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# A Phenomenological Plate Height Equation for Packed Chromatographic Columns

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## Summary

In the present study a general expression for the plate height in packed columns is established. The purpose of this expression is to give a picture of the variation of the column plate height over a very wide range of operating conditions, e.g., laminar and turbulent flow regions, gaseous and liquid mobile phases. The position is taken that it is futile to propose a model of the column processes which cannot be justified by the reliability of available experimental data. A very simple, but meaningful, model based mainly on experimentally measurable parameters has therefore been assumed as the basis for the plate height expression. The proposed (plate height) expression appears to be able both to predict and to interpret the available body of experimental results. Perhaps the most significant features of this expression are first, that it quantitatively takes account of the role of turbulence in band broadening, and second, that it indicates that in the turbulent flow region the plate height becomes a strongly increasing function of the mass distribution coefficient.

The fundamental exposition of the causes underlying band dispersion in packed columns has occupied the attention of a great many chromatographers over many years (*1–15*). This has been particularly true in the field of gas chromatography. The problem has been approached in many ways but most of these have involved the following line of reasoning: Mechanisms or processes, which on the basis of common scientific experience could reasonably cause band spreading, are postulated. Using highly idealized models of these mechanisms, expressions are derived to relate parameters which are considered to be suitable, relevant, or convenient to a plate height. Thus each mechanism is associated with a plate height and the total plate height is considered to be some function of these. Essentially the only means of assessing the validity of a particular expression for the plate height is to compare the theoretically predicted value of the plate height with the experimentally measured one at the outlet. This approach can be extended, in a suitable fashion, to parameters in the expressions for the various proposed band-spreading mechanisms and comparing the theoretically predicted trends with those observed by measurement of the eluted band under the specified circumstances. A necessary and sufficient condition for the success of this approach is that it is possible in practice to so adjust the various column parameters that the measured band spreading is exclusively concerned with a single proposed mechanism. To a greater or lesser extent this condition can be met by the conventional approach being considered here. For example, band-spreading mechanisms associated with the mobile phase can be isolated from those concerned with the stationary phase by carrying out experiments on unretarded and retarded solute bands. However, where the ultimate source of experimental information is limited to band-shape measurement at the column outlet, the extent to which individual mechanisms can be isolated from each other is also limited. The position at present is thus that although there is a certain degree of unanimity on some of the proposed band-spreading mechanisms, there are other proposals between which a choice cannot be made. This is particularly true where the expressions for two different mechanisms are functionally similar (*16*).

Possibly the most attractive solution to this dilemma is to carry out more detailed measurements within the column itself. An approach of this type has been widely adopted by workers outside the field of chromatography—particularly chemical engineers—and it is significant that these researches have been largely ignored by chromatographers. A wealth of information which is pertinent to chromatography has been accumulated in this way on actual phenomena within a packed column. Examples which may be quoted here are studies of dispersion and flow characteristics (*17–41*), velocity profiles (*42–47*), and packing structure

(*48–52*). Although much of this information is highly relevant to chromatography, it is not always readily assimilable into the existing theoretical framework of chromatography.

The purpose of the present study has been to derive a plate height expression valid for the widest possible range of chromatographic circumstances, particularly those unusual conditions (viz., high flow rates and turbulent flow) which appear to be relevant to high-speed liquid chromatography. To ensure that such an expression is practically useful—i.e., that it can be used to predict performance under a particular set of circumstances with reasonable accuracy—as much as possible of the experimental information, referred to above, has been incorporated. In this sense the approach is a phenomenological one. A consequence of it is that the predicted plate height can be related to experimentally measurable parameters more directly concerned with the actual band spreading processes within the column than is the case when the plate height is essentially assessed from a single measurement at the column outlet as is conventionally done.

As a starting point we propose that the band-spreading processes may be visualized on various "scales of observation," and it is possible to focus attention on each of these in turn and at the same time disregard the others (*10*, *24*, *53*). Three such "scales of observation" are considered convenient here. First, the column packing as a whole is considered (i.e., the columnwide region) and band-broadening mechanisms peculiar to columnwide effects are placed in this category. Second, the scale of observation is reduced to a representative portion of the packing (i.e., the intermediate region), and band-spreading mechanisms which are not affected by the column radius are considered here. Finally, the scale of observation is further reduced to the actual interstitial voids of the packing (i.e., the interparticle region).

Although many aspects of the theoretical treatment are sufficiently general to pertain to a wide variety of packing types, it will be ultimately necessary to limit attention to beds of spherical particles for reasons which will become obvious in due course. In addition, the column-to-particle diameter ratio, $\rho$, will be restricted to values larger than 10. The potential advantages (*54*) of packed column with $\rho \lesssim 10$ are recognized but are not explored any further here. It is convenient to develop expressions for band spreading associated with the various individual "scales of observation." These are then, together with an expression for longitudinal diffusion, corrected for compressibility, where necessary, summed to yield the total local plate height.

## THE PLATE HEIGHT FOR THE INTERPARTICLE REGION

The establishment of plate height expressions via the present phenomenological approach tends, by its very nature, to obscure the molecular characteristics of the processes which are involved, and a brief discussion of this aspect is thus appropriate at this point.

First of all, we may observe that it is commonly accepted that the interparticle region actually involves two broad categories of phenomena—those residing in the stationary phase and those associated with the mobile phase. The first of these is physically well understood and our discussion at this point will thus be focused mainly on the mobile phase phenomena.

### Physical Description of the Mobile Phase Portion of the Interparticle Region

One of the most crucial aspects which concerns the plate height in this region is the interstitial flow dynamics. It has become customary to correlate flow dynamic data with the Reynolds number (*55*). Since a number of expressions for the Reynolds numbers are currently used in the literature, it is necessary to clarify this point before proceeding further. In addition to the definitions (*10, 55*)

$$\mathrm{Re} = d_p\bar{u}/\nu$$

and

$$\mathrm{Re} = \epsilon(d_p\bar{u}/\nu)$$

defined for packed beds, Bischoff and Levenspiel (*26*) have proposed

$$\mathrm{Re} = d_e\bar{u}/\nu$$

where

$$d_e = \frac{\epsilon d_t}{\frac{3}{2}(d_t/d_p)(1-\epsilon)+1}$$

Data in the literature are presented using all three definitions. A detailed discussion of which of these is best would be out of place here, although there is some evidence in favor of the form proposed by Bischoff et al. Nevertheless we shall employ the form $\mathrm{Re} = d_p\bar{u}/\nu$ since this definition is most familiar to chromatographers, and all data obtained from the literature has, where necessary, been corrected to conform to this definition.

In spite of the extensive data available on the correlation between the flow dynamics and the Reynolds number, there is a difference of opinion about the Reynolds number at which turbulence in packed columns sets in. In chromatography it has often been claimed that this Reynolds number is as low as 10 (*10, 56–58*). The conclusion is based on observed deviations from Darcy's law at Re = 10. There is reason to believe that this conclusion may be in error since the necessary care has not always been taken to distinguish between other types of "rotational flows," which may lead to a similar effect, and turbulent flow (*19*). The point at which truly unstable turbulent flow sets in can best be determined by a more direct observation of the emergence of unstable flow. Jolls et al. (*17*) have attempted to obtain such independent information and have arrived at a value for the critical Reynolds number of ~500. These workers have investigated the transition to turbulence for flow through a bed of dumped spheres by visual observation of dyes introduced continuously into the mobile phase as well as from the measurement of mass transfer coefficients. They have shown that the flow dynamics in the laminar flow region ($\mathrm{Re} \lesssim 500$) is very stable—the flow lines remaining unchanged for times up to 20 min. In the flow region approaching $\mathrm{Re} \simeq 500$, small fluctuations in the flow lines are observed, but the flow patterns, however, appear to remain stable. Only in the region $\mathrm{Re} \gtrsim 500$ does the flow dynamics become unstable, and violent eddying is observed. Mickley et al. (*20*) have studied quantitatively the structure of interstitial turbulent gas flow in a regular rhombohedral array of spheres at high Reynolds numbers ($\mathrm{Re} \gtrsim 12{,}000$). These authors have found no evidence for eddy shedding in the packing voids. They also indicated that the turbulent intensity near the contact points between the particles is low. Evidently, a dogmatic choice of a particular value of the Reynolds number as an indication of the threshold of turbulence is not simple. We shall assume that turbulence definitely exists at $\mathrm{Re} \gtrsim 500$.

It should be stressed that the interstitial voids are highly irregular and random in character. This irregularity affects the effective lateral mass transport in the interstitial voids in that the boundaries of the elementary flow channels move randomly with respect to a representative solute molecule during its passage through the column. Clearly fluid flow in packed beds—which is in itself a complex phenomena—is further complicated.

### The Plate Height Expression for the Mobile Phase in Terms of Phenomenological Variables

It was realized in the pioneering study of Van Deemter et al. (*53*) that the contribution to the plate height of resistance to lateral mass transfer in the mobile phase can be related to the mass transfer coefficient (*59*) of the packed bed. It is also clear from their work, however, that in this approach lateral flow velocity variations are not taken into account. This assumption of flat velocity profiles in the interstitial voids predicts a zero contribution to the plate height in the case where $k = 0$ (*59*, *53*, *60*). Furthermore, it can be anticipated, for the same reason, that predictions of the magnitude of the plate height based on this approach will be somewhat optimistic even in regions where $k$ is relatively large ($k \gtrsim 1$). In spite of these objections, however, a relation between the plate height and the mass transfer coefficients has the advantage that it implicitly takes account of many phenomena peculiar to packed beds which cannot possibly be incorporated into idealized models. The plate height has been related to the mass transfer coefficient, $\chi$, by (*59*)

$$H(k) = \frac{2k\bar{u}}{(1+k)^2}\frac{d_f K}{\chi} \tag{1}$$

The mass transfer coefficient, $\chi$, for packed columns is readily available in the nonchromatographic literature (*61–68*). For example, Gupta et al. (*64*) and, more recently, Wilson et al. (*62*) have obtained empirical correlations for the mass transfer coefficients in terms of dimensionless groups. The first of these studies reported a very general correlation for both gases and liquids in the Reynolds number range $\text{Re} \gtrsim 1$. Thus,

$$\chi = \frac{\bar{u}}{\text{Sc}^{2/3}}\left[0.010 + \frac{0.863}{(\epsilon\text{Re})^{0.58} - 0.483}\right] \tag{2}$$

The second study, however, pointed out that the values for $\chi$ given by the above correlation are somewhat too large for liquids in the vicinity of $\text{Re} \gtrsim 1$. It was therefore proposed that

$$\chi = \frac{1.09\bar{u}}{(\text{Sc}\epsilon\text{Re})^{2/3}} \tag{3}$$

for liquids in the range $10^{-3} \lesssim \text{Re} \lesssim 10$. For gases in the lower Reynolds number range ($\mathrm{Re} \lesssim 100$), Wilke et al. (*69*) have found

$$\chi = \frac{1.82\bar{u}}{\mathrm{Sc}^{2/3}(\epsilon \mathrm{Re})^{0.51}} \qquad \mathrm{Re} \lesssim 100 \tag{4}$$

This expression appears (*61*) to be in agreement with other studies reported in the same region. The upper limits of the range of Reynolds numbers indicated in Eqs. (3) and (4) are values where these functions coincide, respectively, with Eq. 2. For the present study Eqs. (2), (3), and (4) have been substituted in Eq. (1) for the plate height. For sperical beads covered with a liquid layer of thickness $d_f$, it follows readily that

$$k = \frac{6(1-\epsilon)}{\epsilon}\frac{d_f}{d_p}K \tag{5}$$

TABLE 1

Expressions for the Reduced Plate Height: Interparticle Region

| Fluid | Reynolds number range | Expressions | |
|---|---|---|---|
| Liquid<br>$20 \le \mathrm{Sc} \le 10^4$ | $10^{-3} \le \mathrm{Re} \le 10$ | $h(x) = \frac{1}{3.27}\left(\frac{k}{1+k}\right)^2\left(\frac{\epsilon}{1-\epsilon}\right)$<br>$(\epsilon \mathrm{ScRe})^{2/3}$ | (6) |
| | $10 \le \mathrm{Re} \le 2000$ | $h(x) = \frac{1}{3}\left(\frac{k}{1+k}\right)^2\left(\frac{\epsilon}{1-\epsilon}\right)$<br>$\frac{\mathrm{Sc}^{2/3}}{0.01 + 0.863/[(\epsilon\mathrm{Re})^{0.58} - 0.483]}$ | (7) |
| Gases<br>$\mathrm{Sc} \sim 1$ | $10^{-3} \le \mathrm{Re} \le 100$ | $h(x) = \frac{1}{5.46}\left(\frac{k}{1+k}\right)^2\left(\frac{1}{1-\epsilon}\right)$<br>$\mathrm{Sc}^{2/3}(\epsilon\mathrm{Re})^{0.51}$ | (8) |
| | $100 \le \mathrm{Re} \le 2000$ | $h(x) = \frac{1}{3}\left(\frac{k}{1+k}\right)^2\left(\frac{\epsilon}{1-\epsilon}\right)$<br>$\frac{\mathrm{Sc}^{2/3}}{0.01 + [0.863/(\epsilon\mathrm{Re})^{0.58} - 0.483]}$ | (7) |

Keeping this in mind, the plate height expressions obtained for both gases and liquids in the appropriate flow region have been tabulated in Table 1. Although these expressions have been derived using Eqs. (1) and (5) and apparently would be limited to systems employing a liquid stationary phase, they are actually completely general.

### The Plate Height Expression for the Stationary Phase in Terms of Phenomenological Variables

The nature of the stationary phase, as well as its detailed structure, determines the extent to which band-broadening mechanisms, operative in the stationary phase, contribute to the plate height. It has been found (*1*, *10*, *53*) that under most conditions

$$H_S(x) = C_s\bar{u}(x)$$

and the relation between $C_s$ and the parameters relevant to a description of the stationary phase has been the object of a number of fundamental studies (*10*, *70–72*). It is inconvenient for the present development to consider a detailed study of $C_s$, and a dimensionless stationary phase parameter, $\theta_s$, is introduced as

$$h_S(x) = \frac{k}{(1+k)^2}\,\theta_s(x)\,\mathrm{Re} \tag{9}$$

$\theta_s(x)$ is now analogous in meaning to parameters such as $\lambda$ and $\gamma$. It can be related to $C_s$ by

$$C_s = \frac{k}{(1+k)^2}\,\theta_s(x)\,\frac{d_p{}^2}{\nu(x)} \tag{10}$$

TABLE 2

$C_s$ and $\theta_s$ for Typical Stationary Phase Band Broadening Processes

| $C_s$ | $\theta_s$ | Type of process |
|---|---|---|
| $\frac{2}{3}\frac{k}{(1+k)^2}\frac{d_f{}^2}{D_s}$ | $\frac{2}{3}\left(\frac{d_f}{d_p}\right)^2\frac{\nu}{D_s}$ | Stationary phase existing as uniform film of thickness $d_f$ on solid surface |
| $2\frac{k}{(1+k)^2}\bar{t}_d$ [a] | $2\frac{\bar{t}_d}{d_p{}^2}$ | Adsorption on multisite surfaces |

[a] $\bar{t}_d$ = mean adsorption time.

Various expressions for $\theta_s$ and $C_s$ in terms of more detailed parameters, adapted from expressions derived by Giddings (10), are shown in Table 2.

## THE PLATE HEIGHT FOR THE INTERMEDIATE REGION

### Physical Description of the Intermediate Region

A quantitative description of the packing structure is an essential prerequisite to obtaining an accurate expression of the plate height for the intermediate region. Although some attempts have been made to connect the plate height with the packing structure (*1, 10, 11, 13, 53*), these attempts remain unsatisfactory mainly because the parameters introduced to describe the packing lack a meaning in terms of experimental measurements. In the nonchromatographic literature a number of studies proposed methods whereby the structure of packed beds can be described, mainly in statistical terms (*41, 51*). Although this line of approach is very promising, lack of suitable experimental data prohibits its use in the present study.

### The Plate Height Expression in the Intermediate Region in Terms of Phenomenological Variables

Despite the fact that a general expression for the plate height in this region is hindered by these considerations, several broad outlines of its behavior suggest themselves. First, it can be shown by simple random-walk considerations that the plate height is independent of the flow velocity, i.e., the Reynolds number. This picture is, however, a too drastic oversimplification of reality. More detailed studies indicated (*21–23*) that $h$ depends weakly on Re. Second, the plate height does not depend on the mass distribution coefficient since the mass distribution coefficients cancel when $H$ is determined from

$$H = \frac{2D_r/(1+k)}{u/(1+k)} \tag{11}$$

For the present purpose the following functional dependence will merely be assumed

$$h(x) = \lambda(\text{Re, packing geometry}) \tag{12}$$

The magnitude of $\lambda$ will be evaluated very roughly by subsequent experiments.

## THE PLATE HEIGHT FOR THE COLUMNWIDE REGION

### Physical Description of the Columnwide Region

On this "scale of observation" the physical description itself can only be done in terms of phenomenologically defined variables such as measured radial velocity profiles and radial dispersion coefficients.

### Velocity Profiles

Velocity profiles have been measured experimentally in a large number of studies (*42–47*). Radial variation in the linear flow velocity has been observed not only in the obvious case where a radial variation in particle size is present (*73*, *74*) but also when spherical beads, nearly homogeneous in diameter, have been used as packing material (*42–47*). The nature and origin of the velocity profile in the latter case is of interest. The velocity at the wall is zero on account of wall friction and it increases with increasing distance from the wall to reach a maximum somewhere between the column wall and the center (*42*). At the center the velocity profile goes through a minimum (*42*). The increase of the velocity can be attributed mainly to an increase in the permeability in the vicinity of the column wall (*42*, *48*). This phenomenon results from an attempt by the packing to adjust itself from the basically rectangular packing structure of spheres to the circular shape of the column. The packing structure appears to be well ordered next to the column wall. The order is extending for distances of up to five particle diameters and then changes into an otherwise completely random structure (*48*). Benenati et al. (*48*) have shown that the radial variation of the void fraction with a packed bed of uniform spheres varies from unity at the wall to about 0.38 in the interior of beds with a large column to particle diameter ratio. The voidage distribution takes the form of a damped oscillatory wave with the oscillations damped out at about $4\frac{1}{2}$ to 5 sphere diameters from the container wall.

### Radial Dispersion

When a tracer is introduced on the axis of a column, it is dispersed radially as it is swept through the column. This dispersion process obeys a Ficksian law (*40*, *41*) and this, in turn, defines the radial dispersion coefficient, $D_r$, which is an important characteristic of a packed column. A thorough understanding of the radial dispersion mechanisms is therefore, in addition to its quantitative prediction, of paramount importance and it will be dealt with in some detail.

The radial dispersion coefficient can be expressed by *(7)*

$$D_r = \gamma D_m + \lambda_R d_p \bar{u} + \psi(\mathrm{Re}) \tag{13}$$

where the three terms represent the different mechanisms contributing to $D_r$. $\gamma D_m$ represents molecular diffusion. $\lambda_R d_p \bar{u}$ arises from the so-called side-stepping mechanisms *(41, 58)* whereby the solute is transported randomly in the radial direction as a result of deviations of the mobile phase around the particles; $\psi(\mathrm{Re})$ originates from turbulence in the flow domain $\mathrm{Re} \gtrsim 500$. It is instructive to note *(2)* that the contribution of $\psi(\mathrm{Re})$ to $D_r$ is relatively small—seldom more than 0.1 $(\lambda_R d_p u)$.

Although Eq. (13) is illustrative of the physical processes involved in radial dispersion, experimentally measured data of $D_r$ proves, here again, to be the most reliable way of predicting it over the wide range of parametric values that will be considered in this study. Bernard et al. *(40)* were the first to measure $D_r$ for gases as well as for liquids. They have correlated their data to yield, after rearrangement and upon the addition of $\gamma/\mathrm{Sc}$,

$$\frac{D_r}{\nu} = \frac{\gamma}{\mathrm{Sc}} + \frac{(17.4/\rho^{2.7}) + 0.065}{2.68(\epsilon \mathrm{Re})^{4.28}/(\rho^{1.8} - 0.05)} \mathrm{Re} \tag{14}$$

This correlation is valid only in the higher Re region $(\mathrm{Re} \gtrsim 10)$. For the lower Reynolds number domain $(\mathrm{Re} \lesssim 1)$ the data compiled by Bischoff et al. *(41)* may be used to yield

$$\frac{D_r}{\nu} = \frac{\gamma}{\mathrm{Sc}} + \frac{1}{30} \sqrt{\frac{2\epsilon\rho}{3\rho(1-\epsilon) + 1}}\, \mathrm{Re} \tag{15}$$

Equations (14) and (15) appear to correlate most data excellently at very high $(\mathrm{Re} \gtrsim 50)$ and very low $(\mathrm{Re} \lesssim 0.5)$ Reynolds numbers, respectively, but less well in the intermediate region. The "dividing line" between these equations has been taken at $\mathrm{Re} = 1$.

The variation of $D_r/\nu$ with the various significant parameters is shown in Fig. 1. From this Figure it is evident that $\rho$ does not play a significant role for $\rho > 10$.

## The Plate Height Expression for the Columnwide Region in Terms of Phenomenological Variables

It is important to note at the outset that contributions to the plate height arising from nonequilibrium extending over more than one

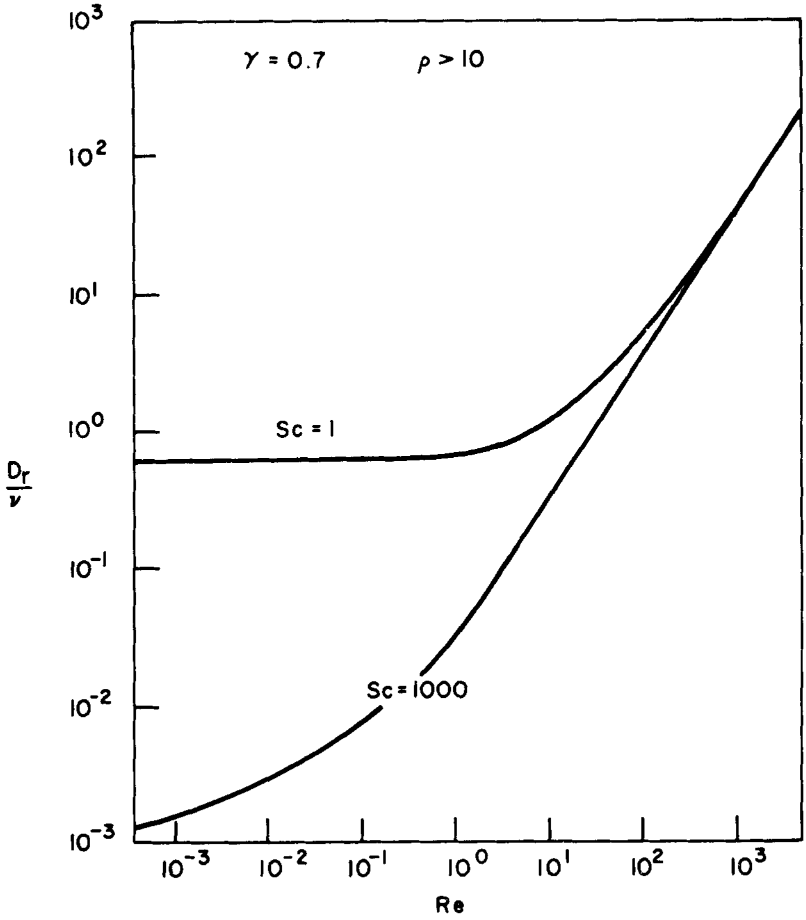

FIG. 1. Variation of $D_r/\nu$ with Re.

particle do not depend on the mass distribution coefficient, $k$ (*1*, *75*). This implies that data available for band spreading at $k = 0$ can be employed to study these effects. Experiments can also be carried out for $k = 0$ and the data extrapolated to the chromatographically significant case of $k > 0$.

On a columnwide scale of observation the detailed packing structure fades and the latter can be taken to be homogeneous. A packed column may thus be regarded as conduit with certain observable properties such as column wide variations in flow velocity where small local velocity variations can be ignored. Material transport in the radial direction is governed by a Ficksian law (*41*) defining, in turn, a radial dispersion coefficient, $D_r$, as is discussed above. In fact the approach now becomes identical to that followed by us (*76*) for the calculation of the plate height for open tubular columns in the turbulent flow region. This approach leads to

$$h = \frac{m\rho^2 \mathrm{Re}}{2D_R/\nu} \tag{16}$$

where

$$m = \int_0^{r_t} \frac{dr}{2r\psi(r)} [\Phi(r) - (r/r_t)^2]^2 \tag{17}$$

and

$$D_r(r) = D_r'\psi'(r) \tag{17a}$$

$$U(r) = \bar{u}\phi(r) \tag{17b}$$

$$\Phi(r) = \int_0^r \frac{2r'\phi(r')dr'}{r_t} \tag{17c}$$

Although it is not possible at this stage to relate $m$ analytically to the various relevant parameters, broad qualitative trends suggest themselves from a consideration of the nature of the velocity profiles. First, the reported (*42*) invariance of the velocity profile with Re [i.e., $\phi(r)$ independent of Re] implies that $m$ is also independent of Re. Second, since the velocity profile becomes flatter as $\rho$ increases, it is to be expected that $m$ will decrease monotonically with increasing $\rho$. Third, one would expect $m$ to be identical for gases and liquids.

## EXPERIMENTAL TEST OF THE PROPOSED PLATE HEIGHT EXPRESSION

A conclusive test for the sufficiency of the approach adopted here would be to measure each of the operationally defined variables in terms of which the plate height has been expressed, i.e., $\chi$, $\lambda$, $\psi'(r)$, $\phi(r)$, $\theta_s$ and, upon substitution into the appropriate plate height expressions, to compare this value with that measured under similar conditions at the column outlet. A simpler, but essentially equally critical, test can be devised for $k = 0$, i.e., where the interparticle contribution to the plate height can be neglected. Here,

$$h(x) = \lambda(\mathrm{Re}) + \frac{m(\mathrm{Re}, \rho)\rho^2\mathrm{Re}}{2D_r/\nu} \tag{18}$$

If it is assumed that $\lambda$, $D_r/\nu$, and $h(x)$ are known from experimental measurement, then

$$m(\mathrm{Re}, \rho) = 2\left[\frac{h - \lambda}{\rho^2\mathrm{Re}}\right]\frac{D_r}{\nu} \tag{19}$$

The test proposed is to show that $m(\mathrm{Re}, \rho)$ is not an arbitrary constant but that it indeed corresponds to the definition of this parameter as given by Eq. (17). Thus the numerical values of this parameter, as obtained by means of Eq. (19), should correspond both qualitatively and quantitatively in their dependence on all relevant parameters with those obtained from Eq. (17). For the evaluation of Eq. (19), $D_r/\nu$ is given by Eqs. (14) and (15). $\lambda = 2$ has been estimated from unpublished experimental data obtained in this laboratory and it has been assumed that $\lambda$ is independent of Re. It is the purpose of the present experimental study to obtain $h$ under controlled conditions.

It is instructive at this stage to summarize the assumptions implicit in the value of $m(\mathrm{Re}, \rho)$ as obtained via Eq. (19), i.e., to summarize what we are actually testing for. First, it must take account of the restricted number of "scales of observation" considered. Second, the experimental inaccuracies in the measurement of $h$ and $D_r/\nu$ must be accounted for. Last, the assumption that $\lambda$ is constant, $\lambda = 2$, and independent of Re may contribute to relegate $m$ to a meaningless empirical constant.

## Experimental Procedure

A very simple liquid chromatograph has been constructed to measure the plate height mainly for unretarded peaks. The general features of the apparatus are shown in Fig. 2.

A syringe type injection system was found to be the most suitable for the present system. The high pressures involved in some operating ranges made sample introduction under stopped-flow conditions necessary. The influence of this procedure on the plate height as measured at the column outlet has been assessed at lower inlet pressures where the sample could also be introduced while the eluate flowed. The measured plate height has been found to be independent of the mode of injection.

Samples of 0.1 *M* KI were used and the volume injected was kept constant at 1 $\mu$l. An increase of this inlet volume up to 5 $\mu$l did not affect the plate height as measured at the column outlet.

For the present purpose the electrolytic oxidation of iodide anions on a carbon electrode served excellently as detector. The linearity of the detector response was determined by adapting the exponential dilution method described by Lovelock (*75*) and it was found to be satisfactory over the range $10^{-4}$–2 *M*.

The fact that the electrodes could be introduced into the packing itself served admirably to reduce detector dead volumes. A number of typical detector constructions used during the course of this investigation are shown in Fig. 2. The time constant could not be measured directly but a rise time from zero to maximum of $5 \times 10^{-2}$ sec was recorded. This implies that the time constant of the detector plus electronics must be smaller than $10^{-2}$ sec, which has been found to be sufficiently low for the present study.

The electrochemical current was measured in a simple bridge circuit and fed onto a Hitachi potentiometric pen recorder. The large time constant of this recorder necessitated the use of an oscillographic recorder (Visigraph FR 201) at higher flow velocities. For this purpose further amplification of the signal by operational amplifiers was found to be necessary. The plate height as measured by both these recorders was the same.

A stainless steel column of internal diameter 0.45 cm and length 300 cm was used.

The column length in this type of study must be sufficient to allow the injected solute to assume a fully Gaussian shape before it is measured at the column outlet (*25*, *26*). The critical length is given by (*26*)

$$L_{\text{cr}} \simeq 0.04\,\frac{\text{Re}\rho^2 d_p}{D_r/\nu}$$

Typically, for $\rho = 40$, $\text{Re} = 100$, $d_p = 10^{-2}$ cm, and $D_r/\nu = 1$ (from Fig. 1)

$$L_{\text{cr}} \simeq 40 \text{ cm}$$

This calculation was checked experimentally by measuring the plate height at a number of points along the column length. These results indicate that *H* increases gradually with distance but it remains constant beyond a certain column length. This distance was found to be always shorter than 100 cm. It should be stressed that for the circumstances

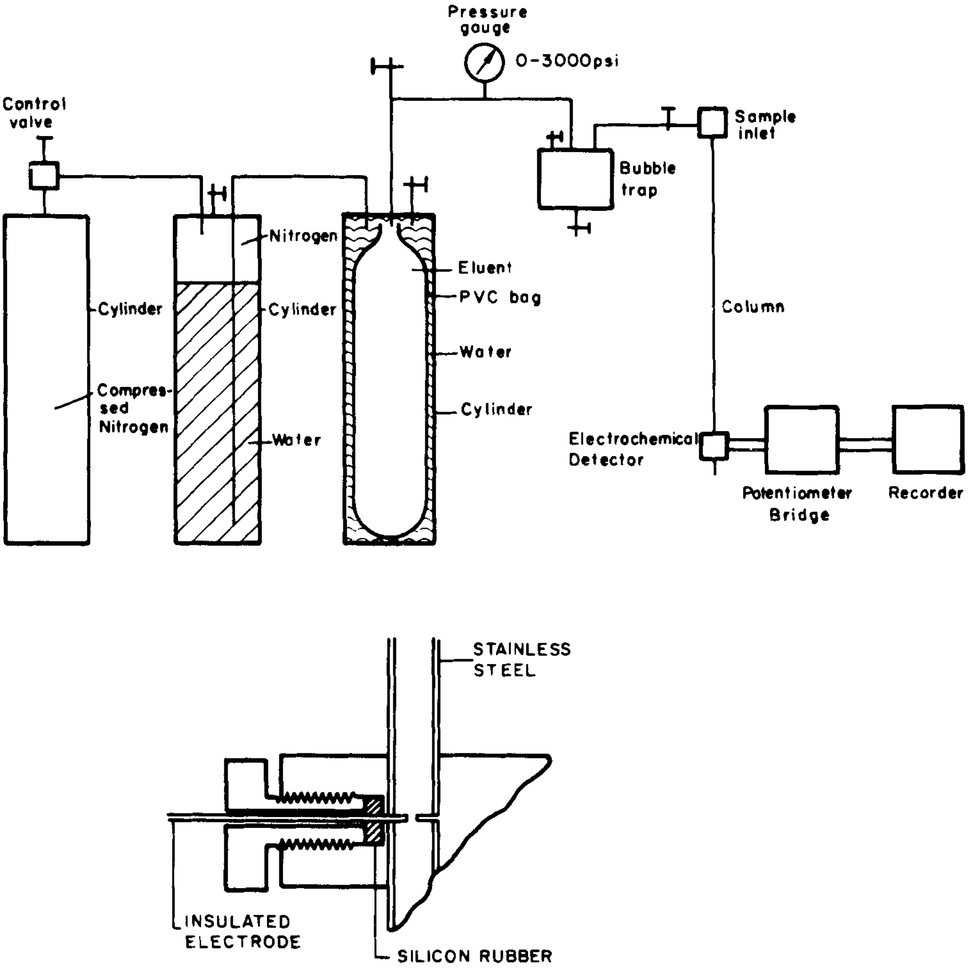

FIG. 2. Some typical features of the liquid chromatography.

used in this study the above-mentioned phenomenon may contribute substantially to reduce the reliability of plate height measurements made in this study and those reported elsewhere.

Spherical glass beads (obtained from Ballotine, England and Microbeads DIV, Cataphote Corp., U.S.A.) have been used for the experiments. The diameters used as well as the range within which 95% of the bead population falls are as follows, $d_p = 114 \pm 7.0$, $150 \pm 10$, $240 \pm 20.0$, $331 \pm 15$, and $493 \pm 30\ \mu$. The column was packed by introducing small amounts of packing successively at the column inlet and subsequently applying high pressure. The column was vibrated for 1 min after each addition.

As mobile phase an aqueous 0.1 *M* $KNO_3$ solution was used. The $KNO_3$ served as supporting electrolyte for the detector. This solvent was placed in a polythene bag which, in turn, was suspended in a steel cylinder connected to a second cylinder to which gas pressure of up to 2400 psi could be applied. The gas pressure was transmitted by means of water to prevent gas diffusion through the plastic bag since dissolved gas tended to boil out in the column packing. A bubble trap inserted prior to the inlet system was found useful.

The reproducibility of plate height measurement was better than 7% for 95% confidence limits.

TABLE 3

Typical Values of *m* Determined from Experimental Data

| $\rho = 13.8$ average $m = 1.26 \times 10^{-3}$ | | | $\rho = 19$ average $m = 0.94 \times 10^{-3}$ | | | $\rho = 40$ average $m = 0.11 \times 10^{-3}$ | | |
|---|---|---|---|---|---|---|---|---|
| Re | $h$ | $m \times 10^3$ | Re | $h$ | $m \times 10^3$ | Re | $h$ | $m \times 10^3$ |
| 0.6 | 7.5 | 0.90 | 0.2 | 6.4 | 0.78 | 0.1 | 4.5 | 0.10 |
| 1.4 | 9.6 | 1.22 | 0.3 | 7.9 | 0. 2 | 0.5 | 5.7 | 0.08 |
| 3.6 | 12.4 | 1.66 | 0.3 | 10.2 | 0.96 | 1.0 | 6.7 | 0.07 |
| 6.8 | 13.5 | 1.84 | 0.5 | 11.3 | 0.89 | 2.1 | 8.6 | 0.10 |
| 7.1 | 13.8 | 1.85 | 0.8 | 14.5 | 0.97 | 2.5 | 9.0 | 0.11 |
| 10.1 | 11.4 | 1.50 | 2.4 | 15.7 | 1.04 | 3.6 | 8.3 | 0.10 |
| 13.1 | 12.2 | 1.63 | 4.7 | 16.8 | 1.14 | 4.21 | 7.8 | 0.09 |
| 16.0 | 10.9 | 1.43 | 7.6 | 16.9 | 1.15 | 5.6 | 9.6 | 0.12 |
| 19.4 | 14.2 | 1.96 | 16.4 | 13.4 | 0.90 | 8.7 | 9.4 | 0.12 |
| 20.4 | 11.1 | 1.47 | 29.4 | 13.1 | 0.89 | 12.6 | 8.1 | 0.10 |
| 20.7 | 9.1 | 1.15 | 59.9 | 11.4 | 0.77 | 16.9 | 9.7 | 0.13 |
| 29.6 | 8.0 | 0.95 | 98.3 | 10.4 | 0.70 | 21.6 | 9.3 | 0.12 |
| 41.6 | 8.5 | 1.06 | | | | | | |
| 42.3 | 6.9 | 0.80 | | | | | | |
| 78.3 | 6.5 | 0.74 | | | | | | |
| 140.4 | 5.8 | 0.63 | | | | | | |
| 202.4 | 5.7 | 0.60 | | | | | | |

## Experimental Results and Discussion

Data obtained by using the techniques described in the foregoing are shown in Fig. 3, as correlated by the dimensionless variables $h$, Re, and $\rho$. The scatter in the data, characteristic of measurements of this type (*41*), would naturally limit the quality of the ultimate information that can be extracted from them. The parameter $m$ has been determined from this data by Eq. (19) together with Eqs. (14), (15), and $\lambda = 2$. Typical data thus obtained is shown in Table 3 for various values of the parameters $\rho$ and Re.

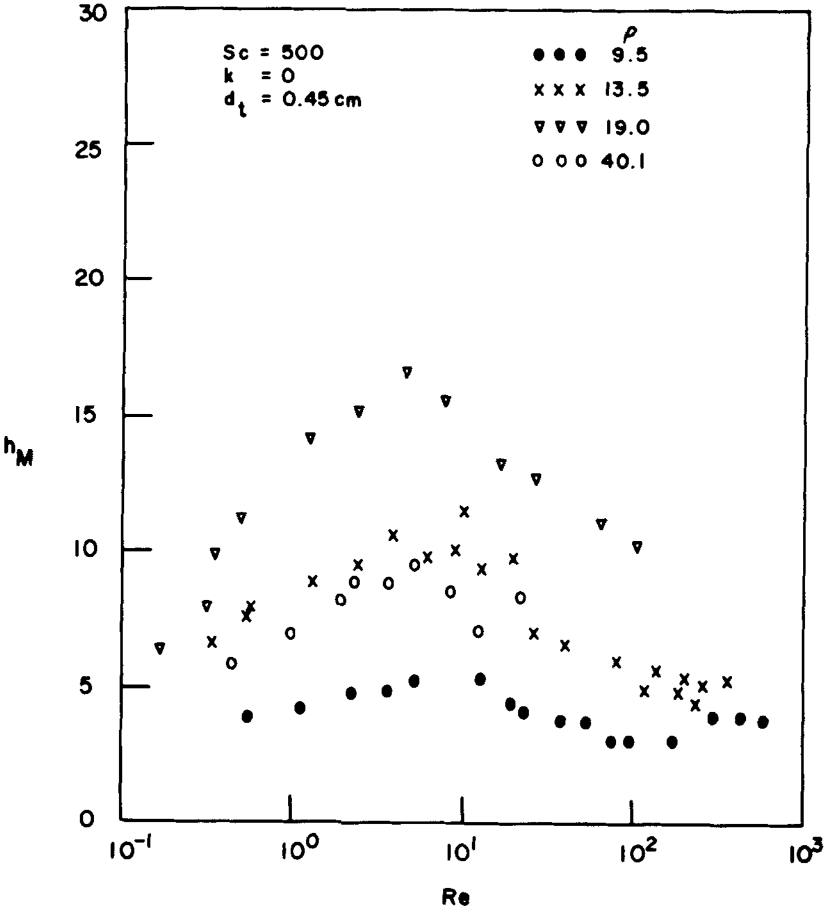

FIG. 3. Experimentally measured values of the reduced plate height.

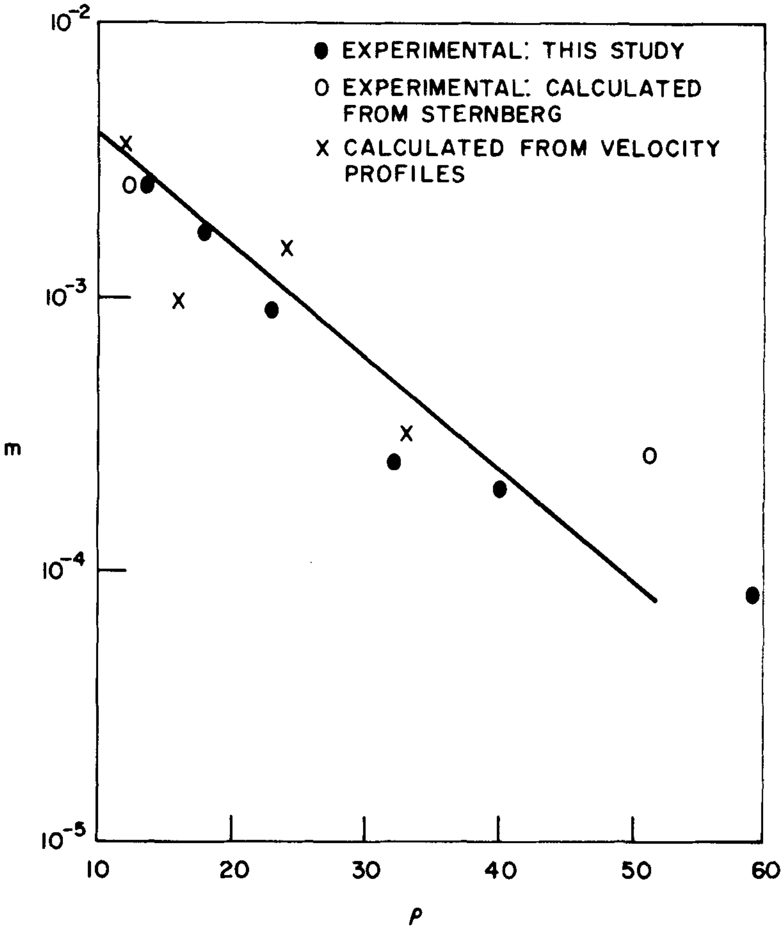

Fig. 4. Compilation of values for $m$ from a wide variety of sources.

These values obtained for $m$ can now, at the outset, be compared with the qualitative trends in $m$ predicted by Eq. (17) and the general characteristics of experimentally measured velocity profiles. First, it is evident from Table 3 that $m$ does not vary significantly with Re. This is especially remarkable if the wide range in the Re values shown is taken into consideration. Second, it is also clear that the average value (not weighted) of $m$ decreases with increasing values of $\rho$.

A more crucial test of the assumptions implicit in the data given in Table 3 would be to evaluate $m$ via Eq. (17) from experimentally measured velocity profiles and by comparing the values of $m$ thus obtained quantitatively with those given in Table 3. For this purpose the data of Schwartz et al. (*42*) has been employed to obtain $\phi(r)$. This, together with the expressions for $\psi(r)$ obtained from Eqs. (14) and (15), has been used to evaluated $m$ as given by Eq. (17). Numerical integration, similar to the methods used previously by us (*76*), has been employed to evaluate the integrals involved. The values of $m$ thus obtained are shown in Fig. 4, together with the average $m$-values obtained experimentally.

In order to obtain values of $m$ for gases, the data of Paulson and Sternberg (*54*) have been used. The values thus obtained are also shown in Fig. 4.

A general consideration of the data compiled in Fig. 4 indicates that, although the correspondence between the various values is not perfect, it is, in the least, encouraging and good enough to validify the approach adopted here for the broad purposes envisaged. The solid line through points is given by

$$m = e^{-\rho/10}/100 \tag{20}$$

and it appears to fit all the data sufficiently well. Equation (20) will be used to relate $m$ and $\rho$ in subsequent work.

## DISCUSSION OF THE PLATE HEIGHT

The results obtained thus far can be summarized by the following expression for the total local plate height

$$\begin{aligned} h(x) &= \lambda + \frac{2\gamma}{\mathrm{ScRe}} + \frac{m\rho^2\mathrm{Re}}{2D_r/\nu} + \frac{C_s\bar{u}(x)}{d_p} \\ &= h_M(x) + h_S(x) \end{aligned} \tag{21}$$

and

$$h_{ip}(x) = \frac{2\gamma}{\mathrm{ScRe}}$$

$$h_c(x) = \frac{m\rho^2\mathrm{Re}}{2D_r/\nu} \tag{22}$$

The value of $m$ is given by Eq. (20) and the relevant expression for $h_{ip}$ can be selected from Table 1.

The evaluation of the success of the proposed plate height expression can be effected the most significantly in relation to experimental data obtained over a very wide range of operating conditions wherever such data exist. Such an evaluation is meaningful, however, only after agreement has been reached on what and how well this expression must be able to predict the plate height. The complete answer to this question may involve one in the philosophy of the status of the theoretical approach in scientific research which, although interesting in itself, will not be pursued any further here. In the present context it is necessary only to point out that the quality of the predictions of the plate height on the basis of theoretical expressions cannot possibly be expected to have a greater accuracy than the existing body of experimental knowledge.

The abundance of empirical data for $k = 0$ makes this situation a natural starting point in this discussion.

### Comparison between Theoretically Predicted and Experimentally Measured Values of the Plate Height for $k = 0$

Theoretical and experimental (*41*, *57*, *58*) values of the local plate height are contrasted in Figs. 5 and 6.

The experimental data shown in Fig. 5 correspond to a large number of independent investigations (*78*, *41*), including those carried out here.

The most striking feature of this data is the relatively weak dependence of $h$ on Re. During a variation of over six orders of magnitude in the Reynolds number, the reduced plate height changes from 2–3 to $\pm 10$, i.e., roughly only a factor 3. It is thus evident that an assumption of $h$ = constant (say roughly 4) will not lead to wild errors where $\rho \geq 20$. It is essentially on this evidence that the $2\lambda d_p$-term in the classical Van Deemter expression (*53*) is based. The theoretical curve shown in Fig. 5 and based on Eq. (21) predicts the experimental data as well as can be expected up to $\text{Re} \simeq 200$. In the higher Re-region the theoretically predicted values of $h_M$ do not decrease as much as those measured experimentally, although it exhibits the same features. Noteworthy among these is that a maximum in the $h_M$ vs. Re curve occurs. The predicted Reynolds number coinciding with the maximum of $h_M$ is about an order of magnitude higher than that found experimentally. This is, however, to be expected since in the establishment of $m$ the flattening of the columnwide velocity profile at high Reynolds

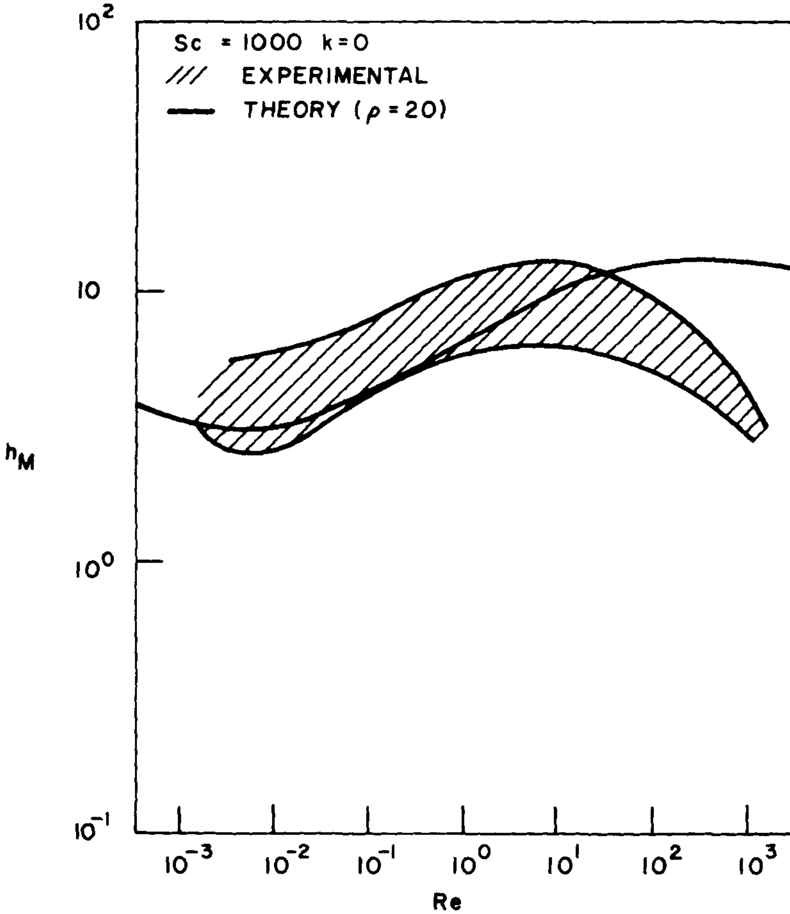

FIG. 5. Comparison between the theoretical prediction of the dependence of $h$ on Re and experimental data.

numbers has not been taken into account. Should sufficient information on velocity profiles in packed columns become available, we are confident that a more detailed evaluation of $m$ will lead to better quantitative prediction of the Re where $h_M$ is a maximum. It must be pointed out, however, that such a study will be interesting in the chromatographic context mainly from an academic point of view since, as will be shown below, in the practical situation, i.e., $k \gtrsim 0$, the contribution to the plate height originating in the interparticle region dominates the others in the high Re-region.

The comparison between the theoretical and experimental predictions of the dependence of $h_M$ on $\rho$, presented in Fig. 6, again shows satisfactory agreement.

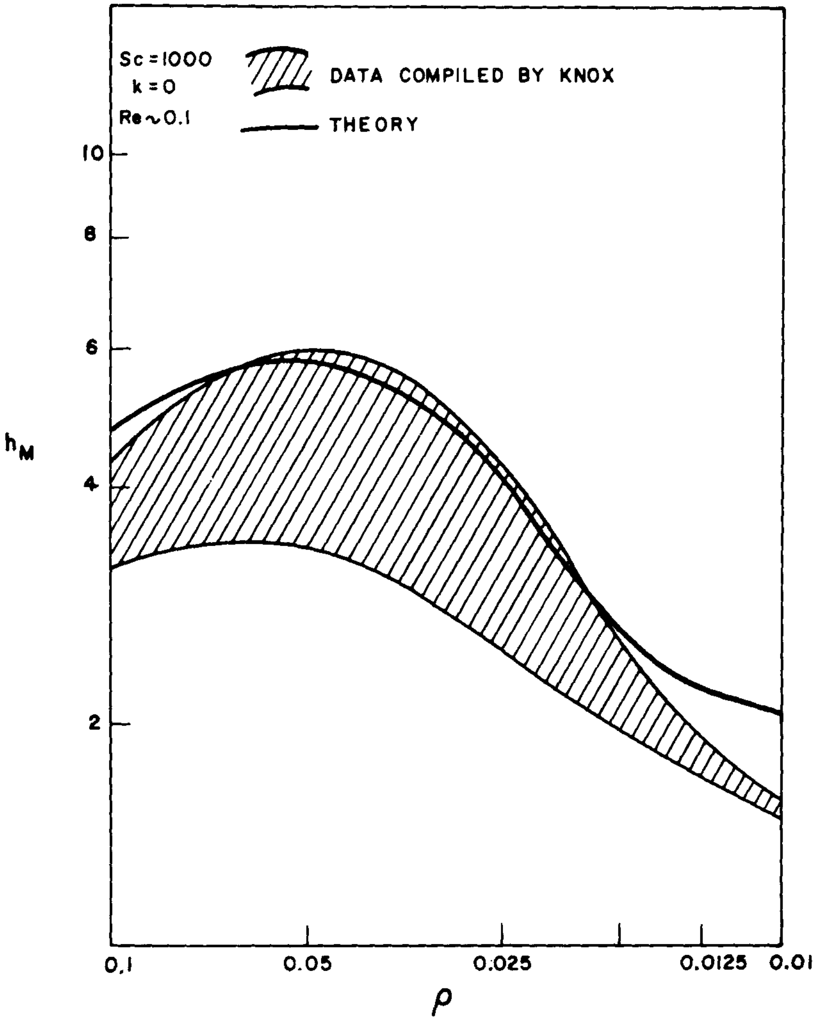

Fig. 6. Comparison between the theoretical prediction of the dependence of $h$ on $\rho$ and experimental data.

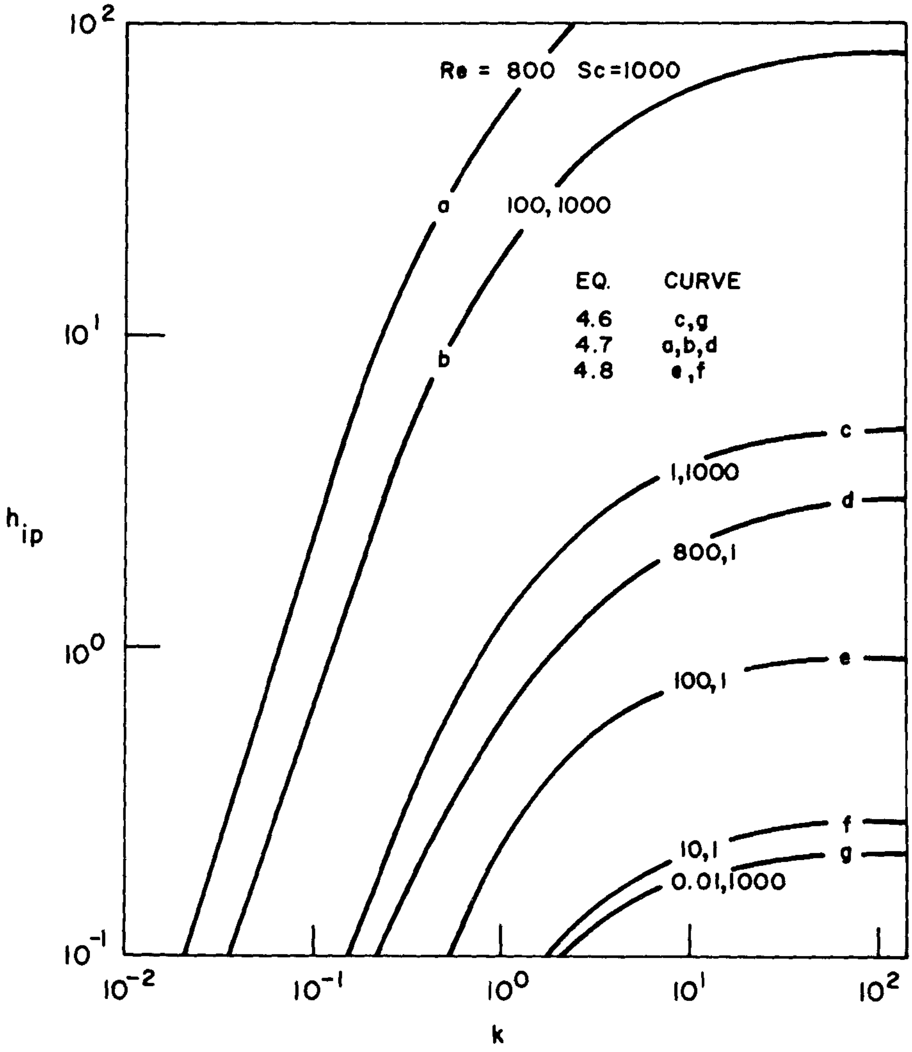

FIG. 7. Dependence on $k$ of the contribution to $h$ originating in the interparticle spaces.

## Consideration of the Case where $k > 0$

Discussion in the present context is largely complicated by a lack of suitable experimental data and recourse must, perforce, be made to fundamental considerations. It would appear that the independence of both λ and $h_c$ from $k$ is fairly well established (*1*, *75*) and the results discussed above for $k = 0$ can be carried over to the present case.

The contribution to the plate height of band-broadening mechanisms residing in the interparticle space, $h_{ip}$, is, on the contrary, strongly

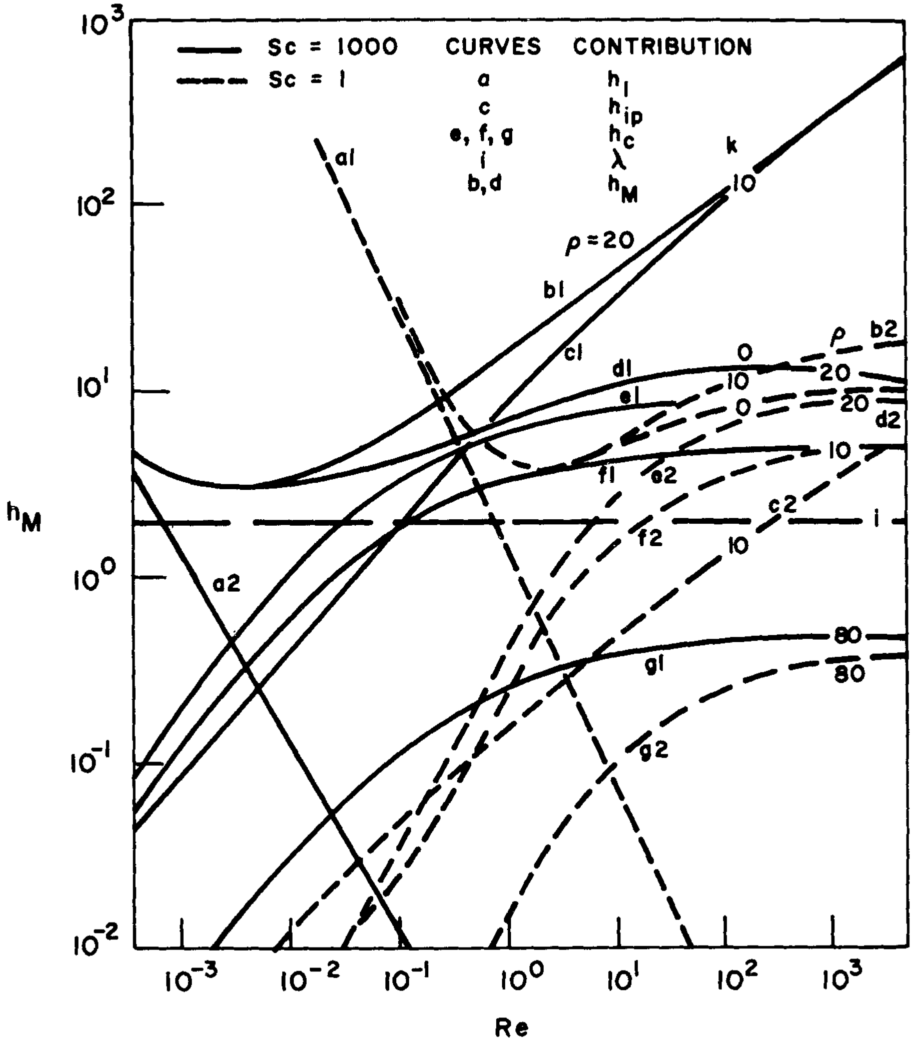

FIG. 8. Comprehensive graphical summary of the behavior of the plate height over a wide range or operating conditions.

influenced by changes in $k$. The extent of this dependence is demonstrated in Fig. 7 from which it is evident that the effect is more pronounced for liquids than for gases and, in both cases, for large values of Re. Although lack of experimental data to test $h_{ip}$ limits the confidence that can be placed in the prediction of its dependence on $k$, it should be stressed that these predictions will, if anything, be too conservative.

This accentuated dependence of $h_M$ on $k$ in the turbulent flow region is one of the most important results of the present investigation. A similar result has been obtained for open tubes (*76*).

Finally, the general trends in $h_M$, as well as of $\lambda$, $h$, $h_c$ and $h_{ip}$, have been summarized in Fig. 8. A few interesting generalizations emerge from these curves. The most striking of these is demonstrated by Curves $b_1$ and $d_1$ from which it is clear that, for liquids, as soon as $k > 0$, $h_M$ increases linearly with increasing Re beyond the Re-value where $h_M$ is a minimum. In the flow region Re $\gtrsim$ 100, $h$ ($k = 10$) is an order or two of magnitude larger than when $k = 0$. It is, furthermore, interesting to note that for gases (Curves $b_2$ and $d_2$) this effect is much less pronounced. Even when $k = 10$ (Curve $b_2$), $h_M$ does not increase linearly with Re but continues to flatten off, although the maximum exhibited by Curve $d_2$ (i.e., $k = 0$) has disappeared.

## CONCLUSIONS

The broad conclusion drawn from the preceding discussion is that the proposed plate height expression, i.e., Eq. (20), is reasonably successful in quantitatively predicting the plate height over a wide range of operating conditions of columns packed with spherical beads. This is particularly satisfying since Eq. (20) is qualitatively founded, molecular longitudinal diffusion aside, on only three simple contributions to the plate height, viz., a velocity independent term, a contribution attributable to columnwide velocity profiles and a $k$-dependent term arising from mechanisms residing in the interparticle region. This simple, but surprisingly accurate, physical picture of the column band-broadening processes is particularly useful since each of the mechanisms proposed, except $h_{ip}$, can experimentally be measured, thereby facilitating the development of better chromatographic columns.

It is significant to note that the proposed expression is an improvement of existing theory in three main respects. First, the expressions for $h_M$ based on the so-called coupling mechanisms proposed by Giddings (*10*) cannot account for the observed maximum of $h_M$ in the high Reynolds number region. These expressions predict an asymptotic approach to an infinitely high-velocity limit. Second, Eq. (20) correctly predicts the dependence of $h_M$ on $\rho$. Third, strong dependence of $h_M$ on $k$, especially for liquids, has not been stressed before for packed beds.

In conclusion it may be worthwhile to explore the implications of this third feature on the practice of liquid chromatography. This equation explains the apparently ambiguous experimental result that while in gas chromatography the plate height differs by about a factor of 4 for peaks eluted with $k = 0$ and $k \gtrsim 10$, in liquid chromatography with a similar stationary phase this factor is much larger. Furthermore, it should also be apparent that the potential advantages of turbulent flow dynamics, from the point of view of analysis speed (*7*, *10*), will be largely offset by the linear increase of $h_M$ with Re in the turbulent flow region. This anticipates the results of a more comprehensive study (*77*) of speed in chromatography, viz., that it is very seldom advantageous to operate a chromatographic column in the turbulent flow region. Finally, since $h_{ip}$ is in the practical case, i.e., $k \gtrsim 0$, the dominating contributor to $h_M$, the plate height in liquid chromatography will be relatively insensitive to $\rho$ i.e., to column diameter for a fixed particle diameter. The consequence in practice is that it will be difficult to construct any column, even of nonspherical particles but provided that $h_{ip}$ still holds, with an $h_M$ value much smaller than those given by Curve $d_1$ of Figure 8. As an example, consider operation at Re = 10. It is irrelevant whether the columnwide contribution to $h_M$ is given by Curve $g_1$, $f_1$, or $e_1$ (Fig. 8) or, for that matter, whether $\lambda = 0$, 1, or 2 since these terms contribute negligibly to $h_M$ for Re $\geq 1$. In the vicinity of the optimum (Re $\simeq 10^{-2}$), however, the various contributions again become comparable, a situation which rarely applies in the current practice using highly efficient chromatographs (*4*).

## LIST OF SYMBOLS

| | |
|---|---|
| $C_s$ | convenient parameter, related to band broadening mechanism residing in the stationary phase |
| $D_m$ | molecular diffusion coefficient in the mobile phase ($L^2T^{-1}$) |
| $D_r$ | radial dispersion coefficient ($L^2T^{-1}$) |
| $D'_r$ | reference value of $D_r$ ($L^2T^{-1}$) |
| $d_e$ | "effective" particle diameter ($L$) |

| | |
|---|---|
| $d_f$ | thickness of a formally uniform layer of stationary phase ($L$) |
| $d_p$ | particle diameter ($L$) |
| $d_t$ | column diameter ($L$) |
| $H$ | plate height measured at the column outlet ($L$) |
| $H_S$ | contribution to $H$ of mechanisms residing in the stationary phase ($L$) |
| $H(x)$ | local plate height ($L$) |
| $h$ | reduced plate height; $H/s$ |
| $h_M$ | $H_M$ measured in units of $s$; $H_M/s$ |
| $h_S$ | $H_S$ measured in units of $s$; $H_S/s$ |
| $h_c$ | contribution to $h$ of band broadening mechanisms peculiar to column wide effects |
| $h_{ip}$ | contribution to $h$ of band broadening mechanisms residing in the interparticle region |
| $K$ | concentration distribution coefficient; ratio of the concentration of solute in the stationary phase to the concentration in the mobile phase at equilibrium |
| $k$ | mass distribution coefficient; ratio of the solute mass in the stationary phase to the solute mass in the mobile phase at equilibrium |
| $L$ | column length ($L$) |
| $m$ | convenient parameter, defined by Eq. (17) |
| Re | Reynolds number; $= d_p\bar{u}(x)/\nu(x)$ |
| $r$ | radial coordinate ($L$) |
| $r_t$ | radius of open tubular column ($L$) |
| Sc | Schmidt number; $= \nu/D_m$ |
| $u$ | linear flow velocity of mobile phase in the axial direction ($LT^{-1}$) |
| $\bar{u}$ | radial average of $u$ ($LT^{-1}$) |
| $x$ | axial column coordinate with the sample inlet point chosen as the origin ($L$) |
| $\gamma$ | packing parameter defined by Eq. (13) |
| $\epsilon$ | porosity of column packing |
| $\theta_s$ | stationary phase parameter defined by Eq. (9) |
| $\lambda$ | contribution to $h_M$ of band broadening mechanisms originating on the intermediate scale of observation |
| $\lambda_R$ | packing parameter, defined by Eq. (13) |
| $\nu$ | kinematic viscosity coefficient of mobile phase ($L^2T^{-1}$) |
| $\rho$ | column to particle diameter ratio; $= d_t/d_p$ |
| $\Phi$ | integral defined by Eq. (17c) |

$\phi$ function, indicative of the lateral variation in the linear velocity, $u$, defined by Eq. (17b)

$\psi$ parameter, dependent upon turbulent intensity in a packed column, defined by Eq. (13)

$\psi'$ function, indicative of the lateral variation in the radial dispersion coefficient, defined by Eq. (17a)

$\chi$ mass transfer coefficient ($LT^{-1}$)

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