

THE ROLE OF LATERAL DIFFUSION AS A RATE-CONTROLLING MECHANISM IN CHROMATOGRAPHY

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A great number of kinetic and diffusion processes influence the resolution obtainable in chromatographic separations. These processes serve to establish local nonequilibrium¹ within the column or paper and consequently smear individual zones. The effect increases as the processes become slower. A first step in improving resolution has followed the basic understanding of the role of these processes as established by GLUECKAUF², THOMAS³, and many others. Until recently, however, no method was available for understanding the role of complex processes involving more than one, or at most two, steps. The basis of the method to be used here for diffusion-controlled processes was evolved for use with complex reaction schemes composed of many simultaneous single-step reactions¹. Application has been made to adsorption chromatography in which the surface is heterogeneous and consists of n different kinds of sites, consecutive reactions (this being an approximation to simultaneous partition and adsorption), the sorption of large molecules, and the simultaneous occurrence of chemical reaction and sorption in chromatography⁴. The solutions obtained by this method are exactly valid only at infinite time, a characteristic which they share with the VAN DEEMTER⁵, GOLAY⁶, and other equations. Fortunately, in chromatography, the equations which apply strictly only at infinite times are usually excellent approximations during most of the running time of an experiment.

As a special case of this method applied to diffusion-controlled processes, results have already been calculated for the effects of bending chromatographic columns⁷. In this case lateral diffusion across the column is the important controlling process. The tubewise nonequilibrium found in that case is in contrast to the nonequilibrium extending over only one or so particle diameters as discussed here.

THEORY

The flow of the mobile phase fluid in chromatography is responsible for establishing nonequilibrium by continually bringing new fluid with varying solute concentration into contact with the fixed bed and its associated stagnant layers. The sorption and desorption processes are opposing this trend by leveling off the concentration excesses and deficiencies. If these processes are rapid, and it is one of the goals in chromatography to make them so, they succeed in establishing a condition with very little

departure from equilibrium soon after a run begins. The nonequilibrium discussed here is always local nonequilibrium, especially that established between mobile stationary phases due to the above processes. This is in contrast to the nonequilibrium always associated with gross concentration gradients such as found in chromatographic zones and boundaries. Assuming simple geometries, the nonequilibrium is established laterally with respect to the flow direction, but with complex media the nonequilibrium is more complicated. Nevertheless the word "lateral" will be used in describing this nonequilibrium and the diffusion acting against it.

If attention is centered on a small volume element in the chromatogram with its coordinates fixed to the stationary support, it can be established that the concentration changes in that element due to three potential sources; the flow of new material directly into the element (operative in the mobile phase only), the longitudinal diffusion into the element due to the gross concentration gradients, and the flux of material due to local nonequilibrium. The equation for these changes in phase i is

$$\frac{\partial m_i}{\partial t} = s_i - v_i \frac{\partial m_i}{\partial z} + D_i \frac{\partial^2 m_i}{\partial z^2} \quad (1)$$

where z is the net flow direction, t the time, m_i the concentration in that phase, D_i the diffusion coefficient of the solute in phase i , and v_i the velocity of phase i at that point. The velocity, of course, must be written as a function of the lateral coordinates since it may vary from point to point across the channel as with parabolic flow. The rate of solute accumulation per unit volume due to local nonequilibrium is designated as s_i . If one assumes the departure from equilibrium to be small, the derivatives of the actual concentration m_i can be replaced by the derivatives of the equilibrium concentration, m_i^* . Thus s_i can be written to a good approximation as

$$s_i = \frac{\partial m_i^*}{\partial t} + v_i \frac{\partial m_i^*}{\partial z} - D_i \frac{\partial^2 m_i^*}{\partial z^2} \quad (2)$$

The first term on the right-hand side can be replaced by the following, provided we again assume conditions near to equilibrium

$$\frac{\partial m_i^*}{\partial t} = -\bar{u} \frac{\partial m_i^*}{\partial z} + \frac{m_i^*}{\sum A_j m_j^*} \sum_j D_j A_j \frac{\partial^2 m_j^*}{\partial z^2} \quad (3)$$

where A_j is the fraction of the cross sectional area occupied by phase j , and the summations extend over all phases. The average downstream velocity of the solute molecules is \bar{u} . This equation can be substituted back into eqn. (2). It can be shown, however, that the longitudinal diffusion terms appearing at the end of both eqns. (2) and (3) are ordinarily negligible¹. Furthermore the two terms tend to cancel one another when the equations are combined. In fact when all values of D_j are equal, the combined term vanishes altogether. We are thus able to write

$$s_i = (v_i - \bar{u}) \frac{\partial m_i^*}{\partial z} \quad (4)$$

An alternate expression for s_i can be written in terms of the "lateral" diffusional transport which it represents (diffusional processes, only, are considered in this paper):

$$s_i = D_i \nabla^2 m_i \quad (5)$$

where the Laplacian operator ∇^2 is to be applied only to local, and not to gross, concentration gradients. The equations are simplified by defining the equilibrium departure term, ε_i , by the equation

$$m_i = m_i^* (1 + \varepsilon_i) \quad (6)$$

Rewriting eqn. (5), and keeping in mind the fact that m_i^* is the local equilibrium concentration and is thus locally invariant, we have

$$s_i = m_i^* D_i \nabla^2 \varepsilon_i \quad (7)$$

Eliminating s_i between eqns. (4) and (7), we have

$$\nabla^2 \varepsilon_i = (v_i - \bar{u}) \frac{1}{D_i} \frac{\partial \ln c}{\partial z} \quad (8)$$

where c is the overall concentration in terms of a unit volume containing a proportionate amount of all the phases. The differential $\partial \ln m_i^*$ has been replaced by $\partial \ln c$ since m_i^* is proportional to c for the linear equilibrium considered here.

A major part of the chromatographic problem is solved if a solution for ε_i can be obtained as a function of the coordinates for each phase i . Eqn. (8) is, mathematically, the well known Poisson's equation, a fact which may be of some use in obtaining solutions to some complex problems. The solutions must be compatible with certain boundary conditions related to the geometry and physical characteristics of the system. The principle types of boundary conditions applying to eqn. (8) are as follows.

(1) The condition that m_i^* results from the local equilibration of all concentrations m_i in the column, and therefore the integral of m_i^* over the total cross sectional area is equal to the integral of m_i over the area. The difference between the terms, $m_i^* \varepsilon_i$, must integrate to zero, $\sum_i \int m_i^* \varepsilon_i dA_i = 0$.

(2) The boundary condition at a non-connecting interface (an interface across which no material flux is possible), $\partial \varepsilon_i / \partial x = 0$.

(3) The boundary condition expressing the equality of fluxes at a connecting interface, $D_i (\partial \varepsilon_i / \partial x) = D_j K_{ij} (\partial \varepsilon_j / \partial x)$, where K_{ij} is the partition coefficient, m_j^* / m_i^* .

(4) The condition expressing equilibrium at an interface (this is usually applicable), $\varepsilon_i = \varepsilon_j$.

(5) Symmetry conditions, which generally lead to expressions of the form $\partial \varepsilon_i / \partial x = 0$ when applied to the center of a symmetrical channel or to the center of a spherical ion exchange bead, etc.

The local nonequilibrium, described above, is responsible for the smearing of zones following the equations of diffusion. The development of this idea is analogous

to that used previously¹, but is summarized here because the equations must be rewritten when the rate-controlling processes are diffusional.

The flux of material through a unit area normal to the flow direction is given by

$$q = \sum_i \int m_i v_i dA_i \quad (9)$$

Using eqn. (6) this rearranges to

$$q = \sum_i \int m_i^* v_i dA_i + \sum_i \int m_i^* \epsilon_i v_i dA_i \quad (10)$$

where the first term on the right-hand side represents the mean convective drift of the zone and the second term on the right-hand side is responsible for zone dispersion and can be equated to $-D_c \partial c / \partial z$.

$$D_c = - \frac{\sum_i \int m_i^* \epsilon_i v_i dA_i}{\partial c / \partial z} \quad (11)$$

Since the ϵ_i terms, obtained from the integration of eqn. (8), are proportional to $\partial \ln c / \partial z$, D_c becomes a diffusion coefficient independent of position and the overall concentration, and proportional to the velocity squared. This coefficient is to be added to the coefficients of ordinary molecular diffusion and eddy diffusion. These terms contribute directly to the flux and when multiplied by the negative of the concentration gradient can, if desired, be added directly on to eqn. (9) as a starting point.

The calculated results for zone spreading can be expressed either in terms of diffusion or plate height. The contribution to plate height due to nonequilibrium effects is $H_c = 2D_c / \bar{u}$. The method outlined above is a very general method for obtaining plate height expressions which can be applied to several special cases now in the literature in addition to numerous other practical cases. Some of these will now be calculated by way of illustration.

CALCULATIONS

Most of the useful models employed in connection with chromatography consist of just two phases; a fluid mobile phase and a fixed stationary phase. While diffusion through these phases is often regarded as the rate-controlling process for mass transfer, it is likely that many actual cases also involve a contribution from single-step reactions. This has been investigated in ion-exchange chromatography, but not in gas and paper chromatography. In the latter cases adsorption, simultaneously with the partitioning process, must often occur in a manner that increases plate height. The methods used in previous papers^{1,4} must be employed to account for single-step reactions of this kind.

The model used to represent the complex geometry of the fixed support and the interstitial fluid is open to some choice, and will ordinarily vary with the kind of

support chosen. The fixed support in ion-exchange chromatography is usually considered to consist of spherical beads, and in gas chromatography, a liquid film of uniform thickness. Randomly oriented cylindrical fibers may be assumed in this role in paper chromatography. The interstitial space, for which order of magnitude estimations are made, is usually not equated to a geometrical model. A model is quite important here, however, since the occurrence of a flow pattern that is essentially parabolic determines the rate-controlling process at high R values. The parabolic nature of laminar flow must consequently be considered in this region. The method used here can easily be applied to a number of simple models, with and without parabolic flow. It is possible to extend the calculations to more complicated models, as shown below, by using a liquid film of variable thickness for gas chromatography. It is anticipated that very realistic results can be obtained by numerical methods applied to a three-dimensional, periodic-lattice model of the fixed phase.

Stationary film of uniform thickness

In this case diffusion in the mobile phase (phase 1) will be considered to be very rapid, and ε_1 will therefore be constant. The geometry of the mobile phase is immaterial in this case. The stationary film is of thickness d_2 . Applying eqn. (8) to this phase we obtain

$$\frac{\partial^2 \varepsilon_2}{\partial x^2} = -\frac{\bar{u}}{D_2} \frac{\partial \ln c}{\partial z} \quad (12)$$

where x is the distance through the film. Integrating with respect to x we get

$$\varepsilon_2 = -\frac{\bar{u}x^2}{2D_2} \frac{\partial \ln c}{\partial z} + g_{02}x + g_{12} \quad (13)$$

where g_{02} and g_{12} are integration constants. The type (1) boundary condition, considering the fact that ε_1 is constant, appears as

$$\varepsilon_1 A_1 = -\frac{KA_2}{d_2} \int_0^{d_2} \varepsilon_2 dx \quad (14)$$

where K is the partition coefficient $K_{12} = (m_2^*/m_1^*)$. The type (2) boundary condition requires that $\partial \varepsilon_2 / \partial x$ must equal zero at the non-connecting interface, $x = d_2$. The type (4) boundary condition requires that the constant ε_1 must equal ε_2 at $x = 0$; $\varepsilon_1 = g_{12}$. These three are sufficient to determine the three constants, ε_1 , g_{02} and g_{12} . Only ε_1 is required in the integral in eqn. (14); ε_2 is multiplied by the velocity $v_2 = 0$, and hence drops out. The constant ε_1 is

$$\varepsilon_1 = \frac{K\bar{u}d_2^2}{3D_2} \frac{\partial \ln c}{\partial z} \frac{A_2}{A_1 + KA_2} \quad (15)$$

Using this in the integral of eqn. (11)

$$D_c = -\frac{m_1^* A_1 \varepsilon_1}{d_1 c \partial \ln c / \partial z} \int_0^{d_1} v_1 dx \quad (16)$$

we obtain

$$D_c = \frac{1}{3} R^2 (1 - R) v^2 \frac{d_2^2}{D_2}, \quad H_c = \frac{2}{3} R (1 - R) v \frac{d_2^2}{D_2} \quad (17)$$

where v is the average mobile phase velocity given by $\int_0^{d_1} (v_1 dx) / d_1$; R is the ratio of zone to mobile phase velocity, \bar{u}/v , and is given by $R = A_1 / (A_1 + A_2 K)$; m_1^*/c is given by R/A_1 ; and K is obtained from the expression for R as $K = A_1(1 - R) / A_2 R$. These expressions will be used in subsequent sections also.

Homogeneous spheres

Again we assume that diffusion in the mobile phase is rapid enough to eliminate lateral concentration gradients in that phase. Consequently each part of the bead's spherical surface will be bathed at the same concentration level. This introduces spherical symmetry into the problem, and we can write eqn. (8) as

$$\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial \varepsilon_2}{\partial r} = - \frac{Rv}{D_2} \frac{\partial \ln c}{\partial z} \quad (18)$$

integration with respect to r gives

$$\varepsilon_2 = - \frac{Rvr^2}{6D_2} \frac{\partial \ln c}{\partial z} - \frac{g_{02}}{r} + g_{12} \quad (19)$$

Boundary conditions of type (1), type (4), and type (5) are applied to evaluate the constants ε_1 , g_{02} , and g_{12} . The value of ε_1 is

$$\varepsilon_1 = - \frac{RvKb^2}{15D_2} \frac{\partial \ln c}{\partial z} \frac{A_2}{A_1 + KA_2} \quad (20)$$

where b is the radius of the bead. When used in connection with eqn. (11), this equation leads to

$$D_c = \frac{1}{15} R^2 (1 - R) v^2 \frac{b^2}{D_2}, \quad H_c = \frac{2}{15} R (1 - R) v \frac{b^2}{D_2} \quad (21)$$

Cylindrical rods

Diffusion into cylindrical paper fibers in paper chromatography must proceed by means of a tortuous path, following the amorphous pathways between the crystalline regions of the fiber. Due to the obstructions the diffusion coefficient is reduced. Since the amorphous and crystalline regions are apparently small compared to the fiber diameter, the diffusion equation still applies. The reasonable assumption is made that the fiber length is great enough to neglect longitudinal gradients in the fiber. Diffusion in the mobile phase is again assumed to be comparatively rapid.

Eqn. (8), written in cylindrical coordinates with the above assumptions, appears as

$$\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial \varepsilon_2}{\partial r} = - \frac{Rv}{D_2} \frac{\partial \ln c}{\partial z} \quad (22)$$

This equation integrates to

$$\varepsilon_2 = -\frac{Rvr^2}{4D_2} \frac{\partial \ln c}{\partial z} + g_{02} \ln r + g_{12} \quad (23)$$

The constant ε_1 is obtained with the application of type (1), (4), and (5) boundary conditions

$$\varepsilon_1 = -\frac{RvKb^2}{8D_2} \frac{\partial \ln c}{\partial z} \frac{A_2}{A_1 + KA_2} \quad (24)$$

where b is the cylinder radius. Use of eqn. (24) with eqn. (11) gives

$$D_c = \frac{1}{8}R^2(1 - R)v^2 \frac{b^2}{D_2}, \quad H_c = \frac{1}{4}R(1 - R)v \frac{b^2}{D_2} \quad (25)$$

Pores of nonuniform depth

In gas chromatography liquid solvent covers rough granular particles and forms a film of nonuniform thickness. The following calculation reveals the nature of the influence of these small, closely spaced heterogeneous regions. Our model calls for $n-1$ pores (each considered to be a different phase) of uniform cross section throughout their length and liquid depth d_i , and each occupying a respective fraction A_i of the total column cross section (or volume). The mobile phase, in which diffusion is assumed to be rapid, is phase 1 whereas the liquid-filled pores are phases 2 through n . For each pore we have, using eqn. (8)

$$\frac{\partial^2 \varepsilon_i}{\partial x^2} = -\frac{Rv}{D_2} \frac{\partial \ln c}{\partial z} \quad (26)$$

where x is the distance of penetration into the pore and D_2 , as previously, is the diffusion coefficient in the stationary phase. This integrates to

$$\varepsilon_i = -\frac{Rvx^2}{2D_2} \frac{\partial \ln c}{\partial z} + g_{0i}x + g_{1i} \quad (27)$$

The type (1) boundary condition appears as

$$\varepsilon_1 A_1 = -K \sum_{i=2}^n \frac{A_i}{d_i} \int_0^{d_i} \varepsilon_i dx \quad (28)$$

The type (2) boundary condition applies at depth d_i and gives

$$g_{0i} = \frac{Rvd_i}{D_2} \frac{\partial \ln c}{\partial z} \quad (29)$$

The type (4) boundary condition gives

$$\varepsilon_1 = g_{1i} \quad (30)$$

These equations can be solved for ε_1 , eliminating the integration constants

$$\varepsilon_1 = - \frac{KRv}{3D_2} \frac{\partial \ln c}{\partial z} \frac{\sum_2^n A_i d_i^2}{A_1 + K \sum_2^n A_i} \quad (31)$$

This equation is analogous to eqn. (15) for a uniform film. Substituting into eqn. (11) and rearranging, we have

$$D_c = \frac{1}{3} R^2 (1 - R) v^2 \frac{\sum A_i d_i^2}{D_2 \sum A_i} \quad (32)$$

where the summations run from 2 to n . The ratio of summations is simply the mean square depth, \bar{d}^2 , averaged over cross-sectional area, or, equivalently, over the total liquid content. It is not the ordinary mean square pore depth as illustrated by the following calculation. If we are considering just two pores of equal radius, and one twice as deep as the other (h and $2h$), the ordinary mean square pore depth is $5h^2/2$, but the proper mean square depth is $3h^2$.

Substituting \bar{d}^2 into eqn. (32), we have

$$D_c = \frac{1}{3} R^2 (1 - R) v^2 \frac{\bar{d}^2}{D_2}, \quad H_c = \frac{2}{3} R (1 - R) v \frac{\bar{d}^2}{D_2} \quad (33)$$

These equations are of the same form as eqn. (17). The introduction of a nonuniform film does not greatly complicate the picture, but does lead to a different interpretation of the film thickness. A similar simplicity has been found to exist with adsorption chromatography on heterogeneous surfaces⁴.

MOBILE PHASE

Calculations for the mobile phase proceed in much the same manner as for the stationary phase. The problem is more complicated, however, for two reasons. First, the geometry is usually more complex as illustrated by comparing the interstitial space with the individual spherical beads in an ion exchange column. Second, the fluid motion in the interstitial space is complicated by viscous forces. For simple geometries, *i.e.*, circular cross sections or flow between parallel faces, the fluid motion is parabolic. It is reasonable to assume that flow of a basically similar type (parabolic) occurs in more complex interstices. Beyond this, the understanding of the non-equilibrium in complex interstitial spaces will probably not be much advanced until numerical solutions to the Navier-Stokes equation and then to eqn. (8) are obtained for some reasonable two and three dimensional lattices. Until then we can only assume the basic correctness of the simpler models.

The problem arising when diffusion in both phases is partially controlling is also important. The contributions to D_c and H_c add*, as will be shown, for some

* Additive terms are those contributing a fixed amount to the plate height irrespective of the rate (diffusion coefficient) in the other phase (see eqn. (49)).

simple geometries. It is questionable if the terms are additive for complex geometries as found in chromatographic columns. This premise is supported by calculations on a model, to be presented shortly.

Mobile-phase fluid with constant thickness and velocity

The simplest assumption for the mobile phase is flow at constant velocity between parallel faces each covered with a stationary partitioning layer. The constant velocity pattern is being used here primarily for comparison with the parabolic profile to be evaluated next. Rapid diffusion is assumed for the stationary phase. The calculations proceed in the same way as shown for the stationary film of uniform thickness. We obtain

$$D_c = \frac{1}{3}R(1-R)^2v^2 \frac{d_1^2}{D_1}, \quad H_c = \frac{2}{3}(1-R)^2v \frac{d_1^2}{D_1} \quad (34)$$

where $2d_1$ is the distance between the faces and D_1 is the diffusion coefficient of solute molecules in the mobile phase. A comparison with eqn. (17) shows a symmetry in D_c such that one is converted into the other if the mobile phase quantities R , d_1 , and D_1 , are exchanged with $(1-R)$, d_2 and D_2 . No such symmetry is exhibited by H_c .

Mobile fluid with constant thickness and parabolic velocity

Laminar flow between parallel faces a distance $2d_1$ apart occurs with a velocity

$$v_1 = \frac{3}{2}v \left(1 - \frac{x^2}{d_1^2}\right) \quad (35)$$

where x is the distance from the center and v , as before, is the average mobile phase velocity. Substituting eqn. (35) into eqn. (8), we obtain

$$\frac{\partial^2 \epsilon_1}{\partial x^2} = \frac{v}{D_1} \frac{\partial \ln c}{\partial z} \left[\left(\frac{3}{2} - R\right) - \frac{3x^2}{2d_1^2} \right] \quad (36)$$

Integration with respect to x gives

$$\epsilon_1 = \frac{v}{2D_1} \frac{\partial \ln c}{\partial z} \left[\left(\frac{3}{2} - R\right)x^2 - \frac{x^4}{4d_1^2} \right] + g_{01}x + g_{11} \quad (37)$$

Application of type (1), (4) and (5) boundary conditions to this gives

$$\epsilon_1 = \frac{v}{2D_1} \frac{\partial \ln c}{\partial z} \left[\left(\frac{3}{2} - R\right)x^2 - \frac{x^4}{4d_1^2} - \frac{d_1^2}{60}(40R^2 - 108R + 75) \right] \quad (38)$$

Eqns. (35) and (38) are substituted into eqn. (11) yielding an equation similar to eqn. (16) except that the term ϵ_1 is under the integral sign. Evaluation of the integral leads to

$$D_c = \frac{1}{3}R \left(R^2 - \frac{12}{5}R + \frac{51}{35} \right) v^2 \frac{d_1^2}{D_1}, \quad H_c = \frac{2}{3} \left(R^2 - \frac{12}{5}R + \frac{51}{35} \right) v \frac{d_1^2}{D_1} \quad (39)$$

These expressions differ from those in eqn. (34), especially at R values approaching unity. An expression equivalent to eqn. (39) has been derived by GOLAY for capillary columns⁶.

Mobile fluid with circular cross section and constant velocity

This problem proceeds along the same lines as the diffusion into cylindrical rods. The results are

$$D_c = \frac{1}{8}R(1-R)^2v^2 \frac{r_0^2}{D_1}, \quad H_c = \frac{1}{4}(1-R)^2v \frac{r_0^2}{D_1} \quad (40)$$

where r_0 is the tube radius. If R and $(1-R)$ are interchanged, this D_c becomes identical in form to the one in eqn. (25).

Mobile fluid with circular cross section and parabolic velocity

This case is analogous to parabolic flow between parallel faces. The important equations are

$$v_1 = 2v \left(1 - \frac{r^2}{r_0^2}\right) \quad (41)$$

$$\frac{1}{r} \frac{\partial}{\partial r} r \frac{(\partial \varepsilon_1)}{\partial r} = \frac{v}{D_1} \frac{\partial \ln c}{\partial z} \left[(2-R) - \frac{2r^2}{r_0^2} \right] \quad (42)$$

$$\varepsilon_1 = \frac{v}{4D_1} \frac{\partial \ln c}{\partial z} \left[(2-R)r^2 - \frac{r^4}{2r_0^2} - \frac{r_0^2}{6} (3R^2 - 10R + 9) \right] \quad (43)$$

These equations take the place of eqns. (35), (36) and (38) for flow between parallel faces. The effective diffusion coefficient and plate height expressions are

$$D_c = \frac{1}{48}R(6R^2 - 16R + 11)v^2 \frac{r_0^2}{D_1}, \quad H_c = \frac{1}{24}(6R^2 - 16R + 11)v \frac{r_0^2}{D_1} \quad (44)$$

This expression for plate height is equivalent to one derived earlier for the influence of lateral diffusion in capillary columns⁶.

The results obtained above for both stationary and mobile phases are summarized in Table I.

TWO OR MORE RATE PROCESSES

The method outlined above can be applied when two or more lateral diffusion processes influence the plate height. However, as already indicated, the calculations become excessively difficult for realistic models of packed columns. It is necessary to choose simple models that still exhibit some of the principle characteristics of the chromatographic nonequilibrium. When dealing with two phases, it is not possible to choose a model for each of the phases independently. It is unreasonable to assemble a model that is geometrically incompatible. Thus one would not assume cylindrical rods for the stationary phase and tubes of circular cross section for the mobile phase since

TABLE I
THE CONTRIBUTION OF VARIOUS GEOMETRIES AND FLOW PATTERNS TO THE PLATE HEIGHT

<i>Rate-controlling diffusion process</i>	<i>Plate height, H_c</i>
<i>Stationary phase</i>	
$D_2 = \infty$, geometry irrelevant	0
Flat film of uniform thickness d_2	$\frac{2}{3}R(1-R)v \frac{d_2^2}{D_2}$
Homogeneous spheres of radius b	$\frac{2}{15}R(1-R)v \frac{b^2}{D_2}$
Cylindrical rods of radius b	$\frac{1}{4}R(1-R)v \frac{b^2}{D_2}$
Pores of nonuniform depth (mean square depth \bar{d}^2)	$\frac{2}{3}R(1-R)v \frac{\bar{d}^2}{D_2}$
<i>Mobile phase</i>	
$D_1 = \infty$, geometry irrelevant	0
Constant velocity and thickness $2d_1$	$\frac{2}{3}(1-R)^2v \frac{d_1^2}{D_1}$
Parabolic velocity and constant thickness $2d_1$	$\frac{2}{3}\left(R^2 - \frac{12}{5}R + \frac{51}{35}\right)v \frac{d_1^2}{D_1}$
Constant velocity in circular tube of radius r_0	$\frac{1}{4}(1-R)^2v \frac{r_0^2}{D_1}$
Parabolic velocity in circular tube of radius r_0	$\frac{1}{24}(6R^2 - 16R + 11)v \frac{r_0^2}{D_1}$

these two geometries are incompatible. The question as to whether all the terms for the stationary phase in Table I are additive to all the terms for the mobile phase when both processes are rate-controlling is meaningless since many of the geometries are incompatible. One cannot tell if the two terms are additive for an ion exchange column of spherical beads since no one has evaluated the nonequilibrium in the interstitial space. Previous assumptions to this effect are unjustified. Hence many of the results in Table I are useful only if the process referred to is rate-controlling. More will be said about rate-controlling processes in the next section.

Simple models, such as flat, adjacent mobile and stationary phases of constant thickness, can be easily evaluated. These models should reveal the nature of *some* of the processes in real columns. The method will be illustrated by a simple model in which fluid of thickness $2d_1$ flows with constant velocity between plates each possessing a retentive layer of thickness d_2 . Integration of eqn. (8) for each phase gives

$$\epsilon_1 = \frac{v(1-R)x^2}{2D_1} \frac{\partial \ln c}{\partial z} + g_{01}x + g_{11} \quad (45a)$$

$$\epsilon_2 = \frac{vRx^2}{2D_2} \frac{\partial \ln c}{\partial z} + g_{02}x + g_{12} \quad (45b)$$

In order to evaluate any or all of the constants, g_{01} , g_{11} , g_{02} , and g_{12} , four boundary

conditions are used: types (1), (2), (4), and (5) are most easily applied. From these, ϵ_1 is obtained as

$$\epsilon_1 = v(1 - R) \frac{\partial \ln c}{\partial z} \left[\frac{x^2 - d_1^2}{2D_1} + \frac{Rd_1^2}{3D_1} - \frac{Rd_2^2}{3D_2} \right] \quad (46)$$

and, with the help of eqn. (11)

$$D_c = \frac{1}{3}R(1 - R)^2v^2 \frac{d_1^2}{D_1} + \frac{1}{3}R^2(1 - R)v^2 \frac{d_2^2}{D_2} \quad (47)$$

These two expressions are the sum of the respective contributions from eqns. (17) and (34). It can similarly be shown that H_c and D_c are composed of additive terms if the flow is parabolic. GOLAY has obtained the latter result, and also finds gas and liquid diffusion terms additive in capillary columns of circular cross section⁶.

In packed chromatographic columns the interstitial space is complicated by the presence of pockets and fissures extending into the support. The diffusion into these will compete with diffusion through the stationary phase to the same general area. That this destroys the additive make-up of plate-height expressions can be shown by the following model, which, while not entirely realistic, does allow for the competition between diffusion in the two phases in getting solute to remote areas of the stationary phase (the high symmetry of the previous cases has disallowed this). Our model consists of deep (depth d_2) narrow pores, alternate ones filled with the mobile phase. These pores each terminate at the boundary of the flat channel occupied by moving fluid. For mathematical convenience it will be assumed that solute exchanges freely back and forth between the pores, and that the pores are sufficiently narrow to prevent any "sideways" nonequilibrium from developing. The relative pore volumes occupied by mobile and stationary phases are a_1 and a_2 respectively. An analysis of this case leads to the following result

$$H_c = \frac{2}{3}(1 - R)^2v \frac{d_1^2}{D_1} \left[\left(\frac{d_1 + a_1d_2}{d_1} \right) \left(\frac{Ka_2 + a_1}{a_2K} \right)^2 \right] \\ + \frac{2}{3}R(1 - R)v \frac{d_2^2}{D_2} \left[\left(\frac{Ka_2 + a_1}{a_2K} \right) \left(\frac{Ka_2D_2 + a_1D_2}{Ka_2D_2 + a_1D_1} \right) \right] \quad (48)$$

where R now equals $(d_1 + a_1d_2)/(d_1 + a_1d_2 + a_2Kd_2)$. The terms in brackets are corrections to eqn. (47). As a_1 and a_2 approach zero and unity, respectively, the bracketed terms approach unity in value. Eqn. (48) is no longer additive in the sense that the kinetics in each phase are responsible for a single term to be added to give H_c . Thus the equality

$$H_c(D_1, D_2) = H_c(D_1, \infty) + H_c(\infty, D_2) \quad (49)$$

is no longer true.

RATE-CONTROLLING PROCESSES

Even though the plate height is not always an additive quantity, an approximate evaluation of the relative importance of the two diffusion processes in the two phases can be obtained by comparing the separate contributions.

Using Table I, and assuming the mobile phase to have parabolic flow between parallel faces, we find the relative contribution to H_c due to the stationary and mobile phases as

$$\frac{H_c(\text{stat})}{H_c(\text{mob})} = \frac{R(1-R)\tau_2}{\left(R^2 - \frac{12}{5}R + \frac{51}{35}\right)\tau_1} = r \frac{\tau_2}{\tau_1} \quad (50)$$

where τ_1 and τ_2 are approximate diffusional relaxation times in the two media; $\tau_1 = d_1^2/D_1$ and $\tau_2 = \bar{d}^2/D_2$ if the nonuniform pore model is being used. It is important to note that the above ratio can be strongly influenced by r as well as the ratio of relaxation times. The quantity r goes to zero as R approaches both zero and one. The limit at $R = 1$ is caused entirely by parabolic flow since if we assume constant flow velocity with the same geometry, we have

$$\frac{H_c(\text{stat})}{H_c(\text{mob})} = \frac{R}{1-R} \frac{\tau_2}{\tau_1} \quad (51)$$

This ratio goes to infinity at $R = 1$. It is clear that it is absolutely necessary to consider the parabolic nature of flow in evaluating the rate-controlling processes at high R values. This result is due to the ability of parabolic flow to cause a dispersion by itself even if absorption is absent. Eqn. (50) must be considered as a reasonably good approximation for actual columns, reflecting the basic nature of viscous flow. The ratio r and $R/(1-R)$ are compared in Fig. 1.

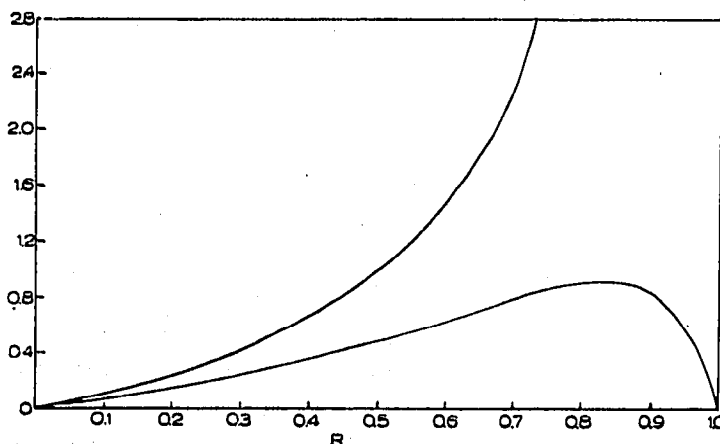


Fig. 1. Relative value of the plate height of the stationary phase to the plate height of the mobile phase for uniform flow (upper curve) and parabolic flow (lower curve).

TABLE OF SYMBOLS

A_i	fraction of cross sectional area occupied by phase i .
a_1, a_2	relative pore volumes occupied by mobile and stationary phases.
b	radius of spherical bead and of rod.
c	overall concentration, with all phases included.
d_1	one half the distance between parallel faces.

d_2	thickness of the stationary film.
\bar{d}^2	mean square pore depth averaged over cross sectional area, eqn. (32).
D_i	diffusion coefficient of solute in phase i .
D_c	nonequilibrium contribution to the diffusion coefficient describing zone spreading.
ϵ_i	equilibrium departure term for phase i , eqn. (6).
g_{02} , etc.	integration constants (see eqn. (13)).
H_c	nonequilibrium contribution to plate height.
K_{ij}	partition coefficient, m_j^*/m_i^* .
K	partition coefficient, m_2^*/m_1^* .
m_i	concentration in phase i .
m_i^*	concentration in phase i under conditions of local equilibrium.
q	material flux for unit area and time.
R	ratio of zone to mobile phase velocity, \bar{u}/v .
r	distance from center of spheres, rods, circular tubes (see also eqn. (50)).
s_i	incoming flux due to lateral diffusion in phase i .
t	time.
τ_1, τ_2	diffusional relaxation times, \bar{d}_1^2/D_1 and \bar{d}^2/D_2 .
u	average downstream velocity of solute molecules.
v_i	local downstream velocity in phase i .
v	average downstream velocity of mobile phase.
x	lateral (or local) coordinate.
z	longitudinal coordinate.

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SUMMARY

A general method is outlined for calculating lateral nonequilibrium when the rate-controlling steps involve lateral diffusion only. The nonequilibrium is responsible for a contribution to the diffusion, or to the plate height, of a zone in a column. The latter is easily calculated from the nonequilibrium. The stationary phase models chosen for calculation include a flat film of uniform thickness, homogeneous spheres, cylindrical rods and pores of nonuniform depth. These models are useful in describing gas, ion exchange and paper chromatography. Mobile phase models include uniform and parabolic flow; both between parallel faces and in circular tubes.

The role of two simultaneous diffusion processes is considered, and the conditions under which these contribute additive terms are discussed. Examples of both additive and nonadditive cases are shown. Finally, the rate-controlling influences of stationary phase and mobile phase diffusion are compared. The importance of parabolic flow, in contrast to uniform flow, is shown at R values near unity.

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