TDS

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TDS = **TPD**

(**T**hermal **D**esorption (mass) **S**pectroscopy) = (**T**hermal **P**rogrammed **D**esorption)

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).

FHI-Berlin, 14.02.2008

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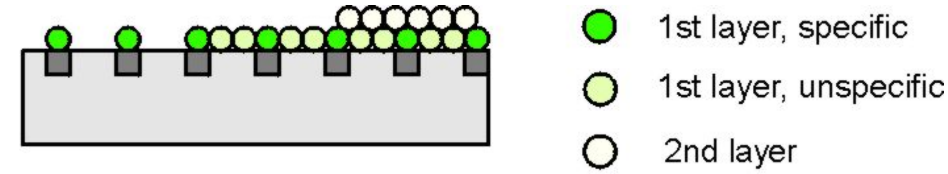
1. Idea, desorption, experimental

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

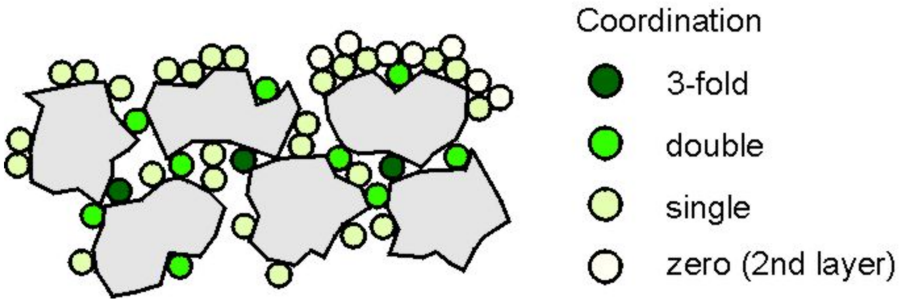
E_d	activation energy for desorption
n	reaction order
ν	frequency- or preexponential factor

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

Desorption from “simple” and “complex” samples:

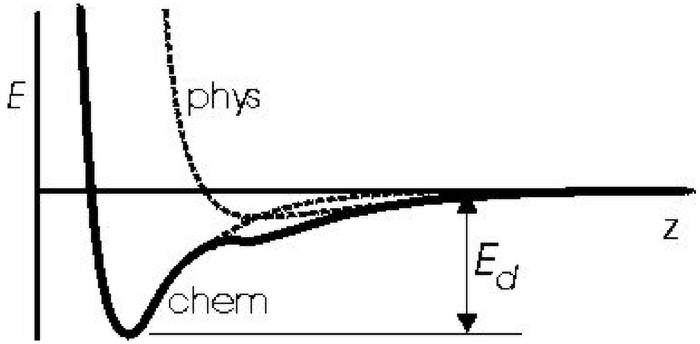


(a) desorption from single crystal surface; site inhomogeneity from crystal structure; no pore diffusion limitation;

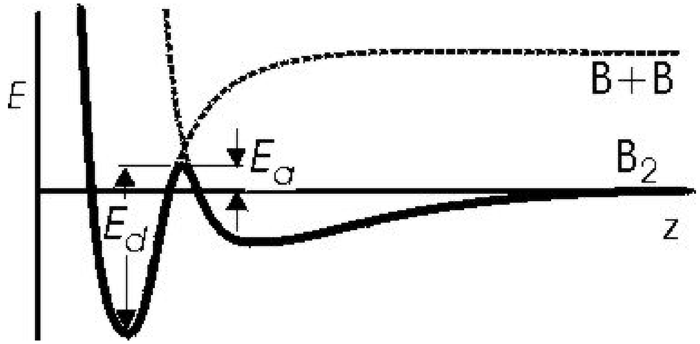


(b) desorption from powder sample; additional inhomogeneity from roughness: sites with different coordination to the substrate; desorption includes pore diffusion;

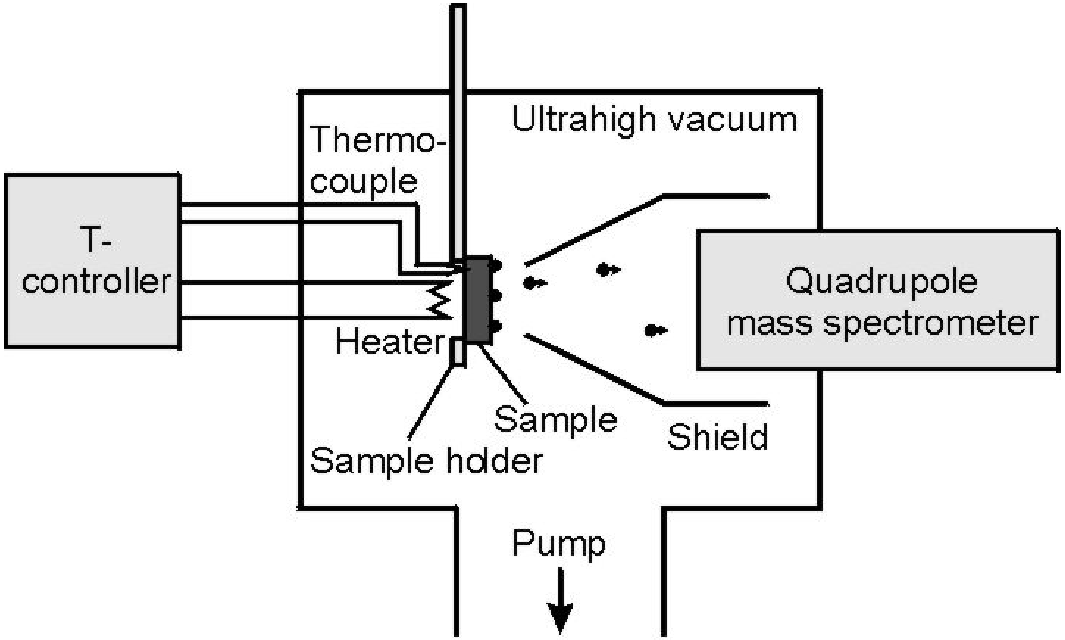
1. Idea, desorption, experimental



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.

2. First model for the desorption rate: Polanyi-Wigner-equation

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

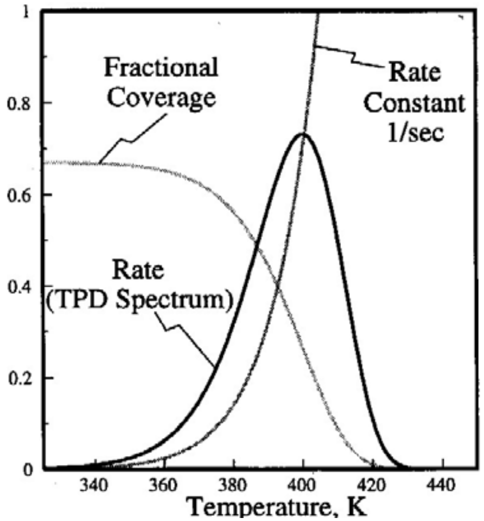
Redhead (1963)

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

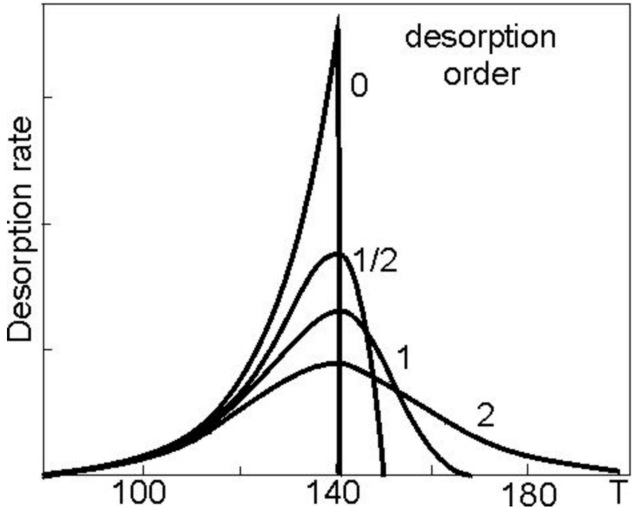
σ_A: density of adsorption sites cm^{-2};
ν_n: the frequency factor for desorption order n;

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

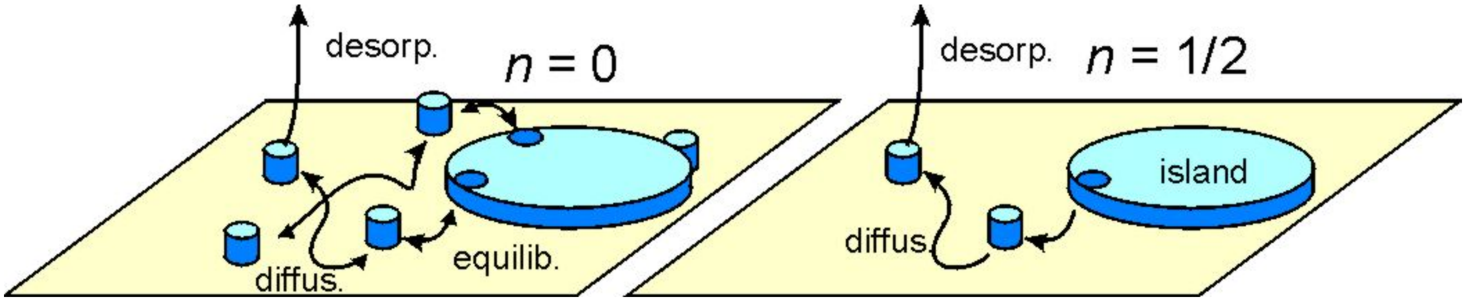
Definition: desorption order = exponent n of $\Theta_r^{\,n}$



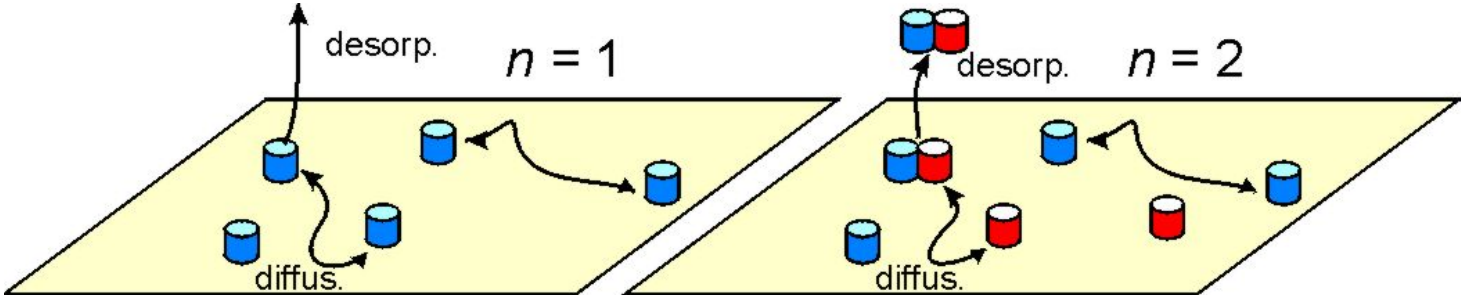
Coverage, rate constant and desorption rate.
$\Theta_{r,0} = 0.67$, $n = 1$, $\nu = 10^{13} s^{-1}$,
$\beta_H = 10$ K/s, $E_d = 100$ kJ/mol.
(Masel fig. 7.11)



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

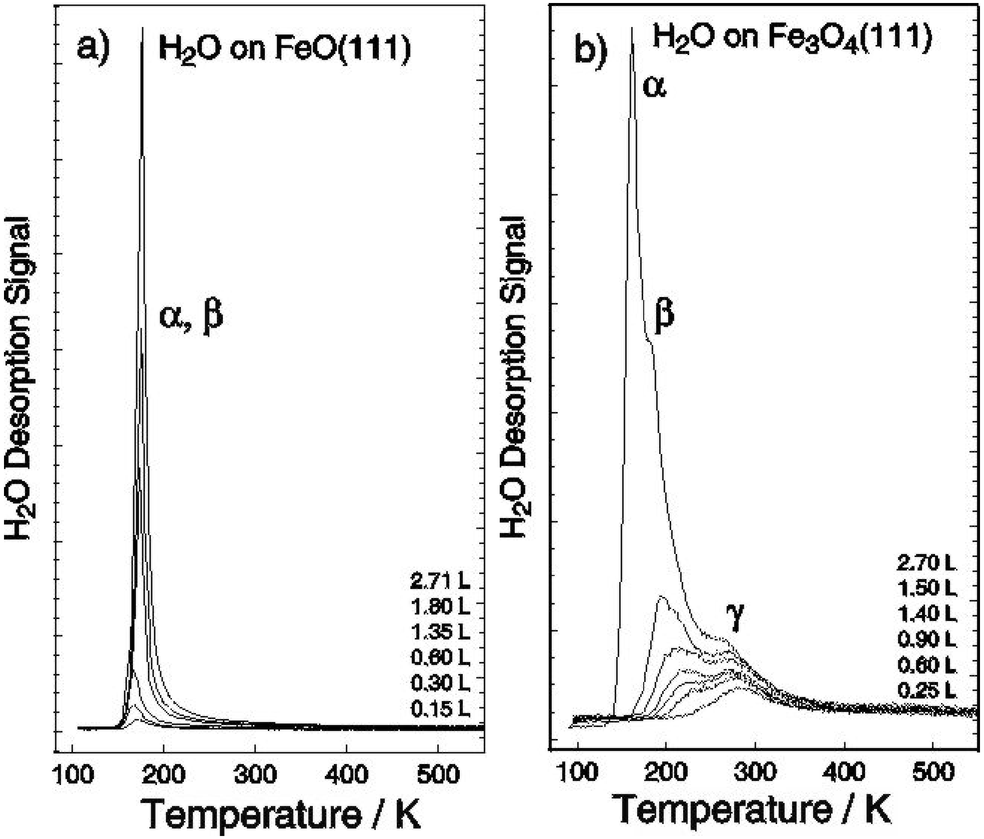


Left: *2D gas with very fast exchange and equilibration with islands (2D vapor pressure in equilibrium with 2D fluid): Desorption rate independent of Θ, as long as islands are left; desorption order* **n=0***. The same order for sublimation of thick condensed layers.*
Right: *The desorption rate is proportional to the circumference of the islands and thus proportional to $\Theta^{1/2}$; desorption order* **n=1/2***.*



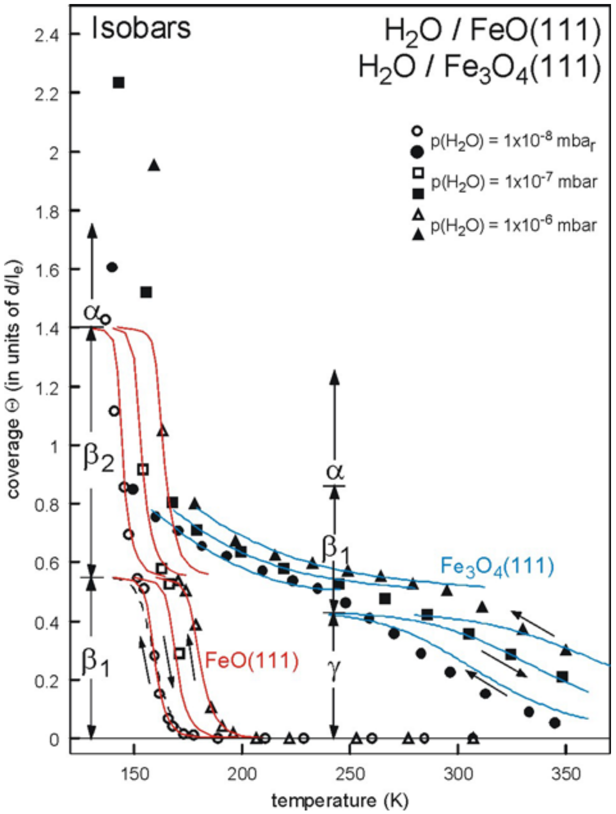
Left: *Molecular desorption, mobile or immobile adsorbate; desorption rate proportional to Θ; desorption order* **n=1***.*
Right: *Associative desorption, at least one of both species must be mobile; desorption rate proportional to Θ^2; desorption order* **n=2***.*

3. Example: H_2O desorption from FeO(111) and Fe_3O_4(111)



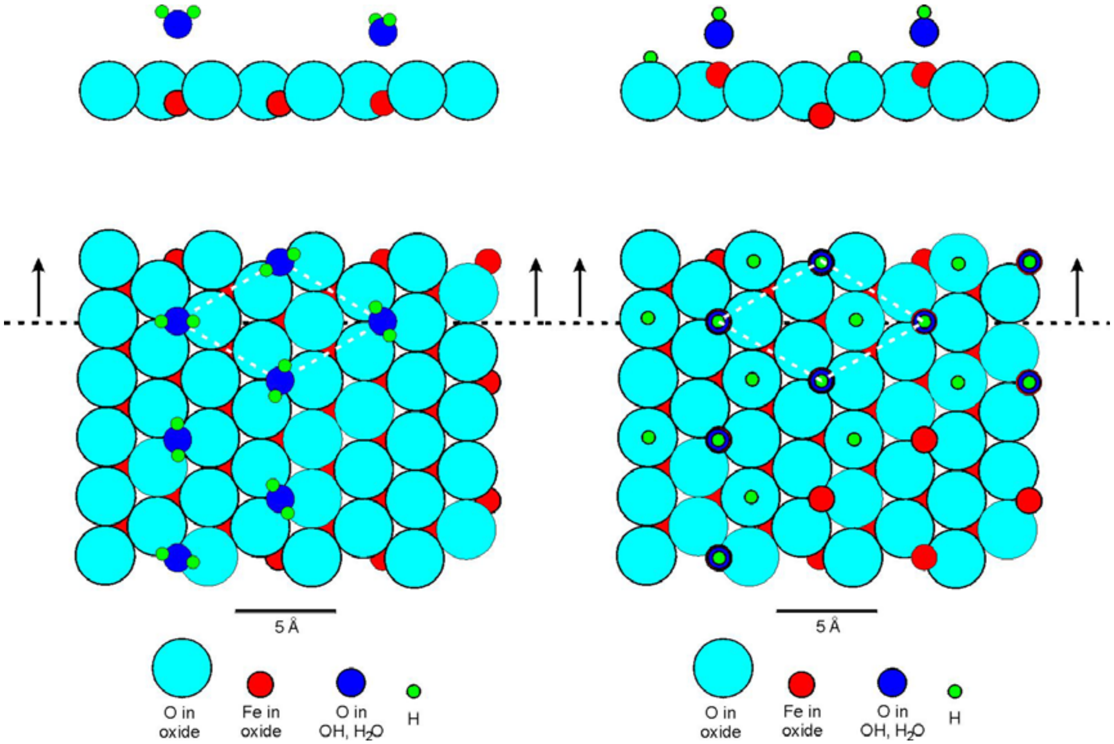
TD-traces for desorption of H_2O from (a) FeO(111) and (b) Fe_3O_4(111). While a small initial peak shift on FeO suggests sequential desorption of physisorbed β-water and condensed α-water, a more tighly bound chemisorbed γ-species saturates first on Fe_3O_4. Exposure at 100 K, exposure in Langmuir units.

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



For comparison:
Isobars for the same system, measured in adsorption-desorption equilibrium

(W. Ranke, Y. Joseph, Phys. Chem. Chem. Phys. 4 (2002) 2483)



Structure and models for the most tightly bound species:
<u>Left</u>: physisorbed β-water on almost inert O-terminated FeO(111);
<u>Right</u>: γ-water on $Fe_3O_4(111)$, 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 $1.33\mathrm{x}10^{-6}$ 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:

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

p in mbar,
t in sec,
M in g/mol,
T in K.

4. 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 $T_{des} >> T_{ads}$**; 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).

5. 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:

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

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

T_P, Θ_P:
values at desorption
peak maximum

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

Approximation (Redhead): $$E_d \approx RT_P\left[\ln\left(\frac{\nu_1 T_P}{\beta_H}\right) - 3.64\right]$$ error < 1.5% for $10^8 < \nu_1/\beta < 10^{13}$ K^{-1}

Only useful if ν_1 is reasonably well known.

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

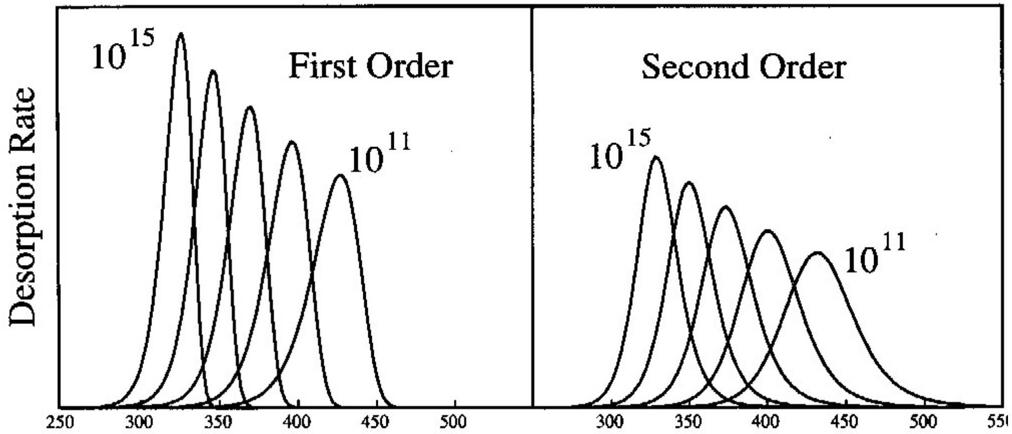
$E_d \approx 0.25 \, T_P$ E_d in kJ/mol, T_P in K.

Error in E_d : ±20% for several orders of magnitude in ν_1.

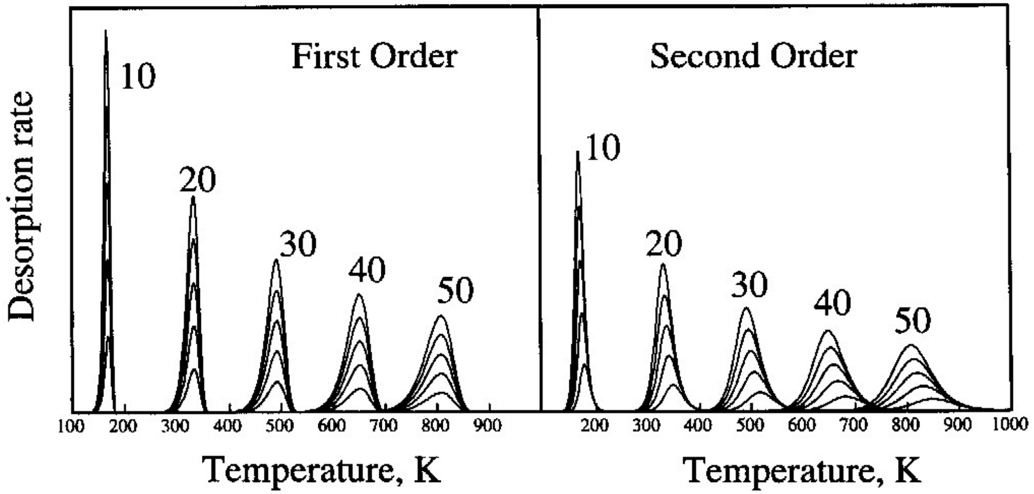
This is usually not acceptable:
For a given (measured) desorption rate at 300 K, an inaccuracy of only ~2.5 kJ/mol (error of 10 K in T) results in an inaccuracy of the frequency factor by a factor of 10!

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
$\Theta_0=0.67,\ n=1,2,$
$\nu_n/\beta_H=10^{11}\ldots10^{15},$
$E_d=100$ *kJ/mol.*
(Masel fig. 7.13)



Variation of E_d *and* $\Theta_{r,0}$
$\Theta_{r,0}=0.2\ldots1.0,\ n=1,2,$
$\nu_n/\beta_H=10^{12},$
E_d *in kcal/mol.*
(Masel fig. 7.14)

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

2. First model for the desorption rate: Polanyi-Wigner-equation

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

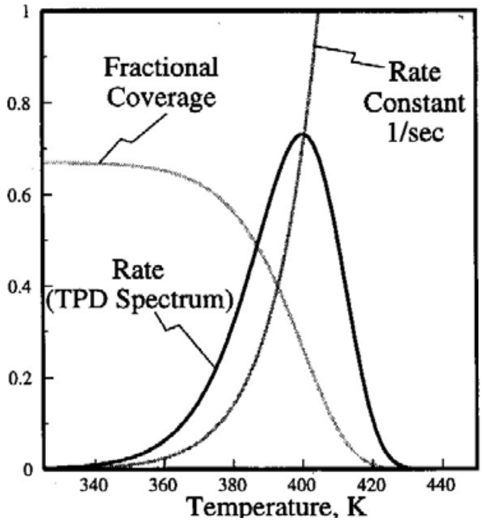
Redhead (1963)

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};
ν_n: the frequency factor for desorption order n;

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

$$\boxed{\text{Definition: desorption order = exponent } n \text{ of } Q_r^n}$$



Coverage, rate constant and desorption rate.
$\Theta_{r,0} = 0.67$, $n = 1$, $\nu = 10^{13} s^{-1}$,
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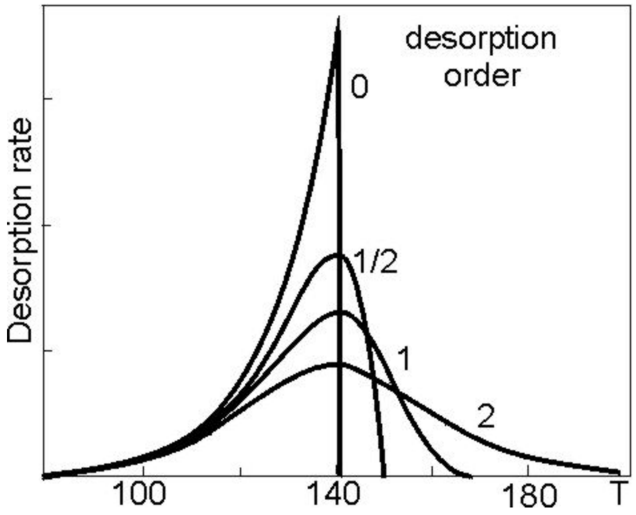
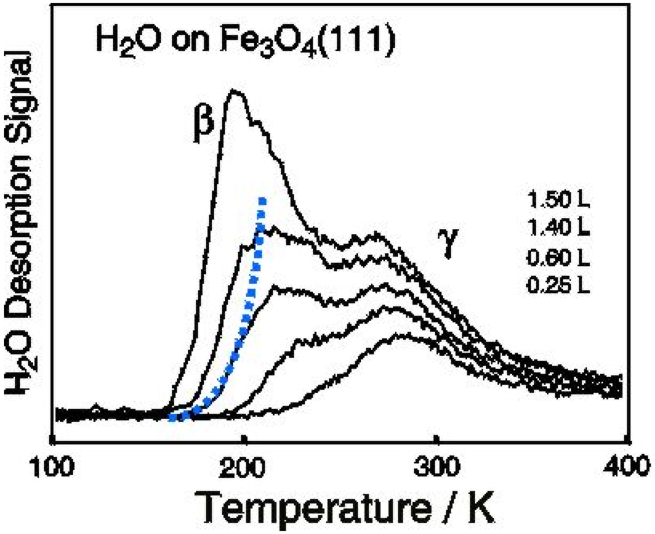


Shape of desorption traces for different desorption orders.
(D. Pöss, Diss., TU Berlin (1980).

6. Leading edge method (E. Habenschaden, J. Küppers, Surf. Sci. 138 (1984) L147)



Low coverage TD-traces of H_2O on $Fe_3O_4(111)$. 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 $$r_d = \nu_n(\Theta_0)\, \sigma_A^n\, \Theta_0^n \exp\left[-E_d(\Theta_0)/kT\right]$$

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, $n \ln(\Theta_0) + \ln(\nu_n)$ 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.

2. First model for the desorption rate: Polanyi-Wigner-equation

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

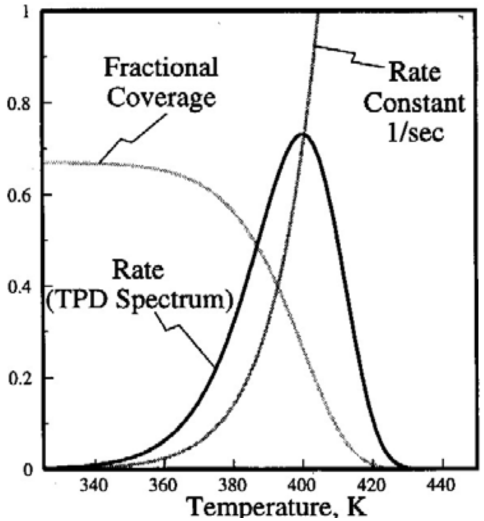
Redhead (1963)

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

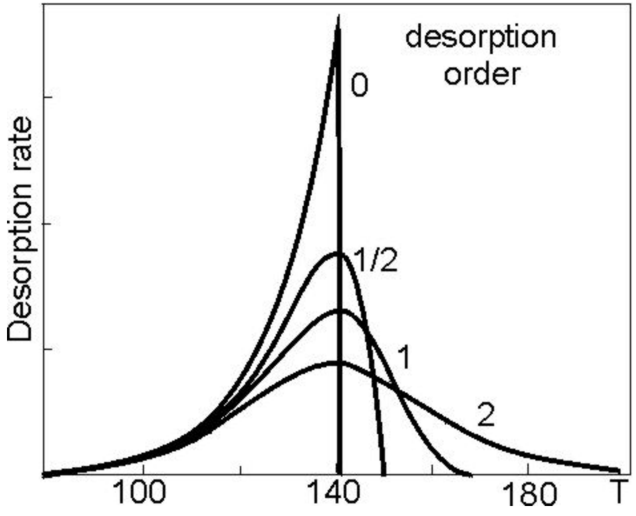
σ_A: density of adsorption sites cm^{-2};
ν_n: the frequency factor for desorption order n;

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

$$\boxed{\text{Definition: desorption order = exponent } n \text{ of } Q_r^n}$$



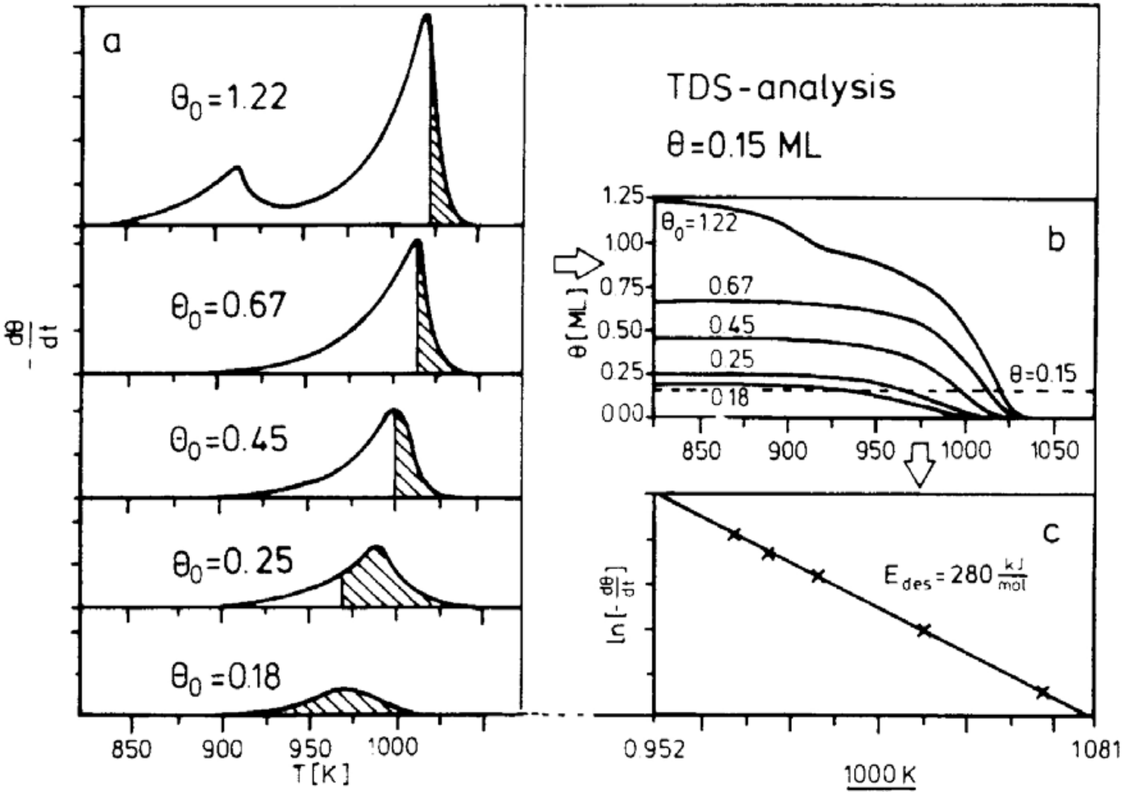
Coverage, rate constant and desorption rate.
$\Theta_{r,0}=0.67$, $n=1$, $\nu=10^{13}s^{-1}$, $\beta_H=10$ K/s, $E_d=100$ kJ/mol.
(Masel fig. 7.11)



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

7. Complete analysis

Goes back to D.A. King et al. (more generally: Weinberg and Taylor)
(D.E. King, T.E. Madey, J.T. Yates, Jr., J. Chem. Phys. 55 (1971) 3236).



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, Θ_r=0.15) is reached at different T.

3. The original TD traces at Θ_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 $\ln(\nu_n) + n\ln(\Theta_r)$.

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

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

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

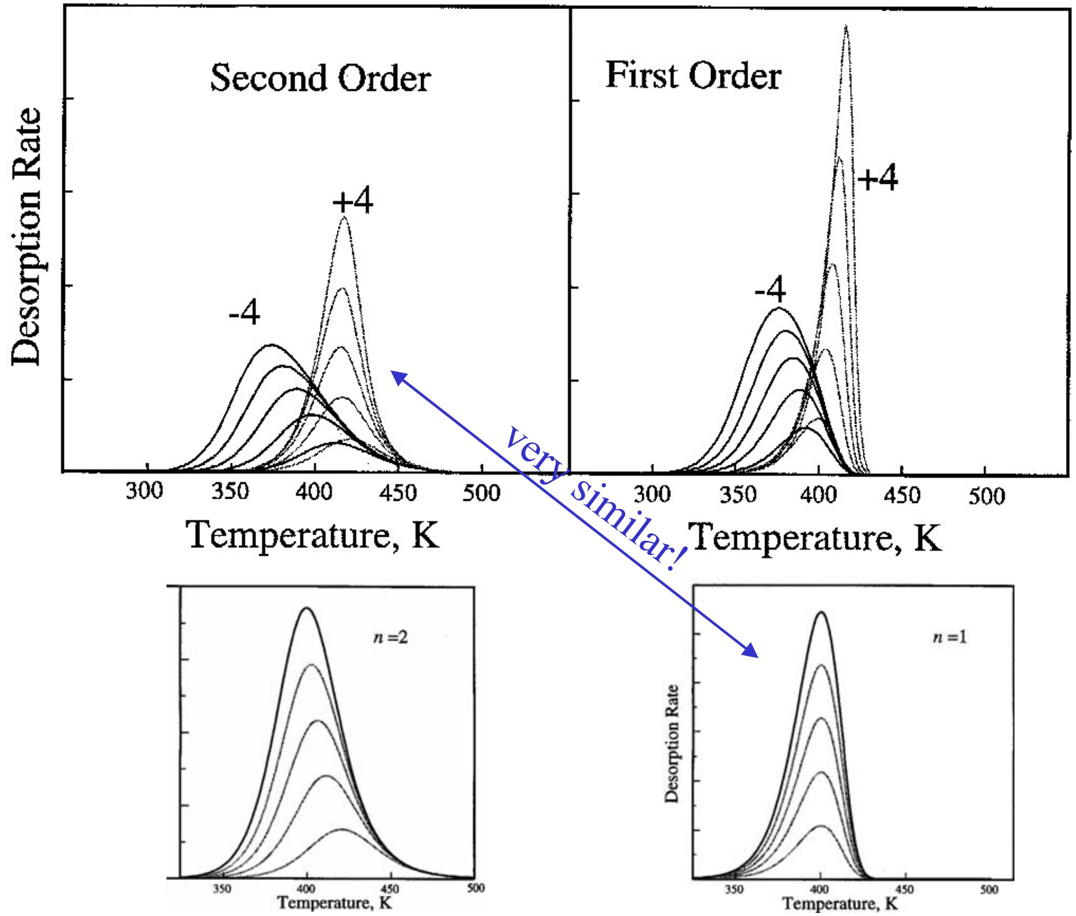
Not often applied, although E_d, ν_n and n can be derived:
Needs an engagement into the understanding of the desorption process and is comparatively complicated.

8. Second Model: Adsorbate-adsorbate interaction, the Elovich-equation

Problem: $E_d = E_d(\Theta)$; $\nu_n = \nu_n(\Theta)$.
Elovich-equation: Assumption: E_d varies linearly with Θ_r.

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

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



very similar!

TD spectra calculated by numerically integrating the Elovich equation.
Θ_0=0.2…1.0,
E_d^0=100kJ/mol,
α_E= ±4 kJ/mol,
$\nu_n/\beta_K = 10^{12}$.
(Masel fig. 7.22).

$\alpha = 0$

9. Third model: Monte Carlo simulations and precursor-moderated desorption

Problem: Elovich-equation assumption: E_d varies linearly with Θ_r is seldom true:

MC with neighbor-neighbor interaction: two peaks for repulsive case!

h > 0 attractive
h < 0 repulsive

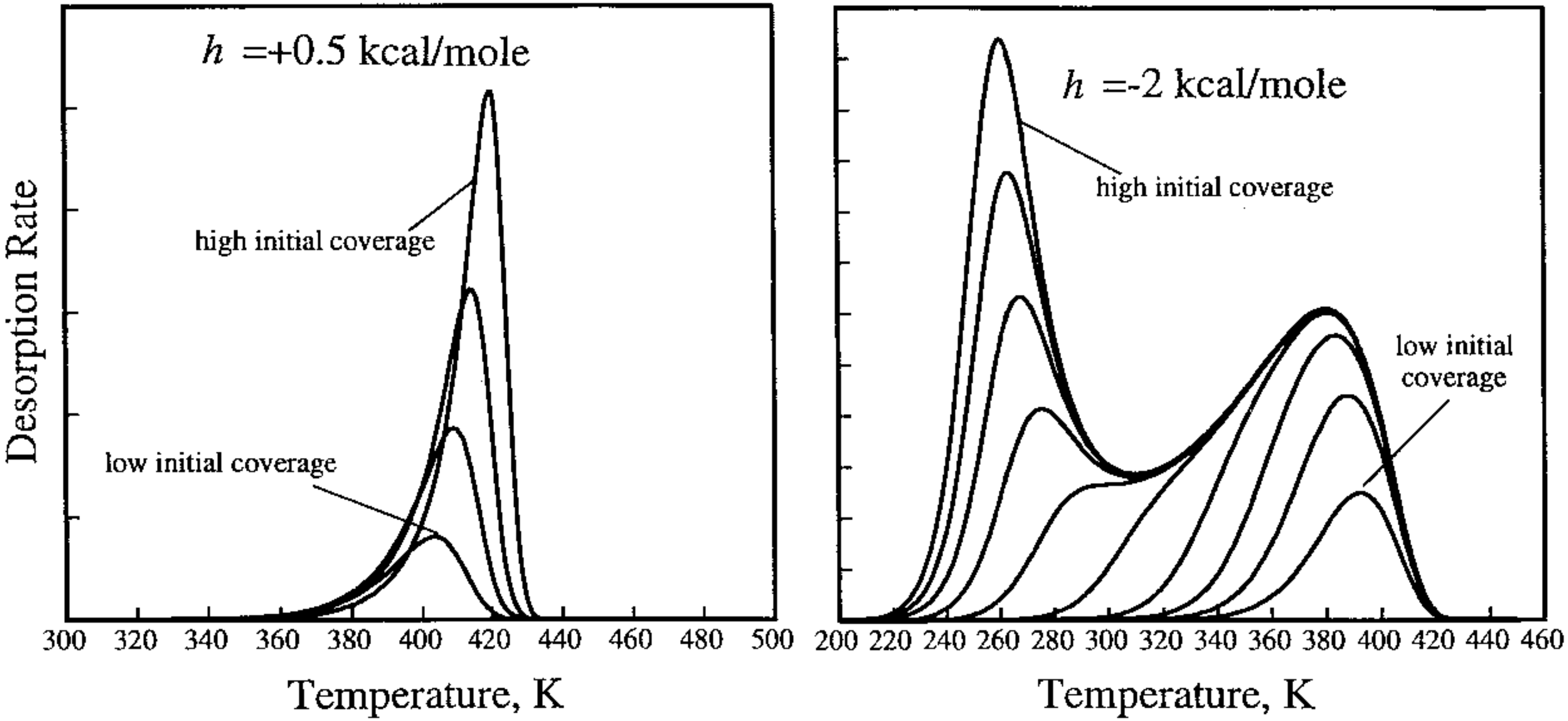


Figure 7.32 A series of TPD spectra calculated by numerically integrating Equation 7.100 for $k_o/\beta_H = 10^{12}$/sec, $E_d^o = 24$ kcal/mole, $\alpha_P = 1.0$.

Masel fig.7.32

10. Conclusions

"Simple" surfaces and "simple model" (Polanyi-Wigner-equation):

Suggestive:	Number of consecutively adsorbing species
Qualitatively:	Distinction of chemisorbed, physisorbed, condensed species
Quantitative:	Evaluation of coverages possible; evaluation of E_d, ν_n and n difficult, many parameters

"Complex" surfaces and order-disorder phenomena:

So far only qualitative evaluation or more complex model.

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