PLATE HEIGHT IN COILED COLUMNS *

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Under a title similar to the above, MAISEN AND HARDING[1] have criticized certain mathematical approximations used by the writer[2] in obtaining the plate height of coiled and bent columns. With one exception, an oversight corrected in the subsequent literature[3,4], the approximations are integral steps in the generalized nonequilibrium theory[3, 5–8], for which coiled columns are only a special case. Thus their criticism can be discussed in part by reference to this broad theory of chromatography. Before discussing details, we may cite the following evidence in support of the generalized nonequilibrium theory.

1. This theory agrees exactly with the results of GOLAY[9], KHAN[10] and JONES[11] for uniform films of liquids (as on a capillary wall).

2. Exact agreement is found with GOLAY[9] AND KHAN[10] on the plate-height contribution of the flowing gas in a capillary column.

3. The results are identical to an independent method[12] used to study diffusion in ion-exchange beads.

4. Other methods[13–16] confirm the validity of this theory in the study of single-step kinetic processes.

5. Experimental results with a diffusion tube[17] (for measuring gaseous diffusion coefficients) have confirmed the theory to within 5 % accuracy.

6. Experimental results with glass-bead columns[18] have confirmed the theory within a 20–50 % margin on plate height.

7. Experimental results on capillary columns[19, 20] verify the theory in a general way, particularly in regard to the gas phase processes.

The approximations of the generalized nonequilibrium theory are made necessary by the extreme complexity of the dynamics of chromatography. It is not a theory for the exact mathematician who would refuse to proceed at the 95 % level just because the other 5 % could not be handled rigorously. In sacrificing a few percent accuracy, highly simplified results are obtained. The exactness in most cases probably well exceeds the limit of experimental accuracy, thus making the theory perfectly adequate for developing the concepts of chromatography in conjunction with experimental work.

The generalized nonequilibrium theory is based on certain judicious approximations which are related to the fundamental nature of chromatographic processes. The near-equilibrium approximation is the main one. With a few exceptions in preparative work, column efficiency would degenerate almost totally if the near-equilibrium ap-

proximation were not valid. Thus for any effective column the equilibrium departure term, ε, is small compared to unity and can be ignored under the proper circumstances.

The magnitude of ε is determined by equating the accumulation rate of solute, s, based on longitudinal flow and diffusion with that based on lateral diffusion. In the former case the overall concentration is important and ε terms may obviously be ignored. In the latter case nonequilibrium is the sole driving force and ε must be retained. The final error is the order of ε, *i.e.*, about 1–5 %*. The argument of MATSEN AND HARDING, that while ε is small, so are the lateral diffusion effects, is not entirely clear. The value of ε is not being compared to some undefined effects whose dimensions were not stated. It is, instead, being compared to unity.

A second question raised was with respect to the overall mass-balance equation, their equation (4). It is contended that equation (5) should be employed. Now equation (4) is used to obtain the s related to longitudinal flow and diffusion, and we shall be satisfied if our relative error in this term is no larger than ε. As a first step, employing their eqn. (4), the concentration, c, is written as c^* $(1 + \varepsilon)$ and ε is ignored. As a second step the flow-velocity profile is approximated as in the original paper, eqn. (1), *i.e.*, $v = v_0$ $(1 - r \sin \theta / R_0)$, and this is substituted into their eqn. (4). (The maximum error in this approximation, if the ratio of coil to column radius is 10, is only 1 %.) The integration of this equation leads to a result identical to our own, *i.e.*, to eqn. (4). In saying that our equation is applicable only in "trivial cases", the authors are therefore implying that any result with a 1–5 % approximation is trivial. This view is especially erroneous in chromatography where many effects are still uncertain by an order of magnitude.

MATSEN AND HARDING conclude that the two steps just discussed are responsible for a final s equation (their eqn. (6)) which is unrealistic because it is independent of lateral diffusivity. The fact that s (the accumulation rate for solute at a given point) is independent of lateral diffusivity under near-equilibrium conditions is, however, extremely clear on physical grounds. The quantity s is governed by the deficiency or excess (with respect to the mean) of solute flowing into a given region (longitudinal diffusion may be ignored for the sake of this argument). If an excess flows into a particular region as a result of a high flow rate (and thus high flow transport), this will be parceled out to neighboring regions until mutual equilibrium is *nearly* reached. The amount transferred, indicated by the s term, will be governed almost entirely by the excesses and deficiencies, not by the diffusivities. The latter will simply change the concentration difference which is the driving force for diffusion. This difference, compared to the mean concentration, is only the order of ε in magnitude, and is thus unimportant for mass-conservation purposes. (We may think of the accumulation term as resulting from a diffusive flux, which, in one dimension, may be written as $J = -D \partial c / \partial x$. Since J is essentially constant, as shown above, a change in D leads to a change in the gradient, $\partial c / \partial x$. MATSEN AND HARDING apparently did not consider the ch in $\partial c / \partial x$, and thus assumed that J must change, contrary to the physical nature o. near-equilibrium processes.)

Finally MATSEN AND HARDING conclude that the use of two different material flux expressions, their eqns. (7) and (8), is incorrect. In fact, however, these two

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* For the analytical column used in the original paper, assuming a length of 2 m, the extreme maximum of ε, a distance σ from the peak center, is only 0.03. The minimum is zero. On the average in this case, ε can be ignored with respect to unity with only a 1–2 % error.

equations differ by only a small fraction, and their use is to be determined by the role they play in the development of the theory. These roles are distinctly different, each involving a different order of approximation, and their respective uses are entirely proper within this framework. They cannot both be right, as stated by MATSEN AND HARDING, but they can both be valid approximations to be used where appropriate.

For the most part the objections to the original theory are based on a few of the approximations made. No proof is given that these approximations are incorrect. Instead, it is stated that such approximations would be more safely reserved for the final equations. By the authors' own admission, however, the final equations cannot even be obtained without first making the approximations. Thus they must limit themselves to such special cases as that of zero diffusivity, the equations for which would be valid only for preparative columns approaching infinite diameter. The necessity to proceed with reasonable assumptions will always be an integral part of chromatographic theory. That the assumptions of this theory are valid is shown by the foregoing arguments and confirmed by the extensive agreement with other theories and data as mentioned at the beginning.

The only valid criticism of the earlier coiled-column equation is related to the equivalence of the length of flow paths. This error has long been recognized by this writer, and was corrected in the literature early in 1963[3,4]. The correction[4] is a simple matter, not requiring the explicit use of toroidal coordinates as suggested. The functional form of the original equation was correct but a numerical correction factor of 4 must be applied. The true plate-height equation is:

$$H = \frac{7\, v r_0^4}{12 R_0^2\, \gamma D_g}$$

where v is flow velocity, r_0 is tube radius, R_0 is coil radius, D_g is gaseous diffusion coefficient and γ is the obstruction factor for molecular diffusion in the gas.

SUMMARY

The main approximations used by the author in an earlier treatment of coiled columns are justified. This refutes the recent arguments of MATSEN AND HARDING[1] on this matter. A corrected equation for plate height in coiled columns is given.

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