A CONTRIBUTION TO THE THEORY OF CHROMATOGRAPHY

LINEAR NON-EQUILIBRIUM CHROMATOGRAPHY WITH A CHEMICAL REACTION OF THE FIRST ORDER

MILAN KOČIŘÍK

Institute of Physical Chemistry, Czechoslovak Academy of Sciences, Prague (Czechoslovakia)

(First received December 23rd, 1966; modified March 23rd, 1967)

The paper of LAPIDUS AND AMUNDSON[1] solves the problem of a linear chromatographic system under conditions of longitudinal diffusion and with slow establishment of equilibrium between the mobile and immobile phases. Their paper gives the final results in the form of functional relations, the practical application of which is somewhat difficult. The present paper is an attempt to solve this system in the presence of a chemical reaction of the first order by moment analysis, the application of the latter to chromatography was suggested by McQUARRIE[2] and used by KUBÍN[3], KUČERA[4], GRUBNER AND KUČERA[5] and WINK[6].

This method makes use of statistical moments[7], to describe the chromatographic curves $c(x,t)$; in particular the first normal moment μ_1' and the central moments μ_n are used. The n-th normal statistical moment is defined by the equation:

$$\mu_n' = \frac{\int_0^\infty c t^n \, \mathrm{d}t}{\int_0^\infty c \, \mathrm{d}t}$$

(1)

The n-th central moment is defined as:

$$\mu_n = \frac{\int_0^\infty c(t - \mu_1')^n \, \mathrm{d}t}{\int_0^\infty c \, \mathrm{d}t}$$

(2)

The n-th central moment can be calculated from the normal moments with the help of the expression:

$$\mu_n = \sum_{k=0}^{n} \binom{n}{k} (-\mu_1')^k \mu_{n-k}'$$

(3)

The normal statistical moments are related to the Laplace transform of the function $c(x,t)$ by a relation known in operator calculus[8]:

$$\mu_n' = (-1)^n \cdot \lim_{p \to 0} \frac{\dfrac{\mathrm{d}^n}{\mathrm{d}p^n} S(x,p)}{S(x,p)}$$

(4)

where $S(x,p)$ is the Laplace transform of the function $c(x,t)$, and which is given in the following form:

$$S(x,p) = \int_0^\infty e^{-pt} c(x,t) \, dt \tag{5}$$

where p is a complex variable.

Let us consider a chromatographic system with a linear separation isotherm having the following characteristics: longitudinal diffusion occurs in the system, the mass transfer between the immobile and mobile phases is carried out at a finite velocity, and a chemical reaction of the first order takes place in the mobile, as well as the immobile phase under isothermal conditions. Neither the influence of pressure drop on the linear velocity, nor the influence of pressure on the diffusion coefficient is considered. The coefficient of longitudinal diffusion and the coefficient of mass transport show a general dependence on the linear velocity of the carrier medium. These relations need not be specified in advance, as it is sufficient for them to be substituted into the final formulae.

The system considered is described by the following set of equations:

$$D \frac{\partial^2 c}{\partial x^2} = u \frac{\partial c}{\partial x} + \frac{\partial c}{\partial t} + \frac{1}{\varPhi} K[\alpha c - a] + \varkappa_1 c \tag{6}$$

$$\frac{\partial a}{\partial t} = K[\alpha c - a] - \varkappa_2 a \tag{7}$$

where c (short for $c(x,t)$) is the volume concentration of the given component in the mobile phase relative to a unit volume in the mobile phase, a (short for $a(x,t)$) is the volume concentration of the given component in the immobile phase relative to a unit volume of the bed, x is the position coordinate along the axis of the column, t is the time coordinate, u is the linear velocity of the carrier medium in the space between the solid particles of the bed, D (short for $D(u)$) is the coefficient of longitudinal diffusion, K (short for $K(u)$) is the coefficient of mass transfer between the mobile and immobile phases, $\varPhi$ is the fraction of the cross-section which is not occupied by the immobile phase, α is the slope of the separation isotherm, $\varkappa_1$ is the rate constant of the chemical reaction in the mobile phase, $\varkappa_2$ is the rate constant of the chemical reaction in the immobile phase.

An example of such a system is a pulse reactor in which a chemical reaction of the first order is taking place, or a chromatographic system separating a compound which is subject to extinction through radioactive decay.

The system is solved for two special types of boundary conditions:

(I) $c(x,t) = a(x,t) = 0$ for $x = +\infty$, $t \geq 0$

    $c(x,t) = c_0(t)$ for $x = 0$, $t \geq 0$

    $c(x,t) = a(x,t) = 0$ for $t = 0$, $0 < x < +\infty$ (8)

(II) $c(x,t) = a(x,t) = 0$ for $x = -\infty$, $t \geq 0$

    $c(x,t) = a(x,t) = 0$ for $x = +\infty$, $t \geq 0$

    $c(x,t) = c_t(x)$ for $t = 0$, $-\infty < x < +\infty$

    $a(x,t) = a_t(x) = 0$ for $t = 0$, $-\infty < x < +\infty$ (9)

The Laplace transform of the function $c(x,t)$, given by eqn. (5), is denoted by S, and the Laplace transform of the function $a(x,t)$ by:

$$L[a(x,t)] = A(x,p) = A \tag{10}$$

Equations (6) and (7) are thus transformed to:

$$D\frac{d^2 S}{dx^2} = u\frac{dS}{dx} + pS + \frac{1}{\Phi}KzS - \frac{1}{\Phi}KA + z_0 S \tag{11}$$

$$pA = KzS - (K + z_2)A \tag{12}$$

By excluding A from the system of eqns. (11) and (12), one has a similar equation to the one found by LAPIDUS AND AMUNDSON[1]:

$$\frac{d^2 S}{dx^2} - \frac{u}{D}\frac{dS}{dx} - \frac{1}{D}\frac{\Phi(p + z_0)(p + K + z_2) + Kz(p + z_2)}{\Phi(p + K + z_2)}S = \frac{c_i(x)}{D} \tag{13}$$

By denoting:

$$\frac{\Phi(p + z_0)(p + K + z_2) + Kz(p + z_2)}{\Phi(p + K + z_2)} = \omega$$

and

$$\frac{c_i(x)}{D} = P(x)$$

it is possible to transcribe eqn. (13) into the following:

$$\frac{d^2 S}{dx^2} - \frac{u}{D}\frac{dS}{dx} - \frac{\omega}{D}S = P(x) \tag{14}$$

The general solution of eqn. (14) is given by[9]:

$$S = \varphi_2 \int \frac{\varphi_1 P(x)}{W} dx - \varphi_1 \int \frac{\varphi_2 P(x)}{W} dx + C_1\varphi_1 + C_2\varphi_2 \tag{15}$$

where C_1 and C_2 are constants which can be determined from the boundary conditions, φ_1 and φ_2 are the so-called fundamental system of the solution of the appropriate homogeneous equation:

$$\varphi_1 = e^{\lambda_+ x} \quad \varphi_2 = e^{\lambda_- x} \tag{16}$$

and

$$\lambda\pm = \frac{u}{2D} \pm \sqrt{\left(\frac{u}{2D}\right)^2 + \frac{\omega}{D}} \tag{17}$$

are the roots of the characteristic equation:

$$\lambda^2 - \frac{u}{D}\lambda - \frac{\omega}{D} = 0 \tag{18}$$

W can be calculated with the help of the following equation:

$$W = \begin{vmatrix} \varphi_1 & \varphi_2 \\ \varphi_1' & \varphi_2' \end{vmatrix} \tag{19}$$

TYPE I BOUNDARY PROBLEM

By introducing type I limiting conditions, the solution for the Laplace transform becomes:

$$S = \tilde{c}_0(p) \exp\left[\frac{ux}{2D} - \sqrt{\left(\frac{u}{2D}\right)^2 + \frac{\omega}{D}} \cdot x\right] \tag{20}$$

where $\tilde{c}_0(p)$ is the Laplace transform of the boundary condition $c_0(t)$. In this case it is convenient to use the terminology of the theory of continuous systems[10]. Thus $S = \tilde{v}(p)$ is the Laplace transform of the out-put quantity of the system $v(t)$; $\tilde{c}_0(p) = \tilde{u}(p)$ is the Laplace transform of the in-put quantity of the system, $u(t)$, and

$$\exp\left[\frac{ux}{2D} - \sqrt{\left(\frac{u}{2D}\right)^2 + \frac{\omega}{D}} \cdot x\right] = \tilde{w}(p) \tag{21}$$

is the transfer function, which is the Laplace transform of the weight function $w(t)$. By the weight function of the system under investigation is meant the response of the system to the transmission of a unit impulse (Dirac's delta function) to the in-put at $t = 0$, while for $t < 0$ the system was undisturbed.

The moments of the out-put quantity have been calculated up to the fourth order, inclusive, under the assumption that an arbitrary concentration impulse has been transmitted to the in-put of the chromatographic system, for which the following is valid: $u(t) \geq 0$ for $0 \leq t < \infty$, and $\int_0^\infty u(t) \, dt$ has a finite value. As:

$$\tilde{v}(p) = \tilde{u}(p) \cdot \tilde{w}(p) \tag{22}$$

it is possible to express the normal moment of the out-put quantity relative to the origin with the help of eqn. (4) by:

$$(\mu_n{}^v)' = (-1)^n \lim_{p \to 0} \frac{\dfrac{d^n}{dp^n}[\tilde{u}(p) \cdot \tilde{w}(p)]}{\tilde{u}(p) \cdot \tilde{w}(p)} =$$

$$= \frac{(-1)^n \sum_{k=0}^{n} \binom{n}{k} \lim_{p \to 0} \dfrac{d^{n-k}}{dp^{n-k}} \tilde{u}(p) \cdot \lim_{p \to 0} \dfrac{d^k}{dp^k} \tilde{w}(p)}{\tilde{u}(p) \cdot \tilde{w}(p)} \tag{23}$$

Therefore,

$$(\mu_n{}^v)' = \sum_{k=0}^{n} \binom{n}{k} (\mu_{n-k}{}^u)' (\mu_k{}^w)' \tag{24}$$

For the first normal moment of the out-put quantity, the following results directly from eqn. (24):

$$(\mu_1{}^v)' = (\mu_1{}^u)' + (\mu_1{}^w)' \tag{25}$$

Using eqns. (3), (24) and (25), the relation for the n-th central moment of the out-put quantity follows:

$$\mu_n{}^v = \sum_{k=0}^{n} \left\{ \binom{n}{k} (-1)^k [(\mu_1{}^u)' + (\mu_1{}^w)']^k \cdot \sum_{l=0}^{n-k} (\iota^{n-k}) (\mu_{n-k-l}{}^u)' (\mu_l{}^w)' \right\} . \tag{26}$$

By executing the indicated operations, and by rearranging the equations, relations currently used in statistics are found[7]:

$$\mu_2{}^v = \mu_2{}^w + \mu_2{}^{wc}$$
$$\mu_3{}^v = \mu_3{}^w + \mu_3{}^{wc}$$
$$\mu_4{}^v = \mu_4{}^w + 6\,\mu_2{}^w\mu_2{}^{wc} + \mu_4{}^{wc} \tag{27}$$

In the case where the in-put quantity is Dirac's function, the Laplace transform of the out-put quantity is equal to the transfer function, and

$$((\mu_n{}^v))' = ((\mu_m{}^{wc}))' \tag{28}$$

$$\mu_m{}^v = \mu_m{}^{wc} \tag{29}$$

is valid. In agreement with eqn. (4) the following is valid for $(\mu_n{}^w)'$:

$$((\mu_m{}^{wc}))' = ((-1)^m \lim_{p \to \mathfrak{p}} \frac{\dfrac{\mathrm{d}^m}{\mathrm{d}p^m}\left\{ \exp\left[\dfrac{ux}{2D} - \sqrt{\left(\dfrac{u}{2D}\right)^2 + \dfrac{\omega}{D} \cdot x}\, \right]\right\}}{\exp\left[\dfrac{ux}{2D} - \sqrt{\left(\dfrac{u}{2D}\right)^2 + \dfrac{\omega}{D} \cdot x}\, \right]} \tag{30}$$

Denoting

$$r = \sqrt{u^2 + 4D\left(x_1 + \frac{K\alpha}{\Phi}\,\frac{x_2}{K + x_2}\right)} \tag{31}$$

the first normal moment and the central moments, second to fourth order inclusive, can be described at a distance of L from the origin by the following relations:

$$((\mu_1{}^{wc}))_1{}' = \frac{L}{r}\left(1 + \frac{K^2\alpha}{\Phi(K + x_2)^2}\right) \tag{32}$$

$$(\mu_2{}^{wc})_1 = \frac{2DL}{r^3}\left(1 + \frac{K^2\alpha}{\Phi(K + x_2)^2}\right)^2 + \frac{2L}{r}\cdot\frac{K^2L}{\Phi(K + x_2)^3} \tag{33}$$

$$(\mu_3{}^{wc})_1 = \frac{12D^2L}{r^5}\left(1 + \frac{K^2\alpha}{\Phi(K + x_2)^2}\right)^3 + \frac{12DL}{r^3}\left(1 + \frac{K^2\alpha}{\Phi(K + x_2)^2}\right)\left(\frac{K^2\alpha}{\Phi(K + x_2)^3}\right) +$$
$$+ \frac{6L}{r}\cdot\frac{K^2\alpha}{\Phi(K + x_2)^4} \tag{34}$$

$$(\mu_4{}^{wc})_1 = \left(\frac{120D^3L}{r^7} + \frac{12D^2L^2}{r^6}\right)\left(1 + \frac{K^2\alpha}{\Phi(K + x_2)^2}\right)^4 +$$
$$+ \left(\frac{144D^2L}{r^5} + \frac{24DL^2}{r^4}\right)\left(1 + \frac{K^2\alpha}{\Phi(K + x_2)^2}\right)^2\left(\frac{K^2\alpha}{\Phi(K + x_2)^3}\right) +$$
$$+ \left(\frac{24DL}{r^3} + \frac{12L^2}{r^2}\right)\left(\frac{K^2\alpha}{\Phi(K + x_2)^3}\right)^2 + \frac{48DL}{r^3}\left(1 + \frac{K^2\alpha}{\Phi(K + x_2)^2}\right)$$
$$\left(\frac{K^2\alpha}{\Phi(K + x_2)^4}\right) + \frac{24L}{r}\cdot\frac{K^2\alpha}{\Phi(K + x_2)^5}. \tag{35}$$

TYPE II BOUNDARY PROBLEM

By using limiting conditions of type II, Laplace's solution is generated:

$$S = \int_{-\infty}^{+\infty} \frac{c_i(\xi)}{2D\sqrt{\left(\frac{u}{2D}\right)^2 + \frac{\omega}{D}}} \exp\left[\frac{u(x - \xi)}{2D} - \sqrt{\left(\frac{u}{2D}\right)^2 + \frac{\omega}{D}} \mid x - \xi \mid \right]d\xi \quad (36)$$

By introducing the initial condition,

$$c_i(x) = \frac{M_0}{\Phi q} \delta(x) \quad (37)$$

where M_0 is the total amount of the compound introduced into the column, q is the total cross-section of the bed and $\delta(x)$ is Dirac's delta function, Laplace's image of the solution takes the form:

$$S = \frac{M}{\Phi q} \frac{\exp\left[\frac{ux}{2D} - \sqrt{\left(\frac{u}{2D}\right)^2 + \frac{\omega}{D}} x\right]}{2D\sqrt{\left(\frac{u}{2D}\right)^2 + \frac{\omega}{D}}} \quad (38)$$

This equation differs from the earlier one found in KUČERA's paper[4] in that $w(p)$ has another form. The first normal moment and the central moments, second to fourth order inclusive, have again been calculated with the help of eqns. (4) and (3) for $x = L$. These moments have been expressed in terms of the moments of Boundary Problem I:

$$(\mu_1')_{II} = \frac{2D}{r^2}\left(1 + \frac{K^2\alpha}{\Phi(K + \varkappa_2)^2}\right) + (\mu_1{}^w)_{I}' \quad (39)$$

$$(\mu_2)_{II} = \frac{8D^2}{r^4}\left(1 + \frac{K^2\alpha}{\Phi(K + \varkappa_2)^2}\right)^2 + \frac{4D}{r^2}\cdot\frac{K^2\alpha}{\Phi(K + \varkappa_2)^3} + (\mu_2{}^w)_{I} \quad (40)$$

$$(\mu_3)_{II} = \frac{64D^3}{r^6}\left(1 + \frac{1}{\Phi}\frac{K^2\alpha}{(K + \varkappa_2)^2}\right)^3 + \frac{48D^2}{r^4}\left(1 + \frac{K^2\alpha}{\Phi(K + \varkappa_2)^2}\right)\left(\frac{K^2\alpha}{\Phi(K + \varkappa_2)^3}\right) +$$

$$+ \frac{12D}{r^2}\cdot\frac{K^2\alpha}{\Phi(K + \varkappa_2)^4} + (\mu_3{}^w)_{I}. \quad (41)$$

$$(\mu_4)_{II} = \left(\frac{960D^4}{r^8} + \frac{96D^3L}{r^7}\right)\left(1 + \frac{K^2\alpha}{\Phi(K + \varkappa_2)^2}\right)^4 +$$

$$+ \left(\frac{960D^3}{r^6} + \frac{144D^2L}{r^5}\right)\left(1 + \frac{K^2\alpha}{\Phi(K + \varkappa_2)^2}\right)^2\left(\frac{K^2\alpha}{\Phi(K + \varkappa_2)^3}\right) +$$

$$+ \left(\frac{144D^2}{r^4} + \frac{48DL}{r^3}\right)\left(\frac{K^2\alpha}{\Phi(K + \varkappa_2)^3}\right)^2 +$$

$$+ \left(\frac{192D^2}{r^4}\right)\left(1 + \frac{K^2\alpha}{\Phi(K + \varkappa_2)^2}\right)\left(\frac{K^2\alpha}{\Phi(K + \varkappa_2)^4}\right) +$$

$$+ \frac{48D}{r^2}\cdot\frac{K^2\alpha}{\Phi(K + \varkappa_2)^5} + (\mu_4{}^w)_{I}. \quad (42)$$

DISCUSSION

The problem formulated above, includes the following special cases:

(1) $\varkappa_1 = \varkappa_2 = 0$

The expressions give the moments of the chromatographic curves, which agree with the moments calculated from the analytical solution given by LAPIDUS AND AMUNDSON[1].

(2) $\varkappa_1 \neq 0, \varkappa_2 = 0$

The component, subject to chromatography, decreases through a first order reaction in the gaseous phase. It is either a question of monomolecular decay of the given component, or of a bimolecular reaction of the component, subject to chromatography, with the carrier gas, which is in excess and, therefore, its concentration is unchanged and is included in the velocity constant $\varkappa_1$.

(3) $\varkappa_1 \neq 0, \varkappa_2 \neq 0$

This case can be turned into the previous by the following transformation:

$$K' = K + \varkappa_2 \tag{43}$$

$$\alpha' = \frac{K\alpha}{K + \varkappa_2} \tag{44}$$

$$\varkappa_1' = \varkappa_1 + \frac{\alpha'}{\phi} \varkappa_2 \tag{45}$$

The expressions for the moments show that in case (2) the rate of the chemical reaction influences the shape of the chromatographic curve only if $D \neq 0$, whereas in case (3) the influence of the chemical reaction can be seen in the shape of the curve, even if $D = 0$. The latter occurs according to the transformation (43–44), given above.

The coefficient of mass transfer includes such phenomena as, e.g. external diffusion, internal diffusion etc. The kinetics of heterogeneous catalytic reactions studied so far, were in most cases under conditions in which either the chemical reaction, or one of the mass transfer phenomena, was the rate determining process. It is expected that the method described above will enable some heterogeneous catalytic reactions of the first order to be studied, even in cases where the velocity of the chemical reaction and the velocity of mass transfer are comparable. The generation of the zero to fourth moment of the out-put chromatographic curve in general allows five independent physical constants of the system to be found.

Equations (27) allow for the moments of the weight function to be found, and in this way make feasible the use of eqns. (32–35) for measuring the physical constants of a given system even in cases, where a quantity of arbitrary form, fulfilling the conditions $u(t) \geq 0$ for $0 \leq t < \infty$ and $\int_0^\infty u(t) \, dt$ has a finite value, is transmitted to the in-put of the system. It is thus sufficient to measure the shape of the in-put concentration with a detector incorporated in the in-put of the column, and to find the moments with the help of the curves. In this way, it is also possible to evaluate experiments carried out by the frontal technique, whereby a rectangular impulse of

such length is transmitted into the system, as to enable the concentration at the out-put to attain a stationary state at least in a short time interval.

The moments in both the boundary problems differ from each other in quantities of higher orders, which can be neglected in the case of a sufficiently long column, so
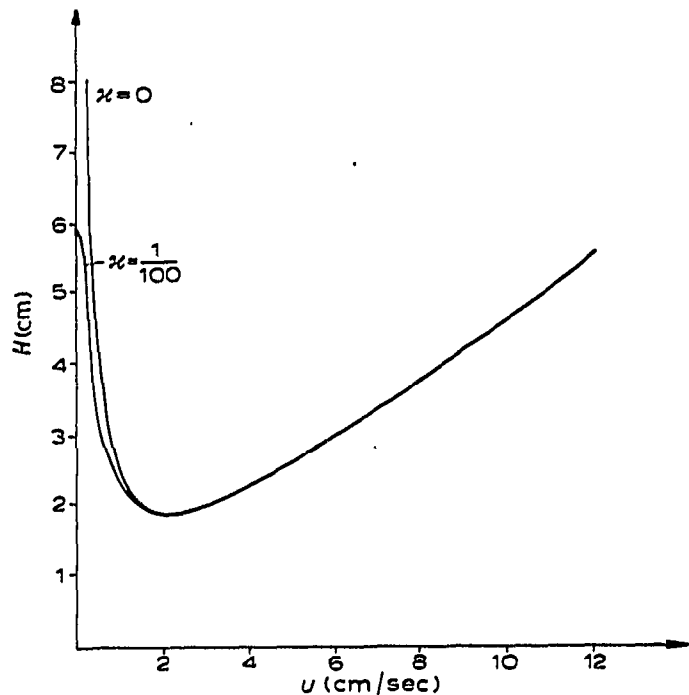

Fig. 1. Dependence of H on u. $D = 1$; $\varkappa_1 = \varkappa_2 = \varkappa$; $K = 1$; $\alpha = 1$; $\Phi = 0.5$.
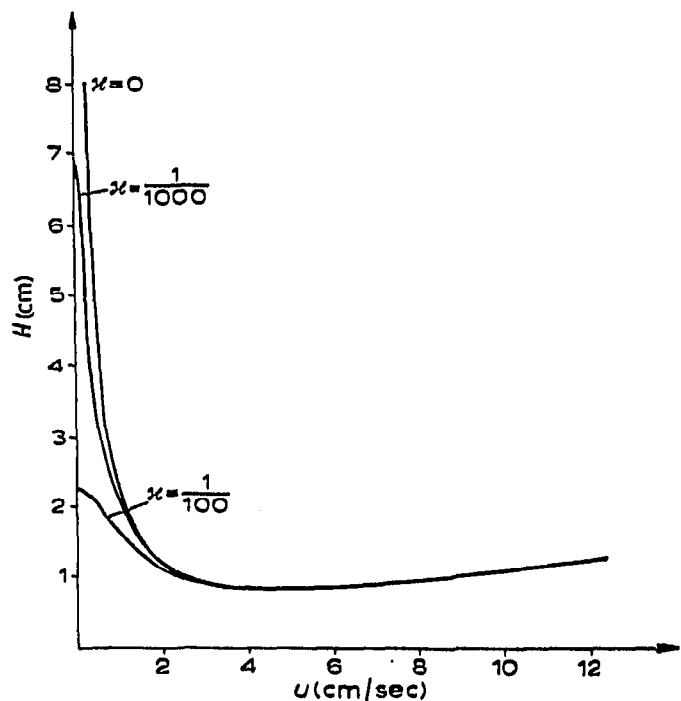

Fig. 2. Dependence of H on u. $D = 1$; $\varkappa_1 = \varkappa_2 = \varkappa$; $K = 1$; $\alpha = 10$; $\Phi = 0.5$.

that the form of the out-put quantity, even in case II, is practically determined by the moments of the weight function.

By carrying out the operation $\lim_{p \to 0} S$, the expression for $\int_0^\infty c(L,t)\,dt$, *i.e.* the zero moment, can be generated in problem I, as well as problem II. In problem I, the areas under the curves $c_0(t)$ and $c(L,t)$ are measured, because the limiting process in this case leads to the expression:

$$\int_0^\infty c(L,t)\,dt = \left[\int_0^\infty c_0(t)\,dt\right] \exp\left[\frac{(u-r)L}{2D}\right] \qquad (46)$$

In the second case the total amount of matter M_0, applied to the column, is measured in its infinitely short section, as well as the area under the curve $c(L,t)$, as the following is valid:

$$\int_0^\infty c(L,t)\,dt = \frac{M_0}{\Phi q}\,\frac{\exp\left[\frac{(u-r)L}{2D}\right]}{r} \qquad (47)$$

For assessing the effectiveness, H, of a given chromatographic system, the following formula is used[5]:

$$H = L\,\frac{\mu_2}{(\mu_1)^2} \qquad (48)$$

By substituting the appropriate expressions for the moments of problem I into eqn. (48), one gets the following equation:

$$H = \frac{2D}{r} + 2r\,\frac{\Phi\alpha K^2(K+\varkappa_2)}{[\Phi(K+\varkappa_2)^2 + K^2\alpha]^2} \qquad (49)$$

The dependence of the quantity H on the linear velocity of the carrier medium u was calculated for a hypothetical case, in which D and K are independent of the carrier medium velocity (*cf.* Figs. 1 and 2). It can be seen that the relation converges to the course described by the van Deemter equation as the values of $\varkappa_1$ and $\varkappa_2$ decrease.

ACKNOWLEDGEMENTS

SUMMARY

A linear chromatographic system was solved, in which longitudinal diffusion, finite velocity of mass transport between mobile and immobile phases and a chemical reaction of the first order in both the phases under isothermal conditions, was considered. The solution was presented as expressions for the moments of the chromatographic curves, with the central moments calculated to the fourth order, inclusive, for two types of limiting conditions.

It is expected that these expressions can be used in studying heterogeneous catalytic reactions in regions where the velocity of the chemical reaction is comparable to the velocity of mass transport. In addition, a method of obtaining constants from a system where an impulse of arbitrary shape has been introduced into the in-put, for both elution and frontal chromatographic techniques, was suggested.

REFERENCES

1 L. LAPIDUS AND N. R. AMUNDSON, *J. Phys. Chem.*, 56 (1952) 984.
2 A. D. McQUARRIE, *J. Chem. Phys.*, 38 (1963) 437.
3 M. KUBÍN, *Collection Czech. Chem. Commun.*, 30 (1965) 1104.
4 E. KUČERA, *J. Chromatog.*, 19 (1965) 237.
5 O. GRUBNER AND E. KUČERA, in H. G. STRUPPE (Editor), *Gas-Chromatographie 1965*, Vorträge des V. Symposiums über Gas-Chromatographie in Berlin, May 1965, Akademie Verlag, Berlin.
6 H. VINK, *J. Chromatog.*, 20 (1965) 305.
7 H. CRAMÉR, *Mathematical Methods of Statistics*, Princeton University Press, Princeton, 1946.
8 G. DOETSCH, *Anleitung zum praktischen Gebrauch der Laplace Transformation*, Oldenbourg, München, 1956.
9 E. KAMKE, *Differentialgleichungen I*, Akad. Verlagsgesellschaft Geest und Portig K.-G., Leipzig, 1951.
10 J. MATYÁŠ, *Metody vyšetřování spojitých systémů a jejich optimální regulace*, SNTL, Prague, 1963.