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## THEORY OF NON-EQUILIBRIUM STOPPED-FLOW GAS CHROMATOGRAPHY

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### SUMMARY

An equation is derived that gives the area under the curve of the stop-peaks, as a function of the time of the stop and of the carrier gas flow-rate, in non-equilibrium stopped-flow gas chromatography. Adsorption-desorption is assumed to take place at two kinds of reactive sites. It is shown that, with certain approximations, the equation derived can be used to determine the rate constants for desorption and the partition coefficients for both kinds of sites. Experiments at various temperatures can then yield desorption activation parameters, as well as enthalpies and entropies of adsorption. Furthermore, the stop-peaks provide a simple method for finding ideal retention times in linear non-ideal (*i.e.* non-equilibrium) chromatography.

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### INTRODUCTION

Stopped-flow gas chromatography (GC) was introduced by Phillips *et al.*<sup>1</sup> as a method of studying heterogeneous catalysis. It was assumed that the chemical reaction took place under conditions of linear equilibrium elution chromatography. Katsanos and Hadzistelios<sup>2</sup> showed that the stopped-flow technique can be used to measure desorption rates in non-equilibrium GC. The latter authors gave a simple theoretical analysis, based on a homogeneous surface, but their experimental data for desorption of various hydrocarbons from an alumina surface suggest the existence of two kinds of adsorption sites with different desorption rates. The idea of a two-sided adsorption-desorption is further explored in the present paper, and it is shown that not only two desorption rate constants, but also the two corresponding partition coefficients, can be derived from the experimental data.

It was observed that the stopped-flow technique can, with advantage, be applied in adsorption-desorption studies if the adsorbate is allowed first to equilibrate between the gas and the solid phases at the inlet end of the chromatographic column, although this step is not always necessary. Thus, the initial conditions here differ from those of conventional pulse chromatography.

In this paper we give a simple mathematical treatment of two-sided non-equilibrium stopped-flow adsorption chromatography, with initial conditions of equilibrium.

The theory has been successfully applied to the adsorption of *n*-hexane and *n*-heptane on modified alumina, as well as to the adsorption of *n*-heptane on porous glass. From the experimental curves two rate constants and two partition coefficients, one for each active site, have been determined using the method described later in the present paper. These results will be reported shortly.

#### THEORETICAL ANALYSIS

Consider a conventional tubular GC column filled with a solid adsorbent. Under isothermal conditions, a small amount of the pure adsorbate (A) is instantaneously introduced as a vapour at the inlet end of the column and allowed to equilibrate with the solid. A flow of carrier gas through the column (at a constant velocity) is now established, thus destroying the equilibrium between the gas and the solid phases, and giving a highly asymmetrical signal at the detector. This signal has a sharp front profile with long tailing.

While the chromatographic signal is decaying, the flow of the carrier gas is stopped and then restored after a definite time interval; this procedure is repeated, the time of each stop being noted. Following each restoration of the carrier gas flow, a sharp symmetrical peak (the so-called stop-peak), having a well defined retention time and "sitting" on the otherwise asymmetrical tailing signal, is detected, as shown in Fig. 1. The stop-peak is caused by the enrichment of the gas phase in the adsorbate owing to slow desorption during the interval when no gas flows. The problem to be solved here is to determine the area under the curve of each stop-peak as a function of the time of the corresponding stop of the carrier gas flow, with the following assumptions:

- (1) Axial diffusion of the gas in the bed is negligible.
- (2) The only slow processes, determining the rates of equilibration of the ad-

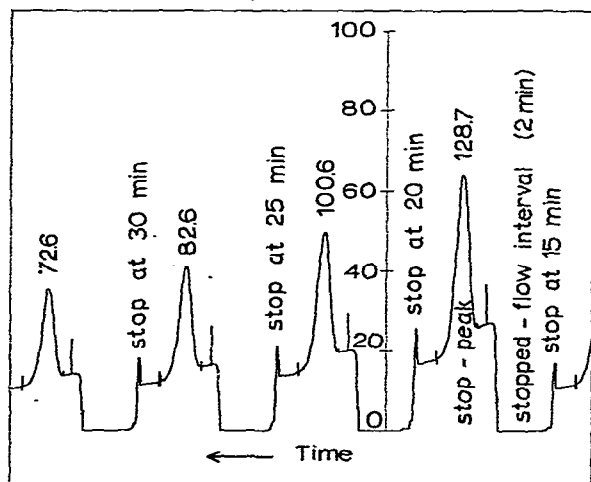


Fig. 1. Section of a typical stopped-flow chromatogram for desorption of *n*-heptane from an alumina surface covered with 10% potassium chloride at 111.0°. Nitrogen was used as carrier gas with a corrected volume flow-rate of 0.43 ml/sec. The number on each stop-peak is the area of the peak in mV-sec.

sorbate between the gas and the solid phases, are adsorption and desorption phenomena, other "resistances", e.g., intraparticle diffusion, being negligible.

The above two assumptions seem reasonable for flow-rates that are high enough and small particle diameters.

(3) Adsorption-desorption takes place at two kinds of active sites,  $S_1$  and  $S_2$ , as dictated by experimental evidence. The adsorption isotherm is assumed to be linear for both kinds of sites, their fractions ( $s_1$  and  $s_2$ ) of the total concentration of sites remaining constant with time. This is not an unreasonable assumption for small adsorbate concentrations.

(4) The adsorbate is introduced in an "infinitesimally" small section of the column, so that the feed band can be described by a Dirac delta function  $\delta(x)$ . The use of a square function, such as the difference of two Heaviside step functions  $u(x) - u(x - b)$ , is more complicated, but leads to equivalent results.

### Notation

$a$	= volume of gas phase per unit length of column ( $\text{cm}^2$ );
$a'$	= volume of solid phase per unit length of column ( $\text{cm}^2$ );
$c$	= concentration of the vapour in the gas phase (mole/ml);
$c_0$	= concentration of the vapour in the gas phase in the interval $t'$ for $t_s = 0$ (mole/ml);
$C$	= Laplace transform of $c$ with respect to $t$ ;
$\bar{c}, \bar{c}_0$	= Laplace transforms of $c$ and $c_0$ with respect to $t'$ ;
$\Delta c, \Delta q_1, \Delta q_2$	= changes in $c, q_1$ and $q_2$ during the stopped-flow interval (mole/ml);
$\overline{\Delta C}$	= Laplace transform of $\Delta c$ with respect to $t$ ;
$\overline{\Delta c}$	= Laplace transform of $\Delta c$ with respect to $t'$ ;
$\overline{\overline{\Delta C}}$	= double Laplace transform of $\Delta c$ with respect to $t$ and $t'$ ;
$f$	= area under the curve of a stop-peak (moles);
$F$	= Laplace transform of $f$ with respect to $t$ ;
$k_1, k_2$	= rate constants for adsorption on sites $S_1$ and $S_2$ ( $\text{sec}^{-1}$ );
$k_{-1}, k_{-2}$	= rate constants for desorption from sites $S_1$ and $S_2$ ( $\text{sec}^{-1}$ );
$K_1, K_2$	= equilibrium constants for adsorption (partition coefficients) on sites $S_1$ and $S_2$ (dimensionless);
$l$	= length of column (cm);
$m$	= total mass of injected vapour (moles);
$m_n$	= integrals defined by eqn. 29;
$p, p'$	= transform parameters with respect to $t$ and $t'$ ;
$q_1, q_2$	= concentration of the vapour adsorbed on sites $S_1$ and $S_2$ per unit volume of solid adsorbent (mole/ml);
$Q_1, Q_2$	= Laplace transforms of $q_1$ and $q_2$ with respect to $t$ ;
$\bar{q}_1, \bar{q}_2$	= Laplace transforms of $q_1$ and $q_2$ with respect to $t'$ ;
$r$	= $a'/a$ = volume ratio of solid and gas phases;
$s_1, s_2$	= fractions of adsorption-active sites $S_1$ and $S_2$ ;
$t$	= time interval from the beginning of the carrier gas flow to the beginning of the stopped-flow interval (sec);
$t_M$	= gas hold-up time (sec);
$t_R$	= retention time (sec);
$t_s$	= stopped-flow time (sec);

- $t'$  = time measured from the end of the stopped-flow interval (sec);  
 $v$  = linear velocity of the carrier gas in the interparticle space (cm/sec);  
 $V$  = volume of carrier gas passed through the column in the interval  $t'$  (ml);  
 $\dot{V}$  = volume flow-rate of carrier gas (ml/sec);  
 $V_s$  =  $a'l$  = total volume of solid adsorbent (ml);  
 $x$  = distance from inlet end of column (cm);  
 $Y_1, Y_2$  = functions defined by eqns. 36 and 37;  
 $\Phi$  = expression defined by eqn. 9;  
 $\Omega_1, \Omega'_1, \Omega_2, \Omega_3$  = expressions defined by eqns. 14, 23, 15 and 26, respectively.

Other symbols are defined as they occur in the text.

For the adsorption-desorption of the adsorbate (A) on the two kinds of reactive sites we can write:



and



where  $A - S_1$  and  $A - S_2$  are the two adsorbed species.

Provided that 1 and 2 are elementary reactions, the equilibrium constants for adsorption are related to the rate constants by the equations:

$$K_1 = \frac{k_1}{k_{-1}} s_1 = \frac{q_1}{c} \quad (3)$$

and

$$K_2 = \frac{k_2}{k_{-2}} s_2 = \frac{q_2}{c} \quad (4)$$

The problem will be considered separately for the three intervals  $t$ ,  $t_s$  and  $t'$  of the time variable.

### Interval $t$

Under the restrictions stated previously, the concentrations  $c(x, t)$ ,  $q_1(x, t)$  and  $q_2(x, t)$ , as functions of  $x$  and  $t$ , are determined by the following system of equations:

Mass balance in the gas phase:

$$\frac{\partial c}{\partial t} + r \frac{\partial q_1}{\partial t} + r \frac{\partial q_2}{\partial t} = -v \frac{\partial c}{\partial x} \quad (5)$$

Rate of adsorption on sites  $S_1$ :

$$\frac{\partial q_1}{\partial t} = k_1 c s_1 - k_{-1} q_1 = k_{-1} (K_1 c - q_1) \quad (6)$$

Rate of adsorption on sites  $S_2$ :

$$\frac{\partial q_2}{\partial t} = k_2 c s_2 - k_{-2} q_2 = k_{-2} (K_2 c - q_2) \quad (7)$$

Initial conditions:

$$c(x,0) = \Phi\delta(x), \quad q_1(x,0) = K_1\Phi\delta(x), \quad q_2(x,0) = K_2\Phi\delta(x) \quad (8)$$

$$\text{where } \Phi = \frac{m}{a + (K_1 + K_2) a'} \quad (9)$$

Conditions 8 are due to the initial equilibration of the vapour between the two phases, taking into consideration eqns. 3 and 4.

Substituting eqn. 6 for  $\partial q_1/\partial t$  and eqn. 7 for  $\partial q_2/\partial t$  in eqn. 5, and taking the Laplace transform with respect to  $t$  of the resulting equation, as well as those of eqns. 6 and 7, we obtain:

$$v \frac{dC}{dx} + (p + rk_{-1}K_1 + rk_{-2}K_2)C - r(k_{-1}Q_1 + k_{-2}Q_2) = c(x,0) \quad (10)$$

$$Q_1 = \frac{k_{-1}K_1C + q_1(x,0)}{p + k_{-1}} \quad (11)$$

and

$$Q_2 = \frac{k_{-2}K_2C + q_2(x,0)}{p + k_{-2}} \quad (12)$$

Substitution of eqn. 11 for  $Q_1$  and of eqn. 12 for  $Q_2$  in eqn. 10, and rearrangement gives:

$$\frac{dC}{dx} + \Omega_1 C = \frac{1}{v} \left[ c(x,0) + \frac{rk_{-1}}{p + k_{-1}} q_1(x,0) + \frac{rk_{-2}}{p + k_{-2}} q_2(x,0) \right] \quad (13)$$

where

$$\Omega_1 = \frac{1}{v} \left( p + rk_{-1}K_1 + rk_{-2}K_2 - \frac{rk_{-1}^2K_1}{p + k_{-1}} - \frac{rk_{-2}^2K_2}{p + k_{-2}} \right) \quad (14)$$

The initial conditions 8 are now substituted for  $c(x,0)$ ,  $q_1(x,0)$  and  $q_2(x,0)$  in eqn. 13, giving the following differential equation in  $C$ :

$$\frac{dC}{dx} + \Omega_1 C = \Omega_2 \delta(x)$$

where

$$\Omega_2 = \frac{\Phi}{v} \left( 1 + \frac{rk_{-1}K_1}{p + k_{-1}} + \frac{rk_{-2}K_2}{p + k_{-2}} \right) \quad (15)$$

This equation can be solved by multiplying it by the integrating factor  $e^{\Omega_1 x}$  and integrating between the limits  $-\infty$  and  $x$ . The result is

$$C = \Omega_2 e^{-\Omega_1 x} \quad (16)$$

By taking the inverse Laplace transform of this equation with respect to  $t$ , we can

find  $c$  as a function of  $x$  and  $t$ . As, however, the explicit form of  $c(x, t)$  is not required for the solution of our problem, the inverse Laplace transform is postponed to a later stage in order to keep the calculations simple.

#### Interval $t_s$

During this time interval the flow of the carrier gas through the column is stopped, so that  $v = 0$ , and the situation is described by the following system of equations, which are analogous to eqns. 5, 6 and 7:

$$\frac{\partial c}{\partial t_s} + r \frac{\partial q_1}{\partial t_s} + r \frac{\partial q_2}{\partial t_s} = 0 \quad (17)$$

$$\frac{\partial q_1}{\partial t_s} = k_{-1} (K_1 c - q_1) \quad (18)$$

and

$$\frac{\partial q_2}{\partial t_s} = k_{-2} (K_2 c - q_2) \quad (19)$$

By keeping the interval  $t_s$  sufficiently small, so that the total change in  $c$  during this interval is small, we can write  $\Delta c/t_s \approx \partial c/\partial t_s$ , and eqn. 17, after substituting in it eqns. 18 and 19 for  $\partial q_1/\partial t_s$  and  $\partial q_2/\partial t_s$ , respectively, gives:

$$\Delta c \approx [k_{-1} (q_1 - K_1 c) + k_{-2} (q_2 - K_2 c)] r t_s \quad (20)$$

The physical meaning of  $\Delta c$  is that it represents the enrichment of the gas phase in the adsorbate, due to slow desorption during the stopped-flow interval  $t_s$ .

Similarly from eqns. 18 and 19 we obtain the relationships:

$$\Delta q_1 \approx k_{-1} (K_1 c - q_1) t_s$$

and

$$\Delta q_2 \approx k_{-2} (K_2 c - q_2) t_s$$

Obviously,  $\Delta c$ ,  $\Delta q_1$  and  $\Delta q_2$  are functions of: (a) the position  $x$  in the column, (b) the time  $t$  when the flow of the carrier gas was stopped and (c) the duration of the stop  $t_s$ , which is required to be kept constant throughout a chromatographic run.

#### Interval $t'$

At the end of the stopped-flow interval, the flow of the carrier gas through the column is restored and the situation is therefore again described by eqns. 5, 6 and 7 with  $t'$  in place of  $t$ , and  $c$ ,  $q_1$ ,  $q_2$  now being functions of  $x$ ,  $t$ ,  $t_s$ ,  $t'$ . The initial conditions for this interval are:

$$\left. \begin{aligned} c(x, t, t_s, 0) &= c(x, t) + \Delta c(x, t, t_s) \\ q_1(x, t, t_s, 0) &= q_1(x, t) + \Delta q_1(x, t, t_s) \approx q_1(x, t) \\ q_2(x, t, t_s, 0) &= q_2(x, t) + \Delta q_2(x, t, t_s) \approx q_2(x, t) \end{aligned} \right\} (21)$$

and

where  $\Delta q_1$  and  $\Delta q_2$ , as a first approximation, are taken to be negligible compared with  $q_1$  and  $q_2$ , respectively.

Substituting eqns. 6 and 7 in eqn. 5, as before, taking the Laplace transform with respect to  $t'$ , and eliminating  $\bar{q}_1$  and  $\bar{q}_2$ , we obtain the following relationship, which is analogous to eqn. 13:

$$\frac{d\bar{c}}{dx} + \Omega'_1 \bar{c} = \frac{1}{v} \left[ c(x, t, t_s, 0) + \frac{rk_{-1}}{p' + k_{-1}} q_1(x, t, t_s, 0) + \frac{rk_{-2}}{p' + k_{-2}} q_2(x, t, t_s, 0) \right] \quad (22)$$

where

$$\Omega'_1 = \frac{1}{v} \left( p' + rk_{-1}K_1 + rk_{-2}K_2 - \frac{rk_{-1}^2K_1}{p' + k_{-1}} - \frac{rk_{-2}^2K_2}{p' + k_{-2}} \right) \quad (23)$$

Now, eqn. 22 can also be written for  $t_s = 0$ , *i.e.*, without stopping the carrier gas, which means that the total time is artificially divided into two intervals,  $t$  and  $t'$ , the second being simply the continuation of the first. Denoting the concentration of the gas phase in this instance by  $c_0$ , we have:

$$\frac{d\bar{c}_0}{dx} + \Omega'_1 \bar{c}_0 = \frac{1}{v} \left[ c(x, t) + \frac{rk_{-1}}{p' + k_{-1}} q_1(x, t) + \frac{rk_{-2}}{p' + k_{-2}} q_2(x, t) \right]$$

If this equation is subtracted from eqn. 22, after substituting in the latter the initial conditions 21, the following relationship is obtained:

$$\frac{d}{dx} \left[ \bar{\Delta c}(x, t, t_s, p') \right] + \Omega'_1 \bar{\Delta c}(x, t, t_s, p') = \frac{1}{v} \Delta c(x, t, t_s, 0) \quad (24)$$

where  $\bar{\Delta c}(x, t, t_s, p') = \bar{c} - \bar{c}_0$ , and  $\Delta c(x, t, t_s, 0)$  is given by eqn. 20.

The above relationship is the Laplace transform with respect to  $t'$  of an equation describing  $\Delta c(x, t, t_s, t')$  as a function of  $x$  and  $t'$ , after restoring the carrier gas flow, *i.e.*, the effect of the chromatographic process on  $\Delta c$ , which is formed during the stopped-flow interval  $t_s$ .

Substituting eqn. 20 for  $\Delta c(x, t, t_s, 0)$  in eqn. 24, taking the Laplace transform with respect to  $t$ , and finally using eqns. 11, 12 and 16, as well as conditions 8, we obtain, after rearrangement:

$$\frac{d(\bar{\Delta C})}{dx} + \Omega'_1 \bar{\Delta C} = \Omega_3 \left[ \Phi \delta(x) - p\Omega_2 e^{-\Omega_1 x} \right] \quad (25)$$

where

$$\Omega_3 = \frac{rt_s}{v} \left( \frac{k_{-1}K_1}{p + k_{-1}} + \frac{k_{-2}K_2}{p + k_{-2}} \right) \quad (26)$$

This relatively simple differential equation can be solved to find  $\bar{\Delta C}$  as a function of  $x$ , by using the Laplace transform with respect to  $x$ . The result is

$$\bar{\Delta C} = \Omega_3 \left( \Phi e^{-\Omega_1 x} - p\Omega_2 \frac{e^{-\Omega_1 x} - e^{-\Omega_1' x}}{\Omega_1 - \Omega_1'} \right) \quad (27)$$

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. The area under the curve of this stop-peak in the form of its Laplace transform with respect to  $t$ , is

$$F = \int_0^\infty \Delta C(l, p, t_s, t') dV = \dot{V} \int_0^\infty \Delta C(l, p, t_s, t') dt' \quad (28)$$

The integral can be evaluated by using the well known property of the Laplace transform (we omit the constants  $l$  and  $t_s$  from the independent variables of  $\Delta C$ ):

$$m_n = \int_0^\infty t'^n \Delta C(p, t') dt' = (-1)^n \lim_{(p' \rightarrow 0)} \frac{d^n [\overline{\Delta C}(p, p')]}{dp'^n} \quad (29)$$

The value of the integral of eqn. 28 is then  $m_0$  and is found from eqn. 27 (with  $x = l$ ) by letting  $p' = 0$ , and using eqns. 14 and 15. The result is  $m_0 = \Omega_3 \Phi e^{-\Omega_1 t}$  and thus

$$F = \dot{V} \Omega_3 \Phi e^{-\Omega_1 t} \quad (30)$$

Before taking the inverse Laplace transform of this equation, so as to find  $f$  as a function of  $t$ , it is interesting to calculate the first absolute moment ( $\mu'_1$ ) of the stop-peak, which (for negligible longitudinal diffusion) is the retention time  $t_R$ . Using eqn. 29 we find that

$$t_R = \mu'_1 = \frac{m_1}{m_0} = \frac{(1 + rK_1 + rK_2)(e^{\Omega_1 t} - 1)}{v\Omega_1} \text{ sec} \quad (31)$$

If  $\Omega_1 l$  is sufficiently small, the approximation  $e^{\Omega_1 t} \approx 1 + \Omega_1 l$  can be made and eqn. 31 thus becomes

$$t_R = \frac{l}{v} (1 + rK_1 + rK_2) \quad (32)$$

Inverse Laplace transform of eqn. 32 with respect to  $t$  is not required, as  $t_R$  is independent of  $p$ , and continuity restrictions require that  $t_R$  be also independent of  $t$ . This is confirmed experimentally (see Fig. 1).

Recognising now that  $l/v = t_M$  and  $rK_1$  and  $rK_2$  are the partition ratios  $k'$  and  $k''$  for active sites  $S_1$  and  $S_2$ , respectively, we can rewrite eqn. 32 as

$$t_R = t_M (1 + k' + k'') \quad (33)$$

Comparing this with the well known relationship  $t_R = t_M (1 + k)$  of linear ideal (*i.e.*, equilibrium) chromatography, we conclude that the stop-peaks provide a simple method for finding *ideal* retention times in linear *non-ideal* (*i.e.*, non-equilibrium) chromatography, accepting, of course, the assumptions and approximations used to derive eqn. 32.

Other moments, such as the second central moment  $\mu_2$ , can easily be calculated with the aid of eqn. 29.

The area under the curve of the stop-peak as a function of  $t$  is found by taking



the inverse Laplace transform with respect to  $t$  of eqn. 30. This is given by the relationship:

$$f = \frac{mrt_s}{1 + r(K_1 + K_2)} e^{-(k_{-1}K_1 + k_{-2}K_2)V_s/\dot{V}} \cdot \left\{ k_{-1}K_1 I_0 [2\omega_1^\ddagger(t-t_M)^\ddagger] e^{-k_{-1}(t-t_M)} + k_{-2}K_2 I_0 [2\omega_2^\ddagger(t-t_M)^\ddagger] e^{-k_{-2}(t-t_M)} + \psi_1 + \psi_2 \right\} \quad (34)$$

where

$$\omega_1 = \frac{k_{-1}^2 K_1 V_s}{\dot{V}} \quad \text{and} \quad \omega_2 = \frac{k_{-2}^2 K_2 V_s}{\dot{V}}$$

$\psi_1$  and  $\psi_2$  are convolutions<sup>3</sup> of two functions, each being enclosed within the brackets { }:

$$\psi_1 = \left\{ k_{-1}K_1 I_0 [2\omega_1^\ddagger(t-t_M)^\ddagger] e^{-k_{-1}(t-t_M)} \right\} * \left\{ \left( \frac{\omega_2}{t} \right)^\ddagger I_1 [2\omega_2^\ddagger t^\ddagger] e^{-k_{-2}t} \right\}$$

and

$$\psi_2 = \left\{ k_{-2}K_2 I_0 [2\omega_2^\ddagger(t-t_M)^\ddagger] e^{-k_{-2}(t-t_M)} \right\} * \left\{ \left( \frac{\omega_1}{t} \right)^\ddagger I_1 [2\omega_1^\ddagger t^\ddagger] e^{-k_{-1}t} \right\}$$

and  $I_0$  and  $I_1$  are hyperbolic Bessel functions of the zeroth and first order, respectively, with the arguments enclosed within the brackets [ ].

Obviously, eqn. 34 must be reduced to a simpler form, so that it can be compared with experimental data, and this can be achieved by using certain approximations: (a) the gas hold-up time  $t_M$ , which is negligible compared with  $t$ , can be omitted, and (b) it can be written  $I_0(z) \simeq 1$  and  $I_1(z) \simeq z/2$ , as was done before<sup>2</sup>, assuming that the argument of the Bessel functions is small. With these approximations eqn. 34 reduces to:

$$f = Y_1 e^{-k_{-1}t} + Y_2 e^{-k_{-2}t} \quad (35)$$

where

$$Y_1 = \frac{mrt_s k_{-1} K_1}{1 + r(K_1 + K_2)} \left( 1 - \frac{k_{-2} K_2 V_s}{\dot{V}} \cdot \frac{k_{-1} + k_{-2}}{k_{-1} - k_{-2}} \right) e^{-(k_{-1}K_1 + k_{-2}K_2)V_s/\dot{V}} \quad (36)$$

and

$$Y_2 = \frac{mrt_s k_{-2} K_2}{1 + r(K_1 + K_2)} \left( 1 + \frac{k_{-1} K_1 V_s}{\dot{V}} \cdot \frac{k_{-1} + k_{-2}}{k_{-1} - k_{-2}} \right) e^{-(k_{-1}K_1 + k_{-2}K_2)V_s/\dot{V}} \quad (37)$$

The area recorded by the instrument should be proportional to  $f$  and if the constant of proportionality is  $\lambda$ , this area is  $\lambda f$ . If several stop-peaks are created by repeatedly stopping and restoring the carrier gas flow, then a plot of  $\ln(\lambda f)$  against  $t$  should initially yield a curve, such as that of Fig. 5 in ref. 2. After a certain time, however, the plot becomes linear because one of the terms, say the first, of eqn. 35 becomes negligibly small. The slope of this straight line then gives the value of  $-k_{-2}$ , and its intercept with the  $y$ -axis equals  $\ln(\lambda Y_2)$ . By constructing a similar plot of the differ-

ences between the experimental points and those found by extrapolation of the first straight line, a new straight line is obtained with slope  $-k_{-1}$  and  $y$ -intercept  $\ln(\lambda Y_1)$ .

The experiment can be repeated, at the same temperature, with various flow-rates ( $\dot{V}$ ), yielding various values of  $\lambda Y_1$  and  $\lambda Y_2$ , from which the two partition coefficients  $K_1$  and  $K_2$  can then be determined as follows. We add eqns. 36 and 37:

$$Y_1 + Y_2 = \frac{mrt_s(k_{-1}K_1 + k_{-2}K_2)}{1 + r(K_1 + K_2)} e^{-(k_{-1}K_1 + k_{-2}K_2)V_s/\dot{V}} \quad (38)$$

and we see that a plot of  $\ln(\lambda Y_1 + \lambda Y_2)$  against  $1/\dot{V}$  should be linear with slope  $-(k_{-1}K_1 + k_{-2}K_2)V_s$ . By using the previously determined values of  $k_{-1}$  and  $k_{-2}$  and the known value of  $V_s$ , we obtain an algebraic equation in  $K_1$  and  $K_2$ . A second equation can be obtained from the ratio of corresponding intercepts  $\lambda Y_1$  and  $\lambda Y_2$ . These two equations then can be solved to find  $K_1$  and  $K_2$ .

Sets of experiments at various temperatures will permit the calculation of desorption activation energies and entropies of activation from the variation of  $k_{-1}$  and  $k_{-2}$  with temperature, as well as adsorption enthalpies and entropies from the variation of  $K_1$  and  $K_2$  with temperature. Data of this kind will be reported elsewhere.

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