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Transfer Characteristics of Packed Columns, Determined by Frontal Gas Chromatography

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Summary

A frontal-gas-chromatographic method is described for the determination of effective gas diffusion coefficients and constants of the first-order rate equation, respectively. The dependence of these parameters on particle size and degree of wetting by the stationary phase in case of supports of different origin makes it probable that the dissolution of the sorbable component can be considered as the rate-governing step in gas-liquid chromatography. Experimental data suggest that the wetting of supports in most cases does not result in a homogeneous liquid film, but rather in liquid droplets and "islands."

The computations allow us to deduce an equation for H involving the slope at the inflexion point of the frontal chromatographic breakthrough curves, instead of the diffusion constant and the constant of the rate equation. The courses of H, measured according to the elution and frontal variant of chromatography, respectively, are similar, but both differ considerably from that computed from the van Deemter equation, when the calculation is performed by using the correct values of D_{eff} and k_t. A correct theory of gas-chromatographic processes ought to take into consideration the asymmetry of the elution or frontal profiles at higher flow rates.

In the well-known van Deemter equation of gas chromatography, the so-called B and C terms involve transport coefficients, one being characteristic of the diffusional spread of the sorbate during its passage through the column, the other one of the rate-governing step of its sorption. This latter step may be—in the case of a wetted column—the diffusion into and out of the stationary phase, and/or the penetration into the inner pores of the solid support. (In the case of gas-solid chromatography, only the latter type of transport can be rate-governing, delay of the desorption process being prohibitive if the method should be practically useful). If the rate-governing mass transfer is assumed to be formally a first-order process, with a "rate constant" k_t, then the simplified van Deemter equation is (symbols defined at the end)

$$H = \frac{2D_{\text{eff}}}{u_0} + \frac{2k}{(1+k)^2 k_t} u_0 \tag{1}$$

applicable upon dropping from consideration the possible contribution of eddy diffusion and the effect of the pressure drop along the column (that is, on assuming a suitably short column, as has been used in our measurements, to be described below).

One (and the most usual) way to attribute actual values to the coefficients D_{eff} and k_t is to determine the actual dependence of H on u_0, at a fixed ratio k, for a given column and carrier-solute system. The values thus obtained are mostly the starting point for theoretical considerations aiming at their explanation, and it is in the light of the latter that one is trying to create experimental conditions as optimal as possible for practical uses. Another way would be to determine the values of the coefficients independently of the course of H, to insert these in (1), and to see whether the resulting equation fits the experimentally found relation between H and u_0. Clearly such a procedure would not only be a means to assess some important performance characteristics of actual column fillings, but could also throw light on the possible limits of validity of the simple van Deemter equation and of the theoretical deductions leading to it. In connection with the latter, we have in mind, first of all, the assumption of a simple rate-governing mass-transfer step of the first order.

In previous publications (*1–3*) we outlined a new, refined theory of the frontal-gas-chromatographic process, on the basis of which we could evolve a method of determining the coefficients D_{eff} and k_t, as these are relevant parameters of these processes too. In the following we first briefly summarize the main points of the theory by which this determination is made possible, and proceed then to its bearing on the van Deemter equation, and to the conclusions to be drawn from actual experimental results.

EXPRESSION FOR *H* DERIVED FROM FRONT CHARACTERISTICS

The main point of the theory referred to is that it takes into account the change of flow rate of the gas mixture (solute + carrier), caused by the sorption process occurring within the proceeding front. It has been pointed out and proved theoretically that, in the case of a single sorbable component being present in the mixture, as a result of two counteracting effects, stationary fronts of the sorbable component in both the gas and sorbed phase and of the flow rate as well should develop. One of these effects is the spreading of the front due to the finite rate of sorption and to common gas diffusion; there is another effect—the changing flow rate acting in the opposite direction and in this way causing the front to sharpen. It is characteristic of these fronts from the physical point of view that they are proceeding along the column with a steady shape and constant velocity v, corresponding to the retention of the sorbable component. As a result, the stationary fronts can mathematically be described instead of the basic variables, the time coordinate t and the coordinate of location z, in terms of only one independent variable ψ, containing the former variables in the combination

$$\psi = t - \frac{z}{v} \tag{2}$$

This process of the fronts becoming stationary takes place asymptotically in time, a statement that could have been proved exactly for several cases (*2*,*4*). Furthermore, there is strong evidence that the transient solutions of the basic differential equation system become for sufficiently long times equivalent to the stationary ones, obtained immediately by introduction of the combined variable ψ into the initial differential equations.

The differential material-balance equation of the sorbable component and the over-all balance equation, respectively, are in this case

$$\begin{aligned} \frac{dx}{d\psi} - \frac{1}{v}\frac{d(xu)}{d\psi} + \frac{1}{v}\frac{du}{d\psi} - \frac{D_{\text{eff}}}{v^2}\frac{d^2x}{d\psi^2} &= 0 \\ \frac{d\alpha}{d\psi} - \frac{1}{v}\frac{du}{d\psi} &= 0 \end{aligned} \tag{3}$$

or

$$dx - \frac{d(xu)}{v} + \frac{du}{v} - \frac{D_{\mathrm{eff}}}{v^2}\frac{dx}{d\psi}\,dx = 0$$
$$d\alpha - \frac{du}{v} = 0 \tag{4}$$

with the boundary conditions that $\alpha = 0$ ahead of the advancing gas-chromatographic front (where $x = 0$), whereas at its rear $\alpha = \alpha_0$, $x = x_0$ (supposing that equilibrium conditions do not set in too slowly). From the first integrals of the above equations it follows then, by elimination of u, that

$$\frac{D_{\mathrm{eff}}}{v^2}\frac{dx}{d\psi} + [\alpha + k(1 - x_0)]x - \alpha = 0 \tag{5}$$

together with

$$v = \frac{u_0}{1 + k} \tag{6}$$

as the common velocity of the procession of the stationary front.

For the description of the transfer rates of the sorbable component from the gas phase into the fixed one, the use of an equation of the form

$$\frac{d\alpha}{d\psi} = k_t(kx - \alpha) \tag{7}$$

is generally accepted, a first-order "rate constant" k_t being taken as characteristic of the process.

The variable α may be eliminated from (5) and (7), to obtain an equation of the concentration front curve alone. For this purpose, we differentiate (5) with respect to ψ, express $d\alpha/d\psi$ and set this expression equal to the right side of (7), solve the resulting equation for α, and reinsert this in (5). After some rearrangement, there results for x the following nonlinear differential equation of second order:

$$(1 - x)y\frac{dy}{dx} + [r(1 - x_0) + (1 - x)]y + y^2 - r(x_0 - x)(1 - x)x = 0 \tag{8}$$

where

$$y \equiv \frac{dx}{d(k_t\psi)}$$
$$r \equiv \frac{kv^2}{k_tD_{\mathrm{eff}}} = \frac{ku_0^2}{k_t(1 + k)^2D_{\mathrm{eff}}} \tag{9}$$

Obviously no general solution of (8) can be found, so we tried an approximate solution in form of the following power series:

$$y = \lambda_0 + \lambda_1 x + \lambda_2 x^2 + \lambda_3 x^3 \tag{10}$$

where the unknown coefficients have also to be determined in a way that will fulfill the boundary conditions. From the condition $y = 0$, where $x = 0$ (before the front) we get $\lambda_0 = 0$ for the first coefficient. Comparison of the coefficients of the terms containing x on the first power gives an equation of the second degree for λ_1, whose solution with physical meaning is

$$\lambda_1 = \frac{1 + r(1 - x_0)}{2}\left(-1 + \left\{1 + \frac{4rx_0}{[1 + r(1 - x_0)]^2}\right\}^{1/2}\right) \tag{11}$$

Similarly, we get for λ_2,

$$\lambda_2 = \frac{\lambda_1 - r(1 + x_0)}{3\lambda_1 + 1 + r(1 - x_0)} \tag{12}$$

Regarding the term containing x on the third power as a correction, λ_3 has to be determined so as to also satisfy the second boundary condition, requiring y to disappear behind the front, where x had already reached the initial concentration x_0. According to Eq. (10), this condition is fulfilled if

$$\lambda_3 = -\frac{\lambda_1 + \lambda_2 x_0}{x_0^2} \tag{13}$$

The expressions (11) to (13) we arrived at for the coefficients λ_i are still too complicated, and it is hardly possible to foresee their consequences. A means of simplification presents itself, however; if we stipulate that r may not be very large (this being mainly a limitation for the flow rate u_0, the other conditions given), and also the initial concentration x_0 does not exceed a proper limit. By expanding the square root in the expression for λ_1 into a power series and omitting terms beyond the first power, the following simple equations result for λ_i:

$$\lambda_1 = \frac{rx_0}{1 + r} \qquad \lambda_2 = -\frac{r}{1 + r} \qquad \lambda_3 = 0 \tag{14}$$

i.e., in this case $dx/d\psi$, or dx_L/dt at the end of the column (where x_L stands for the concentration appearing at the outlet of the column), is represented as a function of x_L by a parabola, and so the breakthrough curve becomes of a symmetrical S shape.

In this case the steepest slope of the breakthrough curve corresponds to $x_0/2$, the half-value of the initial concentration. Denoting this highest value of the derivative with respect to time by x'_m, we have

$$\frac{1}{k_t} x'_m = \lambda_1 \left(\frac{x_0}{2}\right) + \lambda_2 \left(\frac{x_0}{2}\right)^2 \tag{15}$$

and by introducing the expressions (14) of λ_1 and λ_2 and that of r according to (9),

$$\frac{x_0^2}{4x'_m} = \frac{1}{k_t}\left(\frac{1}{r} + 1\right) = \frac{D_{\text{eff}}}{kv^2} + \frac{1}{k_t} \tag{16}$$

Equation (16) means that by plotting $x_0^2/4x'_m$ as a function of $1/kv^2$ we get a straight line, from the slope and intercept of which it is a simple task to determine D_{eff} and k_t, that is, the effective coefficient of gas diffusion and the first-order rate constant of the relevant mass transfer, respectively.

The values thus obtained may enable us to give a definite answer regarding the question of the limits of validity of the simple first-order rate equation underlying our deductions. On the other hand, a knowledge of how the values of these coefficients will be influenced by the preparation of column filling may be helpful to create optimal experimental conditions. By a simple rearrangement of Eq. (16) an expression can also be deduced for H, the height equivalent to one theoretical plate, which also throws light on the main performance characteristic of working chromatographic columns on the basis of frontal-gas-chromatographic data. For this purpose we transform the van Deemter equation (1), by introducing $u_0 = (1 + k)v$ [see (6)], with the result

$$H = \frac{2ku_0}{(1 + k)^2}\left(\frac{D_{\text{eff}}}{kv^2} + \frac{1}{k_t}\right) \tag{17}$$

By comparison with (16) it seems, however, quite reasonable to substitute $x_0^2/4x'_m$ for the right hand term of (17), resulting in an expression for H in terms of frontal-gas-chromatographic data:

$$H = \frac{ku_0x_0^2}{2(1 + k)^2}\frac{1}{x'_m} \tag{18}$$

The fact that expressions (1) and (16) can be transformed simply one into the other does not seem surprising when we consider that the initial differential equations are alike for frontal and elution chromatography, respectively, the only difference lying in the auxiliary conditions, as a natural consequence of the relevant processes. Therefore, the limits of validity of the two expressions for H must also be identical. That means, in other words, that values of H determined according to (18) and those derived by the well-known formula of elution chromatography

$$H = \left(\frac{\Delta t}{4t_R}\right)^2 L \tag{19}$$

should also agree within reasonable limits of experimental error. We repeat that formula (19) is based essentially on a symmetrical peak shape, this being the counterpart of a symmetrical S-shaped front curve in frontal chromatography.

Equations (18) and (19) give a realistic possibility of checking the capabilities of the two expressions for H; on the other hand, the limitations of the elution gas-chromatographic equation show up clearly when we recall the simplifying conditions we felt justified to introduce in deducing the frontal-gas-chromatographic equation for H.

In the following we try to draw conclusions regarding the limits of applicability of the simple rate law widely used in the theory of gas chromatography, mainly based on our k_t values, and try to show some important aspects of a comparison of the values of H determined by the elution and frontal methods, respectively.

CONCLUSIONS TO BE DRAWN FROM THE VALUES OF D_{eff} AND k_t, DETERMINED BY FRONTAL GAS CHROMATOGRAPHY

Before going into a detailed discussion of the kind of information available from data on the influence of different factors on D_{eff} and k_t, it is worthwhile to sum up briefly their exact meaning.

The longitudinal diffusion of the sorbable component in the carrier gas stream is taken into account by the so-called effective diffusion coefficient, D_{eff}. When relating D_{eff} to D_g, the constant of common gas diffusion, one has to bear in mind that (1) the spreading of the front by diffusion does not take place in the whole of the available space (s per unit length, including the inner pore volume, too) but rather in the free voids between the individual support particles (s_0); and (2) as a consequence of the labyrinth structure of these voids, the coefficient of common gas diffusion has to be multiplied by a factor χ ($\chi < 1$). Therefore, the relation between D_{eff} and D_g is given by

$$s_0 D_{\text{eff}} = s\chi D_g \tag{20}$$

The interpretation of k_t and the selection of a suitable rate equation to describe the mass-transfer phenomena in gas chromatography are different aspects of the same problem. It would be desirable to have a definite choice of a kinetic equation giving the dependence on the actual concentration x and sorbed amount α to sort out the rate-governing step from among the possible elementary mass-transfer processes. It is, however, hardly conceivable to find such a relation, because the rate-controlling mass-transfer step must, among others, also depend on different factors related to the structure of the column support, the thickness of the coating, etc. At present there is no rate equation available in which this composite dependence might be expressed in a sufficiently detailed form. The simple first-order rate law generally accepted in gas chromatography represents the result of rough approximations and averagings only, and one tries to account for the nature of the rate-controlling step by attaching different meanings to k_t. For example, for pore diffusion being rate-controlling

$$k_t = \frac{15D_b}{\rho_0^2} \tag{21}$$

However, when the dissolution of the sorbable component into the fixed phase is the slowest step of mass transfer then k_t is given the following meaning:

$$k_t = \frac{3D_f}{\delta^2} \tag{22}$$

When both of the transport velocities have commensurable magnitude,

$$k_t = \frac{3}{\delta^2/D_f + \rho_0^2/5D_b} \tag{23}$$

It remains to be seen whether this dependence of k_t on the pore structure of different supports and on film thickness, etc., will be revealed by suitable experiments.

Experimental Part

For a comparison of the influence exerted on k_t by the factors mentioned, gas-chromatographic supports of different origin, mesh size, and (not least) coated with varied amounts of stationary phase are needed. For a closer investigation we selected two supports: Termolit and Firebrick-22, of Hungarian and English origin, respectively. Some relevant physical properties of the support materials are given in Table 1.

TABLE 1
Physical Properties of the Support Materials Used

Support	Density, g/cm^3		Surface area, m^2/g
	Apparent	Real	
Termolit	0.683	2.37	4.79
Firebrick-22	0.673	2.55	3.46

To ascertain whether k_t will be influenced by the particle size of the support [as could be expected if pore diffusion were rate-controlling according to Eq. (21)], different sieve fractions were prepared from the ground material between 0.2 and 0.5 mm in diameter.

Squalane was used as the stationary phase, the coating being performed on the previously heated (up to 200°C) and evacuated support by use of a solution of squalane in light gasoline. With regard to Eq. (22), the amount of squalane per unit mass of support was varied between 10 and 20%, supposing that this would result in a similar change in the film thickness of the fixed phase. To get a film as homogeneous as possible, the surface of the support was occasionally exposed to hexamethyl-disilasane vapor at 80°C prior to the standard coating procedure.

Preliminary investigations of the coated support by independent physical methods may sometimes be useful to collect information on the physical properties, e.g., on the wetting properties of the stationary phase. For this purpose some surface-area determinations have been performed using the standard krypton-adsorption technique at liquid-N_2 temperature, as is common practice in measuring low surface areas. It is interesting to note that the surface areas of three samples of Firebrick-22 (particle size between 0.31 and 0.41 mm), coated with increasing amounts of squalane (10, 15, and 20%, respectively) happened to be 1.65, 1.11, and 0.79 m^2/g.

Glass tubes of different length (25 to 50 cm) and inner diameter

TABLE 2

D_{eff}, k_t, and Some Other Parameters of Working Chromatographic Columns

Run No.	Col. No.	Support material	Particle size, mm	Amount of squalane, wt %	L, cm	s, ml/cm	m, g/cm	$\frac{a_0}{x_0}$, ml/g	k	D_{eff} cm²/sec	k_t, (sec⁻¹)
I	1	Termolit	0.2 –0.4	15.02	28.8	0.372	0.041	59.1	6.50	0.16	0.42
	2	Termolit	0.2 –0.4	15.02	28.8	0.372	0.041	57.4	6.33	0.18	0.38
	3	Termolit	0.2 –0.4	14.9	25.0	0.344	0.037	56.8	6.11	0.17	0.38
II	4	Firebrick-22	0.2 –0.25	15.05	25.0	0.367	0.031	58.83	5.02	0.16	0.77
	5	Firebrick-22	0.315–0.4	14.96	24.8	0.379	0.031	60.56	4.96	0.16	0.82
	6	Firebrick-22	0.315–0.4	14.96	49.9	0.332	0.029	57.6	5.02	0.20	0.71
	7	Firebrick-22	0.4 –0.5	15.03	25.0	0.365	0.033	58.4	5.22	0.16	0.75
III	8	Firebrick-22	0.315–0.4	9.99	49.8	0.371	0.020	58.2	3.19	0.17	0.65
	9	Firebrick-22	0.315–0.4	9.99	49.8	0.345	0.019	59.4	3.22	0.20	0.69
	10[a]	Firebrick-22	0.315–0.4	10.01	50.0	0.392	0.020	58.7	3.07	0.18	0.75
	5	Firebrick-22	0.315–0.4	14.96	24.8	0.379	0.031	60.56	4.96	0.16	0.82
	6	Firebrick-22	0.315–0.4	14.96	49.9	0.332	0.029	57.6	5.02	0.20	0.71
	11	Firebrick-22	0.315–0.4	20.00	25.0	0.360	0.043	57.86	6.90	0.17	0.61
	12	Firebrick-22	0.315–0.4	20.00	24.7	0.360	0.047	58.39	7.68	0.15	0.57
	13	Firebrick-22	0.315–0.4	20.00	50.0	0.342	0.045	58.78	7.68	0.19	0.51
	14[a]	Firebrick-22	0.315–0.4	20.01	24.7	0.336	0.046	51.20	6.97	0.19	0.64

[a] Hexamethyl-disilasane treated.

(6 to 10 mm) were used as columns. The most important data of the filled gas-chromatographic columns are summarized in Table 2.

In the experiments the carrier gas was hydrogen and the sorbable component *n*-butane. The concentration of *n*-butane in the feed was adjusted differently, according to the needs of the experiment, although it did not in any case exceed 0.32, in mole fractions. The temperature was uniformly 20°C.

The measurement itself consisted of the registration of the recorder deflection vs. time curves and of the continuous reading by a soap-film flowmeter of the gas volume leaving the column. D_{eff} and k_t are to be evaluated from the concentration vs. time curves of the recorder. The curves $W(t)$ vs. t by the flowmeter were used for the determination of such relevant data as the sorption capacity of the filling, the total dead space, the initial concentration of *n*-butane, and the flow rate of the carrier gas, according to a standard method described elsewhere (5,6), where details as to the apparatus used may also be found.

Reliability of the Experimental Method

To give an idea of the reliability of the computation method used for the evaluation of D_{eff} and k_t from experimental data, some results may be shown in advance, permitting some insight into the procedure from this point of view.

One may check the validity of Eq. (16), based on its rearranged form:

$$x_0^2 = \frac{4}{kv^2}\left(D_{\text{eff}} + \frac{k_t}{kv^2}\right) x'_m \tag{24}$$

Equation (16) may be proved simply by ascertaining that under otherwise identical conditions there exists a linear relationship between x_0^2 and x'_m. Another means is the computation of x_0 from (24) using the measured values of x'_m and comparison of these concentrations with those determined by the composition of the feed. All the other parameters occurring in (24), D_{eff} and k_t included, are to be derived from separate measurements for this purpose, and so this is a means to check them.

The result of a comparison of this kind, made with the chromatographic column No. 3 of Table 2 is given in Table 3. In the last column of Table 3 the differences between the squares of the concentrations computed by Eq. (24) and those given by the partial pressures are contained. As can be seen, the errors have no definite trend and (24) reflects the dependence of x'_m on x_0 correctly, provided the experimental conditions have been chosen to justify the simplifications introduced in the derivation of this relation.

TABLE 3

A Comparison of the Initial Concentrations of the Sorbable Component, Computed from the Slope of the Breakthrough Curves at the Point of Inflexion and Measured Manometrically

x_0 (measured)	$x_0^2 \times 10^2$	$x'_m \times 10^4$, sec^{-1}	v, cm/sec	$x_{0,c}$ (computed)	$x_{0,c}^2 \times 10^2$	$(x_{0,c}^2 - x_0^2) \times 10^2$
0.099	0.98	5.15	0.0564	0.114	1.30	0.32
0.161	2.59	8.25	0.0542	0.153	2.34	0.25
0.163	2.66	8.97	0.0570	0.173	2.99	0.33
0.207	4.28	12.14	0.0570	0.210	4.41	0.13
0.227	5.15	12.28	0.0550	0.233	5.43	0.28
0.274	7.51	15.25	0.0542	0.274	7.51	0.00
0.285	8.12	17.66	0.0546	0.293	8.58	0.46
0.322	10.32	22.40	0.0586	0.323	10.43	0.06

A similar comparison is shown in Fig. 1, where $x_0^2/4x'_m$ is plotted against $1/kv^2$ as the suitable independent variable. The solid line corresponds to 20% (column No. 8 in Table 2) and the dashed one to 10% squalane on Firebrick-22 (column No. 13 in Table 2). At flow rates not too high, the experimental points fit straight lines; at higher rates, however, deviations appear (their explanation should be given below).

On the basis of these experiments we may depend on the reliability of (16) to reflect the dependence of x'_m on the experimental parameters in the correct way. Using the same columns and the same experimental arrangement in repeated experiments the errors pertaining to the individual D_{eff} and k_t values could also be determined. Their average error did not exceed 15 and 5 relative per cent, respectively. If by having the particle size and/or the amount of the fixed phase changed, the alteration in the magnitude of the relevant constants would exceed these limits of experimental spread, the change could be considered significant. (For k_t on Firebrick-22, for example, this limit would lie in these experiments at about $|\Delta k_t| > 0.04$, k_t being around 0.8.)

The experimental values of D_{eff} and k_t for our different chromatographic columns are listed in Table 2. From the arrangement of the data in this table it can immediately be seen whether the quality of the support (runs I and II), the change in its particle size (run II), and the amount of fixed phase (run III) exert any influence on these parameters.

Comparing the data of runs I and II of Table 2 it turns out that although the values of D_{eff} are for both supports practically identical, there is a significant difference in k_t by a factor of about 2. At first glance it may be surprising that the support Termolit, having a specific surface area twice as great as that of Firebrick-22, should be inferior from the point of view of gas-chromatographic separation. In addition, it can be stated that diffusion in the pores of the support cannot be the rate-determining mass-transport step because a double increase in the particle size did not exert any influence on k_t, as shown clearly by the data of run II. Our own measurements referred to above as well as those of others [see, e.g., (8)] show that relatively small amounts of the fixed phase may bring about a significant decrease in the specific surface area of wetted gas-chromatographic supports (the surface area of Firebrick-22 after wetting with 10% squalane decreased by 52% of the original value). This is, in all probability, a consequence of an obstruction or filling up, first of the most narrow and then of the transient pores of the support (both giving the main contribution to the total surface area) by the material of the stationary phase, leading to an abrupt diminution of the accessible surface area from the side of the gas phase. Increasing the amount of the wetting material, the curve representing the accessible surface area of the support vs. degree of wetting flattens and levels off at still higher concentrations. At this degree of wetting all the smaller pores are completely filled by the liquid.

In light of these considerations, it is to be supposed that Termolit, with the larger surface area, has more micro and transient pores than Firebrick-22, causing a more pronounced and quicker pore-closure phenomenon. This results in a smaller specific surface area in the case of Termolit at the same degree of wetting. We may suspect, therefore, the dissolution process of the sorbable component into the liquid phase to be the rate-determining step in gas-liquid chromatography. In contradiction to this supposition we failed to detect a quadratic dependence of k_t on the reciprocal value of the *amount* of liquid phase, as would be required were expression (22) to be valid, and at the same time the film thickness could be regarded proportional to the mass of the stationary phase. It must be pointed out, however, that on structured surfaces (geometrically and energetically as well) the thickness calculated by the amount related to the whole surface cannot be but a rough average value, at best. The wetting is in reality inhomogeneous. It is even possible that the liquid phase on the support consists of small droplets and liquid "islands," as has been observed to happen in some independent investigations (7). This may be the reason that no marked dependence of k_t on the amount of liquid could be detected, and from this point of view we could not find any significant difference between the properties of the standard and hydrophobized supports. It may be remembered in this connection that squalane is a very effective tailing reducer in adsorption chromatography, blocking preferentially the most active spots of the surface.

COMPARISON OF *H* VALUES DETERMINED BY THE ELUTION AND FRONTAL CHROMATOGRAPHIC METHODS

We now turn our attention to the discussion of the sort of limitations we are faced with as a natural consequence of the simplifications used in the deduction of Eq. (18) for H; on the other hand, this seems to have also some bearing on another question, i.e., the tailing occurring in elution chromatography at higher flow rates and the part it plays in measuring H values.

As has been mentioned in connection with the curves of Fig. 1,

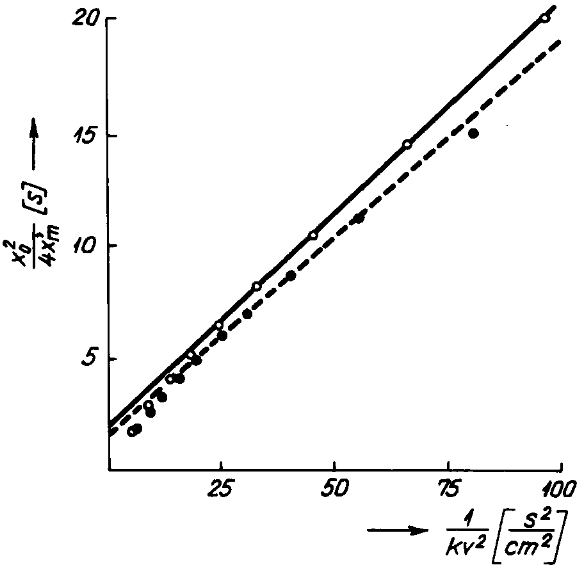

FIG. 1. $x_0^2/4x_m'$ vs. $1/kv^2$ curves for columns Nos. 8 and 13 (Table 2). Support: Firebrick-22; stationary phase: squalane, 10% (—•—•—•—) and 20% (—○—○—○—), respectively.

the experimental values of $x_0^2/4x_m'$ [left side of Eq. (16)] drop below the extrapolated straight lines at the higher flow rates. This can be explained by the failing symmetry of the breakthrough curves at those flow rates, as the parameter r exceeds the limit we had to set as the necessary condition for λ_3 being zero [see Eq. (14)]. In the case of asymmetric S curves the point of inflection is also shifted to concentration values less than $x_0/2$, causing the breakthrough curves to flatten off on the part lying behind the inflection point. This shape of the curves explains why the slopes taken at the point of inflection are greater, consequently $x_0^2/4x_m'$ smaller, than one would expect by extrapolation of the straight lines of Fig. 1. By dropping the simplifications leading to Eq. (14), the actual asymmetry of the front curves can be very well described by using suit-

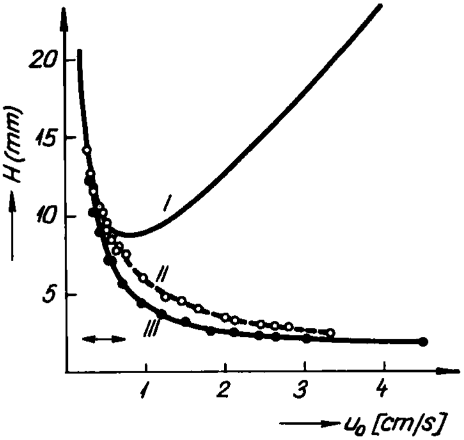

FIG. 2. H vs. u_0 curves for column No. 8 (Table 2). Curves I, II, and III were computed by Eqs. (1), (18), and (19), respectively.

able values of λ_1, λ_2, and $\lambda_3 \neq 0$. In this case, however, the proportionality factor before u_0^2 in the parameter r [see the definition (9)] turns out to be different from that derived from the symmetrical region. As there is no valid reason to suspect a changing k or D_{eff}, there remains only k_t to account for the discrepancy. This leads us to the necessity of a closer examination of the first-order rate equation (7).

In Figs. 2 and 3 the values of H as a function of flow rate are

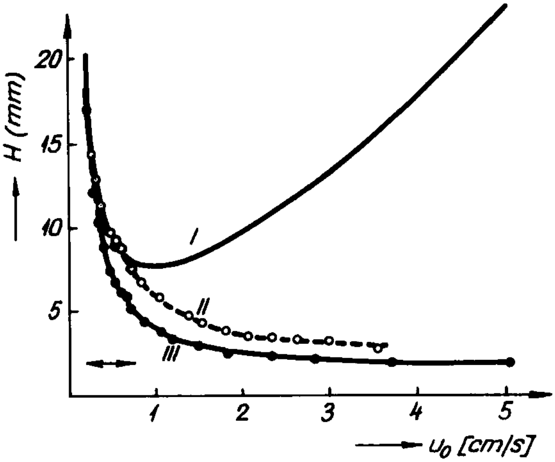

FIG. 3. H vs. u_0 curves for column No. 13 (Table 2). Curves I, II, and III were computed by Eqs. (1), (18), and (19), respectively.

shown for the chromatographic columns Nos. 8 and 13 of Table 2, computed from the steepest slopes of the frontal-gas-chromatographic curves [Eq. (18); curves denoted by II] as well as from the base widths and retention times of elution peaks [Eq. (19); curves denoted by III], determined at nearly identical experimental conditions, with the exception of the concentration range, of course. Complete agreement between curves II and III cannot be expected, because the relevant k values were somewhat different for the elution and frontal cases, the sorption isotherm being slightly curved upward. Apart from this difference, the trend of the curves is mainly the same, so that the two modes of computation give materially equivalent results.

As is well known, the van Deemter equation—at least in its simple form (1)—in the majority of practical cases is not well suited to describe the whole course of the experimental H curves. It is not surprising therefore, that the shapes of our curves II and III differ markedly from the well-known minimum curves one may expect on the basis of the simple van Deemter equation. By assigning suitable arbitrary values to D_{eff} and k_t, it is still possible to enforce a formal agreement between the experimental curves and the van Deemter equation, but only with extremely high figures for k_t, having no real physical meaning. The frontal method offers a simple means to determine the truly relevant D_{eff} and k_t values, with only a small uncertainty, from the steepest slopes of the breakthrough curves measured at lower flow rates. By inserting these constants in the van Deemter Eq. (1), hypothetical curves for H may be computed, resulting in the curves denoted by I on Figures 2 and 3 (k, D_{eff}, and k_t were taken from Table 2). Comparison with the curves II shows clearly that agreement exists only within the intervals of flow rates marked by double arrows, where the frontal S curves are symmetrical and also the requirements of Eq. (16) are fulfilled. Curves *I* are of the orthodox minimum type, whereas no definite tendency for a renewed raise at the higher flow rates appears in the experimental ones, neither in the frontal case nor in the elution case.

This is in our mind a serious discrepancy, requiring explanation. First, we would remind the reader of the fact that the theoretical derivation of the van Deemter equation is based on the assumption of a symmetrical spread, resulting in a gaussian distribution of an elution peak. The conventional computation of H, according to formula (19), is based on this symmetry, too, and in deriving our formulas (17) and (18) we relied on front curves of a symmetrical S shape. At the higher flow rates, the symmetry of the stationary frontal breakthrough curves gets lost, however, and a closer examination of elution peaks reveals an increasing tailing, going sometimes as far as to influence even the retention time corresponding to the peak maximum. Nevertheless, values for *H* were computed by the formulas based on the assumption of symmetry, from the steepest slopes in the frontal case, and from the peak retentions and base widths in elution chromatography. We would not question, of course, the value of this customary standard procedure for estimating column performance for practical purposes, even at higher flow rates (as are applied to an ever-increasing extent for quick analyses), but we would point out that the situation is by far not reassuring from a theoretical point of view.

There is a general tendency in modern literature to try to account for the experimental course of the *H* curves by adding an increasing number of new terms to the van Deemter equation, without any alteration of its fundamental structure. We are convinced, however, that though such corrections may be well founded in themselves, this is not the really correct way toward decisive advance. A revision of the fundamental system of differential equations underlying the theory should be undertaken, by which we could come into the position to be able to account for the loss of symmetry at high flow rates, that is, for the increasing tailing of the elution peaks, and for the distortion of the breakthrough fronts as well. We suspect this problem to be intimately related to the question of validity of the linear transport rate equation, due originally to Glueckauf. As a consequence of the series expansion used by him, it is only in the neighborhood of sorption equilibrium (i.e., after the point of inflexion in the frontal case, and around the peak maximum in elution chromatography), that this equation may be apt to describe the transport rate of the process correctly enough. It seems not impossible that the definition of *H* itself ought to be revised in the light of more exact solutions, taking into account the tailing of the peaks, too.

Unfortunately, we are unable to give any definite suggestions as to how to overcome the mathematical difficulties that might arise from such an attempt, and for the time being have to content ourselves with the above critical remarks.

Nomenclature

$a(z,t)$	mean value of sorbed gas volume at a given cross section of the column per unit mass of the fixed phase, as a function of z and t, ml/g or ml STP/g
a_0	sorbed equilibrium volume at concentration x_0 in the gas phase per unit mass of fixed phase, ml/g
$u(z,t)(= w/s)$	actual rate of gas flow in the column, as a function of z and t, cm/sec
$u_0(= v/s)$	constant linear flow rate of the feed at the inlet end of column, cm/sec
D_b	diffusion constant in the inner pores of the wetted support, cm^2/sec
$D_{\mathrm{eff}}(= s_0/s\chi D_g)$	effective diffusion constant in the gas phase of the column, cm^2/sec
D_g	diffusion constant in the free gas phase, cm^2/sec
H	height equivalent to one theoretical plate, cm
k_l	rate constant of linear rate equation, sec^{-1}
m	mass of fixed phase per unit column length, g/cm
$k[= (m/s)(a_0/x_0)]$	dimensionless partition coefficient of sorbable component in case of a linear isotherm equal to its slope; at curved isotherms it corresponds to the chord taken at the origin and the point (x_0,a_0) of the isotherm, respectively
L	length of column, maximum value of z, cm
$r(= qv^2/k_lD_{\mathrm{eff}})$	composite constant
s	the (geometric) dead space per unit column length (pore volume + interparticle volume), ml/cm
s_0	the (geometric) interparticle volume per unit column length, ml/cm
t	time coordinate, sec
Δt	the base width of an elution peak, sec (viz., cm)

t_R	uncorrected retention time in elution chromatography, sec
v	constant linear velocity of a stationary front or of an elution peak, cm/sec
w	constant volumetric flow rate of feed, ml/sec
$W(t)$	volume of gas that left the column up to time t, ml
z	coordinate of location along the column, cm
$x(z,t)$	mean value of concentration (in mole fractions) of the sorbable component at a given column cross section as a function of z and t, ml/ml
x_0	constant concentration in the feed, ml/ml
$x'_m = (dx_L/dt)_{x=x_0/2}$	steepest slope of the curve $x_L(t)$
$\alpha[\equiv (m/s)a]$	the sorbed amount, in dimensionless form
$\lambda_1,\lambda_2,\lambda_3$	parameters, independent of concentration
δ	film thickness of the fixed phase, cm
ρ_0	particle radius of the support, cm
χ	labyrinth factor
$\psi(\equiv t - z/v)$	combined variable, sec

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