Thermal desorption analysis: Comparative test of ten commonly applied procedures

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THERMAL DESORPTION ANALYSIS:
COMPARATIVE TEST OF TEN COMMONLY APPLIED PROCEDURES

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Simulated thermal desorption spectra have been used to test the performance of ten commonly applied analysis procedures for obtaining the correct activation energy, pre-exponential factor and order of desorption, as a function of adsorbate coverage. In general, simplified procedures based on easily accessible features such as peak maximum temperature, peak width and peak shape, yield unreliable results. The so-called complete methods, however, require considerably more effort, but yield results which are in good agreement with the values used as input for the simulated spectra.

1. Introduction

Temperature programmed desorption (TPD) or thermal desorption spectroscopy (TDS) is one of the most frequently employed techniques in surface science and catalysis. After appropriate calibration it can be used to determine surface coverages of adsorbates and to evaluate the activation energy of desorption.

Thermal desorption is usually described in terms of an Arrhenius expression, often called Polanyi–Wigner equation, as:

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

in which \( r \) is the rate of desorption, \( \theta \) the adsorbate coverage, \( t \) the time, \( \nu \) the pre-exponential factor of desorption, \( n \) the order of desorption, \( E \) the activation energy of desorption, \( R \) the gas constant and \( T \) the temperature. \( T \) and \( t \) are related by \( \frac{dT}{dt} = \beta \), in which \( \beta \) is the heating rate [1]. Lateral interactions between adsorbate particles make the desorption parameters coverage dependent. In its most general form, eq. (1) expresses that \( \nu \) and \( E \) can both be a function of coverage, and that \( E(\theta) \) and \( \nu(\theta) \) are unrelated. Very often, however, the presence of a compensation effect has been noted [2,3].

At least ten different procedures have been proposed in the literature for the evaluation of the desorption parameters from TD spectra [4]. The so-called complete methods are based on eq. (1) without further assumption [1,5]. They usually require a collection of desorption traces. Because the application of complete methods is rather involved, many investigators use simplified, approximate methods, which make use of easily accessible spectral features, such as the temperature at which the peak maximum occurs, \( T_m \), peak widths and parameters which reflect the shape of thermal desorption spectra [6–8]. These methods are attractive because they are rapid, and can be applied to a single spectrum.

The purpose of this paper is to compare the performance of complete and approximate analysis procedures on a number of simulated TDS spectra, for which the desorption parameters \( E(\theta) \), \( \nu(\theta) \) and \( n \) are exactly known.

The test results clearly show the limitations of the approximate methods and suggest that complete procedures should be used wherever possible. A small part of this work has appeared recently [9].
2. TDS analysis procedures

We now present a short overview of the most often used procedures for TDS analysis. An excellent review by Falconer and Schwarz gives a detailed description of most of the methods summarized here [4].

2.1. Complete analysis [1]

This procedure which uses a family of thermal desorption curves corresponding to different initial coverages, is based on the rigorous application of the Polanyi–Wigner equation (1). The quintessence of the method is that the coverage is fixed at some value $\theta'$: points corresponding to $\theta'$ are determined on all spectra with initial coverage higher than $\theta'$. An Arrhenius plot of all $\ln r$ versus $1/T$ values for this particular coverage yields $E(\theta')$ from the slope of the plot.

The prefactor follows from the intercept $n \ln \theta' + \ln \nu(\theta')$, provided that the order $n$ is known. For coverages above 0.1, however, the term $n \ln \theta'$ is much smaller than $\ln \nu(\theta')$, and $\nu(\theta')$ can be determined with reasonable accuracy, independent of the order. The complete method implicitly assumes that the temperature dependence of $\nu(\theta)$ can be ignored.

2.2. The Habenschaden–Küppers (HK) or leading edge analysis [5]

This method acknowledges that $\nu(\theta)$ may depend on temperature. In order to fix both $T$ and $\theta$, a relatively small temperature interval is selected at the low temperature, high coverage side of a TD spectrum, in which the variations in $T$ and $\theta$ are insignificant. An Arrhenius plot of this short interval yields a straight line with slope $-E(\theta)/R$ and intercept $n \ln \theta + \ln \nu(\theta, T)$. The advantage of the HK method is that it rests on a minimum number of assumptions (the desorption parameters may even depend on temperature). The disadvantage, however, is that the method uses the leading edge of the thermal desorption spectrum, where the desorption rate is small and where the accuracy is inherently low. Leading edge analysis can be considered as a special case of line shape analysis as described in ref. [1].

2.3. “Arrhenius” plots: $\ln(r/\theta^n)$ versus $1/T$

In this method a spectrum is plotted as $\ln(r/\theta^n)$ against $1/T$ for three values of $n$: 0, 1, 2. The plot corresponding to the correct order should be close to a straight line. The method gives averages of $E$ and $\nu$ over the spectrum from the slope and the intercept of the Arrhenius plot. An example of this method applied on zeroth order desorption spectra has been given by Niemantsverdriet et al. [10].

2.4. Redhead’s peak maximum method [6]

Redhead derived an easily applicable relation between the temperature of the peak maximum $T_m$, the prefactor $\nu$ and the desorption energy $E$. For coverage-independent desorption parameters and first-order kinetics, differentiation of eq. (1) gives

$$E/RT_m = (\nu/T_m)^{1/2} \exp(-E/RT_m).$$

Plots of $E$ against $T_m$ for certain $\nu$ and $T_m$ are almost linear and are approximated by:

$$E = RT_m[\ln(\nuT_m/\beta) - 3.46].$$

Deviations of eq. (2) from the analytically correct expression are within 1.5% provided that $\nu/\beta$ falls between $10^8$ and $10^{13}$ K$^{-1}$. This equation, valid for first order desorption only, is often applied to determine $E$ from a single spectrum. One must however choose a value for $\nu$. The usual choice is $10^{13}$/s. Another equation proposed by Redhead gives a more general relation between the desorption parameters:

$$\nu = (E\beta/RT_m^2)^{n+1} \exp(E/RT_m), \quad \text{for } n > 0.$$  (3)

This equation can be used to determine $\nu$ when $E$ is already known, for example from an alternative method.

2.5. Chan–Aris–Weinberg (CAW) [7]

Another popular method which is based on easily accessible features in the TD spectrum has
been proposed by Chan, Aris and Weinberg. These authors derived equations which express $E(\theta)$ and $\nu(\theta)$ in terms of the peak maximum temperature $T_m$, and the peak width $W$, either at half or at three quarters of the maximum intensity. See fig. 1a for the parameters involved in the definitions.

The equations are:

$$E = RT_m \left[ -1 + \left( \frac{\gamma_{1/2}}{W_{1/2}} + 5.832 \gamma_{1/2} \right)^{1/2} \right],$$

for $n = 1$,

$$E = RT_m \left[ -1 + \left( \frac{\gamma_{3/4}}{W_{3/4}} + 2.353 \gamma_{3/4} \right)^{1/2} \right],$$

for $n = 1$,

$$E = 2RT_m \left[ -1 + \left( \frac{\gamma_{1/2}}{W_{1/2}} + 3.117 \gamma_{1/2} \right)^{1/2} \right],$$

for $n = 2$,

$$E = 2RT_m \left[ -1 + \left( \frac{\gamma_{3/4}}{W_{3/4}} + 1.209 \gamma_{3/4} \right)^{1/2} \right],$$

for $n = 2$,

with $\gamma_{1/2} = T_m/W_{1/2}$ and $\gamma_{3/4} = T_m/W_{3/4}$.

In which $W_{1/2}$ and $W_{3/4}$ are the peak widths at $\frac{1}{2}$ and $\frac{3}{4}$ of the maximum intensity, respectively.

The thus obtained $E(\theta)$ and $\nu(\theta)$ should then be extrapolated to coverage zero to obtain $E_0$ and $\nu_0$. Note that although Chan et al. [7] developed the method for a determination of the desorption parameters at zero coverage only, the method has been used to determine $E(\theta)$ and $\nu(\theta)$ at higher coverages as well [11].

2.6 Heating rate variations

These methods are particularly attractive for studies in which the substrate is saturated with the adsorbate without formation of multilayers, for example in supported catalysts. The method requires a number of spectra corresponding to the same initial coverage, but recorded at different heating rates. A logarithmic plot of either the peak height $I$ or $\beta/T_m^2$ versus $1/T$ gives a straight line with slope equal to $-E/R$. The method implicitly assumes that the fractional coverage left on the surface when the peak maximum is reached, is the same for all heating rates.

2.7 Order plots

A closer inspection of eq. (1) shows that a plot of $\ln \nu$ versus $\ln \theta$ at constant temperature should
Table 1
Predicted values for the skewness parameters of Chan et al. [7] and the shape index of Konvalinka and Scholten [8], for first and second order desorption kinetics

<table>
<thead>
<tr>
<th>Order</th>
<th>Skewness Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>First order</td>
<td>$-18 &lt; x_{1/2} &lt; -15$</td>
</tr>
<tr>
<td>$-11 &lt; x_{3/4} &lt; 10$</td>
<td></td>
</tr>
<tr>
<td>Second order</td>
<td>$3 &lt; x_{1/2} &lt; 5$</td>
</tr>
<tr>
<td>$2 &lt; x_{3/4} &lt; 3$</td>
<td></td>
</tr>
<tr>
<td>$S = 0.76$</td>
<td>$S = 1.46$</td>
</tr>
</tbody>
</table>

yield a straight line with slope $n$, the desorption order, if $E$ and $v$ do not vary with coverage. This method to determine the desorption order requires a family of desorption spectra at differential initial coverages.

2.8. Shape analysis

Several attempts have been made to characterize the asymmetry of a TD spectrum with one parameter, which then serves as an indicator of the desorption order.

The shape index $S$ is defined as the ratio of $\frac{dr}{dT}|_{T_2}$ to $\frac{dr}{dT}|_{T_1}$, where $T_1$ and $T_2$ are the inflection points of the thermal desorption curves, see fig. 1b. According to Konvalinka and Scholten [8], $S$ not only reveals the desorption order but also indicates whether or not readsorption of the desorbed species occurs. Table 1 gives the expected values for first and second order desorption for the case that readsorption does not take place.

A similar approach but based on a differently defined property called skewness parameter was proposed by Chan et al. [7]. The skewness parameter $\chi$ is calculated from the peak maximum temperature $T_m$ and the two temperatures $T'$ and $T''$ at which the rate is at half or at three quarters of the maximum intensity (fig. 1a):

$$\chi = 100 \times \left[ \frac{(T'' - T_m) - (T_m - T')}{(T'' - T')} \right].$$  \hspace{1cm} (10)

First or second order desorption now each correspond to a certain range of values for the skewness parameter, see table 1.

3. Simulated thermal desorption spectra

Spectra have been simulated by solving eq. (1) with a Runge–Kutta method under the assumption that the pumping speed is infinitely high. We will assume that $E$ varies linearly with $\theta$ as $E(\theta) = E_0 - W\theta$ with $E_0 = 100$ kJ/mol and $W = 10$ kJ/mol. This implies that pair-wise repulsive interactions exist between the adsorbed particles. We will furthermore assume that $v$ varies with coverage according to the well known compensation effect: $\ln v(0) = \frac{E(0)}{RT_c} + c$, in which $T_c$ the isokinetic temperature, determines how strongly $v(0)$ varies. Note that $v$ becomes constant for high values of $T_c$. The occurrence of compensation effects in thermal desorption has been discussed elsewhere [2].

![Fig. 2. Simulated thermal desorption spectra for first (left) and second order desorption kinetics (right).](image-url)
Fig. 3. Simulated thermal desorption spectra for initial coverages of 1 monolayer and different heating rates of 0.1, 0.5, 1.0, 5.0 and 10.0 K/s. All other parameters as in fig. 2.

Four different cases will be considered, corresponding to first and second order desorption, each combined with either an almost constant pre-factor \((T_c = \infty)\) or a varying pre-factor \((T_c = 250\) K). The heating rate is 1 K/s. The four sets of spectra are shown in fig. 2.

In order to test the procedures in which the heating rate is varied, spectra as shown in fig. 3 have been used. These spectra correspond to the same \(E(\theta), \nu(\theta)\) and \(n\) as specified above.

### 4. Results

All procedures described above have been applied to the simulated spectra of fig. 2 or 3, in order to determine \(n, E\) and \(\nu\) as a function of coverage.

#### 4.1. Order of desorption, \(n\)

As explained above, four procedures have been described in the literature to derive the order of desorption from thermal desorption spectra. We will test these procedures on the simulated spectra of fig. 2.

Order plots, i.e. desorption isotherms, have been made for all four sets of spectra in fig. 2. The desorption orders as determined from the slopes of the desorption isotherms are shown in fig. 4. This figure shows that it depends on the temperature at which the isotherm is taken whether or not the orders are predicted correctly. For example, fig. 4 shows that an order plot of the first order desorption spectra with a constant pre-exponential, taken at temperatures between 300 and 340 K, i.e. at the high coverage side, suggests that the order is closer to two than to one. However, if the isotherms are constructed from the high temperature sides of the spectra, where the coverages are low, the order comes out correctly for all four cases simulated in fig. 2. The finding that, at higher coverages, the slope of the desorption isotherm may deviate from the true desorption order is in agreement with Wittrig et al. [13]. These
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authors pointed out that order plots may give unrealistic values for the order when $E$ and $v$ depend on coverage.

Hence, desorption isotherms provide a useful means to determine the desorption order, but only if the isotherm is constructed from the high temperature side of the spectra where the coverages are low. A note of caution is appropriate, however, because in practice the high temperature part of a thermal desorption spectrum may easily be perturbed by inadequate pumping speeds.

If the desorption parameters vary only moderately with coverage, a plot of $\ln(r/\theta^n)$ against $1/T$ yields a straight line for the correct order $n$. This procedure is illustrated in fig. 5 for two of the simulated first order spectra of fig. 2. The plots of $\ln(r/\theta^n)$ for $n = 1$ are indeed closer to a straight line than the plots corresponding to $n = 0$ or 2. Hence, this procedure appears useful for determining the desorption order. As fig. 5 shows, the agreement with a straight line improves for spectra with a lower initial coverage.

The skewness parameters introduced by Chan et al. [7] also appear as useful indicators for determining the desorption orders, provided they are used with care. Fig. 6 shows the values of the skewness parameter at half maximum, $\chi_{1/2}$, for all the simulated spectra of fig. 2. Although almost all values of $\chi_{1/2}$ are strictly speaking outside the expected ranges for first and second order, extrapolation of the values to coverage zero indicates the correct order of desorption for all four cases considered. Hence, this method should not be applied on a single spectrum, but becomes useful if a sufficient number of thermal desorption spectra of different initial coverages is available, such that a reliable extrapolation of $\chi_{1/2}$ to coverage zero can be made. We have also tested the performance of the skewness parameter defined at three quarters of the peak maximum intensity, $\chi_{3/4}$ (results not shown) and arrive at very similar conclusions as for $\chi_{1/2}$.

Finally, we have calculated the shape index $S$ for the four monolayer spectra of fig. 2, see table 2. As this table shows, the shape index does not appear to have any diagnostic value. For example,
Table 2
Values of the shape index proposed by Konvalinka and Scholten [8], for the simulated spectra of fig. 2

<table>
<thead>
<tr>
<th>Prefactor</th>
<th>Order</th>
<th>S predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>1</td>
<td>0.76</td>
</tr>
<tr>
<td>Variable</td>
<td>1</td>
<td>0.42</td>
</tr>
<tr>
<td>Constant</td>
<td>2</td>
<td>1.46</td>
</tr>
<tr>
<td>Variable</td>
<td>2</td>
<td>0.80</td>
</tr>
</tbody>
</table>

The fact that the two first order desorption spectra (one with a constant and the other with a non-constant pre-exponential) give a different shape index illustrates clearly that there is no unique relation between the shape of a spectrum and the desorption order. This method can only be used when both the activation energy and the pre-exponential factor of desorption do not depend on coverage. Such situations are not a priori known and occur rarely.

In summary, three methods for determining the order of desorption appear useful. First, the order of desorption can reliably be determined from the slope of desorption isotherms which are constructed from the high temperature (low coverage) side of a family of thermal desorption traces. Second, constructing plots of ln(r/θ^n) versus 1/T for n = 0, 1, 2 and then deciding which choice of n yields the closest agreement with a straight line, also gives a reliable indication of the desorption order. Third, the skewness parameters of Chan et al. [7] can be used in the limit of zero coverage only. The shape index as proposed by Konvalinka and Scholten [8], however, does not have a diagnostic value.

4.2. Activation energy of desorption, E(θ)

The four plots in fig. 7 show E(θ) as determined with the different procedures for TDS analysis. The heavily drawn line represents E(θ) used as input for the simulation. As fig. 7 shows, the complete method and the Habenschaden–Küppers method yield an excellent reproduction of the correct E(θ) values. Only at low coverages small and hardly significant deviations occur, which are mainly due to the limited number of points used in the calculations.

![Fig. 7. Test results on the determination of the activation energy of desorption. The heavily drawn line represents the input values for the simulation.](image-url)
the temperature of the peak maximum are the same for all heating rates, appears to be correct within a few percent.

Determination of $E$ from the slope of $\ln(r/\theta)$ versus $1/T$ plots cannot be recommended. As fig. 5 shows, such plots may deviate significantly from a straight line, even for the correct choice of the order. If we nevertheless determine $E$ from the slope of the best fitting line to the $\ln(r/\theta)$ plot of the monolayer spectrum, we obtain $E = 120$ kJ/mol. The correct value is 90 kJ/mol. Note that the method is not unambiguous as the answer depends on the particular choice of points from the spectrum used to make the $\ln(r/\theta)$ plot. Only in the limit of $\theta \to 0$ the correct activation energy is obtained. Note also that this method becomes equivalent to the leading edge analysis if one uses only the low temperature part of the $\ln(r/\theta)$ plots.

The simple methods, based either on the peak maximum temperature or on the combination of peak maximum and width, perform rather poorly. Application of the Redhead formula (2) requires knowledge of the order of desorption and a more or less arbitrary choice of the pre-exponential factor. The choice made for the data in fig. 7 is the obligatory $10^{13}$/s, which is a factor 10 less than the input value for $v_0$ used in the simulations. The test results in fig. 7 show that, although for the particular choice of $v$ made in this case $E(\theta)$ is nowhere more than 6% off from the true $E(\theta)$, the trend is not correctly reproduced by the Redhead formula: $E(\theta)$ merely follows the peak shift because $v$ is necessarily constant.

The largest deviations of $E(\theta)$ from the correct value are found by applying the Chan–Aris–Weinberg formulas, (4)–(7), as fig. 7 clearly shows. This, however, does not mean that the method is useless. Note that extrapolation of the calculated $E(\theta)$ data to $\theta = 0$ yields the correct activation energy of desorption at coverage zero, $E_0$. Hence, the merit of the Chan–Aris–Weinberg method is that it provides a rapid and reliable determination of $E_0$ when a series of thermal desorption spectra corresponding to different initial coverages is available. Every value $E(\theta)$ for $\theta > 0$, however, is entirely without meaning, as is the trend in $E(\theta)$.

4.3. Pre-exponential factors, $v(\theta)$

Pre-exponential factors have been determined for all four sets of thermal desorption spectra in fig. 2. We only discuss the test result obtained on one case, namely that of first order desorption kinetics and a coverage dependent pre-exponential factor, see fig. 8. The test results obtained with the other sets of simulated spectra are qualitatively similar.

Both the leading edge or Habenschaden-Küppers and the complete analysis reproduce the input values for the pre-exponential factor, as fig. 8 shows. The general formula of Redhead [3] enables one to calculate a pre-exponential factor when the desorption energy is available and other parameters such as the order of desorption, the peak maximum temperature, the heating rate and the coverage are known. We have tested the applicability of these formulas by using the correct input values for the desorption energies. As fig. 8
shows, the general Redhead formula correctly converts these energies into the expected pre-exponential factors.

Pre-exponential factors determined from the intercept of a straight line fitted to plots of \( \ln(r/\theta^n) \) against \( 1/T \) are only correct in the limit of zero coverage. Severe deviations occur at higher coverages: for the plot corresponding to \( n = 1, \theta = 1 \) in fig. 5 we find \( \nu = 10^{16}/s \), whereas the correct value is \( 10^{12}/s \). The values of \( \nu \) determined with this method depend strongly on the choice of points from the spectrum, used to make the \( \ln(r/\theta) \) plot.

Also included in fig. 8 are the pre-exponential factors calculated according to the Chan–Aris–Weinberg formulas, (8) and (9). Although the value of a prefactor at any particular coverage deviates seriously from the true value, extrapolation to coverage zero yields the correct value for the desorption of one isolated adsorbate molecule from the substrate surface. Note that the trend of \( \nu \) with \( \theta \) is not recognized, and that values of \( \nu \) corresponding to coverages higher than zero have no significance.

5. Discussion

The present test of analysis procedures for thermal desorption data shows clearly that the answer obtained from TDS may strongly depend on the way the spectra have been analyzed. Table 3 summarizes the procedures considered in this paper and indicates under which conditions they are applicable.

In general, simplified procedures which purport to derive desorption parameters from easily accessible properties such as a peak maximum temperature, peak width or shape indicator from one single spectrum, perform poorly. Determination of \( E \) and \( \nu \) from a straight line fitted to plots of \( \ln(r/\theta^n) \) against \( 1/T \) cannot be recommended either. The analysis based on variation of the heating rate gives results which are close to the true values. In practice, the deviations are probably acceptable.

Meaningful data on the activation energy and the pre-exponential factor of desorption and their dependence on adsorbate coverage are only obtained with the so-called complete analysis, first

<table>
<thead>
<tr>
<th>Method</th>
<th>Order of desorption</th>
<th>Activation energy of desorption</th>
<th>Preexponential factor of desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desorption isotherms</td>
<td>Limited to high ( T ), low ( \theta ) side of spectra</td>
<td>All ( \theta ); however, high quality data required</td>
<td>In practice for ( \theta ) up to about 0.7 monolayer</td>
</tr>
<tr>
<td>Skewness parameter</td>
<td>Only valid in the limit for ( \theta = 0 )</td>
<td>Only in the limit for ( \theta = 0 ) or for constant ( E, \nu )</td>
<td>In practice for ( \theta ) up to about 0.7 monolayers</td>
</tr>
<tr>
<td>Shape index</td>
<td>Not applicable; valid for constant ( E ) and ( \nu )</td>
<td>Moderately accurate results</td>
<td>High quality data required</td>
</tr>
<tr>
<td>( \ln(r/\theta^n) ) versus ( 1/T ) plots</td>
<td>Works well for ( \theta \leq 0.5 )</td>
<td>Should only be used when ( \nu(\theta) ) is known</td>
<td>Only for ( L ) at ( \theta = 0 ); meaningless results for ( \theta &gt; 0 )</td>
</tr>
<tr>
<td>Complete analysis</td>
<td>In practice for ( \theta ) up to about 0.7 monolayer</td>
<td>Only for ( \theta = 0 ) or for constant ( E, \nu )</td>
<td>In practice for ( \theta ) up to about 0.7 monolayers</td>
</tr>
<tr>
<td>Leading edge analysis</td>
<td>All ( \theta ); however, high quality data required</td>
<td>Moderately accurate results</td>
<td>High quality data required</td>
</tr>
<tr>
<td>Slope of ( \ln(r/\theta^n) ) versus ( 1/T )</td>
<td>Only in the limit for ( \theta = 0 ) or for constant ( E, \nu )</td>
<td>Moderately accurate results</td>
<td>Only in the limit for ( \theta = 0 ) or for constant ( E, \nu )</td>
</tr>
<tr>
<td>Heating rate variations</td>
<td>Moderately accurate results</td>
<td>Only for ( \nu ) at ( \theta = 0 ); meaningless results for ( \theta &gt; 0 )</td>
<td>Only for ( \nu ) at ( \theta = 0 ); meaningless results for ( \theta &gt; 0 )</td>
</tr>
<tr>
<td>Peak maximum temperature</td>
<td>Only for ( \theta = 0 ); meaningless results for ( \theta &gt; 0 )</td>
<td>Useless if reliable value of ( E ) is available</td>
<td>Useless if reliable value of ( E ) is available</td>
</tr>
<tr>
<td>Peak maximum and width</td>
<td>Useless if reliable value of ( E ) is available</td>
<td>Useless if reliable value of ( E ) is available</td>
<td>Useless if reliable value of ( E ) is available</td>
</tr>
<tr>
<td>Redhead relation</td>
<td>Useless if reliable value of ( E ) is available</td>
<td>Useless if reliable value of ( E ) is available</td>
<td>Useless if reliable value of ( E ) is available</td>
</tr>
</tbody>
</table>
described by King [1], or the leading edge analysis described by Habenschaden and Kipper [5]. These methods directly reveal the activation energy of desorption, but need an independent determination of the order of desorption before the pre-exponential factor can be calculated.

The present paper shows that the slopes of desorption isotherms, often called order plots, give a reliable indication of the order, provided the isotherm is constructed from the low coverage side of the desorption spectra. A necessary condition is, however that the pumping speed is sufficiently high to prevent peak broadening. A more rapid but also reliable alternative to determine the order is to calculate skewness parameters as defined by Chan et al. [7] for all spectra in the set and extrapolate the skewness factors to zero coverage. Here one must however be certain that the spectra correspond to only one desorption state, otherwise the skewness parameters loose their meaning. In this case, an order plot at low coverages would still give the correct order for the desorption state prevailing at low coverages.

Fitting spectra as \( \ln(r/\theta^n) \) against \( 1/T \) for \( n = 0, 1, 2 \) and deciding which choice of \( n \) leads to the best agreement with a straight line is also a useful procedure for determining the order.

In general the leading edge analysis has the advantage that it allows for temperature-dependent desorption parameters and that it is applicable for all coverages. The disadvantage however is that the method uses the low temperature, high coverage edge of the thermal desorption peak, where the rate of desorption is low. Hence, spectra of excellent signal-to-noise ratio are required.

The requirement of spectra with excellent signal-to-noise ratio is somewhat less stringent for application of the complete analysis. This method however has the intrinsic disadvantage that the accuracy of the desorption parameters decreases with increasing coverage, simply because the number of spectra that can contribute a pair of \( \ln r, T \) values to an Arrhenius plot decreases with increasing coverage.

A common advantage of the complete and the leading edge analysis is that these methods yield the true coverage dependence of the desorption parameters. All other procedures give the desorption parameters as a function of initial coverage, \( \theta_0 \), that is the coverage at the start of the desorption process. Such data should be considered as an ill-defined average over the coverage range between 0 and \( \theta_0 \).

A few remarks on the test spectra used may be in order. We have simulated our spectra according to a semi-empirical rate expression based on (i) the Polanyi-Wigner equation, (ii) pair-wise repulsive interactions, and (iii) the presence of a compensation effect, i.e. a linear relation between \( r \) and \( E \). As explained in ref. [2] this leads to a semi-empirical expression which describes a number of thermal desorption systems successfully. We stress that application of this formalism in no way limits the value of the test results. For the purpose of this investigation, the important fact is that the simulated spectra in figs. 2 and 3 have desorption parameters which are known at all coverages between 0 and 1 monolayer.

It is interesting to note that the test results for the four different cases considered, namely first or second order and constant or coverage dependent pre-exponential, are qualitatively very similar. The methods are either successful or unsuccessful, irrespective of the case considered.

Finally, in assessing the value of \( E(\theta) \) and \( \nu(\theta) \) data obtained from thermal desorption, one should keep in mind that the Polanyi-Wigner approach has its limitations, for example that all the temperature dependence is in the exponential term. An alternative and preferable procedure to obtain adsorption energies as a function of coverage is to measure adsorption isotherms or isobars under equilibrium conditions, see for example ref. [14]. If one nevertheless chooses TDS, then the tests in this paper show which methods should be considered for analyzing the data and which not.

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References