LONGITUDINAL DIFFUSION AND RESISTANCE TO MASS TRANSFER AS CAUSES OF NONIDEALITY IN CHROMATOGRAPHY

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Abstract—The mechanisms of band broadening in linear, nonideal chromatography are examined. A development is presented of a rate theory for this process, wherein nonideality is caused by axial molecular diffusion; axial eddy diffusion; finiteness of transfer coefficient. The correspondence with the plate theory is given, so that the results can also be expressed in heights equivalent to a theoretical plate.

The plate theory has been extended to the case of a finite volume of feed; the requirement for this feed volume to be negligible has been examined and a method is presented for evaluating concentration profiles obtained with a larger volume of feed.

An analysis is given of experimental results, whereby the relative contributions to band broadening for various cooperating mechanisms could be ascertained.

Résumé—Une étude a été faite des mécanismes de l’élargissement des bandes dans la chromatographie linéaire non-ideale. On a développé une théorie sur la vitesse de ce processus, selon laquelle la non-idéalité est causée par: la diffusion moléculaire axiale; la diffusion turbulente axiale; le fait que le coefficient de transfert a une valeur finie. La correspondance établie entre cette théorie et celle des plateaux permet d’exprimer les résultats obtenus aussi en termes de la hauteur de colonne équivalente à un étage théorique.

La théorie des plateaux a été rendue applicable sur le cas d’un échantillon de volume fini; les conditions dans lesquelles le volume de cet échantillon est négligeable ont été étudiées et on présente une méthode pour interpréter les profils de concentration obtenus avec des échantillons plus grands.

Une analyse des résultats expérimentaux a permis de déterminer les contributions relatives des différents mécanismes en question à l’élargissement des bandes.

1. INTRODUCTION

For the design of efficient chromatographic columns it is desirable to have a background of theory, in order to know how various factors influence the sharpness of separation.

In the theories of chromatography simplifying assumptions are introduced in order to make the basic differential equations accessible to mathematical treatment. As the nature of the assumption depends on the type of chromatography adopted, a survey of the possible assumptions should first be made. These are:

1. The equilibrium concentrations in the two phases are proportional ("linear chromatography").
2. The exchange process is thermodynamically reversible, i.e. the equilibrium between particle and fluid is immediate—the mass transfer coefficient is infinitely high—and longitudinal diffusion and other processes having a similar effect can be ignored. Such a process is commonly called "ideal chromatography".

By making these assumptions or not in the two cases, respectively, one arrives at the following four possibilities:

<table>
<thead>
<tr>
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<th>Ideal</th>
<th>Nonideal</th>
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<tbody>
<tr>
<td>Linear isotherm</td>
<td>I</td>
<td>III</td>
</tr>
<tr>
<td>Nonlinear isotherm</td>
<td>II</td>
<td>IV</td>
</tr>
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Case I covers the simplest theory still possessing the essential features of chromatography. The retardation of solute with regard to solvent depends on the product of the distribution (partition) coefficient between the phases and the ratio of the amounts of those phases present in the column, but not on concentrations. The shape of a band, during its movement, thus remains unchanged. Furthermore, different solutes behave independently [1].

If a band of mixed solutes is introduced in a column, it is a matter of simple arithmetic to find the requirement for the individual bands to become separated; this point need not be gone into further.


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Case II is of particular importance for adsorption chromatography in liquids where the effect of nonlinearity of the isotherm can usually not be neglected, and where it may be assumed, on the other hand, that mass transfer is sufficiently fast because of the small size of the adsorbent particles, and that, in spite of the low linear velocity of the fluid, axial diffusion is still relatively unimportant. The first author to provide an adequate treatment of the single-solute case was De Vault [2].

The bands change during their passage through the column and usually develop a sharp front and a long tail.

A special complication is introduced by the fact that the solutes may affect each other's movement, so that the case of two or more solutes usually cannot be derived by superposition of single-solute cases. Strictly speaking, it is not even accessible to rigorous treatment [3–5].

Case III is of particular importance for partition chromatography with a moving liquid or gas. Here the assumption of the linear isotherm is usually a good approximation.

Case IV, the most general case, is probably required for adsorption chromatography of gaseous mixtures. Furthermore, certain kinetic theories mentioned by Klinkenberg and Sjenitzer [6] covering adsorption and ion exchange, belong in this category. In these cases, the mathematics become very involved.

In this paper a discussion will be presented of class III of the chromatographic theories. There are two basically different approaches, known from many other transfer processes. In the plate theory, the column is conceived as consisting of a number of stages or plates in each of which there is equilibrium between the two phases. The second approach, which may be called the "rate theory", considers the actual continuous column. Diffusional phenomena, etc., are taken into account for describing the unsharpness of a band.

The plate theory

In the plate theory [7, 8] starting from the assumption of a linear distribution isotherm, the separating efficiency of a chromatographic column is characterized by the height equivalent to a theoretical plate (HETP). This HETP is an empirical quantity and the theory does not deal with the mechanisms which determine it. It is, however, of much practical value for calculating the effects of the column length and the method of feeding the column on the separation obtained. The HETP depends on the flow rate and on the nature of the substances treated just as it does in the packed columns employed in other transfer processes.

The rate theory

The rate theory in principle provides all information on the influence of kinetic phenomena such as rate of mass transfer between phases, rate of adsorption or chemical reaction, longitudinal diffusion and flow behaviour on the history of a band in the column.

Here, the basic difficulty lies in arriving at an adequate physical concept of the phenomena determining the movement of a solute in and around the particles. This is where various authors differ in their way of treatment. Such a concept is of necessity an idealization, and its acceptibility will have to be checked experimentally.

One method of treatment, analogous to well-known work on heat transfer (see review by Klinkenberg [9]) introduces solely a transfer coefficient (e.g. Ketelle and Boyd [10]). It is, however, easy to see that this method lacks detailed physical background, since the usual conditions for the film concept or two-film concept do not apply.

Ketelle and Boyd [10] and Boyd et al. [11] have interpreted this coefficient by a diffusional mechanism through a liquid film.

Band broadening by a finite mass transfer coefficient has been combined with band broadening by axial diffusion in the treatment of Lapidus and Amundson [12].

The use of an empirical mass transfer coefficient has been avoided by Tunitskii [13], who took eddy diffusion and intraparticle diffusion into consideration, and by Glueckauf [8] who related the HETP to particle size, particle diffusion and diffusion through the film surrounding the particles. Glueckauf also showed how his theory may be used to explain many experimental effects in ion-exchange chromatography.

The present paper may be seen as an extension of the work of Glueckauf and partly as an alternative, namely in so far as the relation between HETP and contributing mechanisms is observed.

It also uses the Amundson and Lapidus approach, but with a considerable simplification. It will namely be shown that under certain conditions, which are of practical importance, the Amundson and Lapidus formulae may be simplified to a Gaussian distribution function which is directly comparable with a corresponding formula of the plate theory. A combination of these two lines of thought leads to a simple relation between the HETP and various parameters of the rate theory. The result will be applied to two examples, namely to the ion-exclusion experiments of Simpson and Wheaton [14] and to results for gas-liquid-partition chromatography obtained by Keulemans [15].

Reference is also made to the publication by Klinkenberg and Sjenitzer [6] the subject of which is the distribution of retention times in flow systems, particularly of the Gaussian type.

2. THE THEORY OF THE PLATE COLUMN

Derivation

In its most simple form the plate theory has been developed and applied by Martin and Synge [7]. In this section the plate theory will be extended
As may easily be verified, the solution of eqs (6)-(8) for all stages including the first is

$$y_n = \int_0^w e^{-w'} \frac{(n-1)! w'^{n-1}}{(n-1)!} dw' \text{ for } 0 \leq w \leq \frac{A}{v},$$

$$y_n = \int_{w-A}^w e^{-w'} \frac{(n-1)! w'^{n-1}}{(n-1)!} dw' \text{ for } w > \frac{A}{v},$$

or

$$c_{l,n} = c_0 \int_0^S \frac{1}{v} e^{-S'/v} \left( \frac{S'}{v} \right)^{n-1} dS'$$

for $0 \leq S \leq A$

$$c_{l,n} = c_0 \int_{S-A}^S \frac{1}{v} e^{-S'/v} \left( \frac{S'}{v} \right)^{n-1} dS'$$

for $S > A$.

These formulae are sufficient for calculating the position and shape of a moving band. In the following, formula (12) in particular will be considered more closely, since it represents the situation at the end of the column.

The integrand of eq. (12) is the Poisson distribution function. This function may be approximated by a Gaussian distribution function if the argument $S'/v$ is large (say $S'/v > 100$). This will always be the case when the number of plates is not too small and the band has arrived at the end of the column:

$$\frac{1}{n!} e^{-S'/v} \left( \frac{S'}{v} \right)^n \approx \frac{1}{\sqrt{2\pi nS'/v}} \exp \left\{ -\frac{(S'/v - n)^2}{2S'/v} \right\}. (13)$$

With sufficiently large values of $S'/v$ no serious error is introduced by replacing the Gaussian distribution (13) by

$$\frac{1}{\sqrt{2\pi n}} \exp \left\{ -\frac{(S'/v - n)^2}{2n} \right\}. (14)$$

With eq. (14) and by putting $n - 1 \approx n$, eq. (12) becomes

$$c_{l,n} = \frac{c_0}{v} \sqrt{2\pi nS-A} \int_{S-A}^S \exp \left\{ -\frac{(S'/v - n)^2}{2n} \right\} - dS'. (15)$$

The elution curve of the band according to eq. (15) is indicated in Fig. 2. The concentration is a maximum for

$$S = S_{\text{max}} = nv + \frac{1}{2} A. (16)$$

According to the law of conservation of mass, the area under the elution curve is equal to the feed volume $A$. For small feed volumes ($A \ll S$) the band obtains a Gaussian shape:

$$c_{l,n} = \frac{Ac_0}{v} \sqrt{2\pi n} \exp \left\{ -\frac{(S'/v - n)^2}{2n} \right\}. (17)$$

As will now be shown the condition $A \ll S$ may be brought into a quantitative form.
We found it convenient to define the width $\Delta S$ of the elution curve as the distance between the points of intersection of the tangents in the inflection points with the horizontal axis (Fig. 2). For the Gaussian curve this value of $\Delta S$ is just equal to 4 times the standard deviation.

In order to relate width and height of the elution curve to the number of plates it is convenient to introduce the dimensionless quantities

$$S = \frac{S}{v\sqrt{n}} \quad \text{and} \quad a = \frac{A}{v\sqrt{n}}.$$  \hspace{1cm} \begin{equation} \tag{18} \end{equation}

Expression (15) then becomes

$$\frac{c_{1,n}}{c_0} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-((1/2)(a' - \sqrt{n})^2)} \, da'. \hspace{1cm} \begin{equation} \tag{19} \end{equation}$$

A straightforward calculation shows that

$$\left(\frac{c_{1,n}}{c_0}\right)_{\text{max}} = \text{erf}\left(-\frac{a}{2\sqrt{2}}\right). \hspace{1cm} \begin{equation} \tag{20} \end{equation}$$

and

$$\Delta s = a + 2\delta + \sqrt{2\pi} \frac{a + \delta}{\delta} e^{(1/2)\delta^2} \times \left( \text{erf}\left(\frac{a + \delta}{\sqrt{2}}\right) - \text{erf}\left(\frac{\delta}{\sqrt{2}}\right) \right) \hspace{1cm} \begin{equation} \tag{21} \end{equation}$$

where $\delta$ is given by

$$\delta e^{-(1/2)\delta^2} = (a + \delta) e^{-(1/2)(a + \delta)^2}. \hspace{1cm} \begin{equation} \tag{22} \end{equation}$$

It is seen that height $(c_{1,n}/c_0)_{\text{max}}$ and width $\Delta S = \Delta S/v\sqrt{n}$ are only dependent on the parameter $a = A/v\sqrt{n}$. These relations are graphically represented in Figs 3 and 4.

Figure 4 shows that for $a = A/v\sqrt{n} < 0.5$ \hspace{1cm} \begin{equation} \tag{23} \end{equation} the width $\Delta S$ becomes almost independent of the feed volume. If in this case we denote the width as $\Delta S_0$, we have

$$\Delta S_0 = 4v\sqrt{n}. \hspace{1cm} \begin{equation} \tag{24} \end{equation}$$

This result means that the elution curve is Gaussian. It may further be derived from eqs (21) and (22) that

$$\Delta S = A + v\sqrt{2\pi n} \quad \text{for} \quad \frac{A}{v\sqrt{n}} > 3. \hspace{1cm} \begin{equation} \tag{25} \end{equation}$$

Another interesting characteristic of the elution curve may be derived from the above equations. Let the retention volume, $S_r$, be defined as the volume of mobile phase that has flowed through the column from the instant the feed is stopped until the moment the solute appears in the effluent. The value of $S_r$ at
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Fig. 4. Width of elution curve.

which all the solute is just stripped from the column is then called the final retention volume, $S_f$ (see Fig. 2).

According to this definition

$$ S_f = n\nu - \frac{1}{2} A + \frac{1}{2} \Delta S. $$

If we substitute $\Delta S$ by using eqs (24) and (25) it then follows for $a > 3$ that

$$ S_f = n\nu + 0.31 \Delta S_0. \quad (26) $$

Since $\Delta S_0$ is constant, eq. (26) shows that the final retention volume is independent of the feed volume. The final retention volume and $\Delta S_0$ being easily obtainable experimentally, eq. (26) is very useful for calculating the total stage volume $n\nu$. The subsequent calculation of the number of plates from the width and height of the elution curve is then most easily performed with the aid of Figs 3 and 4.

Number of plates needed for chromatographic separations

The chromatographic technique is generally used for separation of two or more solutes. Therefore, the question arises how large the minimum number of plates is for obtaining such a separation. Obviously, the degree of separation depends on the overlap of the elution curves of the solutes emerging successively from the column. Since this overlap decreases if the elution curves of the solutes become narrower, it immediately follows that for a given degree of separation the minimum plate number is obtained when small feed volumes ($a < 0.5$) are used. In order to obtain a quantitative expression for the minimum plate number the degree of actual separation that results has to be defined. A general solution to this problem has been offered by Glueckauf [16]. However, a simple case is obtained when the tangents of the elution curves of the subsequent solutes just touch at the base of the chromatogram. With $v_1$ and $v_2$ being the effective plate volumes of solutes 1 and 2, the distance between the maxima of the bands is

$$ n_{\text{min}} = 4 \left( \frac{\eta + 1}{\eta - 1} \right)^2 \quad (27) $$

when

$$ \eta = \frac{v_2}{v_1} \approx \frac{k_1}{k_2}. \quad (28) $$

$\eta$ is the ratio of the distribution coefficients; in vapour-liquid operations it is called the relative volatility of the solutes. Equation (26) is valid only for the specified degree of separation. A calculation shows that, for the case of an equimolar mixture of solutes, the purity of the eluted material is about 97.7% if a separation is effected at the minimum between the two concentration peaks.

It is interesting to compare the minimum plate number needed for chromatographic separations with the minimum of plates needed in a countercurrent process; for instance, batch distillation. Figure 5 shows this comparison for the separation of equimolar mixtures; the plate numbers required are plotted as a function of the value of $\eta$. It is seen that in chromatography much higher plate numbers are required than in distillation, especially at low values of $\eta$. This undoubtedly is caused by the fact that in
Application to gas-liquid partition chromatography

The predictions of the effect of feed volume on the width and height of the elution curve have been checked experimentally. Use was made of a chromato-

graphic column 1.80 m long and 6 mm in diameter. It was packed with 50–200 mesh (particle diameter ~ 75–300 μm) ground Sterchamol brick (furnace ins-

ulation brick), impregnated with a lubricating oil fraction in a weight ratio (oil to carrier) of 0.25. Elu-

tion curves were measured for different concentra-

tions of n butane as the feed gas and at varying total amounts of feed gas; nitrogen was used as the carrier gas. The experiments were performed at 0°C and

760 mm exit pressure; the pressure drop over the column at the gas rates applied was 52 mm Hg. The data obtained are given in Table 1.

As predicted it is found that the final retention volume \( V_{f} \) is fairly constant. Extrapolation of the \( A \) values to zero feed volume gives \( A_{S_{0}} = \sim 165 \text{ ml} \). Table 1. Experimental data on width and height of elution curve for gas-liquid partition chromatography

<table>
<thead>
<tr>
<th>( A ) (ml)</th>
<th>% n-butane in feed</th>
<th>( A ) (ml)</th>
<th>( S_{f} ) (ml)</th>
<th>( \left( \frac{H_{e}}{C_{f_{max}}} \right) )</th>
<th>exp.</th>
<th>calc.¹</th>
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</thead>
<tbody>
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<td>32</td>
<td>1.0</td>
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<td>1100</td>
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<td>0.53</td>
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</tbody>
</table>

¹ Calculated for \( n = 650 \).

Accordingly, \( m_{o} = \sim 1055 \text{ ml} \). Using eq. (24), \( n \) is calculated as 650. With this value the width and max-

imum height of the elution curve can be calculated for the case where large feed volumes are used. Compari-

son of calculated and experimental maximum heights in Table 1 shows a satisfactory agreement. Figure

6 shows the comparison for the width of the elution curve. The feed volumes in this figure have been plot-

ted as the total amounts of solute feed, i.e. \( n \) butane. For the cases of 1.0, 3.0 and 4.5% of \( n \) butane the agreement between theory and experiment is excel-

lent¹. For pure \( n \) butane feed the agreement is not so good; strictly speaking the theory cannot be applied in this case, however, since the volume of the moving

and immobile phases will not have been constant.

Figure 6 shows that for obtaining sharp separations (narrow elution bands), the solutes should be intro-

duced into the column in as concentrated a form as possible. This is easily understood, since only in that case is a negligibly small fraction of the column length used for absorbing the solute, the major part of the column being available for the resolution process.

3. THE THEORY OF THE CONTINUOUS COLUMN

General theory

The mathematics for the continuous column, assu-

miming a linear adsorption or absorption equilibrium

isotherm and uniform fluid velocity over each cross-

section, has been given by Lapidus and Amundson

[12]. In this theory longitudinal diffusion has also been taken into account. It may be remarked here that

this longitudinal diffusion may partly be of an eddy

¹The curves in Fig. 6 would coincide if the actual volume of diluted feed gas instead of the \( n \) butane had been plotted along the abscissa.
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Fig. 7. Material balance in continuous column.

character, i.e. irregularities in flow caused by the packing, which are small compared with the size of the band and which are statistically distributed over the column, may be incorporated in the longitudinal diffusion coefficient.

As before, we shall consider the case of partition chromatography with a linear partition isotherm. The material balances per unit cross-sectional area (see also Fig. 7) are

\[ F_1 \frac{\partial c_1}{\partial t} = F_1 D \frac{\partial^2 c_1}{\partial z^2} - F_1 u \frac{\partial c_1}{\partial z} + \alpha (K c_n - c_1) \]  
\[ F_1 u \frac{\partial c_n}{\partial t} = \alpha (c_1 - K c_n). \]  

The solution of these equations, corresponding to the introduction of a concentration pulse \( c_0 \) of sufficiently short duration \( t_0 \), may be derived from the general solution of Lapidus and Amundson. It reads

\[ \frac{c_1}{c_0} = \frac{2 t_0}{2 \sqrt{\pi D t}} \exp \left[ - \frac{(z - u t)^2}{4 D t} \right] \]
\[ + \int_{t_0}^{t} \frac{2 t_0}{2 \sqrt{\pi D t_0}} e^{-\left(z-u(t-t')\right)^2/4D t'} F(t') \, dt' \]  

where

\[ F(t') = \left[ \frac{\sigma^2 K t'}{F_1 F_n(t-t')} \right]^{1/2} \exp \left[ - \frac{a K}{F_n} (t - t') - \frac{a t'}{F_1} \right] \]
\[ \times \left\{ 2 \sqrt{\frac{\sigma^2 K t'}{F_1 F_n(t-t')}} \right\}. \]  

Formulae (31) and (32) may be simplified if the column contains a large number of mixing stages and transfer units. The number of mixing stages for longitudinal diffusion may be defined as that number of ideal continuous mixers in series which yields the same response to a disturbance in concentration as the given length of a column with longitudinal diffusion. From the comparison by Klinkenberg and Sjenitzer [6], it is seen that the number of mixing stages in a column of height \( l \) is \( l u / 2D \). The height of a mixing stage equals \( \frac{2D}{u} \). The number of transfer units, or rather the height of a transfer unit, is used to characterize the effectiveness of mass transfer between two phases. For our case the latter may be defined as \( F_1 u / \alpha \) (compare [6]).

Now it is shown in the Appendix that for locations \( z \) much larger than both \( 2D / u \) and \( F_1 u / \alpha \) the eqs (31) and (32) reduce to a Gaussian function

\[ \frac{c_1}{c_0} = \frac{\beta t_0}{\sqrt{2\pi (\sigma_1^2 + \sigma_2^2)}} \exp \left[ - \frac{(z/u - \beta t)^2}{2(\sigma_1^2 + \sigma_2^2)} \right] \]  

with

\[ \frac{1}{\beta} = 1 + \frac{F_1 u}{\alpha} \quad \sigma_1^2 = \frac{2Dz}{u}, \quad \sigma_2^2 = \frac{2\beta^2 - F_1^2 z}{F_1 K^2 u}. \]  

Since, as already said, \( D \) may depend upon the flow characteristics of the bed, it is not easy to decide to what extent the band broadening is caused by longitudinal diffusion on the one hand and by mass transfer on the other hand. This point will be considered in more detail later.

The comparison of the Gaussian distribution curves as derived from the plate theory and the rate theory

First a number of useful relations will be derived by comparing the Gaussian distribution of the plate theory (17) with the Gaussian distribution of the rate theory (33).

Considering that per unit cross-sectional area the effective plate volume is

\[ v = H F_1 + \frac{1}{K} H F_n = \frac{1}{\beta} F_1 v \]  

and that

\[ S = F_1 u t \]  
\[ z = n H \]

we find from eqs (17) and (33) that

\[ H = 2 \frac{D}{u} + 2 \frac{F_1 u / \alpha}{(1 + F_1/F_n)^2} = L + 2 \frac{h}{(1 + K (F_1/F_n))^2} \]  

where

\[ L = 2 \frac{D}{u} \]  
\[ h = \frac{u F_1}{\alpha} \]

is the height of a transfer unit.

Equation (38) shows how the corresponding heights for longitudinal mixing (diffusion) and mass transfer have to be added to yield the HETP.

For the straightforward derivation of the Gaussian function combining diffusion and mass transfer mechanisms we are indebted to van der Waerden [17]. This result is remarkable from the statistical point of
view. It is evident that longitudinal diffusion will lead to a Gaussian distribution in the concentration. It is also known that close to the equilibrium (corresponding to a large number of transfer units) the frequently repeated process of transfer of solute to the immobile phase and back again may be explained in terms of a random walk with resulting Gaussian distribution. According to eq. (33) these two effects, when occurring simultaneously, are apparently independent for statistical purposes, so that the resulting Gaussian distribution is found by simply adding the component variances. Klinkenberg and Sjoenitzer [6] have computed these component variances and arrived at the same results.

It is believed that the above conditions are applicable in the large majority of practical cases, so that the reduction of the Lapidus and Amundson equation to a more amenable form entails little loss in the field of application.

**Application to the ion-exclusion experiments of Simpson and Wheaton**

In ion exclusion the ion exchange particles in principle act as absorbers for nonionic materials, while the ionic material cannot enter, so that the ionic material travels at a faster rate through the column than the nonionic compounds.

Simpson and Wheaton [14] carried out a series of experiments to determine the HETP as a function of particle size and flow rate for ethylene glycol in water with Dowex 50-X8 (a cation exchange resin) as absorber. The conclusion was that the HETP is proportional to the particle diameter and to the square root of the flow rate. The formula, which has been used to calculate the HETP, however, does not agree with the plate theory developed in the present paper. Since no derivation is given, it is impossible to determine how the discrepancy arises.

The main results of the Simpson and Wheaton's experiments are summarized in Table 2. Figure 8 shows the influence of the feed volume on height and width of the elution curve. It appears that with $nv = 70$ ml and $n = 240$ and 277 a reasonable agreement is obtained between experiment plate theory.

For the other experiments, also, the number of theoretical plates can be easily determined with the aid of Figs 3 and 4. In this way the HETP can be determined for every condition in two independent ways. The results are given in Table 3.

![Figure 8. Height and width of elution curve as a function of feed volume. Comparison with the experimental results of Simpson and Wheaton.](image-url)

<table>
<thead>
<tr>
<th>Feed volume (ml)</th>
<th>Particle size (mesh)</th>
<th>Superficial velocity (mm/s)</th>
<th>Width at base (ml)</th>
<th>Maximum height (fraction of $c_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>50-100</td>
<td>0.091</td>
<td>42</td>
<td>1.00</td>
</tr>
<tr>
<td>20</td>
<td>50-100</td>
<td>0.091</td>
<td>32</td>
<td>0.94</td>
</tr>
<tr>
<td>10</td>
<td>50-100</td>
<td>0.091</td>
<td>21</td>
<td>0.72</td>
</tr>
<tr>
<td>5</td>
<td>50-100</td>
<td>0.091</td>
<td>17</td>
<td>0.44</td>
</tr>
<tr>
<td>5</td>
<td>200-400</td>
<td>0.091</td>
<td>16</td>
<td>0.20</td>
</tr>
<tr>
<td>5</td>
<td>50-70</td>
<td>0.091</td>
<td>16</td>
<td>0.62</td>
</tr>
<tr>
<td>5</td>
<td>30-40</td>
<td>0.091</td>
<td>23</td>
<td>0.29</td>
</tr>
<tr>
<td>5</td>
<td>16-20</td>
<td>0.091</td>
<td>48</td>
<td>0.20</td>
</tr>
<tr>
<td>5</td>
<td>50-100</td>
<td>0.046</td>
<td>14</td>
<td>0.52</td>
</tr>
<tr>
<td>5</td>
<td>50-100</td>
<td>0.182</td>
<td>20</td>
<td>0.37</td>
</tr>
<tr>
<td>5</td>
<td>50-100</td>
<td>0.365</td>
<td>23</td>
<td>0.31</td>
</tr>
<tr>
<td>5</td>
<td>50-100</td>
<td>0.73</td>
<td>30</td>
<td>0.25</td>
</tr>
</tbody>
</table>

*Note: The effective column volume $nv$ is 70 ml.*
In order to arrive at a quantitative interpretation of these results we will have to consider the mass transfer phenomena more closely.

The overall mass transfer resistance $1/\alpha$ may be written as the sum of the resistances in the mobile and the immobile phase

$$\frac{1}{\alpha} = \frac{1}{\alpha_1} + \frac{K}{\alpha_2}.$$  \hfill (41)

For the mass transfer coefficient in the mobile phase the correlation formula proposed by Ergun \[18\] will be used, which for laminar flow reads

$$a_p = a_p k_1 = \frac{25 D_p a_p^2}{6 F_1}.$$  \hfill (42)

$D_p$ is the molecular diffusion coefficient in the mobile phase, $\alpha$ is the specific surface area of the particles per unit volume of the bed; $k_1$ is the mass transfer coefficient per unit surface area of the particles.

For diffusion into a particle the mass transfer coefficient may be defined as

$$-D_p \frac{\partial c}{\partial r}_{\text{surface}} = k_1 (c_{\text{surface}} - c_{\text{average}}).$$  \hfill (43)

A simplified version of the general solution for diffusion into a spherical particle can be obtained if it is assumed that the average concentration ($c_{\text{average}}$) does not differ too much from the concentration at the particle surface ($c_{\text{surface}}$). The result then reads

$$a_p = a_p k_1 = \frac{25 D_p a_p^2}{6 F_1}.$$  \hfill (44)

With eqs (42) and (44) the overall resistance becomes

$$\frac{1}{\alpha} = \frac{6 F_1}{25 D_p a_p^2} + \frac{3 K d_p}{2\pi^2 D_n a_p}.$$  \hfill (45)

For the case of uniform spherical particles,

$$a_p = \frac{6}{d_p} - \frac{1 - F_1}{d_p}.$$  \hfill (46)

The longitudinal diffusivity $D$ will be the sum of molecular diffusivity $D_m$ and eddy diffusivity $E$. In order to account for the irregular pattern along the particles, $D_m$ has to be multiplied by a labyrinth factor $\gamma$ which is of the order of magnitude of 0.5–1.0. A reasonable approach to the eddy diffusivity $E$ is to assume that

$$E = \lambda u d_p.$$  \hfill (47)

where $\lambda$ is a packing characterization factor. In this way

$$D = \gamma D_1 + \lambda u d_p.$$  \hfill (48)

Introduction of eqs (45), (46) and (48) into eq. (38) yields

$$H = \frac{D_1}{d_p} = 2\gamma + 2\lambda + C \frac{u d_p}{D_1},$$  \hfill (49)

where $C$ is a dimensionless factor depending on $F_1$, $F_1$, $K$ and $D_1/d_1$ according to

$$C = \frac{F_1^2}{75(1 - F_1)^2 + 2\pi^2(1 - F_1) d_n}.$$  \hfill (45)

According to eq. (49) the HETP expressed in particle diameters is made up of three terms, a longitudinal molecular diffusion contribution inversely proportional to $u$ times $d_p$, an eddy diffusion contribution presumable independent of $u$ and $d_p$, and a mass transfer resistance contribution proportional to $u$ times $d_p$. This formula suggests that a plot of $H/d_p$ vs $u d_p$ or $1/u d_p$ might decide upon the relative importance of the three terms. Now by a rough estimate it is easily found that longitudinal molecular diffusion was of no importance in the Simpson and Wheaton experiments. In Fig. 9, therefore, $H/d_p$ has been plotted vs $F_1 u d_p$, using the values of Table 3. It appears that for the experiments with varying flow rate (50–100 mesh particles), the linear relationship is fairly well confirmed. The experiments with varying particle size on the other hand seem to follow a completely different curve. The latter might, however, be explained by assuming a variation of $\lambda$ with the particle diameter as indicated by the dashed lines.

It seems reasonable to expect that it is easier to effect a regular packing for large particles than for small particles. The values found for $\lambda$ are 8 for 200–400 mesh, 3 for 50–100 mesh and practically zero for 20–40 mesh.

The particle diffusion coefficient $D_n$ may be calculated from the slope of the straight line in Fig. 9. With $F_1 = F_n = 0.4$ and $K = 1.3$ it is found that $D_n = 1.3 \times 10^{-10}$ m$^2$/s, a value which is about 10 times smaller than the diffusion coefficient in the free liquid.

Application to gas-liquid partition chromatography

In gas-liquid partition chromatography \[19, 20\] a suitable liquid is retained by the pores of solid particles. This liquid absorbs the various components in the flowing gas according to their solubility (Henry coefficient), so that a separation is obtainable which may be compared with extractive distillation.

1In effect, eq. (49) is an example of addition of resistance terms. This manner of expression of overall mass transfer rates is quite common and a particular analogous case is found in the mass transfer in a wetted wall column under laminar flow condition. For distillation, Westhaver \[21\] obtained for the HETP:

$$H = \frac{1}{d} = \frac{11 u d}{192 D_1}.$$  \hfill (49)

in which $d$ is the diameter of the column. The first term in this equation has the same physical significance as the first term in eq. (49), whilst the second term is essentially the same as the third term in eq. (49). Because of the laminar flow conditions and the absence of packing, the eddy diffusion parameter $\lambda$ equals zero in Westhaver's equation.
In order to describe the diffusion in the liquid phase, it will be assumed that the liquid within the particles is present in the form of a film of effective thickness $d_f$. Whether the liquid is actually a continuous film or just fills up the smaller pores and leaves the wider pores unwetted is immaterial for the mathematical description. If the latter is the correct concept it will be found that the effective film thickness is larger than the diameter of the smaller pores. In the first case the film thickness should be very small.

The distribution of fractional volumes of gas, liquid, pore space and particle skeleton in the column is schematically indicated in Fig. 10.

The mass transfer coefficient in the liquid phase may again be found from the simplified solution of the general equation for diffusion into a layer. If $d_f$ is the film thickness and $a_u$ the specific surface of the film,

$$a_u = a_s k_n = \frac{1}{4} \pi^2 \frac{D_u a_p}{d_f^2}.$$  

Considering that $a_u d_f = F_u$ it follows that

$$a_u = \frac{1}{4} \pi^2 \frac{D_u F_u}{d_f^2}.$$  

For the moment it will be assumed that the mass transfer resistance in the gas phase may be neglected. This assumption will be checked later on. Then the general equation (38) becomes

$$H = 2 \frac{D}{u} + \frac{8}{\pi^2} \frac{K F_u {u}^2}{(1 + K F_u F_u)^2 D_u F_u}.$$  

The longitudinal diffusivity $D$ will be written as the sum of molecular diffusivity $\gamma D_1$ and eddy diffusivity $E$. For the latter approach, eq. (47) will again be introduced. In this way, eq. (52) becomes

$$H = 2 \frac{D_1}{u} + 2 \lambda d_p + \frac{8}{\pi^2} \frac{K F_u {u}^2}{(1 + K F_1/F_u)^2 D_u F_u}.$$  

It is seen that, particularly in this case, a variation in gas velocity should demonstrate the contribution to the HETP of gas longitudinal eddy and molecular diffusion and liquid molecular diffusion.

We will next consider some experimental results obtained with two chromatographic columns, both of 1.80 m length and 6 mm internal diameter. In the first, Celite (a diatomaceous earth) with an average particle diameter of about 30 \(\mu\text{m}\) was used as the solid carrier, in the second a narrow fraction of ground Sterchamol (50–80 mesh; $d_p \approx 240 \mu\text{m}$). In both cases the liquid phase was the same, viz., a lubricating oil with an average molecular weight of 312 and a viscosity of 30 cS at 20°C. The weight ratio of oil to solid carrier was 0.3. The feed sample, consisting of a mixture of normal butane (90%) and isobutane (10%), was eluted with N\(_2\) at 30°C and at a pressure close to atmospheric. The HETP was determined by varying the sample size and extrapolating to zero sample size. The results of such experiments at different gas velocities are summarized in Table 4 and graphically represented in Figs 11–14 as a function of gas velocity and reciprocal gas velocity.

For the Celite column the relation between HETP and gas velocity may be described by

$$\text{HETP} = \frac{9}{u} + 0.3 + 0.05 u$$  

for normal butane, and by

$$\text{HETP} = \frac{8}{u} + 0.8 + 0.08 u$$  

for isobutane (HETP in mm, $u$ in mm/s).
As in these experiments $K(F_i/F_n) = 0.019$ and 0.028 for the two components, respectively, the ratio of the slopes of the straight parts of the curves in Fig. 11 according to eq. (53) must be about 1.5. This appears to be in good agreement with the above formulae, where the value of this ratio is 1.6.

The diffusivity $D_n$ in the liquid phase may be estimated from its viscosity. This gives $D_n = 0.3 \times 10^{-10}$ m$^2$/s. Consequently, from eq. (53), the known values of the slopes under discussion and the $K$-values mentioned above the effective film thickness can be calculated. It is found from both curves that $d_f \approx 10$ µm.

Comparison of the formulae (54) with (53) also reveals that

$$2 \gamma D_1 \approx 8 \times 10^{-6} \text{ m}^2/\text{s}.$$ 

This value is of the right order of magnitude as $\gamma$ lies between 0.5 and 1, and $D_1 = 9 \times 10^{-6} \text{ m}^2/\text{s}$ as estimated from the well-known formula of Gilliland [22].

The second term in the right-hand member of eq. (53) is the contribution of eddy diffusion to the HETP. It therefore should obviously have the same value for both components. The formulae (54) do not agree with theory in this respect. It must be mentioned, however, that the values of the constants in eq. (54) are highly uncertain, owing to the relatively small number of experimental data that were available. The value $2 \lambda d_p \approx 0.5$ mm seems to be reasonable, from which it follows that $\lambda \approx 8$. This is in fair agreement with the statement concerning $\lambda$ on p. 3877.

The results of the measurements with normal butane in the Sterchamol column may be represented by the relation

$$\text{HETP} = 0.05u + \frac{7.5}{u}. \quad (55)$$

It will be obvious that the absence of a constant in the right-hand member is not a definite proof that eddy diffusion does not in principle occur. Again, with the small number of experimental data the constant could not be determined accurately. It should not differ much from zero, however, so that the eddy diffusion is

### Table 4. Experimental data on HETP in gas-liquid chromatographic columns

<table>
<thead>
<tr>
<th>Superficial velocity (mm/s)</th>
<th>HETP for normal butane (mm)</th>
<th>HETP for iso-butane (mm)</th>
<th>Solid carrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7</td>
<td>6.0</td>
<td>5.2</td>
<td>Solid carrier</td>
</tr>
<tr>
<td>2.0</td>
<td>4.6</td>
<td>5.1</td>
<td>Solid carrier</td>
</tr>
<tr>
<td>3.4</td>
<td>2.7</td>
<td>3.1</td>
<td>Solid carrier</td>
</tr>
<tr>
<td>3.5</td>
<td>2.7</td>
<td>3.3</td>
<td>Solid carrier</td>
</tr>
<tr>
<td>4.8</td>
<td>2.3</td>
<td>2.4</td>
<td>30 µm Celite</td>
</tr>
<tr>
<td>5.0</td>
<td>2.3</td>
<td>2.7</td>
<td>&gt; 40 µm 24%</td>
</tr>
<tr>
<td>15</td>
<td>1.8</td>
<td>2.6</td>
<td>40-20 µm 52%</td>
</tr>
<tr>
<td>15</td>
<td>2.0</td>
<td>2.7</td>
<td>20-10 µm 18%</td>
</tr>
<tr>
<td>15</td>
<td>1.7</td>
<td>2.8</td>
<td>10-6 µ 41%</td>
</tr>
<tr>
<td>15</td>
<td>1.9</td>
<td>2.4</td>
<td>&lt; 6 µ 1%</td>
</tr>
<tr>
<td>23</td>
<td>1.9</td>
<td>2.8</td>
<td>Sterchamol</td>
</tr>
<tr>
<td>23</td>
<td>1.9</td>
<td>3.5</td>
<td>(180-300 µm)</td>
</tr>
<tr>
<td>1.8</td>
<td>4.1</td>
<td>Sterchamol</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>3.5</td>
<td>Sterchamol</td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>2.5</td>
<td>Sterchamol</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>2.3</td>
<td>Sterchamol</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>1.6</td>
<td>Sterchamol</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>1.6</td>
<td>Sterchamol</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>1.2</td>
<td>Sterchamol</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>1.2</td>
<td>Sterchamol</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>1.2</td>
<td>Sterchamol</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>1.7</td>
<td>Sterchamol</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 12. HETP vs reciprocal gas velocity for the celite column.

Fig. 13. HETP vs gas velocity for the sterchamol column.

certainly smaller than in the Celite column. Consequently, the Sterchamol column is superior to the Celite column from an analytical point of view, as with less eddy diffusion sharper separations will become possible.

The good agreements between the constant in eq. (55) and corresponding constants in the first formula of eq. (54) is considered somewhat incidental. As in the experiments with the Sterchamol column $K(F_t/F_0) = 0.026$ the effective film thickness in this case is found to be $d_f = 9 \mu m$. With respect to the average particle diameter of 240 $\mu m$, this value seems very reasonable.

We will finally discuss the question of where the mass transfer resistance is located. For this purpose we will compare the time spent by the molecules travelling to the gas-liquid interface with the time needed for diffusing into the liquid layer. In the gas phase, the molecules have to travel over a distance which is roughly one-half of the pore width. This pore width is of the order of magnitude of one-fifth of the particle diameter, so the path in the gas phase comes into the
equation as \( \frac{1}{100} d_f \). The path in the liquid phase is \( d_f \). Consequently, the ratio of the two diffusion times becomes

\[
\frac{1}{100} \left( \frac{d_f}{d_p} \right)^2 \frac{D_{ll}}{D_l}.
\] (56)

The resistance in the gas phase may be neglected if this ratio is small in comparison with unity. As in the present problem \( D_{ll}/100 D_l = 3.3 \times 10^{-8} \) the two resistances become of equal order of magnitude in the case of a film thickness smaller than about 0.0001 of the particle diameter. This does not occur in the two columns under discussion. The ratio (56) amounts to \( 3 \times 10^{-7} \) and \( 2.5 \times 10^{-5} \) for the Celite and Sterchamol columns, respectively. Apparently, the resistance to mass transfer is located entirely in the liquid phase.

Acknowledgements—The authors are indebted to the managements of the Koninklijke/Shell-Laboratorium, Amsterdam, and N. V. De Batavische Petroleum Maatschappij, The Hague, for permission to publish this paper.

\[\begin{align*}
\text{NOTATION} \\
a & (A/v\sqrt{n}) \text{ dimensionless feed volume} \\
a_p & \text{specific surface of packing, } m^{-1} \\
A & \text{feed volume, } m^3 \\
c & \text{concentration (suitable unit/m}^3) \\
c_l & \text{concentration in mobile phase (suitable unit/m}^3) \\
c_{ll} & \text{concentration in immobile phase (suitable unit/m}^3) \\
c_o & \text{concentration in feed (suitable unit/m}^3) \\
d_p & \text{particle diameter, } m \\
d_f & \text{effective liquid film thickness, } m \\
D & \text{effective longitudinal diffusivity, } m^2/s \\
D_{ll} & \text{molecular diffusivity in immobile phase, } m^2/s \\
F_l & \text{fractional volume of mobile phase, } m^3/m^3 \\
F_{ll} & \text{fractional volume of immobile phase, } m^3/m^3 \\
h & \text{height of a transfer unit } m \\
H & \text{height equivalent to a theoretical plate, } m \\
k_l & \text{mobile phase mass transfer coefficient per unit surface area of packing, } m/s \\
k_{ll} & \text{immobile phase mass transfer coefficient per unit surface area of packing, } m/s \\
K & \text{distribution factor (} = c_l/c_0 \text{ equilibrium) } \\
l & \text{length of column, } m \\
n & \text{number of theoretical plates} \\
S & \text{(} = S/v\sqrt{n} \text{) } \\
S_f & \text{total volume of mobile phase flowed through, } m^3 \\
t & \text{time, } s \\
u & \text{interstitial velocity, } m/s \\
v_l & \text{effective plate volume, } m^3 \\
v_{ll} & \text{volume of mobile phase in one theoretical plate, } m^3 \\
v_o & \text{volume of immobile phase in one theoretical plate, } m^3 \\
z & \text{longitudinal position, } m \\
\alpha & \text{mass transfer coefficient per unit volume of packing, } s^{-1} \\
\beta & \text{conversion factor [eq. (34)]} \\
\Delta S & \text{width of elution curve at very small feed volume, } (a < 0.5) \\
\Delta S_0 & \text{width of elution curve, } m^3 \\
\gamma & \text{labyrinth factor}
\end{align*}\]
\( \eta \)  
(relative volatility)

\( \lambda \)  
(factor in eddy diffusivity)

\( \sigma \)  
(variance, \( s \))

REFERENCES


APPENDIX

The expression (31) will be simplified to a Gaussian distribution function by introducing a few approximations, where are essentially due to van der Waerden [17].

In the first place the first term of the asymptotic expansion of the Bessel function \( I_n \) will be used. This involves that the argument of \( I_n \) is sufficiently large, a condition which will be verified afterwards. Then eq. (32) reduces with

\[
\frac{1}{\beta} = 1 + \frac{F_n}{K F_n}
\]

to

\[
F(t) = \frac{1}{2\sqrt{\pi}} \left[ \frac{\alpha^2 K t'}{F_n F_{n-1} (t' - t)} \right]^{1/4}
\times \exp \left\{ -\frac{\alpha^2 K^2 F_n}{F_{n-1}} \left( \frac{t - t'/\beta}{\sqrt{(t' - t)/F_n K + \sqrt{t'/F_n}} \right)^2 \right\}
\]

Now in the integral (31) two exponential functions occur. Their maximum values are obtained for \( t' = z/u \) and \( t' = \beta t \), respectively. We will next assume that the effects of longitudinal diffusion and of the deviation from equilibrium are small. This means that all retention times \( t \) are close to the mean \( \bar{t} = z/\mu \), which is that prevailing in ideal linear chromatography. Consequently, the two maxima of the individual exponential functions \( t' = z/u \) and \( t' = \beta t \) are close together, so that the main contribution to the integral depending on the product of those exponential functions will also be located in this small region where \( t' \approx z/u = \beta t \). It follows that it is permissible to replace \( t' \) by \( z/u \) or \( \beta t \), except in the numerators of the exponents. In this way, \( F(t') \) may be further simplified to

\[
F(t') = \frac{1}{\beta} \sqrt{\frac{\alpha^2 K^2 F_n}{F_{n-1}}} \exp \left\{ -\frac{\alpha^2 K^2 F_n}{4F_{n-1}} \left( \frac{t - t'/\beta}{\sqrt{(t' - t)/F_n K + \sqrt{t'/F_n}} \right)^2 \right\}
\]

It also follows that the first term of eq. (31) may be completely neglected, as long as \( z \approx \beta t \) is markedly different from \( t' \), i.e. if there is a sufficient retention of the solute in the column.

Now the expression (31) may be simplified to

\[
\frac{c_1}{c_0} = \frac{\beta \sigma_t}{\sigma_z} = \frac{1}{\sigma_z} \frac{1}{\sigma_t} \exp \left\{ -\frac{\alpha^2 K^2 F_n}{4F_{n-1}} \left( \frac{t - t'/\beta}{\sqrt{(t' - t)/F_n K + \sqrt{t'/F_n}} \right)^2 \right\}
\]

where

\[
\sigma_z^2 = 2 \frac{Dz}{u^2}, \quad \sigma_t^2 = \frac{\beta^2}{K^2} \frac{F_n^2}{xF_n K^2 u^2}
\]

The three assumptions used in this derivation may now be specified as

\[
2 \frac{\alpha^2 K^2 (t - \bar{t})}{F_n F_{n-1}} \approx 2 \frac{\alpha z}{F_n \mu} = 1
\]

\[
\sigma_z^2 = \left( \frac{z}{u} \right)^2 \leq \frac{2Dz}{u} \leq 1
\]

\[
\sigma_t^2 = \left( \frac{\beta^2}{K^2} \frac{F_n^2}{xF_n K^2 u^2} \right) \leq 1
\]

The first condition requires that the height of a transfer unit \( F_n \mu/u \) is much smaller than the height \( z \) of the bed. According to the second condition the height of a longitudinal mixing stage \( 2D/u \) should be much smaller than the height of the bed. The last condition is always fulfilled if the first one is valid, because

\[
\frac{\beta F_n^2}{K F_n} = \frac{1}{(1 + K(F_n/F_{n-1}))^2} < 1
\]

It follows that the simplified expression may be used if the column contains a large number of mixing stages and transfer units, or, in other words, a large number of theoretical plates.