REDUCED PLATE HEIGHT EQUATION: A COMMON LINK BETWEEN CHROMATOGRAPHIC METHODS

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It has long been recognized that a critical requirement for chromatographic separation is the development of zones whose "width" is no greater in magnitude than the distance separating them[1]. Since the plate height is conventionally used to express zone width or zone spreading it is particularly important to understand the physical basis of this parameter and the lower limits to which it can be restrained.

While the first step in improving the resolving power of a method is in understanding the ultimate potential of the system, one hopes to avoid the necessity of treating each variation in technique as a new and separate problem. Since nearly all chromatographic techniques are based on the same molecular physics, it should be possible to relate the different methods to a single plate-height equation. This "universal" equation would then serve to demonstrate the ultimate capabilities of all systems at one and the same time.

In an earlier paper[2] it was shown that inert (non-sorbed) zones in gas and liquid chromatography could be treated by the same equation providing reduced variables were used. The present development is an extension of this concept, along with its practical application, to working chromatographic systems.

The theoretical equation for the plate height of a chromatographic system may be written in the form[3]:

$$H = \frac{2\gamma D_m}{v} + \frac{2\gamma_s D_s (1 - R)}{v \quad R} + Cv + \sum_i \frac{1}{1/2\lambda_i d_p + D_m/\omega_i d_p^2 v} \qquad (1)$$

where v is the average velocity of the mobile phase, γ and γ_s are the longitudinal diffusion parameters for the mobile and stationary phases, respectively, and D_m and D_s the corresponding diffusion coefficients for these phases, R is the retention factor ($\cong R_F$), d_p is the mean particle diameter, ω_i is one of the mass transfer parameters for the mobile phase and λ_i is the corresponding eddy diffusion parameter. The coefficient C, of great importance, is a mass transfer term representing the finite rate of adsorption–desorption in adsorption chromatography and the finite rate of diffusion in the stationary liquid of a partion column. This parameter, representing the total "rate" effects of the stationary phase, has been studied in detail[3], but the numerous forms assumed by C in different circumstances precludes its more specific elaboration here.

Dimensionless variables of the following nature[2] serve to reduce equation (1) to a more universal form:

$$h = H/d_p, \quad v = d_p v/D_m \tag{2}$$

where h is the "reduced plate height" and v the "reduced flow velocity". In addition the two dimensionless parameters:

$$\Omega = CD_m/d_p^2, \qquad \beta_s = (1 - R)\gamma_s D_s/R\gamma D_m \tag{3}$$

are useful. With these changes eqn. (1) gives the following dependence of h upon v:

$$h = \frac{2\gamma}{v} + \frac{2\gamma\beta_s}{v} + \Omega v + \sum \frac{1}{\frac{1}{2}\lambda_i + 1/\omega_i v} \tag{4}$$

The first and the last terms of this equation, representing the mobile phase effects, depend only on the structural parameters γ, the λ_i's and ω_i's (in addition to the reduced velocity). These terms do not depend on the specific properties of the solute and the mobile phase, such as the diffusivity D_m, and they are independent of the mean particle diameter d_p. Since the structural factors are nearly the same for any random packing of particles, the first and last terms of the equation have essentially the same dependence on reduced velocity v irregardless of the nature of the chromatographic system. (This rule is violated when the column diameter to particle diameter ratio becomes excessive and trans-column mass transfer becomes significant[4].). Thus the h — v curve due to mobile phase effects alone shows an irreducible minimum below which the plate height cannot be taken by *any* manipulation of column parameters. An approximation to this minimal curve (using approximate structural parameters for packed media) is shown by the lowest line in Fig. 1. Even at optimum

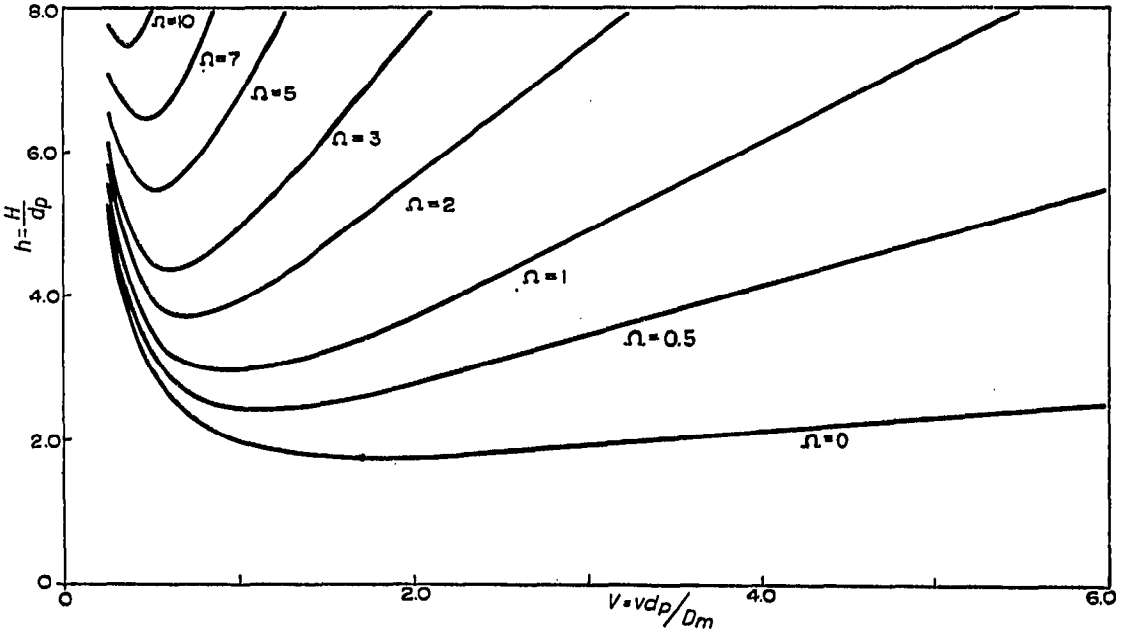

Fig. 1. Reduced plate height as a function of reduced velocity. The curve with $\Omega = 0$ is caused by mobile phase effects only. The other curves show the increase in plate height as the sorption–desorption processes become unduly slow.

velocity the value of h cannot be reduced much below 2, *i.e.*, the plate height H cannot be pushed much below 2 particle diameters.

While the mobile phase contribution to plate height in a packed column is determined within rather inflexible limits, the same is not true for the stationary phase contribution given by the middle two terms of eqn. (4). The $\Omega\nu$ term, particularly, may vary over wide limits. Excessive values of Ω may destroy the resolution of an otherwise excellent column. This is shown in Fig. 1 where the $\Omega\nu$ term is added to the "minimal curve" for different values of Ω. (The β_s term, negligible in many columns, will be assumed as zero in these plots.). The effectiveness of separation, indicated by the smallness of h, is decreased as Ω increases. The plots show that resolving power is seriously hindered for Ω values greater than unity. We will thus regard unity as an upper desirable limit to Ω, and briefly indicate how this limit may be achieved in practical columns.

The parameter C, which has the dimensions of time, is a measure of the speed of the sorption–desorption process in or on the stationary phase. Since the Ω parameter has been limited to a value of unity or less the maximum C value, from equation (3), is:

$$C \leq d_p^2/D_m \tag{5}$$

Two general rules can be formulated from the above expression. They are:

(1) The requirement for rapid equilibration (small C) increases with the square of the particle diameter. If C already contributes a significant part of the plate height there is little use in reducing the particle diameter further. For those systems in which C is naturally small (some forms of adsorption chromatography) a reduction in d_p may be very helpful.

(2) The speed of equilibration must increase as the mobile phase diffusion coefficient increases. Thus gas chromatography, with D_m values about 10^5 times larger than in liquid chromatography, makes much more stringent demands on the equilibration processes. Likewise a hydrogen or helium carrier gas demands more of the system than a nitrogen carrier, but the effect is not so large in this case.

An application of rule (2) serves as a useful example. It is known that gas–liquid partition chromatography operates effectively when the stationary liquid is accumulated in pores about one micron in diameter[5]. Therefore liquid-partition chromatography should operate successfully with the partitioning liquid in units as large as $\sqrt{10^5} \times 1\ \mu \cong 300\ \mu$ in diameter, if necessary. Since particle diameters are usually less than this, it can be concluded that equilibration in the stationary liquid phase, when there are no side effects due to adsorption or other influences, is rapid enough not to hinder chromatographic performance. This conclusion applies, of course, only when the liquid system is operated in the same range of ν values as the gas system. This example does show, however, that empirical results from one chromatographic system may have an important bearing on the performance and limitations of many different techniques.

The curves shown in Fig. 1 demonstrate that the optimum performance of an efficient column occurs at a reduced velocity of between 1 and 2. If the minimum occurs at a point much less than this the system is in need of redesigning. Quite often the velocity will be increased beyond the optimum in order to increase the speed of analysis. This is particularly true in liquid chromatography where the optimum ve-

locity, obtained from equation 2 with $\nu = 1$, is about 10^{-4} cm/sec (the optimum velocity in gas chromatography is about 10 cm/sec). It is especially important in such high-speed chromatography that C be small, perhaps even less than the limit suggested by equation (5).

In summary we may say that the reduced plate-height expression of equation (4) contains a group of structural factors (γ, λ_i, ω_i) which are essentially universal constants. It also contains two parameters, β_s and Ω, characteristic of the stationary phase. The desirability of the stationary phase must be judged in terms of the properties of the mobile phase. This comparison is already made once we have reached the stage of equation (4), and relatively simple criteria thus exist for the effectiveness of the stationary phase, *i.e.*, β_s and Ω should be less than unity. These criteria are not quantitatively rigid because of the varying requirements of the experimentalist; indeed they could not be quantitatively exact because the structural factors are not precisely the same for any two columns. In addition some difficulty might be encountered in determining the molecular diffusion coefficients, and approximate estimates might be required. Nonetheless equation (4) comes very close to forming a practical and quantitative bridge between the different forms of chromatography, and the universal plots of Fig. 1 demonstrate the common goal sought in the resolving power of any systems.

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SUMMARY

In order to correlate the behavior and performance obtained from the many diverse forms of chromatography, a universal plate-height equation is proposed. This equation is based on the fundamental processes which are characteristic of all methods. A plot of reduced plate height versus reduced flow velocity should yield a set of universal curves, approximated by the equation, which will be applicable to any system under any operating conditions (temperature, etc.). This concept shows the possibility for relating experimental results obtained on different systems and thus transferring experimental knowledge from one system to another.

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