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## KINETIC STUDY OF SLOW PROCESSES IN GAS CHROMATOGRAPHY

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### SUMMARY

A method is developed for determining the rate constant of slow diffusion and/or slow adsorption-desorption processes in gas chromatography. Rate-constant measurements have been performed by applying the method to the desorption of *n*-butane and *trans*-2-butene from an aluminium oxide surface modified with cerium trichloride. The kinetic feature of every desorption experiment in the systems studied is two distinct rate constants, which might be attributed to two kinds of active sites on the surface. The activation parameters of desorption corresponding to the two kinds of sites have been determined from Arrhenius plots.

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### INTRODUCTION

Gas chromatography (GC) is well-known as an analytical technique; less well-known are its applications to studies of adsorption and heterogeneous catalysis. Particularly interesting are instances in which the same chromatographic column is used simultaneously as a catalytic reactor and as a separation column for the products and reactants<sup>1-3</sup>. These instances, belonging to the gas-solid type, are based on linear ideal chromatography, *i.e.*, on a linear isotherm and on instantaneous equilibration of the vapour between the stationary and the moving phase. In an actual column, however, the last condition is usually not fulfilled, so that chromatography is non-ideal, despite the fact that the isotherm may remain linear. The non-ideality of the column may be due to slow diffusion of the vapour in the stationary (solid) or in the gas phase, slow adsorption and desorption of the vapour and (probably) other slow processes. The net result of this deviation from ideality is mainly a broadening of the chromatographic peaks, often accompanied by peak asymmetry.

When GC is used as an analytical tool, these phenomena are seldom taken into account, particularly when the deviation from ideality is small. However, when the column is used as a catalytic reactor, the slow diffusion or adsorption-desorption processes of the reactants and products may play an important role, as they may influence or even constitute the rate-determining step for the entire reaction<sup>4,5</sup>.

In this paper, we develop a method for determining the rate of the above-

mentioned slow processes. This may complement already existing GC techniques<sup>6-8</sup> for determining desorption rates.

## THEORY

We shall use the following symbols, as used by Littlewood<sup>9</sup>.

$q$  = concentration of the vapour in the stationary phase (moles/g)\*,

$c$  = concentration of the vapour in the gas phase (moles/ml),

$m$  = mass of stationary phase per unit length of column (g/cm),

$a$  = volume of gas phase per unit length of column (cm<sup>2</sup>),

$x$  = distance from inlet end of column (cm),

$l$  = length of column (cm),

$V$  = volume of carrier gas passed through column (ml),

$\dot{V}$  = volume flow-rate of carrier gas (ml/sec),

$\beta$  = partition coefficient of the vapour between the stationary and the gas phases (ml/g).

If equilibrium is reached exponentially according to a first-order law, we can write:

$$-\frac{dq}{dt} = k(q - q_e) = k(q - \beta c) \quad (1)$$

where  $k$  is the rate constant of the slow process (sec<sup>-1</sup>) and  $q_e$  is the equilibrium concentration of the vapour in the stationary phase; for a linear isotherm,  $q_e = \beta c$ .

The first-order conservation equation of chromatography (De Vault equation), together with eqn. 1 and the initial conditions\*\*  $q(0, x) = 0$  and  $c(V, 0) = \delta(V)$  lead<sup>10</sup> to the following solutions for  $c$  and  $q$  as functions of  $V$  and  $x$ :

$$q(V, x) = \frac{\beta k}{\dot{V}} I_0 \left\{ \frac{2k}{\dot{V}} [m\beta x(V - ax)]^{0.5} \right\} \cdot \exp \left[ -\frac{k}{\dot{V}} (m\beta x + V - ax) \right] \quad (2)$$

$$c(V, x) = \frac{k}{\dot{V}} \left( \frac{m\beta x}{V - ax} \right)^{0.5} I_1 \left\{ \frac{2k}{\dot{V}} [m\beta x(V - ax)]^{0.5} \right\} \cdot \exp \left[ -\frac{k}{\dot{V}} (m\beta x + V - ax) \right] \quad (3)$$

where  $J_0$  and  $I_1$  are the hyperbolic Bessel functions of the zeroth and first order, respectively, with the argument enclosed in the braces { }. From the right-hand side of eqn. 3 we have omitted the term  $\exp[-(k/\dot{V})m\beta x] \cdot \delta(V - ax)$ , as it becomes negligible after the first few millimeters of the column.

When the argument of the Bessel functions in eqns. 2 and 3 is large ( $>10$ ), the chromatographic peaks are broadened, but remain approximately symmetrical and of the Gaussian type. However, if this argument is small, e.g., because  $k$  is small

\* For an adsorbent stationary phase it would be more correct to express  $q$  in moles per unit surface area of adsorbent, but this does not affect our results, as it is assumed that the solid adsorbent is uniform and has the same surface area per gram along the column. Moreover, the treatment given here can be also applied to gas-liquid chromatography, for which moles/g seem appropriate.

\*\* It is assumed that input distribution of the vapour is expressed by the delta function.

or  $\dot{V}$  is large, the peaks become asymmetrical, with sharp front profiles and long "tails". All the above statements are well-known in GC; they have been repeated here to provide the necessary background for what follows.

Let us assume now that the argument of the Bessel functions of eqns. 2 and 3 is very small, so that we can apply the approximate formula of ref. 11, viz.,

$$I_p(z) \approx \frac{1}{\Gamma(p+1)} \cdot \left(\frac{z}{2}\right)^p \quad (4)$$

With this approximation,  $I_0(z) = 1$  and  $I_1(z) = z/2$ . Therefore  $I_0$  in eqn. 2 is equal to 1, and  $I_1$  in eqn. 3 is equal to  $(k/\dot{V}) [m\beta x (V-ax)]^{0.5}$ . Thus, eqns. 2 and 3 become:

$$q(V,x) = \frac{\beta k}{\dot{V}} \cdot \exp\left[-\frac{k}{\dot{V}} (m\beta x + V - ax)\right] \quad (5)$$

$$c(V,x) = \left(\frac{k}{\dot{V}}\right)^2 m\beta x \cdot \exp\left[-\frac{k}{\dot{V}} (m\beta x + V - ax)\right] \quad (6)$$

The distance from equilibrium,  $q - q_e = q - \beta c$ , as a function of  $V$  and  $x$  can be found by substituting  $q$  and  $c$  in this relationship from eqns. 5 and 6.

If, after passage of volume  $V$  of carrier gas through the column, the flow of gas is stopped for a period  $t_s$  (i.e., if  $V$  is kept constant for time  $t_s$ ), at every point  $x$  of the column  $q - \beta c$  will decay exponentially (as do all first-order processes), becoming after time  $t_s$  equal to  $(q - \beta c) \cdot \exp(-kt_s)$ . As a result of this, a fraction of the vapour equal to  $(q - \beta c) [1 - \exp(-kt_s)]$  per unit mass of stationary phase will be expelled from this phase and enter the gas phase. This will be a function of  $x$  for the same value of  $V$ , as  $q$  and  $c$  are both functions of  $V$  and  $x$ . If  $dW$  is the mass of stationary phase contained between points  $x$  and  $x + dx$  of the column, then the fraction of vapour ( $dS$ ) that will be expelled from this section of the column is given by

$$\begin{aligned} dS &= (q - \beta c) [1 - \exp(-kt_s)] dW, \quad \text{or} \\ dS &= (q - \beta c) [1 - \exp(-kt_s)] m dx \end{aligned} \quad (7)$$

By substituting the right-hand sides of eqns. 5 and 6 for  $q$  and  $c$ , respectively, in eqn. 7 and integrating between the limits  $x = 0$  and  $l$ , we can derive the fraction  $S$  of the vapour that is transferred from the total mass of the stationary phase to the gas phase along the entire length of the column during time  $t_s$ . The result is

$$S(V) = ABC \left\{ \frac{\exp[(D - A)l] - 1}{D - A} - Ax \cdot \frac{1 + [(D - A)l - 1] \cdot \exp[(D - A)l]}{(D - A)^2} \right\} \quad (8)$$

where  $A = m\beta k/\dot{V}$ ,  $B = 1 - \exp(-kt_s)$ ,  $C = \exp(-kV/\dot{V})$  and  $D = ka/\dot{V}$

Eqn. 8 can be greatly simplified (although this is not absolutely necessary for its present experimental verification) by assuming that  $D$  is much less than  $A$ , so that  $D - A \approx -A$ . This assumption is justified because the condition that  $D$  is much less

than  $A$  is equivalent to  $a$  being much less than  $m\beta$ , and this multiplied by  $l$  gives  $al$  being much less than  $m\beta l$ . Now  $al = V_M^0$ , the gas hold-up (or dead) volume of the column, and  $ml = W$ , the total mass of the stationary phase, so that  $m\beta l = W\beta = V_R^0 - V_M^0 = V_N$ , the net retention volume of the peak maximum. Thus, it is reasonable to assume that  $V_M^0$  is much less than  $V_N$ , *i.e.*, that the dead volume is negligible compared with the retention volume.

By using this approximation, *i.e.*, neglecting  $D$  compared with  $A$ , in all terms of eqn. 8, we obtain:

$$S(V) = ABCl \cdot \exp(-Al) \quad (9)$$

or, substituting for  $A$ ,  $B$  and  $C$ ,

$$S(V) = \frac{m\beta kl}{\dot{V}} \cdot \exp\left(-\frac{m\beta kl}{\dot{V}}\right) \cdot [1 - \exp(-kt_s)] \cdot \exp\left(-\frac{kV}{\dot{V}}\right) \quad (10)$$

Other useful substitutions are  $ml = W$  as before, and  $V/\dot{V} = t_f$  (the time of flow of carrier gas through the column), by means of which eqn. 10 becomes

$$S(t_f) = \left\{ \frac{W\beta k}{\dot{V}} \cdot \exp\left(-\frac{W\beta k}{\dot{V}}\right) \cdot [1 - \exp(-kt_s)] \right\} \cdot \exp(-kt_f) \quad (11)$$

Eqn. 11 predicts that cessation of the carrier gas flow through the column at time  $t_f$  for a period  $t_s$  will result in a fraction  $S$  of the total amount of vapour being expelled from the stationary phase. On restoring the carrier gas flow, and after a certain time, this fraction will appear as an extra peak "sitting" on the tail of the asymmetrical elution chromatogram of the substance. This prediction is confirmed experimentally, as is shown in Fig. 1.

On repeating the stopping and restoring of the carrier gas at various times  $t_f$ , various "stop-peaks" will appear on the chromatogram. At constant temperature, and for constant values of  $\dot{V}$  and  $t_s$ , the expression in braces in eqn. 11 will be a constant  $S_0$ , thus allowing  $S$  to become a simple exponential function of  $t_f$ :

$$S = S_0 \exp(-kt_f) \quad (12)$$

or, taking logarithms,

$$\ln S = \ln S_0 - kt_f \quad (13)$$

Therefore, a graph of  $\ln S$  against  $t_f$  will be a straight line, from the slope of which  $k$  can be determined.

This method of determining  $k$  resembles the stopped-flow technique of Phillips *et al.*<sup>3</sup> for determining the rate constant of a chemical reaction taking place on the surface. It should be noted, however, that here  $t_f$  is the total time of flow of the carrier gas through the column, *i.e.*, the time between injection of the substance and stopping of the gas, diminished by the time during which the gas was not flowing. If, for example,  $t_s = 60$  sec, the  $t_f$  corresponding to the tenth stop is equal to the total time less

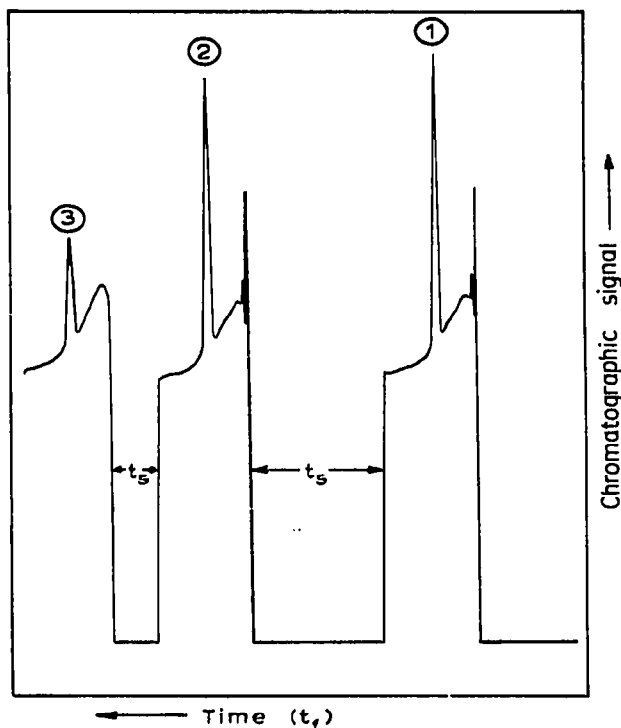


Fig. 1. Section from a typical chromatogram of desorption of *n*-butane from  $\text{Al}_2\text{O}_3$ -10%  $\text{CeCl}_3$  at  $81.1^\circ$ ; peaks 1, 2 and 3 are "stop-peaks".

$9 \times 60$  sec. The magnitude of  $S$  is proportional to the area  $s$  under the "stop-peak", and, if the constant of proportionality is  $\lambda$ , then eqn. 13 gives

$$\ln s = \ln (S_0/\lambda) - kt_f \quad (14)$$

Thus, it is only necessary to plot the logarithm of the "stop-peak" area against time in order to derive  $k$ .

In the rest of this paper we give an example of the application of eqn. 14 using *n*-butane, and *trans*-2-butene adsorbed on aluminium oxide modified with 10% of cerium(III) chloride.

## EXPERIMENTAL

### *Apparatus and materials*

A Pye Unicam Series 104 gas chromatograph was used with a flame ionization detector. A Perkin-Elmer 212D sorptometer was employed for measuring the specific surface area of the adsorbent. A Hamilton four-port valve (Fig. 2) and a Varian seven-port gas-sampling valve (Fig. 3) were used. Vapour samples, of small size, were injected by using disposable 1-ml syringes. Fluka (Buchs, Switzerland) *n*-butane ("purum") and *trans*-2-butene ("purum"), as well as  $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$  (Schuchardt,

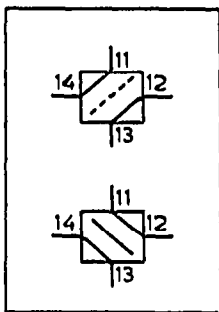


Fig. 2. Schematic flow diagram in the two-position four-port gas valve

Munich, G.F.R.) were used as purchased. Aluminium oxide (BDH, Poole, Great Britain; acidic, Brockmann grade 1) for chromatographic analysis, was used. The following analytical columns, run in nitrogen (99.9%), were used: (a)  $95 \times 0.25$  cm (I.D.) filled with 24% of ethylene glycol-silver nitrate (3.77:1, w/w) on Chromosorb P (60–80 mesh) for the identification of *trans*-2-butene, and (b)  $200 \times 0.25$  cm (I.D.) filled with 15% of dinonyl phthalate on Chromosorb P (80–100 mesh) for the identification of *n*-butane. During desorption runs the aluminium oxide column was run in nitrogen (99.9%) or in argon (99.95%). In both instances, the carrier gas was first passed through a drying tube containing Linde molecular sieve 4A activated at 400°C.

#### Preparation of the stationary phase and conditioning of the column

Aluminium oxide (18 g), sieved (100–120 BSS mesh), was impregnated with a solution containing  $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$  (2 g) in distilled water (15 ml). After 15 h, the resulting mixture was evaporated to a heavy slurry on a steam-bath. The slurry was spread on a filter-paper and allowed to dry for a while before being heated for 0.5 h in an oven at 100°, sieved (100–120 BSS mesh) and stored. The stationary phase so prepared ( $\text{Al}_2\text{O}_3$ -10%  $\text{CeCl}_3$ ) was used to fill a stainless-steel column,  $37 \times 0.25$  cm (I.D.), which was connected to the injector,  $5 \times 0.5$  cm (I.D.), of the chromatograph.

Desorption experiments for *n*-butane were performed using this column (run

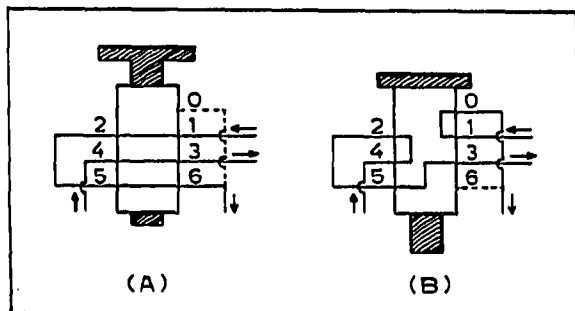


Fig. 3. Schematic flow diagram in the two-position seven-port gas-sampling valve: (A), normal position; (B), feeding position.

in argon) after activation for 1 h at 500° and conditioning *in situ* for 18 h at 80° in an argon stream. Every new setting of temperature was followed by conditioning for at least 12 h.

Desorption experiments with *trans*-2-butene were performed on the same column, but run in nitrogen and pre-treated as follows: activation for 7 h at 500°, cooling in air for 0.5 h, injecting distilled water (100  $\mu$ l), conditioning for 24 h at 78°, again injecting distilled water (100  $\mu$ l) and conditioning for 24 h at 78° in a stream of nitrogen. This column, used in the temperature range 50–75°, exhibited unaltered chromatographic behaviour during 1 week. Every temperature change was followed by a conditioning period of at least 12 h.

The same column was also used in another series of runs, for studying the desorption of *trans*-2-butene from a surface with a higher amount of water than the previous one. For these experiments, the drying tube was removed from the carrier gas line, thus allowing the nitrogen to moisten the column continually. The column was conditioned in this way for 15 days at ambient temperature (20°), and subsequent kinetic runs were performed after the column had been allowed to equilibrate for at least 12 h at each new temperature setting. It was found that olefins isomerized and mainly polymerized to a considerable extent on a dry column; moistening of the stationary phase was necessary to avoid such effects.

#### *Kinetic runs and identification of the desorbing substances*

The kinetic runs for measuring desorption rates of *n*-butane and *trans*-2-butene from the surface of aluminium oxide, modified with cerium trichloride, were performed by using the experimental arrangement shown in Fig. 4 and applying the stopped-flow technique. The flow-rate (30 ml/min) of carrier gas at any column temperature was measured at the exit of the detector and 0.1-ml vapour samples were injected. After the elution peak of the injected substance had emerged, the flow of car-

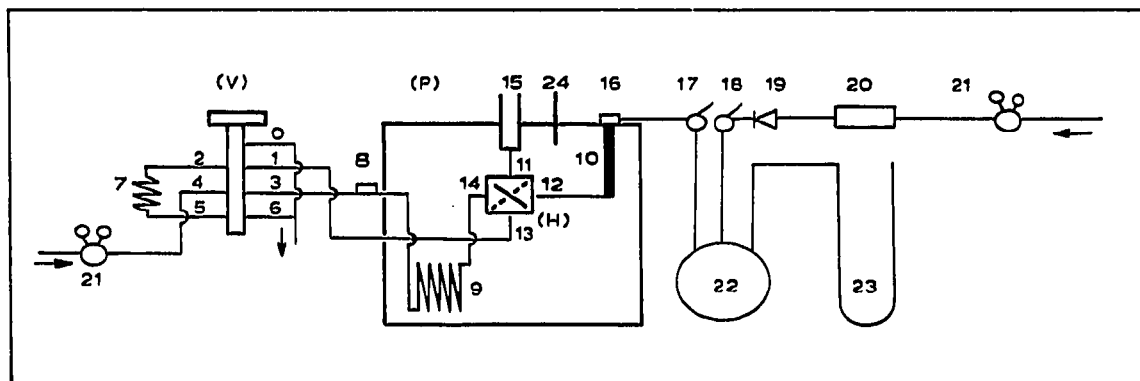


Fig. 4. Schematic arrangement for desorption rate measurements and identification of the desorbing substances: P, gas chromatograph; V, seven-port gas-sampling valve; 0, 1, 2, 3, 4, 5, 6, communication of the ports as in Fig. 3; 7, 5-ml loop; 8, injection port to analytical column; 9, analytical column; 10, experimental column; H, four-port valve; 11, 12, 13, 14, communication of the ports as in Fig. 2; 15, flame-ionization detector; 16, injection port to experimental column; 17, 18, shut-off valves; 19, needle valve; 20, gas-drying tube; 21, pressure regulators; 22, reservoir (1 litre); 23, open manometer; 24, thermometer.

rier gas was stopped by means of the two shut-off valves (17 and 18 in Fig. 4) and re-started after exactly 1 min. This was done repeatedly, at precisely known times after the injection, thus giving rise to stopped-flow peaks of desorption; the retention time of these peaks was always the same during one kinetic run. Moreover, they were symmetrical and had the same width at half peak height. Thus, their height was measured instead of their area, and eqn. 14 was applied in order to calculate  $k$ . After the last kinetic run, approximately 0.1 g of the modified aluminium oxide was transferred from the column to the sorptometer for surface area determinations.

The desorbing substances were analyzed by gas chromatography and found to be identical with those injected into the column in all instances. This identification was made by keeping valve V in the normal position (A in Fig. 3) and switching valve H to the position indicated by the dotted line in Fig. 4, thus venting the content of the experimental column through loop 7 (Fig. 4). Then, by switching valve V to the feeding position (B in Fig. 3), the contents of the loop are transferred to the analytical column connected to the detector.

Stopped-flow peaks were obtained even when *n*-butane was desorbing from the column run in dry hydrogen. Thus, the possibility that the slow desorption observed could be due to formation of an intermediate polymer decomposing slowly was excluded. A substance-spot bleeding, in the injection system, was also excluded by replacing the injector and the injection septum during a run.

## RESULTS AND DISCUSSION

In Fig. 5 we give a plot of  $\log s$  against  $t_f$ . It can be seen that the initial part of the graph is a curve and that linearity is observed only after a certain time. This suggests that the experimentally measured value of  $s$  is equal to the sum of two exponential functions like that of eqn. 12, with two considerably different values of  $k$ .

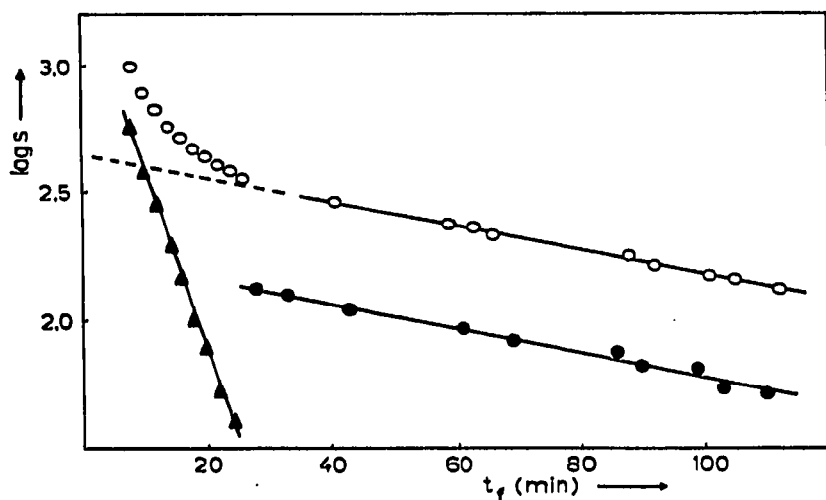


Fig. 5. Kinetics of *n*-butane desorption from  $\text{Al}_2\text{O}_3$ -10%  $\text{CeCl}_3$  at  $81.1^\circ$ . ○, Points corresponding to 3-min stops; ●, points corresponding to 1-min stops; ▲, points calculated from the difference between the straight-line extrapolation and the corresponding experimental points.



TABLE I

RATE CONSTANTS OF SLOW PROCESSES FOR *n*-BUTANE ADSORBED ON Al<sub>2</sub>O<sub>3</sub>-10% CeCl<sub>3</sub>

Temperature (°C)	$k_1 \times 10^3$ (sec <sup>-1</sup> )	$k_{11} \times 10^4$ (sec <sup>-1</sup> )
68.6	—	1.0 ± 0.1
74.2	—	1.33 ± 0.03
81.1	—	1.77 ± 0.08
84.1	1.13 ± 0.02	2.43 ± 0.08
90.6	—	2.88 ± 0.03
95.6	1.70 ± 0.03	3.48 ± 0.08
97.9	2.1 ± 0.2	3.97 ± 0.03
104.2	2.13 ± 0.03	5.02 ± 0.05

This assumption is supported by the fact that the plot can be analyzed in two straight lines, as shown in Fig. 5, thus allowing the determination of two rate constants at each temperature and for each adsorbate. These can be attributed to two kinds of active sites in alumina, as frequently reported in the literature<sup>8,12</sup>.

Tables I and II show rate constants determined at different temperatures for *n*-butane and *trans*-2-butene, respectively.

$k_1$  refers to the faster and  $k_{11}$  to the slower of the two processes. We believe that these processes are slow desorptions from the two kinds of active sites of the surface.

Table III gives the activation parameters for the desorption process from both active sites, determined by conventional Arrhenius plots of  $\log k$  against  $1/T$ .

The values of  $E$  ( $E_1 = 4.5$  kcal/mole and  $E_{11} = 11$  kcal/mole) found by us for the desorption of *trans*-2-butene from sites I and II of the adsorbent are considerably lower than those ( $E_1 = 12.1$  kcal/mole and  $E_{11} = 16.2$  kcal/mole) found<sup>13</sup> by the "flash-desorption" technique for the desorption of *trans*-2-butene from an unmodified

TABLE II

RATE CONSTANTS OF SLOW PROCESSES FOR *trans*-2-BUTENE ADSORBED ON MOISTENED Al<sub>2</sub>O<sub>3</sub>-10% CeCl<sub>3</sub>

Temperature (°C)	Slightly wetted surface		More wetted surface	
	$k_1 \times 10^3$ (sec <sup>-1</sup> )	$k_{11} \times 10^3$ (sec <sup>-1</sup> )	$k_1 \times 10^3$ (sec <sup>-1</sup> )	$k_{11} \times 10^3$ (sec <sup>-1</sup> )
22.6	—	—	7.0 ± 0.1	1.60 ± 0.05
36.0	—	—	10.1 ± 0.1	2.4 ± 0.1
50.2	—	—	13.3 ± 0.5	3.8 ± 0.1
52.5	3.3 ± 0.1	0.62 ± 0.02	—	—
52.5	4.3 ± 0.1	0.93 ± 0.02	—	—
55.2	3.8 ± 0.2	0.77 ± 0.03	—	—
62.7	—	—	15.7 ± 0.1	5.5 ± 0.1
64.2	5.3 ± 0.1	1.22 ± 0.05	—	—
68.9	5.7 ± 0.1	1.33 ± 0.03	—	—
69.0	6.0 ± 0.1	1.28 ± 0.03	—	—
74.0	—	1.90 ± 0.02	—	—
78.3	7.0 ± 0.05	2.31 ± 0.01	—	—

TABLE III

ACTIVATION ENERGIES ( $E$ , kcal/mole) AND FREQUENCY FACTORS ( $A$ , sec<sup>-1</sup>) FOR THE DESORPTION OF *n*-BUTANE AND *trans*-2-BUTENE FROM Al<sub>2</sub>O<sub>3</sub>-10% CeCl<sub>3</sub>

Hydrocarbon	Sites I		Sites II	
	$E$	$\log A$	$E$	$\log A$
<i>n</i> -butane	9.0	2.2	11.5	3.3
<i>trans</i> -2-butene*	4.5	0.62	11.0	4.2
<i>trans</i> -2-butene**	4.0	0.82	6.2	1.7

\* Slightly wetted surface.

\*\* More wetted surface.

alumina surface. This is to be expected, as the characteristics of the alumina surface were different in the two cases mentioned above. The value of the specific surface area of the modified alumina used by us (87 m<sup>2</sup>/g) was about half of that (165 m<sup>2</sup>/g) used in the experiments by the flash-desorption technique. However, the main cause of lowering of the kinetic parameters in our experiments is the water content of the surface; this can be concluded from the results shown for *trans*-2-butene in Table III, which also indicate that traces of moisture affect the adsorbability of sites II more than that of sites I. Moreover, it should be noted that the value of  $A$  for sites I was used in calculating the activation energy of sites II by the flash-desorption technique, whereas in our work the value of  $A$  differed greatly for the two sites.

Finally, it is interesting to see whether the argument of the Bessel functions,  $(2k/\dot{V}) [m\beta x(V-ax)]^{0.5}$ , is consistent with the original assumption that this is "small" during the measurements for determining the  $k$  values. To do this, we need the value of  $\beta$ . This can be found approximately from the corrected retention volumes of the stop-peaks. If we consider the measurements taken from 30 to 120 min during the desorption of *n*-butane (Fig. 5) from the sites II, we have to calculate the values of the argument corresponding to these limits of time. Considering that  $x$  is equal to the total length of the column and  $ax = al = V_{0M}^0$ , we found that the argument of the Bessel functions was increasing from 0.41 to 0.81 during the above measurements. A table of hyperbolic Bessel functions<sup>14</sup> shows that, for such small values of the argument  $I_0 \approx 1$  and  $I_1 \approx \text{argument}/2$  as assumed.

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