



MAX-PLANCK-GESELLSCHAFT



Lecture WS 2002/2003

**Modern Methods in Heterogeneous Catalysis Research:
Theory and Experiment**

Thermal analysis - TDS

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TDS (thermal desorption (mass) spectroscopy)

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TPD (thermal programmed desorption)

Literature:

- R.I. Masel, Principles of adsorption and reaction on solid surfaces, Wiley, New York (1996).
J.W. Niemantsverdriet, Spectroscopy in catalysis, Wiley-VCH, Weinheim (2000).
K. Christmann, Surface physical chemistry, Steinkopff, Darmstadt (1991).
M. Henzler, W. Göpel, Oberflächenphysik des Festkörpers, Teubner, Stuttgart (1991).

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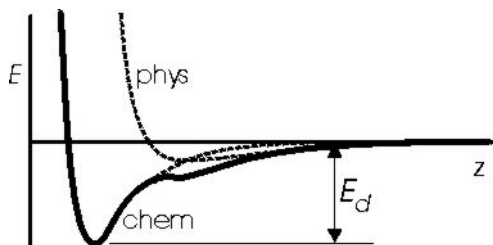
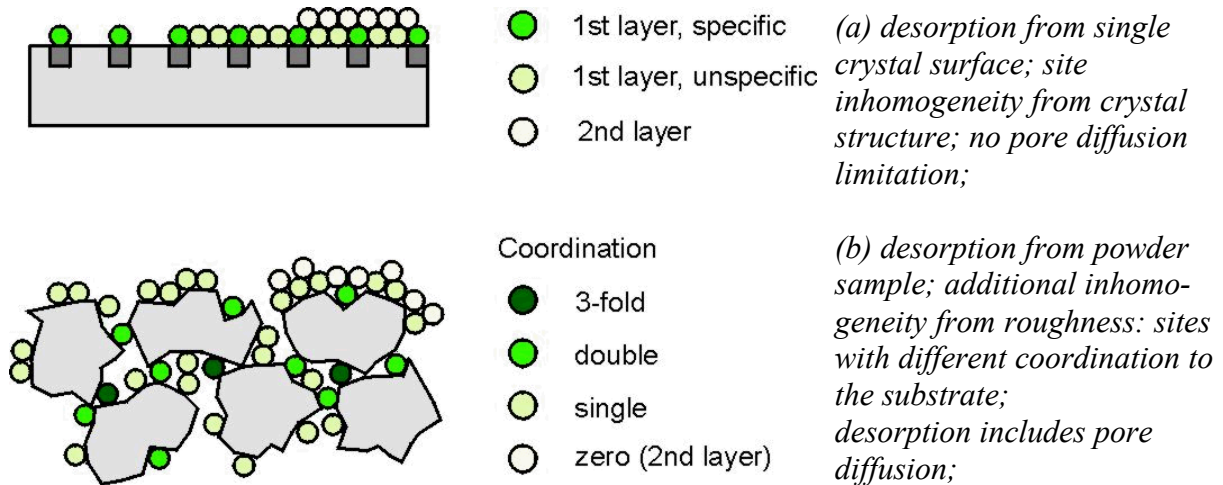
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1. Idea, desorption, experimental, example

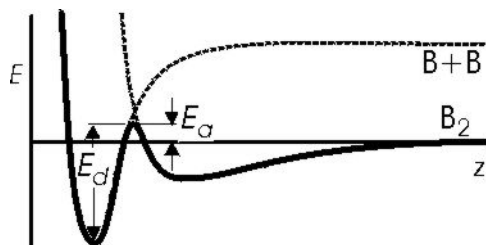
Idea: Adsorbed particles with different E_d (energetics) and n , n (kinetics) will desorb at different T .

Adsorb gas at low T, run a T-ramp, look what desorbs at which T.

Desorption from “simple” and “complex” samples

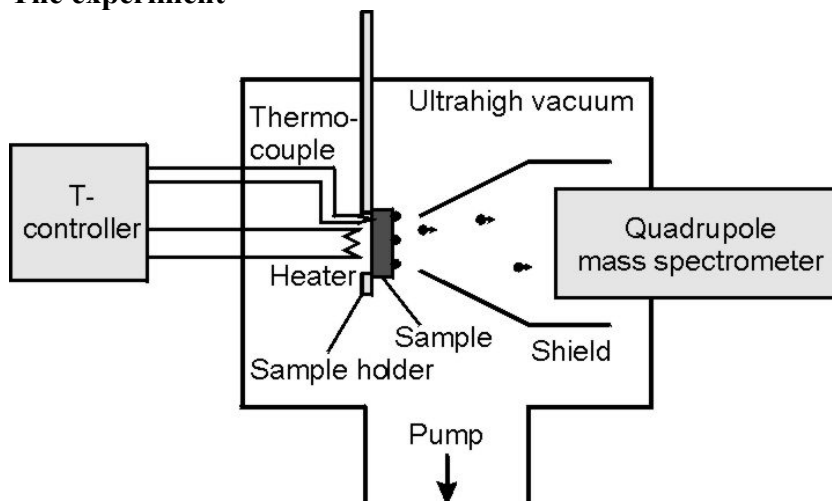


Potential curves for desorption of an undissociated particle: physisorption, chemisorption and sum curve.



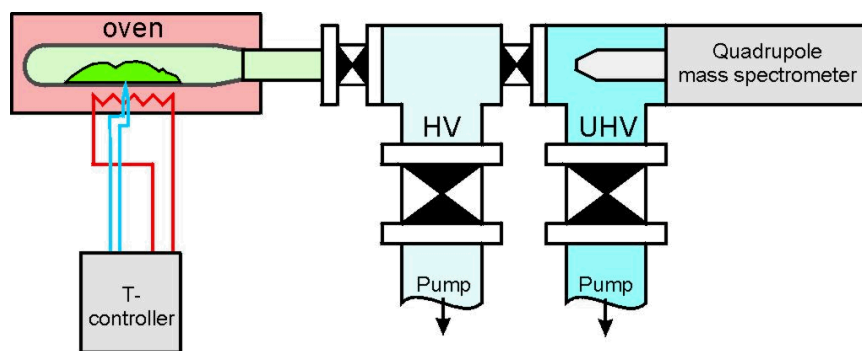
Potential curves for activated recombinative desorption of a dissociated particle: The activation energy $E_d > DH_{ad}$

The experiment



TDS setup, schematic.

The shield should prevent particles from the sample holder to reach the QMS; the pumping speed must be sufficient to suppress readsorption; measurement of the real surface T is not trivial; heat conductivity problems may arise for non-metallic samples.

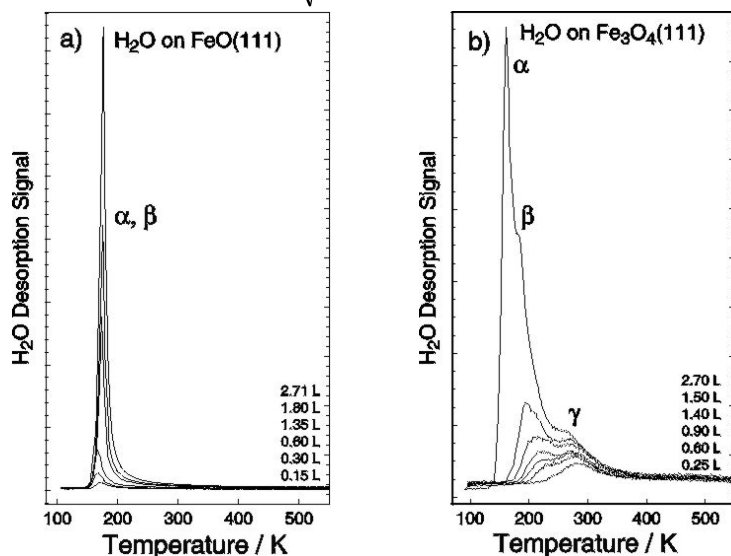


TDS setup for powder samples, schematic

Example: H₂O desorption from FeO(111) and Fe₃O₄(111)

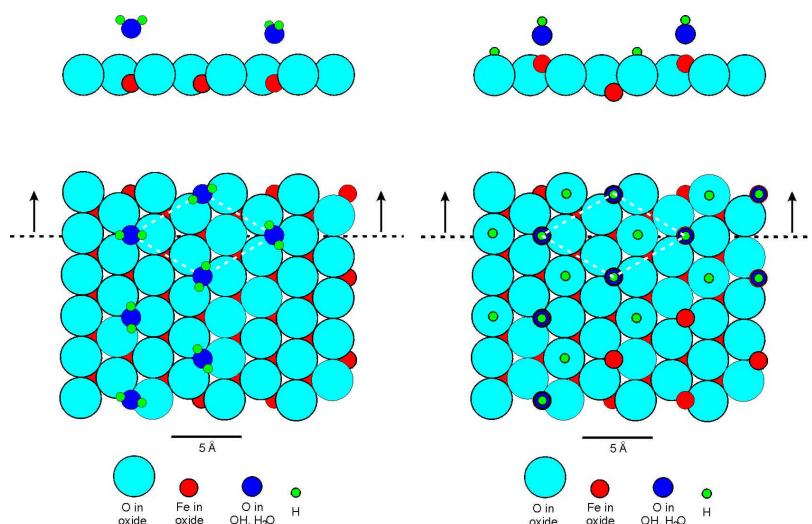
Exposures are often given in Langmuir units. 1 L = 10⁻⁶ Torr s or 1.33x10⁻⁶ mbar s. If the sticking coefficient is 1, it corresponds roughly to 1 ML. The exact value of the exposure e is:

$$e = 2.63 \cdot 10^{22} \frac{p t}{\sqrt{M T}}, \quad (\text{cm}^{-2}) \quad p \text{ in mbar, } t \text{ in sec, } M \text{ in g/mol, } T \text{ in K.}$$



TD-traces for desorption of H₂O from (a) FeO(111) and (b) Fe₃O₄(111). While a small initial peak shift on FeO suggests sequential desorption of physisorbed b-water and condensed a-water, a more tightly bound chemisorbed g-species saturates first on Fe₃O₄. Exposure at 100 K, parameter: exposure in Langmuir units.

(Y. Joseph et al. Chem. Phys. Lett. 314 (1999) 195)



Structure and models for the most tightly bound species: Left: physisorbed b-water on almost inert O-terminated FeO(111);

Right: g-water/Fe₃O₄(111), bound dissociatively with OH to acidic surface Fe sites, H to basic O-sites.

Besides TDS, mainly LEED, STM, UPS, XPS were used to derive these models.

(Y. Joseph et al. J. Phys. Chem. 104 (2000) 3224)

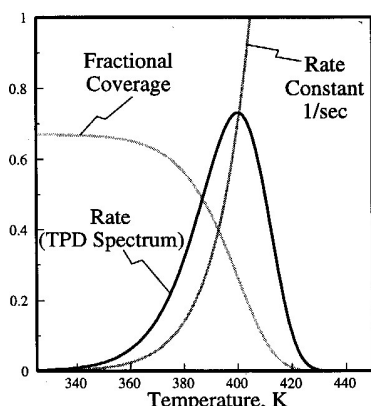
2. Coverage determination, site occupation and warnings

Features (peaks, shoulders) in TDS traces give a suggestive impression of the number of inequivalent adsorption sites which are occupied sequentially. The total area under a TDS trace is proportional to the initial coverage (if everything really desorbs). The area under individual peaks (if separable) gives the occupation of the corresponding sites. This is an important method for determination of (relative) coverages. Absolute coverages are usually deduced from saturation coverages which are ascribed to certain adsorbate configurations.

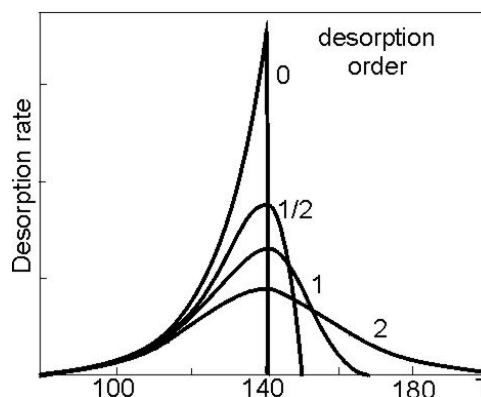
Warnings:

TDS shows you only what is going off the surface. It does not show you what is left. Often, adsorbates decompose irreversibly and eventually form carbonaceous deposits. The sample is exposed at a low temperature where the desorption rate is negligibly small. Often adsorbate mobility is insufficient to fill sequential adsorbate states really sequentially.

3. Desorption order



Coverage, rate constant and desorption rate. $Q_0=0.67$, $n=1$, $n=10^{13} \text{ s}^{-1}$, $b_H=10 \text{ K/s}$, $E_d=100 \text{ kJ/mol}$. (Masel fig. 7.11)



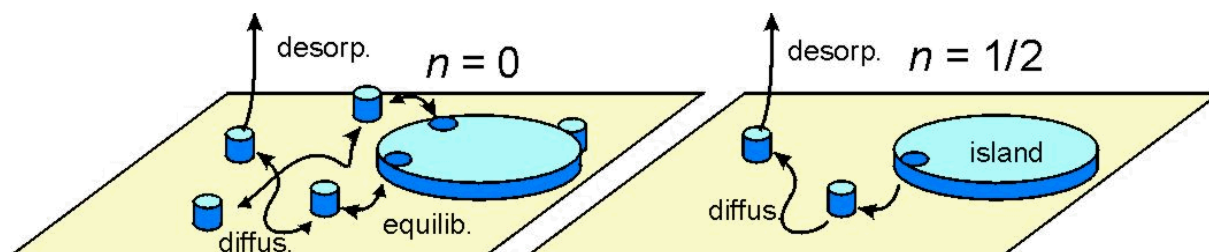
Shape of desorption traces for different desorption orders. (D. Pöss, Diss., TU Berlin (1980).)

The desorption rate is given by:

$$r_d = -\frac{\sigma_A d\Theta_r}{dt} = v_n \sigma_A^n \Theta_r^n \exp(-E_d/kT)$$

E_d : activation energies for adsorption and desorption; S_A : density of adsorption sites cm^{-2} ; $Q_r=Q/Q_{sat}$: relative coverage ($0 < Q_r < 1$); n_n : the frequency factor for desorption order n ; n : order of desorption reaction.

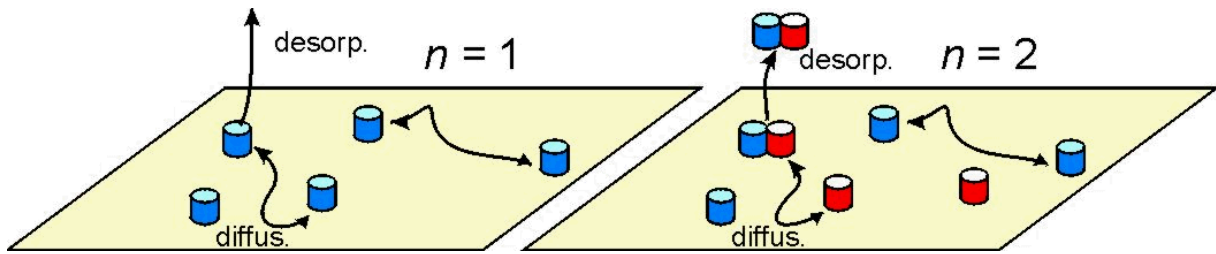
For practical reasons, I divide the total coverage Q into $Q = Q_r S_A$.



Left: 2D gas with very fast exchange and equilibration with islands (2D vapor pressure in equilibrium with 2D fluid): Desorption rate does not depend on Q , as long as islands are left; desorption order $n=0$. The same desorption order is observed for sublimation of thick condensed layers.

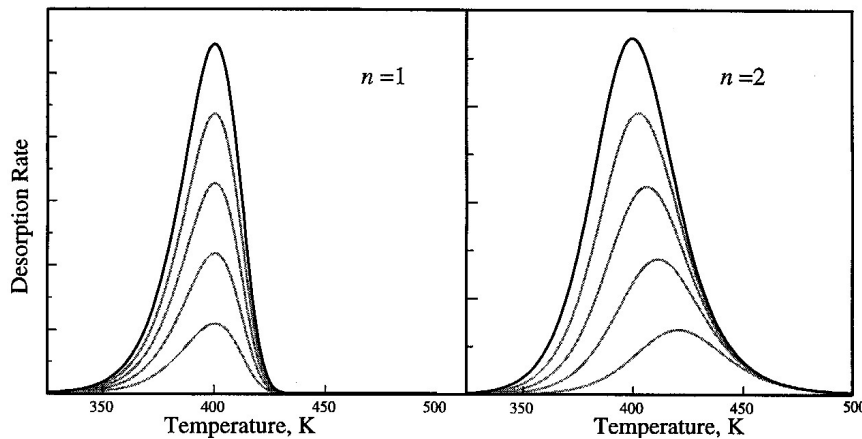
Right: The desorption rate is proportional to the circumference of the islands and thus

proportional to $Q^{1/2}$; desorption order $n=1/2$.



Left: Molecular desorption, mobile or immobile adsorbate; desorption rate proportional to Q ; desorption order $n=1$.

Right: Associative desorption, at least one of both species must be mobile; desorption rate proportional to Q^2 ; desorption order $n=2$.



TDS 1st and 2nd order, for $Q_0=0.2, 0.4 \dots 1.0$, $n=1$, $n=10^{13} \text{ s}^{-1}$, $b_H=10 \text{ K/s}$, $E_d=100 \text{ kJ/mol}$.
(Masel fig. 7.12)

4. Redhead's analysis (P.A. Redhead, Vacuum 12 (1963) 203)

The desorption rate is:

$$r_d = -\frac{\sigma_A d\Theta_r}{dt} = v_n \sigma_A^n \exp(-E_d/kT) \Theta_r^n.$$

Linear temperature ramp:

$$T = T_0 + b_H t.$$

Combining this yields:

$$\frac{r_d}{b_H \sigma_A} = -\frac{d\Theta_r}{dT} = \frac{n_n}{b_H} \Theta_r^n \exp(-E_d / RT),$$

$$\frac{E_d}{RT_p} = \ln\left(\frac{n_n T_p n \Theta_p^{n-1}}{b_H}\right) - \ln\left(\frac{E_d}{RT_p}\right).$$

Approximation (Redhead):

$$E_d \approx RT_p \left[\ln\left(\frac{n_1 T_p}{b_H}\right) - 3.64 \right].$$

This is only valuable if n_1 is reasonably well known.

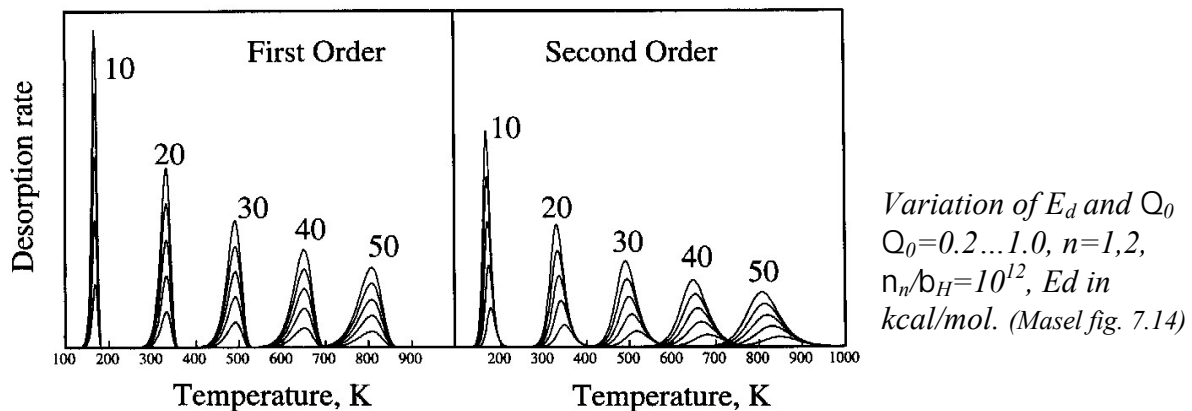
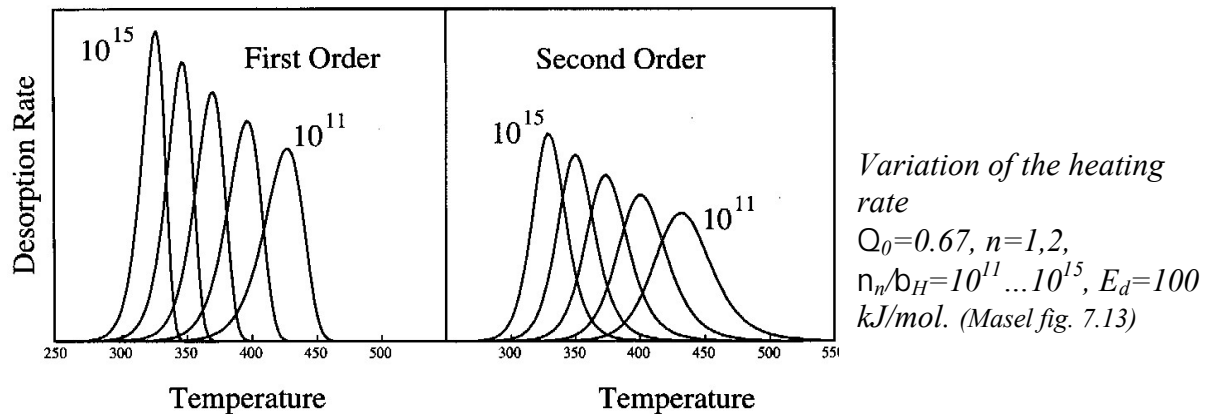
This is often simplified further assuming $n_1=10^{13} \text{ s}^{-1}$ to

$$E_d \approx 0.25 T_p \quad E_d \text{ in kJ/mol, } T_p \text{ in K.}$$

This yields an estimation of E_d to $\pm 20\%$. This seems acceptable but is not. For a given (measured) desorption rate at 300 K, an inaccuracy of only $\sim 2.5 \text{ kJ/mol}$ results in an inaccuracy of the frequency factor by a factor of 10!

Problem: Often the importance of n is underestimated. For every practical problem, one needs both n and E_d .

A number of evaluation methods for E_d and n are based on variation of heating rate b_H and Q_0 -dependence of T_P , the position of the desorption peak maximum.



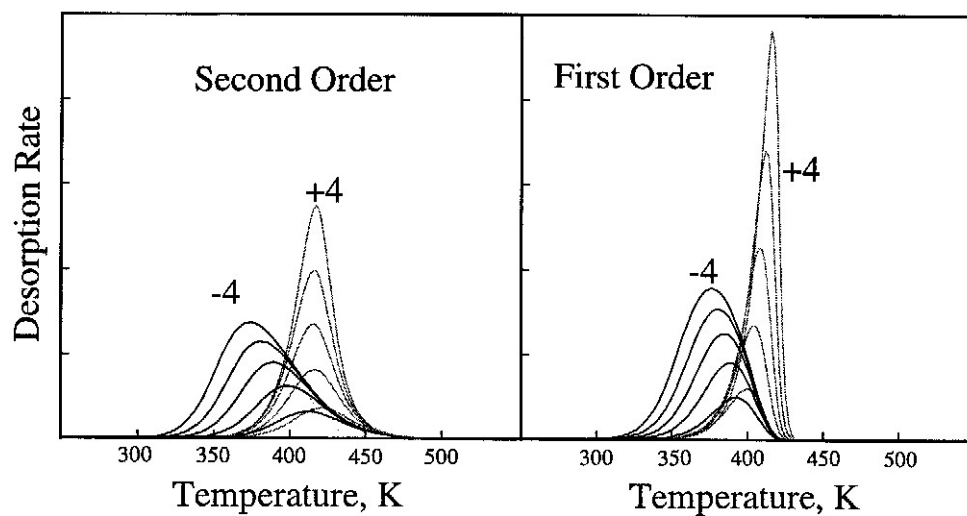
Problem: This applies for one (equilibrated) adsorption state with Θ -independent E_d and v . In general, this is not fulfilled.

5. Adsorbate-adsorbate interaction: the Elovich-equation

Problem: $E_d = E_d(Q)$; $n_n = n_n(Q)$.

Elovich-equation: Assumption: E_d varies linearly with Q_r .

$$r_d = v_n \sigma_A^n \Theta_r^n \exp\left[-(E_d^0 - \alpha_E \Theta_r)/kT\right].$$



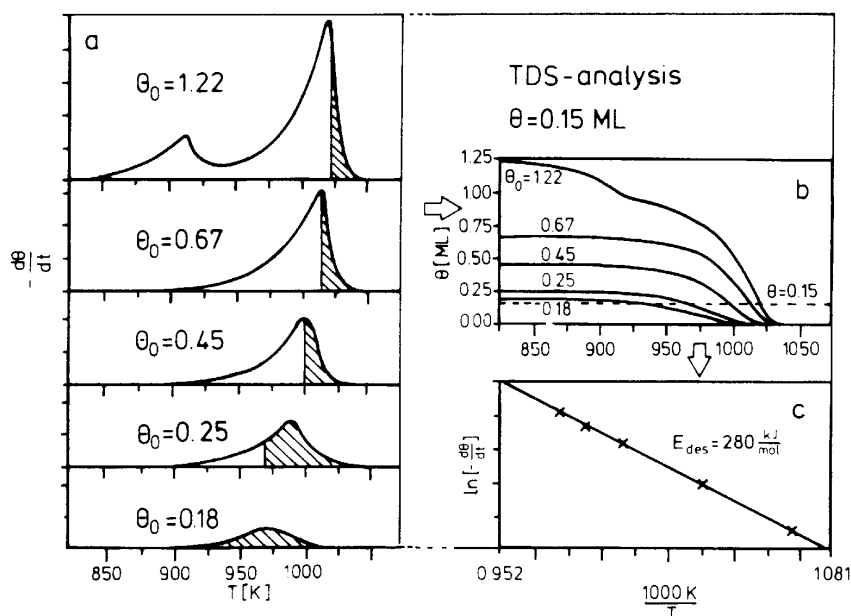
*TD spectra
calculated by
numerically
integrating the
Elovich
equation.
 $Q_0=0.2 \dots 1.0$,
 $E_d^0=100\text{kJ/mol}$,
 $a_E=17 \text{ kJ/mol}$,
 $n_n/b_K=10^{12}$.
(Masel fig. 7.22).*

6. “Complete analysis”

The method uses the rate equation for desorption and allows for a coverage dependence of both n_n and E_d :

$$r_d = v_n(\Theta_r) \sigma_A^n \exp[-E_d(\Theta_r)/kT] \Theta_r^n .$$

Although E_d , n_n and n can be derived, this method is not often applied, probably because it needs an engagement into the understanding of the desorption process and is comparatively complicated. It goes back to D.A. King et al. (D.E. King, T.E. Madey, J.T. Yates, Jr., J. Chem. Phys. 55 (1971) 3236).



“Complete analysis” of TD data of Ag from Ru(0001):

1. The spectra of (a) are integrated from the right (b) yielding also the initial coverage Θ_0 .
2. Depending on Θ_0 , a certain coverage (as example, $\Theta_r=0.15$ is chosen) is reached at different temperatures.
3. The original TD traces at $\Theta_r=0.15$ give the corresponding values of the desorption rate r_d .
4. For this coverage, one obtains pairs of (r_d, T) . An Arrhenius-plot $\ln(r_d)$ vs. $1/T$ is made (c).
5. The slope yields E_d and the intercept equals $\ln(n_n) + n \ln(\Theta_r)$.

(J.W. Niemantsverdriet et al., J. Vac. Sci. Technol. A5 (1987) 857).

7. “Leading edge” method

(E. Habenschaden, J. Küppers, Surf. Sci. 138 (1984) L147)

Idea: In the region of the first data points at the leading edge of a TD trace (low-T onset of the curves), the total coverage Q_r is almost unchanged and can be considered as constant:

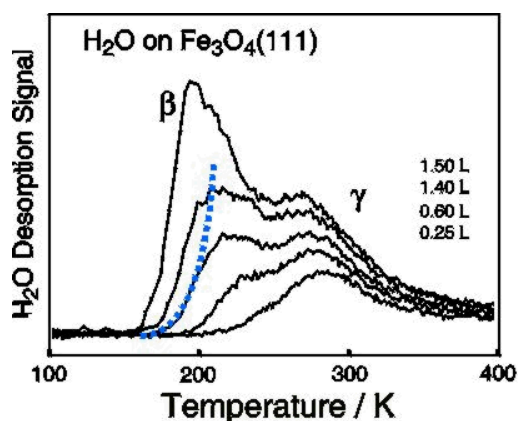
$$Q_r \approx Q_0 .$$

The rate equation becomes

$$r_d = v_n(\Theta_0) \sigma_A^n \Theta_0^n \exp[-E_d(\Theta_0)/kT] .$$

For each (known) Q_0 , an Arrhenius plot $\ln(r_d)$ vs. $1/T$ of this short interval should yield a straight line. From the slope, $E_d(Q_0)$ and from the intercept, $n \ln(Q_0) + \ln(n_n)$ can be deduced.

If it is known that $n=1$, one may plot $\ln(r_d/Q_r)$ vs. $1/T$ allowing use of a larger part of the desorption curve.



Low coverage TD-traces of H₂O on Fe₃O₄(111). The first data points at the leading edge can be approximated by a simple Polanyi-Wigner (exponential) behaviour.

Problem: Need for extremely good data for the small used interval.

8. Conclusions

“Simple” surfaces:

Suggestive: Number of consecutively adsorbing species

Qualitatively: Distinction of chemisorbed, physisorbed, condensed species

Quantitative: Evaluation of coverages possible;

evaluation of E_d , n_n and n difficult, many parameters.

“Complex” surfaces:

So far only qualitative evaluation.