TDS

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TDS = TPD

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

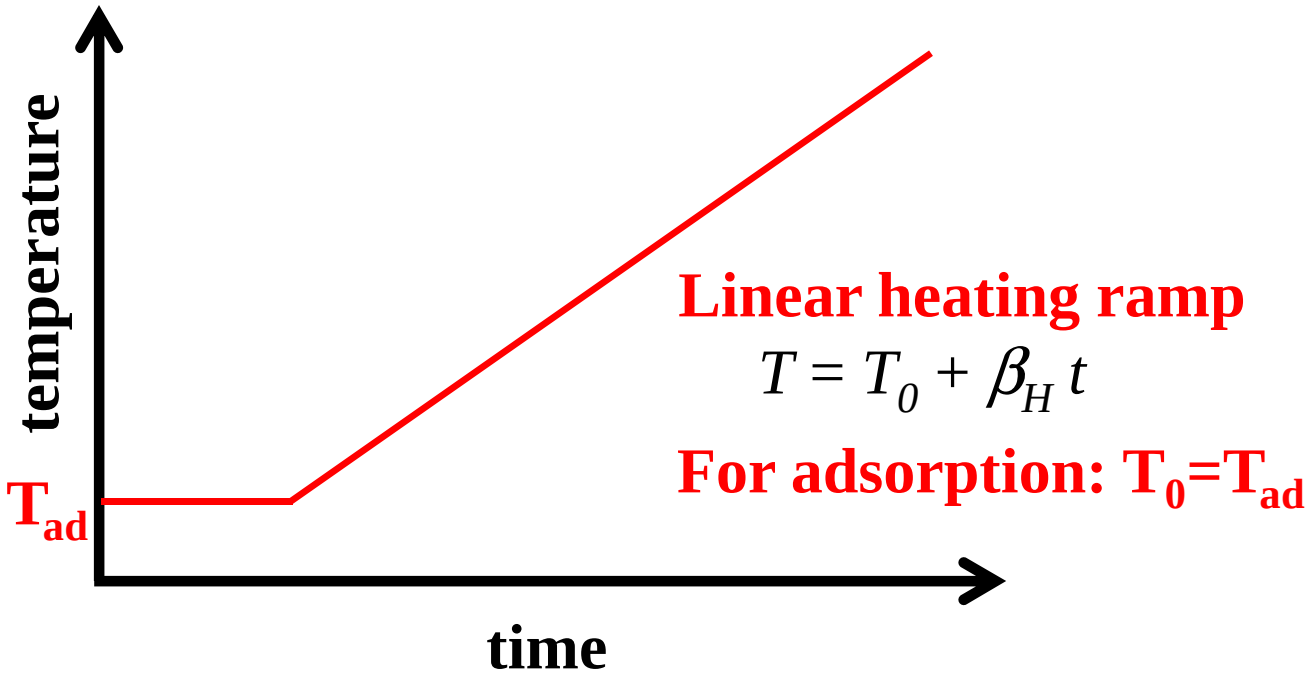
Literature:

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).

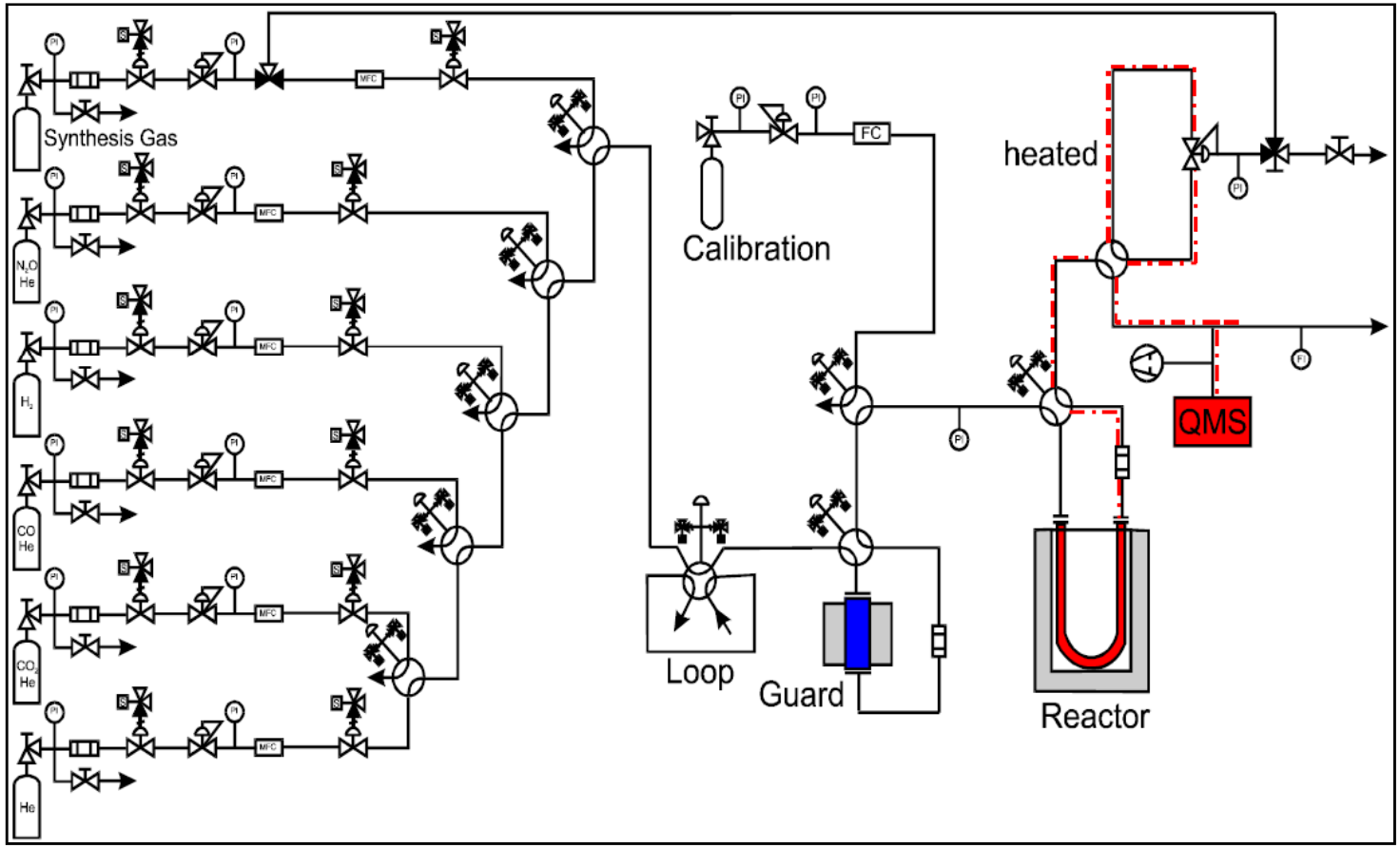
Why TDS?

Simple idea:

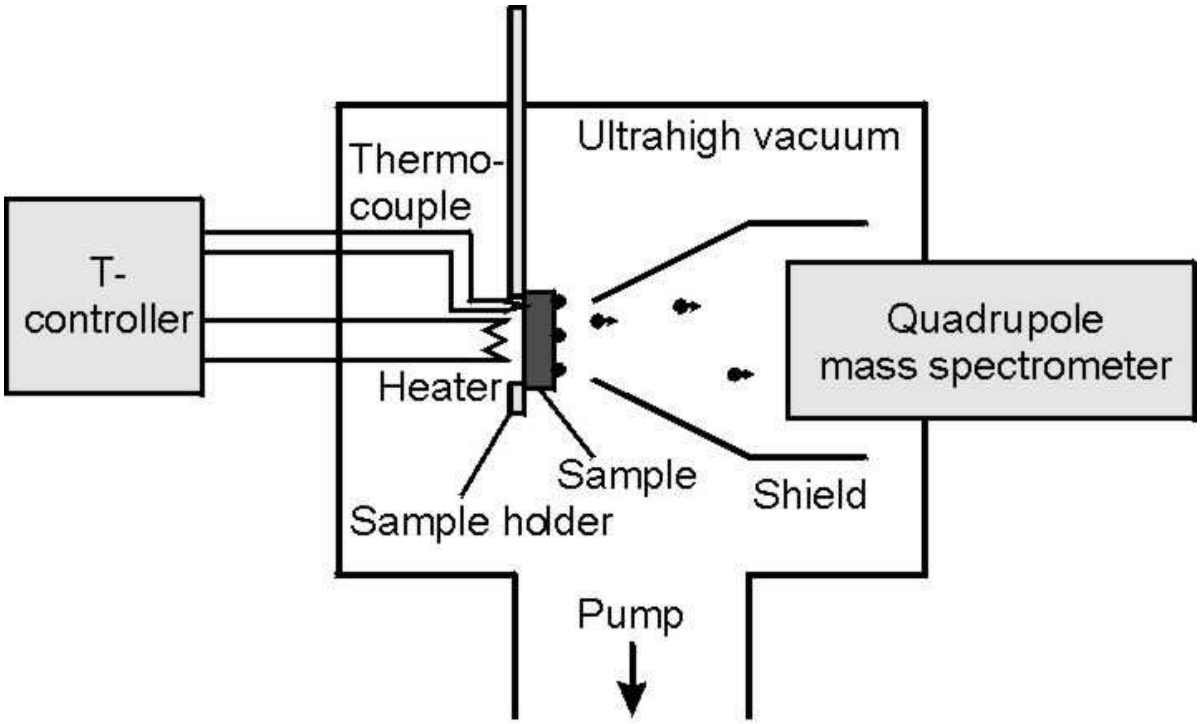
Adsorbed particles with different *binding energies* will desorb at different *temperature*.



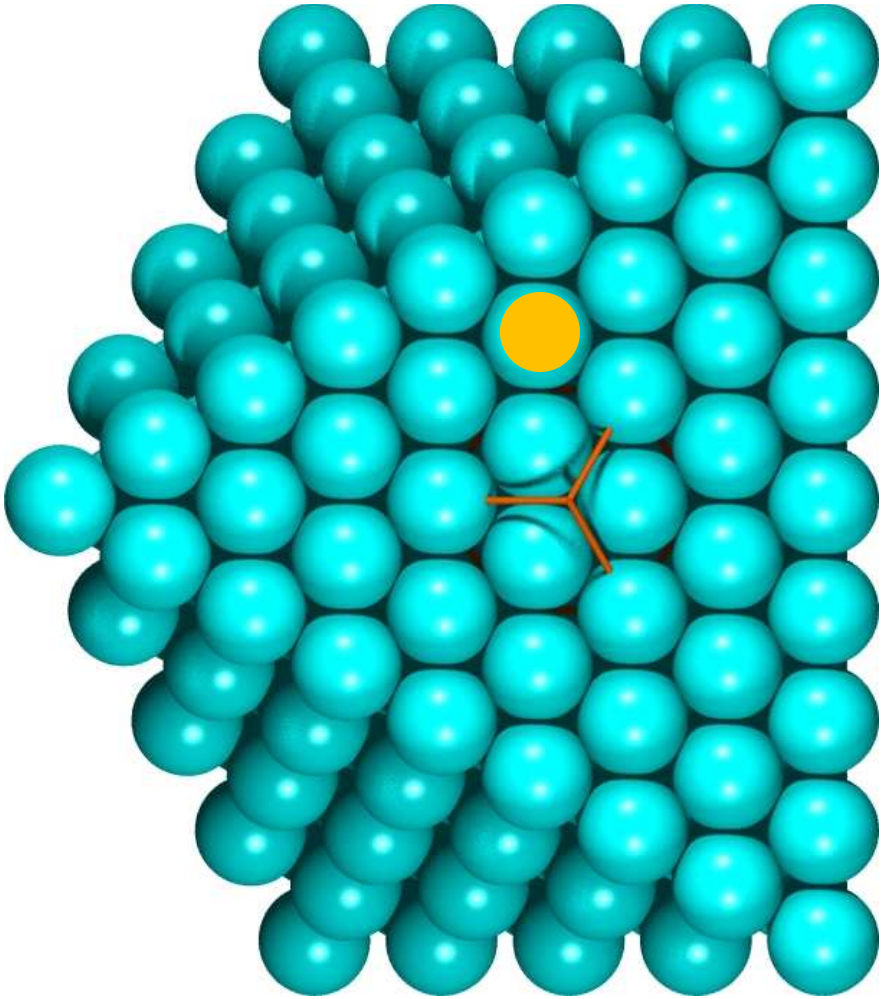
How?
Flow-system (Hinrichsen, Muhler etc.)

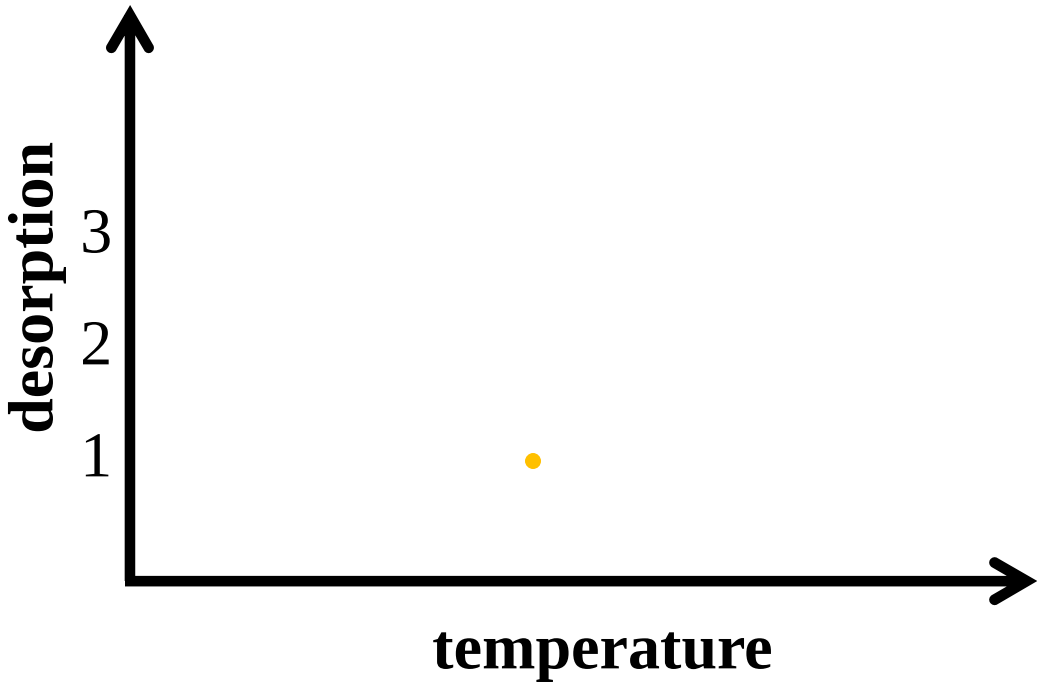


How?
Vacuum-setup

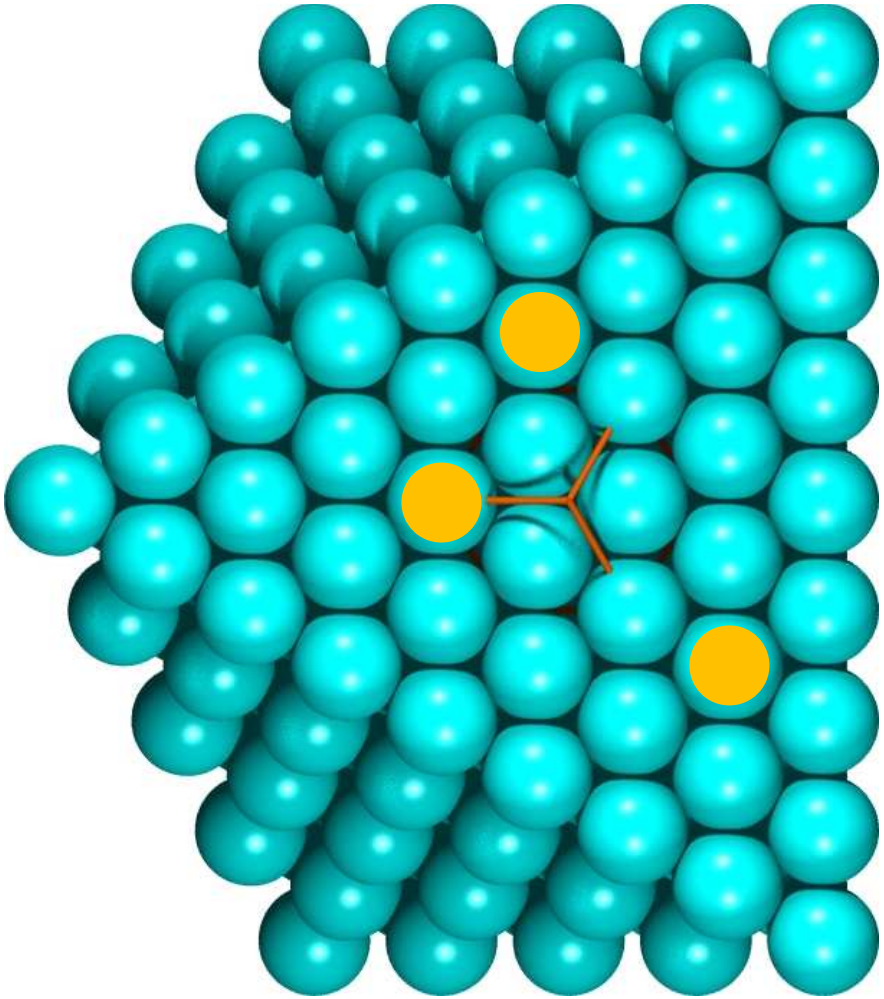


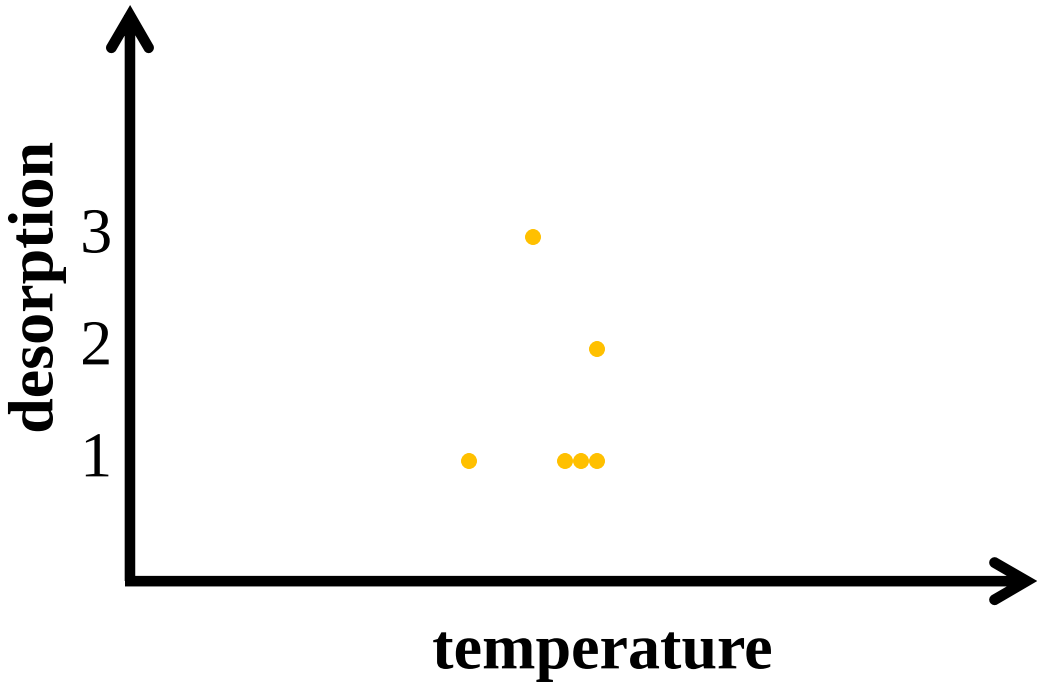
TDS on atomic level





TDS on atomic level

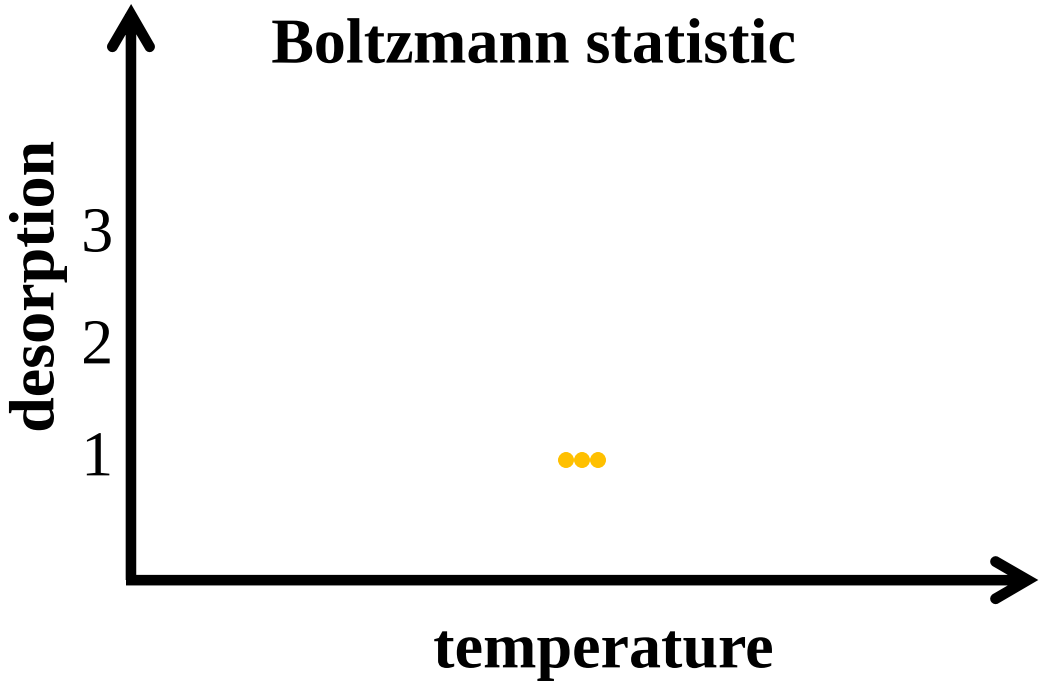




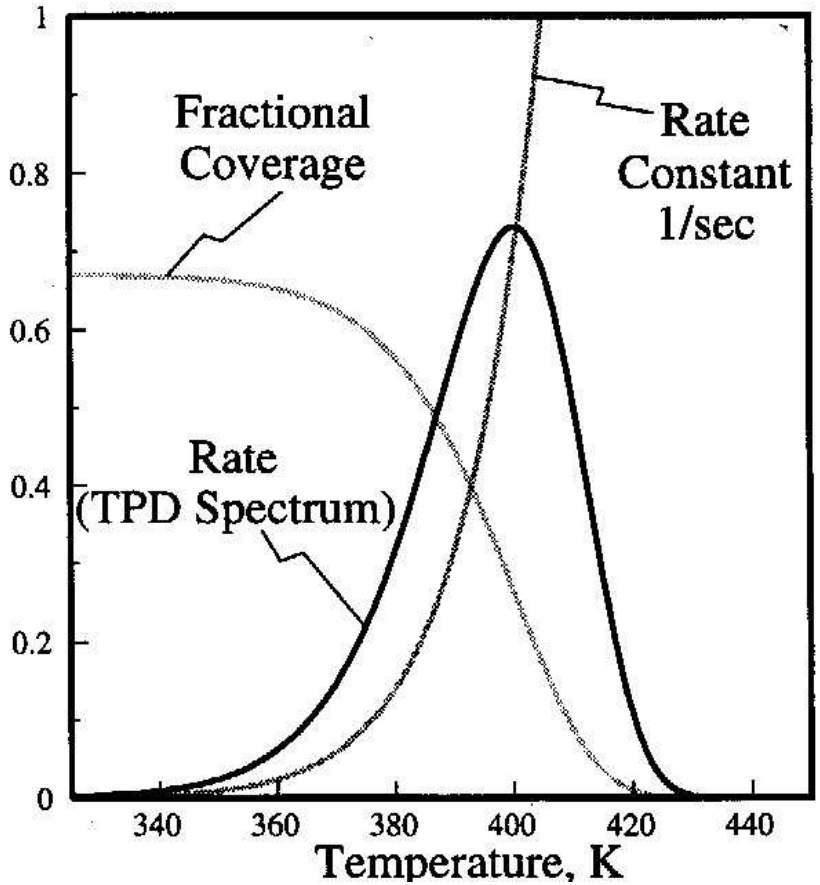
TDS on atomic level

TDS on atomic level is statistics:

- temperature – vibration of the surface atoms:



From atomic level to TD-spectrum
Polanyi-Wigner equation



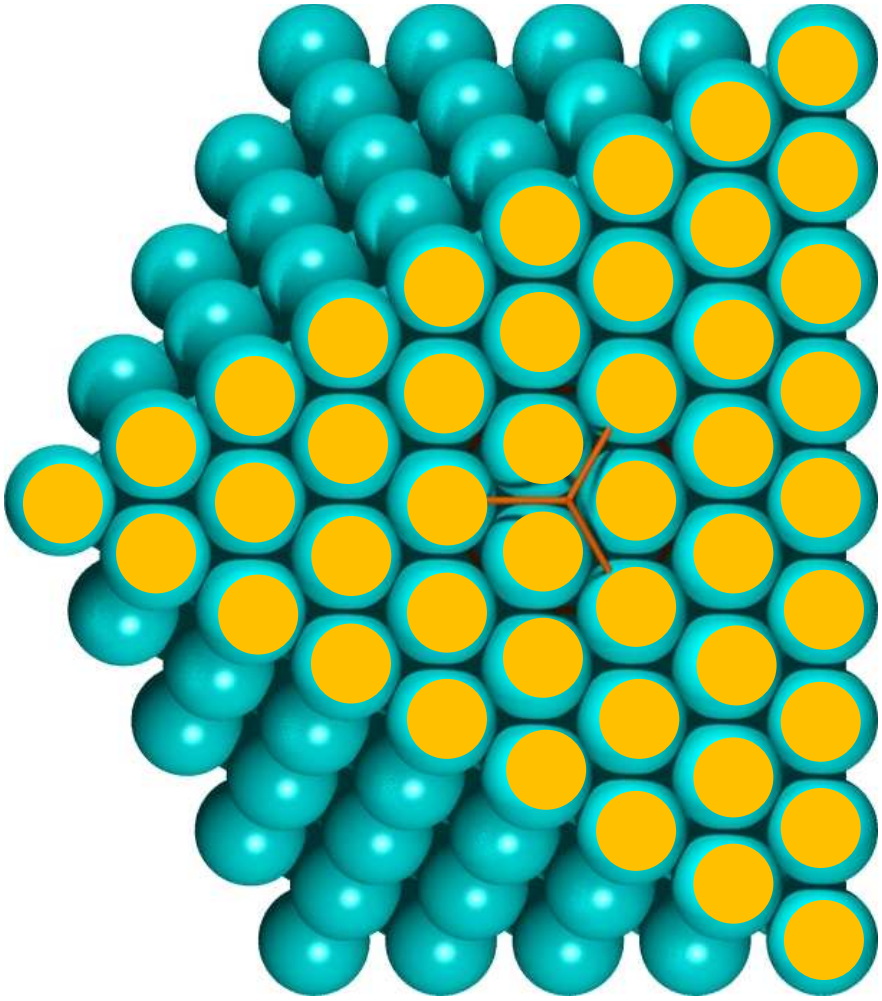
Redhead (1963)

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

E_d: activation energies for desorption;
σ_A: density of adsorption sites cm^{-2};
$\Theta_r = \Theta / \Theta_{sat}$: relative coverage ($0 < \Theta_r < 1$);
ν_n: the frequency factor for desorption order n;
n: order of desorption reaction.
For practical reasons, I divide the total coverage Θ into $\Theta = \Theta_r \, \sigma_A$.

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

Adsorption sites and $\Theta_r = \Theta / \Theta_{sat}$: relative coverage ($0 < \Theta_r < 1$)

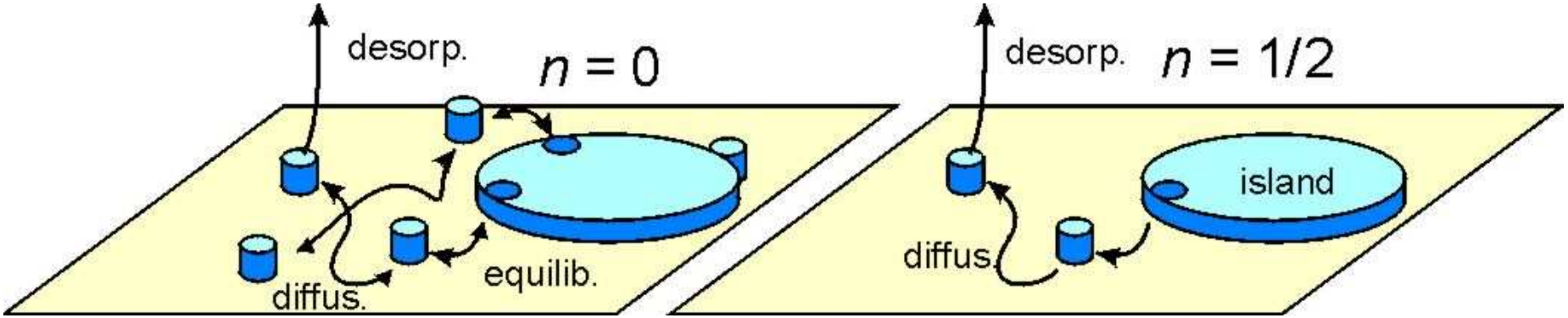


On top $\Theta_r = 1$

p(2x2):

$\Theta_r = 1/4$

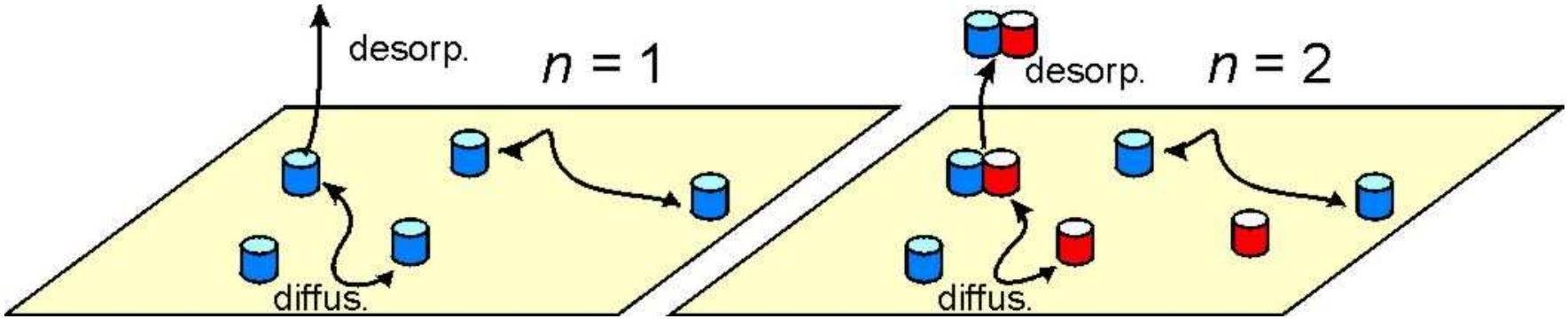
n: order of desorption reaction



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****.*

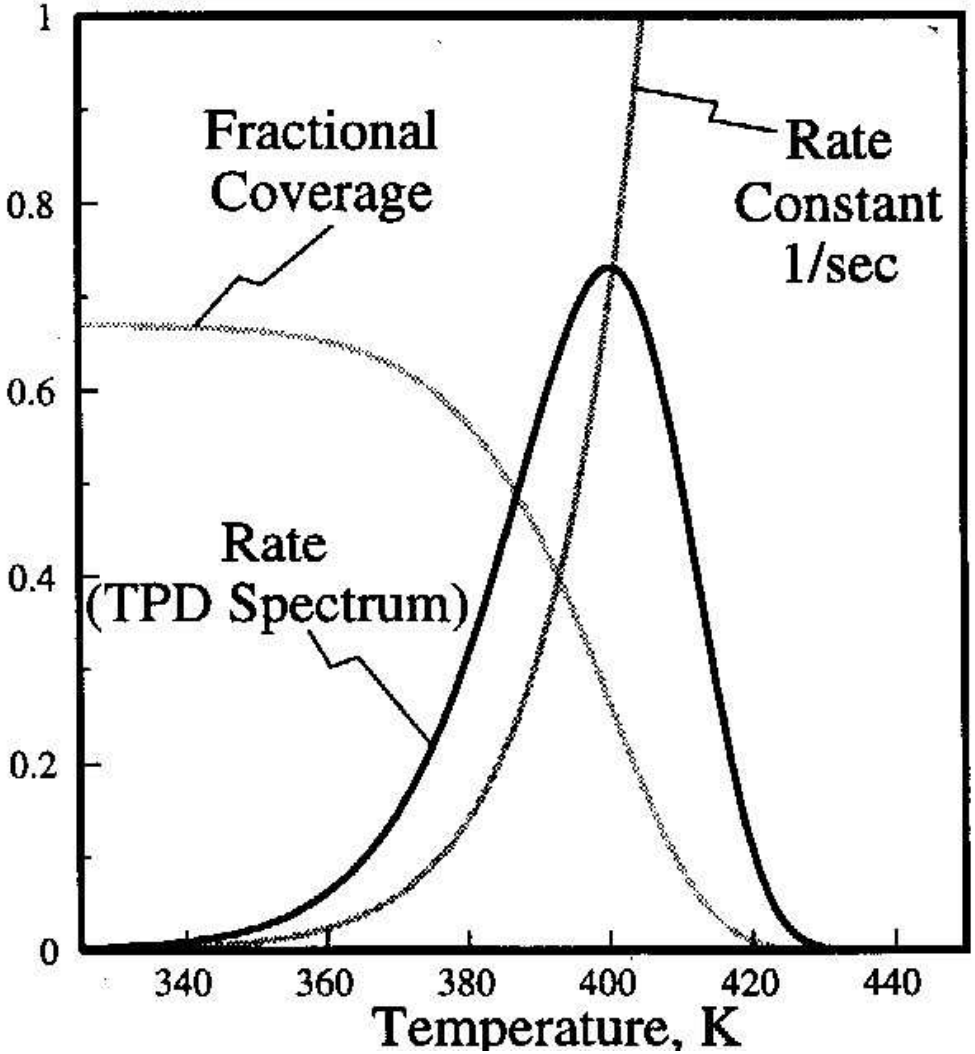
n: order of desorption reaction



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***.

Analysis of TD-spectra relying on the Polanyi-Wigner equation



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

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

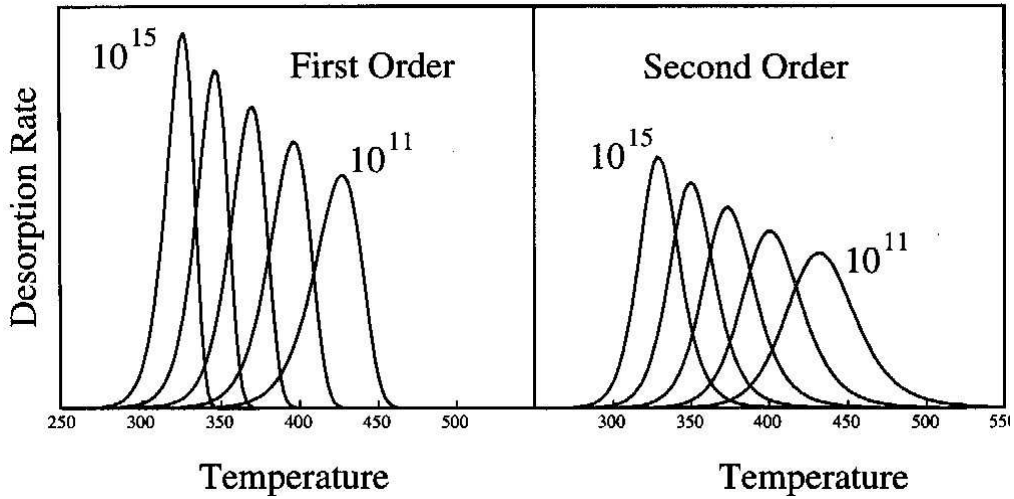
Approximation (Redhead): $E_d \approx RT_P \left[\ln\left(\frac{\nu_1 T_P}{\beta_H} \right) - 3.64 \right]$

T_P, Θ_P:
values at desorption peak maximum

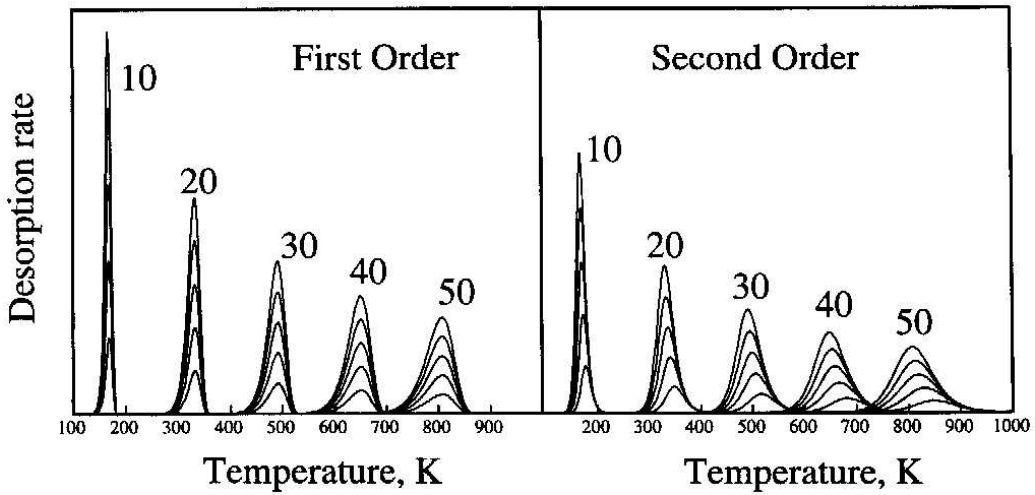
error < 1.5% for $10^8 < \nu_1/\beta < 10^{13}$ K^{-1}

Rule of thumb assuming $\nu_1 = 10^{13}$ s^{-1}: $E_d \approx 0.25 \, T_P$ (E_d in kJ/mol, T_P in K)

Series of TD-spectra



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)

Logarithmic forms of the Polanyi-Wigner equation

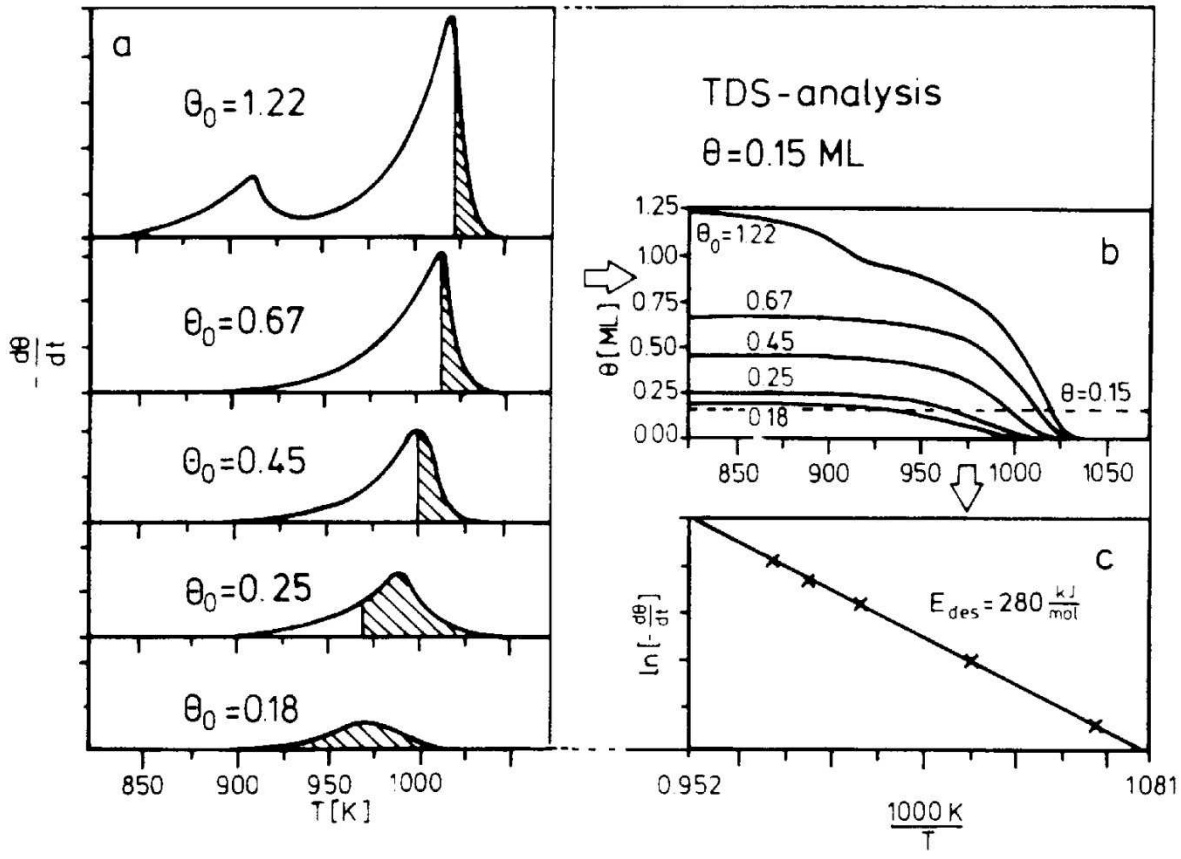
$$r_d = \frac{\sigma_A \, d\Theta_r}{dt} = -\nu_n \, \sigma_A^n \, \Theta_r^n \exp(-E_d/kT)$$

1. Leading edge analysis, after Habenschaden and Küppers,
2. Complete analysis, after King and Bauer

$$\ln(r_d) = -E_d/kT + \ln(\nu_n) + n \ln(\sigma_A \, \Theta_r)$$

Complete analysis, after King

(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.

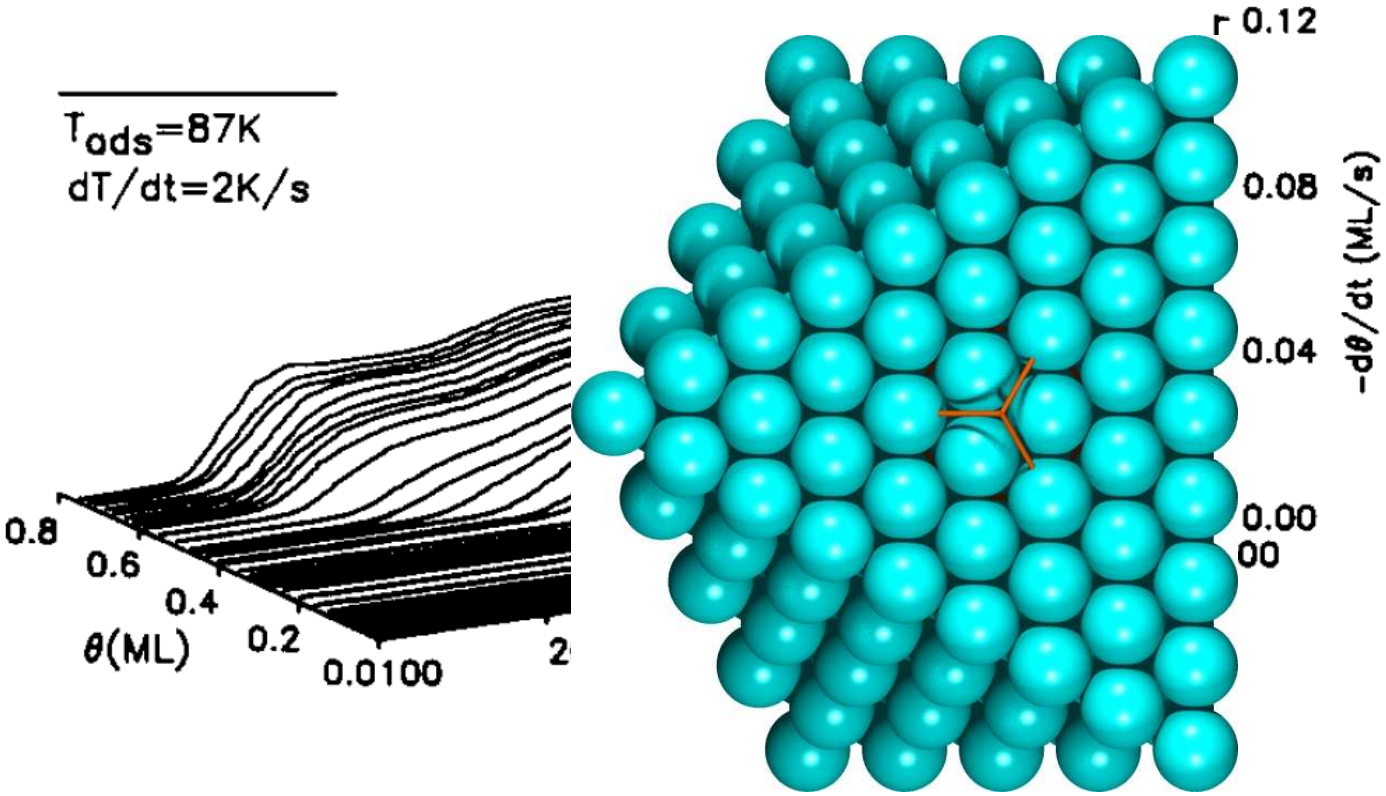
4. From pairs of (r_d, T), ln(r_d) vs. 1/T is plotted (Arrhenius c).

5. The slope yields E_d and the intercept equals ln(ν_n) + n ln(Θ_r). (J.W. Niemantsverdriet et al., J. Vac. Sci. Technol. A5 (1987) 857).

Complicate example

Guo XC, Yates JT. J Chem Phys 1989;90(11):6761-6

THERMAL DESORPTION RATE vs. TEMPERATURE AND COVERAGE



Complicate example?

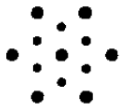
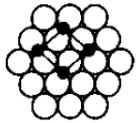
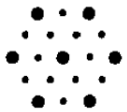
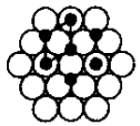
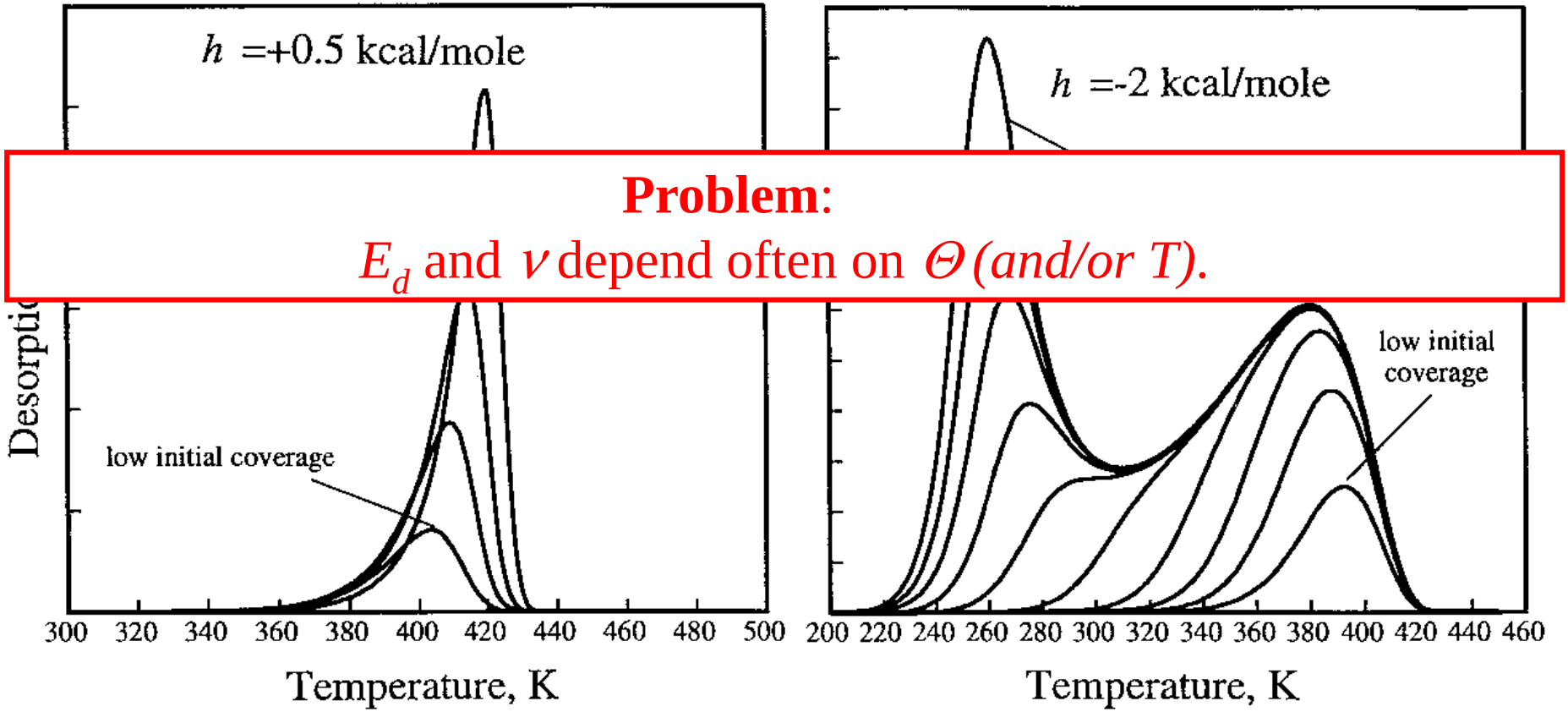
CO Coverage (ML)	Vibrational Frequency (cm^{-1})	LEED Pattern	Structure Model
0.33	1849		
0.50	1918		
0.60	1951		
0.63	1951 2097		
0.66	1951 2097		
0.75	1951 2097		

FIG. 1. CO stretching frequencies, LEED patterns and surface structure models as a function of CO coverage on Pd(111). Results are from Refs. 4 and 5.

Monte Carlo simulations and precursor-moderated desorption

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



Problem:

E_d and ν depend often on Θ *(and/or T)*.

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

Catalytic systems: porous systems

- Pd(111) was already complicated – but understandable

Now: **porous systems**

- **readsorption**
- **diffusion (inter- and intra-particle)**

Simulation results

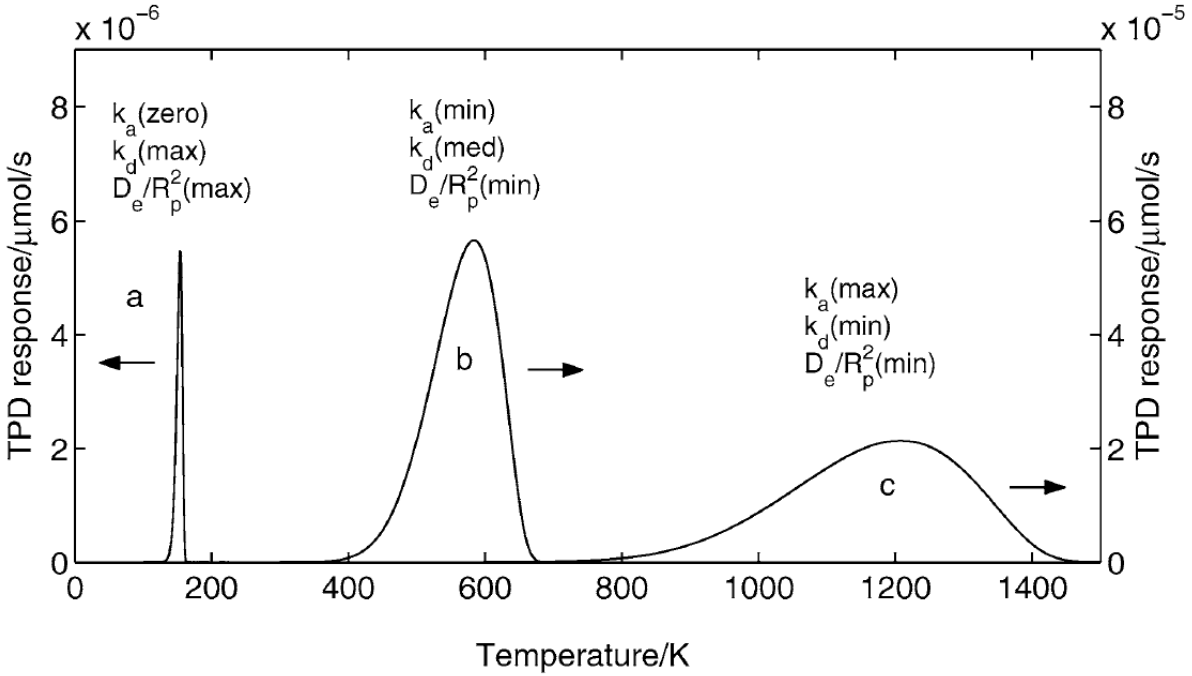
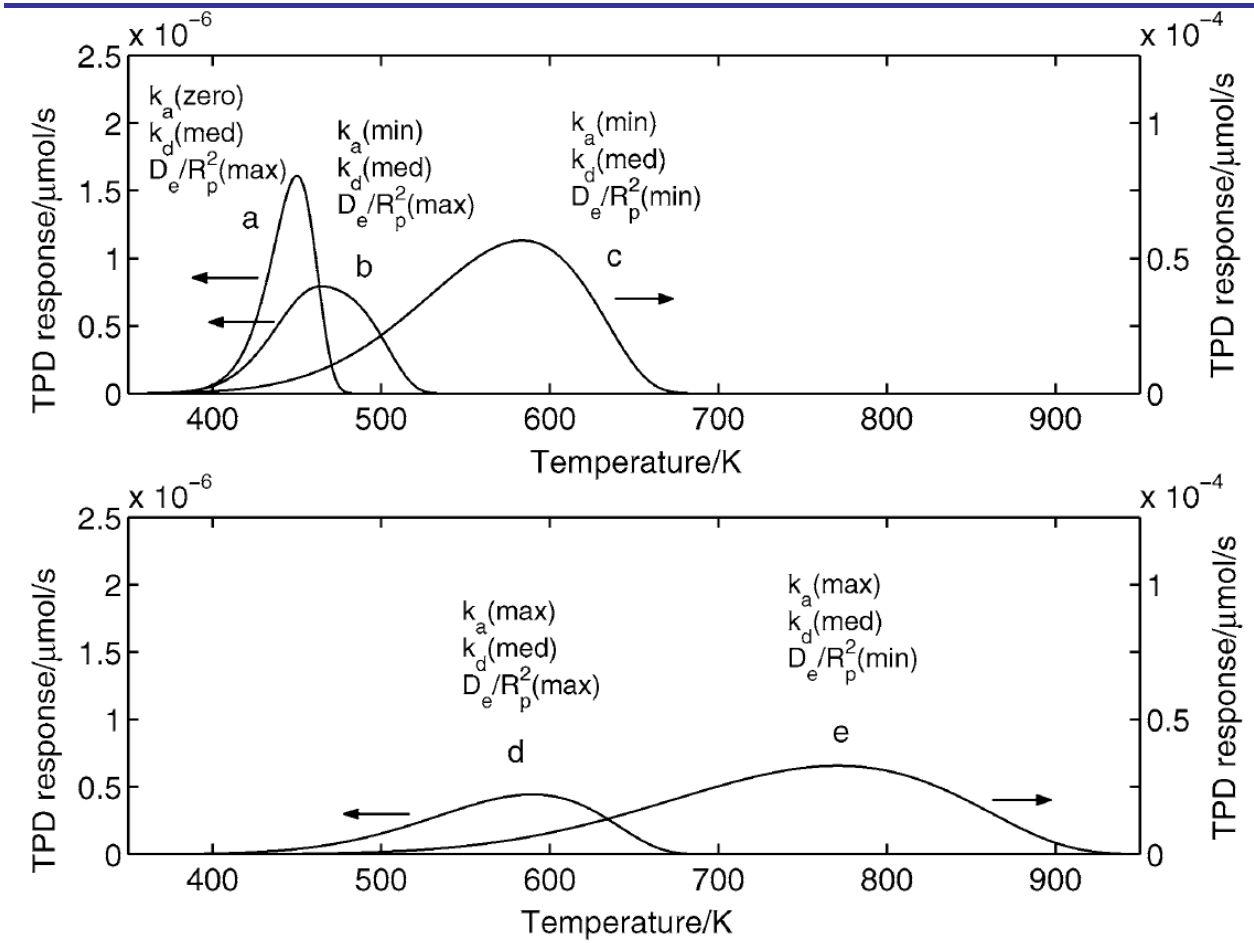


Fig. 1. Possible TPD responses in single particle simulations. TPD response in the lowest temperature range (a), an intermediate TPD response (b), and TPD response in the highest temperature range (c).

Kanervo, J. M.; Keskitalo, T. J.; Shoor, R. I.; Krause, A. O. I. Temperature-Programmed Desorption as a Tool to Extract Quantitative Kinetic or Energetic Information for Porous Catalysts. *J. Cat.* **2006,** *238,* 382-393

Simulation results



Kanervo, J. M. et al., *J. Cat.* **2006,** *238*, 382-393

Fig. 4. TPD responses: without readsorption (a), minimum rate of adsorption (k_a(min)), medium rate of desorption (k_d(med)) and the two extreme values of D_e/R_p^2 (b and c), maximum rate of adsorption (k_a(max)), medium rate of desorption (k_d(med)) and the two extreme values of D_e/R_p^2 (d and e).

H_2 TPR of vanadia/alumina

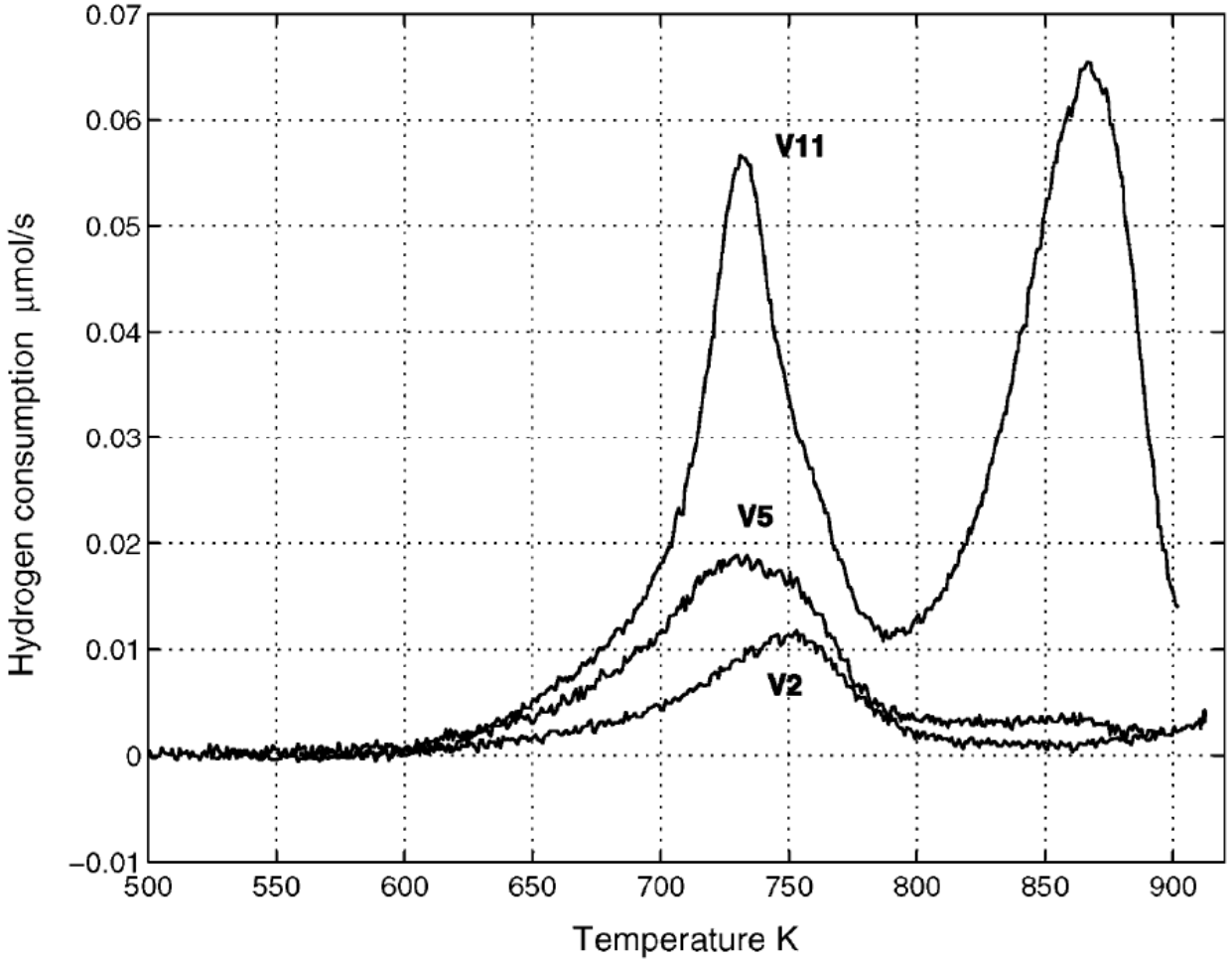


Fig. 5. H2-TPR of the catalysts V2, V5 and V11 (β = 6°C/min, xH2= 10.7% and F = 30 cm^3 NTP/min).

Surface versus bulk reduction

Kanervo, J. M.; Harlin, M. E.; Krause, A. O. I.; Banares, M. A. Characterisation of Alumina-Supported Vanadium Oxide Catalysts by Kinetic Analysis of H-2-TPR Data. *Catal. Today* **2003,** *78,* 171-180.

Flow-system versus vacuum TDS

- In flow set-up TPD responses occur at higher temperatures than in vacuum
- TPD responses may be qualitatively different
- Different mass transfer patterns in reaction cell
- More effective external mass transfer in vacuum setups - can re-adsorption be ignored?
- The intraparticle mass transfer even more relevant in vacuum than in flow TPD
- controlled particle size

Conclusions I

"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 with readsorption and diffusion necessary.

Conclusions II

For catalysts a well calibrated setup is useful:

- Fingerprint method
- Comparison with single crystals data
- Usage of E_{ad} from microcalorimetry
- Combination with other methods (XPS)
- Flow setup enables kinetic and TPD experiments in one setup