

STATISTICAL MOMENTS THEORY OF GAS-SOLID CHROMATOGRAPHY DIFFUSION CONTROLLED KINETICS

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(Received September 26th, 1966)

A new theory of non-equilibrium linear gas-solid chromatography (GSC) following the work of GIDDINGS¹ and MCQUARRIE² has been recently published³⁻⁵. This theory is based on the "exact" solution of a system of partial differential equations describing the mass-balance in the gas chromatographic column. The solution is first obtained in Laplace coordinates, from which statistical moments can be evaluated. By means of a suitable function, these statistical moments can be arranged in a series, which presents the solution of the original system of differential equations in normal coordinates. The expressions for statistical moments up to the fifth order have been calculated³. In this paper only the first four moments defined by the following equations will be used.

$$\mu_1 = \left(\frac{L}{u} + \frac{2D_p}{u^2} \right) [1 + \phi K_c (1 + K_n)] \quad (1)$$

$$\begin{aligned} \mu_2 = & \left(\frac{2D_p L}{u^3} + \frac{8D_p^2}{u^4} \right) [1 + \phi K_c (1 + K_n)]^2 + \\ & + \left(\frac{2L}{u} + \frac{4D_p}{u^2} \right) \phi K_c \left[\frac{R^2 (1 + K_n)^2}{D_r v (v + 2)} + \frac{\phi (1 + K_n)^2}{H_c} + \frac{K_n}{H_n} \right] \end{aligned} \quad (2)$$

$$\begin{aligned} \mu_3 = & \left(\frac{12 D_p^2 L}{u^5} + \frac{64 D_p^3}{u^6} \right) [1 + \phi K_c (1 + K_n)]^3 + \\ & + \left(\frac{12 D_p L}{u^3} + \frac{48 D_p^2}{u^4} \right) \phi K_c [1 + \phi K_c (1 + K_n)]. \end{aligned}$$

$$\left[\frac{R^2 (1 + K_n)^2}{D_r v (v + 2)} + \frac{\phi (1 + K_n)^2}{H_c} + \frac{K_n}{H_n} \right] + \left(\frac{6L}{u} + \frac{12 D_p}{u^2} \right) \phi K_c.$$

$$\begin{aligned} & \left[\left(\frac{R^2}{D_r} \right)^2 \frac{2 (1 + K_n)^3}{v^2 (v + 2) (v + 4)} + \frac{R^2}{D_r} \frac{2 (1 + K_n)}{v (v + 2)} \left(\frac{\phi (1 + K_n)^2}{H_c} + \frac{K_n}{H_n} \right) + \right. \\ & \left. + \frac{\phi^2 (1 + K_n)^3}{H_c^2} + \frac{2\phi K_n (1 + K_n)}{H_c H_n} + \frac{K_n}{H_n^2} \right] \end{aligned} \quad (3)$$

$$\begin{aligned}
\mu_4 = & \left(\frac{12 D_p^2 L^2}{u^6} + \frac{216 D_p^3 L}{u^7} + \frac{960 D_p^4}{u^8} \right) [1 + \phi K_c (1 + K_n)]^4 + \\
& + \left(\frac{24 D_p L^2}{u^4} + \frac{288 D_p^2 L}{u^5} + \frac{960 D_p^3}{u^6} \right) [1 + \phi K_c (1 + K_n)]^2 \left[\frac{R^2}{D_r} \frac{(1 + K_n)^2}{v(v+2)} + \right. \\
& + \left. \frac{\phi (1 + K_n)^2}{H_c} + \frac{K_n}{H_n} \right]^2 + \left(\frac{12 L^2}{u^2} + \frac{72 D_p L}{u^3} + \frac{144 D_p^2}{u^4} \right) \phi^2 K_c^2 \left[\frac{R^2}{D_r} \frac{(1 + K_n)^2}{v(v+2)} + \right. \\
& + \left. \frac{\phi (1 + K_n)^2}{H_c} + \frac{K_n}{H_n} \right] + \left(\frac{48 D_p L}{u^3} + \frac{196 D_p^2}{u^4} \right) \phi K_c [1 + \phi K_c (1 + K_n)]. \\
& \left[\left(\frac{R^2}{D_r} \right)^2 \frac{2(1 + K_n)^3}{v^2(v+2)(v+4)} + \frac{R^2}{D_r} \frac{2(1 + K_n)}{v(v+2)} \left(\frac{\phi (1 + K_n)^2}{H_c} + \frac{K_n}{H_n} \right) + \right. \\
& + \left. \frac{\phi^2 (1 + K_n)^3}{H_c^2} + \frac{2\phi K_n (1 + K_n)}{H_c H_n} + \frac{K_n}{H_n^2} \right] + \left(\frac{24 L}{u} + \frac{48 D_p}{u^2} \right) \cdot \\
& \phi K_c \left[\left(\frac{R^2}{D_r} \right)^3 \frac{(5v+12)(1+K_n)^4}{v^3(v+2)^2(v+4)(v+6)} + \left(\frac{R^2}{D_r} \right)^2 \frac{(1+K_n)^2}{v^2(v+2)^2(v+4)} \cdot \right. \\
& \cdot \left(\frac{(5v+12)\phi(1+K_n)^2}{H_c} + \frac{(6v+12)K_n}{H_n} \right) + \frac{R^2}{D_r} \frac{1}{v(v+2)} \left(\frac{3\phi^2(1+K_n)^4}{H_c^2} + \right. \\
& + \frac{6\phi K_n(1+K_n)^2}{H_c H_n} + \left. \frac{(2+3K_n)K_n}{H_n^2} \right) + \frac{\phi^3(1+K_n)^4}{H_c^3} + \frac{3\phi^2 K_n(1+K_n)^2}{H_c^2 H_n} + \\
& + \left. \frac{\phi K_n(2+3K_n)}{H_c H_n^2} + \frac{K_n}{H_n^3} \right] \tag{4}
\end{aligned}$$

where v is the particle shape factor; $v = 3$ for spheres.

The GC column of length L , through which flows the carrier gas with velocity u , is homogeneously filled with a porous sorbent of particle radius R . The column has the external porosity ε_e (interparticle void volume in unit volume), and the internal porosity ε_i (intraparticle void volume in unit volume), the porosity function ϕ being defined by $\varepsilon_i/\varepsilon_e$. The molecules of the chromatographed compound can be subject to the following transport processes during passage through the column:

(i) Longitudinal diffusion in the carrier gas characterized by the coefficient D_p in which case $D_p = D_g + Au$, D_g being the gaseous phase diffusion coefficient and A a constant comprising effects of eddy diffusion.

(ii) Mass transfer across the interface around the external grain surface characterized by the rate constant H_c .

(iii) Radial diffusion into the pores with the coefficient D_r .

(iv) Mass transfer from the internal volume of the pores to the internal adsorbent surface with the rate constant H_n .

When the concentration of the compound to be separated is different in the interparticle space from that in the pore volume (volumetric adsorption) then the equilibrium is given by the constant $K_c = c_i/c_e$, where c_i is the equilibrium adsorbate concentration in the pore volume, and c_e is the concentration in the interparticle

volume. The adsorption equilibrium between the internal surface and the concentration in the pore volume is characterized by the constant $K_n = n/\epsilon_1 c_1$; n being the amount adsorbed on the surface of the pore volume unit. The equations (1)–(4) contain well defined physical constants and describe a rather complex model of GSC. In reality, however, it is improbable, that all the transport phenomena considered take place simultaneously in the GS column. In many cases the adsorption kinetics will be controlled by intrinsic (radial) diffusion. Thus the constants H_c and H_n are close to infinity and the terms containing these constants may be neglected. If we further consider only the surface adsorption characterized by the equilibrium constant K_n , there is no adsorption in the pore volume and the constant $K_c = 1$. In GSC we usually have the velocity u so large that the term $D_p/u < 1$. Under this condition it can be assumed, that in the individual products of the polynomes only the terms with the lowest power of D and u are significant and the terms with higher powers can be neglected. If we further normalize the moments by dividing the second moment about the mean by the square of the first moment μ_1 , the third moment by μ_1^3 , and the fourth moment by μ_1^4 , we may obtain from (1)–(4):

$$H = \frac{\mu_2}{\mu_1^2} \cdot L = 2A + \frac{2D_0}{u} + \frac{2}{15} \frac{\phi(1+K_n)^2}{(1+\phi+\phi K_n)^2} \frac{R^2}{D_r} \cdot u \quad (5)$$

$$Z = \frac{\mu_3}{\mu_1^3} \cdot L^2 = 12 \frac{D_0^2}{u^2} + 24 \frac{AD_0}{u} + 12A^2 + \frac{4}{5} \frac{D_0 R^2}{\phi D_r} + \frac{4ARu}{5\phi D_r} + \frac{4}{105} \frac{R^4 u^2}{D_r^2 \phi^2} \quad (6)$$

assuming $K_n \gg 1$.

$$\begin{aligned} F = \frac{\mu_4}{\mu_1^4} \cdot L^3 = & \frac{12 D_0^2 L}{u^2} + 12 A^2 L + \frac{24 AD_0 L}{u} + \frac{8 D_0 R^2 L}{5 D_r \phi^3} + \\ & + \frac{8 ALR^2}{5 D_r \phi^3} \cdot u + \frac{32}{105} D_0 \left(\frac{R^2}{D_r}\right)^2 \frac{1}{\phi^2} \cdot u + \frac{32}{105} A \left(\frac{R^2}{D_r}\right)^2 \frac{1}{\phi^2} \cdot u^2 + \\ & + \frac{4}{75} L \left(\frac{R^2}{D_r}\right)^2 \frac{1}{\phi^2} \cdot u^2 + \frac{8}{525} \left(\frac{R^2}{D_r}\right)^3 \frac{1}{\phi^3} \cdot u^3 \end{aligned} \quad (7)$$

assuming $K_n \gg 1$,

where $D_0 + Au$ has been inserted for D_p . It is clear, that equations (5)–(7) are less complex than equations (1)–(4). In the simpler form they can be used for the experimental verification of the theory outlined.

EXPERIMENTAL

The individual experiments were carried out with columns packed with activated carbon, pumice and glass beads. The physical properties of these columns are summarized in Table I.

For individual packings these materials were screened through sieves into individual fractions representing a certain particle size. The internal and external porosities of the individual packings were determined on basis of measurements of helium and mercury densities. The elution curves of CO_2 were recorded (Perkin Elmer—

TABLE I
COLUMN PARAMETERS

No. of column	Material	Fraction particle radius (mm)	Sample weight (g)	Length of column (cm)	Cross section of empty column (cm ²)	Interstitial porosity	Total porosity
1	Activated carbon	0.15-0.21	21.1	78.5	0.73	0.406	0.843
2	Activated carbon	0.30-0.375	20.1	79.3	0.70	0.421	0.858
3	Activated carbon	0.50-0.60	20.1	79.0	0.70	0.422	0.851
4	Activated carbon	0.75-1.0	19.6	79.8	0.68	0.422	0.847
5	Pumice	0.15-0.21	30.3	81.2	0.67	0.341	0.761
6	Pumice	0.30-0.375	29.10	78.8	0.67	0.361	0.781
7	Pumice	0.50-0.60	27.2	78.8	0.69	0.420	0.840
8	Pumice	0.75-1.0	15.15	46.8	0.70	0.322	0.742
9	Glass	0.15-0.21	90.20	79.0	0.67	0.364	0.364
10	Glass	0.75-1.0	94.8	79.6	0.72	0.386	0.386

Model E) on these columns. The system active carbon-CO₂ represented the case in which the adsorbate is strongly adsorbed on an adsorbent with high internal porosity; pumice-CO₂ represented the case where porous solid is interacting with the non-adsorbing gas. Glass beads were used as materials without internal porosity and without adsorption properties. The carrier gas used in all experiments was hydrogen and its velocity was varied in the range from 3 to 25 cm/sec. The chromatographic curves obtained from all combinations of velocities of the carrier gas and the particle size of individual solids were repeated several times in order to restrict possible experimental errors. The curves were measured and treated by means of a computer. The calculation gave the statistical moments μ_1 - μ_4 and some of their functions. From these moments the functions: $(\mu_2/\mu_1^2)L$; $(\mu_3/\mu_1^3)L^2$; $(\mu_4/\mu_1^4)L^3$, in dependence on the velocity u for individual materials with a given particle size have been plotted. Resulting curves are shown in Figs. 1, 2, 3, 4 and 5.

DISCUSSION

First statistical moment

The meaning of the first statistical moment has already been discussed elsewhere⁶. It should be emphasized, that the first moment gives us the location of the centroid of the area under the chromatographic elution curve (which in general differs from t_{\max}). The position of this centroid depends on the adsorption equilibrium constant, on the porosity of the solids, on the porosity of the bed, and on the longitudinal diffusion constant D_p . The first moment does not depend on any kinetic constant and thus not on the rate at which the equilibrium is established in the column. If we insert in eqn. (1):

$$D_p = D_0 + Au$$

and neglect the term D_0/u^2 we obtain:

$$\mu_1 = \frac{L + 2A}{u} (1 + \phi + \phi K_n) \quad (8)$$

From this it is obvious that the position of the centroid of the area under the chromatographic elution curve (which is better defined as t_{max}) may be influenced by the constant of eddy diffusion A and by the porosity ϕ of the column and of the solid. This expression may be of considerable significance for interpreting the chromatographic data, in particular those obtained on materials with a high internal porosity.

Second statistical moment

In Figs. 1-3 the function $(\mu_2/\mu_1^2)L$ (denoted as H) is plotted in dependence on the velocity u . The function H is in some respects analogous⁸ to the expression for the HETP, which for GLC was introduced by VAN DEEMTER *et al.*⁷. The relationships presented in Fig. 1 show a number of interesting facts:

(i) The increase of the quantity H with increasing u is noticeable over the entire range of the velocities employed only for the largest particle sizes, the dimensions of which considerably exceed those usually employed in gas chromatography.

(ii) The quantity H does not depend, in the employed range of velocities of the carrier gas, upon the material used or, in a certain velocity range, on the velocity itself. For instance, under the condition $u = 10-25$ cm/sec, $R < 0.37$ mm, the quantity H has a constant value amounting very approximately to 0.2 cm. From these experiments we can draw a somewhat surprising conclusion regarding the constant A characterizing the eddy diffusion in gas chromatography. (The $2A$ from our equations is equal to A from the VAN DEEMTER equation⁷.) It appears, that the constant A is neither dependent on the character of the surface of the grain nor on its porosity, and that in the range of chosen experimental conditions it is no function of R . Since the constant A is of considerable importance not only in the case of the second moment but also for higher moments, we have paid great attention to this question. The experiments were analysed in various possible ways for elucidating the dependence of A on R , however, all these analyses only confirm the foregoing statement.

The determination of the term D_g/u whose significance in examining the theory is not very great, has not been studied in detail. For the magnitude of D_g of carbon dioxide in hydrogen we have taken the value of a preceding paper⁶ *i.e.* $D_g = 0.55$ cm²/sec. On the other hand considerable importance was attached to the determination of the coefficient of radial diffusion D_r . For this coefficient in the system CO₂-active charcoal, we obtained the value 2.1×10^{-2} cm²/sec, and in the system CO₂-pumice for $[(\epsilon_e + \epsilon_i)^2/\epsilon_e\epsilon_i]D_r = 8 \cdot 10^{-2}$ cm²/sec, which follows from (5) if $K_n = 0$. This is in good agreement with the theory, which shows, that the influence of porosity for a non-adsorbing gas is such that H decreases to a quarter of the H value of a strongly adsorbing gas. Concerning the nature of the radial diffusion coefficient D_r we have shown elsewhere⁹, that D_r is an effective diffusion coefficient, which is independent of the adsorption constant K_n .

Third statistical moment

On inspecting the expression for the third statistical moment, given by the relation (3) we find, that it is again a function of all constants characterizing the properties of the bed and the packing, the velocity of the carrier medium, the kinetic properties and the equilibrium constants of adsorption. The expression consists only of positive terms, which means (if we place zero into the mean), that the po-

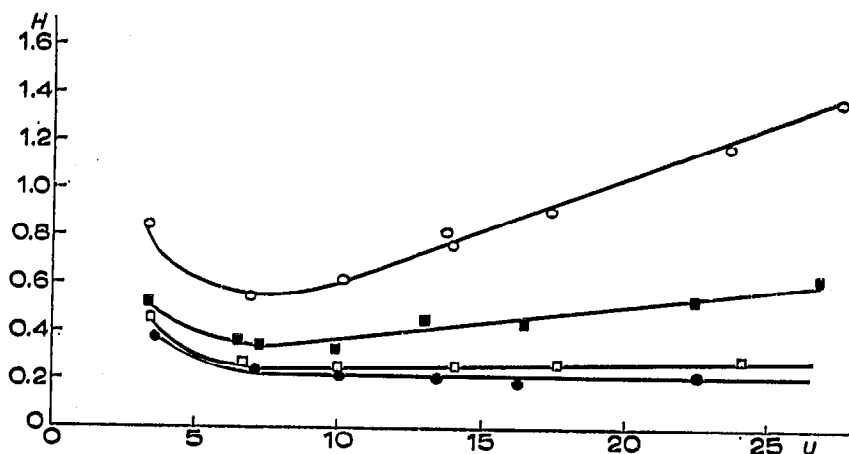


Fig. 1. Dependence of the term H on the velocity of the carrier gas u . Column charged with activated carbon particles of different radius. (●) 0.15–0.21 mm; (□) 0.30–0.375 mm; (■) 0.50–0.60 mm; (○) 0.75–1.0 mm.

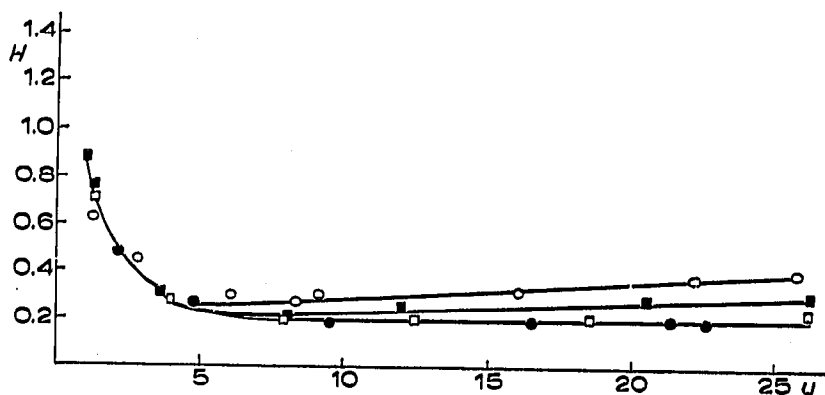


Fig. 2. Dependence of the term H on the velocity of the carrier gas u . Column charged with pumice particles of different radius. (●) 0.15–0.21 mm; (□) 0.30–0.375 mm; (■) 0.50–0.60 mm; (○) 0.75–1.0 mm.

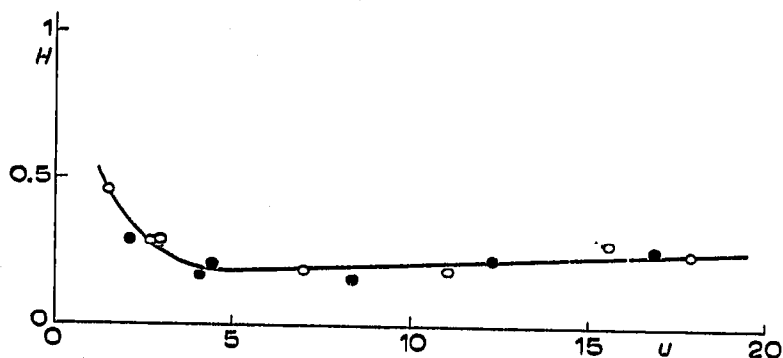


Fig. 3. Dependence of the term H on the velocity of the carrier gas u . Column charged with glass beads of different radius. (●) 0.15–0.21 mm; (○) 0.75–1.0 mm.

sitive deviations predominate over the negative ones. Moreover since the third statistical moment never equals zero, this means that the chromatographic curve in GSC as described by the model under consideration must always be asymmetrical. Multiplying the term μ_3/μ_1^3 , which can be denoted as specific asymmetry by the term L^2 , we obtain the constant Z , which is given by the sum of six terms containing characteristic constants. On examination of these terms we find, that also in the case of a linear adsorption isotherm the asymmetry increases with rising particle radius R , with increasing constant D_0 and A and with decreasing constant D_r . As far as the dependence of the constant Z on the velocity u is concerned, we see that the expression will have a minimum. Since two terms are independent of u , the value of the minimum is likely to be near the values of these terms. The curve of the dependence of Z on u will have a shape similar to that of the dependence H on u . As far as the magnitude and significance of the individual terms is concerned, we must first of all point out the significance of the constant A characterizing the eddy diffusion for the quantity Z . A clear survey of the magnitude of the individual terms in the expression for Z is provided by Table II. From this table it is obvious that the terms containing A largely participate in the overall expression. The large terms with R arise because in this case the experiments were undertaken with relatively large particles.

TABLE II

Z TERMS CALCULATED FROM THE THEORETICAL RELATIONSHIPS

$R = 8.75 \cdot 10^{-2}$ cm; $D_r = 2.1 \cdot 10^{-2}$ cm²/sec; $D_0 = 5.5 \cdot 10^{-1}$ cm²/sec; $A = 1 \cdot 10^{-1}$ cm; $L = 80.0$ cm; $\phi = 1$

u	$\frac{12 D_0}{u^2}$	$\frac{24 A D_0}{u}$	$12 A^2$	$\frac{4}{5} D_0 \frac{R^2}{D_r}$	$\frac{4}{5} A \frac{R^2}{D_r} u$	$\frac{4}{105} \frac{R^4}{D_r^2} u^2$	$\frac{\mu_3}{\mu_1^3} \cdot L^2 = Z$
5	0.26	0.26	0.12	0.16	0.15	0.13	1.08
10	0.07	0.13	0.12	0.16	0.29	0.50	1.27
15	0.03	0.09	0.12	0.16	0.44	1.14	1.97
20	0.02	0.07	0.12	0.16	0.58	2.02	2.96
25	0.01	0.05	0.12	0.16	0.73	3.16	4.24

Experimental examination of the theory

Up to now, we have dealt with considerations following from theoretical conclusions and possible simplifications of the individual relations. It is extraordinarily important and interesting, however, to compare the validity and applicability of the theoretical statements with experimental results. Of principal importance for examining the theory were the experiments with CO₂ on carbon. The dependence of H on u was utilized for determining the constants A and D_r ($A = 0.1$ cm, $D_r = 2.1 \cdot 10^{-2}$ cm²/sec). In accordance with the foregoing explanation the constant A was regarded as independent of R . As magnitude of the particle radius R we introduced the mean value of the respective range of closely limited fractions obtained by screening. The linear velocity of the carrier gas was calculated on the basis of the knowledge of the volumetric flow rate, of the column cross section and the external porosity ϵ_e . Utilizing experimental data we calculated the dependence of Z upon u according to formula (6). The calculated dependence marked by dashed lines is

TABLE III
F TERMS CALCULATED FROM THE THEORETICAL RELATIONSHIPS

u	$\frac{12 D_g^2 L}{u^2}$	$12 A^2 L$	$\frac{24 A D_g L}{u}$	$\frac{8 D_g L R^2}{5 D_r}$	$\frac{8 A L R^2}{5 D_r}$	$\frac{32}{105} D_g \frac{R^4}{D_r^2} u$	$\frac{32}{105} A \frac{R^4}{D_r^2} u^2$	$\frac{4}{75} L \frac{R^4}{D_r^2} u^2$	$\frac{8}{505} \frac{R^6}{D_r^3} u^3$	$\frac{\mu^4}{\mu^4} L^3 = F$
5	11.61	9.60	21.12	25.67	23.33	0.11	0.10	14.17	0.07	105.79
10	2.90	9.60	10.56	25.67	46.67	0.22	0.40	56.70	0.57	153.30
15	1.29	9.60	7.04	25.67	70.00	0.33	0.91	127.57	1.94	244.36
20	0.72	9.60	5.28	25.67	93.34	0.44	1.62	226.80	4.60	368.08
25	0.46	9.60	4.22	25.67	116.67	0.55	2.53	354.37	8.99	523.08

compared with experimental measurements in Fig. 4. A comparison of the results of the calculations and the experimental data shows an agreement, which can be regarded as very good, because the divergence between theory and experiment is smaller than the assumed range of experimental and calculation errors.

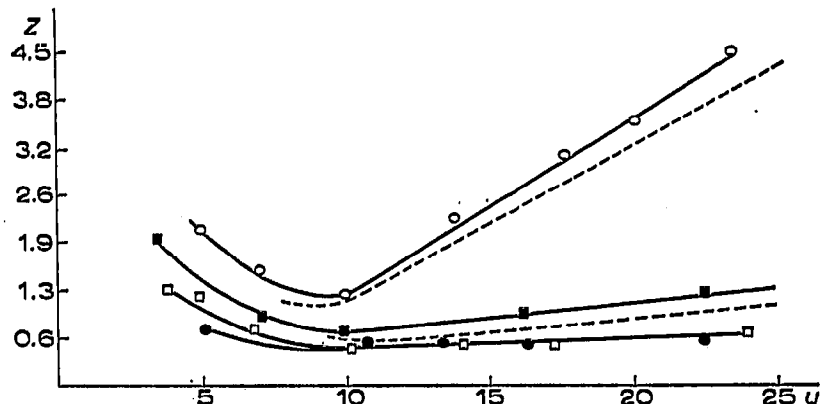


Fig. 4. Dependence of the term Z on the velocity of the carrier gas u. Carbon columns as in Fig. 1. Dashed curves represent the values of the term Z, derived from the theoretical relationships.

Fourth statistical moment

The fourth statistical moment for the Gaussian curve has the value of 3 if we divide this moment by μ_2^2 . The deviation from this value shows the excess or flattening of the distribution curve under investigation. A sufficiently simple expression for the ratio μ_4/μ_2^2 is difficult to derive from the relations for the individual moments. We can, however, easily express the ratio $(\mu_4/\mu_1^4)L^3$, which we denote by F. An examination of the relations mentioned shows clearly that this quantity—contrary to the foregoing characteristics of this type—depends in a more complex way on the column length L. Its dependence on the velocity u is again similar to the preceding relationships *i.e.* it passes through a minimum. The significance of the individual terms can be estimated by means of Table III.

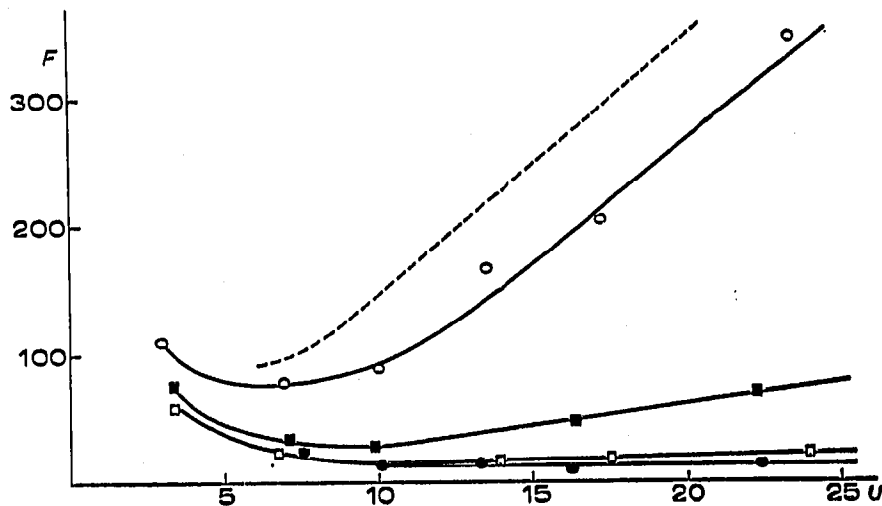


Fig. 5. Dependence of the term F on the velocity of the carrier gas u. Carbon column as in Fig. 1. The dashed curve represents the values of the term F, derived from the theoretical relationships.

As in the case of the third moment, it was also very interesting to compare the experimental results with the theoretical predictions for the fourth moment. For this we utilized experimental data concerning the passage of CO₂ through the column packed with activated carbon, as described earlier, for plotting the expression $(\mu_4/\mu_1^4)L^3$ (this ratio is denoted by F) against the velocity u (Fig. 5). By means of the constants already mentioned we then calculated the values for the expression according to eqn. (7). The calculated results are denoted in Fig. 5 by a dashed line.

It is obvious that in this case too, the agreement between experiment and theory is very good. It may be assumed, therefore, that the chosen model and its mathematical description indicate the behaviour of at least certain GSC systems on porous materials and that the simplifications employed are permissible. The theoretical model and its interpretation may be of importance not only for presenting gas chromatographic data, but also for obtaining important physico-chemical constants. On the other hand it must be pointed out that experimental verification and utilization of the theory have overcome only the first steps and that the conclusions so far drawn must be verified also for other adsorbate-adsorbent systems.

ACKNOWLEDGEMENTS

We are indebted to Dr. M. PÍČEK, PhMr. V. BENEŠOVÁ and L. VIKTOROVÁ for their help in the numerical calculations. The computer programme for calculation of the statistical moments was proposed by Dr. E. KUČERA.

SUMMARY

By means of the system CO₂-activated carbon the applicability of the statistical moments theory to gas-solid chromatography was verified under the assumption that the adsorption rate is controlled by interparticle diffusion. The experimental results are in very good agreement with theoretical predictions.

The theory shows that all the gas chromatographic characteristics may be influenced by the column and solid porosity and by the eddy diffusion constant. This fact has to be respected in presenting the gas chromatography data.

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