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TDS spectra analysis

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Abstract

Methods of TDS spectra analysis start usually from the Polanyi–Wigner desorption rate equation. The Redhead approximative solution of the equation can be rearranged into a reduced form in which it serves as an analytical expression for the desorption rate versus time or temperature. Fitting the analytical form to an experimental curve we can confirm or deny the invariability of kinetic parameters – a desorption energy E_d and a preexponential factor v_l – and determine their values. If the parameters depend on a surface coverage Θ the application of the reduced form allows us to determine their values at $\Theta \to 0$ and $\Theta \to \Theta_0$ and estimate the dependence $E_d(\Theta)$, $v(\Theta)$ from a single TDS spectrum. The method proposed in this paper is valid for the first-order kinetics of desorption; for the estimation mentioned above an assumption is made that desorption sites are identical and that E_d as well as v_l changes with Θ monotonously.

Keywords: Adsorption kinetics; Carbon monoxide; Thermal desorption

1. Introduction

In studies of gas–surface interactions, thermodesorption (TDS) or thermoprogrammed (TPD) spectroscopy is often used despite the fact that many other methods of surface analysis have been developed, some of them more sensitive and more precise. There are at least two reasons for TDS to be attractive: the TDS technique is relatively simple and the method can be applied even to electrically insulated samples without further difficulties. Excellent surveys of TDS methods are available from the literature [1–3].

One of the goals of TDS measurements is the determination of the kinetic parameters of desorption – energy of desorption E_d, preexponential factor v_l, and order of kinetics, l. In the simplest case when multiple steps and multiple adsorption sites can be ignored the parameters are bound together in the Polanyi–Wigner equation

$$r = v_l n^l \exp\left(-\frac{E_d}{kT}\right), \qquad (1)$$

where r is the desorption rate $r = -\mathrm{d}n/\mathrm{d}t$, n is the concentration of admolecules and E_d refers to one molecule. For the first-order kinetics, i.e. $l = 1$, n can be easily replaced by the surface coverage Θ without any changes in the preexponential factor; $r = -\mathrm{d}\Theta/\mathrm{d}t$.

Desorption measurements are often carried out in UHV conditions. Usually, the pumping speed of the apparatus is constant and sufficiently high and the increase p of a partial pressure which

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occurs during the desorption cycle is proportional to the desorption rate r. The whole area of the desorption peak then corresponds to the initial number of admolecules; the concentration at moment t can be obtained by integration of $p(t)$

$$n(t) = \text{const.} \int_t^\infty p \, \mathrm{d}t, \tag{2}$$

where const. is given by the parameters of the UHV system and by the sample area. Moreover, in TPD measurements the temperature rate $T(t)$ is known, it follows that the pressure–time curve $p(t)$ can be transformed into $p(T)$ and (1) can be applied for interpretation. Of course, the peak shape and its area, N, depend now on the heating regime [4]. In the simplest case of a linear heating rate, $T = T_0 + \beta t$, we have

$$n(T) = \frac{1}{\beta} \text{const.} \int_T^\infty p \, \mathrm{d}T = \frac{1}{\beta} \text{const.} \, N(T). \tag{3}$$

With $l = 1$, we need not know the value of the const. in (2) or (3) to determine the parameters listed above (except the surface concentration n); p (or r) can be given in arbitrary units and (n,ν_l) may be replaced by $(N,\gamma \equiv \nu_l/\beta)$:

$$p(T) = \gamma N(T) \exp\left(-\frac{E_\mathrm{d}}{kT}\right),$$

$$p(T) = -\frac{\mathrm{d}N(T)}{\mathrm{d}T}, \tag{4}$$

or – if we introduce the quantity Θ_T analogous to Θ –

$$r(T) = \gamma \Theta_T(T) \exp\left(-\frac{E_\mathrm{d}}{kT}\right),$$

$$r(T) = -\frac{\mathrm{d}\Theta_T(T)}{\mathrm{d}T}. \tag{5}$$

The analysis may be quite simple if the desorption parameters do not depend on the coverage Θ. Numerous methods of the spectra analysis are based on the work of Redhead [5] and Carter [6]. The Arrhenius plot is often used to calculate the desorption energy E_d, the preexponential factor ν_l, and the order of kinetics, l. In an effort to find an easier way how to extract the values of the kinetic parameters from an experimental spectrum, many approximative formulas have been found [5,7–11] which work with the relations of E_d and ν_l to some features of the spectrum: to the position of the peak maximum T_m, to the temperature width of the spectrum, to its shape etc. A method of the reaction order determination together with typical shapes of the spectra for different l are given in Ref. [12]. If the parameters change with Θ a set of TDP profiles is usually required which start from different initial coverages Θ_0. The present work offers a procedure valid for $l = 1$ which allows us – under some conditions – to determine (or at least estimate) $E_\mathrm{d}(\Theta)$, $\nu_l(\Theta)$ from a single desorption trace.

The methods listed above – with the exception of Refs. [1] and [6], where the problem of multiple peaks is discussed – must assume the surface to be homogeneous in E_d and ν_l even if they are applied in the differential form (e.g. the threshold TPD – TTPD – method, [2]). The method proposed below does not require the equivalence of adsorption sites if applied to the small interval of the spectrum. It is because it works with the desorption rate and its temperature dependence and not with the actual coverage. If the desorption comes from sites characterized by different E_d and ν_l parts of the spectrum may be revealed where the desorption from one type of sites prevails. Not ony the values of corresponding parameters but also the relative number of the respective sites can be determined.

2. Dimensionless desorption peak

In Ref. [5], approximative solutions of (1) valid for $E_\mathrm{d} = \text{const}$, $\nu_l = \text{const}$, for a linear temperature rate $T = T_0 + \beta t$, and for $l = 1$, $l = 2$ can be found. For $l = 1$, the formula taken from Ref. [5] reads

$$\ln \frac{r_\mathrm{m}}{r} = \frac{E_\mathrm{d}}{k}\left(\frac{1}{T} - \frac{1}{T_\mathrm{m}}\right) + \left(\frac{T}{T_\mathrm{m}}\right)^2 \times \exp\left[-\frac{E_\mathrm{d}}{k}\left(\frac{1}{T} - \frac{1}{T_\mathrm{m}}\right)\right] - 1. \tag{6}$$

Index m indicates the value corresponding to the peak maximum. Introducing a parameter $\alpha = E_d/kT_m$ and a variable $x = (T - T_m)/T_m$ we can rearrange (6) into the form $r/r_m \equiv R(\alpha,x)$. Analytical expressions not only for the reduced desorption rate r/r_m (or p/p_m) but also for its derivatives and for the peak area $A(\alpha,x)$ could be now obtained as functions of one variable (x) and one parameter (α):

$$R(\alpha,x) = \exp\left[\frac{\alpha x}{1+x} - (1+x)^2 \exp\left(\frac{\alpha x}{1+x}\right) + 1\right], \tag{7a}$$

$$A(\alpha,x) = A_0 \exp\left[-(1+x)^2 \exp\left(\frac{\alpha x}{1+x}\right)\right], \tag{7b}$$

$$A_0(\alpha,x) = \frac{\mathrm{e}}{\alpha+2}, \tag{7c}$$

$$A_m = \frac{A_0}{\mathrm{e}}, \tag{7d}$$

where

$$A(\alpha,x) = \int_x^\infty R(\alpha,x)\,\mathrm{d}x,$$

and the whole peak area

$$A_0 = \int_{-1}^\infty R(\alpha,x)\,\mathrm{d}x.$$

The index 0 stands for the initial values, $\mathrm{e} \equiv \exp\{1\}$.

Forming the expressions (7b)–(7d) we had to take into account the expression (5), the relations between the quantities of the real spectrum ($r,\Theta_T,\mathrm{d}r/\mathrm{d}T$) and the dimensionless functions ($R,\mathrm{d}R/\mathrm{d}x,A$),

$$r(T) = r_m R(\alpha,x(T)),$$

$$\Theta_T(T) = r_m T_m A(\alpha,x(T)),$$

$$\frac{\mathrm{d}r}{\mathrm{d}T} = \frac{r_m}{T_m}\frac{\mathrm{d}R}{\mathrm{d}x}, \tag{8}$$

and the behaviour of R at the point $x = 0$. At that point, $R = 1$ and $\mathrm{d}R/\mathrm{d}x = -2$; the maximum value of R is slightly larger than 1 and its position is at some point $x_m \neq 0$. Both, the maximum position x_m and the height $R(x_m)$ are determined by the parameter α. An overwhelming number of experimental data obtained for many combinations of metallic substrates and CO, NO, O_2, N_2, H_2 adsorbates give $23 < \alpha < 40$ [13]. In that region of α, $|x_m| < 0.003$ and $R(x_m) < 1.01$.

R and A are schematically shown in Fig. 1. The symbol w_x represents the width of the spectrum at half the peak maximum. It can be determined numerically as a function of one parameter, α, and easily transformed into the temperature width of the spectrum: $w_T = T_m w_x$. The data obtained by this procedure fully agree with those given in Ref. [8].

3. Approximation of $r(T)$ spectra

To approximate a real TDS spectrum by R we must respect three parameters: the position of the spectrum on the temperature scale (T_m), the height of the spectrum (r_m), and its width (characterized by α). The method of least squares in which three parameters have to be searched for is quite acceptable with the standard computer fitting programmes (Easy Plot, Origin etc.); it does not take more than several minutes with PC.

For the fitting, it is now convenient to reintroduce T, T_m into Eq. (7) instead of x and find α, T_m, and r_m. With the values obtained, we can

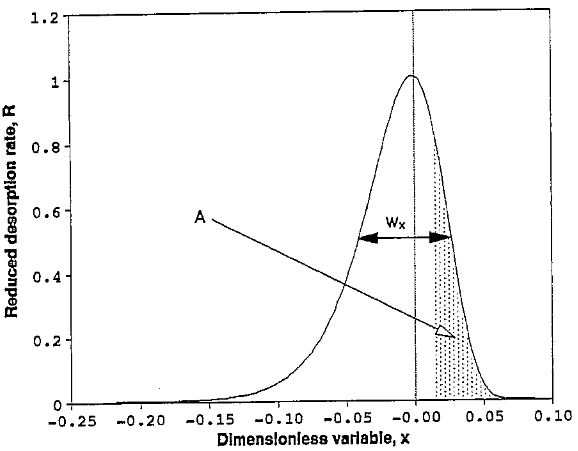

Fig. 1. $R(x)$ for $\alpha = 34.8$. w_x is the peak half-width, A is the peak area corresponding to some actual coverage.

calculate the parameters E_d and γ (as with the Arrhenius plot or other methods) and, in addition, the initial coverage Θ_{T_0}. The last parameter may give us important information about the presence and relative numbers of adsorption sites described by different kinetic parameters.

The relations between (α, r_m, T_m) and $(E_d, \gamma, \Theta_{T_0})$ as obtained from the definition of α, from (7a) and (8), and from the condition $dR/dx = -2$ at $x = 0$, are as follows:

$$E_d = \alpha k T_m,$$

$$\gamma = \frac{\alpha + 2}{T_m} \exp\{\alpha\},$$

$$\Theta_{T_0} = A_0 r_m T_m. \tag{9}$$

The expressions (9) can also help us to understand the fact of the small dispersion of α over a wide range of substrate–adsorbate combinations. They give the relation $E_d \gamma = k\alpha(\alpha + 2)\exp\{\alpha\}$; then for $23 \leq \alpha \leq 40$, $\alpha_{\text{average}} = 29$ [13] we have

$$\alpha = \ln \frac{E_d}{k} + \ln \gamma - (6.8 \pm 0.6), \tag{10a}$$

and the change of α with E_d and γ is

$$\frac{\delta\alpha}{\alpha} \approx \frac{1}{29} \left(\frac{\delta E_d}{E_d} + \frac{\delta\gamma}{\gamma} \right). \tag{10b}$$

It is seen that α is influenced only slightly by changes in E_d and γ.

The fitting can be applied to the whole spectrum ("integral" approximation) or to a small interval δT, δp about a point $[T_s, p_s]$ ("differential" approximation). In the first case, it can be deduced from a good agreement between the real spectrum and R that the order of kinetics has been chosen properly and that the parameters are constant (or a perfect compensation effect takes place which is not very probable). In the case of the differential approximation, the parameters can be determined at every point of the spectrum. In that case, α, T_m, and r_m describe the spectrum which "completes" the fitted interval and – if $E_d = E_d(\Theta)$, $\nu_l = \nu_l(\Theta)$ takes place or if the adsorption sites are not identical – they can differ substantially from those of the whole spectrum. The correctness of their values will be discussed in Section 4.1.

4. Application of $R(\alpha, x)$

4.1. Simulated spectra

To verify the applicability of the approximation simulated spectra have been analyzed because their basic parameters are perfectly known. The spectra have been obtained by the numerical solutions of (5) for $l = 1$ and for different input values γ, Θ_{T_0}, and E_d; the Runge–Kutta numerical solution (step 0.1 K) has been used. Both E_d and γ can generally be functions of different parameters of the surface, its coverage, temperature, and of the properties of different adsorption sites. In all our examples the assumption has been made that the kinetic parameters do not depend explicitly on the surface temperature.

4.1.1. Homogeneous surface with all adsorption sites identical, constant parameters

$\gamma = 10^{14}\,\mathrm{K}^{-1}$, $E_d = 1.38$ eV, the initial coverage (i.e. the peak area) $\Theta_{T_0} = 1$. The spectrum is identical with that on Fig. 1. Both types of analyses – the integral as well as the differential fitting of the spectrum with the function $r_m R$ – has been carried out. As a result of the integral approximation, the parameters $\alpha = 34.7$, $T_m = 460.25$ K, $r_m = 0.0293$, i.e. $\gamma = 9.37 \times 10^{13}\,\mathrm{K}^{-1}$ ($\log \gamma = 13.972$), $E_d = 1.378$ eV, $\Theta_{T_0} = 0.9998$ have been obtained. The differential approximation (in which the intervals $\delta T = 6$ K were taken) gives the parameters which are demonstrated in Fig. 2 in dependence on the relative coverage Θ_T corresponding to the points $[T_s, p_s]$; the value T_s was always situated in the middle of δT. The average values of the parameters are as follows: $\log \gamma = (13.957 \pm 0.009)\,\mathrm{K}^{-1}$, $\alpha = 34.72 + 0.02$, $E_d = 1.3784 \pm 0.0006$ eV, $\Theta_{T_0} = 1.003 \pm 0.003$. The results agree with the input values within an error of 0.05–0.3%.

In the present case of the homogeneous surface, it is not necessary to analyze the spectrum with the function $r_m R$. Some simpler method can be applied which utilizes the fact that the desorption rate $r(T)$ is proportional to the total actual coverage $\Theta_T(T)$ obtained by the peak integration. One of the convenient methods is the method of the Arrhenius plot which is most often used not only in the integral form but which also makes a base

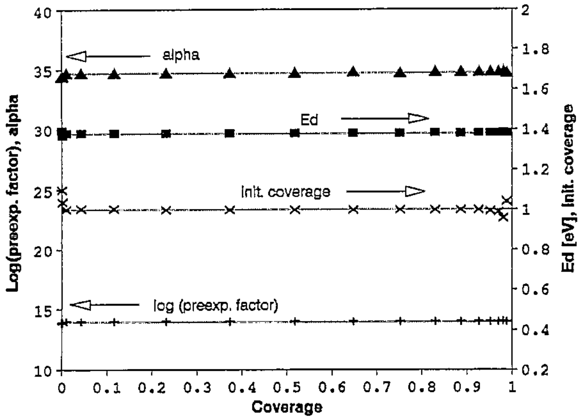

Fig. 2. Parameters α, $\log\gamma$, E_d, and Θ_{T_0} obtained from the differential fitting of the simulated TDS spectrum ($\gamma = 10^{14}\ \mathrm{K}^{-1}$, $E_d = 1.38$ eV, $\Theta_{T_0} = 1$) in dependence on the coverage.

for the differential TTPD method. To compare the results, the Arrhenius plot technique has been used to the spectrum described above, i.e. the linear regression of $\ln r/\Theta_T$ versus $1/T$ has been carried out.

The regression can be performed not only in terms of an Arrhenius plot, i.e. in the form $\ln(r/\Theta_T) = \ln\gamma - E_d/kT$ but also in terms of the dimensionless functions (7a)–(7d):

$$\ln\frac{r}{\Theta_T} = \alpha + \ln\frac{\alpha+2}{T_m} - \alpha T_m\frac{1}{T}, \tag{11}$$

which is equivalent to the fitting of r/Θ_T (linearized in that case) with the dimensionless function $(1/T_m)(R/A)$. Both interpretations give the same values of E_d and γ which confirms again the applicability of dimensionless functions and the relations (9). The results are for integral fitting (the whole spectrum): $E_d = 1.380$ eV, $\gamma = 9.95 \times 10^{13}\ \mathrm{K}^{-1}$ ($\log\gamma = 13.984$); for differential fitting (with the same intervals as before): $E_d = 1.380 \pm 0.0034$ eV, $\gamma = (8.41 \pm 0.2) \times 10^{13}\ \mathrm{K}^{-1}$ ($\log\gamma = 13.925 \pm 0.04$).

4.1.2. Adsorption sites identical, E_d depends on Θ, $\nu = const.$

The spectra with parameters $E_d = 1.38\,(1 - 0.1\Theta_T)$ eV, $\gamma = 10^{14}\ \mathrm{K}^{-1}$, and $\Theta_{T_0} = 1$ or $\Theta_{T_0} = 0.5$ have been analyzed. The analysis has been made as follows:

Eq. (5) is still valid at every point $r(T)$, $\Theta_T(T)$ of the spectrum; unfortunately, with an infinite number of pairs (E_d,γ). We are not able to identify the pair of the proper actual values $E_d(\Theta_T)$ and $\gamma(\Theta_T)$. The derivatives of $r(T)$ or $(r/\Theta_T)(T)$ now contain the changes of E_d and γ. Making use of the differential fitting with functions $r_m R$ or $(1/T_m)(R/A)$ we misinterpret the derivatives on the interval of approximation δT and the parameters obtained are generally incorrect. The first derivatives are given by the expressions

$$\frac{dr}{dT} = r\left[\frac{E_d}{kT^2} - \gamma\exp\left(-\frac{E_d}{kT}\right)\right] + r^2\left(\frac{1}{kT}\frac{dE_d}{d\Theta_T} - \frac{d\ln\gamma}{d\Theta_T}\right),$$

$$\frac{d(r/\Theta_T)}{dT} = \frac{r}{\Theta_T}\frac{E_d}{kT^2} + \frac{r^2}{\Theta_T} \times \left(\frac{1}{kT}\frac{dE_d}{d\Theta_T} - \frac{d\ln\gamma}{d\Theta_T}\right). \tag{12}$$

The first terms in Eq. (12) are the same as in the case of constant E_d and γ (with their actual values $E_d(\Theta_T)$, $\gamma(\Theta_T)$). The "correct" (unknown) functions R and R/A which would respect the proper values of E_d and γ at T would have the derivatives proportional only to that first terms. Their values at the point T would be $R = r/r_m$, $A = (1/T_m)(\Theta_T/r_m)$, but the area $A_0 = e/(\alpha+2)$ would differ from $\Theta_{T_0}/r_m/T_m$. It is because the desorption process has been ruled by the changing parameters before the point T is reached.

Unfortunately again, we do not know the way how to separate the terms in Eq. (12). Of course, even if it is not possible to find the correct functions R and R/A we can use them formally. Comparing the derivatives of r, r/Θ_T with the derivatives of R, R/A and neglecting $2x$ against $(\alpha+2)$ we can rewrite Eq. (12) into the form

$$\frac{dr}{dT} = \frac{r_m}{T_m}R'\left(1 + r_m T_m\frac{R^2}{R'}D\right),$$

$$\frac{d(r/\Theta_T)}{dT} = \frac{1}{T_m^2}\left(\frac{R}{A}\right)'\left(1 + r_m T_m\frac{(R^2/A)}{(R/A)'}D\right), \tag{13}$$

where $D = (dE_d/d\Theta_T)(1/kT) - d(\ln\gamma)/d\Theta_T$ and R',

$(R/A)'$ mean the derivatives with respect to x. The correct functions R, R/A can be obtained by the differential approximation only if the second terms – i.e. D or (R^2/R'), $(R^2/A)/(R/A)'$ (or all) – equal zero. The condition $D=0$ is fulfilled in the special case when the so-called compensation effect [17] is very strong, i.e. when E_d and γ simultaneously increase or decrease; their changes have the opposite influence on r. More promising is the behaviour of $R^2/(R)'$, $(R^2/A)/(R/A)'$. Making use of the analytic expressions for R, A ((7a), (7b)) and the derivatives

$$\frac{\mathrm{d}R}{\mathrm{d}x}=R\left[\frac{\alpha}{(1+x)^2}-\exp\left(\frac{\alpha x}{1+x}\right)[2(1+x)+\alpha]\right],$$

$$\frac{\mathrm{d}(R/A)}{\mathrm{d}x}=(\alpha+2)\frac{\alpha}{(1+x)^2}\exp\left(\frac{\alpha x}{1+x}\right), \qquad (14)$$

we can easily show that R^2/R', $(R^2/A)/(R/A)'$ go to zero at both edges of the spectrum; they decrease faster than the functions $\mathrm{d}R/\mathrm{d}x$ or $\mathrm{d}(R/A)/\mathrm{d}x$ themselves. If D is not too large the second terms in (13) cease and the derivatives $\mathrm{d}r/\mathrm{d}T$, $\mathrm{d}(r/\Theta_T)/\mathrm{d}T$ go to the "constant parameters" values; so we can expect that the fitting will go to the "correct" functions R, R/A. The parameters if extrapolated to $\Theta_T=0$, $\Theta_T=\Theta_{T_0}$ will then reach their proper values.

The results of the differential fitting of the spectrum with $\Theta_{T_0}=1$ are presented in Figs. 3a–3c for both fitting procedures r with $r_\mathrm{m}R$ (symbols) and r/Θ_T with $(1/T_\mathrm{m})(R/A)$ (symbols and lines). A similar procedure has been carried out for $\Theta_{T_0}=0.5$. A new variable, $\pm\delta\Theta_T$, has been introduced which seems to be more convenient than Θ_T or T for the extrapolation of α, E_d, and γ to $\Theta_T=\Theta_{T_0}$ and to $\Theta_T=0$: $\delta\Theta_T$ represents the change of Θ_T on the interval δT and goes to zero at both ends of the spectrum. The artificial introduction of signs allows us to differentiate between the case $\Theta_T\to 0$ and $\Theta_T\to\Theta_{T_0}$.

We can see that at the high-temperature end ($\Theta_T\to 0$) all parameters reach the input values. In the low-temperature part of the spectrum, the deviations in the derivatives still lead to errors in the parameters if obtained by fitting r with $r_\mathrm{m}R$. Although the change in Θ_T is very slow at this end of the spectrum and E_d and γ are nearly constant the extrapolated parameters differ from the input ones. The only exception makes E_d which is less sensitive to the deviations – maybe because of the logarithmic relation to r. The application of the alternative in which r/Θ_T is fitted with $(1/T_\mathrm{m})(R/A)$ shifts the extrapolated parameters quite close to the input values. As the rates of decrease of second terms in both expressions (13) are practically identical the only explanation for the better results seem to be in the simpler form (only two parameters) of the fitting function $(1/T_\mathrm{m})(R/A)$.

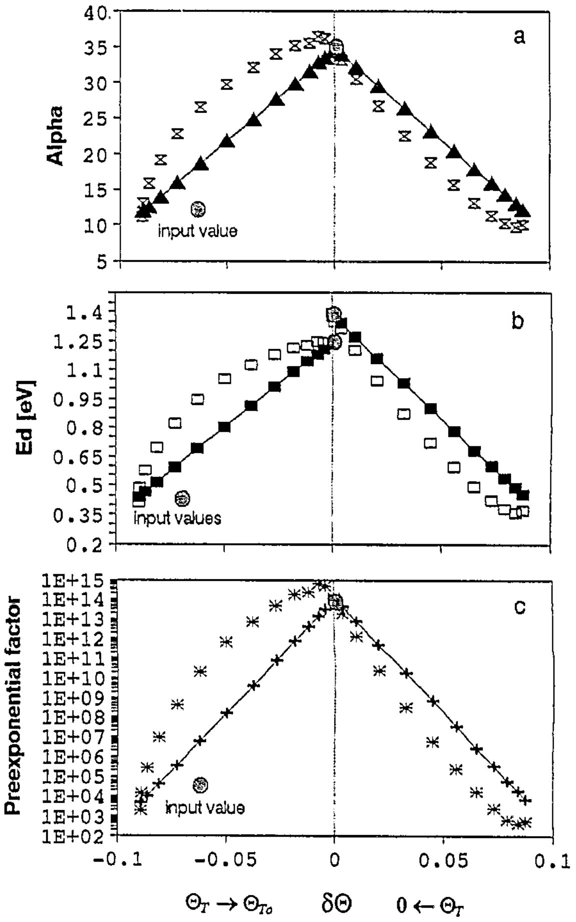

Fig. 3. Parameters α (a), E_d (b), and γ (c) versus $\pm\delta\Theta_T$. The results of the differential approximation of the spectrum with $\Theta_{T_0}=1$. The sign *minus* holds for $T\leq T_\mathrm{m}$, *plus* for $T>T_\mathrm{m}$. The parameters are extrapolated to $\delta\Theta_T=0$, i.e. $\Theta_T\to\Theta_{T_0}$ and $\Theta_T\to 0$.

If we can assume that E_d as well as γ changes with Θ_T monotonously (as it is in many cases) all values of the parameters lie within the limits of their (extrapolated) values for $\Theta_T=\Theta_{T_0}$ and $\Theta_T=$

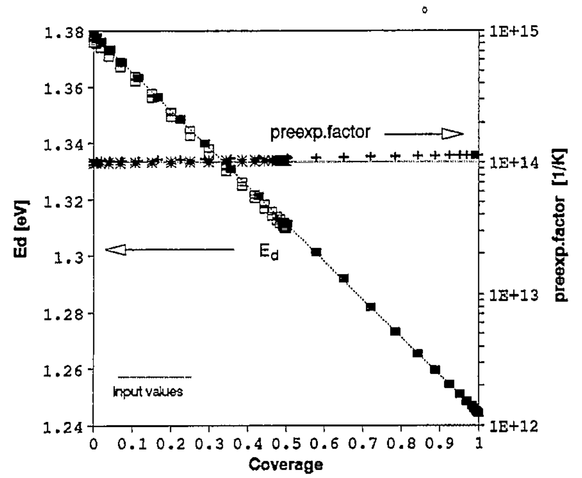

Fig. 4. Results of the analysis: $E_d(\Theta_T)$ and $\gamma(\Theta_T)$. The calculations have been performed for $\Theta_{T_0}=1$, $\alpha(0)=\alpha(1)=34.785$ (■, +) and for $\Theta_{T_0}=0.5$, $\alpha(0)=34.77$, $\alpha(0.5)=34.72$ (□, ∗).

0. If E_d and γ decrease or increase simultaneously then α also changes monotonously and – as follows from Eqs. (10a), (10b) – only slightly. When the decrease (increase) of E_d is accompanied by the increase (decrease) of γ the changes of α need not be monotonous, but they are even less than before because the variations of E_d and γ partly compensate each other.

With the assumption of monotonous changes of E_d, γ, and α the values $E_d(\Theta_{T_0})$, $E_d(0)$ etc. represent the limits of all values belonging to arbitrary coverage between 0 and Θ_{T_0}. It follows that the parameter which reaches the same value at both ends of the spectrum can be considered as a constant. We can use it as an information supplementary to Eq. (5) and calculate proper values of other parameters at every point (r,Θ_T) of the spectrum. If α is the constant $E_d(\Theta_T)$ and $\gamma(\Theta_T)$ are to be calculated. To do it we first determine numerically $T_m(\alpha,\Theta_T)$ from the experimental value r/Θ_T with the help of (11); then the relations (9) are used. If E_d or γ are constant we can use Eq. (5) and directly determine the complementary parameter.

If all – α, E_d, and γ – depend on Θ_T we take the parameter with the least relative difference in its border values. The procedure described above if carried out for both border values gives now only the limits of regions in which the remaining two parameters can be found.

In our case, the fitting with $(1/T_m)(R/A)$ gave border values of α which exhibit a very low dispersion: 34.72 and 34.77 for $\Theta_{T_0}=0.5$, 34.79 and 34.78 for $\Theta_{T_0}=1$. α has then been chosen as a nearly constant parameter. E_d and γ have been calculated as functions of the coverage from both spectra and for all border values of α and compared to the input functions $E_d=1.38(1-0.1\Theta_T)$ eV and $\gamma=10^{14}$ K^{-1}. Fig. 4 demonstrates the results of our calculations.

4.1.3. *Different adsorption sites, E_d and v const.*

When adsorbate particles occupy adsorption sites characterized by different energies of desorption E_{di} and preexponential factors γ_i several peaks can occur on the spectrum. If the desorption from different sites runs independently the total desorption rate can be expressed as a sum of rates from individual types of sites. The components are ruled by (5) with Θ_{Ti}, E_{di}, and γ_i; Θ_{Ti} is the coverage of the respective type of sites. A detailed analysis is given in Refs. [1] and [6]. The situation can be much easier to solve if the difference between the desorption energies is so large than some parts of the spectrum correspond to only one pair of constant parameters. The application of differential

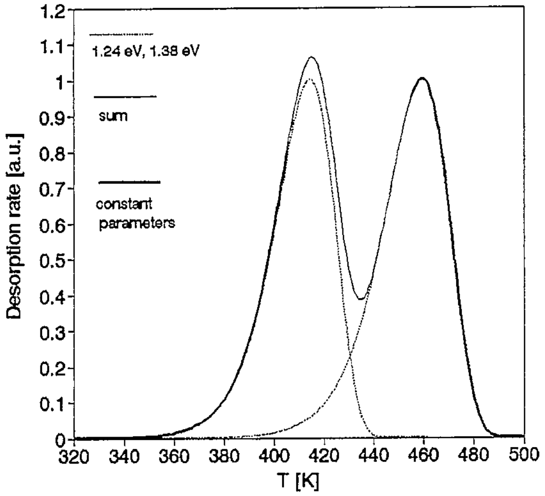

Fig. 5. Spectrum for two different types of adsorption sites. Heavy lines are the regions of constant parameters (taken from Fig. 6).

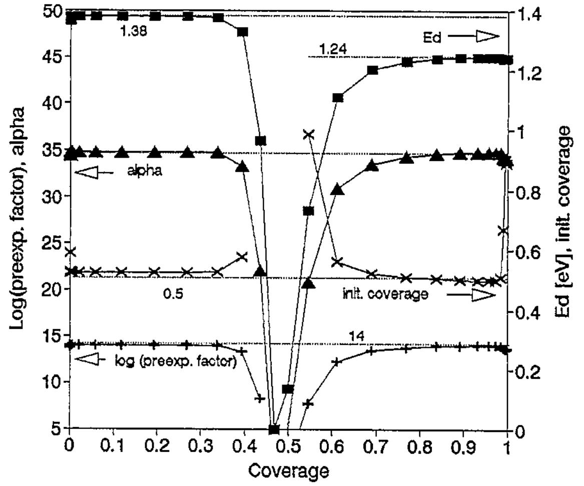

Fig. 6. Parameters obtained by the differential fitting of the spectrum in Fig. 5. The regions of constant parameters correspond to the desorption from one type of adsorption positions.

fitting can reveal the values of the parameters and also the initial coverage of the corresponding sites. Obtaining this data, we can construct the respective spectrum, subtract it from the total profile and try to continue in this procedure.

As a trivial example, a spectrum consisting of two peaks is analyzed (energies 1.23 and 1.38 eV, preexponential factor $10^{14}\,K^{-1}$, initial coverages $\Theta_{T_01} = \Theta_{T_02} = 0.5$; Fig. 5). The parameters resulting from the differential fitting have constant values at both edges of the spectrum (Fig. 6), the agreement between them and the input values is quite satisfying.

4.2. *Experimental spectra*

As an illustration, the analysis of some experimentally obtained TDS spectra has been carried out. As examples the spectra of CO desorbed from a single crystal Pd(111) [14] has been taken. The spectra were obtained from the experiments performed in an UHV system with a base pressure $< 3 \times 10^{-8}$ Pa; the CO exposure at the room temperature was made by means of a molecular beam doser. A linear heating rate ($\beta = 5.1$ K/s) has been achieved with the thermoelectric programmer. The apparatus is described elsewhere [16].

Many studies of the CO/Pd system can be found in the literature (e.g. Refs. [16,17] and references therein). The assumption of the first order kinetics of desorption from a CO/Pd single crystal is usual. The changes in the shape and peak position of the desorption spectrum which accompany the increase in the initial coverage may be ascribed to the adsorbate lateral interactions and to the multiple adsorption sites. The satisfactory description of the desorption process by constant E_d and ν_l can be expressed only if the initial coverage is very low.

This situation is demonstrated in Figs. 7a and 7b where the spectra with different initial coverages are presented (symbols) together with their approximation by $r_m R$ (lines). The spectrum in Fig. 7a corresponds to the initial coverage $\Theta_0 = 7 \times 10^{-3} \Theta_{sat}$, the spectrum in Fig. 7b started from the saturation coverage Θ_{sat}.

The approximation of the spectrum in Fig. 7a has given a very good result – a correlation coefficient of 0.99991 and a standard deviation 0.6% of the maximum value (r_m) which is comparable with the experimental error. The resulting values of the parameters are quite realistic: $\alpha = 37.6$, $T_m = 542.3$ K, $r_m = 162.2$, i.e. $E_d = 1.76$ eV and $\nu_l =$

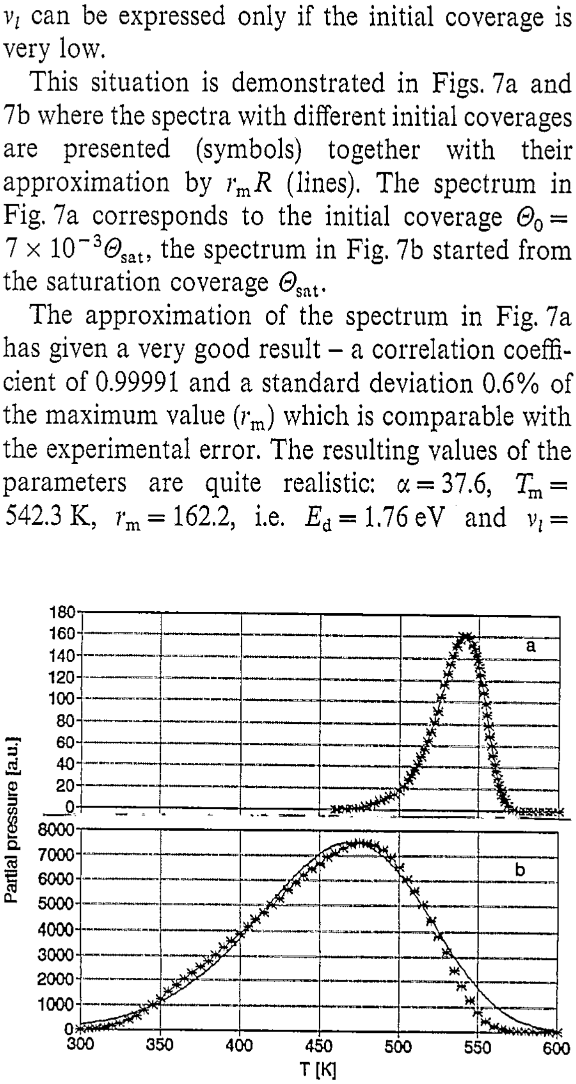

Fig. 7. TDS spectra of CO desorbed from Pd(111). (a) Exposure from a residual gas atmosphere, coverage $7 \times 10^{-3} \Theta_{sat}$ (markers); approximation (line) gives the parameters $\alpha = 37.6$, $T_m = 542.3$ K, $r_m = 162.2$, i.e. $E_d = 1.76$ eV, $\nu = 7.55 \times 10^{15}\,s^{-1}$. (b) Exposure 10^{-3} Pa s, coverage $\Theta_0 = \Theta_{sat}$ (markers); approximation (line): $\alpha = 7.6$, $T_m = 481.1$ K, $r_m = 7373$, *i.e.* $E_d = 0.32$ eV, $\nu_l = 161\,s^{-1}$.

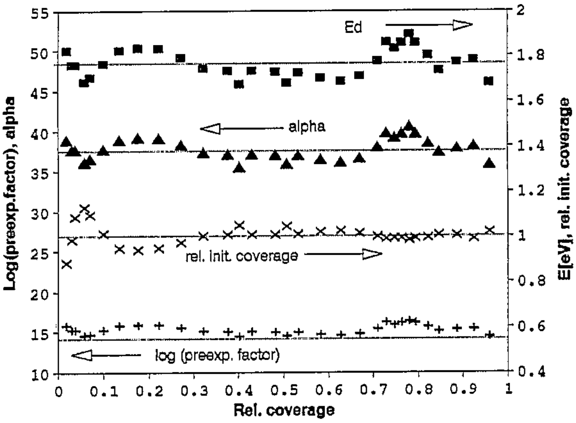

Fig. 8. Parameters α, $\log\gamma$, E_d, and Θ_{T_0} obtained from the differential approximation of the experimental TDS spectrum with $\Theta_0 = 7 \times 10^{-3}\Theta_{sat}$ in dependence on the relative coverage Θ/Θ_0.

$7.55 \times 10^{15}\ s^{-1}$. The values can be compared with results presented in Ref. [17] for CO on Pd(111), TTPD method, adsorption temperatures 87 and 200 K: E_d and ν_l given there for the same coverage are ~ 1.6 eV and $\sim 1 \times 10^{15}\ s^{-1}$, respectively. As it was expected the spectrum for the saturation coverage (Fig. 7b) where E_d and ν_l very probably are not constant has been fitted with a worse correlation coefficient – 0.996 – and a larger standard deviation – about 5% of the maximum value. The results $E_d = 0.32$ eV, $\nu_l = 161\ s^{-1}$ differs significantly from those given in Ref. [17] ($E_d \approx 0.56$ eV, $\nu_l \approx 10^9\ s^{-1}$).

In Fig. 8, the results of the differential fitting of the spectrum from Fig. 7a are demonstrated. The parameters obtained are constant along the whole spectrum within an error of 5–15%. Their mean values are $\alpha = 37.75 \pm 0.24$, $\log\gamma = 15.2 \pm 0.10$ ($\nu_l = (9.2 \pm 0.4) \times 10^{15}\ s^{-1}$), $E_d = 1.78 \pm 0.01$ eV, $\Theta_0 = (7.03 \pm 0.008) \times 10^{-3}\Theta_{sat}$.

5. Summary

A desorption process in which identical adsorption sites take part is usually described by the Polanyi–Wigner equation. When the properties of a vacuum chamber in which the process is investigated save the proportionality between the desorption rate and the pressure increase and when the increase of temperature T provoking the desorption is linear in time (with the rate β) some simplifications are possible. At least for the first-order kinetics the change of variables from time to temperature does not change the form of the equation; only the preexponential factor is now $\gamma = \nu_l/\beta$.

If the process is characterized by constant kinetic parameters the desorption rate r versus T can be expressed analytically. To do so we rearrange the Redhead approximation of the Polanyi–Wigner equation and fit it to the real spectrum. The rearrangement gives us the reduced desorption peak $R(\alpha,x)$ in which R represents the reduced desorption rate and x is a dimensionless variable – the reduced temperature centered about the peak maximum position, T_m. The dimensionless parameter α is given by the ratio of the desorption energy E_d to kT_m and determines the width of the peak. Analytic expressions for the peak area (total or partial) and, of course, for the derivatives of R are also attainable. The fitting procedure gives values of three parameters: α, T_m, and the proportionality factor r_m; the first two determine unambiguously E_d and the preexponential factor γ. We can fit the whole spectrum ("integral" approximation) or only small parts of it ("differential" approximation); the second – when done by turns for the whole spectrum – can confirm (or argue against) the invariability of the parameters.

The differential fitting can be even more helpful if the parameters change their values with surface coverage or if several types of adsorption sites are present. In the last case, the desorption peak represents a sum of individual peaks if the condition is fulfilled that the desorption from different sites runs independently. With the differential fitting the part of the total spectrum can be made visible where the desorption from one type of sites prevails. The relative number of these sites can be obtained as well.

When the parameters are dependent on the surface coverage the differential fitting gives false values except at the ends of the spectrum. If there is a ground to assume that the parameters change monotonously with Θ then their boundary values make limits for all values possible. Taking the quantity from the triad α, E_d, T_m which exhibits the smallest relative difference in its boundary values we can determine – or at least estimate – the dependence on Θ for the remaining two parameters.

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