

KINETIC PROCESSES AND ZONE DIFFUSION IN CHROMATOGRAPHY*

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It has long been realized that kinetic processes involved in the sorption and desorption of solute molecules are in a large part responsible for the smearing of solute zones. The processes that have been especially studied are those in which (1) single step sorption and desorption reactions are important, and (2) diffusion through the stationary or mobile phases is rate controlling. Along with the rapid growth of experimental technique an extended theoretical treatment is needed which will deal in a general way with the complex kinetics which occur in most heterogeneous media such as found in chromatography. An attempt to establish the basis for such a theory is reported elsewhere¹. We will be concerned here with the discussion of kinetic schemes which more closely approximate real chromatographic systems. Included are the effects of adsorption on heterogeneous surfaces, simultaneous partition and adsorption, adsorption of large molecules, and chemical reactions not directly related to sorption. In some cases simple kinetics are assumed which, although more extensive than found in previous treatments, still are only approximations to some of the very complex systems. Nonetheless this permits us to investigate the gross effects of certain kinds of kinetic processes. The complete theory is briefly outlined which permits the extension to other systems. The general method is applicable to nonlinear kinetics and diffusion-controlled processes, as will be shown.

THEORY

The theory¹ which permits the evaluation of zone spreading with complex, underlying kinetics is based upon the assumption that the various kinetic steps are proceeding near equilibrium. With only a few exceptions the departure from equilibrium must remain small unless poor resolution is to be tolerated².

Each of the various kinetic steps in chromatography can be represented by



where A_i and A_j represent different states of the solute molecule (sorbed, desorbed, hydrogen-bonded etc.). The first order rates of transition between the states are shown

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as k_{ij} and k_{ji} . Let the concentration of i , referred to a unit volume of the overall column material, be c_i , and the total concentration be c . The ratio c_i/c is the mole fraction X_i . Furthermore each state is characterized by a velocity, v_i , relative to the fixed phase. This, of course, is zero if the i^{th} state is a sorbed state.

The rate of reaction of molecules in the i^{th} state is obtained by summing over all reaction paths

$$r_i = \sum_j k_{ji}c_j - c_i \sum_j k_{ij} \quad (2)$$

At equilibrium $r_i = 0$ and each concentration is at its equilibrium value c_i^* . In an operating chromatogram the flow of liquid acts to maintain a slight departure from equilibrium. The departure term for the i^{th} species, ε_i , is defined by

$$c_i = c_i^* (1 + \varepsilon_i) \quad (3)$$

Substituting this into eqn. (2) and subtracting out the equilibrium terms, which add to zero, we have

$$r_i = \sum k_{ji}c_j^* \varepsilon_j - c_i^* \varepsilon_i \sum k_{ij} \quad (4)$$

since at equilibrium forward and reverse rates are equal for each step

$$k_{ji}c_j^* = k_{ij}c_i^* \quad (5)$$

we have

$$\frac{r_i}{c_i^*} = \sum k_{ij}\varepsilon_j - \varepsilon_i \sum k_{ij} \quad (6)$$

Since the set of equations represented in (6) are linear equations, the ε 's are easily solved for. In order to effect this solution we will assume, as previously stated, that the reactions are proceeding near equilibrium. This assumption is equivalent to saying either that c_i approximately equals c_i^* , or that $\varepsilon_i \ll 1$.

The left hand side of eqn. (6) can be approximated in the following way. The mass balance equation for i is

$$r_i = \frac{\partial c_i}{\partial t} + v_i \frac{\partial c_i}{\partial z} - D_i \frac{\partial^2 c_i}{\partial z^2} \quad (7)$$

where D_i is the diffusion coefficient of i in the longitudinal direction measured by z . Since the system is close to equilibrium, $\partial c_i/\partial z$ and $\partial c_i/\partial t$ can be replaced by $\partial c_i^*/\partial z$ and $\partial c_i^*/\partial t$. Furthermore it can be shown that the last term is ordinarily negligible. Hence

$$r_i \cong \frac{\partial c_i^*}{\partial t} + v_i \frac{\partial c_i^*}{\partial z} \quad (8)$$

Since c_i^* is a definite fraction, X_i^* , of the total concentration c , and since

$$\frac{\partial c}{\partial t} \cong -\bar{u} \frac{\partial c}{\partial z} \quad (9)$$

where \bar{u} is the average velocity of the solute zone, then to a good approximation

$$\frac{r_i}{c_i^*} = (v_i - \bar{u}) \frac{\partial \ln c}{\partial z} \quad (10)$$

With this evaluation of r_i/c_i^* , the various equations shown in (6) become a set of linear algebraic equations in the various ε_i 's. If there are n states, $i = 1, 2, \dots, n$,

we use $n - 1$ of these equations along with the one equation stating that the total concentration adds to c . The final equations for the values of ε are, then

$$\sum X_i^* \varepsilon_i = 0 \quad (11a)$$

$$(v_i - \bar{u}) \frac{\partial \ln c}{\partial z} = \sum k_{ij} \varepsilon_j - \varepsilon_i \sum k_{ij} \quad (11b)$$

Once the values of ε are known, the zone structure can be related to the ε -dependent flux term. The flux of material through a unit cross section is given by

$$q = \sum_i c_i v_i \quad (12)$$

Combined with eqn. (3) and the definition of mole fraction, $X_i^* = c_i^*/c$, we have

$$q = c \sum X_i^* v_i + c \sum X_i^* \varepsilon_i v_i \quad (13)$$

The first summation is merely the average velocity, \bar{u} , of the solute zone.

$$q = c\bar{u} + c \sum X_i^* \varepsilon_i v_i \quad (14)$$

The term $c\bar{u}$ represents the flux due to the drift of material along with the solvent.

The significance of the last term, $c \sum X_i^* \varepsilon_i v_i$, becomes clear with a closer look at the ε values. From eqns. (11) we see that each ε is proportional to $\partial \ln c / \partial z$. Since this occurs in each term in the summation it can be factored out and combined with the coefficient c to yield a coefficient $\partial c / \partial z$. Hence the flux is proportional to $\partial c / \partial z$ just as in diffusion processes. Thus it is possible to use an effective diffusion coefficient, D_c , in describing the spreading of a zone².

Equating the last term in eqn. (14) to $-D_c \partial c / \partial z$, we obtain

$$D_c = \frac{-\sum X_i^* \varepsilon_i v_i}{\frac{\partial \ln c}{\partial z}} \quad (15)$$

where the ε_i values are to be obtained from eqns. (11). It must be remembered that molecular diffusion and "eddy" diffusion also contribute so that the overall coefficient, D , is the sum of the three. In those cases where it is advantageous to relate zone structure to the height equivalent to a theoretical plate, H , we use the equations

$$H = \frac{2D}{\bar{u}} \quad \text{and} \quad H_c = \frac{2D_c}{\bar{u}} \quad (16)$$

HETEROGENEOUS SORPTION

The sorption media encountered in chromatography are rarely expected to be homogeneous. The rates of sorption and desorption would ordinarily vary considerably from one place to another. The 2-site problem in which two different sorption sites with different rate constants are assumed, has been introduced to allow for heterogeneous effects^{3,4}. It is possible, however, using the theory just presented, to obtain D_c for the general multi-site sorption problem. This problem allows for the kinetics

of sorption on any number of different kinds of sites. The kinetic steps may be written as follows:



In this kinetic scheme, A_1 represents a solute molecule in the desorbed state, and A_2, A_3, \dots, A_n represent different sorption states of the molecule. There are $2n - 2$ different rate constants of the form k_{ij} .

Eqns. (11a) and (11b) can be applied to evaluate the ε 's. For the $n - 1$ equations of the form (11b), it is convenient to choose those for which $i = 2, 3, \dots, n$. Each v_i equals zero for this range of i 's. The n simultaneous equations are

$$\begin{aligned} g &= k_{21}\varepsilon_1 - k_{21}\varepsilon_2 \\ g &= k_{31}\varepsilon_1 - k_{31}\varepsilon_3 \\ &\vdots \\ g &= k_{n1}\varepsilon_1 - k_{n1}\varepsilon_n \\ 0 &= X_1^*\varepsilon_1 + X_2^*\varepsilon_2 + X_3^*\varepsilon_3 + \dots + X_n^*\varepsilon_n \end{aligned} \quad (18)$$

where g has been substituted for $-\bar{u} \partial \ln c / \partial z$. Eqn. 15 tells us which of the ε 's must be evaluated. Since v_i is in each term of the summation, and $v_i = 0$ for all but $i = 1$, it is only necessary to obtain ε_1 . Cramer's rule can be applied to this problem, and yields the following ratio of determinants.

$$\varepsilon_1 = \frac{\begin{vmatrix} g & -k_{21} & 0 & 0 & \dots & 0 \\ g & 0 & -k_{31} & 0 & & 0 \\ \vdots & & & & & \vdots \\ g & 0 & 0 & 0 & & -k_{n1} \\ 0 & X_2^* & X_3^* & X_4^* & \dots & -X_n^* \end{vmatrix}}{\begin{vmatrix} k_{21} & -k_{21} & 0 & 0 & \dots & 0 \\ k_{31} & 0 & -k_{31} & 0 & & 0 \\ \vdots & & & & & \vdots \\ k_{n1} & 0 & 0 & 0 & & -k_{n1} \\ X_1^* & X_2^* & X_3^* & X_4^* & \dots & X_n^* \end{vmatrix}} \quad (19)$$

This can be reduced by the standard methods to yield

$$\varepsilon_1 = g \sum_{i=2}^n \frac{X_i^*}{k_{i1}} \quad (20)$$

Substituting this back into eqn. (15) we obtain

$$D_c = \bar{u}^2 \sum \frac{X_i^*}{k_{i1}} \quad (21)$$

which is the effective coefficient of diffusion due to the kinetics. This result will now be expressed in a form directly related to desorption kinetic measurements.

A convenient parameter in the study of desorption kinetics is the average time

required for desorption, \bar{t}_d . This is equal to the mean sorption life time of a collection of molecules sorbed at equilibrium and which can be irreversibly desorbed, *i.e.*, removed from further sorption after desorption. An expression for \bar{t}_d is

$$\bar{t}_d = \frac{\int_0^{\infty} \Sigma X_i dt}{1 - R} \quad (22)$$

where R is the fraction of molecules initially desorbed (in the mobile phase), and X_i is the mole fraction in the i^{th} sorbed state at the time t . At $t = 0$, $X_i = X_i^*$ for all i . Since the desorption is irreversible, each X_i follows the first order rate law

$$X_i = X_i^* e^{-k_{i1}t} \quad (23)$$

Substituting this back into eqn. (22) and evaluating the integral, we obtain

$$\bar{t}_d = \Sigma \frac{X_i^*}{k_{j1}} / (1 - R) \quad (24)$$

where all summations run from $i = 2$ to $i = n$. This in turn can be substituted into eqn. (21), which yields

$$D_c = \bar{u}^2 (1 - R) \bar{t}_d \quad (25)$$

An equivalent form is obtained when Rv is substituted for \bar{u} . The quantity v is the average stream velocity of the mobile phase while R is the ratio of zone to stream velocity.

$$D_c = R^2 v^2 (1 - R) \bar{t}_d \quad (26)$$

Eqns. (25) and (26) are interesting since the only kinetic quantity appearing is the mean desorption time, \bar{t}_d . This result permits a more realistic interpretation of chromatographic experiments since it is no longer necessary to account for the entire kinetic effect by one or two hypothetical reactions. It would be desirable, however, to isolate the various rate contributions to \bar{t}_d . This would probably require the combined data from several fields of study, including chromatography. It appears that chromatography might be useful in studying desorption phenomena as well as several other reaction rate processes in porous media.

The above equations for D_c are, of course, limited to kinetics near equilibrium. If any of the desorption steps are significantly slow, then the influence of that step cannot be included in eqns. (25) and (26). The procedure then is to account for all the steps possible by means of eqns. (25) or (26), and then include the effect of the nonequilibrium step or steps separately. This can be done if the nonequilibrium steps are sufficiently simple to apply the exact theories of chromatography. Some promise has been found by this method in interpreting double spots in paper chromatography⁶.

CONSECUTIVE REACTIONS

A large number of kinetic processes in chromatography involve a series of consecutive reactions. The following kinetic scheme roughly approximates many of these processes:



Let the flow velocities be v_1 , v_2 and v_3 respectively. Any one of these may again be zero if the state is a sorbed one. Eqns. (11a) and (11b) can be applied to the above kinetics with the result

$$g_1 = -k_{12}\varepsilon_1 + k_{12}\varepsilon_2 \quad (28a)$$

$$g_3 = k_{32}\varepsilon_2 - k_{32}\varepsilon_3 \quad (28b)$$

$$0 = X_1^*\varepsilon_1 + X_2^*\varepsilon_2 + X_3^*\varepsilon_3 \quad (28c)$$

where

$$g_1 = (v_1 - \bar{u}) \frac{\partial \ln c}{\partial z}, \quad g_3 = (v_3 - \bar{u}) \frac{\partial \ln c}{\partial z}, \quad \text{etc.} \quad (29)$$

Applying Cramer's rule we obtain ε_1 and ε_3

$$\varepsilon_1 = -\frac{g_1}{k_{12}} + \frac{g_1}{k_{12}} X_1^* + \frac{g_3}{k_{32}} X_3^* \quad (30a)$$

$$\varepsilon_3 = -\frac{g_3}{k_{32}} + \frac{g_3}{k_{32}} X_3^* + \frac{g_1}{k_{12}} X_1^* \quad (30b)$$

These can be substituted into eqn. (15) for D_c . First, however, we obtain the ε_2 term in the summation directly from eqn. (28c).

$$-X_2^*\varepsilon_2 = X_1^*\varepsilon_1 + X_3^*\varepsilon_3 \quad (31)$$

The result is

$$\frac{\partial \ln c}{\partial z} D_c = (v_2 - v_1) X_1^*\varepsilon_1 + (v_2 - v_3) X_3^*\varepsilon_3 \quad (32)$$

Using eqns. (30) for ε_1 and ε_3 , and an expression for the mean velocity

$$\bar{u} = X_1^*v_1 + X_2^*v_2 + X_3^*v_3 \quad (33)$$

we obtain

$$D_c = \frac{X_1^* (v_1 - \bar{u})^2}{k_{12}} + \frac{X_3^* (v_3 - \bar{u})^2}{k_{32}} \quad (34)$$

It will be noticed that in the special case where $v_1 = v_3 = 0$ we have the 2-site sorption problem with A_2 representing the mobile species. Under these circumstances eqn. (34) reduces to eqn. (21).

Eqn. (34) may be used in describing reactions that occur in either the mobile or stationary phase independent of the phase transfer process. The additional reaction might be an association reaction with a species present in one of the phases. It is necessary that the reaction remains first order in the solute concentration, although the overall order of the reaction may be different.

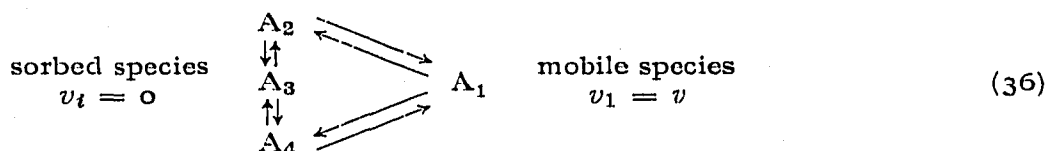
The occurrence of some adsorption in a process that is primarily partition has concerned workers in both gas and paper chromatography. This example is a valid application of eqn. (34) as long as the isotherm remains linear. The use of a single reaction step to describe the partition-diffusion process must be considered as an approximation. Let A_1 be the mobile phase species, A_2 the adsorbed, and A_3 the adsorbed species. The respective velocities are $v_1 = v$, $v_2 = v_3 = 0$. Furthermore $X_1^* = R$ and $X_2^* + X_3^* = 1 - R$. With these values D_c becomes

$$D_c = \frac{R (1 - R)^2 v^2}{k_{12}} + \frac{X_3^* R^2 v^2}{k_{32}} \quad (35)$$

The first term on the right is the one obtained when no adsorption is occurring. The second term is the contribution of adsorption. It is seen that this increases with the amount, X_3^* , adsorbed at equilibrium, and furthermore is generally significant when the adsorption process is slow. As a rough rule for cases with intermediate R values, the contributions to D_c will be in proportion to the time of reaction, or inversely proportional to the reaction rate constants.

LARGE MOLECULES

The sorption of large molecules is by itself a complex phenomenon. The sorption process consists of a series of steps in which one segment attaches itself to the sorbent followed by the sorption of additional segments. Since the general problem is exceedingly complex⁶, we will show the nature of a simple prototype involving bi-functional sorption. This is a case in which only two parts of a molecule are active in attaching to the surface (molecules such as dicarboxylic acids with two polar ends would have kinetics approaching that of the prototype). The following kinetic scheme describes the situation.



The detached molecule A_1 becomes A_2 if it anchors by means of one of its active groups, and A_4 if it anchors by means of the other. The two active groups are not necessarily the same. The molecule can then desorb back to A_1 or complete the sorption of the other active group to form the completely sorbed molecule A_3 .

The methods used in previous sections can be applied to the present example to yield the following D_c

$$D_c = \frac{Rv^2 \left[(1 - R) (k_{23}k_{40}X_2^* + k_{20}k_{40}X_3^* + k_{43}k_{20}X_4^*) + R (k_{12} (k_{23} - k_{43}) X_4^* + k_{14} (k_{43} - k_{23}) X_2^* - k_{12}k_{40}X_3^* - k_{14}k_{20}X_3^*) \right]}{k_{12}k_{23}k_{40} + k_{14}k_{43}k_{20}} \quad (37)$$

where k_{20} and k_{40} have been substituted for $(k_{21} + k_{23})$ and $(k_{41} + k_{43})$, respectively.

Eqn. (37) simplifies considerably under certain limiting circumstances. Consider for example a molecule in which the intermediates A_2 and A_4 have a short lifetime. Such would occur especially when the activation energy for further sorption is small. Under these circumstances X_2^* and X_4^* become negligible compared to X_3^* while $k_{23} \gg k_{12}$ and $k_{40} \gg k_{14}$. Also X_3^* becomes equal to $(1 - R)$. When these assumptions are used in eqn. (37) we have

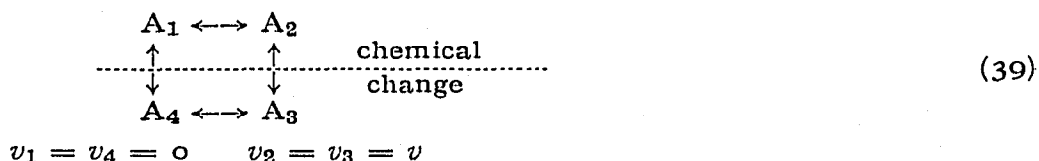
$$D_c = \frac{R(1 - R)^2 v^2}{k_{12}f_2 + k_{14}f_4} \quad (38)$$

where $f_2 = k_{23}/k_{20}$ is the fraction of times that a molecule in the form A_2 proceeds to the completely sorbed state A_3 . A like interpretation holds for f_4 .

CHEMICAL CHANGES

Chemical changes in a chromatographic column lead to a variety of phenomena depending upon the nature and rates of the reactions. If the rates of chemical change are slow, large nonequilibrium effects are observed. These effects include the formation of double and triple zones, and also tailing⁵. If the reactions proceed rapidly enough to effect a large number of chemical changes during the running time of the experiment, the departure from equilibrium will be small, and the present procedure valid. In addition to predicting chromatographic performance from reaction kinetics, it is suggested that the inverse process of obtaining reaction rate data from chromatography might be fruitful.

One type of chemical change can be given as follows



where A_1 and A_4 are the sorbed species which can react to form one another. The mobile phase species are A_2 and A_3 . The horizontal arrows represent the phase changes and the vertical arrows represent chemical changes. This scheme would apply to isomerization reactions (*cis-trans*, etc.) which occur in both the mobile and stationary phases. It would also be applicable to a solute that combines with and dissociates from some species at constant concentration within the column.

The evaluation of D_c for the above scheme involves detailed manipulations too long to reproduce here. The result is

$$D_c = \frac{v^2 \left\{ (1 - R) \left[X_1^* X_2^* k_{14} (k_{30} + k_{23}) + X_1^* X_3^* (k_{14} (k_{20} + k_{32}) - k_{12} k_{34}) \right] \right.}{\left. + R [k_{23} k_{34} X_1^* X_2^* + k_{34} k_{20} X_1^* X_3^* - k_{21} k_{30} X_2^* X_4^* - k_{21} k_{32} X_3^* X_4^*] \right\}}{k_{14} k_{21} k_{30} + k_{23} k_{34} k_{10}} \quad (40)$$

where, again, $k_{30} = k_{32} + k_{34}$, etc. This equation can be simplified by making the following approximations. We will assume that the phase change reactions are much more rapid than the chemical reactions, *i.e.*, k_{12} , k_{21} , k_{43} , $k_{34} \gg k_{14}$, k_{41} , k_{23} , k_{32} . With this approximation we obtain

$$D_c = \frac{v^2 (X_1^* X_3^* - X_2^* X_4^*)^2}{k_{14} X_1^* + k_{23} X_2^*} + \frac{v^2 X_1^* X_2^*}{(X_1^* + X_2^*) (k_{12} + k_{21})} + \frac{v^2 X_3^* X_4^*}{(X_3^* + X_4^*) (k_{34} + k_{43})} \quad (41)$$

The terms in this equation can be interpreted as follows. The second term is the contribution due to the phase change of the chemical species (A_1 , A_2), and as such contains only k_{12} and k_{21} . The third term has an analogous meaning for (A_3 , A_4). The first term accounts for the effects of chemical change. This term can alternately be derived by assuming that each of the two chemical species is moving with its own particular velocity characterized by its own R value (it must be assumed, also, that

the sorption or partitioning process is near equilibrium). This derivation proceeds from the fact that any two interconverting species moving at different velocities gives rise to a diffusion effect. In fact, the simplest kinetic picture of chromatography is based on this fact: the sorbed and desorbed molecules are moving at different downstream velocities, and are, of course, interconverting.

Examination of the first term in eqn. (41) shows that a zero value is acquired when $(X_1^*X_3^* - X_2^*X_4^*) = 0$. This is found when the separate R values $(X_2^*/(X_1^* + X_2^*))$ and $X_3^*/(X_3^* + X_4^*)$ are equal, or when the separation factor is unity. The importance of the chemical change term, then, depends on two factors; the difference in R values appearing in the numerator and the reaction rate constants appearing in the denominator.

It is expected that gas chromatography (especially with capillary columns) will prove a useful medium to exhibit the chemical change term, even with fairly rapid reaction rates. This is a result of the small contribution of the second and third terms of eqn. (41) as illustrated by the fact that the order of 10^6 theoretical plates can now be obtained on capillary columns.

CONCLUSIONS

While the above examples have been concerned primarily with rate processes involving discrete kinetic steps, the nonequilibrium method is also applicable to diffusion controlled processes. These processes lead to a nonequilibrium in the form of lateral concentration gradients. Since the departure from equilibrium is generally small, the same approximations can be used in the mass conservation equations. The rate of reaction, r_i , becomes the rate of accumulation due to the lateral diffusion. Both particle-wide (referring to the particles of the porous media) and tube-wide nonequilibrium can exist in a chromatographic column. An example of the latter is the concentration gradient existing laterally across a coiled column⁷. Particle-wide nonequilibrium will be the subject of a later communication.

The nonequilibrium method can also be used in the description of nonlinear kinetics. While the rate equations (2) are nonlinear, the situation is still tractable as long as $\varepsilon_i \ll 1$. With this condition applying, we can make approximations of the following kind

$$\begin{aligned} c_i^2 &= c_i^{*2} (1 + 2\varepsilon_i) \\ c_i c_j &= c_i^* c_j^* (1 + \varepsilon_i + \varepsilon_j) \end{aligned} \quad (42)$$

where terms the order of ε^2 have been discarded. When these expressions are substituted back into the rate equations they are still linear in the ε 's.

The final results obtained for the various examples have been presented in terms of an effective diffusion coefficient, D_e . This can be written in terms of plate height by eqn. (16). The concentration profiles observed in chromatography, which have not been derived here, are obtained by applying Fick's laws of diffusion to the entering zone. The final profile differs with the nature of the original zone. Since the mathematics of diffusion is such a highly developed discipline, it is felt that concentration

profiles can be effectively derived by its use rather than by means of a separate mathematical derivation using the plate-height concept. The use of diffusion in describing zone structure has been shown by GLUECKAUF⁸. One case of zone structure is found so universally that its relation to the present treatment should be mentioned. When the solute is started as a narrow zone and there are no outside gradients, diffusion leads to a "Gaussian" peak in which the root-mean-square deviation, σ , is equal to $\sqrt{2Dt}$.

The methods used to derive D_c in this paper are not limited to chromatography, but can be applied to a large class of differential migration problems in which rate processes are occurring. Electrophoresis and sedimentation are examples in which zone diffusion results from kinetics processes⁹.

TABLE OF SYMBOLS

A_i	chemical species of the i^{th} type
c	total solute concentration, referred to unit volume of overall chromatogram
c_i	concentration of species i
c_i^*	equilibrium concentration of species i
D	total diffusion coefficient in the direction of flow
D_c	diffusion coefficient in flow direction due to nonequilibrium effects
D_i	diffusion coefficient in flow direction of species i
ϵ_i	equilibrium departure term
f_2, f_4	defined following eqn. (38)
g_i	abbreviation for $(v_i - \bar{u}) \partial \ln c / \partial z$
H	total plate height
H_c	plate height due to nonequilibrium effects
k_{ij}	rate constant for the A_i to A_j transition
n	the number of reacting species
q	solute flux in flow direction
R	equilibrium fraction of molecules in the mobile phase
r_i	rate of accumulation of i due to the kinetic processes
t	time
\bar{t}_d	mean desorption time of sorbed molecules
\bar{u}	mean velocity of solute zone
v_i	velocity of species i in flow direction
X_i	mole fraction of solute in the i^{th} form
X_i^*	equilibrium mole fraction of i

SUMMARY

Equations have been obtained which give the effective diffusion coefficient or plate height due to kinetic processes. It is assumed that the departure from equilibrium is only slight corresponding to the situation usually found in chromatography. The

theory is applied to sorption on heterogeneous media, consecutive reactions, the chromatography of large molecules, and the occurrence of chemical change simultaneous with chromatography. The extension of the theory to diffusion-controlled processes and nonlinear kinetics is discussed. The applicability to other differential migration methods is noted.

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