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Time-resolved determination of surface diffusion coefficients for physically adsorbed or chemisorbed species on heterogeneous surfaces, by inverse gas chromatography

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Abstract

A new simple method is developed for measuring surface diffusion coefficients D_s of gases adsorbed on heterogeneous surfaces, using the reversed-flow version of inverse gas chromatography. The D_s values are found in a time-resolved way, together with the corresponding adsorption energy values, the local adsorbed concentrations, and the local adsorption isotherm values. A relative dynamic adsorption rate constant, an adsorption/desorption rate constant, and a surface reaction rate constant are also found in the same experiment, together with the total diffusion coefficient of the gas in the solid bed. The method has been applied for carbon monoxide, oxygen gas, and carbon dioxide as adsorbates on 75% Pt+25% Rh catalyst supported on SiO_2, at 593.8 K.

Keywords: Inverse gas chromatography; Surface diffusion; Adsorption

1. Introduction

According to the type of surface species, surface diffusion may involve physically adsorbed molecules, chemisorbed species, and self-diffusing atoms, ions, and clusters on the surfaces of their own crystal lattices. All three categories are important to catalysis.

Several techniques have been used to measure surface diffusion, the most common one for physically adsorbed and chemisorbed species being the diffusion cell technique [1]. As stated in a recent review on surface diffusion [2], 'any technique of monitoring local adsorbate concentrations can be used to measure surface diffusion'. However, Smith [3] states that 'Experimental verification of surface diffusion is usually indirect, since concentrations of adsorbed molecules on a surface are difficult to measure. When gas concentrations are obtained, the problem arises of separating the surface and pore volume transport rates'. Radioactive labelled adsorbates, infrared and electron spectroscopies, low energy electron diffraction, field emission microscopy (FEM) and field ion microscopy (FIM) enabled the observation of migration of individual adatoms, but these techniques have been limited to refractory metals, mostly to tungsten surfaces. The FEM, FIM, and many other techniques have been employed to study self-diffusion. They are not

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applicable to studying surface diffusion of physically adsorbed and chemisorbed species.

It was in 1999 [4] that local surface concentrations c_s^* (mol/g), local monolayer capacities c_{max}^* (mol/g) and hence local adsorption isotherms $\theta_t = c_s^*/c_{max}^*$ for ethylene and propene on ZnO, PbO and $CaCO_3$ (marble) were experimentally measured by an inverse gas chromatographic tool, namely, reversed-flow gas chromatography (RF-GC). The term local means with respect to time passing from the moment of injection of the adsorbate onto the solid bed. By looking at Table 1 of the above work [4], one sees the time-resolved values of c_{max}^* and θ_t ranging from 1.18×10^{-6} to 1.22×10^{-2} mol/g, and 0.877–0.001, respectively, for the system C_2H_4/ZnO in the time interval 6–120 min. The respective values of c_s^* can be found from the product $\theta_t c_{max}^*$. Analogous were the results obtained with the other systems, i.e. C_2H_4/PbO, C_3H_6/PbO, and C_3H_6/$CaCO_3$. It is seen from Table 1 of Ref. [4] that, together with c_{max}^* and θ_t, the adsorption energy values ε were measured as time-resolved experimental variables between 6 and 120 min. Since surface diffusion coefficients are generally functions of surface coverage and adsorption energies, it seems a good choice to try an extraction of their value from the same kind of experimental data as those leading to the values of c_{max}^*, θ_t and ε. This is the objective of the present work, for CO, CO_2 and O_2 as adsorbates on a Pt/Rh catalyst, at 593.8 K.

2. Experimental

The materials used have been described in detail in previous publications [5,6]. A short description of them follows.

2.1. Materials

The catalyst used, supplied by Dr. Nieuwenhuys at the Leiden University (The Netherlands), was a platinum–rhodium alloy catalyst containing 75% Pt+25% Rh supported on SiO_2 (3% w/w). The catalyst was reduced at 628 K for 10 h, in flowing hydrogen, at a flow-rate of 1.0 $cm^3\ s^{-1}$, before use.

Carbon monoxide from Linde (99.97% pure), carbon dioxide from Matheson Gas products (99.97% pure) and oxygen from BOC Gases (99.999% pure) were used as adsorbates.

Helium (99.999% pure) from BOC Gases was used as carrier gas, while hydrogen (99.999% pure) for the reduction of the catalysts was obtained from Linde.

The chromatographic material, used for the separation of carbon monoxide and carbon dioxide, was silica gel, 80–100 mesh, from Supelco.

2.2. Apparatus and procedure

The experimental arrangement of RF-GC used here is repeated in Fig. 1. The lengths l' and l of the stainless-steel sampling column were 38 cm×4 mm I.D. each and the length L_1 of the diffusion column, which was connected perpendicularly to the middle of the column $l' + l$, was 117.6 cm×4 mm I.D. All columns (sampling cell) were accommodated inside the oven of a usual gas chromatograph (Pye-Unicam, Series 104) and were empty of any solid material, except for a short length L_2 (~1.0 cm) at the closed end, which contained the catalyst (~0.1 g). The separation column (stainless-steel) was in another oven of a Shimadzu 8A gas chromatograph and its end was connected to a thermal conductivity detector system. This column was filled with 7.6 g silica gel 80–100 mesh. The flow reversals were effected by means of the four-port valve, which connected the ends of the sampling column with the carrier gas inlet and the reference injector.

Before measurements, the whole system was conditioned by heating in situ the catalyst bed at 743 K and the silica gel at 423 K, both for 20 h, under a carrier gas helium flow of 1 $cm^3\ s^{-1}$. At these temperatures, preliminary injections of 1 cm^3 of the absorbates CO, O_2 and CO_2 (at atmospheric pressure) were made, with a gas-tight syringe, in order to establish constant catalytic activity. The working temperature was kept constant in all experiments at 593.8 K while the pressure drop along the whole system was 0.33 atm. After conditioning, 1 cm^3 of CO, O_2 or CO_2 was rapidly introduced through the adsorbate gas injector at L_2. After 5 min, a continuous concentration–time curve, increasing initially and decreasing after a maximum was recorded, due to the adsorbate and the possible products. During this period, flow reversals for 5 s were effected by

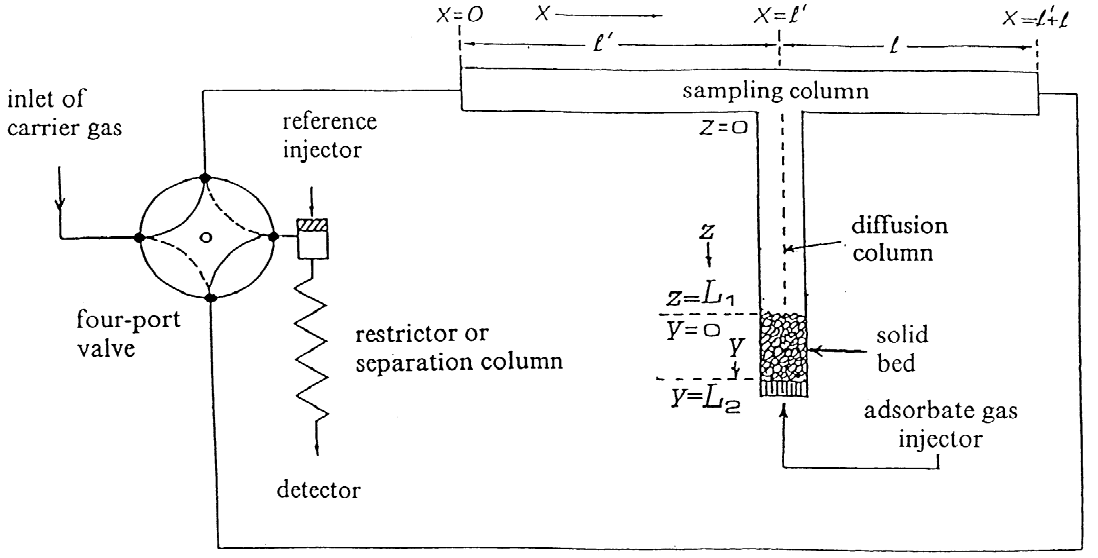

Fig. 1. Outline of the experimental arrangement in the reversed-flow gas chromatography method.

means of the four-port valve. One or two symmetrical 'sample peaks' (in case that the absorbate reacts on the catalytic surface and gives a product) were recorded corresponding to various times from the beginning.

3. Theoretical

3.1. The mathematical model

Since the objective of the present work is to measure a difficult physicochemical quantity very important in catalytic studies, it is rather better to develop the necessary mathematical equations, starting from the very beginning and pointing out where the theoretical analysis is more advanced than the previously published one, used for the measurements of other quantities. One can start from a general GC equation with five terms:

$$\underset{(1)}{\frac{\partial c_g}{\partial t}} = \underset{(2)}{-\upsilon \frac{\partial c_g}{\partial x}} + \underset{(3)}{D_g \frac{\partial^2 c_g}{\partial x^2}} \underset{(4)}{- r \frac{\partial c_s}{\partial t}} + \underset{(5)}{k_R \frac{a_s}{a_y}(c_s - c_s^*)} \quad (1)$$

where c_g is the concentration of the analyte A in the gas (mol/cm^3); c_s is the concentration of A in the adsorbed state (mol/g); c_s^* is the equilibrium adsorbed concentration of A (mol/g); t is the time (s); x is the length coordinate along the column (cm); υ is the linear velocity of carrier gas (cm/s); D_g is the diffusion coefficient of A in the carrier gas (cm^2/s); r is the volume ratio of stationary and mobile phase; k_R is the rate constant for adsorption/desorption on the bulk solid (s^{-1}); a_s is the amount of solid adsorbent (g/cm); a_y is the cross sectional area in the solid bed (cm^2).

Then, one can conclude from the experimental arrangement of Fig. 1 that three kinds of chromatography are conducted, namely: one usual separation chromatography in the separation column, described by the three terms (1), (2), (4), of Eq. (1); a second kind of movement described by the terms (1) and (3) of Eq. (1) in the diffusion column z, empty of solid material; and an inverse chromatographic phenomenon in the solid bed y, described by the terms (1), (3) and (5) of Eq. (1). Needless to say that the characteristic chromatographic term $-\upsilon\ (\partial c_g/\partial x)$ disappears in the columns z and y, since the latter are placed perpendicularly to the direction of the carrier gas, flowing only through the sampling column and

the separation column. This was done on purpose, so that v does not interfere with the rate phenomena in column sections z and y.

What experimental quantity does one measure by injecting a small volume (0.5–1 cm^3 at atmospheric pressure) of the adsorbate gas A through the gas injector at $y = L_2$? The gaseous concentration entering the sampling column at $z = 0$, being transferred by the carrier gas to the detector, either via the separation column or directly, gives a long asymmetrical chromatographic band, as if an unsharp extended input distribution of a vapor were introduced into the sampling column at $x = l'$. If, however, the four-port valve is turned to the other position for 5–60 s, and then returned to its original position, one or more sharp symmetrical and narrow peaks are recorded (cf. Fig. 2 of Ref. [5]). Repetition of the flow reversal may give a long series of such narrow *sample peaks*, their height H from the continuous background line being a function of the time, when the reversal was made:

$$H^{1/M} = \sum_i A_i \exp(B_i t) \tag{2}$$

where M is the response factor of the detector and A_i, B_i are functions of physicochemical quantities pertaining to the various phenomena taking place in columns y and z. The summation index i ranges from 1 to 2, 3 or 4 depending on the mathematical model employed for the description of the various physicochemical processes, and the approximations used to solve the relevant system of partial differential equations. In some cases that have been studied [5,6] two exponential terms in Eq. (2), i.e. $i = 1$, 2, were enough. In other cases [4,7–14] the solution of the system was obtained for $i = 1$–3 and $i = 1$–4. In all cases, A_i and B_i were calculated by PC programs in GW-BASIC, written for non-linear least-squares regression analysis [4,7–11,15] and based on the experimental pair values H, t in cm and s, respectively.

The form of Eq. (2) is not an assumption made a priori, but the result of solution of a system of partial differential equations and a local isotherm, with certain initial and boundary conditions. For the present objective, namely, the experimental determination of surface diffusion coefficients of the adsorbate on a heterogeneous solid surface, at various times, the starting model chosen was that of Ref. [8]. It consists first of the terms (1) and (3) of Eq. (1) written for the column z of Fig. 1 (cf. Eq. (127) of Ref. [8]), where c_g is the gaseous concentration (mol/cm^3) of the adsorbate in column z, and D_g its diffusion coefficient in the carrier gas, not running but filling section z as a stagnant gaseous column.

Secondly, one writes an equation comprising terms (1), (3) and (5) of Eq. (1) valid in column y, i.e. in the solid bed (cf. Eq. (124) of Ref. [8]), where c_g is now the gaseous concentration of the adsorbate A in region y (mol/cm^3), D_g the effective diffusion coefficient of A in the solid bed, and the meaning of the other symbols having been explained after Eq. (1).

A third equation describes the rate of change of the adsorbed concentration of A (cf. Eq. (125) of Ref. [8]), where $k_{-1} = k_R$, and k_2 (s^{-1}) is the rate constant of a possible first-order or pseudo-first-order surface reaction of the adsorbed A.

The fourth equation of the system is a non-linear local adsorption isotherm defined by Eq. (123) of Ref. [8].

The solution of the above system of equations is given analytically in Ref. [7], under the initial conditions of Eq. (126) of Ref. [8], and boundary conditions of Eqs. (16), (18) and (19) of Ref. [7].

If $c(l', t)$ is the gaseous concentration of the adsorbate in the sampling column at the point $x = l'$ and time t, the diffusion column and the sampling column having the same cross sectional area a_z, the solution of the above system is based on double Laplace transformations with respect to t, and with respect to z or y. The result, before the final inverse Laplace transformation with respect to p, was [7]

$$C(l', p) = \frac{A}{\dot{V}} \cdot \frac{n_A - n_s q_3}{A \cdot \cosh q_1 L_1 \cdot \cosh q_2 L_2 + J \cdot \sinh q_1 L_1 \cdot \sinh q_2 L_2} \tag{3}$$

where $C(l', p)$ is the Laplace transform of $c(l', t)$ with respect to t; A is the ratio of cross sectional areas a_z, a_y; $\dot{V} = v\, a_z$ is the volumetric flow-rate of the carrier gas ($cm^3\ s^{-1}$); n_A is the amount (mol) of A introduced as a pulse at $y = L_2$; n_s is the initially adsorbed concentration of A (if any); q_1, q_2, q_3 are given by the relations:

$$q_1^2 = p/D_z \tag{4}$$

$$q_2^2 = \frac{1}{D_y}\left[p + \frac{k_1 k_R (p + k_2)}{p(p + k_R + k_2)} \right] \tag{5}$$

$$q_3 = \frac{k_R (p + k_2)}{p(p + k_R + k_2)} \tag{6}$$

$$J = \frac{D_y q_2}{D_z q_1} \tag{7}$$

where p is the parameter of Laplace transformation with respect to t, and D_z, D_y the diffusion coefficients in section z and y, respectively.

Expanding both $\cosh qL$ and $\sinh qL$ in the denominator of Eq. (3) in McLaurin series in qL, and retaining only the first two terms, namely, $\cosh qL \approx 1 + q^2 L^2/2$ and $\sinh qL \approx 0 + qL \simeq qL$, one obtains Eq. (23) of Ref. [7]:

$$C(l', p) = \frac{n_A a_1 a_2}{\dot{V}} \cdot \frac{p^2 + [k_R(1 - n_s/n_A) + k_2]p - n_s k_R k_2 / n_A}{(p - B_1)(p - B_2)(p - B_3)(p - B_4)} \tag{8}$$

where

$$a_1 = \frac{2D_z}{L_1^2}; \qquad a_2 = \frac{2D_y}{L_2^2} \tag{9}$$

and B_1, B_2, B_3 and B_4 are the roots of the fourth degree polynomial in the denominator $p^4 + Xp^3 + Yp^2 + Zp + W$, with the following physical meaning of X, Y, Z and W:

$$X = a_1 + a_2 + a_2 Q_2 + k_R + k_2 = -(B_1 + B_2 + B_3 + B_4) \tag{10}$$

$$Y = a_1 a_2 + (a_1 + a_2 + a_2 Q_2)(k_R + k_2) + k_1 k_R = B_1 B_2 + B_1 B_3 + B_1 B_4 + B_2 B_3 + B_2 B_4 + B_3 B_4 \tag{11}$$

$$Z = a_1 a_2 (k_R + k_2) + a_1 k_1 k_R + a_2 Q_2 k_1 k_R + k_1 k_R k_2 = -(B_1 B_2 B_3 + B_1 B_2 B_4 + B_1 B_3 B_4 + B_2 B_3 B_4) \tag{12}$$

$$W = (a_1 + a_2 Q_2)\, k_1 k_R k_2 = B_1 B_2 B_3 B_4 \tag{13}$$

The a_1 and a_2 are given by Eq. (9) above, and

$$Q_2 = 2a_y L_2 / a_z L_1 \tag{14}$$

Eqs. (8)–(13) are the same as Eqs. (128)–(132) of Ref. [8] written in a slightly different way. Since H is the height of the extra chromatographic peaks, obtained by the repeated flow reversals of the carrier gas, and this is proportional to the concentration $c(l', t)$ at the junction of the sampling column and the diffusion column, $H^{1/M} = gc(l', t)$, M being the response factor mentioned with Eq. (2), and g a calibration factor of the detector determined as described elsewhere [16]. Thus, the result of the inverse Laplace transformation with respect to p of Eq. (8) is Eq. (2) with $i = 1$–4:

$$H^{1/M} = gc(l', t) = \sum_{i=1}^{4} A_i \exp(B_i t) \tag{15}$$

where the exponential coefficients of time B_1, B_2, B_3 and B_4 satisfy Eqs. (10)–(13), while the pre-exponential factors A_1, A_2, A_3 and A_4 are explicit functions of $gn_A a_1 a_2/\dot{V}$, of B_1, B_2, B_3, B_4, k_R, k_2, n_A and n_s, the analytical form of which is not needed.

Although Eqs. (10)–(13) constitute a system of four algebraic equations, with the values of X, Y, Z, W calculated from the experimentally found values of B_1, B_2, B_3, B_4 as shown, it is difficult, if not impossible to find from that the four out of the five unknowns a_1, a_2, k_1, k_R, k_2, even if $a_1 = 2D_z/L_1^2$ (cf. Eq. (9)) is obtained from the literature or from otherwise calculated values of D_z [17]. The roots of the above system come out as complex numbers. In order to overcome this difficulty, a steady-state in Eq. (125) of Ref. [8], i.e. $\partial c_s/\partial t = 0$, was assumed, and, following exactly the same route as before, one reaches the same form of Eq. (15) but with $i = 1$, 2, 3. This leads to another system of three algebraic equations, which are combined with the four Eqs. (10)–(13) and the calculation of all unknowns becomes possible [7,8]. This route, however, is not permissible here, since the surface diffusion coefficients are known to be strongly dependent on the surface concentration c_s of the adsorbates [2]. How then can one assume a constant c_s by the steady-state assumption $\partial c_s/\partial t = 0$? Another route was sought and this was found by using a different expansion of $\cosh qL$ and $\sinh qL$ in the denominator of Eq. (3),

as follows. The two terms were first written, without any approximation, as

$$A\cosh q_1L_1\cdot\cosh q_2L_2=\frac{A}{2}[\cosh(q_1L_1+q_2L_2)+\cosh(q_1L_1-q_2L_2)] \quad (16)$$

$$J\sinh q_1L_1\cdot\sinh q_2L_2=\frac{J}{2}[\cosh(q_1L_1+q_2L_2)-\cosh(q_1L_1-q_2L_2)] \quad (17)$$

If the expansion in McLaurin series used before for the left-hand sides of the above functions giving Eq. (8), is now performed on the right-hand sides of Eqs. (16) and (17), it gives a different result, namely

$$C(l',p)=\frac{n_Aa_1a_2}{\dot{V}(a_1+a_2+a_2Q_2)}\cdot\frac{p^2+[k_R(1-n_s/n_A)+k_2]p-n_sk_Rk_2/n_A}{(p-B_5)(p-B_6)(p-B_7)} \quad (18)$$

where a_1, a_2 and Q_2 have the same meaning as before (cf. Eqs. (9) and (14)), the numerator is exactly the same as that of Eq. (8), but the denominator is different, since B_5, B_6 and B_7 are now the roots of the third degree polynomial $p^3+X_1p^2+Y_1p+Z_1$, with the following physical meaning of X_1, Y_1 and Z_1:

$$X_1=\frac{a_1a_2}{a_1+a_2+a_2Q_2}+k_R+k_2=-(B_5+B_6+B_7) \quad (19)$$

$$Y_1=\frac{a_1a_2(k_R+k_2)+(a_1+a_2Q_2)k_1k_R}{a_1+a_2+a_2Q_2}=(B_5B_6+B_5B_7+B_6B_7) \quad (20)$$

$$Z_1=\frac{a_1+a_2Q_2}{a_1+a_2+a_2Q_2}k_1k_Rk_2=-(B_5B_6B_7) \quad (21)$$

As before [7], we are left with the values of B_1, B_2, B_3, B_4, B_5, B_6 and B_7, using slightly different approximations not involving a steady-state of the adsorbed concentration, on which the surface diffusion coefficient exhibits a strong dependence [2].

3.2. Calculation of the rate constants

The rate constants k_R, k_2, k_1, and the diffusion coefficient D_y, as defined in the foregoing text can be calculated in various ways from the values of X, Y, Z, W, and X_1, Y_1, Z_1, found from B_1, B_2, B_3, B_4, and B_5, B_6, B_7 according to Eqs. (10)–(13), and (19)–(21), respectively. The values of B's are derived from the experimental pairs H, t (H is the height of sample peaks in cm; t is the time of reversal) by non-linear least-squares regression analysis based on Eq. (2), with $i=1$–4 and $i=1$–3, independently.

It was found that the best way for calculating k_R, k_2, k_1 and D_y is that which gives the minimum value of % difference between the experimental values of X, Y, Z, W, X_1, Y_1, Z_1 found from B's, and those found by using the calculated k_R, k_2, k_1 and D_y values using the diffusion coefficient in the gas phase D_z as calculated by the traditional method [17]. The calculation is as follows. Firstly, the $A=a_z/a_y$ is found, taking into account the external porosity of the solid bed. Then, the $a_1=2D_z/L_1^2$ is found. The calculation from Eq. (14) of $Q_2=2a_yL_2/a_zL_1$ follows, and then from the ratio $W/Z_1=a_1+a_2+a_2Q_2$, $a_2=2D_y/L_2^2=(W/Z_1-a_1)/(1+Q_2)$ is found, and from this the value of D_y.

The following relations are easily derived from Eqs. (19)–(21) and (13):

$$k_R+k_2=X_1-a_1a_2Z_1/W \quad (22)$$

the product

$$k_1k_R=\frac{Y_1W/Z_1-a_1a_2(k_R+k_2)}{a_1+a_2Q_2} \quad (23)$$

and

$$k_1k_Rk_2=\frac{W}{a_1+a_2Q_2} \quad (24)$$

From the above, it easily follows that the value of k_2 is equal to the ratio of Eq. (24)/Eq. (23), the k_R is found from the difference Eq. (22) $-k_2$, and finally k_1 from the ratio Eq. (23)/k_R.

3.3. Calculation of time-resolved adsorption energies, local adsorption concentrations and local isotherms

This is achieved as recently published [4] for

heterogeneous surfaces, the term 'local' meaning with respect to time t, i.e. involving not all adsorption sites, but only those active at time t. For convenience, the necessary equations for the above calculations are repeated below without derivation.

The adsorption energy ε is calculated from Eq. (8) of Ref. [4]:

$$K = K^0 \exp(\varepsilon/RT) \tag{25}$$

where K is calculated experimentally from Eq. (5) of Ref. [10]:

$$KRT = \frac{gD_z}{\upsilon L_1}\left\{ \frac{\sum_{i=1}^{4} A_i B_i^2 \exp(B_i t)}{\left[\sum_{i=1}^{4} A_i B_i \exp(B_i t)\right]^2} - \frac{1}{\sum_{i=1}^{4} A_i \exp(B_i t)} \right\} \tag{26}$$

dividing by RT and correcting by multiplying with the gaseous standard state of 101,325 Pa. The K^0 is found from the formula (9) of Ref. [4], and the local adsorption equilibrium concentration c_s^* is found from Eq. (4) of Ref. [12].

The local isotherm θ_t, and the local monolayer capacity c^*_{max} are found by Eqs. (10) and (16), respectively, of Ref. [4]. The $\partial c_s^*/\partial c_y$ value needed in the latter calculation is given by Eq. (6) of Ref. [12].

3.4. Calculation of surface diffusion coefficients

According to Jaroniec and Madey [18], in the majority of papers concerning adsorption kinetics on solids, the models of mass-transfer kinetics (involving external, internal, and surface diffusion of adsorbate molecules) were studied. According to Eq. (5.3) of Ref. [18]:

$$D_i = D_o + D_s\, \partial\theta/\partial p \tag{27}$$

i.e. the diffusion coefficient is divided into two parts: the term D_o describing diffusion in the bulk phase, and the second term referring to the diffusion in the surface phase. The pressure p reflects the concentration of the adsorbate in the bulk phase, and the adsorption isotherm θ reflects the concentration of the adsorbate in the surface phase. The surface diffusion coefficient D_s in Eq. (27) is the physicochemical quantity sought in the present work, and this can be easily calculated, since all other quantities in this equation are either known physical quantities, or can be obtained quite easily from the pairs H, t of the RF-GC experiments, as follows. The total diffusion coefficient D_i should be equal to $D_z\varepsilon_M^2$, i.e. to that of the adsorbate in the carrier gas in the absence of solid D_z, multiplied by the square of the macro void fraction in the bed ε_M, according to the random-pore model (Ref. [3], p. 467). This is required for boundary condition reasons at $z = L_1$, $y = 0$. The D_o term of Eq. (27) is equal to the experimental D_y, calculated from the H, t pairs as described in Section 3.2, together with the rate constants.

There remains the partial derivative $\partial\theta/\partial p$ of Eq. (27) to be found. This is most easily done from Eq. (7) of Ref. [4]:

$$\theta = 1 - \exp(-Kp) \tag{28}$$

where K is Langmuir's constant given by Eq. (25) and K^0 being given by Eq. (9) of Ref. [4]. Taking the partial derivative of θ with respect to p in Eq. (28) above, one simply finds

$$\partial\theta/\partial p = K \exp(-Kp) = K(1-\theta) \tag{29}$$

and, substituting in it Eq. (25) for K, there results

$$\partial\theta/\partial p = K^0(1-\theta)\exp(\varepsilon/RT) \tag{30}$$

All three factors on the right-hand sides of Eqs. (29) and (30) above are easily calculated, namely, K by Eq. (26), K^0 by Eq. (9) of Ref. [4], θ by Eq. (10) of Ref. [4], and ε or ε/RT by Eq. (25). Except for K^0, all other quantities are found from the values of A_1, A_2, A_3, A_4, B_1, B_2, B_3 and B_4 of Eq. (15), and the time parameter t. Thus, $\partial\theta/\partial p$ is found with a time-resolved procedure from the experimental chromatographic data H, t of the RF-GC method. Finally, the relation giving D_s is easily obtained from Eq. (27):

$$D_s = \frac{D_z\varepsilon_M^2 - D_y}{\partial\theta/\partial p} = \frac{D_z\varepsilon_M^2 - D_y}{K^0(1-\theta)}\exp(-\varepsilon/RT) \tag{31}$$

It is worth noticing that this equation coincides in form with the equation of Higashi et al. [19]:

$$D_s = \frac{D_{so}}{1-\theta}\exp(-E/RT) \quad (32)$$

if $D_{so} = (D_z\varepsilon_M^2 - D_y)/K^0$ and our adsorption energy ε behaves like the activation energy E of the surface diffusion process.

All calculations described in Sections 3.2, 3.3 and 3.4 can be carried out simultaneously by the GW-BASIC PC program listed in Appendix A, by entering the H, t pairs in the DATA lines 3000–3040, together with some auxiliary physical quantities, like T, L_1, L_2, ε_M, a_z, a_y, a_s, $\dot{V}$, υ, n_A, D_z, in the INPUT lines 170–335.

Needless to say that the application of the rule of error propagation in a long sequence of steps does not give reliable final errors, as already pointed out in the past [7].

4. Representative results and discussion

The methodology and calculations described in the preceding sections are demonstrated by their application to the adsorption of carbon monoxide, oxygen gas and carbon dioxide on a platinum–rhodium alloy catalyst containing 75% Pt+25% Rh supported on SiO_2 (3% w/w), at a temperature of 593.8 K. The values of the pairs H, t (in number, 35 for CO, 35 for O_2, and 31 for CO_2) obtained experimentally, have been introduced into the lines 3000–3040 of the PC program listed in Appendix A, together with the other experimentally determined quantities in the INPUT lines 170–335. The diffusion coefficients D_z in the carrier gas helium, required in line 310, were calculated by the well-known equations of Ref. [17], and found to be 1.73, 1.82 and 1.81 $cm^2\ s^{-1}$ for CO, O_2 and CO_2, respectively, at 593.8 K.

Firstly, the rate constants k_1, k_R, k_2 and the total diffusion coefficient D_y in the solid bed were computed by the program, as described in Section 3.2. Then, it follows the calculation of time-resolved adsorption energies ε, local adsorption concentrations c_s^*, local isotherm values θ_t, and surface diffusion coefficients D_s, based on the descriptions given in Sections 3.3 and 3.4. The time period arbitrarily chosen was from 8 to 106 or 130 min, with 2 or more minutes apart from each other. The results are listed in Tables 1–3 for CO, O_2 and CO_2, respectively, although one could plot them by using the PC program MATHEMATICA 3 between the two chosen time limits, with a number of plot points say 1000. The same equations of Sections 3.3 and 3.4 are required for those plots.

Table 1
Time distribution of adsorption energy (ε), equilibrium adsorbed concentration (c_s^*), local adsorption isotherm (θ_t), and surface diffusion coefficient (D_s) for carbon monoxide adsorbed on 75% Pt+25% Rh catalyst, at 593.8 K. $k_1 = 4.72\times10^{-3}\ s^{-1}$, $k_R = 7.53\times10^{-3}\ s^{-1}$, $k_2 = 2.49\times10^{-4}\ s^{-1}$, $D_y = 2.02\times10^{-4}\ cm^2/s$

Time (min)	ε (kJ/mol)	c_s^* (μmol/g)	θ_t	D_s (cm^2/s)
8	157.9	2.90	0.801	0.104
10	158.6	3.30	0.765	7.69×10^{-2}
12	159.2	3.90	0.729	5.87×10^{-2}
14	160.4	4.66	0.721	4.45×10^{-2}
16	162.2	5.55	0.736	3.26×10^{-2}
18	164.7	6.53	0.770	2.24×10^{-2}
20	168.3	7.57	0.820	1.38×10^{-2}
22	174.2	8.64	0.887	6.72×10^{-3}
24	190.7	9.73	0.976	1.10×10^{-3}
26	178.9	10.8	0.920	3.69×10^{-3}
28	170.6	11.9	0.826	9.04×10^{-3}
30	166.1	13.0	0.741	1.51×10^{-2}
32	163.0	14.0	0.662	2.19×10^{-2}
34	160.5	15.1	0.589	2.98×10^{-2}
36	158.4	16.1	0.520	3.90×10^{-2}
38	156.5	17.0	0.453	5.02×10^{-2}
42	153.0	18.9	0.324	8.32×10^{-2}
46	149.2	20.7	0.202	0.151
50	143.9	22.3	0.086	0.387
56	141.5	24.6	0.061	0.605
60	144.9	26.0	0.119	0.324
64	146.3	27.3	0.157	0.256
72	147.4	29.6	0.198	0.217
80	147.6	31.7	0.214	0.211
88	147.5	33.6	0.218	0.216
96	147.3	35.2	0.214	0.227
104	146.9	36.6	0.206	0.243
112	146.4	37.9	0.196	0.262
120	145.9	39.0	0.184	0.285

From the results listed in Tables 1–3, it is clear that the new method of determining surface diffusion coefficients D_s presented here is a time-resolved procedure, showing clearly the dependence of D_s on the adsorption energy ε, the fraction of active surface covered θ_t, and the surface concentration c_s^* of the adsorbate, all in the very same experiment.

The form of the above dependences does not coincide, however, exactly with that usually de-

Table 2
Time distribution of adsorption energy (ε), equilibrium adsorbed concentration (c_s^*), local adsorption isotherm (θ_t), and surface diffusion coefficient (D_s) for oxygen gas adsorbed on 75% Pt+25% Rh catalyst, at 593.8 K. $k_1 = 7.05\times10^{-3}$ s^{-1}, $k_R = 7.29\times10^{-3}$ s^{-1}, $k_2 = 2.74\times10^{-4}$ s^{-1}, $D_y = 4.19\times10^{-4}$ cm^2/s

Time (min)	ε (kJ/mol)	c_s^* (μmol/g)	θ_t	D_s (cm^2/s)
8	164.0	14.2	0.990	0.758
10	161.2	14.6	0.954	0.294
12	161.3	15.3	0.917	0.162
14	162.4	16.2	0.893	0.94×10^{-2}
16	164.3	17.4	0.885	6.28×10^{-2}
18	167.0	18.6	0.891	3.86×10^{-2}
20	171.0	20.0	0.913	2.14×10^{-2}
22	178.0	21.4	0.949	8.89×10^{-3}
24	212.5	22.8	0.998	2.29×10^{-4}
26	177.4	24.2	0.934	7.72×10^{-3}
28	170.7	25.5	0.867	1.50×10^{-2}
30	166.6	26.9	0.798	2.23×10^{-2}
32	163.7	28.3	0.728	3.00×10^{-2}
34	161.4	29.6	0.659	3.85×10^{-2}
36	159.3	30.8	0.590	4.81×10^{-2}
38	157.6	32.1	0.522	5.99×10^{-2}
40	155.9	33.3	0.456	7.31×10^{-2}
42	154.3	34.4	0.392	9.02×10^{-2}
46	151.2	36.7	0.275	0.141
50	147.9	38.7	0.173	0.241
54	144.0	40.7	0.090	0.490
58	137.1	42.5	0.025	1.85
62	139.1	44.2	0.023	1.23
66	141.5	45.7	0.053	0.789
72	142.8	47.9	0.080	0.616
80	143.3	50.5	0.097	0.563
88	143.5	52.7	0.104	0.544
106	143.4	56.8	0.108	0.561
114	143.2	58.3	0.107	0.578
122	143.1	59.6	0.105	0.597

Table 3
Time distribution of adsorption energy (ε), equilibrium adsorbed concentration (c_s^*), local adsorption isotherm (θ_t), and surface diffusion coefficient (D_s) for carbon dioxide adsorbed on 75% Pt+25% Rh catalyst, at 593.8 K. $k_1 = 1.14\times10^{-2}$ s^{-1}, $k_R = 8.12\times10^{-3}$ s^{-1}, $k_2 = 2.42\times10^{-4}$ s^{-1}, $D_y = 1.02\times10^{-3}$ cm^2/s

Time (min)	ε (kJ/mol)	c_s^* (μmol/g)	θ_t	D_s (cm^2/s)
8	165.8	4.36	0.922	0.110
10	163.7	4.82	0.812	7.03×10^{-2}
12	163.1	5.68	0.726	5.42×10^{-2}
14	163.4	6.90	0.685	4.41×10^{-2}
16	164.3	8.44	0.677	3.57×10^{-2}
18	165.7	10.2	0.690	2.81×10^{-2}
20	167.6	12.2	0.718	2.12×10^{-2}
22	170.0	14.3	0.758	1.51×10^{-2}
24	173.3	16.4	0.809	9.76×10^{-3}
26	178.4	18.7	0.873	5.23×10^{-3}
28	189.5	20.9	0.953	1.51×10^{-3}
30	188.8	23.2	0.948	1.58×10^{-3}
32	178.2	25.5	0.858	4.93×10^{-3}
34	173.2	27.7	0.779	8.72×10^{-3}
36	169.8	29.9	0.708	1.30×10^{-2}
38	167.3	32.1	0.644	1.77×10^{-2}
40	165.3	34.3	0.586	2.31×10^{-2}
42	163.5	36.4	0.533	2.90×10^{-2}
44	162.0	38.4	0.485	3.57×10^{-2}
46	160.7	40.4	0.440	4.33×10^{-2}
48	159.4	42.4	0.399	5.18×10^{-2}
50	158.3	44.3	0.361	6.14×10^{-2}
54	156.2	48.0	0.294	8.50×10^{-2}
58	154.3	51.5	0.237	0.116
62	152.5	54.8	0.189	0.158
66	150.7	57.9	0.149	0.213
70	149.0	60.9	0.117	0.289
76	146.6	65.0	0.079	0.456
82	144.2	68.8	0.053	0.724
86	142.6	72.3	0.035	0.987

scribed in the past literature, although the orders of magnitude found are acceptable. For example, Sladek et al. [20] state that for chemisorption systems, the magnitudes of reported D_s values range from 10^{-5} to 10^{-13} cm^2/s, usually considered below those characteristic of physical adsorption systems, which are typically 10^{-2} to 10^{-5} cm^2/s. Our results presented in Tables 1–3 range from 10^{-1} to 10^{-4} cm^2/s at a relatively high temperature (ca. 600 K), except for the long time values being an order of magnitude higher. But the values of the adsorption energy found (in kJ/mol) fall in the range 142–191 for CO, 137–213 for O_2, and 143–190 for CO_2. These values are similar for the three adsorbates, but not the same, particularly their maxima. They indicate rather chemisorption processes, unless they are taken as activation energies for migration of the adsorbed species by means of hopping movements on the surface. It is generally assumed that the hopping mechanism is an activated process [2]. In support of this, Eq. (31) by means of which D_s was calculated here, is an Arrhenius type relation, coinciding exactly with that of Higashi (cf. Eq. (32)). Of course the latter was criticised because it fails when $\theta = 1$, and a correction factor f was added in the denominator of Eq. (32), becoming $1 - f\theta$ [2]. It seems that such a correction factor is not necessary in our Eq. (31), since in all calculations of D_s from

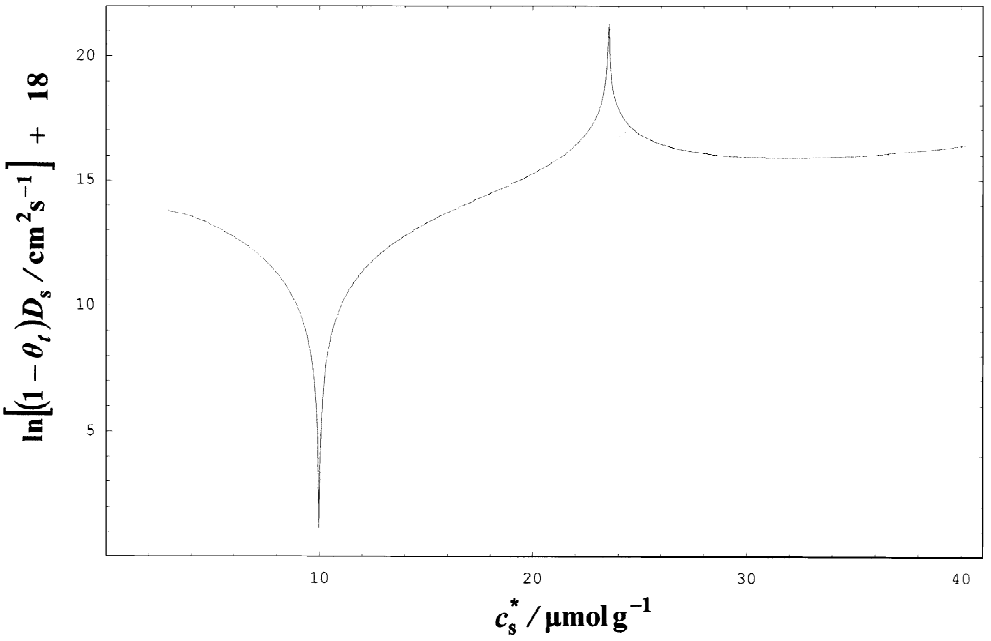

Fig. 2. Dependence of surface diffusion coefficient of carbon monoxide on its equilibrium surface concentration on 75% Pt+25% Rh catalyst, at 593.8 K.

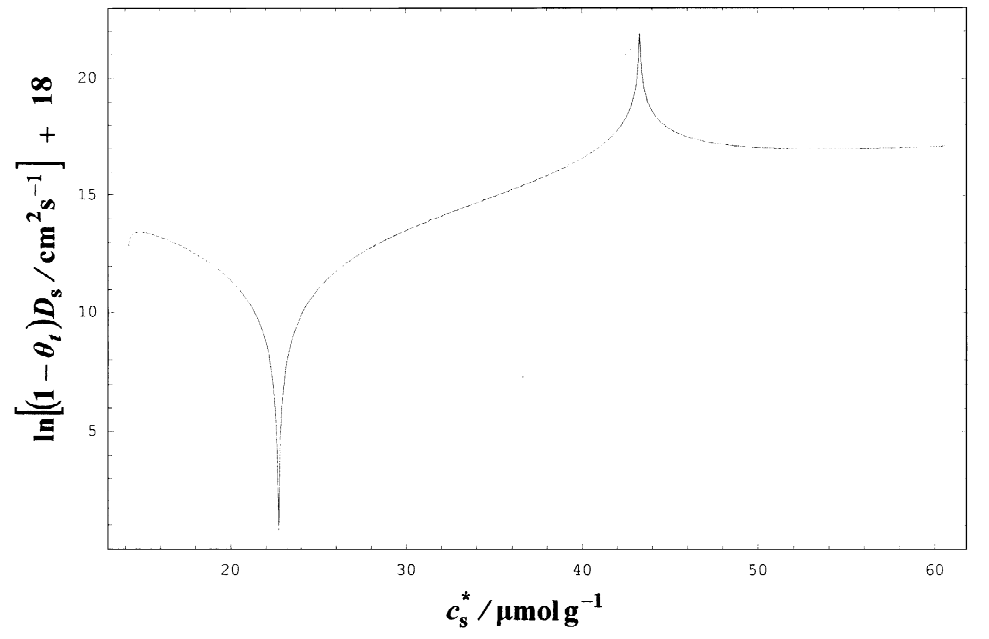

Fig. 3. Dependence of surface diffusion coefficient of oxygen on its equilibrium surface concentration on 75% Pt+25% Rh catalyst, at 593.8 K.

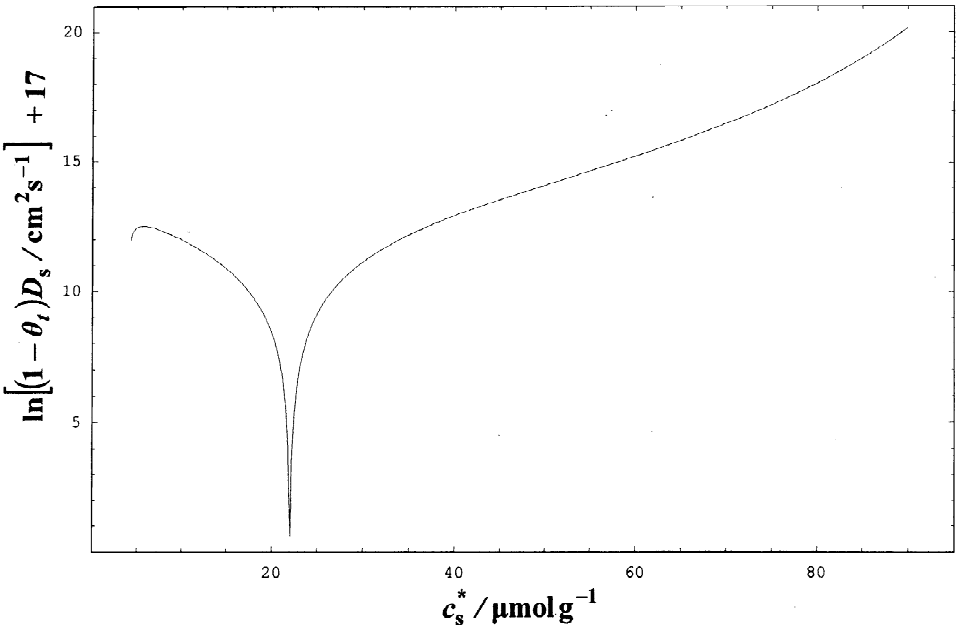

Fig. 4. Dependence of surface diffusion coefficient of carbon dioxide on its equilibrium surface concentration on 75% Pt + 25% Rh catalyst, at 593.8 K.

experimental data θ_t never reached a value bigger than 0.999.

Coming back now to the form of the dependence of D_s on ε and θ_t, one finds from Eq. (31) that a plot of ln $[D_s(1-\theta_t)]$ against ε should be linear with slope $-1/RT$. It is not necessary, however, to test this fact, since D_s has been calculated by means of that relation. In contrast to the above, the dependence of $\log_{10} D_s$ on q/mRT, where q is the heat of adsorption and $m = 1$, 2 or 3 for various classes of solids [2,20] has been found to be linear, all substances examined falling on the same straight line, with considerable spreading out of that line. In other words, the parameter q/mRT resolves the data into three sets differing in m. The effect of θ on the dependence of D_s on $1/T$ [20] is very complicated.

The continuous increase of c_s^* with time is probably due to multilayer adsorption. The dependence of D_s on c_s^* is shown in Figs. 2–4 for CO, O_2 and CO_2, respectively. These figures show the same minima and maxima with those appearing if ε, in a diminishing scale, were plotted against c_s^*. Thus, one may conclude that it is the energy variation with c_s^* that indirectly causes the variation of D_s with c_s^*.

5. Conclusion

With a very simple modification of a commercial gas chromatograph, one can measure in a single experiment the surface diffusion coefficient in a time-resolved way, combined with a simultaneous measurement of the adsorption energy, the local adsorbed concentration, and the local adsorption isotherm, for gaseous adsorbates on heterogeneous solid surfaces.

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Appendix A

```
10 REM Calculation of Rate constants, Diffusion coefficient in the
13 REM solid bed, Adsorption quantities, and Surface diffusion coefficient
16 REM with the experimental setup of Adv. Chromatogr. 40(2000)234
20 REM Non-Linear Regression Analysis of Functions:
30 REM H^(1/M)=A1*EXP(B1*T)+S*A2*EXP(B2*T)+P*A3*EXP(B3*T)+X*A4*EXP(B4*T)
40 REM H^(1/M)=A5*EXP(B5*T)+S*A6*EXP(B6*T)+P*A7*EXP(B7)
50 REM N2     = Minimum number of points of first exponential function
60 REM MAX    = Square of maximum correlation coefficient
70 REM OPT    = Final optional choice of variables when OPT=1
80 REM J      = Number of points of first exponential function
90 REM G      = Number of points of second exponential function
100 REM F     = Number of points of third exponential function
110 REM K,L   = First and last point of linear regression in subroutine
120 REM SA,SB = Standard errors of A and B in each linear regression
130 REM Y(I)  = Ordinate for each linear regression in the subroutine
140 REM U(I)= Variable remaining by  removal of the previous one, two or

            three exponential functions
150 REM D(I)= Function for calculating the squared correlation coefficient
160 CLEAR ,,10000
170 INPUT "Total number of pairs H,T=";N
180 DIM H(N),T(N),Y(N),U(N),D(N)
190 INPUT "Response Factor=";M
200 INPUT "Factor to divide H(I)=";H1
210 INPUT "Temperature in K=";T0
220 INPUT "Lenth L1(cm) of Section z=";L1
230 INPUT "Length L2(cm) of Section y=";L2
240 INPUT "Macro Void Fraction in the Solid Bed eM=";E
250 INPUT "Cross Sectional Area Az(cm^2) of Empty Section L1 =";AZ
260 INPUT "Cross Sectional Area Ay(cm^2) of Filled Section L2=";AY
270 INPUT "Amount of Adsorbent per Unit Length of Bed AS(g/cm)=";AS
280 INPUT "Linear Flow-velocity of the Carrier Gas v(cm/s)=";LV
290 INPUT "Molar Mass MB(kg/mol) of the Analyte B=";MB
300 INPUT "Volumetric Flow-rate of Carrier Gas V'(cm^3/min)=";V0
310 INPUT "Molecular Diffusion Coefficient in the Gas Dz(cm^2/s)=";D1
320 INPUT "Amount of Reactant injected nA(mol)=";NA
330 INPUT "Initial Time for the Calculations t1(min)=";T1
335 INPUT "Final Time for the Calculations t2(min)=";T2
340   FOR I=1 TO N
350    READ H(I),T(I)
360    H(I)=H(I)/H1
370   NEXT I
380 N2=INT(N/7+.5)
390 MAX=0:OPT=0
400 REM Calculation of A1 and B1 with H,T pairs ranging from N2 to N-2*N2-3
410 FOR J=N2 TO N-2*N2-3
420    K=N-J+1
430    L=N
440    FOR I=K TO L
450       Y(I)=(1/M)*LOG(H(I))
460    NEXT I
470    GOSUB 4000       :REM Subroutine for linear regression analysis
480    A1=EXP(A)
490    B1=B
500    SA1=SA
510    SB1=SB
520    IF OPT=1 THEN  560
530 REM Calculation of A2 and B2 with H,T pairs ranging from N2 to N-J-N2-3

       with both prefixes -1 or +1
540    FOR S=-1 TO +1 STEP 2
550       FOR G=N2 TO N-J-N2-3
560          K=N-J-G+1
570           L=N-J
580          FOR I=K TO L
590             U(I)=S*H(I)^(1/M)-S*A1*EXP(B1*T(I))
```

```
600             Y(I)=LOG(ABS(U(I)))
610          NEXT I
620          GOSUB 4000 :REM Subroutine for linear regression analysis
630          A2=EXP(A)
640          B2=B
650          SA2=SA
660          SB2=SB
670          IF OPT=1 THEN 710
680 REM Calculation of A3 and B3 with H,T pairs ranging from N2 to N-J-G-3

       with both prefixes -1 or +1
690          FOR P=-1 TO +1 STEP 2
700            FOR F=N2 TO N-J-G-3
710               K=N-J-G-F+1
720                L=N-J-G
730               FOR I=K TO L
740                  U(I)=P*(H(I)^(1/M)-A1*EXP(B1*T(I))-S*A2*EXP(B2*T(I))
750                  Y(I)=LOG(ABS(U(I)))
760               NEXT I
770           GOSUB 4000:REM Subroutine for linear regression analysis
780               A3=EXP(A)
790               B3=B
800               SA3=SA
810               SB3=SB
820               IF OPT=1 THEN 850
830 REM Calculation of A4 and B4 with H,T pairs ranging from 1 to N-J-G-F

       with both prefixes -1 or +1
840               FOR X=-1 TO +1 STEP 2
850                  K=1
860                  L=N-J-G-F
870                  FOR I=K TO L
880 U(I)=X*(H(I)^(1/M)-A1*EXP(B1*T(I))-S*A2*EXP(B2*T(I))-P*A3*EXP(B3*T(I))
890                     Y(I)=LOG(ABS(U(I)))
900                  NEXT I
910          GOSUB 4000  :REM Subroutine for linear regression analysis
920                  A4=EXP(A)
930                  B4=B
940                  SA4=SA
950                  SB4=SB
960                  IF OPT=1 THEN 1180
970                  C1=0
980                  C2=0
990                  C3=0
1000                  FOR I=1 TO N
1010                   D(I)=H(I)^(1/M)-A1*EXP(B1*T(I))-S*A2*EXP(B2*T(I))

                            -P*A3*EXP(B3*T(I))-X*A4*EXP(B4*T(I))
1020                     C1=C1+D(I)^2
1030                     C2=C2+H(I)^(2/M)
1040                     C3=C3+H(I)^(1/M)
1050                   NEXT I
1060                   R=1-C1/(C2-C3^2/N)
1070      IF R>MAX THEN MAX=R:SMAX=S:PMAX=P:XMAX=X:JMAX=J:GMAX=G:FMAX=F
1080 PRINT MAX
1090                NEXT X
1100             NEXT F
1110          NEXT P
1120       NEXT G
1130    NEXT S
1140 NEXT J
1150 S=SMAX:P=PMAX:X=XMAX:J=JMAX:G=GMAX:F=FMAX:OPT=1
1160 GOTO 420
1170 LPRINT
1180 LPRINT "Intercept Ln(A1) and its Standard error =";LOG(A1*H1) "+-"SA1
1190 LPRINT "Slope B1 and its Standard error=";B1 "+-"SB1
```

```
1200 LPRINT
1210 LPRINT "Intercept Ln(A2) and its Standard error=";LOG(A2*H1) "+-"SA2
1220 LPRINT "Slope B2 and its Standard error=";B2 "+-"SB2
1230 LPRINT
1240 LPRINT "Intercept Ln(A3) and its Standard error=";LOG(A3*H1) "+-"SA3
1250 LPRINT "Slope B3 and its Standard error=";B3 "+-"SB3
1260 LPRINT
1270 LPRINT "Intercept Ln(A4) and its Standard error=";LOG(A4*H1) "+-"SA4
1280 LPRINT "Slope B4 and its Standard error=";B4 "+-"SB4
1290 LPRINT
1300 LPRINT "Square of maximum correlation coefficient r^2=";MAX
1310 LPRINT "Optimum values of points for 1st, 2nd , 3rd and 4th exponential

       functions,respectively=";JMAX","GMAX","FMAX"and"N-JMAX-GMAX-FMAX
1320 LPRINT "Values of S,P and X,respectively ="; SMAX","PMAX"and"XMAX
1330 S0=SMAX:P0=PMAX:X0=XMAX
1340 LPRINT
1350 N2=INT(N/6+.5)
1360 MAX=0:OPT=0
1370  REM Calculation of A5 and B5 with H,T pairs ranging from N2 to N-N2-3
1380 FOR J=N2 TO N-N2-3
1390    K=N-J+1
1400    L=N
1410    FOR I=K TO L
1420       Y(I)=(1/M)*LOG(H(I))
1430    NEXT I
1440    GOSUB 4000 : REM Subroutine for linear regression analysis
1450    A5=EXP(A)
1460    B5=B
1470    SA5=SA
1480    SB5=SB
1490    IF OPT=1 THEN  1530
1500  REM Calculation of A6 and B6 with H,T pairs ranging from N2 to N-J-3

        and both prefixes -1 and +1
1510    FOR S=-1 TO +1  STEP 2
1520       FOR G=N2 TO N-J-3
1530          K=N-J-G+1
1540          L=N-J
1550          FOR I=K TO L
1560             U(I)=S*H(I)^(1/M)-S*A5*EXP(B5*T(I))
1570             Y(I)=LOG(ABS(U(I)))
1580          NEXT I
1590          GOSUB 4000: REM Subroutine for linear regression analysis
1600          A6=EXP(A)
1610          B6=B
1620          SA6=SA
1630          SB6=SB
1640          IF OPT=1 THEN 1670
1650  REM Calculation of A7 and B7 with H,T pairs ranging from 1 to N-J-G,

        with both prefixes -1 and +1
1660          FOR P=-1 TO +1 STEP 2
1670             K=1
1680             L=N-J-G
1690             FOR I=K TO L
1700                U(I)=P*(H(I)^(1/M)-A5*EXP(B5*T(I))-S*A6*EXP(B6*T(I)))
1710                Y(I)=LOG(ABS(U(I)))
1720             NEXT I
1730          GOSUB 4000  : REM Subroutine for linear regression analysis
1740             A7=EXP(A)
1750             B7=B
1760             SA7=SA
1770             SB7=SB
1780             IF OPT=1 THEN 1970
1790             C1=0
```

```
1800            C2=0
1810            C3=0
1820            FOR I=1 TO N
1830               D(I)=H(I)^(1/M)-A5*EXP(B5*T(I))-S*A6*EXP(B6*T(I))
```

References

[1] E. Vicke, R. Kallenbach, Kolloid-Z. 17 (1941) 135.
[2] A. Kapoor, R.T. Yang, C. Wong, Catal. Rev.-Sci. Eng. 31 (1–2) (1989) 129.
[3] J.M. Smith, in: 3rd ed, Chemical Engineering Kinetics, McGraw-Hill, New York, 1981, p. 471.
[4] N.A. Katsanos, E. Arvanitopoulou, F. Roubani-Kalantzopoulou, A. Kalantzopoulos, J. Phys. Chem. B 103 (1999) 1152.
[5] D. Gavril, A. Koliadima, G. Karaiskakis, Langmuir 15 (1999) 3798.
[6] D. Gavril, G. Karaiskakis, J. Chromatogr. A 845 (1999) 67.
[7] Ch. Abatzoglou, E. Iliopoulou, N.A. Katsanos, F. Roubani-Kalantzopoulou, J. Chromatogr. A 775 (1997) 211.
[8] N.A. Katsanos, R. Thede, F. Roubani-Kalantzopoulou, J. Chromatogr. A 795 (1998) 133.
[9] N.A. Katsanos, F. Roubani-Kalantzopoulou, Adv. Chromatogr. 40 (2000) 231.
[10] N.A. Katsanos, E. Iliopoulou, F. Roubani-Kalantzopoulou, E. Kalogirou, J. Phys. Chem. B 103 (1999) 10228.
[11] N.A. Katsanos, N. Rakintzis, F. Roubani-Kalantzopoulou, E. Arvanitopoulou, A. Kalantzopoulos, J. Chromatogr. A 845 (1999) 103.
[12] F. Roubani-Kalantzopoulou, Th. Artemiadi, I. Bassiotis, N.A. Katsanos, V. Plagianakos, Chromatographia 53 (2001) 315.
[13] N.A. Katsanos, E. Iliopoulou, V. Plagianakos, H. Mangou, J. Colloid Interf. Sci. 239 (2001) 10.
[14] N.A. Katsanos, F. Roubani-Kalantzopoulou, E. Iliopoulou, I. Bassiotis, V. Siokos, M.N. Vrahatis, V.P. Plagianakos, Colloid Surf. A 201 (2002) 173.
[15] N.A. Katsanos, F. Roubani-Kalantzopoulou, J. Chromatogr. A 710 (1995) 191.
[16] V. Sotiropoulou, G.P. Vassilev, N.A. Katsanos, H. Metaxa, F. Roubani-Kalantzopoulou, J. Chem. Soc. Faraday Trans. 91 (1995) 485.
[17] R.B. Bird, W.E. Stewart, E.N. Lightfoot, in: Transport Phenomena, Wiley, Chichester, 1960, p. 511.
[18] M. Jaroniec, R. Madey, in: Physical Adsorption on Heterogeneous Solids, Elsevier, Amsterdam, 1988, p. 227.
[19] K. Higashi, H. Ito, J. Oishi, J. Nuclear Sci. Tech. 1 (1964) 293.
[20] K.J. Sladek, E.R. Gilliland, R.F. Baddour, Ind. Eng. Chem. Fundam. 13 (1974) 100.