

DETERMINATION OF THE REACTION ORDER AND ACTIVATION ENERGY FOR DESORPTION KINETICS USING TPD SPECTRA: APPLICATION TO D₂ DESORPTION FROM Ag(111)

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Received 24 July 1989; accepted for publication 12 December 1989

For desorption kinetics which follow the Polanyi–Wigner rate expression, plots of $[\ln(-d\theta/dt) - n\ln(\theta)]$ versus $(1/T)$ obtained from TPD spectra can be used to determine both the reaction order and the desorption activation energy for the desorption kinetics of molecules from surfaces. We present a mathematical justification for this method and apply this method to a wide variety of simulated TPD spectra. The plots are linear for all temperatures when the correct value of the reaction order, n , is chosen. When n is incorrectly chosen, the direction of curvature of the plots yields information which can be used in determining the correct reaction order. Compared to the true value of n , the plots curve upward at high temperature when the trial n is too large, and downward when the trial n is too small. This method of determining the reaction order is most sensitive to the choice of n in the region *near the desorption peak maximum*. We show that the plots are approximately linear for all choices of n at low temperatures and caution others to discontinue using this method over this range of data. We also point out the importance of comparing the measured TPD spectra with computer simulations of TPD spectra using the parameters determined from any analysis method in order to validate the determination of these parameters. In order to illustrate the application of these methods, we reexamine recent TPD data for the desorption of D₂ from Ag(111) [X.-L. Zhou, J.M. White and B.E. Koel, *Surface Sci.* 218 (1989) 201]. The desorption of D₂ from D adatoms chemisorbed on Ag(111) is found to follow second order kinetics, with a desorption activation energy of 10.5 kcal/mol at low D coverage.

1. Introduction

Temperature programmed desorption (TPD) is a powerful technique for determining the kinetics of desorption of molecules from surfaces [1–3]. In principle, each desorption curve in TPD spectra contains information about the rate law for desorption: the reaction order, pre-exponential factor, the activation energy for desorption in the desorption rate constant, and the variation of each of these factors with adsorbate coverage. Many techniques exist for extracting this information. The simplest method is that described by Redhead [1], which requires only the knowledge of the desorption peak maximum temperature in order to determine the activation energy for desorption. The drawback of this method is that the values of the pre-exponential factor and reaction order must be assumed, and this can cause large errors if the assumptions are incorrect. Redhead [1] also de-

scribes a method for determining the reaction order which compares the areas under the TPD curves on either side of the peak maximum. The drawbacks of this method are that a knowledge of the pumping speed of the experimental system is required and the method can only be applied to non-overlapping peaks and systems for which the desorption activation energy is independent of coverage. Another method which has gained popularity is leading edge analysis [4,5]. This technique allows the determination of both the activation energy and the pre-exponential factor (at low coverage). This method gives no information about the reaction order. The activation energy for desorption is independent of the choice of reaction order, but the value of the pre-exponential factor is dependent on the choice of reaction order. Leading edge analysis is a powerful approach but has one drawback in that the TPD data must be of very high quality because only a small initial por-

tion (< 5%) of the spectrum is used over a very narrow range of temperatures and in the region where the signal to noise ratio is the worst. Another well-known method is that proposed by Chan et al. [6] which uses the peak width and peak maximum temperature to determine the activation energy for desorption and the pre-exponential factor. In this method, a skewness parameter is also calculated which provides a test for determination of the reaction order. There are many other methods of TPD analysis that are discussed in an excellent review by Schwarz and Falconer [7].

In this paper we examine a method of analysis that uses a modified Arrhenius plot of the form $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$, where θ is the adsorbate concentration on the surface and $(-d\theta/dt)$ is the desorption rate, to extract the reaction order, n , and activation energy for desorption, E_a . This method has been used previously, for example, to extract E_a [8,9] and both E_a and n [10,11]. A recent paper by Miller et al. [5] also discusses this approach. In this work we present the mathematical justification of the method and present plots of this form obtained for a variety of simulated TPD spectra in order to illustrate the scope and limitations of the method. We are limiting our discussion to the case where pumping speed is high so that readsorption is minimized and to the case of a linear temperature ramp. Finally, we show the utility of this method and the importance of simulation studies using derived desorption parameters by reexamining recent D₂ TPD spectra from Ag(111).

2. Results and discussion

2.1. Mathematical justification

For desorption kinetics which follow the Polanyi–Wigner rate expression [12], we have the following equation:

$$\text{rate} = -\frac{d\theta}{dt} = \nu_n \theta^n \exp\left(-\frac{E_a}{RT}\right), \quad (1)$$

where θ is the adsorbate coverage, n is the reaction order, ν is the pre-exponential factor and E_a

is the activation energy for desorption. For a linear temperature ramp of rate β

$$T = T_0 + \beta t, \quad (2)$$

the rate expression becomes

$$-\frac{d\theta}{dT} = \frac{\nu_n \theta^n}{\beta} \exp\left(-\frac{E_a}{RT}\right). \quad (3)$$

Taking the logarithm of eq. (1) yields:

$$\ln\left(-\frac{d\theta}{dt}\right) = \ln(\nu_n) + n \ln(\theta) - \frac{E_a}{RT}. \quad (4)$$

Rearranging (4) gives:

$$\ln\left(-\frac{d\theta}{dt}\right) - n \ln(\theta) = \ln(\nu_n) - \frac{E_a}{RT}. \quad (5)$$

This expression is linear with respect to $(1/T)$ since ν and E_a vary only slowly with T , and plotting the left-hand side of this expression $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ yields a line with slope $(-E_a/R)$ and intercept $\ln(\nu_n)$. If an incorrect value of n is used in constructing the plots, the expression will retain a term containing θ and the plot will not be linear with respect to $(1/T)$. This can be shown easily by rewriting the left-hand side of (5) to give

$$\ln\left[\left(-\frac{d\theta}{dt}\right)/\theta^n\right] = \ln(\nu_n) - \frac{E_a}{RT}. \quad (6)$$

Substituting for $-d\theta/dt$ from eq. (1) leads to:

$$\ln\left[\nu_n \theta^n \exp\left(-\frac{E_a}{RT}\right)/\theta^n\right] = \ln(\nu_n) - \frac{E_a}{RT}. \quad (7)$$

Choosing an incorrect value for the reaction order, n , leads to the following expression:

$$\begin{aligned} \ln\left[\nu_n \theta^n \exp\left(-\frac{E_a}{RT}\right)/\theta^m\right] \\ = \ln(\nu_n) - \frac{E_a}{RT} + (n - m) \ln(\theta). \end{aligned} \quad (8)$$

Since θ is not linear with respect to T or $(1/T)$, this expression will not be linear with respect to either T or $(1/T)$ for all possible values of T .

Investigation of the behavior of the curves in the plots described above resulting from incorrect choices of reaction order is best done by examining the derivative of the left-hand side of eq. (5) with respect to $(1/T)$. As an example, we will examine the case of first order desorption kinetics

where $n = 1$. Similar derivations can be completed for any value of n .

For convenience we now define a parameter γ so that

$$\gamma = \ln\left(-\frac{d\theta}{dt}\right) - n \ln(\theta). \quad (9)$$

For first order desorption spectra $n = 1$ and $\gamma = \ln(\nu_1) - E_a/RT$ from eq. (5). Thus,

$$\frac{d\gamma}{d(1/T)} = -\frac{E_a}{R}, \quad (10)$$

which is a constant and is simply the slope of the plot of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ for all values of T . If n is incorrectly assumed to be 0, then

$$\frac{d\gamma}{d(1/T)} = -\frac{E_a}{R} + \frac{\nu_1 T^2}{\beta} \exp\left(-\frac{E_a}{RT}\right). \quad (11)$$

The explicit temperature dependence of the right-hand side of this expression means that the plot of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ will not be linear for large values of T . Since the second term is small for small T , the slope of the function will be $(-E_a/R)$ for small T . Furthermore, the second term will be positive for all values meaning that the slope will increase with increasing temperature. An increase in the derivative means that the plot of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ with n incorrectly assumed to be zero for first order desorption kinetics will curve downward.

If n is incorrectly assumed to be 2, then

$$\frac{d\gamma}{d(1/T)} = -\frac{E_a}{R} - \frac{\nu_1 T^2}{\beta} \exp\left(-\frac{E_a}{RT}\right). \quad (12)$$

Again, the temperature dependence means that the plot will not be linear for all values of T . The slope of the function again will be $(-E_a/R)$ for small T . Furthermore, the second term will be negative for all values meaning that the slope will decrease with increasing temperature. A decrease in the derivative means that the plot of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ with n incorrectly assumed to be 2 will curve upward for first order desorption kinetics.

This proof can be extended for all possible values of n . A plot of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ will curve downward as T increases

$(1/T)$ decreases) for any value of n greater than the correct value that actually describes the desorption kinetics. The plot will curve upward for any chosen value of n which is smaller than the correct value. For small values of T , the curves for all choices of n will be approximately linear and will have the same slope.

Applying this method to experimental TPD data requires careful thinking about the effect of unit conversion on the analysis technique. The derivation until now has assumed compatible units for θ and $(-d\theta/dt)$. This is not the case for the raw data obtained in TPD. To test the effect of an arbitrary scale factor on the plot of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ we can rewrite (5) including an arbitrary multiplicative factor, σ , as

$$\gamma = \ln\left(-\frac{d\theta}{dt}\right) - n \ln(\sigma\theta) = \ln\left[\left(-\frac{d\theta}{dt}\right)/(\sigma\theta)^n\right]. \quad (13)$$

For a correctly described desorption order, γ reduces to

$$\gamma = \ln\left(\frac{\nu_n}{\sigma^n}\right) - \frac{E_a}{RT}. \quad (14)$$

This expression is linear with $(1/T)$ and the slope of a plot of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ is unaffected by the factor σ . Therefore, an arbitrary multiplicative factor has no effect on our ability to extract the desorption activation energy. A consequence of this observation is that the choice of units for θ and $(-d\theta/dt)$ is completely arbitrary. No matter what units are chosen, the plot for the correct value of n will be linear with a slope of $(-E_a/R)$. The intercept, however, is affected by the factor σ and is not immune to the effects of changing units. As a result, care must be taken to convert the units of the measured signals in TPD to the units for both rate (molecule $\text{cm}^{-2} \text{s}^{-1}$) and coverage (molecule cm^{-2}), for determining frequency factors. In the event that the value of n chosen does not correctly describe the desorption kinetics being modelled, σ serves only to displace the curves relative to one another on the $[\ln(-d\theta/dt) - n \ln(\theta)]$ axis without altering their respective shapes. This can be of great utility since the curves can be moved such that their linear regions overlay each other. We have found that

positioning the curves in such a manner can be a tremendous aid in determining the direction of curvature for the plots using experimental TPD data which contains noise.

As a final point concerning the application of the method to experimental TPD data, we note the importance of accurately determining the desorption rate by proper background subtraction. Errors that result from this uncertainty have been discussed [3].

2.2. TPD spectra simulations

To show the feasibility and limitations of using plots of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ to obtain the values of n and E_a for desorption processes, we have performed numerous numerical simulations of TPD data to produce computer generated data which has no noise, has a wide dynamic range, and the activation energy, pre-exponential, and reaction order can be forced analytically to be completely independent of cover-

age. We simulated TPD spectra for zero order, half order, first order and second order kinetics. We chose a value of $E_a = 30$ kcal/mol for the desorption activation energy for all cases, and reasonable values for the pre-exponential factor given by $(kT/h)/N^n$ [13]: $\nu_0 = 1.0 \times 10^{28}$ molecule/cm² · s, $\nu_{1/2} = 3.2 \times 10^{20}$ molecule^{1/2}/cm · s, $\nu_1 = 1.0 \times 10^{13}$ s⁻¹, and $\nu_2 = 1.0 \times 10^{-2}$ cm²/molecule · s. The coverage was chosen to be 1 ML ($= 1.5 \times 10^{15}$ atoms/cm²). These simulated curves are shown in fig. 1. For these simulations we have chosen E_a to be independent of coverage. The method discussed here is still valid if E_a is coverage dependent and in a separate paper [14], we will present an extension of this method which enables the coverage dependence of E_a to be determined.

The spectra shown in fig. 1 were integrated to determine the remaining coverage at each temperature and plots of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ were made for each simulated TPD spectrum. We chose n to be 0, 1/2, 1, and 2 so that we

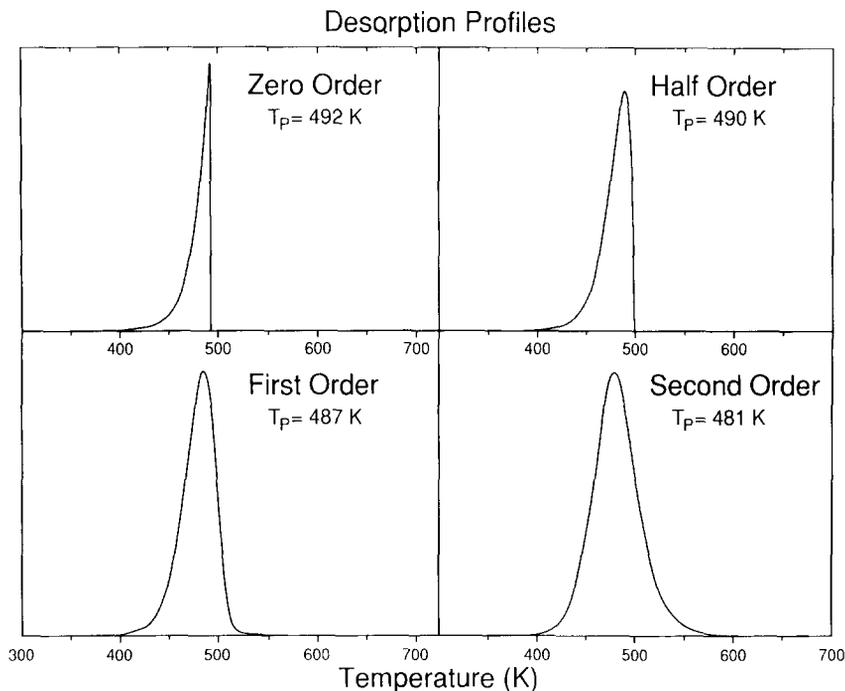


Fig. 1. Computer simulations of TPD spectra calculated for $E_a = 30$ kcal/mol with $\beta = 5$ K/s for zero, half, first, and second order kinetics. The values used for the pre-exponential factor were $\nu_0 = 1.0 \times 10^{28}$ molecule/cm² · s, $\nu_{1/2} = 3.2 \times 10^{20}$ molecule^{1/2}/cm · s, $\nu_1 = 1.0 \times 10^{13}$ s⁻¹, and $\nu_2 = 1.0 \times 10^{-2}$ cm²/molecule · s. The coverage used was 1 ML ($= 1.5 \times 10^{15}$ atoms/cm²).

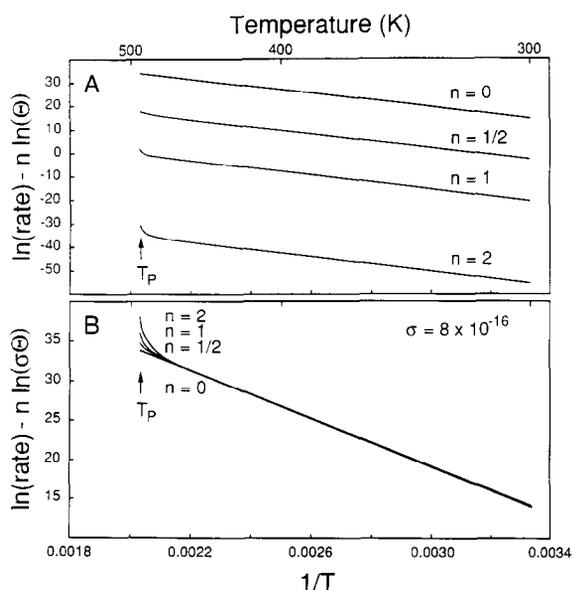


Fig. 2. Plots of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ for simulated TPD spectra with zero order desorption using $n = 0, 1/2, 1,$ and 2 . Panel A shows plots using absolute units of rate (molecules/cm²·s) and coverage (molecules/cm²), and panel B shows the same data plotted in arbitrary units of rate and coverage.

could see the effect of choosing the incorrect value of n in each case. Fig. 2A shows plots of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ for the simulated zero order data for $n = 0, 1/2, 1,$ and 2 for the rate and coverage expressed in absolute units. Fig. 2B shows plots for the same simulated TPD spectrum, but using arbitrary units for rate and coverage. All of the plots can be made to overlap at small values of T making it easier to see the deviation from linearity for incorrect choices of n .

Fig. 2 shows that only the plot for $n = 0$ is linear. The slope of this plot gives an activation energy for desorption of 30 kcal/mol, the value used for E_a in the simulation. The curve for $n = 2$ deviates severely but the curves for $n = 1/2$ and $n = 1$ are only slightly curved. For actual TPD data obtained in experiments, which will have some level of noise this curvature could possibly be obscured. An important point to note is that all choices for the reaction orders give approximately linear plots up until very near the peak maximum. If only the leading edge of experimental data were

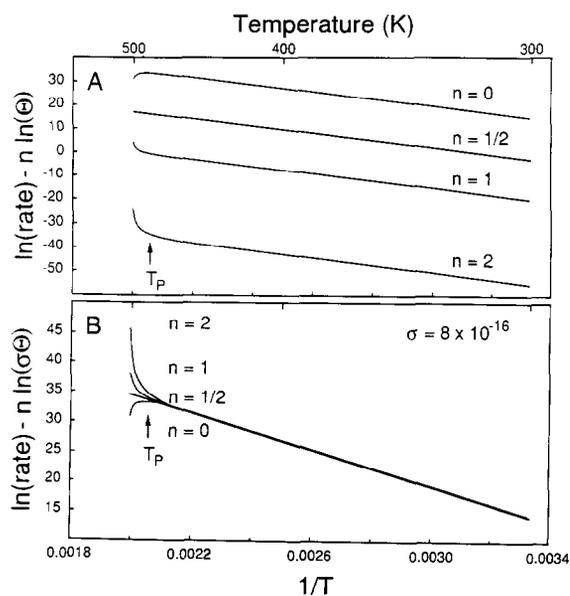


Fig. 3. Plots of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ for simulated TPD spectra with half-order desorption using $n = 0, 1/2, 1,$ and 2 . Panel A shows plots using absolute units of rate (molecules/cm²·s) and coverage (molecules/cm²), and panel B shows the same data plotted in arbitrary units of rate and coverage.

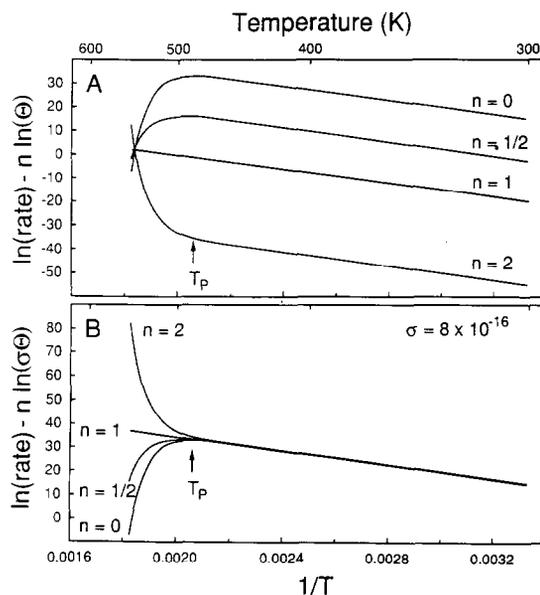


Fig. 4. Plots of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ for simulated TPD spectra with first order desorption using $n = 0, 1/2, 1,$ and 2 . Panel A shows plots using absolute units of rate (molecules/cm²·s) and coverage (molecules/cm²), and panel B shows the same data plotted in arbitrary units of rate and coverage.

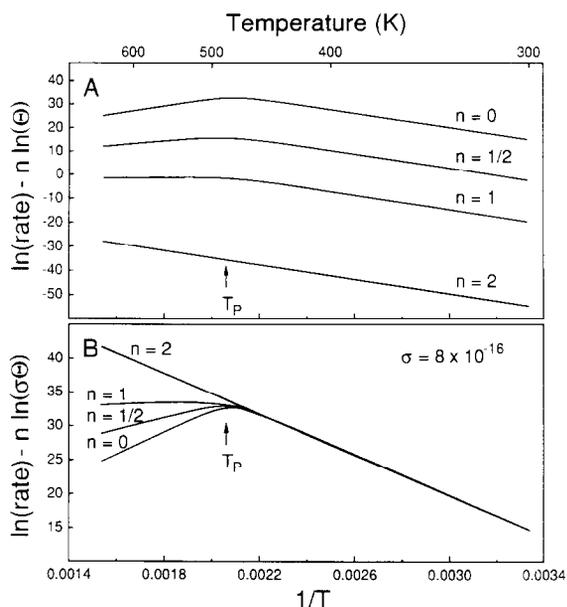


Fig. 5. Plots of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ for simulated TPD spectra with second order desorption using $n = 0, 1/2, 1,$ and 2 . Panel A shows plots using absolute units of rate (molecules/cm²·s) and coverage (molecules/cm²), and panel B shows the same data plotted in arbitrary units of rate and coverage.

to be used, the plot would be linear for any choice of n . Thus, this method cannot be used in this manner to determine the value of n . Plotting only the leading edge in this fashion, however, will allow determination of E_a . Plotting data from the entire desorption spectrum allows determination of both the reaction order and E_a . As predicted in the previous section, the incorrect choices of n curve upward after the peak maximum.

Figs. 3–5 show plots of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ for the simulated TPD spectra shown in fig. 1 that are described by half, first, and second order kinetics, respectively. The same caution given above for data described by zero order applies to that for half-order kinetics, i.e., the deviation from linearity for incorrect choices of n is not highly pronounced, especially for the choices $n = 0$ or 1 . This is due in part to the large asymmetry of the half-order and zero order desorption peaks; once T rises above the peak maximum, the rate quickly drops to zero. Plots of data described by first and second order kinetics show marked

deviations from linearity when the incorrect value of n is chosen, particularly in the region surrounding and above the peak maximum. Again, for all reaction orders, the plots are linear up to near the peak maximum, irrespective of the true reaction order.

As mentioned in the preceding section, the incorrect values of n have a predictable curvature. We show this graphically in fig. 6 where we have plotted the derivative of $[\ln(-d\theta/dt) - n \ln(\theta)]$ with respect to $(1/T)$ versus $(1/T)$ of a simulated desorption spectrum with first order kinetics. For $n = 1$, the derivative plot is a horizontal line and for $n = 0$, the derivative increases, predicting that the plot of $[\ln(-d\theta/dt) - n \ln(\theta)]$ will curve downward (as seen in fig. 4). Note that all of the lines overlap the $n = 1$ line for large values of $(1/T)$ (small T), indicating that all plots have the same slope over this temperature region.

Additionally, we have examined the effect of noise on the ability to distinguish between chosen values of n . Using the same conditions of $E_a, \nu,$

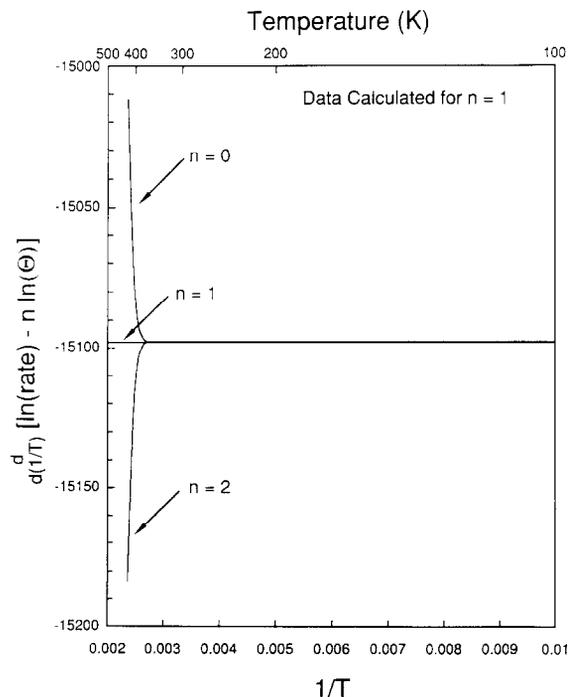


Fig. 6. Plot of $d[\ln(-d\theta/dt) - n \ln(\theta)]/d(1/T)$ versus $(1/T)$ for a calculated TPD spectrum described by first order desorption kinetics for trial values of $n = 0, 1,$ and 2 .

and coverage as given in fig. 1 for the first order desorption trace, we added random noise to the spectrum at a level of up to 10% p-p of the maximum signal ($S/N = 10$). Panel A of fig. 7 shows the simulated first order TPD spectrum at this noise level. Panel B shows plots of $[\ln(-d\theta/dt) - n \ln(\theta)]$ for the noisy TPD data shown in panel A and for all choices of n . This shows that the method is sensitive enough to distinguish the true reaction order even when this high level of noise is present.

We have also examined the ability of this method to distinguish the kinetic parameters for overlapping TPD peaks. There are, of course, endless possibilities for the choice of conditions for the overlapping peaks. For illustration, we used various combinations of two states described by first order kinetics with constant E_a and ν . All of the simulations used $\nu = 10^{13} \text{ s}^{-1}$, $\beta = 5 \text{ K/s}$ and equal initial coverages in the two states. Fig. 8A

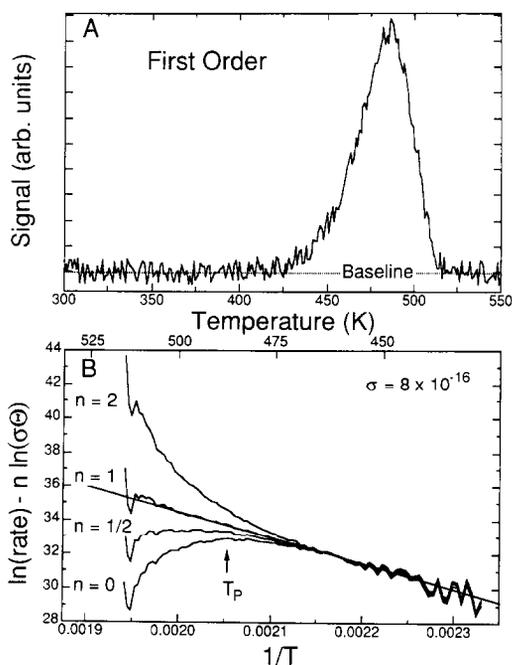


Fig. 7. Panel A: simulated TPD spectrum for $E_a = 30 \text{ kcal/mol}$, $\nu_1 = 1.0 \times 10^{13} \text{ s}^{-1}$, $\theta = 1 \text{ ML}$ and $\beta = 5 \text{ K/s}$. Noise level is about 10% of the peak maximum. Panel B: plot of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$ for all choices of n . The line indicates the best fit to $n = 1$ and yields $E_a = 30 \text{ kcal/mol}$.

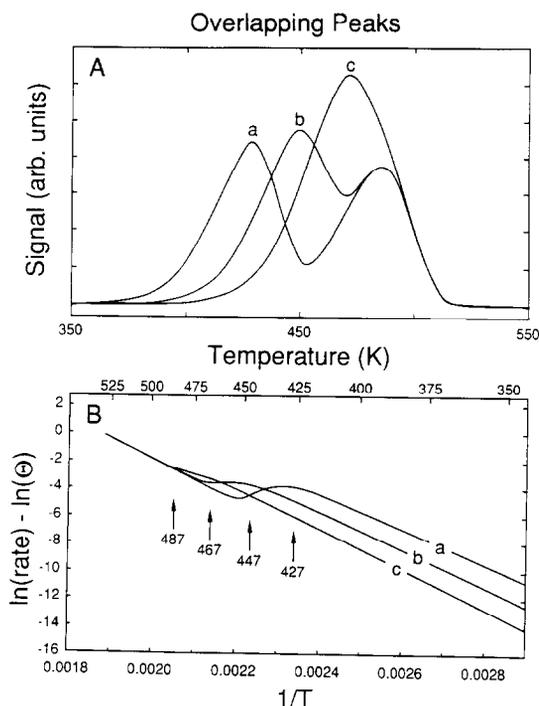


Fig. 8. Panel A shows TPD spectra for three cases of overlapping first order desorption peaks: (a) peaks at 487 K ($E_a = 30 \text{ kcal/mol}$) and 467 K ($E_a = 28.67 \text{ kcal/mol}$), (b) peaks at 487 and 447 K ($E_a = 27.57 \text{ kcal/mol}$), and (c) peaks at 487 and 427 K ($E_a = 26.33 \text{ kcal/mol}$). All calculations used $\nu = 10^{13}$, $\beta = 5 \text{ K/s}$ and equal initial coverages in the two states. Panel B: plots of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $1/T$ for the calculated desorption profiles shown in A.

shows the TPD spectra for three cases of overlapping first order TPD peaks: (a) peaks at 487 K ($E_a = 30 \text{ kcal/mol}$) and 467 K ($E_a = 28.7 \text{ kcal/mol}$), (b) peaks at 487 and 447 K ($E_a = 27.6 \text{ kcal/mol}$), and (c) peaks at 487 and 427 K ($E_a = 26.3 \text{ kcal/mol}$). Fig. 8B shows the plots of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $1/T$ for the calculated desorption spectra shown in 8A. In each case, the plots show two linear regions with an intermediate curved region. The curved region is near the peak maxima and is sharpest for the low temperature peak. The slopes of the two linear regions each give the correct value of E_a for the corresponding TPD peak. This analysis indicates that in many cases it may be possible to extract E_a in the case of overlapping peaks, particularly when

the peaks are fairly well separated. Even the value of n for the high temperature state can probably be determined even for overlapping TPD peaks.

2.3. Experimental data: D_2 desorption from Ag(111)

Recently Zhou et al. [11] have reported TPD spectra for the desorption of H_2 and D_2 from clean and Cl-covered Ag(111). The authors report that the desorption of D_2 from Ag(111) follows half-order kinetics. This determination was made from a plot of $[\ln(-d\theta/dt) - n \ln(\theta)]$ for the leading edge of the TPD data which was linear for $n = 1/2$. As we have seen in the previous sections, for small values of T (the leading edge of the desorption trace) plots of this kind are approximately linear even for the incorrect choices of n . We have reanalyzed the data from fig. 1b in ref. [11] corresponding to $\theta = 0.36$ (relative to $\theta_{\text{sat}} = 1$), in the region around the peak maximum in order to determine if the reaction is indeed well described by half-order kinetics. We chose to analyze this low coverage since it is free from complications arising from an overlapping peak which grows in at higher coverages.

Fig. 9 shows the TPD data for $\theta_D = 0.36\theta_{\text{sat}}$ (from fig. 1b in ref. [11]) plotted using various choices of n . The data surrounding the desorption peak maximum was used since this region is the most sensitive to the choice of n . Fig. 9 clearly shows that only the plot for $n = 2$ is linear, and the slope of this plot gives $E_a = 10.5$ kcal/mol. The other choices of n ($n = 0, 1/2, 1$) have a marked curvature in the predicted direction for incorrect choices of n if the desorption kinetics were truly second order. Clearly a misleading result is obtained by using only the leading edge of the TPD spectrum. We note that second order kinetics have also been observed for the desorption of H_2 from Au(111), with kinetic parameters $E_d = 3$ kcal/mol, $\nu_2 = 1 \times 10^{-10}$ cm²/molecules · s, and the desorption peak maximum occurring at 110 K [15].

As an independent check on the validity of this method, we have simulated TPD spectra using the parameters determined from fig. 9 as a starting point in modeling the TPD spectra. Fig. 10 shows computer simulations compared with experimen-

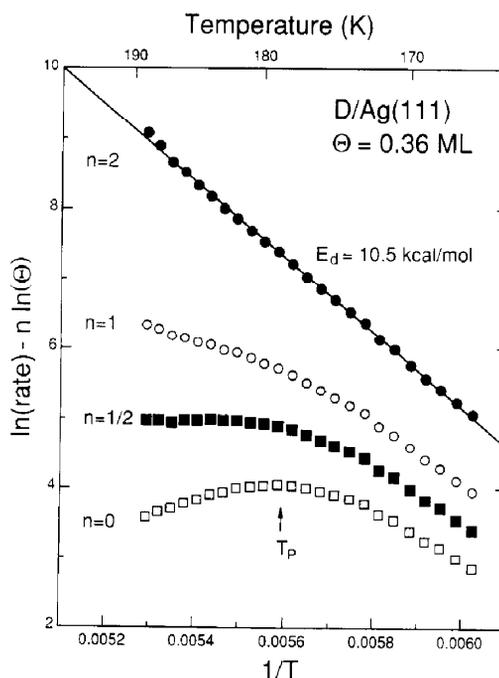


Fig. 9. Reaction order plot for deuterium desorption from Ag(111) for $\theta = 0.36\theta_{\text{sat}}$ [11]. The line is the least-squares fit through the data points and from the slope gives a value of 10.5 kcal/mol for E_d .

tal data for $\theta = 0.36\theta_{\text{sat}}$. Excellent agreement with the experimental data is obtained with $E_a = 10.5$ kcal/mol and $\nu_2 = 1 \times 10^{-2}$ cm²/molecule · s for second order desorption kinetics, i.e., $n = 2$. Fig. 10 also shows the computer simulation compared with the experimental data for $\theta = 0.74\theta_{\text{sat}}$. Good agreement is obtained in this case with $E_a = 11.5$ kcal/mol and $\nu_2 = 1 \times 10^{-2}$ cm²/molecule · s for second order desorption kinetics. The experimental trace is simulated very well except on the low temperature side where there is a contribution from a low temperature shoulder which begins to grow in at this coverage. This low temperature shoulder is seen more clearly in fig. 1c of ref. [11].

Fig. 10 also shows computer simulations using half-order reaction kinetics using the values reported by Zhou et al. [12] and a reasonable pre-exponential factor for half-order desorption kinetics of $\nu_{1/2} = 3.2 \times 10^{20}$ molecule^{1/2}/cm · s. The simulated spectra using half-order kinetics do not match either the shape or position of the experi-

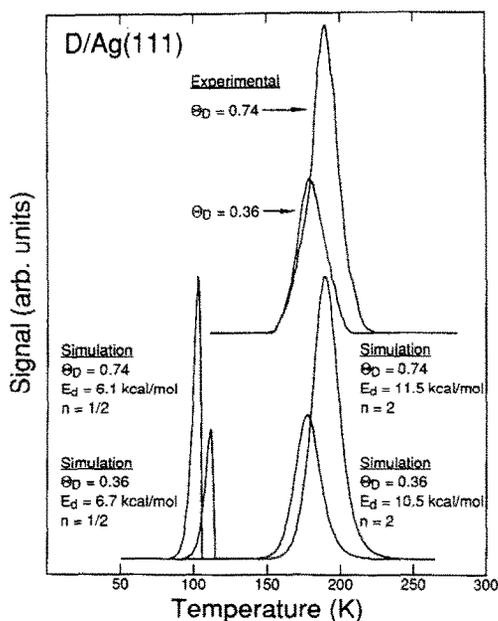


Fig. 10. Comparison of experimental TPD spectra [11] at coverages of $\theta = 0.36\theta_{\text{sat}}$ and $0.72\theta_{\text{sat}}$ (top traces) and computer simulations (bottom traces). The two simulation traces at lower left were obtained using the kinetic parameters in ref. [11]. The two simulation traces at lower right were obtained using the kinetic parameters determined by our analysis.

mental spectra. Furthermore, the simulation shows a shift of the peak maximum to lower temperatures with increasing coverage. This is opposite to the shift observed in the experimental data. The value of E_a used in the simulation is clearly too low to predict the peak maximum of the experimental data. In order to simulate the experimentally observed peak maximum using half-order desorption kinetics, values of $E_a = 10.7$ kcal/mol (rather than the value of 6.8 kcal/mol determined in ref. [11]) and $\nu_{1/2} = 1.0 \times 10^{14}$ molecule^{1/2}/cm²·s are required. This value of the pre-exponential factor required for a reasonable fit to the experimental data is 6 orders of magnitude lower than the expected pre-exponential factor given by $(kT/h)/N^n$. Comparisons of these simulations give further evidence that our reaction order method discussed herein has correctly determined n and E_a . These results clearly show how important it is to use the region of TPD data around the peak maximum in order to determine the reaction order by this method of data analysis.

The importance and utility of computer simulation of TPD spectra using extracted parameters is also clearly indicated.

3. Conclusion

We have shown that TPD data can be used to correctly predict desorption reaction orders from plots of $[\ln(-d\theta/dt) - n \ln(\theta)]$ versus $(1/T)$. It is necessary to use the entire range of data (particularly the region about the peak maximum) in order to correctly determine the reaction order. All choices of n should be plotted since the direction of curvature of the plots constructed using the incorrect values of n provides additional data useful for the determination of the correct reaction order. In the application of this method chosen for illustration here, we have shown that the desorption of D_2 from Ag(111) is described well by second order kinetics with an activation energy near 11 kcal/mol. This analysis is confirmed by computer simulation of the experimental TPD spectra.

Acknowledgement

Acknowledgement is made to the US Department of Energy, Office of Basic Energy Science, Chemical Sciences Division for partial support of this work. M.E.J. gratefully acknowledges support from an Arizona State Research Institute Postdoctoral Fellowship.

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