



Thermal analysis - TDS

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TDS = TPD

(**Thermal Desorption (mass) Spectroscopy**) = **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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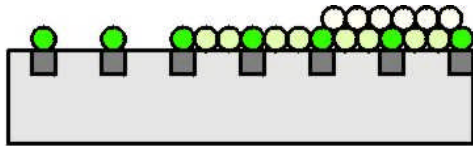
1. Idea, desorption, experimental, example

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

E_d	activation energy for desorption
n	reaction order
ν	frequency- or prefactor

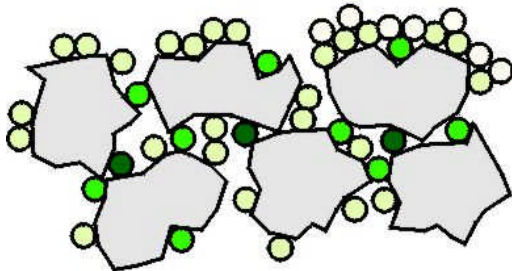
Adsorb gas at low T , run a T -ramp, look what desorbs at which T .

Desorption from “simple” and “complex” samples:



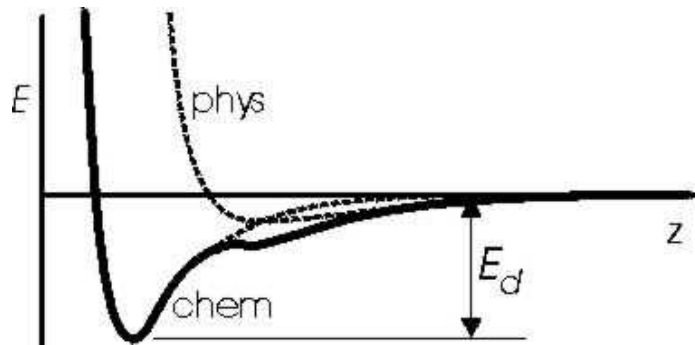
- 1st layer, specific
- 1st layer, unspecific
- 2nd layer

(a) desorption from single crystal surface; site inhomogeneity from crystal structure; no pore diffusion limitation;

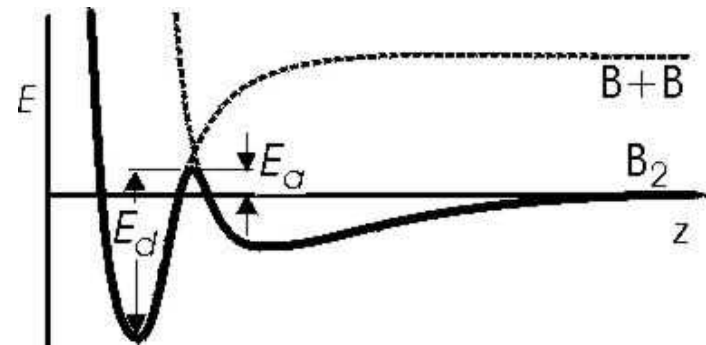


- Coordination
- 3-fold
 - double
 - single
 - zero (2nd layer)

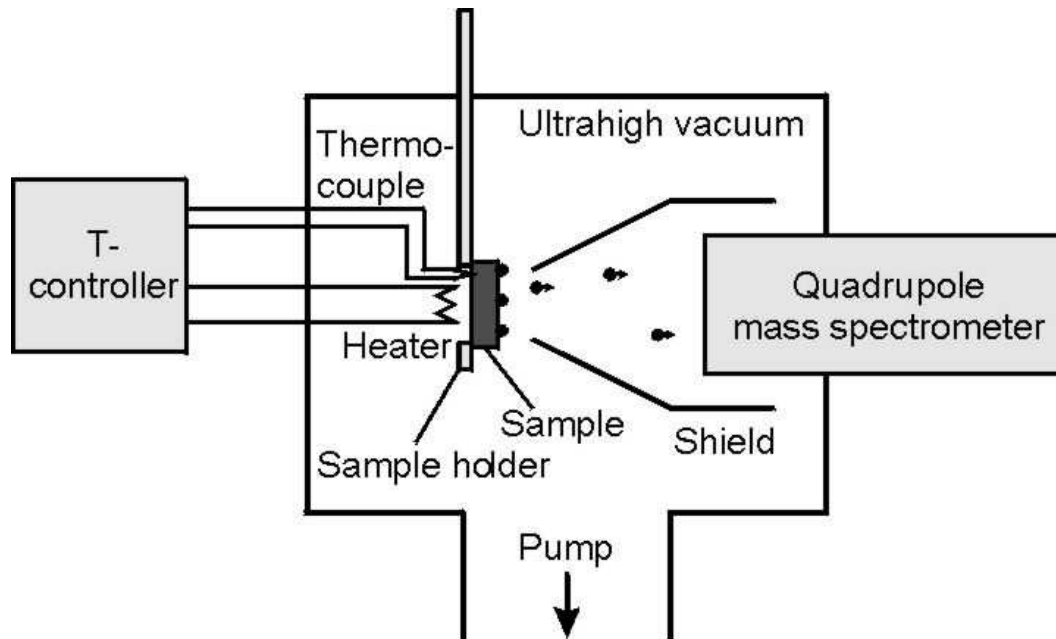
(b) desorption from powder sample; additional inhomogeneity from roughness: sites with different coordination to the substrate; desorption includes pore diffusion;



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

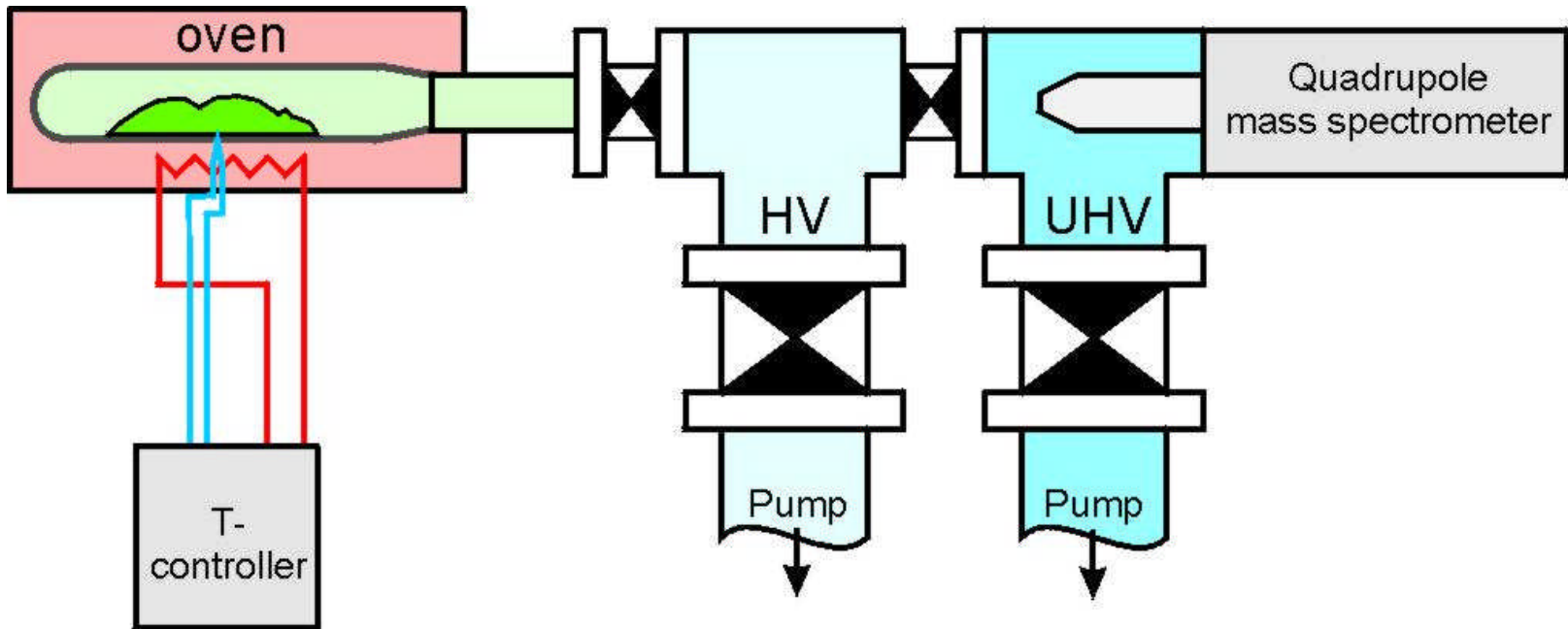


Potential curves for activated recombinative desorption of a dissociated particle: The activation energy $E_d > \Delta H_{ad}$



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

Problems:

T – measurement

T – homogeneity

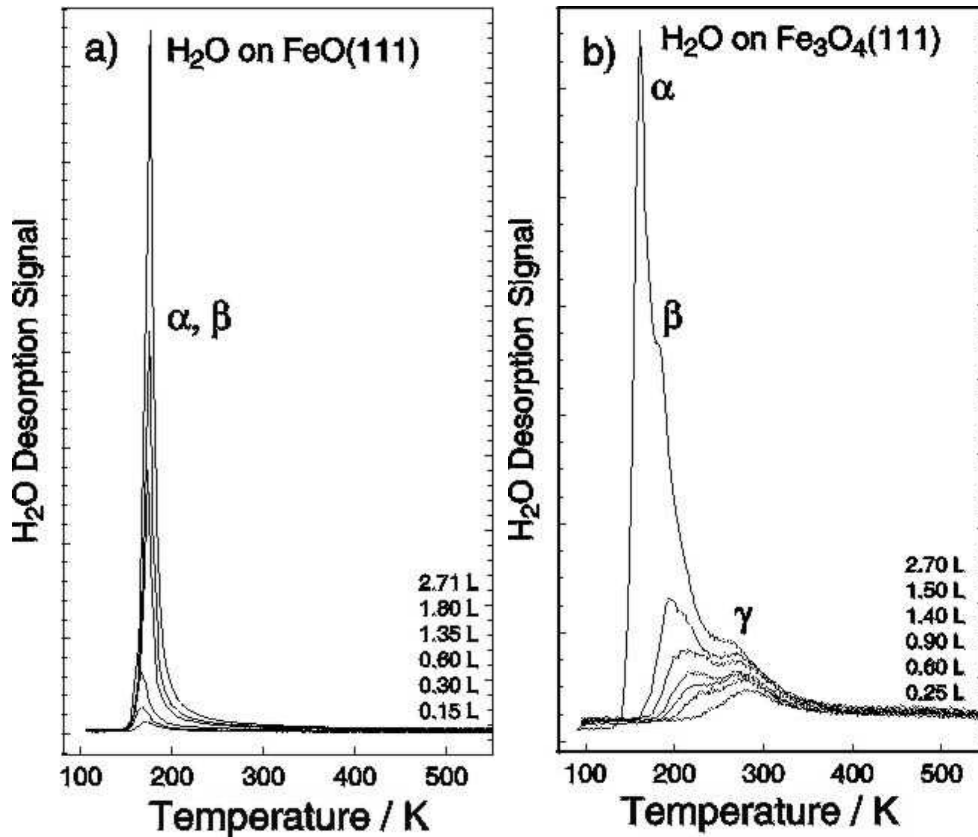
Sample inhomogeneity

Gas release retarded by pore diffusion

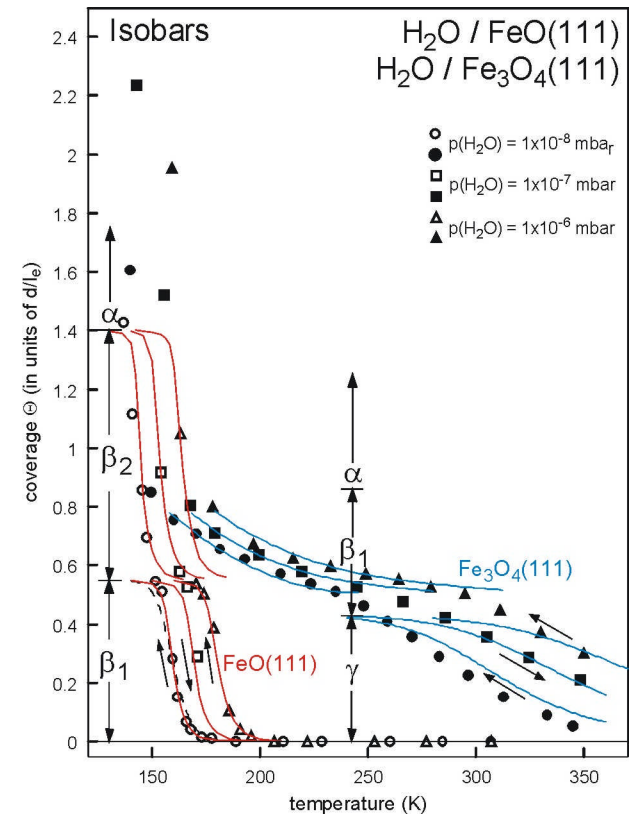


**broader peaks
unspecific
only qualitative**

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

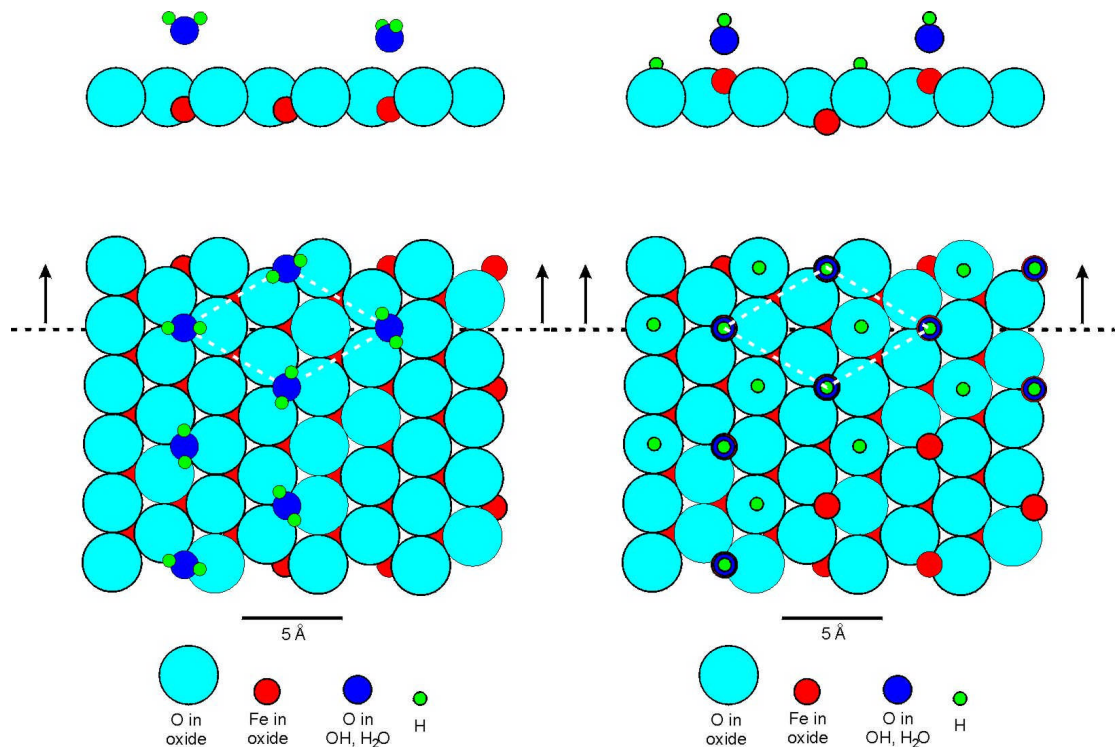


TD-traces for desorption of H₂O from (a) FeO(111) and (b) Fe₃O₄(111). While a small initial peak shift on FeO suggests sequential desorption of physisorbed β -water and condensed α -water, a more tightly bound chemisorbed γ -species saturates first on Fe₃O₄. Exposure at 100 K, exposure in Langmuir units.



For comparison:
Isobars for the same system,
measured in adsorption-
desorption equilibrium
(W. Ranke, Y. Joseph,
Phys. Chem. Chem. Phys. 4 (2002) 2483)

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



Structure and models for the most tightly bound species:

Left: physisorbed β -water on almost inert O-terminated FeO(111);

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

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

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

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 depends on the molecular mass number M and on T . The exposure ε is:

$$\varepsilon = 2.63 \cdot 10^{22} \frac{p t}{\sqrt{M T}} \text{ cm}^{-2}$$

p in mbar,

t in sec,

M in g/mol,

T in K.

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**.
- 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 only **what is going off** the surface and **not what is left**.

TDS shows **what is going off at $T_{des} \gg T_{ads}$** ; changes may have occurred during heating. Often, adsorbates decompose irreversibly and eventually form carbonaceous deposits.



Complementary methods necessary (e.g. XPS, AES)

The sample is exposed at a low temperature in order to keep the desorption rate negligibly small. Often **adsorbate mobility is insufficient for** sequential filling of adsorbate states (equilibration).

3. Desorption order

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;
 $\Theta_r = \Theta / \Theta_{sat}$: relative coverage ($0 < \Theta_r < 1$);
 n : order of desorption reaction.

σ_A : density of adsorption sites cm^{-2} ;
 v_n : the frequency factor for desorption order n ;

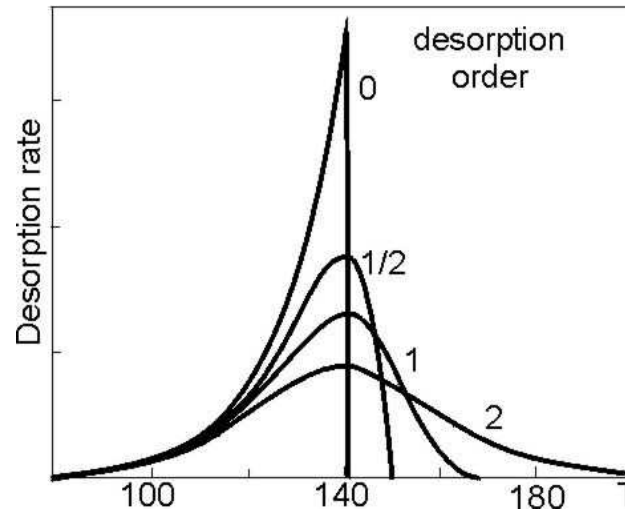
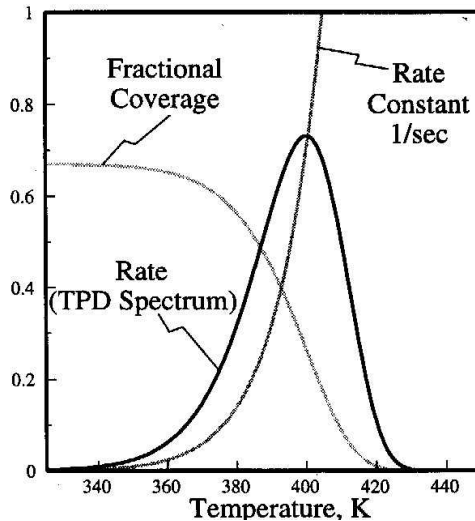
For practical reasons, I divide the total coverage Θ into $\Theta = \Theta_r \sigma_A$.

Definition: desorption order = exponent n of Q_r^n

Mind the sign!

Often the minus sign is omitted:

QMS-signal = $-r_d$

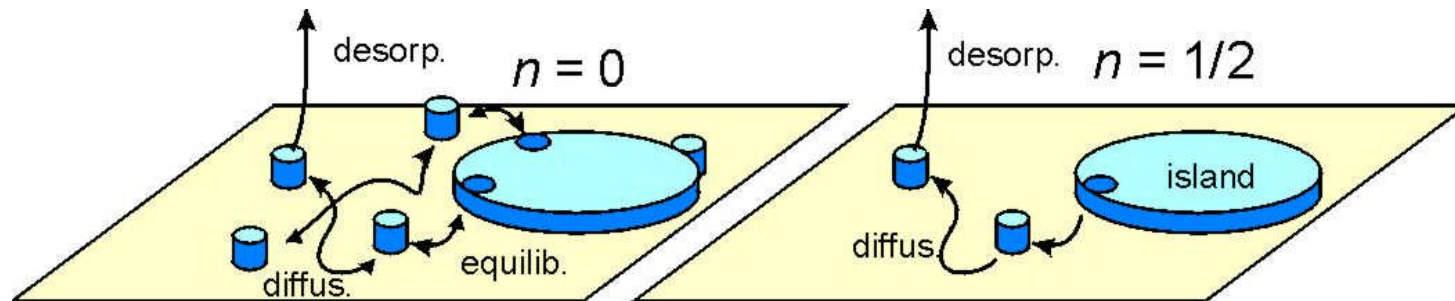


Coverage, rate constant and desorption rate.

$\Theta_{r,0} = 0.67$, $n = 1$, $v = 10^{13} \text{ s}^{-1}$,
 $\beta_H = 10 \text{ K/s}$, $E_d = 100 \text{ kJ/mol}$.
 (Masel fig. 7.11)

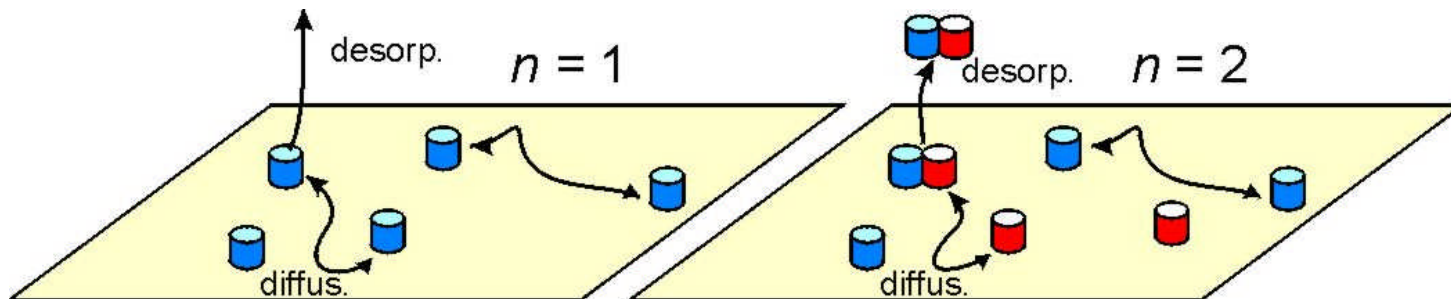
Shape of desorption traces for different desorption orders.

(D. Pöss, Diss., TU Berlin (1980).)



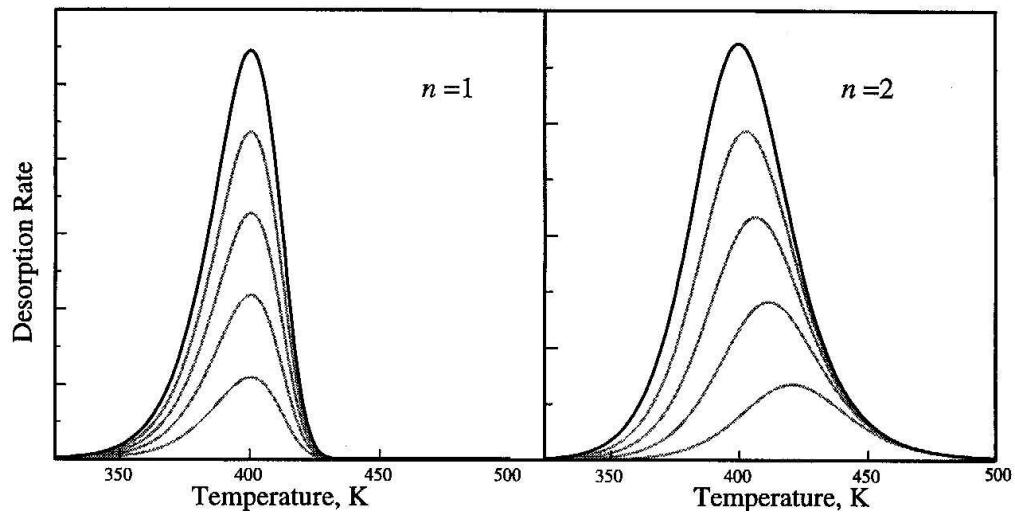
Left: 2D gas with very fast exchange and equilibration with islands (2D vapor pressure in equilibrium with 2D fluid): Desorption rate *independent of* Θ , as long as islands are left; desorption order $n=0$. The same order for sublimation of thick condensed layers.

Right: The desorption rate is proportional to the circumference of the islands and thus *proportional to* $\Theta^{1/2}$; desorption order $n=1/2$.



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

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



TDS 1st and 2nd order, for

$\Theta_{r,0} = 0.2, 0.4 \dots 1.0.$

$n = 1, 2$

$\nu = 10^{13} \text{ s}^{-1}$,

$\beta_H = 10 \text{ K/s}$,

$E_d = 100 \text{ kJ/mol}$.

(Masel fig. 7.12)

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

The desorption rate is: $r_d = -\frac{\sigma_A d\Theta_r}{dt} = \nu_n \sigma_A^n \Theta_r^n \exp(-E_d/kT)$

Linear temperature ramp: $T = T_0 + \beta_H t$.
Combining this yields:

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

$$\frac{E_d}{RT_P} = \ln\left(\frac{\nu_n T_P n \Theta_P^{n-1}}{\beta_H}\right) - \ln\left(\frac{E_d}{RT_P}\right)$$

Approximation (Redhead): $E_d \approx RT_P \left[\ln\left(\frac{\nu_1 T_P}{\beta_H}\right) - 3.64 \right]$

Only useful if ν_1 is reasonably well known.

This is often simplified further, assuming $\nu_1 = 10^{13} \text{ s}^{-1}$:

$$E_d \approx 0.25 T_P \quad E_d \text{ in kJ/mol, } T_P \text{ in K.} \quad \text{Error in } E_d : \pm 20\% .$$

This is **not** acceptable:

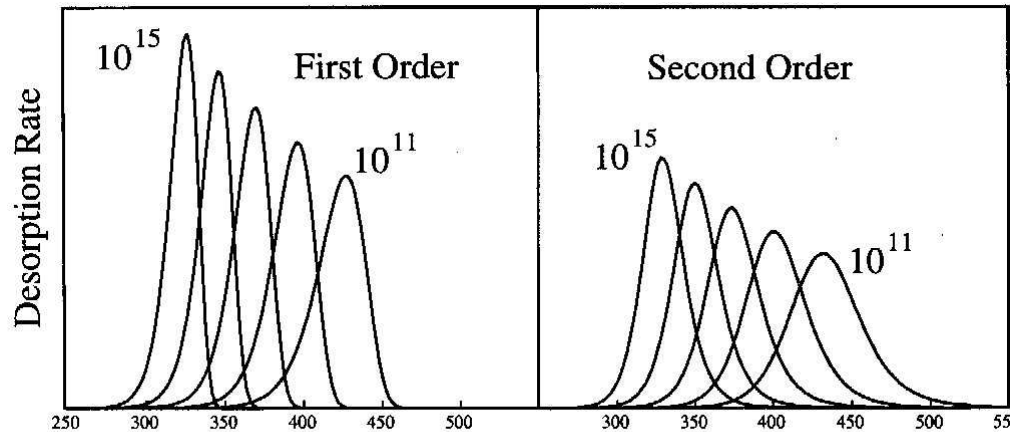
For a given (measured) desorption rate at 300 K, an inaccuracy of only $\sim 2.5 \text{ kJ/mol}$ results in an inaccuracy of the frequency factor by a factor of 10!

Mind the sign!
Here the minus sign is omitted:
QMS-signal = $-r_d$

T_P, Θ_P :
values at desorption
peak maximum

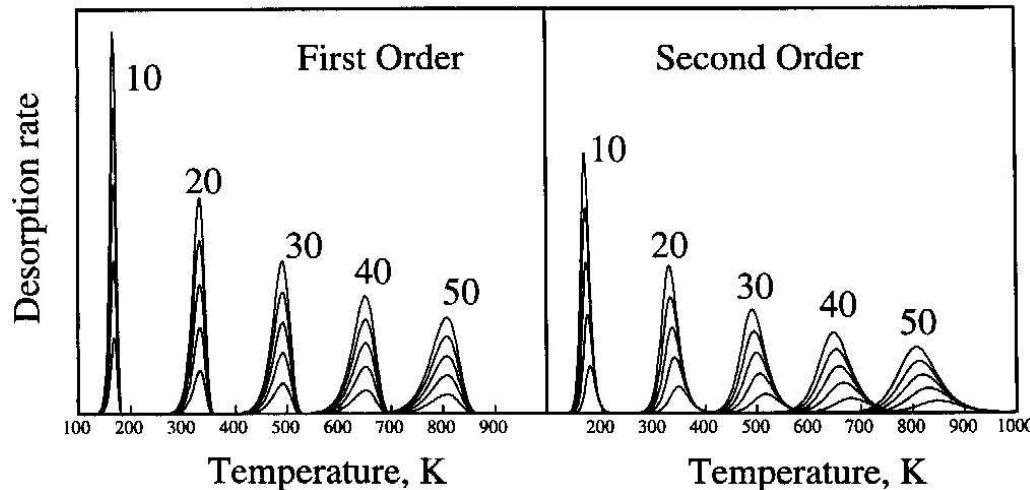
Often the importance of ν is underestimated.
For every practical problem, one needs both ν and E_d .

A number of evaluation methods for E_d and n are based on **variation of heating rate** β_H and Θ -dependence of T_p (position of desorption peak maximum).



Variation of the heating rate

$\Theta_0 = 0.67$, $n = 1, 2$,
 $v_n/\beta_H = 10^{11} \dots 10^{15}$,
 $E_d = 100 \text{ kJ/mol}$.
 (Masel fig. 7.13)



Variation of E_d and $\Theta_{r,0}$

$\Theta_{r,0} = 0.2 \dots 1.0$, $n = 1, 2$,
 $v_n/\beta_H = 10^{12}$,
 E_d in kcal/mol.
 (Masel fig. 7.14)

Problem:

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

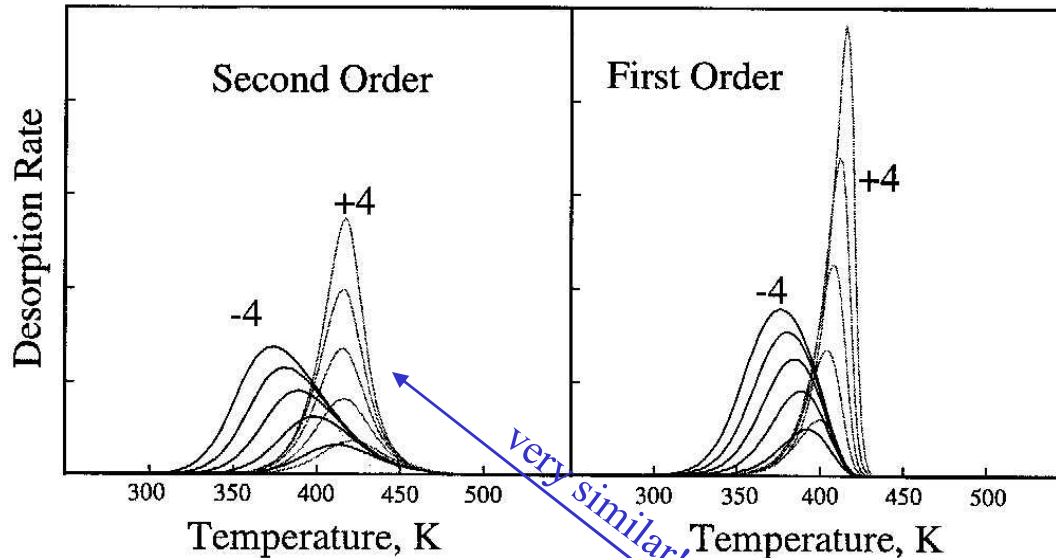
5. Adsorbate-adsorbate interaction: the Elovich-equation

Problem: $E_d = E_d(\Theta)$; $v_n = v_n(\Theta)$.

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

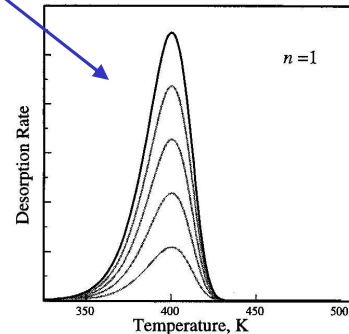
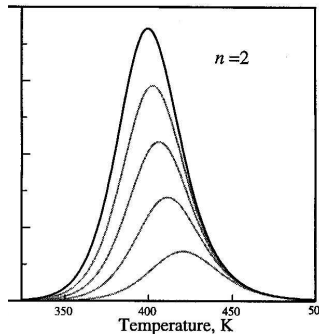
$$r_d = v_n \sigma_A^n \Theta_r^n \exp\left[-(E_d^0 - \alpha_E \Theta_r)/kT\right]$$

$\alpha > 0$ attractive
 $\alpha < 0$ repulsive



TD spectra calculated by numerically integrating the Elovich equation.

$\Theta_0 = 0.2 \dots 1.0$,
 $E_d^0 = 100 \text{ kJ/mol}$,
 $\alpha_E = \pm 4 \text{ kJ/mol}$,
 $v_n / \beta_K = 10^{12}$.
 (Masel fig. 7.22).

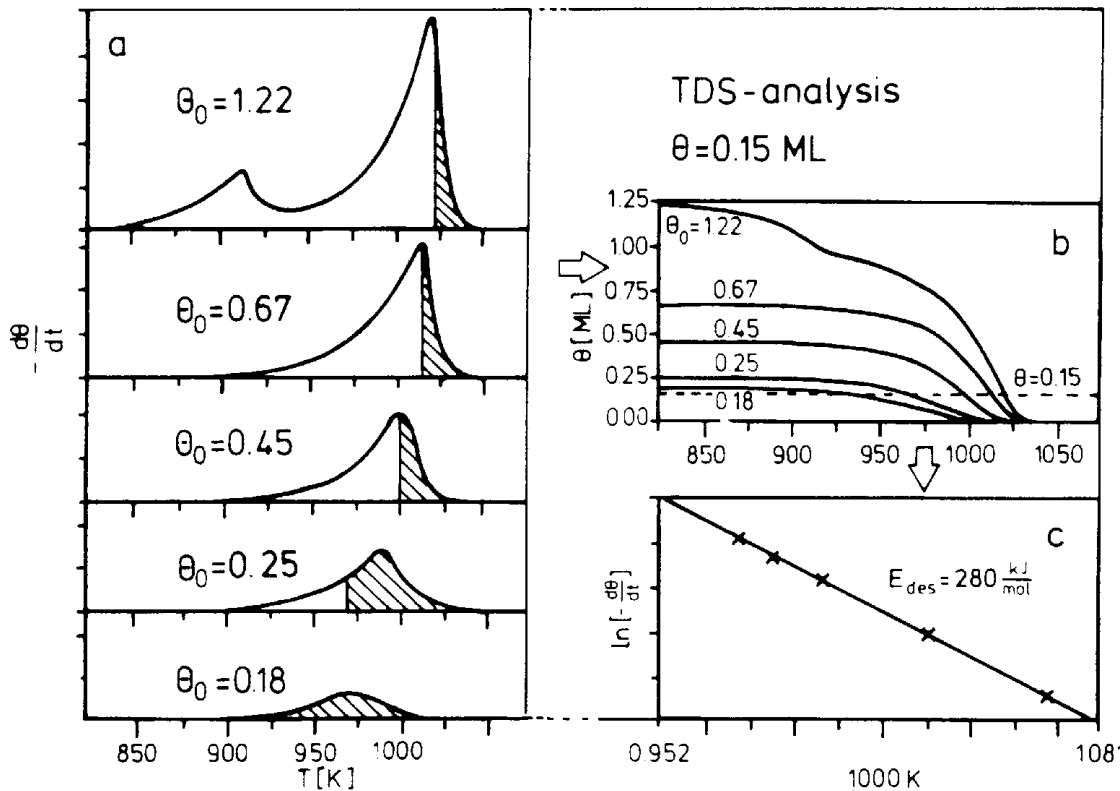


$\alpha = 0$

6. "Complete analysis"

Goes back to D.A. King et al.

(D.E. King, T.E. Madey, J.T. Yates, Jr., J. Chem. Phys. 55 (1971) 3236).



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

Use of the rate equation for desorption, yields coverage dependence of both v_n and E_d .

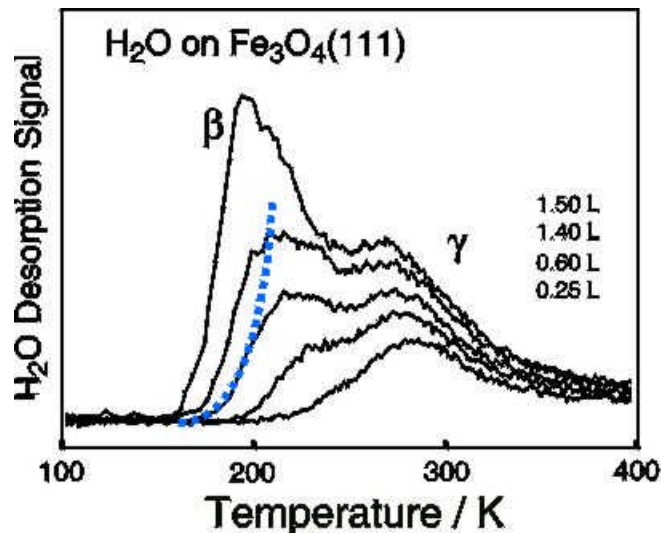
Not often applied, although E_d , v_n and n can be derived:

Needs an engagement into the understanding of the desorption process and is comparatively complicated.

TD data of Ag/Ru(0001):

1. Spectra of (a) are integrated from the right (b) which also yields the initial coverage Θ_0 .
 2. Depending on Θ_0 , a certain coverage (example, $\Theta_r = 0.15$) is reached at different T .
 3. The original TD traces at $\Theta_r = 0.15$ give the corresponding desorption rates r_d .
 4. From pairs of (r_d, T) , $\ln(r_d)$ vs. $1/T$ is plotted (Arrhenius c).
 5. The slope yields E_d and the intercept equals $\ln(v_n) + n \ln(\Theta_r)$.
- (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)



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.

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

$$\Theta_r \approx \Theta_0.$$

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) Θ_0 , an Arrhenius plot $\ln(r_d)$ vs. $1/T$ of this interval should yield a straight line. From the slope, $E_d(\Theta_0)$ and from the intercept, $n \ln(\Theta_0) + \ln(v_n)$ can be deduced. If it is known that $n=1$, one may plot $\ln(r_d/\Theta_r)$ vs. $1/T$ allowing use of a larger part of the desorption curve.

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 , v_n and n difficult, many parameters.

“Complex” surfaces:

So far only qualitative evaluation.

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