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PEAK MOMENTS FOR GAS CHROMATOGRAPHIC COLUMNS WITH A PRESSURE DROP

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SUMMARY

Relationships have been derived for the first absolute and the second and third central moments of the chromatographic curve from a non-isobaric column for the Kubín and Kučera model (axial dispersion, external diffusion, internal diffusion, rate of adsorption). The dependence of the axial dispersion coefficient, mass transfer coefficient and effective diffusion coefficient on the pressure or carrier gas velocity is taken into account. In expressing the internal diffusion, the transition region between Knudsen and bulk diffusion is considered. By using the relationships for the moments, the dependence of the plate height on the carrier gas velocity is expressed (a modified Van Deemter equation for the non-isobaric case). If the rate of adsorption is not significant and internal diffusion takes place in the bulk region, it is possible to use the isobaric form of the Van Deemter equation with a corrected plate height.

INTRODUCTION

The driving force for the flow of a carrier gas through a packed chromatographic column is the pressure drop, Δp ($\Delta p = p_0 - p_e$, where p_0 and p_e are the column inlet and outlet pressures, respectively). Consequently, the pressure $p(z)$ decreases and the interstitial linear velocity $v(z)$ increases along the column since because of the constancy of carrier gas mass flux, the following relationship holds* (on the assumption of ideal behaviour of the carrier gas):

$$p(z) v(z) = p_e v_e = \text{constant} \quad (1)$$

Recently, gas chromatography has been increasingly employed to determine the physico-chemical and chemical engineering parameters of rate processes taking place in a packed column. Therefore, it is necessary to include into the relevant relationships also the effect of varying linear velocity and pressure of the carrier gas

* The change in total mass flux due to the injected substance is considered to be negligible.

because a number of parameters depend on these quantities (axial dispersion, external diffusion, internal diffusion).

So far attention has been paid, from this point of view, to some simpler models of processes in chromatographic columns (see, e.g., refs. 1–4) or a solution has been obtained by using simplifying assumptions⁵. For the most general model of gas chromatography (the Kubín and Kučera model^{6,7}), the expression for the first absolute moment of the outlet chromatographic curve has recently been obtained by Carleton *et al.*⁸.

The aim of this work is to express the first absolute (μ'_1) and the second and third central moments (μ_2, μ_3) of chromatographic curves in a non-isobaric column for the Kubín and Kučera model.

THEORETICAL

Pressure and velocity profiles

Even at relatively high carrier gas velocities, the Reynolds number in a packed column is usually low so that the Darcy equation is sufficient for the description of the carrier gas flow:

$$N = B^* (p/\mu) (1/R_g T) (-dp/dz) \quad (2)$$

where N is the molar density of the carrier gas flow, R_g the gas constant, T the absolute temperature, μ the viscosity of the carrier gas, B^* a constant characteristic of the packed column and z the length coordinate of the column ($z = 0$ at the inlet, $z = L$ at the outlet). On integrating this equation, we obtain the following expression for the dependence of pressure and linear velocity on the position in the column:

$$p(z)/p_e = v_e/v(z) = \left[1 + (2 \mu L a v_e / B^* p_e) \left(1 - \frac{z}{L} \right) \right]^{1/2} \quad (3)$$

or

$$p(z)/p_e = v_e/v(z) = \left[1 + (P^2 - 1) \left(1 - \frac{z}{L} \right) \right]^{1/2} \quad (4)$$

where the subscript e denotes the values at the column outlet and P is the relative pressure at the column inlet ($P = p_0/p_e$).

Non-isobaric column

If we divide the chromatographic column into differential segments of length dz , the pressure and velocity of the carrier gas can be considered to be constant in each segment. The contributions to moments due to a differential segment dz are therefore the same as in an isobaric column in which the velocity and pressure are $v(z)$ and $p(z)$, respectively, and in which an identical shape of the input signal is used. Therefore,

$$\mu'_n(L) - \mu'_n(0) = \int_0^L \frac{d}{dz} (\mu'_n)_{\text{isobar}} dz \quad (n = 0, 1, 2, \dots) \quad (5)$$

$$\mu_n(L) - \mu_n(0) = \int_0^L \frac{d}{dz} (\mu_n)_{\text{isobar}} dz \quad (n = 0, 1, 2, \dots) \quad (6)$$

where μ'_n and μ_n denote the n th absolute and central moment, respectively, of the chromatographic curve at the position z [$\mu'_n(L)$ and $\mu_n(L)$ are the moments of the outlet chromatographic curve at $z = L$] and the subscript isobar denotes the moments for a column with a negligible pressure drop.

The moments μ'_n and μ_n for the isobaric and non-isobaric cases are defined in the usual way as

$$\mu'_n(z) = \int_0^\infty t^n c(z,t) dt / \int_0^\infty c(z,t) dt \quad (n = 0, 1, 2, \dots) \quad (7)$$

$$\mu_n(z) = \int_0^\infty (t - \mu'_1)^n c(z,t) dt / \int_0^\infty c(z,t) dt \quad (n = 0, 1, 2, \dots) \quad (8)$$

where $c(z,t)$ is the time dependence of the concentration of an injected substance at the position z .

Regardless of the pressure conditions in the column, for an input signal in the shape of a rectangular pulse of width t_0 it holds that

$$\mu'_1(0) = t_0/2; \mu_2(0) = t_0^2/12; \mu_3(0) = 0 \quad (9)$$

If we use an input signal in the form of a Dirac function, all of the input moments are zero:

$$\mu'_n(0) = \mu_n(0) = 0 \quad (n = 1, 2, \dots) \quad (10)$$

Kubín and Kučera isobaric model

In the Kubín and Kučera model, the processes in a chromatographic column can be described by the following mass balances of the injected substance^{6,7,9,10}:
column

$$E(\partial^2 c / \partial z^2) - v(\partial c / \partial z) - (\partial c / \partial t) - (3\gamma/\beta)(D/R)(\partial q / \partial r|_R) = 0 \quad (11)$$

particles of the column packing:

$$D[(\partial^2 q / \partial r^2) + (2/r)(\partial q / \partial r)] - \beta(\partial q / \partial t) - \rho_p(\partial w / \partial t) = 0 \quad (12)$$

Because of the low concentration, a linear rate equation is assumed for the rate of adsorption of the injected substance:

$$\partial w / \partial t = k_a[(K\beta/\rho_p)q - w] \quad (13)$$

If the adsorption is in equilibrium, this equation turns into the linear (Henry) adsorption isotherm.

The partial differential eqns. 11 and 12 are supplemented by the following boundary and initial conditions:

$$D(\partial q / \partial r|_R) = k_c[c - q(R)] \quad (14)$$

$$r = 0 \quad \partial q / \partial r = 0 \quad (15)$$

$$t \leq 0 \quad c = q = w = 0 \quad (16)$$

$$z = 0 \quad t > 0 \quad c = c_0(t) \quad (17)$$

In eqns. 11–17, c and q denote the molar concentrations of the injected substance in the carrier gas in the space between the particles of the packing and in the pores of these particles, respectively, w is the molar amount of injected substance adsorbed per unit mass of packing particles, r is the length coordinate of the spherical particles of the packing ($r = 0$ at the centre, $r = R$ at the external surface), t is the time from the beginning of input signal, E is the axial dispersion coefficient, which is usually expressed as

$$E = (\mathcal{D}/\tau) + \varkappa Rv \quad (18)$$

\mathcal{D} is the binary bulk diffusion coefficient of the injected substance–carrier gas pair, τ is the tortuosity of the space between the particles of the packing, \varkappa is a numerical coefficient characterizing the contribution of turbulent diffusion to axial dispersion, R is the radius of the particles of the packing, k_d and K are the rate constant of desorption and the dimensionless equilibrium constant of adsorption of the injected substance on the internal surface of the particles of the packing, respectively, k_c is the mass transfer coefficient of the injected substance between the bulk of the carrier gas and the external surface of the particle, D is the effective diffusion coefficient in the packing particle, α is the external porosity (void volume between particles per unit column volume), β is the internal porosity (pore volume in a particle per unit of its volume) and γ is the ratio of the void volume in the particle (pores) to that between particles [$\gamma = (1 - \alpha)\beta/\alpha$].

By solving the system of eqns. 11–17 by Laplace transformation, it is possible to obtain the following expressions for moments^{6,7,9,11,12}:

$$[\mu'_1(z)]_{\text{isobar}} = \mu'_1(0) + (z/v)(1 + \delta_0) \quad (19)$$

$$[\mu_2(z)]_{\text{isobar}} = \mu_2(0) + (2z/v) [\delta_1 + (E/v^2)(1 + \delta_0)^2] \quad (20)$$

$$[\mu_3(z)]_{\text{isobar}} = \mu_3(0) + (6z/v) [\delta_2 + 2(E/v^2)\delta_1(1 + \delta_0) + 2(E/v^2)^2(1 + \delta_0)^3] \quad (21)$$

where

$$\delta_0 = \gamma(1 + K) \quad (22)$$

$$\delta_1 = \delta_a + \delta_f + \delta_d \quad (23)$$

$$\delta_a = (\delta_0^2/\gamma)(K/k_d)/(1 + K)^2 = \gamma K/k_d \quad (24)$$

$$\delta_f = (\delta_0^2/\gamma)(R\beta/3k_c) \quad (25)$$

$$\delta_d = (\delta_0^2/\gamma)(R^2\beta/15D) \quad (26)$$

$$\delta_2 = [\delta_1^2 + (3/7)\delta_d^2 + (\delta_d^2/K)]/\delta_0 \quad (27)$$

Non-isobaric model

Under non-isobaric conditions it is necessary to take into account the change in the carrier gas velocity along the column and, simultaneously, the corresponding changes in transport parameters which depend on the carrier gas velocity or pressure.

Using eqn. 18 for the description of axial dispersion, then, with respect to eqn. 1 and to the fact that $\mathcal{D} \approx 1/p$, it holds that

$$E/E_e = v/v_e = p_e/p \quad (28)$$

The mass transfer coefficient, k_c , is usually correlated in the form of the Sherwood number with the Schmidt and Reynolds numbers, *i.e.*, as $Sh = f(Re, Sc)$. Here neither Re nor Sc depends on the position in the column [$Sc = (Sc)_e$, $Re = (Re)_e$], so that $Sh = (Sh)_e$ and hence

$$k_c/(k_c)_e = v/v_e = p_e/p \quad (29)$$

With internal diffusion the situation is more complicated. If diffusion takes place in the Knudsen region the effective diffusion coefficient does not change along the column and $D = D_e$. If diffusion occurs in the bulk region then $D/D_e = v/v_e = p_e/p$. For the transition between these regions it is therefore possible to write approximately

$$D/D_e = (v/v_e)^m = (p_e/p)^m \quad (30)$$

where m takes values between 0 and 1 ($m = 0$ in the Knudsen region, $m = 1$ for the bulk diffusion). With the exception of porous particles containing only very narrow pores in which the Knudsen diffusion occurs (see, *e.g.*, ref. 9), it can be expected that the diffusion transport will take place mostly in wider transport pores (see, *e.g.*, refs. 10 and 13) close to the bulk region.

The parameters describing the rate and equilibrium of adsorption of an injected substance (k_d , K) do not depend on the pressure and velocity of the carrier gas.

Non-isobaric moments

By integrating according to eqns. 5 and 6 on using relations 19–21 and dependences 28–30, it is possible to obtain the following relationships for the moments of the outlet chromatographic curve from a non-isobaric column:

$$\mu'_1(L) = \mu'_1(0) + (L/v_e) f_1 (1 + \delta_0) \quad (31)$$

$$\mu_2(L) = \mu_2(0) + (2L/v_e) [f_1 \delta_a + f_2 (\delta_f)_e + f_{m+1} (\delta_d)_e + f_2 (E_e/v_e^2) (1 + \delta_0)^2] \quad (32)$$

$$\begin{aligned} \mu_3(L) = \mu_3(0) + (6L/v_e) \{ & (1/\delta_0) [f_1 \delta_a^2 (1 + K)/K + f_3 (\delta_f)_e^2 + (10/7) f_{2m+1} (\delta_d)_e^2 + \\ & + 2\delta_a (f_2 (\delta_f)_e + f_{m+1} (\delta_d)_e) + 2f_{m+2} (\delta_f)_e (\delta_d)_e] + 2(E_e/v_e^2) (1 + \delta_0) [f_2 \delta_a + \\ & + f_{m+2} (\delta_d)_e + f_3 (\delta_f)_e] + 2f_3 (E_e/v_e^2)^2 (1 + \delta_0)^3 \} \quad (33) \end{aligned}$$

where δ_0 and δ_a are given by eqns. 22 and 24 and

$$(\delta_f)_e = (\delta_0^2/\gamma) [R\beta/3(k_c)_e] \quad (34)$$

$$(\delta_d)_e = (\delta_0^2/\gamma) (R^2\beta/15 D_e) \quad (35)$$

The correction factors f_k ($k = 1-3$) can be expressed as functions of the relative inlet pressure, P :

$$f_k = \int_0^1 (v_e/v)^k d(z/L) = [2/(k+2)] (P^{k+2} - 1)/(P^2 - 1) \quad (36)$$

The dependences f_k vs. P are illustrated in Fig. 1; it can be seen that the correction factors can take comparatively high values. It can also be seen that for lower P holds $f_k(P) \approx [f_1(P)]^k$.

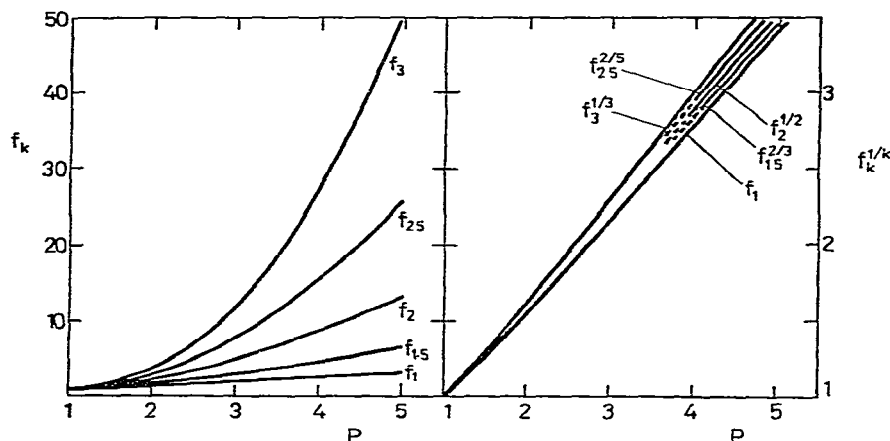


Fig. 1. Correction factors for moments.

First absolute moment. The factor f_1 in eqn. 31 for $\mu'_1(L)$ is identical with the James–Martin correction for retention times^{14,15} and has recently been derived by Carleton *et al.*⁸ for the Kubín and Kučera model by solving a system of balance equations for a non-isobaric column. On introducing the corrected linear velocity v_{corr} , as

$$v_{\text{corr}} = v_e/f_1 \quad (37)$$

the dependence $[\mu'_1(L) - \mu'_1(0)]$ vs. L/v_{corr} must be linear and pass through the origin as in the isobaric case (*cf.*, eqn. 19). From the slope of this dependence it is possible to determine the adsorption parameter, δ_0 , or the equilibrium adsorption constant of injected substance, K .

From a comparison of first absolute moments in the non-isobaric ($P > 1$) and isobaric ($P = 1$) cases at the same outlet velocity, v_e , it follows that $\mu'_1(L)$ in the non-isobaric case is always higher because $f_1 > 1$. This is a consequence of lower linear carrier gas velocities in the upstream parts of column in comparison with v_e .

Second central moment. Under otherwise identical conditions, at the same velocity v_e , the second central moment in the non-isobaric column is always higher than in the isobaric case (corrections $f_1, f_2, f_{m+1} > 1$). The existence of a pressure drop consequently contributes to the peak spreading. The relative increase in the contributions of axial dispersion and external diffusion is the same; the increase in the internal diffusion contribution depends on the region in which internal diffusion takes place (parameter m). With bulk diffusion ($m = 1$), this increase is the same as for

axial dispersion and external diffusion. If the Knudsen diffusion is significant ($m < 1$) the contribution of internal diffusion decreases.

If adsorption is very rapid ($\delta_a \rightarrow 0$) and internal diffusion is of the bulk type ($m = 1$), the relative increase in the second central moment due to the pressure drop in the column is $f_2 - 1$. Consequently, at $P = 1.1, 1.5$ and 2 it represents 10.5%, 62.5% and 150%, respectively.

Third central moment. The third central moment, $\mu_3(L)$, characterizes the asymmetry of the outlet chromatographic curve. It is evident from eqn. 33 and from the values of the correction factors in Fig. 1 that the pressure drop increases the asymmetry considerably. For instance, for $\delta_a \rightarrow 0$ and internal diffusion in the bulk region ($m = 1$), the relative increase in the third moment compared with the isobaric value is $f_3 - 1$. Thus, for $P = 1, 1.5$ and 2 it amounts to 16.3%, 111% and 313%, respectively. The increase in contributions to the third moment due to the external and internal diffusion and axial dispersion is the same as with the second central moment.

Plate height. When evaluating the parameters of processes taking place in a chromatographic column, the plate height, H , is often used. It is defined as

$$H = L[\mu_2(L) - \mu_2(0)]/[\mu_1'(L) - \mu_1'(0)]^2 \quad (38)$$

The dependence of H on the carrier gas velocity, v_e , can easily be obtained even in the non-isobaric case by combining eqns. 38 and 18 and 31 and 32 in the form

$$H = Ag_2 + (Bg_2/v_e) + Cv_e \quad (39)$$

where

$$A = 2 \kappa R \quad (40)$$

$$B = 2 \mathcal{D}_e/\tau \quad (41)$$

$$C = C_a g_1 + C_f g_2 + C_d g_{m+1} \quad (42)$$

$$C_a = 2 \delta_a/(1 + \delta_0)^2 \quad (43)$$

$$C_f = 2 (\delta_f)_e/(1 + \delta_0)^2 \quad (44)$$

$$C_d = 2 (\delta_d)_e/(1 + \delta_0)^2 \quad (45)$$

and the corrections g_k ($k = 1-2$) are defined as

$$g_k = f_k/f_1 = [9/(2k + 4)](P^2 - 1)(P^{k+2} - 1)/(P^3 - 1)^2 \quad (46)$$

The dependence $g_k(P)$ is illustrated in Fig. 2*. Eqn. 39 is related to the modified Van Deemter equation, into which it turns in the isobaric case ($P = 1$, i.e., $g_1 = g_2 = g_{m+1} = 1$).

* The slight dependence of g_2 on P is a consequence of the approximate validity of the relationship $f_2 \approx f_1^2$ ($g_2 = f_2/f_1^2 \approx 1$).

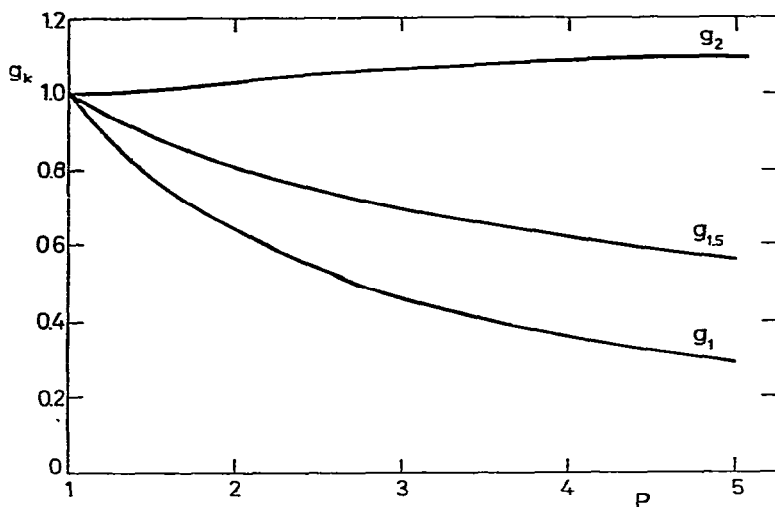


Fig. 2. Correction factors for the Van Deemter equation (eqn. 38).

The contributions to constant C (eqn. 42) change in the non-isobaric case in a different way. In comparison with the isobaric case, the contribution of the rate of adsorption diminishes ($C_a g_1$; $g_1 < 1$), as the contribution of internal diffusion diminishes in the case when the Knudsen diffusion plays a more significant role ($C_d g_{m+1}$; e.g., for $m = 0.5$ $g_{1.5} < 1$). The contribution of external diffusion ($C_f g_2$) is influenced only slightly by the change in the pressure drop over the column (e.g., for $P = 5$, $g_2 = 1.095$); the same holds for internal diffusion in the bulk region ($C_d g_2$). Likewise the terms characterizing the turbulent ($A g_2$) and the diffusion ($B g_2$) parts of axial dispersion change slightly.

It often occurs that the rate of adsorption plays a negligible role ($C_a \rightarrow 0$) and the internal diffusion in close to the bulk region ($m \rightarrow 1$). Then it is possible to rewrite eqn. 39 in the form

$$H/g_2 = A + (B/v_e) + (C_d + C_f)v_e \quad (47)$$

The corrected plate height, H/g_2 , therefore exhibits a dependence on velocity, v_e , identical with that for isobaric conditions. Since for $P < 5$ the correction function g_2 differs from 1 at most by 10%, it is possible to use, in a rougher approximation, the uncorrected values of H on the left-hand side of eqn. 47.

CONCLUSION

Using the relationships for moments of outlet chromatographic curves in non-isobaric columns, it is possible to estimate the effect of pressure drop on the separation efficiency of the column: the retention times [$\sim \mu'_1(L)$] of components of the separated mixture increase in the same way (factor f_1); however, the peaks are simultaneously spread [$\sim \mu_2(L)$] and their asymmetry is increased [$\sim \mu_3(L)$]. Consequently, partial overlapping of peaks takes place and the quality of separation is reduced.

The presence of pressure drop does not cause any problems in chromatographic measurements aimed at evaluating the adsorption equilibrium constant of

an injected substance (K in the parameter δ_0 , eqn. 22). Provided that the corrected carrier gas velocity, v_{corr} , (eqn. 37) is used, it is possible to evaluate the parameter δ_0 from the dependence $[\mu'_1(L) - \mu'_1(0)]$ vs. L/v_{corr} in the same way as under isobaric conditions.

A more complicated situation occurs when it is necessary to evaluate transport parameters by using higher moments of outlet chromatographic curves or plate heights. Then we usually start from the measurements at a number of linear velocities and/or particle sizes of the packing and a graphical procedure or numerical fitting of experimentally determined moments is used. Eqns. 32, 33 and 39 contain, in addition to constant parameters, the correction functions f_k and g_k (eqns. 36 and 46), which are expressed through the easily measurable inlet pressure. Then it is necessary to express P in eqns. 36 and 46 from the relationship

$$P = [1 + (2\mu L \alpha v_e / B^* p_e)]^{1/2} \quad (48)$$

which follows from eqns. 2 and 3. Further, it is necessary to express the dependence of E_e on v_e , e.g., by using eqn. 18*, and the dependence of $(k_c)_e$ on v_e by employing the chemical engineering correlations for packed beds. As external diffusion usually represents a negligible resistance, the last step is not decisive.

Under the usual conditions, adsorption is in the vicinity of equilibrium ($\delta_a \rightarrow 0$), external diffusion plays only a negligible role and transport in the packing particles takes place mostly in wide transport pores ($m \rightarrow 1$). Then it is possible to evaluate easily the effective diffusion coefficient, D_e , from the slope of linear asymptote of the dependence of H/g_2 vs. v_e for higher linear velocities of the carrier gas (C_d , eqn. 45). For the usual pressure drops the correction g_2 can also be omitted and the part of the dependence H vs. v_e for higher velocities can be used directly.

The validity of eqns. 5 and 6 is substantiated by the additivity of moments. Further proof follows from the identity of correction functions f_1 and f_2 obtained for the case of a linear pressure decrease along the column with corrections obtained via the exact solution of the non-isobaric column material balance (partial differential) equations; for this simple pressure profile this can be easily done in a manner similar to that proposed by Carleton *et al.*³.

SYMBOLS

A, B, C	term of the Van Deemter equation (cm, cm ² /sec, sec)
B^*	constant characteristic of the packed column (cm ² /sec)
$c(z, t)$	time dependence of the concentration of the injected substance at position z in the interstitial volume (mol/cm ³)
C_a, C_d, C_f	contributions to the constant C in the Van Deemter equation (sec)
\mathcal{D}	binary bulk diffusion coefficient (cm ² /sec)
D	effective diffusion coefficient of injected substance in particles of the packing (cm ² /sec)
E	axial dispersion coefficient (cm ² /sec)

* This dependence is already incorporated in eqn. 39.

f_k	correction factor, eqn. 36
g_k	correction factor, eqn. 46
H	plate height (cm)
k_c	mass transfer coefficient (cm/sec)
k_d	desorption rate constant for the injected substance (sec^{-1})
K	adsorption equilibrium constant for the injected substance
L	column length (cm)
m	exponent, eqn. 30
N	molar density of the carrier gas flow ($\text{mol}/\text{cm}^2 \cdot \text{sec}$)
$p, p(z)$	column pressure at position z (dyn/cm^2)
P	relative pressure at the column inlet ($P = p_0/p_e$)
q	concentration of injected substance in pores of the particles of the packing (mol/cm^3)
r	length coordinate in spherical packing particle (cm)
R	radius of the particles of the packing (cm)
R_g	gas constant ($\text{erg}/\text{mol} \cdot ^\circ\text{K}$)
Re	Reynolds number, $Re = 2Rv_0/\mu$
Sc	Schmidt number, $Sc = \mu_0/\mathcal{D}$
Sh	Sherwood number, $Sh = 2Rk_c/\mathcal{D}$
t	time (sec)
t_0	width of the input rectangular pulse (sec)
T	absolute temperature ($^\circ\text{K}$)
$v, v(z)$	interstitial carrier gas velocity at position z (cm/sec)
w	molar amount of injected substance adsorbed per unit particle mass (mol/g)
z	length coordinate of column; $z = 0$ at inlet (cm)
α	external porosity
β	internal porosity
γ	ratio of void volume in particle (pores) and between particles; $\gamma = (1 - \alpha)\beta/\alpha$
δ_0	contribution to moments
$\delta_a, \delta_d, \delta_f, \delta_1$	contributions to moments (sec)
δ_2	contribution to moments (sec^2)
κ	numerical coefficient (eqn. 18)
μ	carrier gas viscosity ($\text{g}/\text{cm} \cdot \text{sec}$)
$\mu'_n(z)$	n th absolute moment at position z (sec^n)
$\mu_n(z)$	n th central moment at position z (sec^n)
ρ	carrier gas density (g/cm^3)
ρ_p	apparent packing density (g/cm^3)
τ	tortuosity of the interparticle space

Subscripts

0	column inlet
e	column outlet
isobar	negligible pressure drop
a	adsorption
d	internal diffusion
f	external diffusion

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