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IDEAL STOPPED-FLOW GAS CHROMATOGRAPHY WITH CHEMICAL REACTIONS IN THE STATIONARY PHASE

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SUMMARY

By assuming a general mechanism for surface reactions on a chromatographic column, equations are derived from which can be calculated the elution curves of the reactant, the products and the peaks produced by stopping the carrier-gas flow for a short time. Particularly, the area under the curve of these stop-peaks can be calculated as a function of the time of cessation of the gas flow, and this can be used to determine, from experimental values, the rate constants of the surface reactions. Application of the method requires specification of the mechanism assumed in each case. As an example, the equations derived are applied for a simple first-order non-opposing reaction on one kind of active sites, with no intermediate. In this limiting case, two of the final equations coincide with the results of earlier static derivations.

INTRODUCTION

Stopped-flow gas chromatography was introduced in 1967[1] and can now be used to study the kinetics and mechanism of surface reactions, or to determine rate constants for desorption from two kinds of active sites of a surface, together with the corresponding partition coefficients[2,3]. The application of the method is very simple. A conventional gas chromatograph with a high-sensitivity detector, *e.g.*, a flame ionization detector, is equipped with one or two shut-off valves and a pressure stabilizer (such as a volume reservoir) in the carrier-gas line. After introduction of a small amount (*ca.* 1 mg) of the vapour under study on to the chromatographic column containing the catalyst or other solid material, the flow of carrier gas is stopped and then re-started after a known time; this procedure is repeated, noting the exact time of each stop. Sharp symmetrical peaks (the stop-peaks) follow the restorations of the carrier-gas flow, and these peaks have definite retention times and "sit" on the continuous chromatographic signal (see, *e.g.*, Fig. 1 in ref. 3).
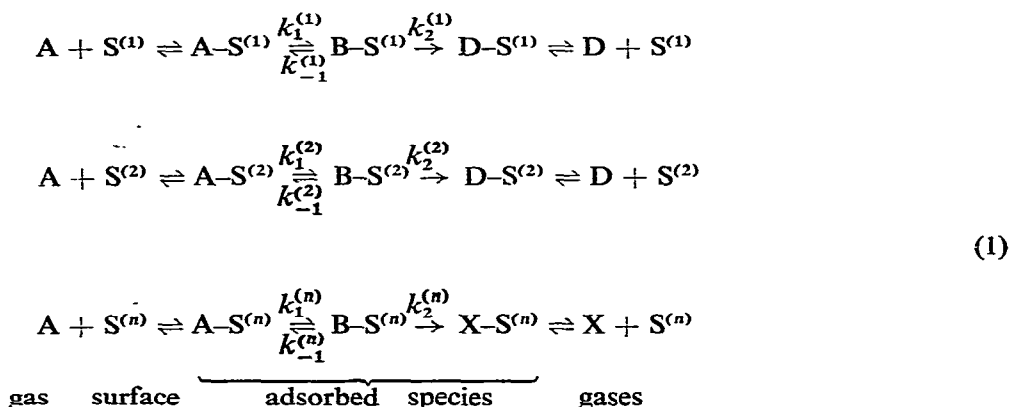
The area under the stop-peaks is a finite function of the time when the corresponding stop was made, and, if the analytic form of this function is known, we can calculate rate constants and other physical quantities from the chromatogram. The analytic form of this function depends on the phenomenon being studied, its detailed mechanism, and other factors. We have derived this function for the case of slow

desorption of a substance adsorbed on two kinds of sites of an active surface, without chemical reaction[3].

For catalytic reactions, two derivations have been made[1,4]; in each, a simple first-order surface reaction was assumed to take place under *static* conditions. However, extensive application of the stopped-flow technique in this laboratory, some results of which have been reported[5-7], has shown that the analytic function mentioned above can be complicated, obviously because of a complex reaction mechanism and/or the dynamic character of the chromatographic process. We therefore decided to derive the various chromatographic equations and the above-mentioned function for a fairly general mechanism and a flow system, and then to show that the results of previous derivations[1,4] coincide with that of a limiting case of the function pertinent to this general mechanism.

THEORETICAL ANALYSIS

The following general mechanism is assumed to describe most cases of stopped-flow chromatography with chemical reactions taking place on the surface of the column material:

$$A + S^{(1)} \rightleftharpoons A\text{-}S^{(1)} \underset{k_{-1}^{(1)}}{\overset{k_1^{(1)}}{\rightleftharpoons}} B\text{-}S^{(1)} \overset{k_2^{(1)}}{\rightarrow} D\text{-}S^{(1)} \rightleftharpoons D + S^{(1)}$$

$$A + S^{(2)} \rightleftharpoons A\text{-}S^{(2)} \underset{k_{-1}^{(2)}}{\overset{k_1^{(2)}}{\rightleftharpoons}} B\text{-}S^{(2)} \overset{k_2^{(2)}}{\rightarrow} D\text{-}S^{(2)} \rightleftharpoons D + S^{(2)}$$

$$(1)$$

$$A + S^{(n)} \rightleftharpoons A\text{-}S^{(n)} \underset{k_{-1}^{(n)}}{\overset{k_1^{(n)}}{\rightleftharpoons}} B\text{-}S^{(n)} \overset{k_2^{(n)}}{\rightarrow} X\text{-}S^{(n)} \rightleftharpoons X + S^{(n)}$$

gas   surface $\underbrace{\hspace{4cm}}_{\text{adsorbed species}}$ gases

The surface is assumed to contain one or more kinds of active sites, $S^{(1)}$, $S^{(2)}$, ..., $S^{(n)}$, which are responsible for chromatographing the reactant A and the products D, ..., X, as well as for the chemical reactions of the adsorbed species. The same product, *e.g.* D, may be produced and/or chromatographed on more than one kind of active sites. The concentration of the various kinds of sites is considered to be large compared with those of the respective adsorbed species, in view of the very small amounts of the reacting vapours being used. Additional assumptions made are:

(1) The adsorption isotherm is linear for all kinds of sites.

(2) Axial diffusion of the gas in the bed is negligible, which is not unrealistic for high enough flow-rates.

(3) The reacting vapour is introduced at the inlet end of the column as an instantaneous pulse, the distribution in time of which can be described by a Dirac delta function, $\delta(t)$.

(4) Equilibration of the reactants and products between the gas and the solid phases is instantaneous, *i.e.*, chromatography is ideal.

Notation

c_A, c_D	= concentrations of A and D in the gas phase (mole/cm³)
C_A, C_D	= Laplace transforms of c_A and c_D with respect to t
Δc_D	= increase in gas-phase concentration of D during the stopped-flow interval (mole/cm³)
ΔC_D	= Laplace transform of Δc_D with respect to t
$\overline{\Delta C_D}$	= double Laplace transform of Δc_D with respect to t and t'
f_A	= area under elution curve of A (mole)
f_s	= area under the curve of a stop-peak (mole)
g	= fraction of A in the adsorbed form (dimensionless)
$k_1^{(i)}$, $k_{-1}^{(i)}$, $k_2^{(i)}$	= rate constants for reaction on sites i (sec⁻¹)
$k_A^{(i)}$, $k_D^{(j)}$	= partition ratios of A and D on sites i or j (dimensionless)
$K_A^{(i)}$, $K_D^{(j)}$	= partition coefficients of A and D on sites i or j (dimensionless)
l	= length of column (cm)
m	= total mass of A injected (mole)
m_n	= integrals defined by eqn. 17
p, p'	= transform parameters with respect to t and t'
$q_A^{(i)}$, $q_B^{(i)}$, $q_D^{(j)}$	= concentrations of adsorbed species A–S$^{(i)}$, B–S$^{(i)}$, D–S$^{(j)}$ on sites i or j per unit volume of solid (mole/cm³)
$Q_B^{(i)}$	= Laplace transform of $q_B^{(i)}$ with respect to t
r	= volume ratio of solid and gas phases
t	= time interval from the injection of A to the beginning of the stopped-flow interval (sec)
t_M	= gas hold-up time (sec)
$t_{R,A}$, $t_{R,D}$	= retention times of A and D (sec)
t_s	= stopped-flow time (sec)
t'	= time measured from the end of the stopped-flow interval (sec)
v	= linear velocity of carrier gas in interparticle space (cm/sec)
V	= volume of the carrier gas passed through the column (cm³)
$\dot{V}$	= volume flow-rate of carrier gas (cm³/sec)
x	= distance from inlet end of column (cm)
λ	= expression defined by eqn. 32
Φ_D	= expression defined by eqn. 12
Ω_A, Ω_D, Ω_D'	= expressions defined by eqns. 10, 11 and 24, respectively.

Other symbols are defined as they occur in the text.

We artificially divide the time variable into three intervals, t, t_s and t', defined above and shown in Fig. 1. In each interval, the various concentrations (as functions of time and distance x) are determined by one or more differential equations with certain initial and/or boundary conditions. The problem will be considered separately for each of the three intervals.
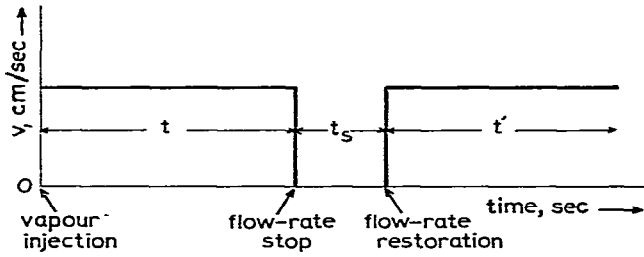
Fig. 1. Ideal variation of carrier-gas linear velocity, v, with time in the stopped-flow technique.

Interval t

The concentrations $c_A(x,t)$, $q_B^{(i)}(x,t)$, and $c_D(x,t)$, where $i = 1, 2, \ldots n$, are determined by the following system of equations.

Mass balance for A and A–S$^{(i)}$:

$$\frac{\partial c_A}{\partial t} + r \sum_{i=1}^{n} \frac{\partial q_A^{(i)}}{\partial t} = -v \frac{\partial c_A}{\partial x} - r \sum_{i=1}^{n} k_1^{(i)} q_A^{(i)} + r \sum_{i=1}^{n} k_{-1}^{(i)} q_B^{(i)} \tag{2}$$

Rate of change of B–S$^{(i)}$:

$$\frac{\partial q_B^{(i)}}{\partial t} = k_1^{(i)} q_A^{(i)} - k_{-1}^{(i)} q_B^{(i)} - k_2^{(i)} q_B^{(i)} \tag{3}$$

Mass balance for D and D–S$^{(j)}$:

$$\frac{\partial c_D}{\partial t} + r \sum_j \frac{\partial q_D^{(j)}}{\partial t} = -v \frac{\partial c_D}{\partial x} + r \sum_j k_2^{(j)} q_B^{(j)} \tag{4}$$

where the index j applies to all sites producing D and/or equilibrating with it.

Initial and boundary conditions:

At $x = 0$, $c_A = \dfrac{m}{\bar{V}} \delta(t)$ $\tag{5}$

At $x > 0$ and $t = 0$, $c_A = q_B^{(i)} = c_D = 0$

Adsorption isotherms:

$$q_A^{(i)} = K_A^{(i)} c_A, \quad q_D^{(j)} = K_D^{(j)} c_D \tag{6}$$

By substituting these expressions for $q_A^{(i)}$ and $q_D^{(j)}$ in eqns. 2, 3 and 4, taking the Laplace transform with respect to t of the resulting three equations under the initial conditions 5, and then combining the three transformed equations, we obtain:

$$\frac{dC_A}{dx} + \frac{\Omega_A}{v} C_A = 0 \tag{7}$$

$$Q_B^{(i)} = \frac{k_1^{(i)} K_A^{(i)}}{p + k_{-1}^{(i)} + k_2^{(i)}} \cdot C_A \tag{8}$$

$$\frac{dC_D}{dx} + \frac{\Omega_D}{v} C_D = \frac{\Phi_D}{v} C_A \tag{9}$$

where

$$\Omega_A = (1 + \sum_i k_A^{(i)})p + \sum_i k_1^{(i)}k_A^{(i)} - \sum_i \frac{k_{-1}^{(i)}k_1^{(i)}k_A^{(i)}}{p + k_{-1}^{(i)} + k_2^{(i)}} \tag{10}$$

$$\Omega_D = (1 + \sum_j k_D^{(j)})p \tag{11}$$

$$\Phi_D = \sum_j \frac{k_2^{(j)}k_1^{(j)}k_A^{(j)}}{p + k_{-1}^{(j)} + k_2^{(j)}} \tag{12}$$

and $k_A^{(i)} = rK_A^{(i)}$, $k_D^{(j)} = rK_D^{(j)}$ are the partition ratios of A and D, respectively, for the active sites i and j.

The solution of eqn. 7 with respect to x, subject to conditions 5, is:

$$C_A = \frac{m}{\dot{V}} \exp\left(-\frac{\Omega_A x}{v}\right) \tag{13}$$

If this is substituted for C_A in eqn. 9 and the resulting equation is solved, e.g., by Laplace transformation with respect to x, we obtain:

$$C_D = \frac{m}{\dot{V}} \Phi_D \frac{\exp(-\Omega_D x/v) - \exp(-\Omega_A x/v)}{\Omega_A - \Omega_D} \tag{14}$$

We are interested in the chromatographic signals of A and D at the detector, which are $c_A(l,t)$ and $c_D(l,t)$, and these can be found by putting $x = l$ (so that $x/v = l/v = t_M$) in eqns. 13 and 14, and taking the inverse Laplace transforms with respect to p. Thus:

$$c_A(l,t) = \mathcal{L}_p^{-1} \left[\frac{m}{\dot{V}} \exp(-\Omega_A t_M) \right] \tag{15}$$

$$c_D(l,t) = \mathcal{L}_p^{-1} \left[\frac{m}{\dot{V}} \Phi_D \frac{\exp(-\Omega_D t_M) - \exp(-\Omega_A t_M)}{\Omega_A - \Omega_D} \right] \tag{16}$$

Evaluation of these inverse transformations for the general case is difficult, but they can be easily found for a number of special or limiting cases, one of which is discussed later in this paper. Further, one can find for the general case the characteristics of the elution curve, from the statistical moments m_n, calculated by means of the well-known property of the Laplace transform:

$$m_n = \int_0^\infty t^n c(l,t)dt = (-1)^n \lim_{(p \to 0)} \frac{d^n[C(l,p)]}{dp^n} \tag{17}$$

Thus, the area under the elution curve of unreacted A is

$$f_A = \int_0^\infty c_A dV = \dot{V} \int_0^\infty c_A dt = \dot{V} m_0 = m \cdot \exp\left[-\left(\sum_i k_1^{(i)}k_A^{(i)} - \sum_i \frac{k_{-1}^{(i)}k_1^{(i)}k_A^{(i)}}{k_{-1}^{(i)} + k_2^{(i)}}\right) t_M\right] \tag{18}$$

Two interesting special cases arise when all values of $k_2^{(i)} = 0$, *i.e.*, no products are formed, and when all values of $k_{-1}^{(i)} = 0$, *i.e.*, non-opposing reactions occur. In the first case, $f_A = m$, *i.e.*, all of the injected vapour is eluted. In the second case, $f_A = m \cdot \exp(-\sum_i k_1^{(i)} k_A^{(i)} t_M)$, *i.e.*, the amount of reactant A is diminished according to a first-order law, since $k_A^{(i)} t_M$ is the adjusted retention time, $t_{R,A}^{(i)'}$, and therefore the contact time the substance would have if only sites i were present.

The mean retention time of A is given by

$$t_{R,A} = \frac{m_1}{m_0} = \left[1 + \sum_i k_A^{(i)} + \sum_i \frac{k_{-1}^{(i)} k_1^{(i)} k_A^{(i)}}{(k_{-1}^{(i)} + k_2^{(i)})^2} \right] t_M \tag{19}$$

and therefore depends on the various rate constants. Only when $k_{-1}^{(i)} = 0$ (non-opposing reactions) or $k_1^{(i)} = 0$ (no reaction) is $t_{R,A} = (1 + \sum k_A^{(i)}) t_M$, *i.e.*, the expected ideal retention time.

Interval t_s

If this stopped-flow interval is very small, the various concentrations are approximately governed by eqns. 2, 3 and 4 with $v = 0$ and $t = t_s$. The initial conditions are now the inverse Laplace transforms of eqns. 13, 8 and 14 for c_A, $q_B^{(i)}$ and c_D, respectively. It is necessary to keep t_s very small, so that the effects of longitudinal diffusion are minimized during this interval. Whenever the stopped-flow technique was used by us[5-7], the stop-peaks obtained were very narrow, indicating that the effects of longitudinal diffusion can be made negligible.

With the interval t_s sufficiently small, we can make another approximation, which, although not absolutely necessary, keeps the calculations simple. This is to assume that c_A and $q_B^{(i)}$ do not change appreciably during the interval t_s. Then, the only mass balance required is that of D and D–S$^{(j)}$:

$$\frac{\partial c_D}{\partial t_s} + r \sum_j \frac{\partial q_D^{(j)}}{\partial t_s} = r \sum_j k_2^{(j)} q_B^{(j)} \qquad \bullet \tag{20}$$

After substitution of the isotherm 6 for $q_D^{(j)}$ and integration with respect to t_s, we obtain:

$$\Delta c_D = c_D - (c_D)_{t_s=0} = \frac{t_s \, r \sum_j k_2^{(j)} q_B^{(j)}}{1 + \sum_j k_D^{(j)}} \tag{21}$$

Thus, Δc_D is the increase in concentration of D in the gas phase during the stopped-flow interval t_s. It is noteworthy that Δc_D is also a function of x and t, having the same distribution in these variables as $q_B^{(j)}$. Therefore, by forcing Δc_D out of the column, one can see the actual distribution of $q_B^{(j)}$ at the time t when the stop was made, distorted only by the chromatographic process on D. This is the role of the next time interval.

Interval t'

This starts by restoring the flow of carrier gas at the end of the stopped-flow interval t_s. Here we are interested only in Δc_D at the detector, *i.e.*, at $x = l$. We can imagine that at $t' = 0$ a distribution in c_D described by eqn. 21 is introduced into the column, and it is chromatographed with the same partition ratios $k_D^{(j)}$. Thus we can write the mass balance:

$$(1 + \sum_j k_D^{(j)}) \frac{\partial(\Delta c_D)}{\partial t'} = -v \frac{\partial(\Delta c_D)}{\partial x} \tag{22}$$

A double Laplace transformation, first with respect to t' (with initial condition eqn. 21) and then with respect to t, gives:

$$\frac{d(\overline{\Delta C_D})}{dx} + \frac{\Omega_D'}{v} \cdot \overline{\Delta C_D} = \frac{t_s \, r \sum_i k_2^{(j)} Q_B^{(j)}}{v} \tag{23}$$

where

$$\Omega_D' = (1 + \sum_j k_D^{(j)}) p' \tag{24}$$

If eqn. 13 is now substituted for C_A in eqn. 8, and the resulting expression is substituted for $Q_B^{(j)}$ in eqn. 23, the latter can be integrated with respect to x, giving

$$\overline{\Delta C_D} = \frac{m}{\hat{V}} \, t_s \, \Phi_D \cdot \frac{\exp(-\Omega_D' x/v) - \exp(-\Omega_A x/v)}{\Omega_A - \Omega_D'} \tag{25}$$

For $x = l$ (*i.e.*, at the detector), this equation gives the double Laplace transform (with respect to t and t') of the stop-peak. It is only necessary to take the inverse transform, first with respect to p (included in Φ_D and Ω_A), and then with respect to p' (included in Ω_D'), in order to find $\Delta c_D = \Delta c_D(t,t_s,t')$. This is the extra chromatographic signal above the continuous signal of D, which is due to a stop of the carrier-gas flow made at time t and having duration t_s.

It is worth noting that eqn. 25 has exactly the same form as eqn. 14, which, on inversion, gives the continuous chromatographic signal of the product D. The important difference between the two equations, however, is that in eqn. 25 the time parameter is split into two independent parapeters p and p', and this facilitates the inverse Laplace transformation. Moreover, one can find the area under the curve of each stop-peak (f_s) as a function of the time t of the corresponding stop of the carrier-gas flow, by using eqn. 17:

$$\mathcal{L}_t f_s = \dot{V} \int_0^\infty \Delta C_D(p,t') dt' = \dot{V} m_0 = \dot{V} \lim_{(p' \to 0)} (\overline{\Delta C_D}) \tag{26}$$

Thus, from eqns. 26 and 25

$$f_s = \mathcal{L}_p^{-1} \left[m t_s \Phi_D \frac{1 - \exp(-\Omega_A t_M)}{\Omega_A} \right] \tag{27}$$

This is as far as one can proceed with the general case. Further development of the equations requires an exact specification of the mechanism as dictated by experi-

mental evidence, *e.g.*, two kinds of active sites and non-opposing reactions forming only one product or, expressed in terms of partition ratios and rate constants, $k_A^{(3)}$, $k_A^{(4)}$, ..., $k_A^{(n)} = 0$ and all values of $k_{-1}^{(i)} = 0$ ($i = 1, 2, ..., n$). Under the specified conditions, the basic eqns. 15 (for c_A), 16 (for c_D), 25 (for $\overline{\Delta c_D}$), and 27 (for f_s), together with the definitions 10, 11, 12 and 24 for Ω_A, Ω_D, Φ_D and Ω_D', respectively, assume a simpler form and can be manipulated more easily for inverse Laplace transformations with respect to p and p'. Particularly, f_s can be expressed as an analytic function of t, so permitting calculation of the rate constants of the reactions from experimental data. It is hoped that some of these specified cases will be reported in the near future, in conjunction with experimental results.

A LIMITING CASE

We shall examine here the simplest possible case of mechanism 1 and show that the ultimate equations coincide with those derived earlier in a static manner[1,4]. This case is a simple first-order non-opposing reaction, on one kind of active sites and with no intermediate B–S:

$$A + S \rightleftharpoons A\text{–}S \xrightarrow{k_1} D\text{–}S \rightleftharpoons D + S \tag{28}$$

The situation is expressed by $k_A^{(2)}, k_A^{(3)}, ..., k_A^{(n)} = 0$, $k_D^{(2)}, k_D^{(3)}, ..., k_D^{(n)} = 0$, $k_{-1}^{(i)} = 0$ ($i = 1, 2, ..., n$) and $k_2^{(i)} = \infty$ ($i = 1, 2, ..., n$).

Under these conditions, $\Omega_A = (1+k_A)p + k_1 k_A$, $\Omega_D = (1+k_D)p$, $\Phi_D = k_1 k_A$ and $\Omega_D' = (1+k_D)p'$; eqn. 15 then becomes:

$$c_A(l,t) = \mathcal{L}_p^{-1} \left\{ \frac{m}{V} \exp(-k_1 k_A t_M) \cdot \exp[-(1 + k_A)t_M p] \right\}$$

$$= \frac{m}{V} \exp(-k_1 k_A t_M) \cdot \delta[t - (1 + k_A)t_M] \tag{29}$$

or, since from eqn. 19 $t_{R,A} = (1+k_A)t_M$, and $k_A t_M = t_{R,A}'$ (the adjusted retention time):

$$c_A(l,t) = \frac{m}{V} \exp(-k_1 t_{R,A}') \cdot \delta(t - t_{R,A}) \tag{30}$$

This is the expected equation for linear ideal chromatography with the signal at the detector being diminished because of the factor $\exp(-k_1 t_{R,A}')$, describing a first-order reaction with contact time $t_{R,A}'$.

Eqn. 16 becomes

$$c_D(l,t) = \mathcal{L}_p^{-1} \left\{ \frac{m}{V} k_1 k_A \cdot \frac{\exp[-(1 + k_D)t_M p] - \exp(-k_1 k_A t_M) \cdot \exp[-(1 + k_A)t_M p]}{(k_A - k_D)p + k_1 k_A} \right\}$$

$$= \frac{m}{V} k_1 \lambda \left\{ \exp[-k_1 \lambda (t - t_{R,D})] \cdot u(t - t_{R,D}) - \exp(-k_1 t_{R,A}') \cdot \right.$$

$$\left. \cdot \exp[-k_1 \lambda (t - t_{R,A})] \cdot u(t - t_{R,A}) \right\} \tag{31}$$

where $t_{R,D} = (1+k_D)t_M$ is the ideal retention time that D would have if it were injected directly on to the column,

$$\lambda = \frac{k_A}{k_A - k_D} = \frac{t'_{R,A}}{t'_{R,A} - t'_{R,D}} = \frac{t'_{R,A}}{t_{R,A} - t_{R,D}} \tag{32}$$

and $u(t - t_R)$ is the Heaviside unit step function, which is 0 for $t < t_R$ and 1 for $t \geqslant t_R$, with $t_R > 0$.

For $t < t_{R,D} < t_{R,A}$, both terms within the braces { } of eqn. 31 are zero and $c_D = 0$, i.e., no signal is recorded at the detector. The first signal should appear abruptly at $t = t_{R,D} < t_{R,A}$, when the first term becomes 1, whereas the second remains 0. The maximum in the signal is therefore $(c_D)_{max} = mk_1\lambda/\dot{V}$, i.e., inversely proportional to $\dot{V}$. For $t_{R,D} < t < t_{R,A}$, the signal decreases exponentially with t, so that, from eqn. 31

$$\ln c_D = \ln\left(\frac{mk_1\lambda}{\dot{V}}\right) + k_1\lambda t_{R,D} - k_1\lambda t \tag{33}$$

Thus, a plot of the logarithm of the height of the elution curve of D against t should be linear, with slope $-k_1\lambda$. This conclusion coincides with the "simple elution technique" of Phillips et al.[1].

Finally, when $t > t_{R,A}$, both terms in eqn. 31 come into play, and again $c_D = 0$, as can be seen by substituting for λ the expression on the far right of eqn. 32 and performing the calculations.

We consider next the most important eqn. 25, which, when $x = l$, reduces to:

$$\overline{AC_D} = \frac{m}{\dot{V}} t_s k_1 k_A \cdot \frac{\exp(-t_{R,D}p') - \exp(-k_1 t'_{R,A}) \cdot \exp(-t_{R,A}p)}{(1 + k_A)p + k_1 k_A - (1 + k_D)p'} \tag{34}$$

Taking the inverse Laplace transform, first with respect to p and then with respect to p', we find for $t < t_{R,A}$:

$$\Delta c_D(t,t_s,t') = \frac{m}{\dot{V}} t_s k_1 g \cdot \exp(-k_1 g t) \cdot \delta\left[t' - t_{R,D}\left(1 - \frac{t}{t_{R,A}}\right)\right] \tag{35}$$

where g is the fraction of reactant A in the adsorbed form A–S:

$$g = \frac{k_A}{1 + k_A} \tag{36}$$

and $(1+k_D)/(1+k_A)$ has been replaced by $t_{R,D}/t_{R,A}$.

Eqn. 35 predicts the elution of a stop-peak, since Δc_D has a non-zero value only when

$$t' = t_{R,D}\left(1 - \frac{t}{t_{R,A}}\right) \tag{37}$$

which thus is the retention time of the stop-peak. This retention time does not remain constant, but decreases as t increases and becomes zero when $t = t_{R,A}$. Only when $t \ll t_{R,A}$ is $t' \approx t_{R,D}$. i.e., the retention of the stop-peak is approximately equal to

the ideal retention time of the product D only when the stop is made early in the run or when the retention time of the reactant is very large.

Finally, we find the area under the curve of the stop-peak as a function of t from eqn. 27, which here becomes

$$f_s = \mathcal{L}_p^{-1} \left[mt_s k_1 k_A \frac{1 - \exp(-k_1 t'_{R,A}) \cdot \exp(-t_{R,A} p)}{(1 + k_A)p + k_1 k_A} \right]$$

giving

$$f_s = mt_s k_1 g \cdot \exp(-k_1 g t) \left[1 - u(t - t_{R,A}) \right] \tag{38}$$

where the expression in square brackets [ ] is 1 for $t < t_{R,A}$ and 0 for $t > t_{R,A}$. This result is exactly as previously found[1,4] using other derivations.

A graph of the logarithm of the stop-peak area against t is predicted to be linear with slope $-k_1 g$; we have confirmed this experimentally in certain cases[4-7].

ACKNOWLEDGEMENT

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