THE COMPENSATION EFFECT AND THE MANIFESTATION OF LATERAL INTERACTIONS IN THERMAL DESORPTION SPECTROSCOPY

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Received 11 May 1987; accepted for publication 14 October 1987

If thermal desorption spectra are analysed in terms of the Polanyi–Wigner equation lateral interactions between the adsorbates may lead to coverage (θ) dependent pre-exponential factors, τ, and activation energies of desorption, E. Evidence from the literature shows that E and τ often satisfy the well-known compensation effect in τ(θ) = bE(θ) + c, with constants b and c. Here we insert this compensation effect into the rate equation of desorption and simulate spectra which illustrate the influence of the compensation effect in thermal desorption spectra of adsorbate systems where pairwise lateral interactions prevail.

1. Introduction

Thermal desorption spectroscopy (TDS) constitutes an important tool in order to study interactions between adsorbates and substrates as well as lateral interactions between adsorbates on surfaces [1–5]. On an otherwise homogeneous substrate the presence of lateral interactions can be inferred from the coverage dependence of the activation energy of desorption, E(θ). In the case of pairwise interactions one may assume

\[ E(\theta) = E_0 - w\theta \]

with \( E_0 = E(\theta = 0) \), \( w \) the interaction energy (negative for attractive and positive for repulsive interactions), and \( \theta \) the adsorbate coverage in monolayers (ML) [1–5]. Calculated desorption traces based on pairwise lateral interactions between the adsorbed particles by Golze et al. [5] show that in the case of first-order desorption kinetics, attractive interactions shift the desorption peaks to higher temperatures, whereas repulsive interactions shift the peaks to lower temperatures. These calculations, however, rest on the assump-
Compensation effect and lateral interactions in TDS

Fig. 1. Plots of \( \ln \nu(\theta) \) against \( E(\theta) \) for thermal desorption of Ag and Au from W(110), W(100) [3] and Ru(001) [8,9] reveal the presence of the compensation effect.

Fig. 2. When the compensation effect operates in thermal desorption, Arrhenius plots corresponding to different coverages intersect at a critical reciprocal temperature \( 1/T_c \) (after Clark [10]).
Table 1
Critical compensation effect temperatures for thermal desorption of metals from metals [3,8,9]

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Substrate</th>
<th>$T_c$ (K)</th>
</tr>
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<tbody>
<tr>
<td>Ag</td>
<td>W(110)</td>
<td>1145</td>
</tr>
<tr>
<td>Ag</td>
<td>W(100)</td>
<td>1295</td>
</tr>
<tr>
<td>Au</td>
<td>W(110)</td>
<td>1255</td>
</tr>
<tr>
<td>Au</td>
<td>W(100)</td>
<td>1565</td>
</tr>
<tr>
<td>Cu</td>
<td>W(110)</td>
<td>1635</td>
</tr>
<tr>
<td>Ag</td>
<td>Ru(001)</td>
<td>1095</td>
</tr>
<tr>
<td>Ag</td>
<td>Ag/Ru(001) a)</td>
<td>940</td>
</tr>
<tr>
<td>Au</td>
<td>Ru(001)</td>
<td>1115</td>
</tr>
</tbody>
</table>

a) Second layer Ag on Ru(001).

in which $b$ and $c$ are constants, and $T_c$ is defined as $1/bR$, with $R$ the gas constant [10]. A few examples which comply with this compensation effect relate to the desorption of metal layers and have been compiled in fig. 1. From these plots the values of $b$, $c$ and $T_c$ can be determined. The parameter $T_c$ has a clear physical interpretation. It represents the temperature at which the Arrhenius plots for different adsorbate coverages intersect (see fig. 2). Values of $T_c$ calculated from $E(\theta)$ and $\nu(\theta)$ data published for Ag and Au desorption from three different substrates reported by Bauer et al. [3] and ourselves [8,9] are given in table 1.

The purpose of this paper is to illustrate the influence of the compensation effect on the shape of simulated thermal desorption spectra, when lateral interactions between the atoms are present in the adsorbate layer.

2. Rate equation

The rate of thermal desorption of adsorbed particles from a single adsorption state is generally described by the Polanyi–Wigner equation:

$$r = -\frac{d\theta}{dt} = \nu(\theta) \theta^n \exp\left(-\frac{E(\theta)}{RT}\right),$$

in which $r$ is the rate of desorption, $\theta$ the coverage in monolayers (ML), $t$ the time (s), $\nu$ the pre-exponential factor, $n$ the order of the desorption kinetics, $E$ the activation energy of desorption (equals the adsorption energy when the adsorption is a non-activated process), $R$ the gas constant and $T$ the temperature. Most generally, the coverage dependence of $E$ can formally be expressed as:

$$E(\theta) = E_0 + \Delta E(\theta),$$

where $E_0$ is the activation energy of desorption for a single adatom ($\theta \to 0$) and $\Delta E(\theta)$ represents the coverage dependent part of $E$. In agreement with
the experimental evidence cited above we assume that the coverage dependence of \( \nu \) is determined by the compensation effect:

\[
\ln \nu(\theta) = bE(\theta) + c = \ln \nu_0 + \frac{\Delta E(\theta)}{RT_c},
\]

in which \( \nu_0 \) is the pre-exponential factor at coverage zero. The combined influence of the lateral interactions and the compensation effect is then obtained by combining eqs. (3)–(5):

\[
r = -\frac{d\theta}{dt} = \nu_0 \theta^n \exp\left(-\frac{E_0}{RT}\right) \exp\left[\frac{\Delta E(\theta)}{R} \left(\frac{1}{T_c} - \frac{1}{T}\right)\right].
\]

Fig. 3. Simulated thermal desorption spectra for first-order desorption with coverage-independent pre-exponential factor. Top: coverage-independent activation energy of desorption. Middle and bottom: attractive and repulsive pairwise interactions, \( E(\theta) = E_0 - w\theta \). The coverages for each set of spectra vary from 0.1 to 1 ML in steps of 0.1 ML.
In order to illustrate the influence of the compensation effect, we will present model calculations of thermal desorption spectra for the special case of first-order desorption kinetics and pairwise interactions (see eq. (1)), for which the following modification of eq. (6) holds:

$$r = -\frac{d\theta}{dt} = v_0\theta \exp\left(-\frac{E_0}{RT}\right) \exp\left[\frac{w\theta}{R} \left(\frac{1}{T} - \frac{1}{T_c}\right)\right],$$

with $T = T_0 + \beta t$, where $\beta$ is the linear heating rate. We stress that eqs. (6) and (7) are nothing but empirical expressions, which, however, describe a number of TDS observations successfully.

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Fig. 4. Simulated thermal desorption spectra for first-order desorption kinetics and attractive (left) and repulsive (right) lateral interactions, and different values of the compensation effect temperature $T_c$. The desorption energy varies with coverage as $E(\theta) = E_0 - w\theta$ and the pre-exponential factor varies according to the compensation effect as $\ln \nu = -\frac{w\theta}{RT_c} + \ln v_0$. Parameter values: $E_0 = 300$ kJ/mol, $w = \pm 25$ kJ/mol, $v_0 = 10^{13}$ s$^{-1}$. The coverages for each set of spectra vary from 0.1 to 1 ML in steps of 0.1 ML.
3. Results

The spectra have been calculated by solving eq. (7) with a Runge-Kutta method for the following parameters: $E_0 = 300$ kJ/mol, $\nu_0 = 10^{13}$ s$^{-1}$, $\beta = 1$ K s$^{-1}$, $w = \pm 25$ kJ/mol, and different values of $T_c$. Fig. 3 shows, for reasons of comparison, the influence of lateral interactions of the shape of first-order thermal desorption spectra when the pre-exponential factor is constant, that is when $T_c = \infty$. In the absence of lateral interactions ($w = 0$) the temperatures $T_m$ at peak maximum and the peak widths (FWHM) are independent of the initial coverages. When $W < 0$ (attractive interactions), $T_m$ increases and FWHM decreases with $\theta$, for repulsive interactions the opposite behavior is observed. Note that, although the interaction energy $w$ is only small compared to $E_0$, the spectra deviate appreciably from those for $w = 0$. In practice such extreme shapes are rarely observed.

Fig. 5. Variation of the peak maximum temperature $T_m$ and the full width at half maximum FWHM of thermal desorption spectra with initial coverage for first-order desorption kinetics, for attractive and repulsive lateral interactions, and for different values of the compensation effect temperature $T_c$. The desorption energy varies with coverage as $E(\theta) = E_0 - w\theta$ and the pre-exponential factor varies according to the compensation effect as $\ln \nu = - w\theta/RT_c + \ln \nu_0$. Parameter values: $E_0 = 300$ kJ/mol, $w = \pm 25$ kJ/mol, $\nu_0 = 10^{13}$ s$^{-1}$. 
Fig. 4 shows calculated TD spectra for the case of attractive and repulsive pairwise interactions ($\omega = \pm 25$ kJ/mol), when the pre-exponential factor changes according to the compensation effect eq. (2). The corresponding peak maximum temperatures and the widths of the spectra are shown in fig. 5. The top curves of fig. 4 correspond to those shown in fig. 3, for $T_c = \infty$. The next three sets of spectra show the influence of the compensation effect. As $T_c$ decreases the compensation becomes stronger and the spectra look more and more like simple first-order desorption curves with coverage-independent desorption parameters. At a certain critical temperature $T_c$ around 1000 K, compensation is almost perfect. Note that, although both $E$ and $\nu$ depend on coverage, $T_m$ and FWHM are virtually constant. At lower values of $T_c$, the behavior of $T_m$ and FWHM reverses, and the spectra corresponding to attractive interactions look similar to those for weakly compensated repulsive interactions, and vice versa. Such a situation has been observed experimentally for thermal desorption of Au from W(110) and from Ru(001), in which $E$ decreases but $T_m$ increases with increasing coverage [3,8,9].

4. Discussion

An important conclusion from the model calculations is that the temperature of maximum desorption and the width of the spectrum are by no means reliable indicators for the bond strength between adsorbate and substrate. As a particularly interesting example we note that a set of $T_m$ and FWHM values which are virtually constant with initial coverage can in principle correspond to three cases: first-order desorption kinetics with (1) coverage-independent $E$ and $\nu$, (2) attractive and (3) repulsive interactions between the adsorbates, provided that $\nu(\theta)$ and $E(\theta)$ are related by a compensation effect of appropriate strength. It is important to realize that attractive interactions do not necessarily correspond to $dT_m/d\theta > 0$ and repulsive interactions not to $dT_m/d\theta < 0$, as figs. 4 and 5 demonstrate.

This reinforces that TD spectra of systems where lateral interactions play a role should always be analyzed by those procedures which are based on a minimum number of simplifying assumptions. Several procedures for the analysis of TDS data are presently used [2,3,11–14]; table 2 lists the assumptions involved. A useful and rapid test proposed by Pervan et al. [14] indicates which of the assumptions are allowed for a given set of TD spectra.

The popular peak temperature method of Redhead [11] and the procedure of Chan, Aris and Weinberg [12], which is based on the $T_m$ and FWHM of the TD spectra, are inappropriate for adsorbates exhibiting lateral interactions; only the model-independent procedures proposed by King [2], Bauer et al. [3] and Habenschaden and Küppers [13] should be used in those cases in which $E$ and $\nu$ may depend on coverage and in which the order of desorption is not a
Table 2
Assumptions in various methods of TDS analysis

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<tbody>
<tr>
<td>$E$ and $v$ do not</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>depend on $\theta$</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$n$ known</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$v$ known</td>
<td>+</td>
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$p$ priori known. The essential feature of these procedures is that the factor $\theta^n$ in expression (3) is kept constant. For fixed values of $\theta$, a plot of $\ln r$ against $1/T$ should then yield a straight line with slope $-E(\theta)/R$ and intercept $\ln v(\theta) + n \ln \theta$. In this way $E(\theta)$ can be determined without ambiguity. However, in order to separate $v(\theta)$ and $n$, further assumptions, usually on the value of $n$, are required.

The present simulations are justified by the experimental observation that in many desorption systems $E(\theta)$ and $v(\theta)$ satisfy the compensation effect. Although in principle the formalisms including lateral interactions between adsorbates, as those proposed by Cassuto and King [4], Adams [1] and Zhdanov [15] allow for non-constant pre-exponential factors, they do not seem to lead to a strict compensation effect as exhibited by the systems Ag and Au on Ru(001), W(100) and W(110) in fig. 1. The theory of Zhdanov, for example, predicts that $v$ should vary even when $E$ is constant [15], which would be a violation of the compensation effect.

A qualitative explanation of the compensation effect can easily be given when it is realized that $E$ corresponds to the depth of an interatomic potential, and $v$ to its curvature or steepness. As a deeper potential is automatically also a steeper potential, it is clear that $v$ will increase when $E$ increases. However, for Lennard-Jones or Morse potentials this principle is not equivalent with the mathematical expression of the compensation effect $\ln v = bE + c$. For other explanations of the compensation effect we refer to Clark [10].

In conclusion, several desorption systems including metallic and gaseous adsorbates, exhibit compensation effects between the pre-exponential factor and the activation energy of desorption. Simulated desorption spectra, based on an empirical rate equation for desorption which includes pairwise lateral interactions and a compensation effect, show that direct correlations between the shape of the spectra and the nature of the lateral interactions cannot be made. Thermal desorption spectra should therefore be analysed with procedures which rest on a minimum of further simplifying assumptions about the parameters of the Polanyi–Wigner equation.
Acknowledgement

J.W.N. acknowledges financial support from a Huygens-fellowship granted by the Netherlands Organization for the Advancement of Pure Research (ZWO).

References