

LATERAL DIFFUSION AND LOCAL NONEQUILIBRIUM IN GAS CHROMATOGRAPHY

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In the previous paper¹ a general equation describing local nonequilibrium in chromatographic media is derived and applied to certain models. The equation relating nonequilibrium to zone spreading (plate height) is also obtained. The application of these concepts to gas chromatography is especially interesting because of the mushrooming interest and intensive theoretical effort applied to the technique. The valid comparison of theoretical and experimental work has proceeded further in this area than in any of the fields of chromatography.

We will be concerned here with the effect of nonequilibrium in gas chromatographic columns. An equation for plate height will be obtained and the contributing terms will be compared to find the rate-controlling step. Of particular interest is the contribution of the controversial "eddy" diffusion term, to be discussed shortly.

THE RATE-CONTROLLING STEP

The relative contribution of diffusion in the stationary phase compared to the mobile phase is given approximately by eqn. (50) of ref. ¹. In gas chromatography, where ordinarily $R \ll 1$, r approaches $35R/51$. In view of the approximate nature of this result, equal confidence can be established for the simpler expression, $r = 2R/3$. Thus

$$\frac{H_c(\text{stat})}{H_c(\text{mob})} = \frac{2R\tau_2}{3\tau_1} \quad (1)$$

An evaluation of τ_2 and τ_1 is more difficult than it appears since it is not clear how the liquid distributes itself over the common solid supports. It is often assumed that the liquid surrounds the support particle with a layer of nearly uniform thickness, but other evidence² shows the importance of deep narrow pores which may easily penetrate to the center.

The ratio τ_1/τ_2 has been estimated at $3.3 \cdot 10^6$ and $4 \cdot 10^4$ for two different cases by VAN DEEMTER, ZUIDERWEG AND KLINKENBERG³. For R values in the neighborhood of 0.01, the ratio in eqn. (1) becomes $2.2 \cdot 10^4$ and $2.7 \cdot 10^2$ for the two cases, indicating the dominant influence of stationary phase diffusion.

If one assumes that the liquid distributes itself as a layer of constant thickness on the outside of a support particle of radius r_0 , then the layer depth is approximately

$d_2 = r_0 f/3$, where f is the volume fraction of liquid referred to the support. This will differ only by a numerical constant from the weight fraction (usually given as weight percent). The depth d_1 (effective thickness of the mobile phase) will be assumed to equal r_0 . While the channels are actually smaller than this, the effect of some non-equilibrium over one or more particle diameters must be allowed for. With the above assumptions the relative contribution to plate height, eqn. (1), becomes

$$\frac{H_c(\text{stat})}{H_c(\text{mob})} = \frac{2RD_1f^2}{27D_2} \quad (2)$$

This clearly depends on the amount of liquid present as well as the other parameters. Assuming $R = 10^{-2}$, $D_1/D_2 = 10^4$, and $f = 0.3$, the above ratio equals $2/3$. This would indicate an even balance between the two diffusion processes.

If now we assume that the pores penetrate to the center of the support particle, and that these are gradually filled up by capillary forces from smallest to largest, then it is reasonable to let both $d_1 = r_0$ and $d_2 = r_0$. Using the same R and D_1/D_2 values, we obtain the ratio of plate heights as 67. This result is independent of the amount of stationary liquid diffusion. It is likely that the actual behavior of stationary liquid is intermediate between the two models given. Thus the plate height ratio increases with f , but not as rapidly as the square of f . Because of the dependence on both R and diffusion coefficients, different solutes in the same run might exhibit the predominance of different diffusion processes. Evidence accumulated in this laboratory indicates the predominance of liquid diffusion by a six to one ratio under typical conditions.

THE PLATE HEIGHT EQUATION

The equation given by VAN DEEMTER, ZUIDERWEG AND KLINKENBERG³ can be written as

$$H = 2\lambda d_p + \frac{2\gamma D_1}{v} + \frac{8}{\pi^2} R(1 - R)v \frac{d_f^2}{D_2} \quad (3)$$

where d_p is the particle diameter and d_f is an effective film thickness. It is assumed here that lateral diffusion into the liquid is rate-controlling. It must also be assumed that longitudinal diffusion in the liquid is not important. This assumption is usually valid with gas chromatography. The eddy diffusion term, $2\lambda d_p$, is assumed to be independent of velocity.

Several questionable points have arisen with respect to eqn. (3). Foremost among these is the repeated appearance of small and even negative eddy diffusion terms⁴. The rate of lateral diffusion in the gas has also been questioned. Several investigators have suggested adding another term for this effect. This at first seems reasonable if we can assume that gas and liquid contributions add. Even though this assumption is fairly good, the assumption that the eddy diffusion and lateral gas-phase diffusion terms add is erroneous. In order to establish this, the respective roles of the two processes will be examined.

The assumption that lateral gas-phase diffusion contributes an additive term

to the plate height, independent of other processes, is based on the picture of a simple, symmetrical interstice model with straight parallel walls. The theoretical behavior of such a model is approached in practice by capillary columns. If a molecule is started in a given streamline within a capillary column, the only mechanism by which it can change its location relative to the wall is lateral diffusion. If the diffusion coefficient, D_1 , were zero, the molecule would remain the same distance from the wall, and due to the lack of lateral equilibration, the plate height would approach infinity.

A different situation exists in a packed column where the streamlines follow tortuous paths. A given streamline will alternately pass near to and far away from the adjacent walls (of the support particles). The distance of nearest approach to a wall can be made arbitrarily small by waiting a sufficient time. Hence there is an effective lateral equilibration even if the extent of lateral diffusion is negligible (since the stream velocity approaches zero at the walls, it may be necessary to postulate the existence of lateral diffusion for a few mean free paths at this location). As a result of this, the plate height remains at a finite value even though the diffusion coefficient approaches zero. It is consequently impossible to have an additive plate height term proportional to d^2_1/D_1 .

The tortuous streamlines just referred to are responsible for the effect known as "eddy diffusion". Two adjacent streamlines may have quite different histories, each one changing randomly from a high to a low axial velocity depending on the configuration of the neighboring support particles. A low velocity, for instance, may be caused by the nearness of the streamline to a particle boundary, or by the presence of a predominating lateral component of the velocity. Each new change in velocity persists for a distance the order of the particle diameter, and this may be considered the length of step in a random walk process⁵. The eddy diffusion is proportional to the length of step as discussed here, and consequently proportional to the particle diameter. At this point it is useful to again consider the role of lateral diffusion. Lateral diffusion serves to shuttle molecules back and forth from one streamline to another. Thus a velocity bias for an individual molecule may not persist for an entire particle diameter, particularly at low velocities where sufficient time exists for several diffusional transfers. This reduction in the length of step causes a reduction in the coefficient of eddy diffusion. The eddy diffusion effect, from this argument, would not contribute a constant, velocity-independent term to the plate height.

The two interrelated effects discussed above, lateral diffusion in the gas phase and eddy diffusion, can both be accounted for in the following picture. In any chromatographic medium, packed or capillary, the axial streamline velocity varies widely from point to point. This variation tends to establish nonequilibrium. Both lateral diffusion and the effective exchange of streamlines in a packed medium act to re-establish equilibrium by redistributing solute molecules relative to the gas-liquid interface. These processes compete with one another in this role. The contributions to plate height by competing processes add as resistances in parallel rather than in series (this is shown, for example, in the calculations on the chromatographic sorption of large molecules where the attachment to the surface can occur in different ways⁶).

this can explain the disappearance of the eddy diffusion term when it is large compared to the lateral gas-phase diffusion term.

The above problem reduces to the correct calculation of local nonequilibrium, in common with the examples of ref. ¹. While considerably more difficulty might be encountered in an accurate analysis of this problem, much can be gained by a closer look at the processes involved. It has been established that two distinct processes are responsible for lateral equilibration in the gas phase. Lateral diffusion itself operates equally near channel boundaries or in the center of channels where the velocity is much larger. The lateral equilibration due to the effective exchange of streamlines operates more rapidly in the higher velocity regions since, to an approximation, a new velocity is assumed after the passage of a constant distance (the particle diameter). There is very little interchange due to this effect in the stagnant layers immediately adjacent to the channel walls. Consequently a situation can exist in which lateral diffusion controls the equilibration rate in the slow moving regions, and the effective exchange of streamlines predominates in the faster moving regions. Although we have assumed that the processes compete throughout, and thus add in parallel, we see that the actual situation is more complicated.

We are now in a position to comment on the name given to the dispersion of solute due to tortuous paths in a packed medium; namely, "eddy diffusion". The name is usually justified because of the tortuous path of flow in analogy to true eddy diffusion. The name has also been attacked as misleading since the Reynold's number is ordinarily far below that necessary for turbulent flow. The preceding discussion has revealed another similitude between true eddy diffusion and the chromatographic process. In certain heterogeneous reaction studies the liquid contents of a vessel are vigorously stirred in order to facilitate equilibration throughout the liquid. It has been found necessary, however, to postulate a diffusion layer adjacent to the surface where molecular diffusion rather than eddy diffusion controls the rate of mass transfer⁷. The thickness of the diffusion layer is inversely proportional to the stirring velocity. In the analysis of chromatography just presented, it was determined that molecular diffusion was controlling the equilibration in a slow moving zone that may likewise be called a diffusion layer. When the layer is shallow compared to the channel dimensions, this diffusion layer, as before, is inversely proportional to the flow velocity. At very low velocities the diffusion layer expands to fill the entire channel, in close analogy to the transition from turbulent to laminar flow. All of these chromatographic processes, of course, occur without the actual presence of turbulence.

Although the picture of eddy diffusion just given might suggest the conclusion that the two mass-transfer resistance terms add in series, it is still believed, when the velocity dependence of the diffusion layer thickness is considered, that the addition as parallel resistances is the best approximation available at this time. Using this approximation and several of the expressions from Table I of ref. ¹ (assuming parabolic flow between parallel faces and nonuniform pore depths), we obtain the following plate height equation:

$$H = \frac{1}{\frac{1}{2\lambda d_p} + \frac{1}{\frac{2}{3}\left(R^2 - \frac{12}{5}R + \frac{51}{35}\right)\nu\frac{d_1^2}{D_1}}} + \frac{2\gamma D_1}{v} + \frac{2}{3}R(1-R)v\frac{\overline{d_2^2}}{D_2} \quad (4)$$

which can be written as

$$H = \frac{1}{1/A + 1/E\phi v} + \frac{B}{\phi v} + Cv \quad (5)$$

The terms A , B , C and E can be obtained by direct comparison of the two equations. The pressure ϕ arises from the inverse pressure dependence of D_1 . The expression for C is admittedly an approximation describing nonequilibrium in a complex system. No matter how this nonequilibrium manifests itself (as long as it remains small), the general equations show us that the contribution to plate height is always proportional to velocity.

The first term of the equation shows several expected characteristics. At high velocities where molecules exchange from fast to slow stream paths almost entirely by following the flow, the term approaches A , the usual eddy diffusion expression. At low velocities where the exchange is due to lateral diffusion, the term approaches $E\phi v$. It is very possible that the average experiment is run in this regime⁵ and that the measured values of $A = 2\lambda d_p$, using eqn. (3), would be near zero. This observation has been often verified. Much careful experimentation is needed before these results can be stated conclusively, however.

SOME UNSOLVED PROBLEMS

While the gross features of the chromatographic process are well understood, many of the finer details, which may involve subtle influences making better separations possible, lack a theoretical interpretation. One need only look at the field of gas-solid chromatography (GSC) where surface adsorption forces predominate, or to gas-liquid chromatography (GLC) where adsorption forces often contribute, to realize that many areas have not been explored. This brief discussion of unsolved problems, along with possible theoretical approaches, deals mainly with kinetics and non-equilibrium in gas chromatography.

One of the unsolved problems in the area of GLC concerns the effect of the kinetics of adsorption at the stationary phase-solid support interface. This is known to occur particularly with polar solutes and nonpolar stationary phases. Adsorption of this kind is usually assiduously avoided even though it might be profitably used if understood. Surface adsorption is potentially capable of offering the most versatile and selective characteristics of any of the known retentive mechanisms. With the advent of extremely sensitive detectors, the problem of overloading adsorption columns is no longer a serious one.

Another problem in this area is the increase in plate height due to using a mixed mesh support⁸. This increase occurs partly in the rate term, H_c . Such an effect is

possibly due to a nonequilibrium extending over several particle diameters caused by an excessive heterogeneity established in the flow and adsorption pattern. It is felt that calculations on a reasonable model, compared to experimental data, might be an important clue here. Finally, in GLC (as in all other chromatography), it is important to acquire more realistic models showing the influence of nonequilibrium in complex media and how this departs from the simple models commonly employed. A two or three dimensional lattice model is proposed for this purpose.

Gas-solid chromatography has received much recent attention. The rate effects include single-step reactions at the surface and lateral diffusion in the gas phase. While these have been treated singly^{1,6}, a combined approach is desired. With highly porous media like charcoal, diffusion into deep narrow pores with adsorption on the pore walls must be accounted for. If the adsorption-desorption process at the wall is rapid enough to essentially eliminate sideways nonequilibrium in the pore, the narrow, adjacent pore model (eqn. (48) of ref. 1) should be used as a first approximation. Again a major challenge occurs in adequately representing a complex geometry—this time, the pore structure of an adsorbent particle.

The influence of "nonuniform" adsorption sites in gas-solid chromatography has been discussed in several places^{9,10}. Nonuniformity is often considered to be objectionable without a proper qualification of the reasons. It is true that if some sites are extremely tenacious, tailing (not related to nonlinearity) may result. Furthermore, the average exchange rate should be maintained as large as possible consistent with good adsorption. Otherwise nonuniformity, *per se*, is not to be avoided (see ref. 6), and may sometime be used as another degree of freedom leading to adsorbent versatility.

Several other techniques introduce complications into the calculation of nonequilibrium. Gas-adsorption layer chromatography, described by CREMER¹¹, must be treated analogously to simultaneous adsorption-partition, as discussed earlier. The use of two or more stationary liquids, especially if these are immiscible, means that up to three phases share the diffusion and nonequilibrium. Nonlinear kinetics, while making the calculation of zone profiles difficult, does not greatly increase the difficulty in calculating local nonequilibrium.

Large columns, used for preparative work, inherit in magnified form some of the nonequilibrium that is unimportant in ordinary columns. The bending of such columns, for instance, introduces a large lateral nonequilibrium that can seriously impair resolution¹². The extent of nonequilibrium is almost negligible in small columns since equilibration occurs rapidly. If the column packing is not uniform in large columns, either with respect to its permeability to gas flow or its relative solute retentivity (R value), nonequilibrium can be serious. Suppose, for example, that a column is uniformly packed except that numerous fine particles accumulate on one side. That side is less permeable and more retentive (lower R value) than the other if it is assumed that the same weight fraction of stationary phase is present on all support particles. A large nonequilibrium will develop since the equilibration is slow. In order to theoretically predict the nonequilibrium, a detailed knowledge of the

packing would have to be available. Information on column packing, realizing that it is not entirely reproducible from one laboratory to the other, might come from visual observations, density and grain size measurements in individual sections, the visual tracking of colored substances flowing through the column (a suggestion by MARTIN¹³), and by measuring the peak spreading due to nonequilibrium and tracing this back to the original nonuniformity. An assumed model of nonuniform packing has been treated by GOLAY¹⁴. His suggestion of speeding up equilibration with mixing washers might not be necessary if more effort were applied to finding uniform packing methods.

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SUMMARY

The occurrence of local nonequilibrium in gas chromatography is investigated. The question as to whether liquid or gas-phase lateral diffusion is the rate-controlling step is discussed in the light of theoretical equations. It is found that this depends, to a large extent, on the distribution of stationary liquid over the solid support. Allowing for both liquid and gas diffusion, and also for the influence of tortuous streamlines leading to eddy diffusion, a new, approximate plate height equation is obtained. Finally, some of the important unsolved problems in the field of gas chromatography are discussed.

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