COILED COLUMNS AND RESOLUTION IN
GAS CHROMATOGRAPHY*

J. CALVIN GIDDINGS

Department of Chemistry, University of Utah, Salt Lake City, Utah (U.S.A.)

(Received August 5th, 1959)

There are a large number of ways in which nonequilibrium effects can arise in chromatography, and each serves to increase the height equivalent to a theoretical plate (H). The best known sources of nonequilibrium are in the adsorption or partitioning processes themselves[1]. However, nonequilibrium will be found in general whenever molecules can exist in different states traveling with different velocities, and which convert into one another at a finite rate. Molecules in the mobile and in the stationary phases represent these states in the ordinary case. In the case of coiled columns, used particularly in gas chromatography, molecules near the inside are traveling at a greater velocity than those near the outside, leading to a nonequilibrium laterally across the column. Nonequilibrium of this type also arises as a result of wall effects and column inhomogeneity[2]. This effect can easily be calculated for coiled columns under the assumption that the departure from equilibrium is not large. The method used for this calculation is an extension of that used to describe nonequilibrium between the stationary and mobile phases[3]. The method can be used for nonequilibrium effects in general.

Let us assume that a column has a circular cross section of inside radius r_0 and that the packing is essentially homogeneous so that no other nonequilibrium effects arise. The column is bent with a radius of curvature at the center of the tube, R_0. For the purpose of deriving the equations, R_0 does not have to remain constant along the length of the column as it is for coiled columns. We will also assume that the radius of curvature R_0 is much larger than the tube radius r_0. This simplifies the equations which are obtained.

The mean local carrier velocity v in the tube is related to the velocity v_0 at the center by the equation

$$\frac{v}{v_0} = \frac{R_0}{R_0 + r \sin \theta} \cong 1 - \frac{r \sin \theta}{R_0} \tag{1}$$

where r is the distance from the tube center and θ is the angle measured from a line extending through the tube center and perpendicular both to the tube direction and to a line joining the tube to the center of curvature. Lateral concentration gradients are established because of the nonuniform character of the velocity, and lateral

diffusion results from this. The accumulation of solute per unit time and volume due to lateral diffusion is given by

$$s = RD \left(\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial c}{\partial r} + \frac{1}{r^2} \frac{\partial^2 c}{\partial \theta^2} \right) \tag{2}$$

where c is the overall concentration of solute per unit volume of the column, R is the equilibrium fraction of molecules in the mobile phase, and D is the coefficient of lateral diffusion. The latter quantity, while approximately equal to the diffusion coefficient of the solute, is altered to some extent by the presence of a porous media.

The total rate of accumulation of solute at a given point is given by the sum of all contributions including convection (second term) and longitudinal diffusion (last term)

$$\frac{\partial c}{\partial t} = s - vR \frac{\partial c}{\partial z} + D_z R \frac{\partial^2 c}{\partial z^2} \tag{3}$$

The overall coefficient of diffusion D_z, in the tube direction, z, is the sum of coefficients due to molecular diffusion, eddy diffusion and the diffusion due to rate effects.

It is now assumed that the departure from equilibrium is not large. Thus the difference between the actual concentration c and the concentration assuming complete lateral equilibration, c^*, is small. If we write $c = c^* (1 + \varepsilon)$, then ε is small compared to unity. This permits us to replace each partial derivative of c by a partial derivative of c^* in eqn. (3).

$$s = \frac{\partial c^*}{\partial t} + vR \frac{\partial c^*}{\partial z} - DR \frac{\partial^2 c^*}{\partial z^2} \tag{4}$$

The overall mass balance equation gives an alternate expression for $\partial c^*/\partial t$

$$\frac{\partial c^*}{\partial t} = - v_0 R \frac{\partial c^*}{\partial z} + DR \frac{\partial^2 c^*}{\partial z^2} \tag{5}$$

Combining this with eqn. (4) we obtain

$$s = (v - v_0) R \frac{\partial c^*}{\partial z} \tag{6}$$

Eliminating s/R between eqns. (2) and (6), and using $(v - v_0)$ as obtained from eqn. (1)

$$\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial c}{\partial r} + \frac{1}{r^2} \frac{\partial^2 c}{\partial \theta^2} = - \frac{v_0 r \sin \theta}{R_0 D} \frac{\partial c^*}{\partial z} \tag{7}$$

Since $c = c^* (1 + \varepsilon)$ and $\partial c^*/\partial r$ and $\partial c^*/\partial \theta$ are zero because c^* is an equilibrium concentration, we have

$$\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial \varepsilon}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \varepsilon}{\partial \theta^2} = - \frac{v_0 r \sin \theta}{R_0 D} \frac{\partial \ln c^*}{\partial z} \tag{8}$$

The boundary condition on this equation requires that the concentration gradient disappear at the wall, $(\partial \varepsilon/\partial r)_{r_0} = 0$, and furthermore it is required that ε integrated over the cross sectional area of the tube be zero. The solution to eqn. (8) which satisfies these conditions is found to be

$$\varepsilon = \frac{- v_0 r \sin \theta}{8 R_0 D} \frac{\partial \ln c^*}{\partial z} (r^2 - 3 r_0^2) \tag{9}$$

The effect of the nonequilibrium shown quantitatively in eqn. (9) can be evaluated by obtaining the material flux, q, per unit area averaged over the column or tube cross section.

$$q = \frac{\iint cRvr \, d\theta \, dr}{\pi r_0^2} = \frac{c^* R \iint vr \, d\theta \, dr}{\pi r_0^2} + \frac{c^* R \iint v\varepsilon r \, d\theta \, dr}{\pi r_0^2} \tag{10}$$

The range of integration for θ is 0 to 2π, and for r is 0 to r_0. Using eqn. (1) for v and eqn. (9) for ε, and integrating, we obtain

$$q = c^* R v_0 - \frac{7 v_0^2 r_0^4 R}{96 R_0^2 D} \frac{\partial c^*}{\partial z} \tag{11}$$

The first term on the right is the flux that would be found if there were no nonequilibrium. The second term on the right is proportional to the equilibrium (average) concentration gradient, and therefore behaves identically to diffusion. The effective diffusion coefficient is

$$D_c = \frac{7 v_0^2 r_0^4 R}{96 R_0^2 D} \tag{12}$$

This parameter describes the smearing of a solute zone due to column bending, and is an effect over and above usual smearing effects. Instead of writing this as an effective diffusion coefficient we can write it in terms of plate height[1] where $H = 2D_c/Rv_0$, or

$$H = \frac{7 v_0 r_0^4}{48 R_0^2 D} \tag{13}$$

These expressions, in common with all nonequilibrium effects, show H to be proportional to v_0 and D_c to be proportional to v_0^2. The best known example of this dependence is found in the last term of the van Deemter equation.

A result analogous to the above can be derived for tubes with a flat cross section. If w is the distance from the near to the far wall, and R_0 is again the distance from the center of curvature to the center of the tube, the nonequilibrium parameter ε becomes

$$\varepsilon = \frac{- v_0 x}{24 R_0 D} \frac{\partial \ln c^*}{\partial z} (4x^2 - 3w^2) \tag{14}$$

Using this, as before, to get the flux, we then obtain the effective diffusion coefficient and H

$$D_c = \frac{v_0^2 w^4 R}{120 R_0^2 D}, \qquad H = \frac{v_0 w^4}{60 R_0^2 D} \tag{15}$$

These expressions differ only by a constant factor from those for circular cross sections.

The influence of column coiling is not great for the usual dimensions employed in gas chromatography. However, for columns used for preparative work it can be very significant since H increases with the fourth power of the tube radius. Let us calculate the order of H for a column in which $r_0 = 0.3$ cm, $R_0 = 5$ cm, $v_0 = 10$ cm sec^{-1} and $D = 0.1$ cm^2 sec^{-1}. For this case, which is not atypical, eqn. (13) yields $H = 0.006$ cm or 0.06 mm. A well packed column will yield an overall H something less than 1 mm; hence this effect is of the order of 10 % for the parameters stated.

Now suppose we have a preparative column in which $r_0 = 4$ cm, $R_0 = 40$ cm, and D and v_0 are as before. In this case we obtain $H = 2.3$ cm which certainly cannot be tolerated as far as resolution goes. In cases of this kind, where H is calculated to be excessively large, the assumption that the system is near equilibrium is not correct. This does not help the situation, however, since the degree of smearing is of the order calculated except that a great deal of asymmetry will also be introduced into the zone. It would be advisable to always keep such columns straight, for even a single bend through 90° or less would destroy the resolution obtained through careful packing.

SUMMARY

Equations have been derived for the effect of coiling and bending chromatographic columns. Examples from gas chromatography are used to calculate the plate height due to bending. The plate height is small in most cases, but for the larger preparative columns it is sufficient to annul an otherwise good separation.

REFERENCES

[1] J. C. GIDDINGS, *J. Chromatog.*, 2 (1959) 44.
[2] M. J. E. GOLAY, *Proc. Second Intern. Gas Chromatography Symposium, Michigan State University,* June 1959.
[3] J. C. GIDDINGS, *J. Chromatog.*, 3 (1960) 443.