

MATHEMATICAL SIMULATION OF CONTINUOUS GAS CHROMATOGRAPHY I.

A SET OF GENERAL DIFFERENTIAL EQUATIONS DESCRIBING THE BEHAVIOUR OF A CONTINUOUS CHROMATOGRAPHIC COLUMN

By

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Introduction

The classical gas chromatography has proved to be a highly effective method for the separation of volatile mixtures, but it is essentially a discontinuous operation, using only a small part of the column at any time. There have been a lot of attempts to eliminate this inconvenience [1 to 10], [15]. In most cases a countercurrent motion of the "stationary" phase is maintained, making the process similar to continuous distillation or rather extractive distillation or countercurrent extraction. The general principle of operation may be demonstrated by the "hypersorber" of BERG [1], which was utilized by BERG [1], BENEDEK and SZEPESY [2] to industrial-scale separations.

In general parameters of these devices are calculated by analogies. In the simplest case [10] the concepts of elution chromatography (migration velocity, retention values etc.) are used. From the retention factors and capacity ratios determined on a non-moving stationary phase one can determine the velocity ratios of the stationary and gas phases at which separation takes place.

A number of methods are using distillation and extraction analogies. The pure distillation analogy [11, 12] ignores the velocity of the "stationary" phase or the lack of constant molar overflow. BENEDEK et al. [13] do consider these factors, but essentially they are using distillation analogies, too. According to BARKER [14] continuous chromatography is analogous to countercurrent extraction, where one of the "solvents" is the carrier gas. In all of these methods theoretical plates or transfer units are playing an important role, but neither of them takes into account the fact that, because of sorption, the gas velocity may considerably change along the column, and longitudinal diffusion is always neglected as well.

GLASSER's "dynamic" method [5] does not care of HTU and HETP values, but considers the sorption rates to be proportional to the difference in phase boundary and bulk concentrations. Like in other methods, longi-

tudinal diffusion is neglected. A set of differential equations can be set up, which reduces to a set of linear equations at low concentrations. From these equations the concentration distribution of the components can be determined. At higher concentrations the solution cannot be given but numerically.

The method seems to be advantageous because this set of equations gives all the needed quantities. Its drawback is the difficulty of the solution of equations with boundary conditions, especially in the non-linear case. We are trying this way, however, since the equations can easily be modified, taking into account previously neglected factors. Once having made a general computer program for the solution, the modifications do not raise, in general, greater difficulties.

In this first communication, sets of equations will be set up, allowing for longitudinal diffusion in the gas phase, and boundary conditions will be defined. Numerical solution and results will be discussed in a separate paper.

A general model of the continuous chromatography

A line diagram of the device is given in Fig. 1. The actual realizations may differ more or less, but in fact most of them can be reduced to this simple case.

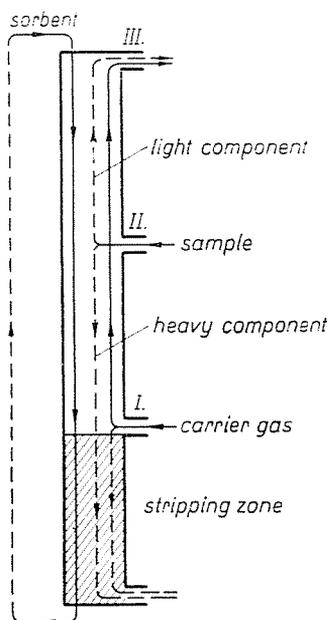


Fig. 1. Flow pattern of a continuous column

The carrier gas is introduced at inlet I, in the lower part of the column. A portion of it may depart downwards forming a gas seal, then only the remainder constitutes the carrier moving upwards at a linear velocity v . The condensed phase, in the form of grains or a bundle of threads, moves downwards at a velocity v_L . After leaving the column it is generally carried back to the top and reused. The sample is introduced in the middle, at inlet II. The strongly adsorbing components are moving downwards and are stripped from the condensed phase in the stripping zone below inlet I. The lighter components are departing with the carrier gas at the top of the column (outlet III). We consider now only the so-called rectification section, from I to III.

In most cases the carrier is not fed at I but through the stripping zone, so that a portion of it saturated with the heavy components *leaves* the column at I. This does not modify the equations at all, but makes the boundary conditions somewhat complicated because a mixture rather than pure carrier gas is fed to the rectification section at I.

Time t and distance from inlet I, z are taken as independent variables. It is assumed that there are no radial gradients in concentration and velocity, so the problem is one-dimensional in space. This assumption is justified, however, only if diffusion coefficients are high enough, and it entails that longitudinal diffusion is *not* negligible [16].

Dependent variables are the linear gas velocity:

$$v = v(t, z),$$

the mole fractions of the components in the gas phase except that of the carrier gas:

$$y_i = y_i(t, z),$$

and the adsorbed quantities per unit length of the same components:

$$a_i = a_i(t, z).$$

In case of k different components:

$$i = 1, 2, \dots, k.$$

The mole fraction of the carrier gas may be given as

$$y_0 = 1 - \sum_{i=1}^k y_i \tag{1}$$

so it is not be treated as a separate variable.

Other parameters thought to be constant along the column are

- T = absolute temperature (K);
 p = pressure;
 q = free cross-sectional area;
 v_L = linear velocity of the condensed phase;
 L_0 = amount of solvent per unit length (only in case of gas — liquid chromatography).

The before-named quantities definitely describe the state of the system. Our task is to find relationships giving the dependent variables versus t and z . To this aim, further specific parameters and relationships are needed, namely the diffusion coefficients D_i (or, properly speaking, the effective binary diffusivities D_{im} [17]) and the sorption rates per unit length:

$$S_i = S_i(y_i, a_i).$$

The problem is similar to that of frontal chromatography with the difference that here the "stationary" phase is moving as well. The fundamental differential equations of frontal chromatography had been given earlier by SCHAY [16]. These equations are applicable to our problem when completed by a term relating to the moving condensed phase. With regard to the following considerations, they will be given below in a slightly different form.

Setting-up of the equations

The equation of continuity for the source-free flow of an incompressible fluid completed by Fick's second law to account for longitudinal diffusion may be written as:

$$\frac{\partial(dn_i)}{\partial t} = D_i \frac{\partial^2(dn_i)}{\partial z^2} - \frac{\partial(vdn_i)}{\partial z}. \quad (2)$$

Here dn_i is the amount of component i in the infinitesimal volume

$$dV = qdz$$

i.e.

$$dn_i = \frac{p_i dV}{RT} = \frac{y_i pq}{RT} dz. \quad (3)$$

Sorption acts as a sink (or source) so in case of sorption the total balance is

$$\frac{\partial(dn_i)}{\partial t} = D_i \frac{\partial^2(dn_i)}{\partial z^2} - \frac{\partial(vdn_i)}{\partial z} - S_i dz \quad (4)$$

or with regard to Eq. (3) and neglecting the differences in difussivities

$$\frac{\partial y_i}{\partial t} = D \frac{\partial^2 y_i}{\partial z^2} - \frac{\partial(vy_i)}{\partial z} - \frac{RTS_i}{pq}. \quad (5)$$

From Eqs (1) and (5) follows for the inert carrier:

$$\sum_{i=1}^k \frac{\partial y_i}{\partial t} = D \sum_{i=1}^k \frac{\partial^2 y_i}{\partial z^2} - \sum_{i=1}^k \frac{\partial(vy_i)}{\partial z} + \frac{\partial v}{\partial z}. \quad (6)$$

Eqs (5) and (6) give

$$\frac{\partial v}{\partial z} = - \sum_{i=1}^k \frac{RT}{pq} S_i, \quad (7)$$

expressing that any change in gas velocity results exclusively from sorption (or desorption). This last equation is simpler than Eq. (6), therefore Eqs (5) and (7) will be further on considered, instead of (5) and (6).

In setting up the equation of continuity for the condensed phase, the role of diffusion, for the moment, will be neglected. This assumption seems quite reasonable for gas-liquid chromatography, because diffusion in the liquid phase is by orders of magnitude slower than in the gas phase. In case of gas-solid chromatography, however, it may be questionable [16].

The equation of continuity for the condensed phase is

$$\frac{\partial(dn_i^s)}{\partial t} = - \frac{\partial(v_L dn_i^s)}{\partial z} + S_i dz \quad (8)$$

where

$$dn_i^s = a_i dz$$

is the amount of the species *i* in an infinitesimal portion of height *dz* of the condensed phase. So Eq. (8) may be rewritten in the more customary form

$$\frac{\partial a_i}{\partial t} = - v_L \frac{\partial a_i}{\partial z} + S_i. \quad (9)$$

Strictly speaking, the sorption is accompanied by an increase in the amount of the condensed phase, i.e. by a decrease in the free cross-sectional area *q*. This effect is, in general, negligible, so it will not be considered. However, it can be accounted for, if necessary, by a relationship like

$$q = q(a_1, a_2, \dots, a_k)$$

to be substituted into Eqs (5) and (7). This does not make the numerical solution of the system much more difficult.

Eqs (5), (7) and (9) constitute a set of equations determining the functions y_i , a_i and v , if the boundary conditions and the concrete forms of the sorption terms S_i are known. A complete solution is, however, very complicated, therefore only steady-state solutions will be considered. In this case the partial differential equations turn into ordinary ones:

$$D \frac{d^2 y_i}{dz^2} = \frac{d(vy_i)}{dz} + \frac{RTS_i}{pq} \quad (i = 1, 2, \dots, k) \quad (10a)$$

$$\frac{dv}{dz} = - \frac{RT}{pq} \sum_{j=1}^k S_j \quad (10b)$$

$$\frac{da_i}{dz} = \frac{1}{v_L} S_i \quad (i = 1, 2, \dots, k) . \quad (10c)$$

The expressions for the sorption rates S_i may depend on the given case but, in general, one of the two limiting cases may be assumed as approximately valid:

- a) Equilibrium chromatography,
- b) linear sorption kinetics.

In case of equilibrium chromatography there are direct relations between y_i and a_i :

$$y_i = f_i(a_i) \quad (11)$$

or

$$a_i = \varphi_i(y_i) . \quad (11')$$

To be more exact, the components do not adsorb independently:

$$y_i = f_i(a_1, a_2, \dots, a_k) \quad (11a)$$

and

$$a_i = \varphi_i(y_1, y_2, \dots, y_k) \quad (11'a)$$

but the effect of the other components is generally negligible. In case of gas-solid chromatography at higher concentrations, however, only equations like (11a) or (11'a) are to be applied.

Eqs (11) or (11') represent k new relationships, so the sorption rates expressed from (10c)

$$S_i = v_L \frac{da_i}{dz}$$

can be written as

$$S_i = v_L \varphi'_i \frac{dy_i}{dz} \quad (12)$$

and thus the sorption rates S_i as well as the adsorbed quantities a_i have been eliminated. The new set of equations is

$$D \frac{d^2 y_i}{dz^2} = \frac{d(vy_i)}{dz} + \frac{RTv_L}{pq} \varphi'_i \frac{dy_i}{dz} \quad (i = 1, 2, \dots, k) \quad (13a)$$

$$\frac{dv}{dz} = - \frac{RTv_L}{pq} \sum_{j=1}^k \varphi'_j \frac{dy_j}{dz}. \quad (13b)$$

Having determined the mole fractions y_i , the values of a_i can be calculated from (11').

In the non-equilibrium case the sorption rates are determined by differences in concentrations or better, activities. According to the two-film theory [18], the overall resistance to absorption is the resultant of the resistances gas-interface and interface-liquid, the interface being in equilibrium. In most cases the rate of sorption can be expressed as

$$S_i = \alpha_i (y_i - y_i^*) \quad (14)$$

or

$$S_i = \beta_i (a_i^* - a_i) \quad (14')$$

where y_i^* and a_i^* are equilibrium values to a_i and y_i , respectively, determined by Eqs (11) or (11'); α_i and β_i are proportionality factors.

Gas-liquid chromatography

In case of gas-liquid chromatography the above equations are suitably rewritten in a slightly different form. Instead of a_i it seems more advantageous to use the mole fractions in the liquid phase, x_i , because the relationship between x and y is linear up to higher concentrations. According to Henry's law:

$$py_i^* = H_i x_i \quad (15)$$

or

$$x_i^* = \frac{P}{H_i} y_i = \gamma_i y_i. \quad (15')$$

If L_0 is the amount of solvent, L is the total amount of liquid per unit length, then

$$L \left(1 - \sum_{j=1}^k x_j \right) = L_0$$

and

$$a_i = Lx_i = L_0 \frac{x_i}{1 - \sum_j x_j} \quad (16a)$$

or

$$\frac{da_i}{dz} = \frac{da_i}{dx_i} \frac{dx_i}{dz} = L_0 \frac{1 - \frac{x_i}{1 - \sum_j x_j}}{1 - \sum_j x_j} \frac{dx_i}{dz}. \quad (16b)$$

Substituting Eq. (16b) into (10c) we get

$$\frac{dx_i}{dz} = \frac{1}{v_L L_0} \frac{1 - \sum_j x_j}{1 - \frac{x_i}{1 - \sum_j x_j}} S_i \quad (16c)$$

and the set (13) of equations becomes, considering also Eq. (15'):

$$D \frac{d^2 y_i}{dz^2} = \frac{d(vy_i)}{dz} + \frac{RTv_L L_0}{pq} \frac{1 - \frac{\gamma_i y_i}{1 - \sum_j \gamma_j y_j}}{1 - \sum_j \gamma_j y_j} \gamma_i \frac{dy_i}{dz} \quad (17a)$$

$$\frac{dv}{dz} = - \frac{RTv_L L_0}{pq} \sum_{i=1}^k \frac{1 - \frac{\gamma_i y_i}{1 - \sum_j \gamma_j y_j}}{1 - \sum_j \gamma_j y_j} \gamma_i \frac{dy_i}{dz}. \quad (17b)$$

In this set of equations all the parameters are known or measurable, so numerical solution is possible. It seems a bit more complicated than set (13), but it is only so because concrete expressions for φ'_i have been substi-

tuted. Moreover, in case of dilute solutions, or better, for

$$\sum_{j=1}^k \gamma_j y_j \ll 1$$

these equations simplify, since then

$$\varphi'_i \approx L_0 \gamma_i. \tag{18}$$

In some cases, however, high concentrations seem to be desirable — e.g. for preparative scale separations — so set (17) has to be examined.

In case of non-equilibrium chromatography, expressions like (14) are to be substituted into set (10). From (10a), (10b), (10c), (14) and (16b) one obtains

$$D \frac{d^2 y_i}{dz^2} = \frac{d(vy_i)}{dz} + \frac{RT}{pq} k_i \left(y_j - \frac{H_i}{p} x_i \right) \quad (i = 1, 2, \dots, k) \tag{19a}$$

$$\frac{dv}{dz} = - \frac{RT}{pq} \sum_{j=1}^k k_j \left(y_j - \frac{H_j}{p} x_j \right) \tag{19b}$$

$$\frac{dx_i}{dz} = \frac{1}{v_L L_0} \frac{1 - \sum_j x_j}{1 - \frac{x_i}{1 - \sum_j x_j}} k_i \left(y_i - \frac{H_i}{p} x_i \right) \quad (i = 1, 2, \dots, k) \tag{19c}$$

k_i being the overall mass transfer coefficient for the species i .

Equilibrium chromatography means that sorption rates are very high, therefore solutions of (19) with growing k_i values must approach the solution of (17). It is to be noted, however, that the numerical solution of (19) for high values of k_i may be very difficult because of stability problems.

Boundary conditions (non-equilibrium case)

There are three places where materials can enter or leave the column: at the bottom, in the middle and at the top (Fig. 2). The quantities relative to these points will be designated by superscripts 0 , m and t , respectively. The general material balance for non-equilibrium chromatography under steady state may be written as

$$v_L (a_i^t - a_i^0) + \frac{pq}{RT} (v^0 y_i^0 - v^t y_i^t) + \frac{pI_v^m}{RT} y_i^m = 0 \tag{20}$$

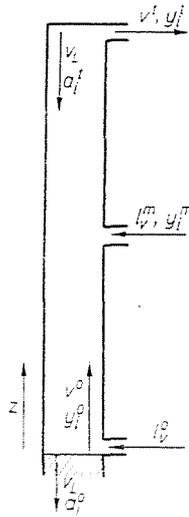


Fig. 2. Material balance of a continuous column

if diffusion is negligible. I_v^m is the flow rate of the sample introduced in the middle.

Assuming that the feed at the bottom is pure carrier gas and the condensed phase before entering the column contains no component to be separated, Eq. (20) reduces to

$$v_L a_i^0 + \frac{P}{RT} (qv^t y_i^t - I_v^m y_i^m) = 0 \quad (21)$$

Further conditions:

$$a_i^t = 0 \quad (22)$$

$$y_i^0 = 0 \quad (23)$$

$$v^0 = I_v^0/q \quad (24)$$

where I_v^0 is the flow rate of the carrier gas introduced at the bottom.

Eqs (20) to (24) are true only if diffusion is negligible. If diffusion (in the gas phase) is to be accounted for, some of the boundary conditions are to be modified. Since there are finite concentration gradients at the boundaries, material can be transferred not only by flow but also by diffusion.

The equations are fully analogous to those for a continuous tubular reactor with longitudinal diffusion, the only difference being that in our

case sinks and sources are represented by sorption and desorption, instead of chemical reaction. This latter case has been discussed in detail by WEHNER and WILHELM [19]. Their communication imply that in our case the condition

$$\frac{dy_i^t}{dz} = 0 \tag{25}$$

is to be used instead of (23). It is to be noted, however, that Eq. (25) is *not* valid for systems without diffusion [19].

The generalized form of Eq. (20) is

$$v_L(a_i^t - a_i^0) + \frac{pq}{RT} \left(v^0 y_i^0 - D \frac{dy_i^0}{dz} - v^t y_i^t + D \frac{dy_i^t}{dz} \right) + \frac{pI_v^m}{RT} y_i^m = 0. \tag{26}$$

It has been shown [19] that

$$v^0 y_i^0 - D \frac{dy_i^0}{dz} = 0. \tag{27}$$

The other diffusion term also vanishes according to Eq. (25); Eq. (22) remains unchanged since diffusion in the condensed phase is neglected, so Eq. (21) remains valid as well. Eq. (24) does not change either, since diffusion does not influence the flow rate.

The problem of central feeding

In the central feeding zone the given sets of equations do not describe the system. Special relationships have to be found to account for the changes in v , y_i , a_i and dy_i/dz due to the central feeding.

It may seem self-evident to assume an infinitesimally thin mixing zone as a first approximation. In this case the following material balance could be written:

$$v^+ = v^- + \frac{I_v^m}{q} \tag{28a}$$

$$y_i^+ = \frac{v^- y_i^- + \frac{I_v^m y_i^m}{q}}{v^+} \tag{28b}$$

$$a_i^+ = a_i^-. \tag{28c}$$

Superscripts - and + refer to the upper boundary of the lower section and the lower boundary of the upper section, respectively.

Eqs (28) represent $2k + 1$ relationships giving definite values to v^+ , y_i^+ and a_i^+ but there is no equation giving values to dy_i/dz . As a matter of fact, the feeding orifice has finite dimensions and, on the other hand, a jump in concentration is incompatible with diffusion: it would mean infinite concentration gradients, i.e. infinite diffusion rates. So it has to be accepted that there is a mixing zone of finite thickness, to which our equations do not apply.

Let superscripts $-$ and $+$ henceforth refer to the lower and upper boundaries of this zone. From the material balances we obtain

$$v^+ = v^- + \frac{I_v^m}{q} + \frac{v_L RT}{pq} \sum_{i=1}^k (a_i^+ - a_i^-) \quad (29a)$$

and

$$y_i^+ v^+ = y_i^- v^- + \frac{I_v^m y_i^m}{q} + \frac{v_L RT}{pq} (a_i^+ - a_i^-). \quad (29b)$$

Eq. (28c) is not valid because on a finite length finite sorption or desorption may take place. To be correct, also diffusion terms should have been considered in Eq. (29b), but it would not alter the fact that we have altogether $k + 1$, rather than $3k + 1$, relationships.

In order to get unique solutions, some definite structure has to be assumed for this zone. It is hoped, however, on the basis of chromatographic practice, that in sufficiently long columns any reasonable structure gives approximately the same results except in the vicinity of the feeding.

In short, the structure and width of the central inlet zone may be chosen arbitrarily to an extent. But it is advisable to check, whether different structures give similar results. In any case, however, the variables should be continuous in the transition layer, the boundaries included, possible by continuously distributing the feed through an inlet zone of length Δz , using a weighting function which vanishes at the boundaries.

A rather realistic weight function may be obtained by assuming the feed uniformly distributed in a circular cross-section of radius

$$r = \Delta z/2.$$

If the centre of the circle is at a height z^m , then the flow rate of the feed at a height z ($z^m + r \geq z \geq z^m - r$) in a layer of thickness dz (Fig. 3) may be written as

$$dI_v = \frac{2 \sqrt{r^2 - (z - z^m)^2}}{r^2} I_v^m dz, \quad (30)$$

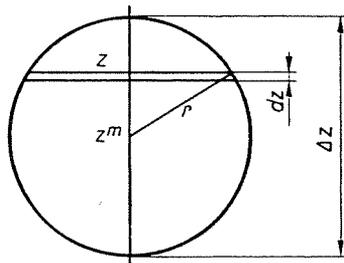


Fig. 3. Cross-section of inlet II

i.e., in this case

$$w(z) = \frac{2\sqrt{r^2 - (z - z^m)^2}}{r^2} \tag{31}$$

It is easy to show that

$$\int_{z^m - r}^{z^m + r} w dz = 1 \tag{32}$$

i.e., the total feed is I_v^m .

The weight function (31) is not the only possible one, it is even unfavourable because of its complexity and singularities of its first derivative at the boundaries. In principle, every function satisfying Eq. (32) and vanishing at the boundaries is suitable. A rather satisfactory function is, for instance:

$$w(z) = \frac{\pi}{2\Delta z} \cos \frac{\pi}{\Delta z} (z - z^m) \tag{33}$$

The application of a weight function has the additional advantage of eliminating any boundary condition problem at the central zone. w may be zero along the whole column except the feeding zone, and then Eq. (4) can be written as

$$\frac{\partial(dn_i)}{\partial t} = D_i \frac{\partial^2(dn_i)}{\partial z^2} - \frac{\partial(vdn_i)}{\partial z} - \left(\frac{wpI_v^m y_i^m}{RT} - S_i \right) dz, \tag{34}$$

accordingly Eqs (5) and (7) become

$$\frac{\partial y_i}{\partial t} = D \frac{\partial^2 y_i}{\partial z^2} - \frac{\partial(vy_i)}{\partial z} - \frac{RT}{pq} S_i + \frac{I_v^m y_i^m}{q} w \quad (i = 1, 2, \dots, k) \tag{35}$$

$$\frac{\partial v}{\partial z} = \frac{I_v^m}{q} w - \frac{RT}{pq} \sum_{i=1}^k S_i. \quad (36)$$

The set (10) turns into

$$D \frac{d^2 y_i}{dz^2} = \frac{d(vy_i)}{dz} + \frac{RT}{pq} S_i - \frac{I_v^m y_i^m}{q} w \quad (i = 1, 2, \dots, k) \quad (37a)$$

$$\frac{dv}{dz} = \frac{I_v^m}{q} w - \frac{RT}{pq} \sum_{j=1}^k S_j \quad (37b)$$

$$\frac{da_i}{dz} = \frac{1}{v_L} S_i \quad (i = 1, 2, \dots, k) \quad (37c)$$

and similarly sets (13), (17) and (19) may be transformed.

Set (37) and the modified set (19) may be solved numerically without any boundary problem in the central zone, considering the boundary conditions given by Eqs (21), (22), (24) and (25).

Equilibrium chromatography

In case of equilibrium chromatography the boundary conditions given above do not apply. In this case the functions a_i have a jump at the upper boundary of the column since the condensed phase enters free from solutes while the gas leaving the column contains finite amounts of them.

Designating the upside and column-side limiting values at the top of the column by superscripts t^+ and t^- :

$$a_i^{t^-} \neq a_i^{t^+} = 0 \quad (38)$$

i.e. at the upper boundary, finite amounts of the components are adsorbed on an infinitesimal length:

$$\Delta \dot{n}_i^t = v_L a_i^t. \quad (39)$$

This entails a jump in the velocity v :

$$\Delta v = - \frac{RT}{pq} \sum \Delta \dot{n}_i^t. \quad (40)$$

At the same time, due to diffusion, there is no concentration jump in the gas phase:

$$y_i^{t^+} = y_i^{t^-}. \quad (41)$$

There is, however, a break in y_i and a jump in dy_i/dz , necessary condition for the finite sorption given by Eq. (39).

It follows from WILHELM and WEHNER's reasoning [19] that

$$\frac{dy_i^{t+}}{dz} = 0 \tag{42}$$

since the components are of finite concentration in the departing gas and there is no sorption after the column. So the excess transported to the boundary by diffusion and to be adsorbed there:

$$\Delta \dot{n}_i = - \frac{Dpq}{RT} \frac{dy_i^{t-}}{dz} \tag{43}$$

Eqs (39), (43) and (11') give the boundary conditions

$$v_L \varphi_i(y_i^t) + \frac{Dpq}{RT} \frac{dy_i^{t-}}{dz} = 0 \tag{44}$$

It is still to be examined, whether the conditions given by Eqs (20), (21) or (26) are valid. They have been set up on the assumption that all the functions were continuous at the boundaries. It was seen, however, that in equilibrium chromatography neither a_i nor dy_i/dz were continuous at the upper boundary.

Designating the column-side and downside limiting values at the lower boundary by superscripts $^{0+}$ and $^{0-}$, Eq. (26) becomes:

$$v_L(a_i^{t+} - a_i^{0-}) + \frac{pq}{RT} \left(v^{0-} y_i^{0-} - D \frac{dy_i^{0-}}{dz} - v^{t+} y_i^{t+} + D \frac{dy_i^{t+}}{dz} \right) + \frac{pI_v^m}{RT} y_v^m = 0 \tag{45}$$

a_i^{t+} and dy_i^{t+}/dz were seen to be zero; WEHNER and WILHELM's communication [19] implies that

$$v^{0-} y_i^{0-} - D \frac{dy_i^{0-}}{dz} = 0 \tag{46}$$

v^{t+} from Eqs (40) and (43) may be substituted:

$$v^{t+} = v^{t-} + \Delta v = v^{t-} + D \sum_j \frac{dy_j^{t-}}{dz} \tag{47}$$

The only undefined term is a_i^{0-} , since Eqs (11) and (11') are not necessarily valid outside the column.

There is no accumulation under steady-state conditions, i.e. the algebraic sum of the material transported to a certain point by convection, diffusion and sorption or desorption has to be zero. For the lower boundary, regarding Eq. (46):

$$v_L(a_i^{0+} - a_i^{0-}) - \frac{Pq}{RT} \left(v^{0+} y_i^{0+} - D \frac{dy_i^{0+}}{dz} \right) = 0 \quad (48)$$

or

$$v_L a_i^{0-} = v_L a_i^{0+} - \frac{Pq}{RT} \left(v^{0+} y_i^{0+} - D \frac{dy_i^{0+}}{dz} \right) \quad (48')$$

so Eq. (45), substituting also Eqs (11') and (47), may be written as:

$$\begin{aligned} -v_L \varphi_i(y_i^0) + \frac{Pq}{RT} \left[v^{0+} y_i^0 - \left(v^{i-} + D \sum_j \frac{dy_j^{i-}}{dz} \right) y_i^i - D \frac{dy_i^{0+}}{dz} \right] + \\ + \frac{pI_v^m}{RT} y_i^m = 0. \end{aligned} \quad (49)$$

Eqs (44) and (49) represent $2k$ boundary conditions. The missing one may be obtained considering that

$$v^{0-} = \frac{I_v^0}{q}$$

and

$$v^{0+} = v^{0-} + \frac{RT}{pq} \sum v_L (a_i^{0+} - a_i^{0-})$$

since there is no source before the column and diffusion does not influence v . Substituting Eq. (48), the boundary condition takes the form

$$v^{0+} \left(1 - \sum_j y_j^0 \right) = \frac{I_v^0}{q} - D \sum_j \frac{dy_j^{0+}}{dz}. \quad (50)$$

Summary

A set of differential equations have been set up in order to calculate the concentration profiles along a continuous chromatographic column. Diffusion in the gas phase has been taken into account, considering both equilibrium and non-equilibrium cases. Boundary conditions are also given. There is no need for boundary conditions at the central feeding, if a feeding zone of definite thickness and structure rather than a point or infinitesimal thin layer is assumed.

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