying respectively stripping part of the column. The concentrations of feed, product and waste are respectively denoted by  $N_0$ ,  $N_p$  and  $N_w$ . Equation (17) states that the total length of the column is a constant, equal to  $l$ . The conservation of mass for one component is given by equation (18); use has already been made of the conservation of mass for the mixture, and it is assumed that  $c_1$  is a constant throughout the column. We restrict ourselves to symmetric operation, which condition is expressed by equation (19).

A further restriction is given by the assumption that the separation of the column is small, that is  $(q-1) \ll 1$ .

It then follows from equations (18) and (19) that

$$\frac{\psi_p}{\psi_w} = \frac{N_0 - N_w}{N_p - N_0} = \frac{1+q}{q+R_0} \frac{R_0+1}{R_0+q} \rightarrow 1,$$

while for the ratio  $N_p \psi_p$  over  $N_w \psi_w$

$$\frac{N_p \psi_p}{N_w \psi_w} = q = 1 + (q-1) \rightarrow 1.$$

So in first approximation we can put

$$\psi_p = \psi_w, \quad N_p \psi_p = N_w \psi_w.$$

The argument of the arctanh from equation (15) can be rewritten, using (19)

$$\frac{(N_p - N_0) A_p(\psi)}{(N_p - 2N_p N_0 + N_0) - (N_p - N_0) \psi} = \frac{\beta A_p(\psi)}{1 - \beta \psi}$$

where  $\beta$  equals  $\beta = (q-1)/(q+1)$ .

The same applies to equation (16).

Using the series development for the arctanh, equations (15) and (16) are transformed to

$$\varepsilon l_p = \frac{\beta}{1-\beta\psi} \left\{ 1 + \frac{1}{3} \frac{\beta^2 A_p^2(\psi)}{(1-\beta\psi)^2} + \dots \right\}, \quad (22)$$

$$\varepsilon l_w = \frac{\beta}{1-\beta\psi} \left\{ 1 + \frac{1}{3} \frac{\beta^2 A_w^2(\psi)}{(1-\beta\psi)^2} + \dots \right\}. \quad (23)$$

Summation gives the equation for the total column

$$\varepsilon l = \frac{\beta}{1-\beta\psi} \left\{ 2 + \frac{2}{3} \frac{\beta^2}{(1-\beta\psi)^2} (1+\psi^2) + \dots \right\}. \quad (24)$$

Taking only the linear part of the series would lead to a value of the argument of the arctanh which

tends to one, which is clearly not legitimate. A solution, found by iteration, taking into account the third power of  $\beta$  suffices.

$$\beta = \frac{\varepsilon l}{2 + \varepsilon l \psi + \frac{1}{3} \varepsilon^2 l^2 (1+\psi^2)} \approx \frac{\varepsilon l}{2 + \varepsilon l \psi + \frac{1}{3} \varepsilon^2 l^2 \psi^2}. \quad (25)$$

For the separative power of the column we use the expression for the symmetric element, which is developed to powers of  $\beta$ .

$$\delta U = G \frac{q-1}{q+1} \ln q = G \frac{q-1}{q+1} \cdot 2 \left( \frac{q-1}{q+1} + \dots \right) = 4 P \beta^2.$$

So the separative power of the column is given by

$$\delta U = 4 c_1 \frac{\varepsilon^2 l^2 \psi}{(2 + \varepsilon l \psi + \frac{1}{3} \varepsilon^2 l^2 \psi^2)^2} \quad (26)$$

which expression as a function of  $\psi$  has a maximum for

$$(\psi)_{\text{opt.}} = \frac{\sqrt{5}-1}{\varepsilon l} \quad (27)$$

with the corresponding value for  $\delta U$

$$(\delta U)_{\text{opt.}} = 4 c_1 \frac{\varepsilon l (\sqrt{5}-1)}{(2+2\sqrt{5})^2} = 0.81 \frac{c_1^2}{4 c_s} l. \quad (28)$$

The separation factor  $q$  follows from equation (25)

$$\alpha = \frac{1 + \varepsilon l / (2 + \varepsilon l \psi + \frac{1}{3} \varepsilon^2 l^2 \psi^2)}{1 - \varepsilon l / (2 + \varepsilon l \psi + \frac{1}{3} \varepsilon^2 l^2 \psi^2)} = \exp \left\{ \frac{2 \varepsilon l}{2 + \varepsilon l \psi + \frac{1}{3} \varepsilon^2 l^2 \psi^2} \right\} + \dots \quad (29)$$

For maximum separative power the separation factor becomes

$$(q)_{\text{opt.}} = \exp \left\{ 2 \varepsilon l / (2 + \frac{2}{3} \sqrt{5}) \right\} \quad (30)$$

which is more than the square root of  $q$  at total reflux.

Until now, the lengths of rectifier and stripper are still undefined. Subtraction of equation (23) from equation (22), and substitution of the optimal values of  $\beta$  and  $\psi$  gives

$$l_p - l_w = 0.15 (1 - 2N) \varepsilon l.$$

Given the small value of  $\varepsilon l$  this means that the feed point is in the middle of the column.

Concluding, we can say that a column with an internal countercurrent can only obtain 80% of the maximum separative power. In contradiction to type I the optimal operation conditions are not given by the square root law, the separation factor being greater than according to the square root law.

### Application

In the column parameters as given by (2) the flow function

$$Q(r) = 2\pi \int_{r_1}^r Q w r dr \quad (31)$$

depends as well on the strength as on the pattern of the flow. Therefore COHEN<sup>2</sup> introduces the quantity  $L$ ,

$$L = 2\pi \int_{r_1}^{r_2} Q w r dr$$

which is the flow up the column plus the flow down the column. The parameters  $c_1$  and  $c_3$  are then written in terms of  $L$ ;  $c_1 = a_1 L$ ,  $c_3 = a_3 L^2$ , where  $a_1$  and  $a_3$  are independent of  $L$ .

The ratio  $c_1/c_3$  is now a function of  $L$ ,

$$\frac{c_1}{c_3} = 2\varepsilon = \frac{a_1 L}{(c_2 + a_3 L^2)} \quad (32)$$

which function has a maximum with respect to  $L$ ,

$$2\varepsilon_0 = a_1/2 \sqrt{c_2 a_3} \quad (33)$$

with the corresponding value of  $L$ ,

$$L_0 = \sqrt{c_2/a_3}. \quad (34)$$

Measuring the strength in terms of  $L_0$ ,

$$m = L/L_0 \quad (35)$$

we find the following substitutions

$$c_1 = m P_0, \quad 2\varepsilon = \frac{2m}{1+m^2} 2\varepsilon_0, \quad \psi = \frac{P}{m P_0}$$

with  $P_0 = a_1 L_0 = 4\varepsilon_0 c_2$ . (36)

Separation factor and separative power for a column with an internal countercurrent, operated symmetrically now follow from (29) respectively (26).

$$q = \exp \left\{ \frac{2m}{1+m^2} 2\varepsilon_0 l \left/ \left[ 2 + \frac{2\varepsilon_0 l}{1+m^2} \frac{P}{P_0} + \frac{1}{6} \left( \frac{2\varepsilon_0 l}{1+m^2} \frac{P}{P_0} \right)^2 \right] \right\} \quad (37)$$

$$\delta U = 16\varepsilon_0 c_2 \left( \frac{2\varepsilon_0 l}{1+m^2} m \right)^2 \frac{P}{P_0} \cdot \left[ 2 + \frac{2\varepsilon_0 l}{1+m^2} \frac{P}{P_0} + \frac{1}{6} \left( \frac{2\varepsilon_0 l}{1+m^2} \frac{P}{P_0} \right)^2 \right]^{-2}. \quad (38)$$

From equations (27) and (28) it can be deduced that for a value of

$$\frac{P}{P_0} = \frac{\sqrt{5}-1}{2\varepsilon_0 l} (1+m^2) \quad (39)$$

the separative power with respect to the product stream is a maximum

$$(\delta U)_{\text{opt.}} = 0.81 \frac{m^2}{1+m^2} 4\varepsilon_0^2 c_2 l. \quad (40)$$

The corresponding value for  $q$  follows from (30)

$$(q)_{\text{opt.}} = \exp \left\{ \frac{2m}{1+m^2} 2\varepsilon_0 l \left/ \left[ 2 + \frac{2}{3} \sqrt{5} \right] \right\}. \quad (41)$$

Considering the optimal separative power (40) of a type II column, operated symmetrically, the term  $m^2/(1+m^2)$  is the well known factor for the flow strength which tends to one for  $m$  going to infinity. The factor  $4\varepsilon_0^2 c_2$ , which by virtue of (33) also can be written as  $c_1^2/4 c_3$  is only a function of the shape, and of the separative mechanism.

$$\frac{c_1^2}{4 c_3} = \left[ \int_{r_1}^{r_2} \alpha(r) Q(r) dr \right]^2 / \int_{r_1}^{r_2} \frac{Q^2(r)}{2\pi Q D r} dr. \quad (42)$$

For a given separation process, that is for a given  $\alpha(r)$ , this function can be maximized with respect to  $Q(r)$ . We could express the separative power in terms of this maximum, by introducing the shape factor  $\gamma$ , which is the ratio of the actual value of  $c_1^2/4 c_3$  to its maximum value. Then

$$(\delta U)_{\text{opt.}} = 0.81 \frac{m^2}{1+m^2} \gamma (\delta U)_{\text{max.}} \quad (43)$$

Apart from maximizing  $c_1^2/4 c_3$  the maximum separative power can be found along other lines, as was shown by DIRAC<sup>2</sup>.

At last the factor 0.81 is given by the symmetric stripper-rectifier combination of the column.

### Conclusions

Although it is mainly assumed that in a countercurrent separating element the separative power can be made a maximum throughout the column, in most practical circumstances this is not the case. It only applies to those columns for which the countercurrent is part of the total circulation of the cascade. When however the countercurrent is internally closed, the separative power is reduced to about 80% of its optimal value. The reason for this is that the net material transport  $P(N_p - N)$  is varying along the length of the column, from  $P(N_p - N_0)$  at the feed point, to zero at both ends of the column.

For maximum separative power this net material transport should be equal to  $c_1/2 \cdot N(1-N)$ . Although on the average this condition is approximately fulfilled, the aberrations lead to a loss of separative power which counts to about 20%.

Whenever the separation process is given, for example mass diffusion or countercurrent centrifuge, the formula (37) till (41) can be applied in order to obtain separative power and separation factor of the column.