

Time separation of surface heterogeneity through experimental measurement of adsorption energies, local monolayer capacities, local isotherms, and energy distribution functions by inverse gas chromatography

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The inverse gas chromatography version of Reversed-Flow is described for experimental determination of local adsorption energies, local monolayer capacities, local isotherms, energy distribution functions, and lateral molecular interactions of gaseous adsorbates on heterogeneous solid surfaces. This method circumvents altogether the traditional integral equation of the three functions

$\Theta(p, T)$, $\theta(p, T, \varepsilon)$ and $f(\varepsilon)$ used in various approximations for finding energy distribution functions. Based on some explicit functions of time derived from the solution of a simple mathematical model, all physicochemical quantities mentioned above can be determined as functions of experimental time by means of simple PC programmes. This creates a domain of time-resolved chemistry of surfaces, used to reach important conclusions regarding adsorption sites. Some representative results are explicitly given.

1. INTRODUCTION

Inverse gas chromatography (IGC) has the stationary phase of the system as the object of its investigation, using the same procedures as the usual gas chromatography (GC). Among others, it was used to calculate the distribution

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function $f(\varepsilon)$ of the adsorption energy ε of gases on heterogeneous surfaces through the well-known integral equation

$$\Theta(p, T) = \int_0^{\infty} \theta(p, T, \varepsilon) f(\varepsilon) d\varepsilon \quad (1)$$

by providing the overall experimental adsorption isotherm $\Theta(p, T)$. For the local adsorption isotherm $\theta(p, T, \varepsilon)$ usually the crude CA (Condensation Approximation) or the ACCA (Asymptotically Correct Condensation Approximation) was employed, as described by Rudzinski and Everett [1]. Naturally, this methodology reminds the view of Adamson [2] that “it is misleading to talk about a true $f(\varepsilon)$, and any pair of $f(\varepsilon)$ and $\theta(\varepsilon, p, T)$ functions that reproduces $\Theta(p, T)$ within about the experimental error must be acceptable”.

Although IGC calculations of any kind are reached through retention time measurements, they do not constitute “time-resolved chemistry”, unless they are disengaged from the carrier gas flow through the stationary phase. Then, they cancel the axial flow velocity term $-v(\partial c/\partial z)$ from the chromatographic mass balance equation, leaving only diffusion, adsorption/desorption and surface reaction terms. This disengagement can be achieved by placing the solid bed in a cylindrical tube perpendicular to the carrier gas flow direction, leaving the latter to conduct only sampling work at a certain position, and transfer the sample taken at a certain time to the detector. This arrangement constitutes the basis of a new version of IGC called Reversed-Flow Gas Chromatography (RF-GC), an outline of which is shown in Figure 1.

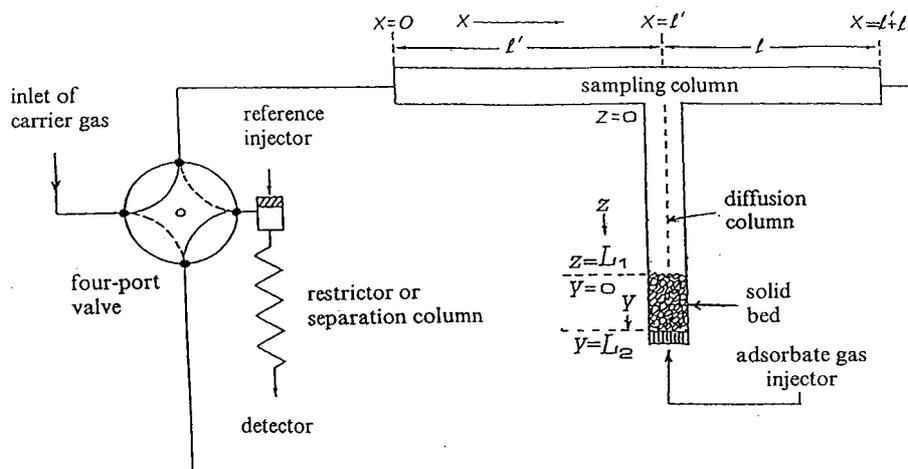


Fig. 1. Schematic representation of the columns and gas connections showing the principle of the Reversed-Flow technique as an inverse gas chromatographic tool

A small volume of the adsorbate gas is injected onto the solid bed of adsorbent particles, and by means of the four-port valve one makes repeated flow reversals of duration 10-60 s of the carrier gas, flowing only through the sampling column perpendicular to the tube containing the solid. These reversals create a long series of extra chromatographic peaks (*sample peaks*), which are narrow and fairly symmetrical with a height H depending on the time t when the reversal was made. An example is given in Figure 2.

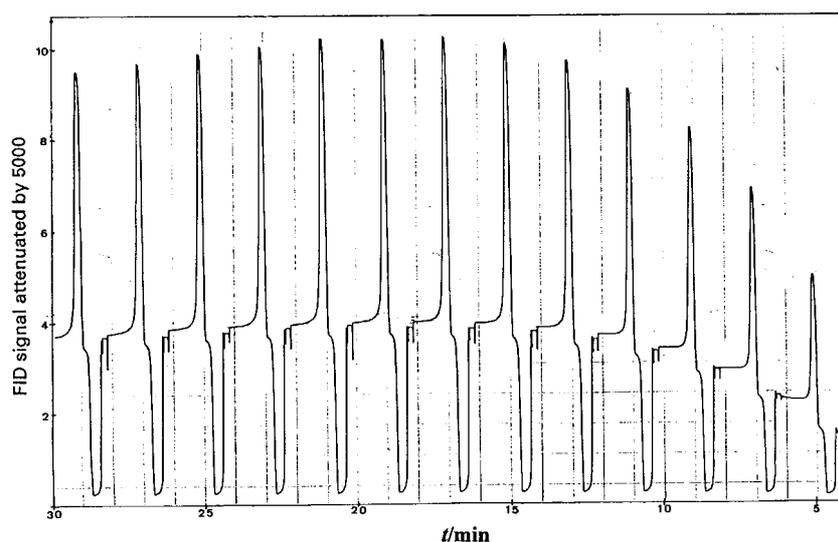


Fig. 2. Sample peaks of propene in nitrogen carrier gas, with section L_2 (9.6 cm) containing 0.67 g TiO_2 , at 323.2 K, and a flame ionization detector

The series of sample peaks, so easily obtained and measured experimentally, constitutes a time-resolved study of adsorption chemistry, by means of which eq. (1) can be circumvented altogether. Only the mathematical equation describing the peak height H as an analytic function of time t , and a model for the local isotherm $\theta(p, T, \varepsilon)$ are needed to calculate as explicit functions of time the physicochemical quantities appearing in the title of this paper. These are described in detail in the Theoretical and Calculations sections below.

2. THEORETICAL

The calculation of the physicochemical quantities pertaining to the adsorption of gases on heterogeneous surfaces as a function of time starts with the following mathematical model:

Two mass balance equations for the gaseous concentrations of the adsorbate gas A in the solid bed y and in the diffusion column z (cf. Figure 1), both expressed as mol/cm³.

The rate of change of the adsorbed concentration (mol/g).

The isotherm for the local adsorbed equilibrium concentration (mol/g) of A on the solid, at time t (s). The term “local” means with respect to t , i.e., involving only adsorption sites active at time t .

The analytical form of (1) and (2) above can be found in the original publication [3] or a recent review [4], while the isotherm (3) was first published in 1995 [5] assuming independent experimental isotherm over a wide range of concentrations, without specifying *a priori* an isotherm equation.

The solution of the above system (1) and (2) of partial differential equations, combined with the isotherm (3), leads to the result that the height H of the sample peaks like those of Figure 2 is given by the following explicit function of time:

$$H^{1/M} = \sum_{i=1}^4 A_i \exp(B_i t) \quad (2)$$

where M is the response factor of the chromatographic detector (1 for F.I.D.), whereas the pre-exponential factors A_i and the exponential coefficients of time B_i are easily calculated from the experimental pairs H, t by means of a GW-BASIC PC programme based on non-linear least-squares regression [3, 4, 6]. The physicochemical content of B_i is given analytically by Eqs. (128)-(133) of ref. [4]. From these, combined with the various geometrical characteristics of the diffusion column and the solid bed, and the diffusion coefficient of the adsorbate in the carrier gas D_1 (cm² s⁻¹), one calculates the adsorption rate constant k_1 (s⁻¹) of the gas adsorbate on the solid surface, together with its calibration factor of the detector g (cm/mol cm³). The above calculations can be easily carried out by a relatively simple PC programme in GW-BASIC, already published as Appendix in refs. [4] and [6].

Two other quantities at the end point $y = 0$ of the solid bed, namely, c_y (gaseous concentration above the solid in mol/cm³), and c_s^* (local adsorbed equilibrium concentration in mol/g of the adsorbate) are given by the relations [6]:

$$c_y = \frac{vL_1}{gD_1} \sum_{i=1}^4 A_i \exp(B_i t) \quad (3)$$

$$c_s^* = \frac{a_y}{a_s} k_1 \frac{vL_1}{gD_1} \sum_{i=1}^4 \frac{A_i}{B_i} [\exp(B_i t) - 1] \quad (4)$$

where v (cm/s) is the corrected linear flow velocity of the carrier gas running only in the sampling column (cf. Figure 1), L_1 (cm) the length of the diffusion column, a_y (cm²) the cross sectional area of the void space in the solid bed, and a_s (g/cm) the amount of solid per unit length of L_2 .

After the above, one may come to the objectives of the present review, namely: (a) Calculation of adsorption energies ε (kJ/mol); (b) calculation of local monolayer capacities c_{\max}^* (mol/g); (c) calculation of local isotherm values θ_i ; (d) calculation of energy distribution functions $f(\varepsilon)$ (mol² kJ⁻¹ g⁻¹) and $\varphi(\varepsilon; t)$ (mol kJ⁻¹ min⁻¹); (e) calculation of lateral molecular interaction parameter β (dimensionless).

All the above are found as functions of time from the experimental information contained in eq. (2). The translation of the above findings of the RF-GC methodology, from the domain of time t to the domain of adsorption energy ε as independent variable, is easily made by reading off any variable under (b), (c), (d) and (e) above together with the respective ε values at the same time t . This was exemplified by a recent publication [7].

3. CALCULATIONS

One can start from the equilibrium differential isotherm already published [5]:

$$\frac{\partial c_s^*}{\partial c_y} = \frac{a_y}{a_s} k_1 \frac{\sum_i^4 A_i \exp(B_i t)}{\sum_i^4 A_i B_i \exp(B_i t)} \quad (5)$$

but the two experimental isotherms described by Eqs. (4) and (5) are not enough for energetic measurements. In addition, an isotherm model is required and a fairly general one for our purposes is that of Jovanovic [8]:

$$\theta(p, T, \varepsilon) = 1 - \exp(-Kp) \quad (6)$$

going over to Langmuir isotherm in middle pressures and to a linear form at low pressures. The K is Langmuir's constant given by the relation [9]

$$K = K^0(T) \exp(\varepsilon/RT) \quad (7)$$

where ε is the adsorption energy, R the gas constant, and $K^0(T)$ is described by statistical mechanics [10] as

$$K^0 = \frac{h^3}{(2\pi m)^{3/2} (kT)^{5/2}} \frac{v_s(T)}{b_g(T)} \quad (8)$$

k being the Boltzmann constant, m the molecular mass, h the Planck constant, $b_g(T)$ the partition function for the rotations and vibrations of the free gas molecule, and $v_s(T)$ the partition function of the adsorbed molecule over all possible quantum states. As a low temperature approximation, we adopt that $v_s(T) \approx b_g(T)$, as was done before [9].

Although the physical foundations of eq. (6) have been criticized [11], this isotherm gives a good representation of experimental gas adsorption and behaves correctly at a wide range of surface coverages. An exhaustive numerical investigation of the differences in the behavior of the Jovanovic isotherm compared with that of Langmuir [12] led to the conclusion that, for the system krypton-pyrex, there is nothing to choose between the two and both give very similar values of the monolayer capacities. Also, Sircar [13] used the Jovanovic isotherm as the kernel $\theta(\varepsilon, T, p)$ in the integral equation (1) to calculate the energy distribution function $f(\varepsilon)$, and this resulted in the same form of $f(\varepsilon)$ as that obtained by using the Langmuir isotherm as the kernel. Only the variance of the calculated function was affected. More details on this point can be found in ref. [14].

The fraction of the surface covered at a given time t is denoted as $\theta_t = c_s^*/c_{\max}^*$, c_{\max}^* being the local with respect to time monolayer capacity (i.e., the maximum adsorbed concentration of the gaseous substance A on the collection of sites being active at time t and having a mean adsorption energy ε). Instead of the partial pressure of the adsorbate A, p , we write $c_y RT$, considering A as an ideal gas. Therefore, according to eq. (6),

$$\theta_t = \frac{c_s^*}{c_{\max}^*} = 1 - \exp(-KRTc_y) \quad (9)$$

From this, one can calculate the first two derivatives of θ_t with respect to c_y , keeping in mind that c_{\max}^* is a constant for each collection of sites i active at time t :

$$\frac{\partial \theta_t}{\partial c_y} = \frac{1}{c_{\max}^*} \frac{\partial c_s^*}{\partial c_y} = KRT \frac{c_{\max}^* - c_s^*}{c_{\max}^*} \quad (10)$$

$$\frac{\partial^2 \theta_t}{\partial c_y^2} = \frac{1}{c_{\max}^*} \frac{\partial^2 c_s^*}{\partial c_y^2} = -(KRT)^2 \frac{c_{\max}^* - c_s^*}{c_{\max}^*} \quad (11)$$

Dividing Eqs. (10) and (11), using also eq. (7), we find

$$-\frac{\partial^2 c_s^*}{\partial c_y^2} \bigg/ \left(\frac{\partial c_s^*}{\partial c_y} \right) = KRT = RTK^0 \exp\left(\frac{\varepsilon}{RT}\right) \quad (12)$$

Thus, the calculation of the two derivatives $\partial c_s^*/\partial c_y$ and $\partial^2 c_s^*/\partial c_y^2$ from the experimental results as a function of time leads directly to the mean value of ε for the sites i being responsible for the adsorption at time t , because everything else on the RHS of eq. (12) is known. The first derivative is given by eq. (5), whereas the second derivative of eq. (12) is found from eq. (2) as a function of time t as follows:

$$\frac{\partial^2 c_s^*}{\partial c_y^2} = \frac{\partial^2 c_s^*}{\partial c_y \partial t} \left(\frac{\partial c_y}{\partial t} \right)^{-1} \quad (13)$$

The second mixed derivative on the right-hand side is simply obtained from eq. (5) by differentiating with respect to time t :

$$\frac{\partial^2 c_s^*}{\partial c_y \partial t} = \frac{a_y}{a_s} k_1 \left\{ 1 - \frac{\left[\sum_i A_i \exp(B_i t) \right] \left[\sum_i A_i B_i^2 \exp(B_i t) \right]}{\left[\sum_i A_i B_i \exp(B_i t) \right]^2} \right\} \quad (14)$$

The $\partial c_y/\partial t$ of eq. (13) is obtained by differentiating eq. (3) with respect to t :

$$\frac{\partial c_y}{\partial t} = \frac{\nu L_1}{g D_1} \sum_i A_i B_i \exp(B_i t) \quad (15)$$

Division of eq. (14) by eq. (15), according to eq. (13), gives the desired second derivative as a function of time:

$$\frac{\partial^2 c_s^*}{\partial c_y^2} = \frac{a_y}{a_s} k_1 \frac{g D_1}{\nu L_1} \left\{ \frac{1}{\sum_i A_i B_i \exp(B_i t)} - \frac{\left[\sum_i A_i \exp(B_i t) \right] \left[\sum_i A_i B_i^2 \exp(B_i t) \right]}{\left[\sum_i A_i B_i \exp(B_i t) \right]^3} \right\} \quad (16)$$

Using Eqs. (5) and (16) in eq. (12), one calculates KRT as a function of time and, from this, the value of ε at any chosen time t of the experiment:

$$KRT = \frac{gD_1}{\nu L_1} \left\{ \frac{\sum_i A_i B_i^2 \exp(B_i t)}{\left[\sum_i A_i B_i \exp(B_i t) \right]^2} - \frac{1}{\sum_i A_i \exp(B_i t)} \right\} \quad (17)$$

$$\varepsilon = RT [\ln(KRT) - \ln(RT) - \ln K^0] \quad (18)$$

From eq. (10), one finds

$$c_{\max}^* = c_s^* + \frac{\partial c_s^*}{\partial c_y} (KRT)^{-1} \quad (19)$$

Thus, the local monolayer capacity of each collection of active sites is computed as a function of time, knowing c_s^* from eq. (4), $\partial c_s^* / \partial c_y$ from eq. (5), and KRT from eq. (17).

The local (with respect to time) adsorption isotherm $\theta_t = c_s^* / c_{\max}^*$ for each time t is found by a simple rearrangement of eq. (19):

$$\theta_t = 1 - \frac{1}{c_{\max}^*} \frac{\partial c_s^* / \partial c_y}{KRT} \quad (20)$$

According to Jaroniec and Madey [15], the function $f(\varepsilon)$ of eq. (1) describing the adsorption energy distribution, is defined as the derivative of the number of adsorption sites with respect to the adsorption energy. Because the first is analogous to c_{\max}^* , one may write

$$f(\varepsilon) = \frac{\partial c_{\max}^*}{\partial \varepsilon} = \frac{\partial c_{\max}^* / \partial t}{\partial \varepsilon / \partial t} \quad (21)$$

Finding the numerator of eq. (21) from eq. (19) and the denominator from eq. (18), with the help of eq. (17), their ratio gives $f(\varepsilon)$, after simple algebraic manipulations:

$$f(\varepsilon) = \frac{1}{RT} \left[\frac{KRT (\partial c_s^* / \partial t) + \partial^2 c_s^* / \partial c_y \partial t}{\partial (KRT) / \partial t} - \frac{\partial c_s^* / \partial c_y}{KRT} \right] \quad (22)$$

All derivatives with respect to time in the above relation have been explicitly and analytically calculated from relations already given, namely, $\partial c_s^*/\partial t$ from eq. (4), $\partial^2 c_s^*/\partial c_y \partial t$ is eq. (14), $\partial(KRT)/\partial t$ from eq. (17); $\partial c_s^*/\partial c_y$ is eq. (5), and KRT is eq. (17).

Equation (22) above was the central theme of publication [16] pointing out that $f(\varepsilon)$ is a function of two independent variables, ε and t , the t appearing as a structural parameter rather than a random variable of the distribution function. However, in a later publication [7] it was shown that the combination of $f(\varepsilon)$ with θ_t and c_{\max}^* , as given by Eqs. (22), (20) and (19), respectively, in the form

$$\phi(\varepsilon; t) = \frac{\theta_t f(\varepsilon)}{c_{\max}^*} \quad (23)$$

is a better choice for the true energy distribution function, behaving like a continuous probability density function for the variate ε and the structural parameter t , with respect to which can be normalized to unity by finding the value of the integral

$$\int_{t_1}^{t_2} \phi(\varepsilon; t) dt = 1 \quad (24)$$

between the two limits t_1 and t_2 of the experimental time.

Finally, lateral molecular interactions on heterogeneous surfaces can be found from the same experimental eq. (2) by correcting eq. (7) to include this type of energy:

$$K' = K^0 \exp\left(\frac{\varepsilon}{RT} + \beta\theta_t\right) = K \exp(\beta\theta_t) \quad (25)$$

where $\beta = z\omega/RT$ is a dimensionless parameter, ω denoting the lateral interaction energy and z the number of neighbours for each adsorption site. Thus, $z\omega\theta_t$ is the added to ε differential energy of adsorption due to lateral interactions.

Jovanovic isotherm (6) is modified accordingly, and from it a new derivative $\partial\theta_t/\partial c_y$ is calculated instead of eq. (10). Then, using this and some

approximations, we reach the result

$$\beta = \frac{1}{c_y} \left[\frac{\exp(KRTc_y) - 1}{KRT} - \frac{c_s^*}{\partial c_s^* / \partial c_y} \right] \quad (26)$$

in which all variables of the right-hand side are known as functions of time: c_y is given by eq. (3), KRT by eq. (17), c_s^* by eq. (4), and $\partial c_s^* / \partial c_y$ by eq. (5). Thus, β is easily calculated and the result is improved by some iterations [17].

In summary, starting from the experimental pairs H , t , as shown in Figure 2, one calculates A_i and B_i ($i = 1-4$) of eq. (2) by a non-linear least-squares method. Then: (a) the adsorption energy ε is calculated by means of Eqs. (17) and (18); (b) the local monolayer capacity c_{\max}^* is found by Eqs. (4), (5), (17) and (19); (c) the local isotherm θ_t is computed by using eq. (20), since c_{\max}^* has already been found, $\partial c_s^* / \partial c_y$ is given by eq. (5) and KRT by eq. (17); (d) the energy distribution function $\varphi(\varepsilon; t)$ is given by eq. (23), finding first $f(\varepsilon)$ by means of eq. (22), and then multiplying the result by θ_t already found and dividing it by c_{\max}^* found before; (e) finally, β is obtained from eq. (26) all functions on the right-hand side being given before as a function of time, namely, Eqs. (3), (17), (4) and (5).

Auxiliary quantities like v , L_1 , D_1 , a_y , a_s are known experimentally or from literature, whereas g and k_1 are found together with A_i and B_i of eq. (2). All calculations above can be carried out by a relatively simple PC programme in GW-BASIC available from the authors.

4. REPRESENTATIVE RESULTS

It should be stressed that the relations given in this work describe ε , c_{\max}^* , θ_t , $\varphi(\varepsilon; t)$ and β as analytic functions of time t . An example of their calculation is given in Table 1 for the experimental time 10-100 min chosen 2-10 minutes apart.

Naturally, based on the given relations one can plot graphically ε , c_{\max}^* , θ_t , $f(\varepsilon)$, $\varphi(\varepsilon; t)$ and β or $\beta\theta_t$ as functions of time t , using the programme MATHEMATICA 3 with a big number of plot points, say 3000. This has been done before [6, 7, 14, 16, 17, 18] and some examples are given here in Figure 3.

To compare energy distribution functions and other quantities as determined through the integral eq. (1) with those calculated by RF-GC as described here through Eqs. (2)-(26), a "translation" of the various findings here from the domain of time t to the domain of adsorption energy ε , as independent variable is required. This can easily be done by reading off at the same time the quantity required and the respective energy value, and constructing the relevant curve against ε . This is accomplished by simple PC calculations and plottings in the

frame of the programme MATHEMATICA 3, choosing a number of plot points (say 1500) between two limits of the experimental time. Three examples are given in Figure 4. In Figure 5 a combination of plots against ε and t is shown.

Tab. 1. Time distribution of adsorption energy, ε , local monolayer capacity, c_{\max}^* , local adsorption isotherm, θ_t , energy distribution function, $\varphi(\varepsilon; t)$, and lateral molecular interaction, $\beta\theta_t$, for *cis*-2-butene adsorbed on Penteli marble, at 333.2 K

Time (min)	ε (kJ/mol)	c_{\max}^* ($\mu\text{mol/g}$)	θ_t	$\varphi(\varepsilon; t)$ (cmol/kJ min)	$10\beta\theta_t$ (dimensionless)
10	90.67	15.06	0.831	5.06	-44.8
12	91.13	16.92	0.809	5.59	-21.9
14	91.57	19.41	0.784	6.11	-11.7
16	92.20	22.05	0.774	6.31	-6.95
18	93.06	24.61	0.779	6.22	-4.57
20	94.18	26.93	0.796	5.86	-3.21
22	95.66	28.89	0.825	5.21	-2.30
24	97.75	30.40	0.866	4.20	-1.58
26	101.18	31.41	0.919	2.69	-0.889
28	111.98	31.83	0.987	0.466	-0.138
30	103.03	36.37	0.934	2.21	0.680
32	98.65	42.48	0.860	4.35	1.46
34	96.21	49.50	0.789	6.01	2.23
36	94.48	57.63	0.721	7.26	3.03
38	93.11	67.22	0.655	8.17	3.92
40	91.95	78.82	0.589	8.75	4.69
42	90.89	93.28	0.523	9.01	5.16
44	89.90	112.0	0.456	8.96	5.25
46	88.92	137.6	0.388	8.57	4.96
48	87.90	174.7	0.318	7.83	4.46
50	86.77	234.1	0.246	6.71	3.73
52	85.42	344.4	0.174	5.18	2.79
54	83.55	618.4	0.100	3.25	1.70
56	79.55	2414	0.0264	0.930	0.474
58	80.80	1564	0.0420	1.45	0.789
60	83.11	719.8	0.0940	3.08	1.83
64	84.73	437.0	0.163	4.93	3.36
68	85.37	368.0	0.203	5.85	4.38
72	85.65	347.1	0.225	6.30	5.05
78	85.70	350.8	0.236	6.51	5.60
84	85.52	378.4	0.230	6.40	5.78
90	85.17	425.2	0.215	6.09	5.69
100	84.38	550.4	0.177	5.26	5.17

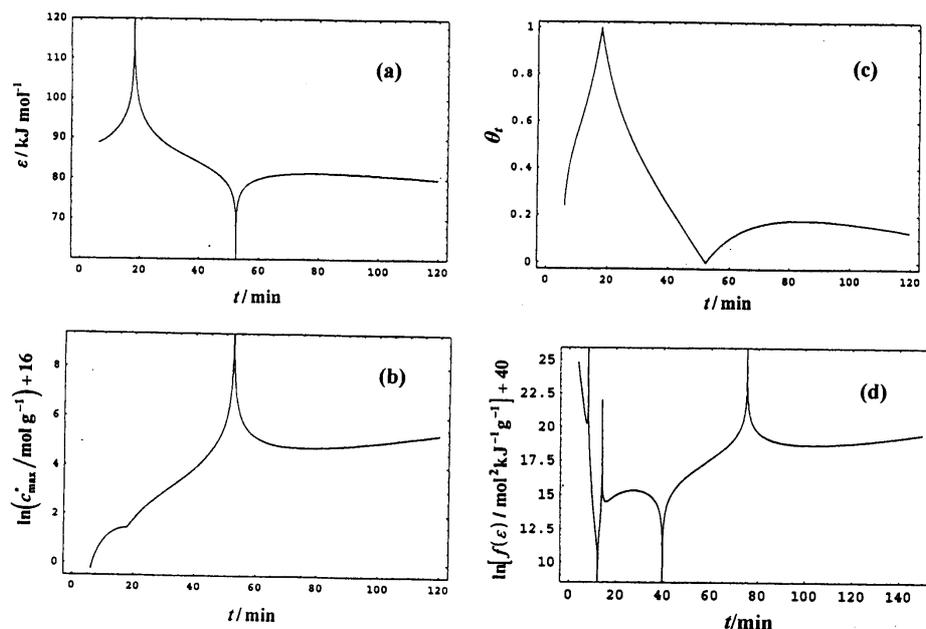


Fig. 3. Plots of adsorption parameters of two adsorbates on heterogeneous surfaces as a function of experimental time, on nitrogen atmosphere, at 323.2 K: (a) Adsorption energy ε of propene on PbO; (b) local monolayer capacity c_{\max}^* of propene on PbO; (c) local isotherm θ_t of propene on PbO; (d) energy distribution function $f(\varepsilon)$ of dimethyl sulfide on CaCO_3 (marble) covered with carbon black powder

5. CONCLUSIONS

Various conclusions can be drawn from the comparison of the plots in Figure 3 with those of Figure 4. Take, for example, the local isotherms θ_t plots. Two maxima and one minimum appear in Figure 3(c) with $\theta_t = 0.980, 0.006, 0.180$ at $t = 18, 52, 83$ min, respectively. In other cases more maxima and minima are recorded [6]. In Figure 4(a) an S shape curve appears resembling the same plots constructed by the method of Adamson and Ling as shown in ref. [1, page 430]. The same form of plots were obtained with both isomers *cis*-2-butene and *trans*-2-butene on the same surface, at temperatures 302, 314, 323 and 333 K [7].

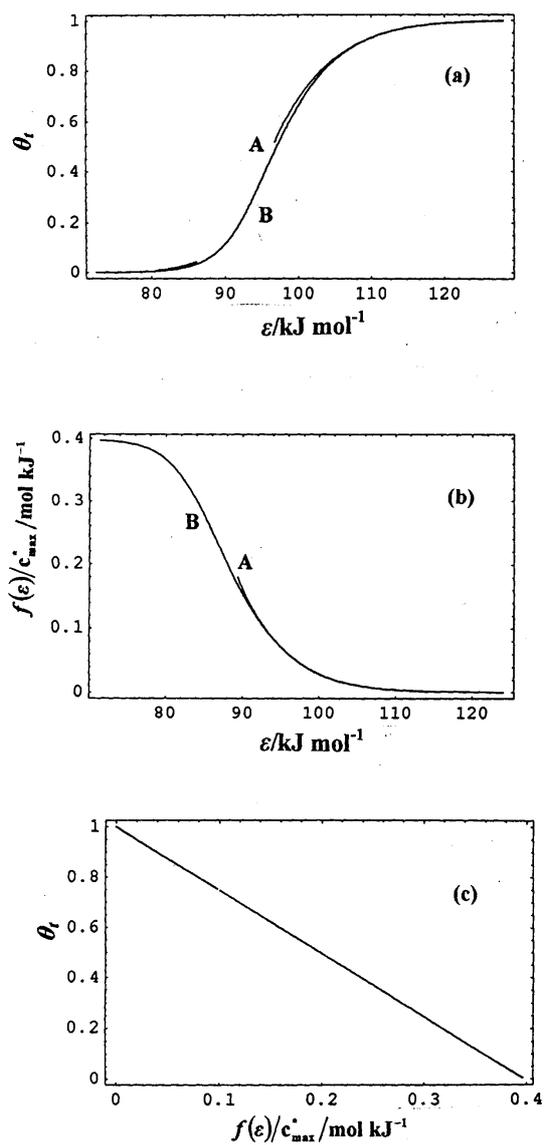


Fig. 4. Plots of adsorption parameters against each other for *cis*-2-butene as adsorbate on the heterogeneous surface of CaCO_3 (marble), in nitrogen atmosphere, at 302 K: (a) Local isotherm θ_t as a function of adsorption energy ϵ ; (b) fractional change of adsorption sites $f(\epsilon)/c_{\max}^*$ as a function of adsorption energy ϵ ; (c) local isotherm θ_t as a function of fractional change of adsorption sites $f(\epsilon)/c_{\max}^*$

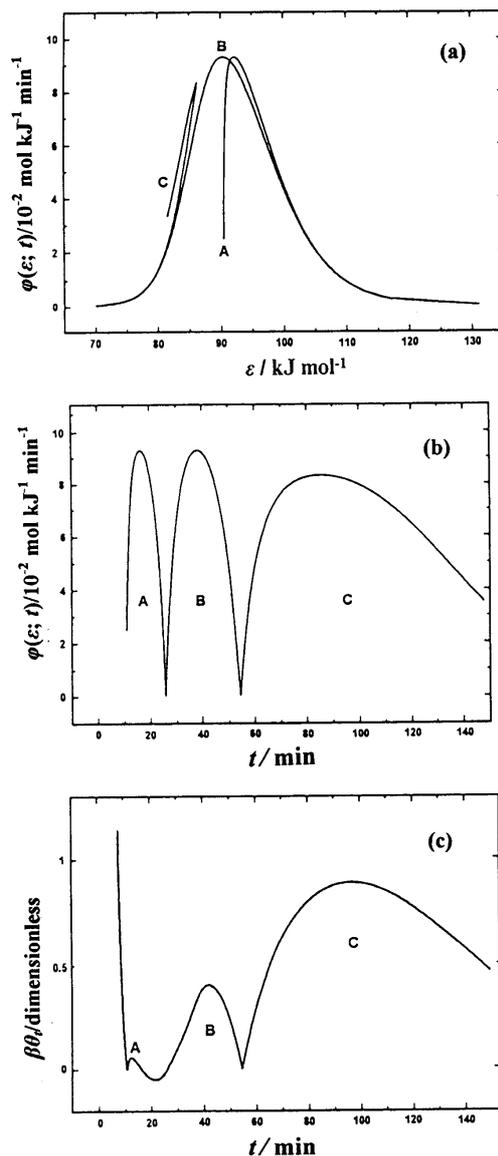


Fig. 5. Experimental behaviour of the adsorption energy distribution function and the lateral molecular interaction for the adsorption of 1-butene on cadmium sulphide, at 323.2 K: (a) The distribution function $\varphi(\varepsilon; t)$, as defined by eq. (23), plotted against the adsorption energy ε ; (b) the function $\varphi(\varepsilon; t)$ plotted against the structural parameter of time t ; (c) the lateral molecular interaction energy $\beta\theta_t$ (dimensionless), defined by eq. (25), plotted against the experimental time t

The plot in Figure 4(b) resembles that of Ref. 1, p. 430, where the integral distribution function F of Adamson and Ling is plotted against adsorption energy. The ratio $f(\varepsilon)/c_{\max}^*$ plotted here is a similar fractional quantity expressing the fractional change of the number of adsorption sites with respect to the adsorption energy. By reading off θ_t and $f(\varepsilon)/c_{\max}^*$ values at the same ε and plotting them one against the other, the straight line of Figure 4(c) is obtained. This resembles the plot of θ against F of Adamson and Ling method, as exemplified by Figure 11.4c of ref. [1], with two noticeable differences. First, the abscissa does not extend here to unity, and second, that the plot here is linear. Thus, the area under the total plot can be easily found by elementary geometry, giving the mean total amount adsorbed per unit adsorption energy [7].

Last but not least are the plots of Figure 5 with the new energy distribution function $\varphi(\varepsilon; t)$, defined by eq. (23). In all systems studied so far [7, 17, 19], this function plotted against the random variate ε , as in Figure 5(a) here, has the appearance of three superimposed Gaussian curves A, B and C. It should be stressed that this Gaussian like shape is an experimental fact, and not an assumption for the distribution function to solve eq. (1), as done several times in the past, e.g., by Steele [20], Ross and Olivier [21], and more recently by Jagiello [22].

In some cases the superposition is much closer, so that curves A and C look like experimental errors of curve B. The plot in Figure 5(b) shows an almost perfect way to separate the three Gaussian-shape probability distributions A, B and C by plotting the distribution function $\varphi(\varepsilon; t)$ against the structural parameter t , instead of the variate ε . This looks like the photographic development of a film. The times of maxima t_A, t_B, t_C correspond to maximum energies 92.2, 90.4, 86.2 kJ/mol, respectively, and these coincide with the maxima in Figure 5(a). The times of minima at 25.9 and 54.4 min correspond to almost zero value of $\varphi(\varepsilon; t)$, and the relative percentages in the areas under the curves A, B and C have been calculated to be 11.48, 20.84 and 67.68%, respectively [17]. Comparing this plot with a respective one of $f(\varepsilon)$ in Figure 3(d), one easily comes to the conclusion that $\varphi(\varepsilon; t)$ is a better probability density function for the adsorption energy ε than $f(\varepsilon)$.

Finally, the time profile of the dimensionless lateral interaction energy $\beta\theta_t$, calculated by means of eq. (26), and shown in Figure 5(c) using the same abscissa scale as that of Figure 5(b), reminds us of the model of Bakaev and Steele [23], who used a computer simulation of the argon adsorption on titanium oxide. They used the assumption that, after filling some (or all) minima of adsorption potential, the adsorbed molecules create new adsorption sites by providing support of favourable lateral interactions with new molecules held at positions which were initially saddle points maxima of the surface. A third kind of adsorption was attributed to molecules loosely bound to the substrate in its

second layer. Bands C of Figure 5(b) and 5(c) may be due to the latter kind of molecules, while bands A and B to adsorption at potential minima, and at newly created adsorption sites by lateral interactions, respectively.

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CURRICULA VITAE



Born in Greece, **Prof. N. A. Katsanos**, Chem FRSC received his first Degree in Chemistry (1954) from Aristotelian University of Thessaloniki, Greece, and his Doctorate in Chemistry (1963) from the same University. In between he went to England on a fellowship and received the Post-Graduate Diploma in Radiochemistry from the Leicester College of Technology. He is Fellow and Chartered Chemist of the Royal Society of Chemistry (England), Member of the Greek Chemists' Association, Member of the Chromatographic Society, and Member of the American Association for the Advancement of Science.

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