LECTURE SERIES
HETEROGENEOUS CATALYSIS

Thermal Desorption Spectroscopy on powders

12th January 8

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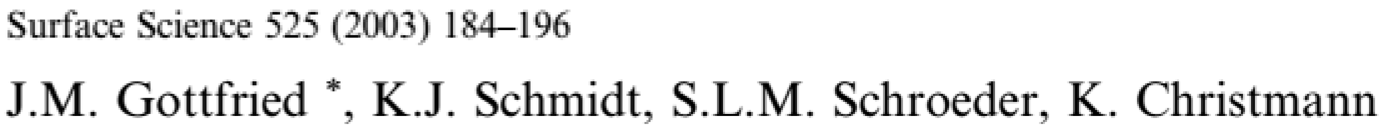
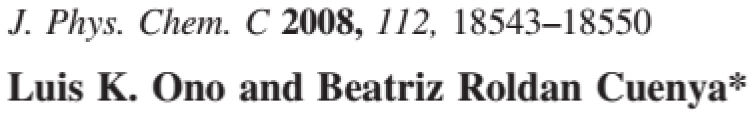
Literature

- R.I. Masel, Principles of adsorption and reaction on solid surfaces, Wiley, 1996.
- J.W. Niemantsverdriet, Spectroscopy in catalysis, Wiley, 2000
- Previous TDS seminras by D. Teschner, W. Ranke and D. Rosenthal
- K. Christmann, Introduction to Surface Physical Chemistry, Steinkopff-Verlag, Darmstadt 1991



Surface Science 525 (2003) 184–196

J.M. Gottfried *, K.J. Schmidt, S.L.M. Schroeder, K. Christmann

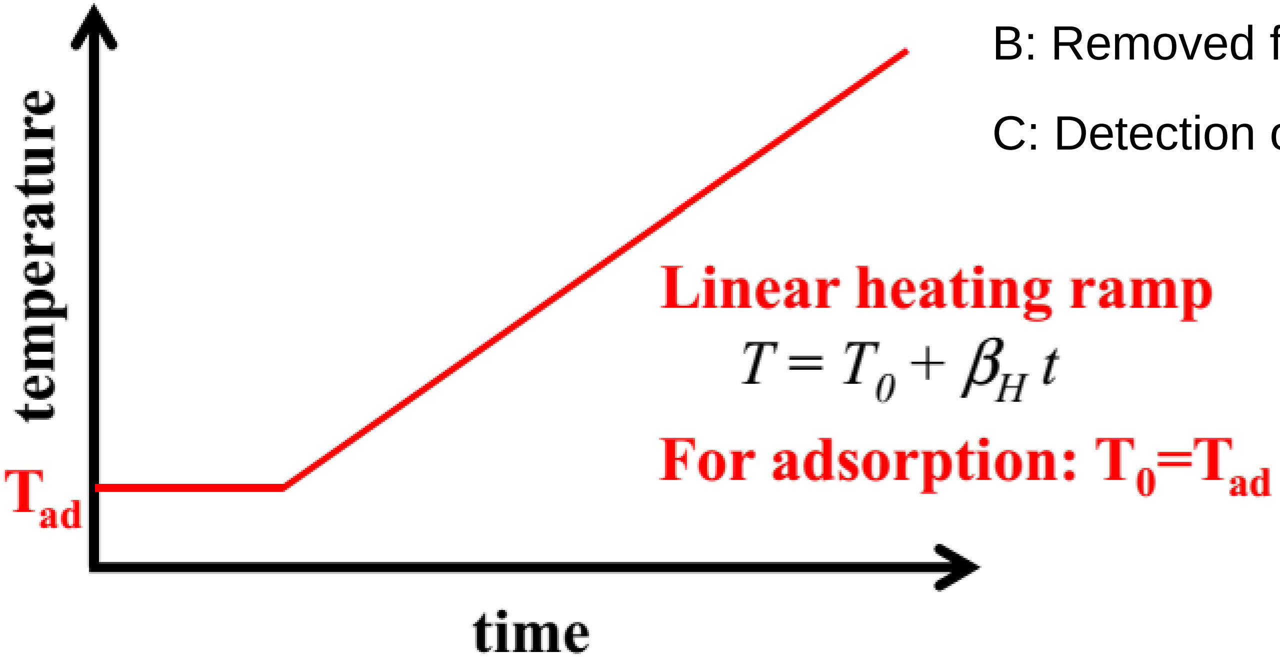


J. Phys. Chem. C **2008,** *112,* 18543–18550

Luis K. Ono and Beatriz Roldan Cuenya*

The idea behind TDS!

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



Linear heating ramp

$$T = T_0 + \beta_H t$$

For adsorption: $T_0 = T_{ad}$

A: Pre-adsorbed species

B: Removed from the surface by T

C: Detection of the desorbing species

TDS signal / curve:
Peaks can be analyzed, qualitatively and quantitatively!

Outline

1. Fundamentals of adsorption/desorption
2. Different TDS/TPD Setups
3. Curves and Evaluation methods
4. A new TDS setup: Between UHV and TPD!
5. Results and Limitations!
6. Summary

Fundamentals: Adsorption kinetics

Rate of Adsorption $R_{ads} = S * F$ in $1/(m^2*s)$

$$F = P / (2\pi m k_b T)^{1/2}$$

Hertz-Knudsen equation:
Flux of incident molecules

Sticking probability: $S = f(\theta) . \exp(-E_a / RT)$

$$R = \frac{f(\theta).P}{\sqrt{2\pi mkT}} \exp(-E_a / RT)$$

Fundamentals: Adsorption/Desorption Thermodynamics

Gibbs energy decreases for spontaneous processes,
$\Delta G < 0$.

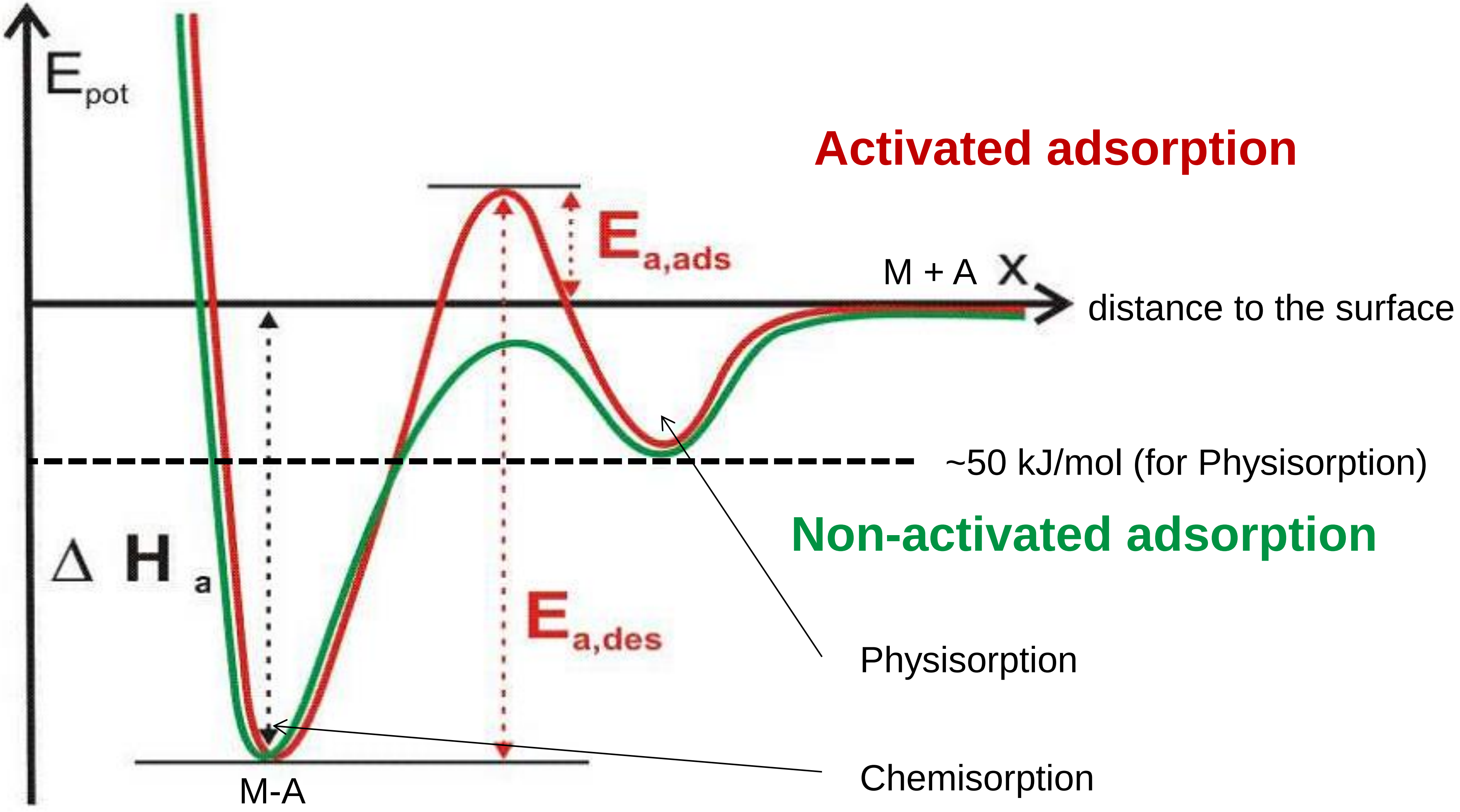
$$\Delta G = \Delta H - T\Delta S$$

Adsorption confines the gas to the surface: $\Delta S < 0$.

- for spontaneous adsorption ΔH is negativ (exothermic).
- for desorption extra energy is needed.

Reversibility: At microscopic scale depending on the energy,
at macroscopic scale averaging in equilibrium.

Fundamentals:
Adsorption Thermodynamics



Activated adsorption

~50 kJ/mol (for Physisorption)

Non-activated adsorption

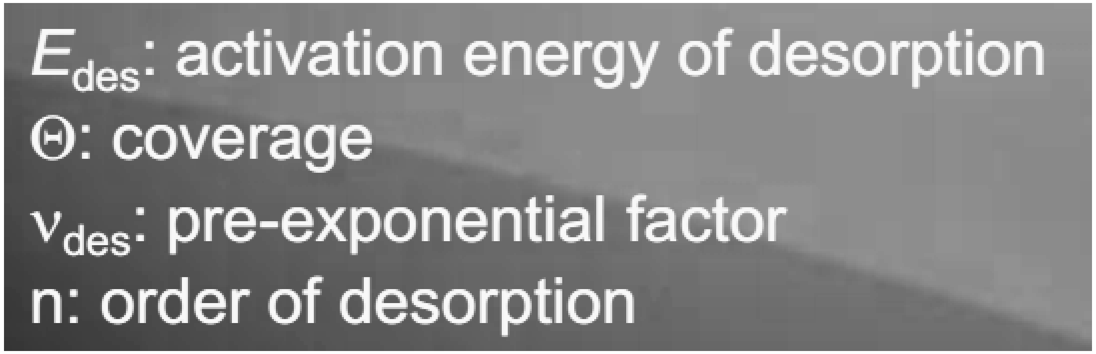
Physisorption

Chemisorption

Fundamentals: Desorption Kinetics

Polanyi-Wigner equation

$$r_{des} = -\frac{d\Theta}{dt} = \nu_n \cdot \exp\left(-\frac{\Delta E_{des}^{PW}}{RT}\right) \cdot \Theta^n$$



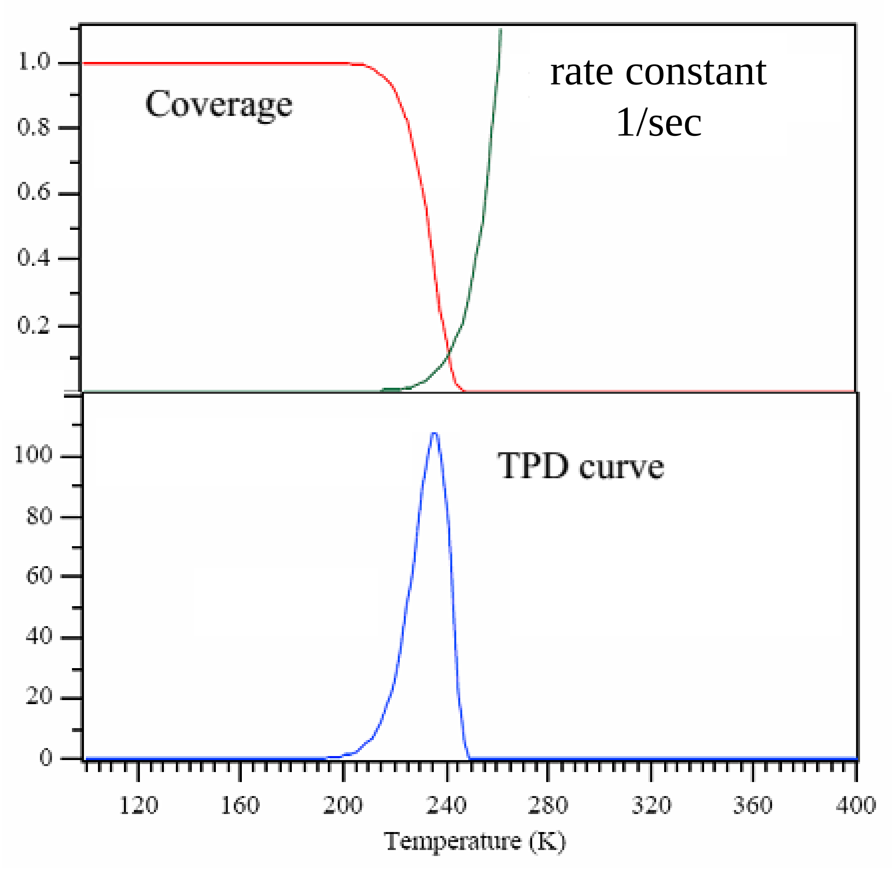
E_{des}: activation energy of desorption

Θ: coverage

ν_{des}: pre-exponential factor

n: order of desorption

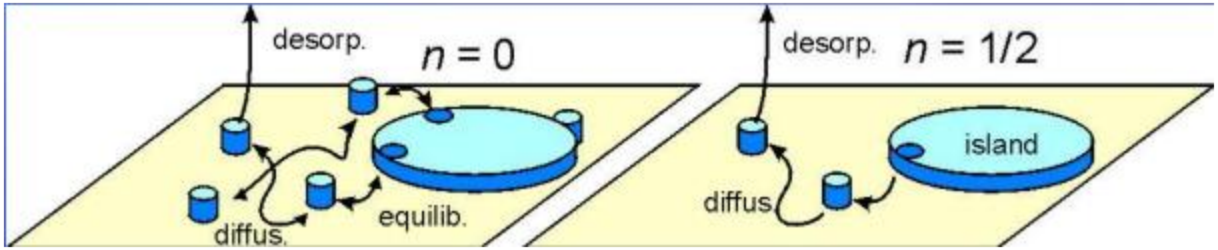
Fundamentals: Desorption Kinetics



$$r_{des} = -\frac{d\Theta}{dt} = \nu_n \cdot \exp\left(-\frac{\Delta E_{des}^{PW}}{RT}\right) \cdot \Theta^n$$

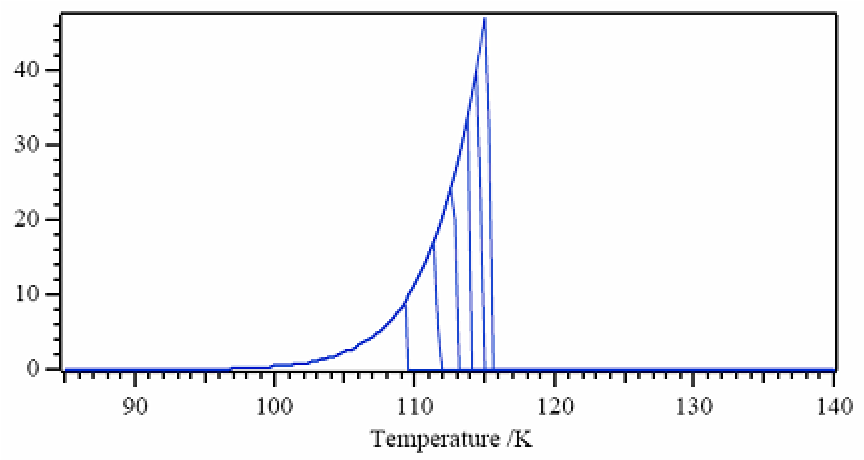
TPD curve represents the desorption rate

Order of Desorption



0: rate independent of coverage; fast exchange with an “infinite” reservoir; e.g. evaporation, sublimation, surface species replenished from bulk

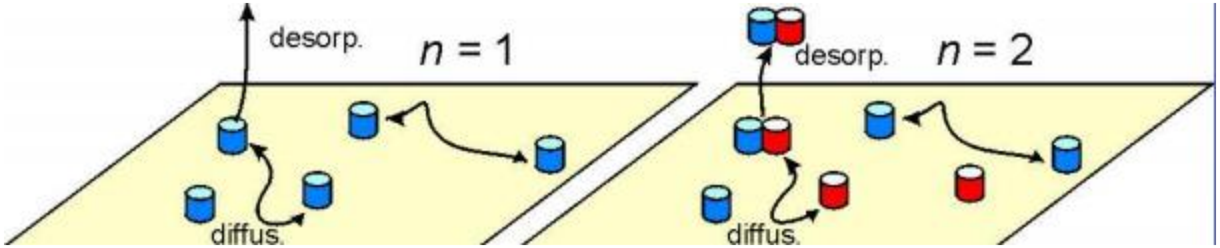
0.5: desorption occurs from the perimeter of i.e. a cluster/edge of a cluster



i) Zero-order kinetics:

multilayer desorption
unlimited supply of particles
(no coverage dependence)
common leading edges

Order of Desorption



1: classical molecular desorption: **rate proportional to Θ^1**

2: associative desorption, the coverage of 2 species matters, mobility of 1 species is needed: **rate proportional to Θ^2**

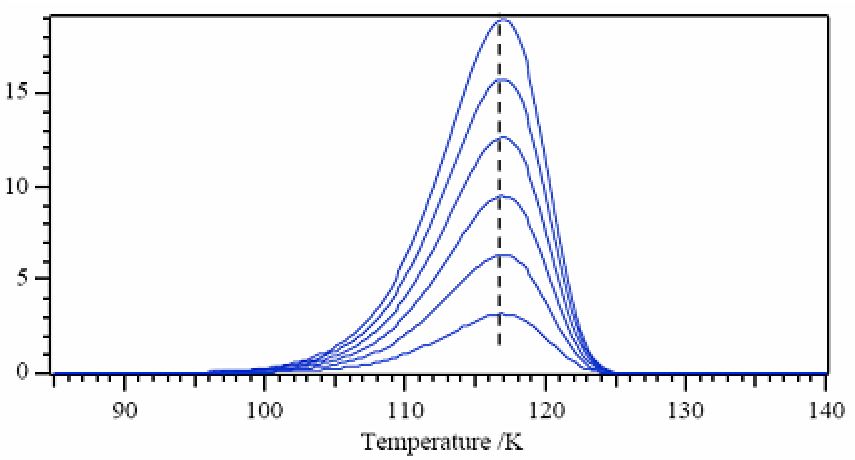
ii) First-order kinetics:

unimolecular desorption

$I(T) \sim$ no. of particles

peak position independent of θ

asymetric peak shape



iii) Second-order kinetics:

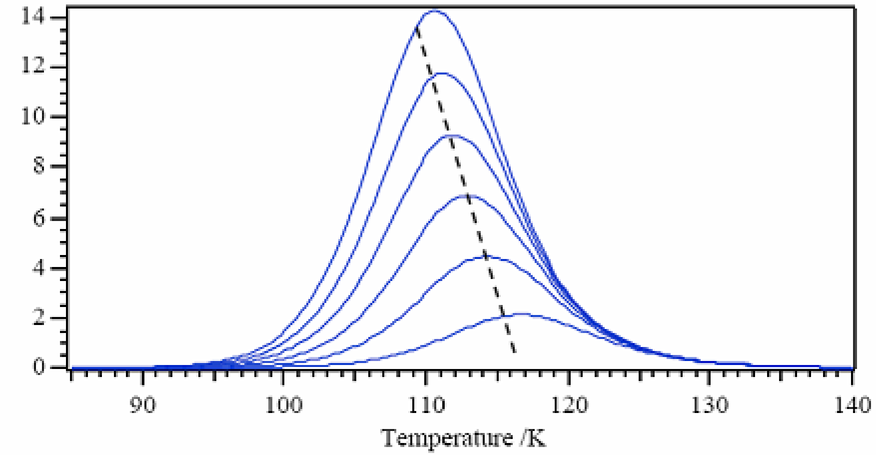
recombinative desorption

$I(T) \sim$ no. of particles (no. of particles $-1) \sim \theta^2$

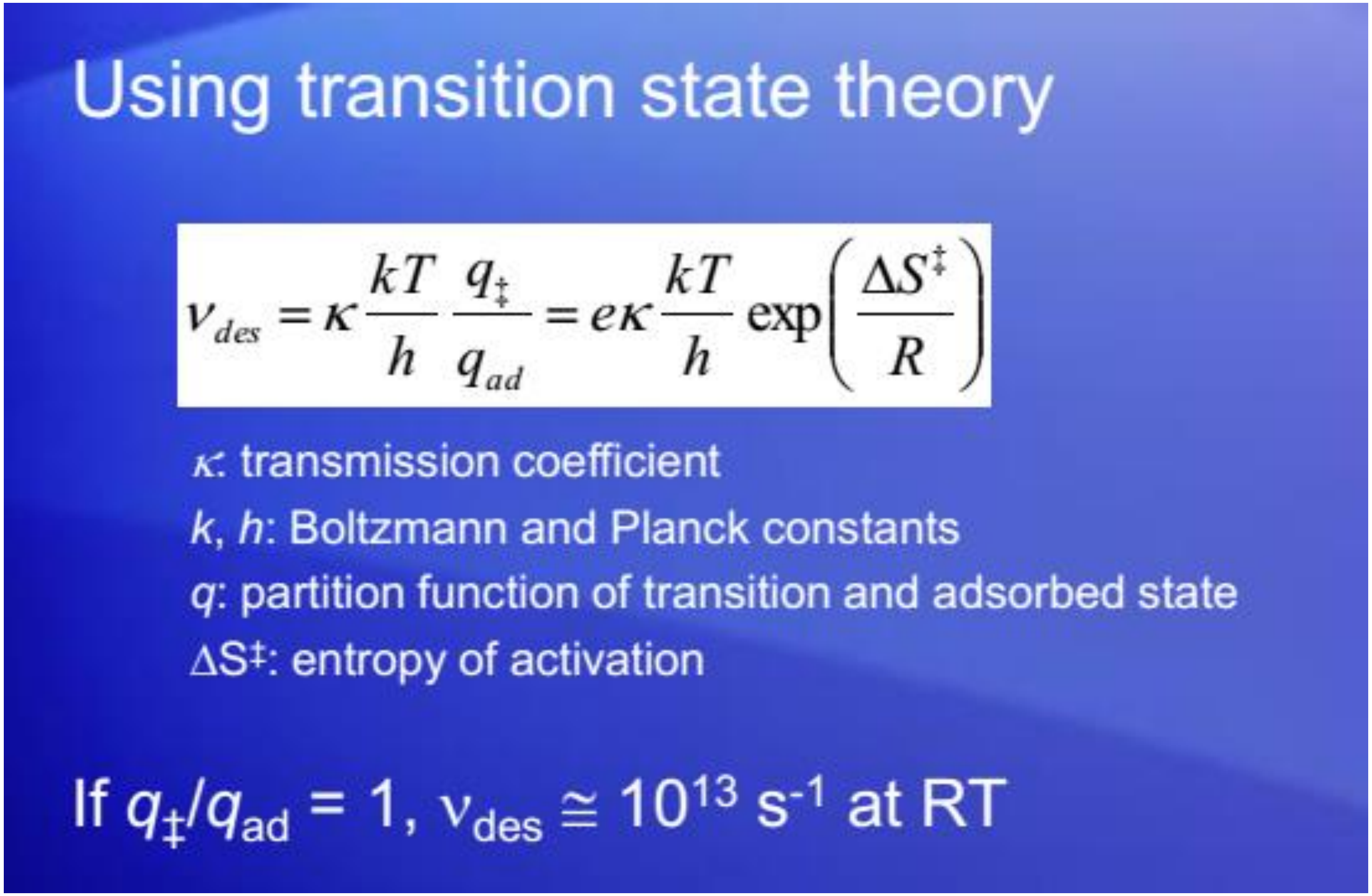
peak position shifts to lower T with increasing θ

symmetric peak shape

common trailing edges



The pre-exponential or frequency factor



Using transition state theory

$$\nu_{des} = \kappa \frac{kT}{h} \frac{q_\ddagger}{q_{ad}} = e\kappa \frac{kT}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right)$$

κ: transmission coefficient

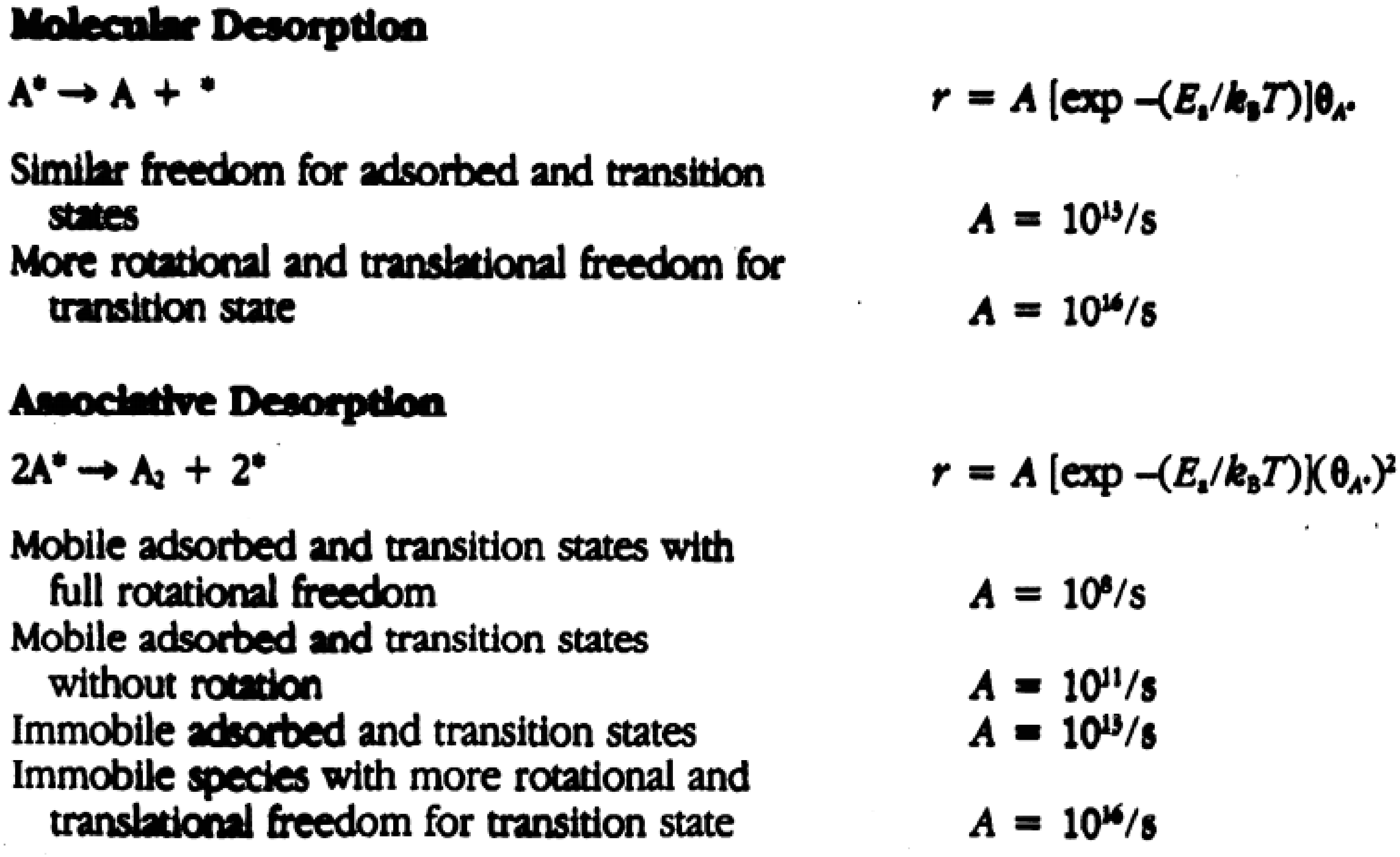
k, h: Boltzmann and Planck constants

q: partition function of transition and adsorbed state

$\Delta S^\ddagger$: entropy of activation

If $q_\ddagger/q_{ad} = 1$, $\nu_{des} \cong 10^{13}\ \mathrm{s}^{-1}$ at RT

The pre-exponential or frequency factor



Molecular Desorption	
$A^* \rightarrow A + *$	$r = A[\exp -(E_a/k_BT)]\theta_{A^*}$
Similar freedom for adsorbed and transition states	$A = 10^{13}/s$
More rotational and translational freedom for transition state	$A = 10^{16}/s$
Associative Desorption	
$2A^* \rightarrow A_2 + 2^*$	$r = A[\exp -(E_a/k_BT)](\theta_{A^*})^2$
Mobile adsorbed and transition states with full rotational freedom	$A = 10^{8}/s$
Mobile adsorbed and transition states without rotation	$A = 10^{11}/s$
Immobile adsorbed and transition states	$A = 10^{13}/s$
Immobile species with more rotational and translational freedom for transition state	$A = 10^{16}/s$

J.A. Dumesic et al., The Microkinetics of Heterogeneous Catalysis, ACS Professional Ref. Book, Washington, DC 1993.

Information from TPD curves

Parameters governing TDS peak T

- E_{des}
- Pre-exponential
- Coverage
- Desorption order
- Heating rate

Differential and integral methods for data analysis

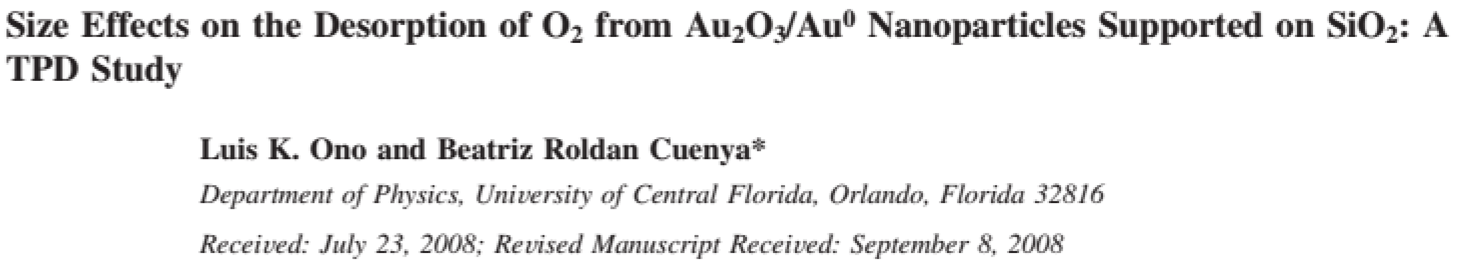
Complete analysis, after King
(D.E. King, T.E. Madey, J.T. Yates, Jr., J. Chem. Phys. 55 (1971) 3236).

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

HRV Method Falconer, J. L.; Madix, R. J.Surf. Sci.1975,48, 393

CAW-Method Chan, C. M.; Aris, R.; Weinberg, W. H.Appl.Surf.Sci.1978,1,360.

Single TD-spectrum: Redhead's analysis
(P.A. Redhead, Vacuum 12 (1963) 203)



Size Effects on the Desorption of O_2 from Au_2O_3/Au^0 Nanoparticles Supported on SiO_2: A TPD Study

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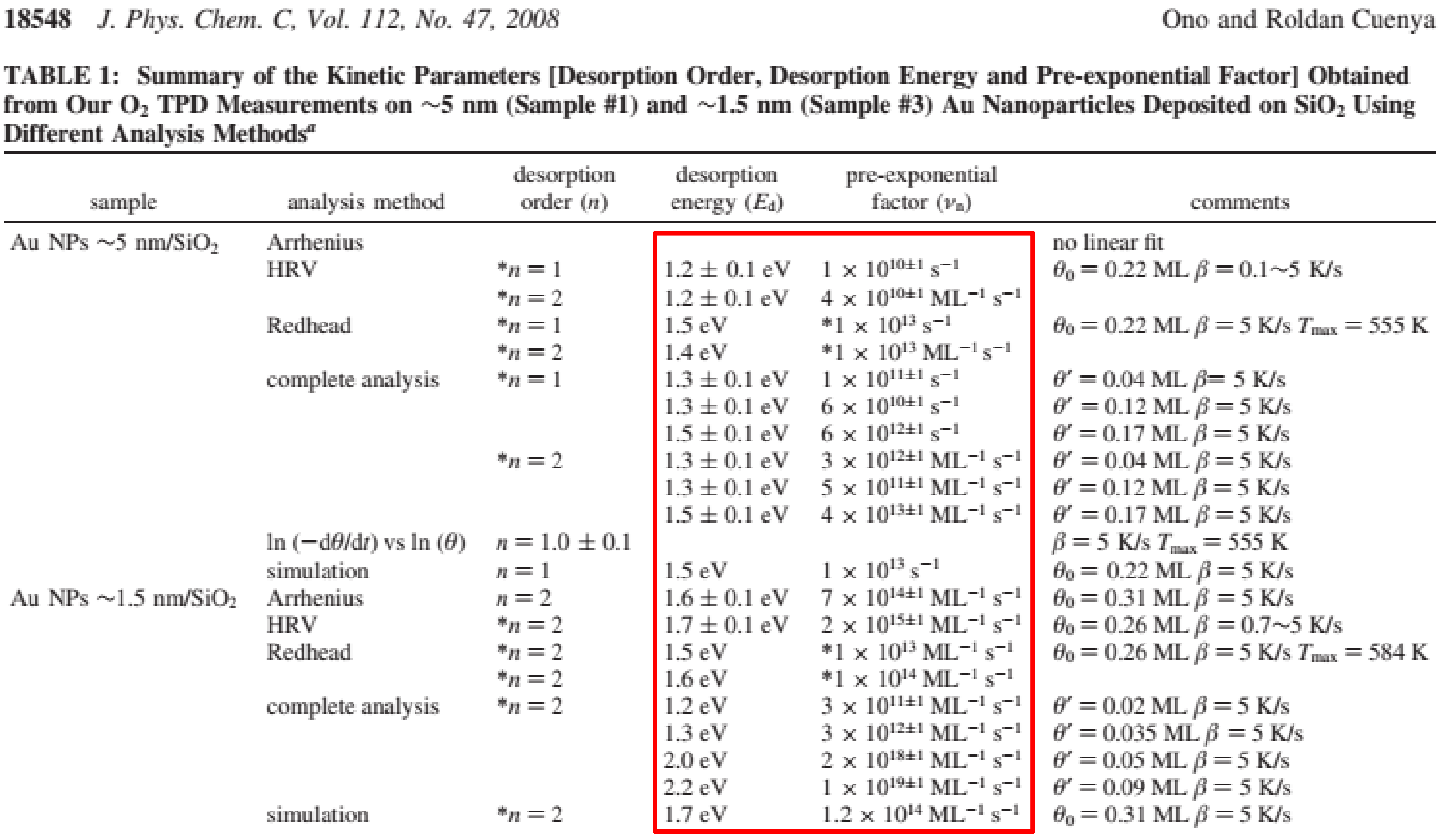
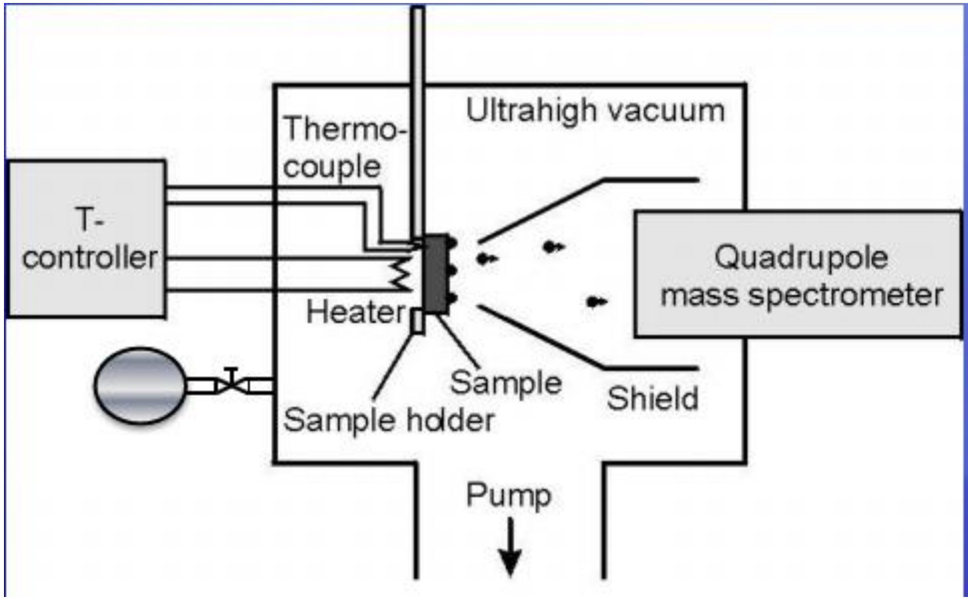
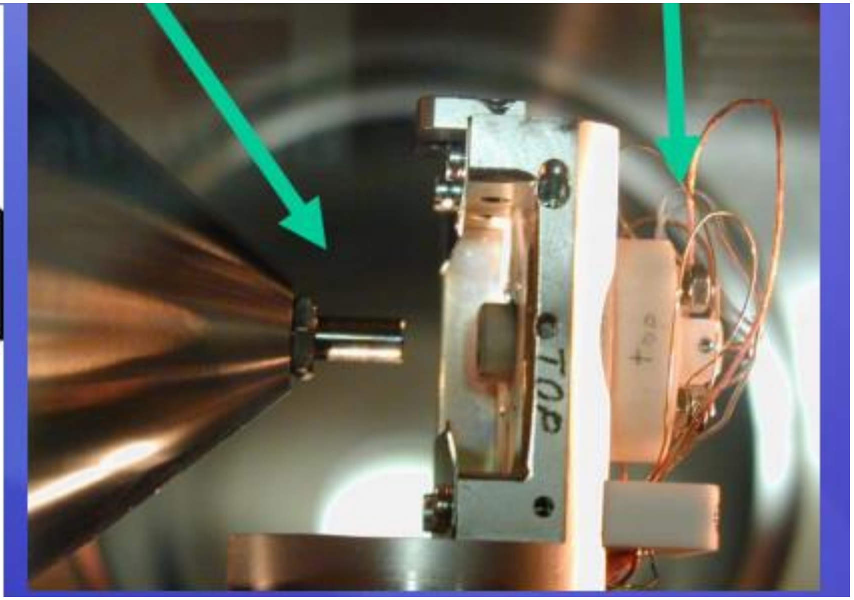


TABLE 1: Summary of the Kinetic Parameters [Desorption Order, Desorption Energy and Pre-exponential Factor] Obtained from Our O_2 TPD Measurements on ~5 nm (Sample #1) and ~1.5 nm (Sample #3) Au Nanoparticles Deposited on SiO_2 Using Different Analysis Methods[a]

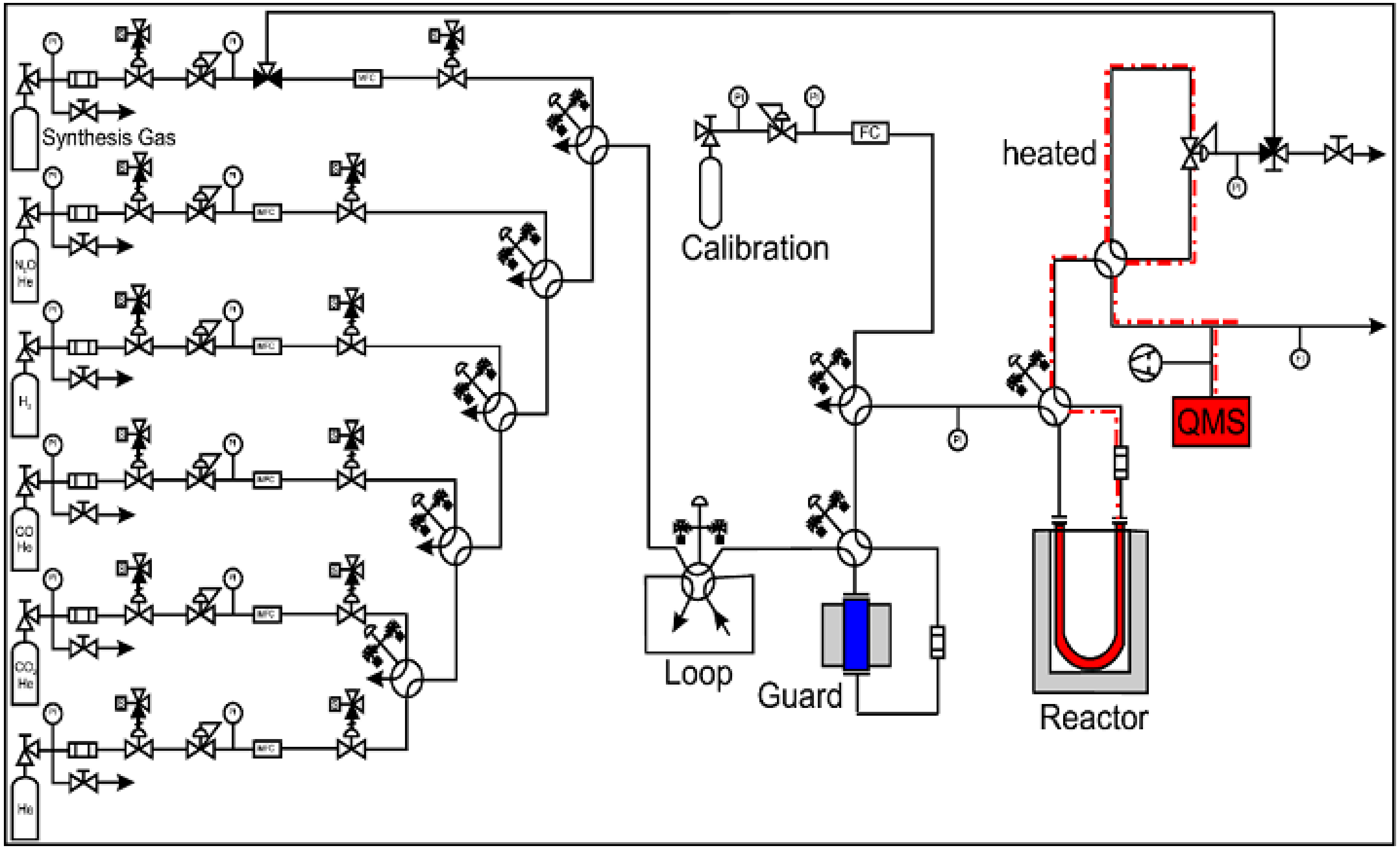
sample	analysis method	desorption order (n)	desorption energy (E_d)	pre-exponential factor (ν_n)	comments
Au NPs ~5 nm/SiO_2	Arrhenius				no linear fit
	HRV	$*n = 1$	1.2 ± 0.1 eV	$1 \times 10^{10\pm1}\ s^{-1}$	$\theta_0 = 0.22$ ML $\beta = 0.1\sim5$ K/s
		$*n = 2$	1.2 ± 0.1 eV	$4 \times 10^{10\pm1}\ ML^{-1}\ s^{-1}$	
	Redhead	$*n = 1$	1.5 eV	$*1 \times 10^{13}\ s^{-1}$	$\theta_0 = 0.22$ ML $\beta = 5$ K/s $T_{max} = 555$ K
		$*n = 2$	1.4 eV	$*1 \times 10^{13}\ ML^{-1}\ s^{-1}$	
	complete analysis	$*n = 1$	1.3 ± 0.1 eV	$1 \times 10^{11\pm1}\ s^{-1}$	$\theta' = 0.04$ ML $\beta = 5$ K/s
			1.3 ± 0.1 eV	$6 \times 10^{10\pm1}\ s^{-1}$	$\theta' = 0.12$ ML $\beta = 5$ K/s
			1.5 ± 0.1 eV	$6 \times 10^{12\pm1}\ s^{-1}$	$\theta' = 0.17$ ML $\beta = 5$ K/s
		$*n = 2$	1.3 ± 0.1 eV	$3 \times 10^{12\pm1}\ ML^{-1}\ s^{-1}$	$\theta' = 0.04$ ML $\beta = 5$ K/s
			1.3 ± 0.1 eV	$5 \times 10^{11\pm1}\ ML^{-1}\ s^{-1}$	$\theta' = 0.12$ ML $\beta = 5$ K/s
			1.5 ± 0.1 eV	$4 \times 10^{13\pm1}\ ML^{-1}\ s^{-1}$	$\theta' = 0.17$ ML $\beta = 5$ K/s
	$\ln(-d\theta/dt)$ vs $\ln(\theta)$	$n = 1.0 \pm 0.1$			$\beta = 5$ K/s $T_{max} = 555$ K
	simulation	$n = 1$	1.5 eV	$1 \times 10^{13}\ s^{-1}$	$\theta_0 = 0.22$ ML $\beta = 5$ K/s
Au NPs ~1.5 nm/SiO_2	Arrhenius	$n = 2$	1.6 ± 0.1 eV	$7 \times 10^{14\pm1}\ ML^{-1}\ s^{-1}$	$\theta_0 = 0.31$ ML $\beta = 5$ K/s
	HRV	$*n = 2$	1.7 ± 0.1 eV	$2 \times 10^{15\pm1}\ ML^{-1}\ s^{-1}$	$\theta_0 = 0.26$ ML $\beta = 0.7\sim5$ K/s
	Redhead	$*n = 2$	1.5 eV	$*1 \times 10^{13}\ ML^{-1}\ s^{-1}$	$\theta_0 = 0.26$ ML $\beta = 5$ K/s $T_{max} = 584$ K
		$*n = 2$	1.6 eV	$*1 \times 10^{14}\ ML^{-1}\ s^{-1}$	
	complete analysis	$*n = 2$	1.2 eV	$3 \times 10^{11\pm1}\ ML^{-1}\ s^{-1}$	$\theta' = 0.02$ ML $\beta = 5$ K/s
			1.3 eV	$3 \times 10^{12\pm1}\ ML^{-1}\ s^{-1}$	$\theta' = 0.035$ ML $\beta = 5$ K/s
			2.0 eV	$2 \times 10^{18\pm1}\ ML^{-1}\ s^{-1}$	$\theta' = 0.05$ ML $\beta = 5$ K/s
			2.2 eV	$1 \times 10^{19\pm1}\ ML^{-1}\ s^{-1}$	$\theta' = 0.09$ ML $\beta = 5$ K/s
	simulation	$*n = 2$	1.7 eV	$1.2 \times 10^{14}\ ML^{-1}\ s^{-1}$	$\theta_0 = 0.31$ ML $\beta = 5$ K/s

Different **TDS**/TPD Setups!

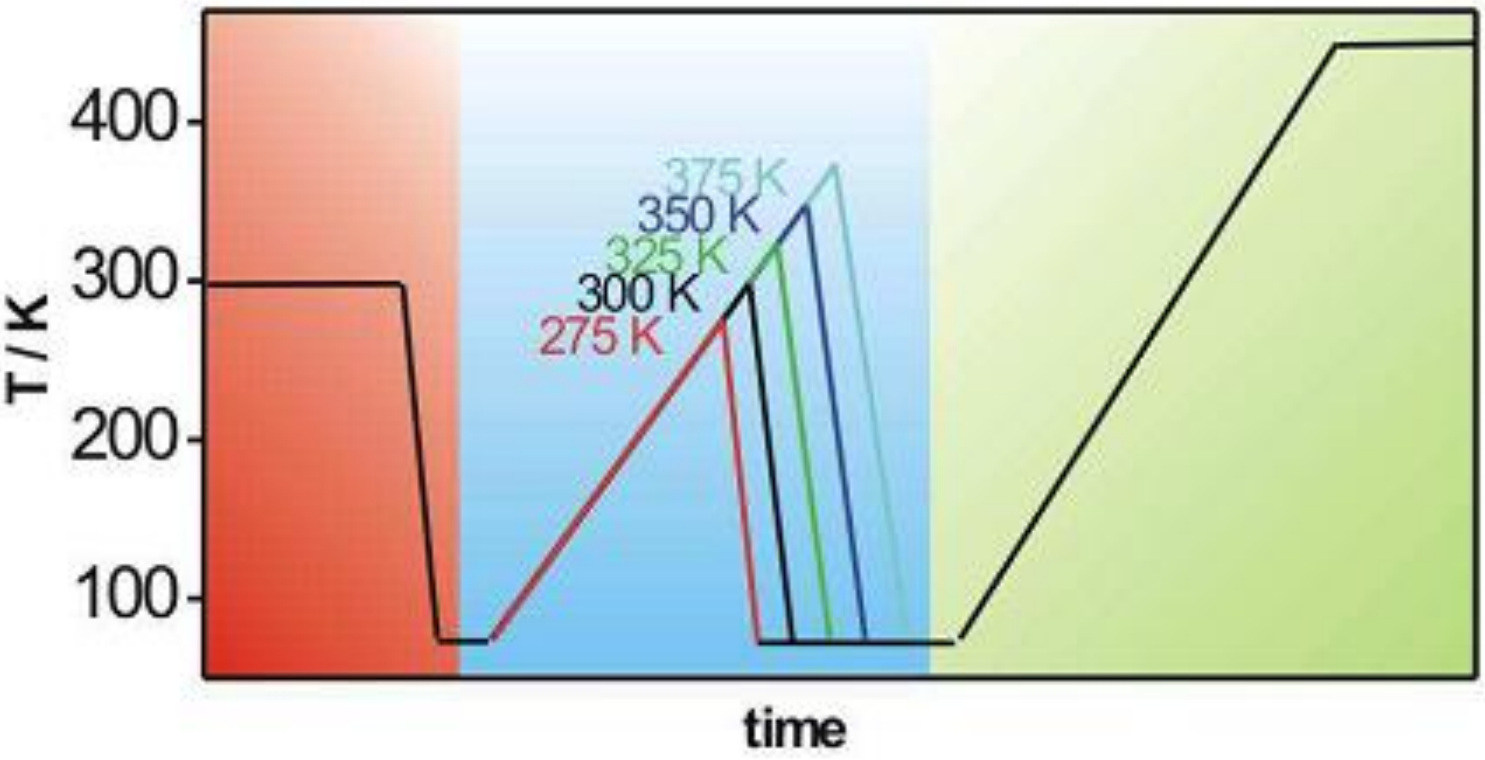




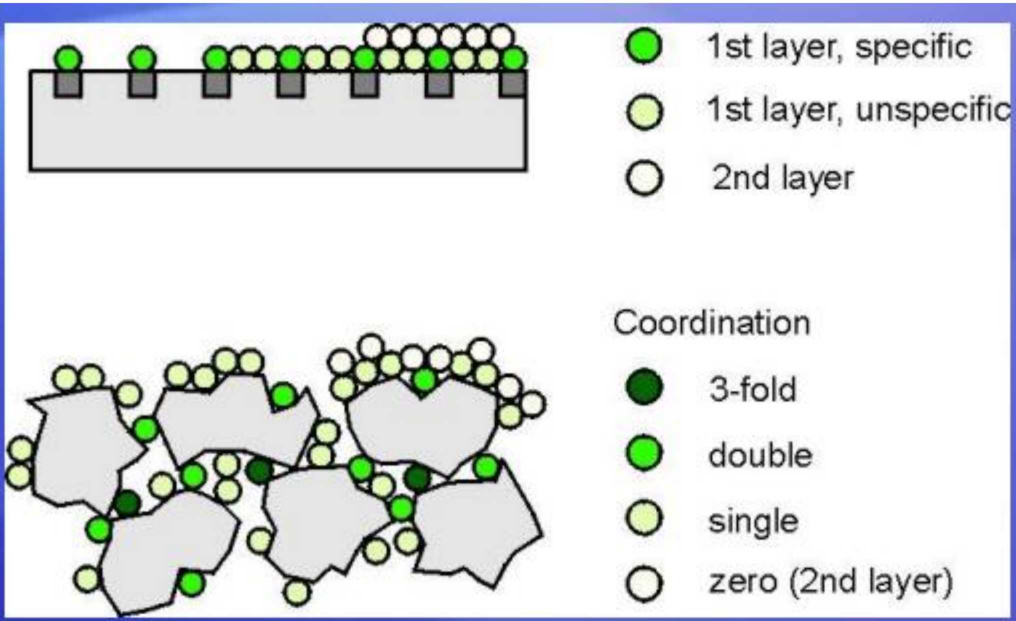
Different TDS/**TPD** Setups!



Different Coverages in TPD



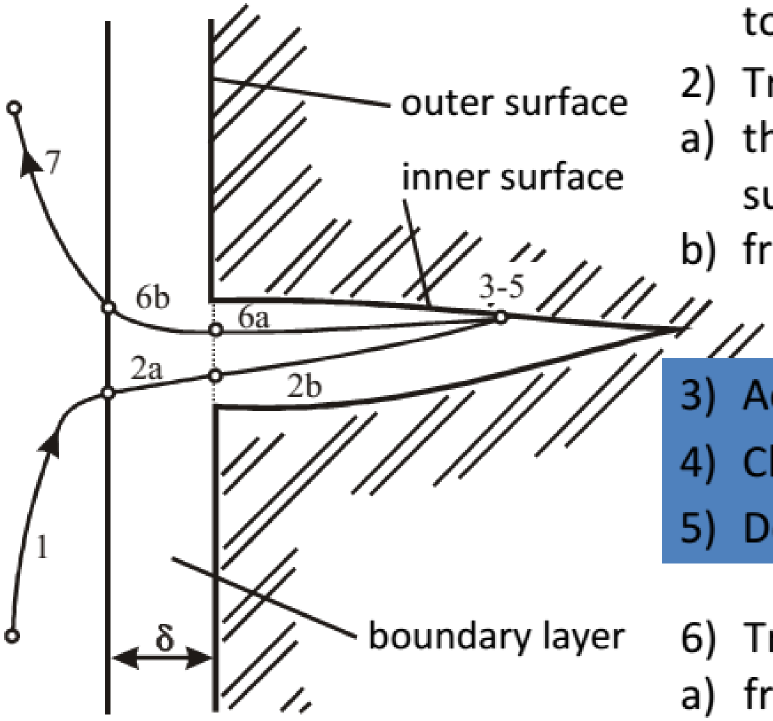
Challenges for powder TDS/TPD



Powder: additional inhomogeneity from roughness: sites with different coordination to the substrate; desorption includes pore diffusion even in UHV.

During TPD with inert gas flow, pore diffusion an issue: peak form is largely affected by the rate of diffusion.

Challenges for powder TDS/TPD



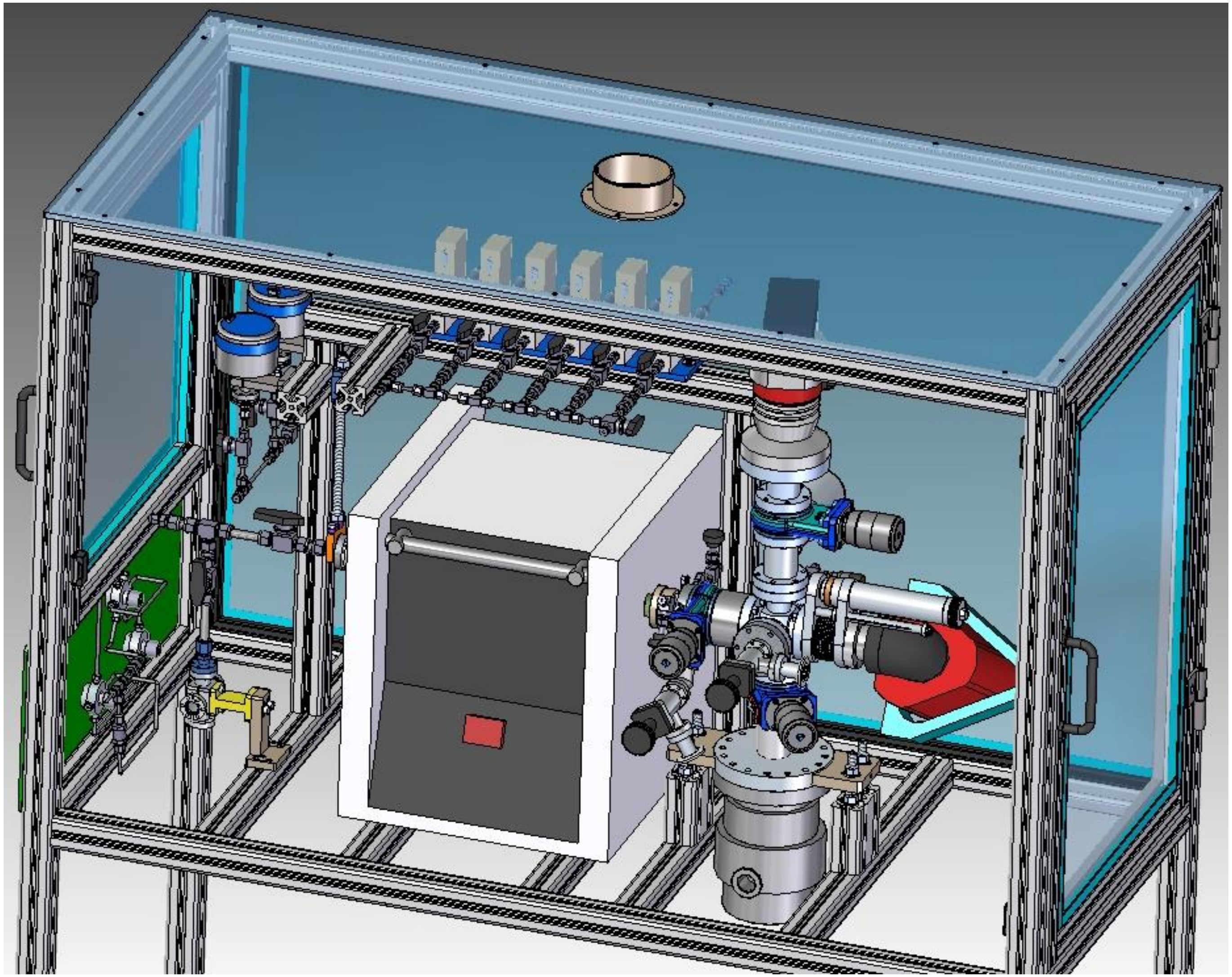
Very frequently:
inner surface >> outer surface

1) Transport of the reactants from the fluid bulk to the boundary layer
2) Transport of the reactants to the surface
a) through the boundary layer to the outer surface
b) from the outer surface to the inner surface

3) Adsorption (chemisorption) of the reactant
4) Chemical reaction
5) Desorption of the product

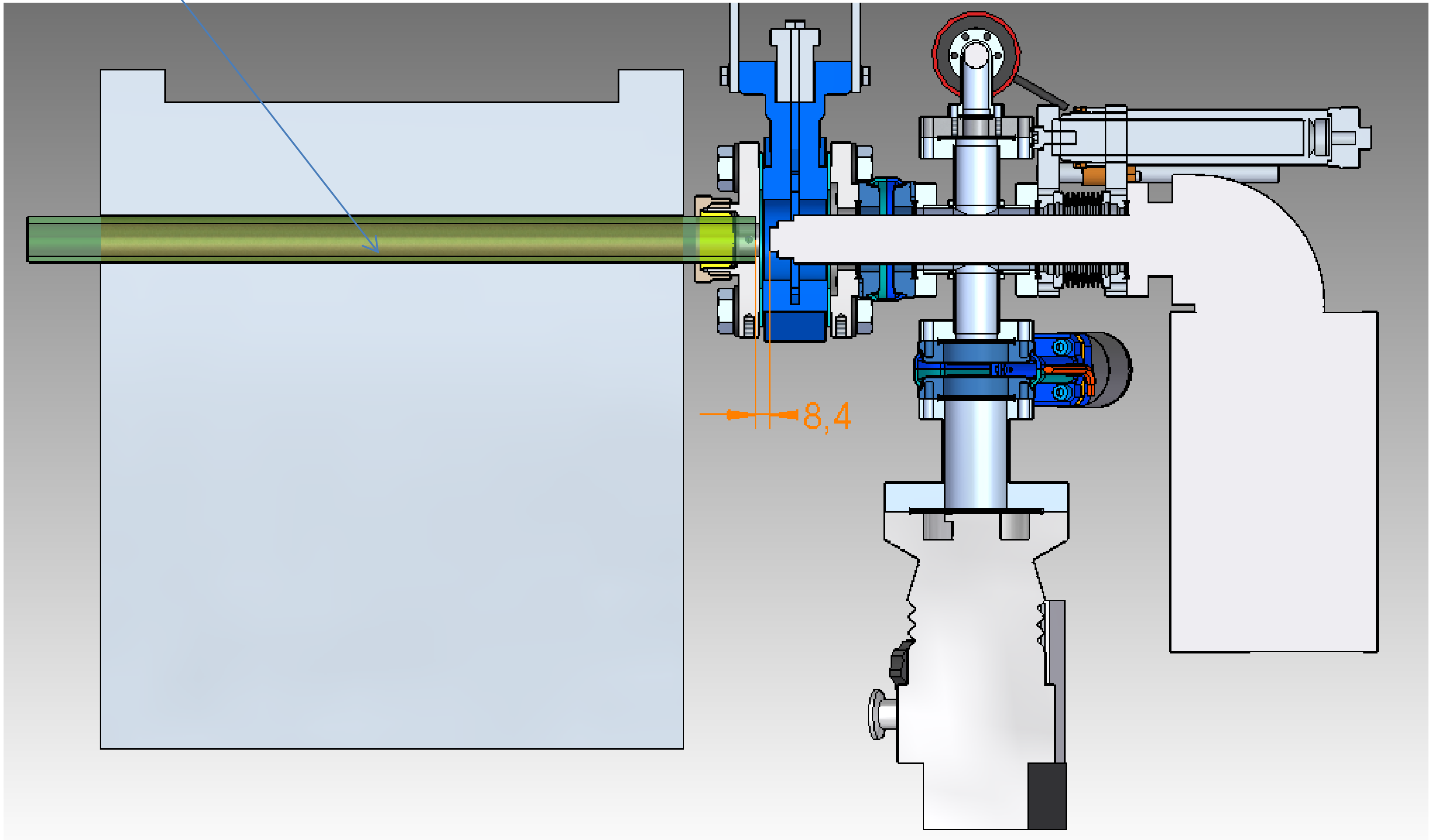
6) Transport of the products to the fluid bulk
a) from the inner surface to the outer surface
b) from the outer surface through the boundary layer
7) Transport of the products from the boundary layer to the fluid bulk

A new TDS setup!



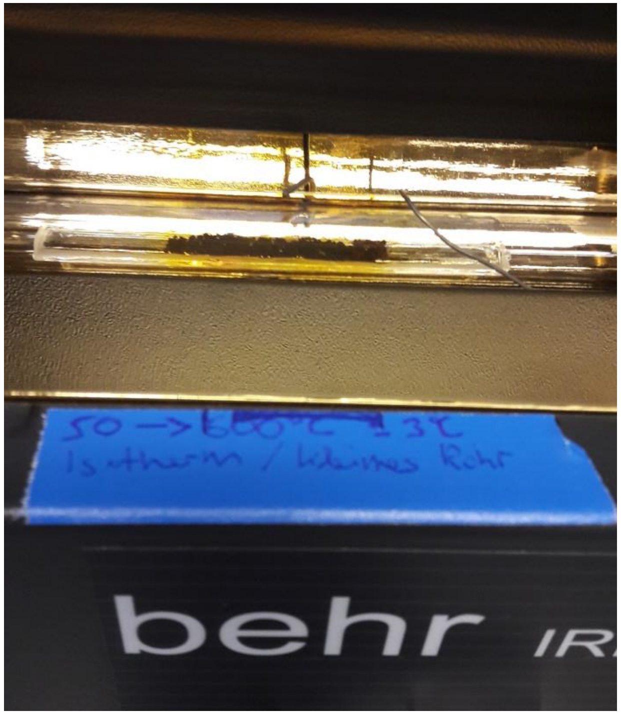
A new TDS setup!

sample



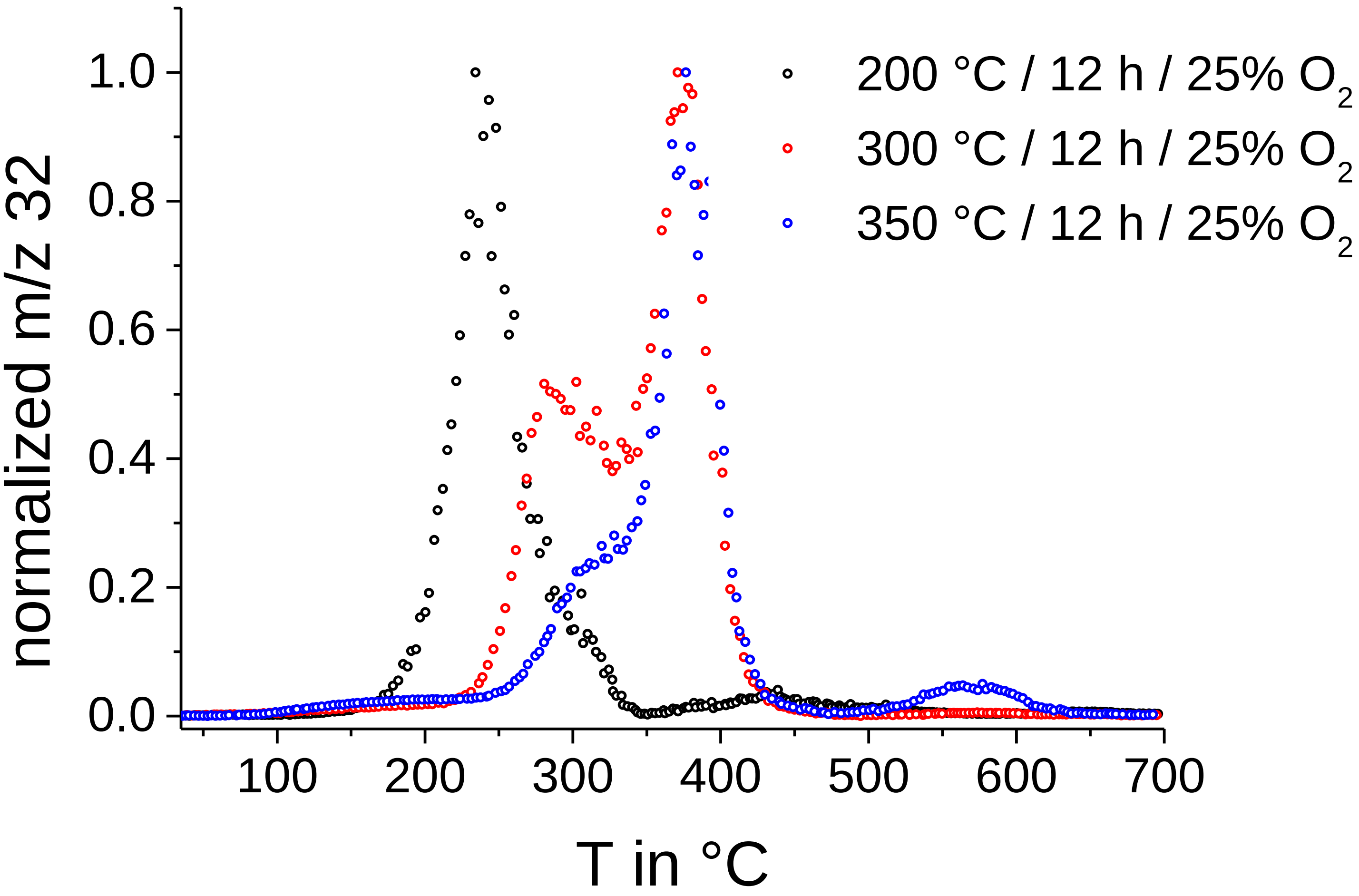
A new TDS setup!

1. Sample has to be properly pre-treated: Activated / cleaned / reduced etc.
2. Adsorption process at dedicated T and t!
3. Bring from 1 bar to $2 \cdot 10^{-6}$ mbar!
4. Move MS to the end of the oven!
5. Start Desorption with constant heating rate!



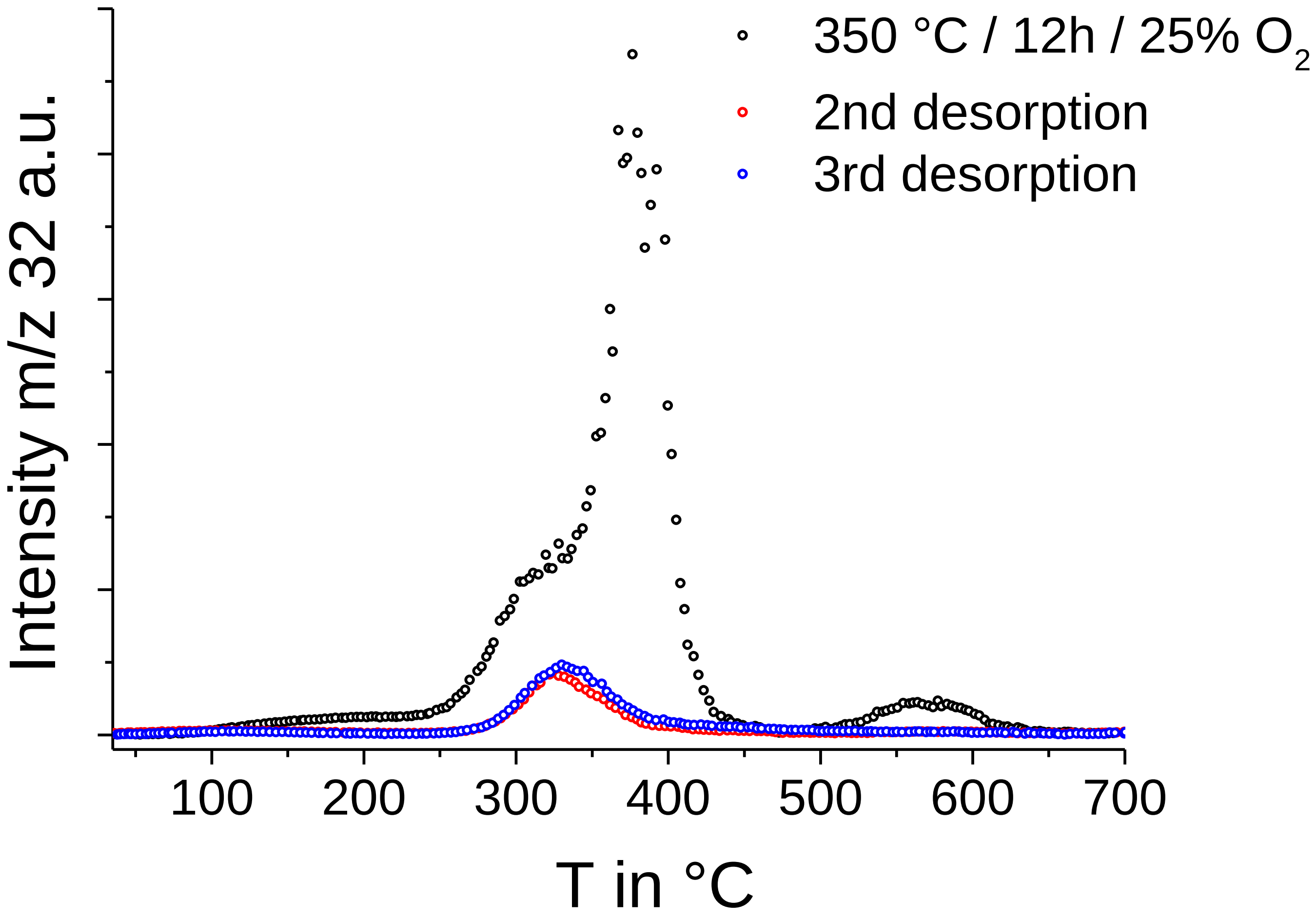
Oxygen TDS on Ag powder

The pretretament temperature (200-350 °C) shifts the desorption maximum to higher temperatures and new desoption events are created.



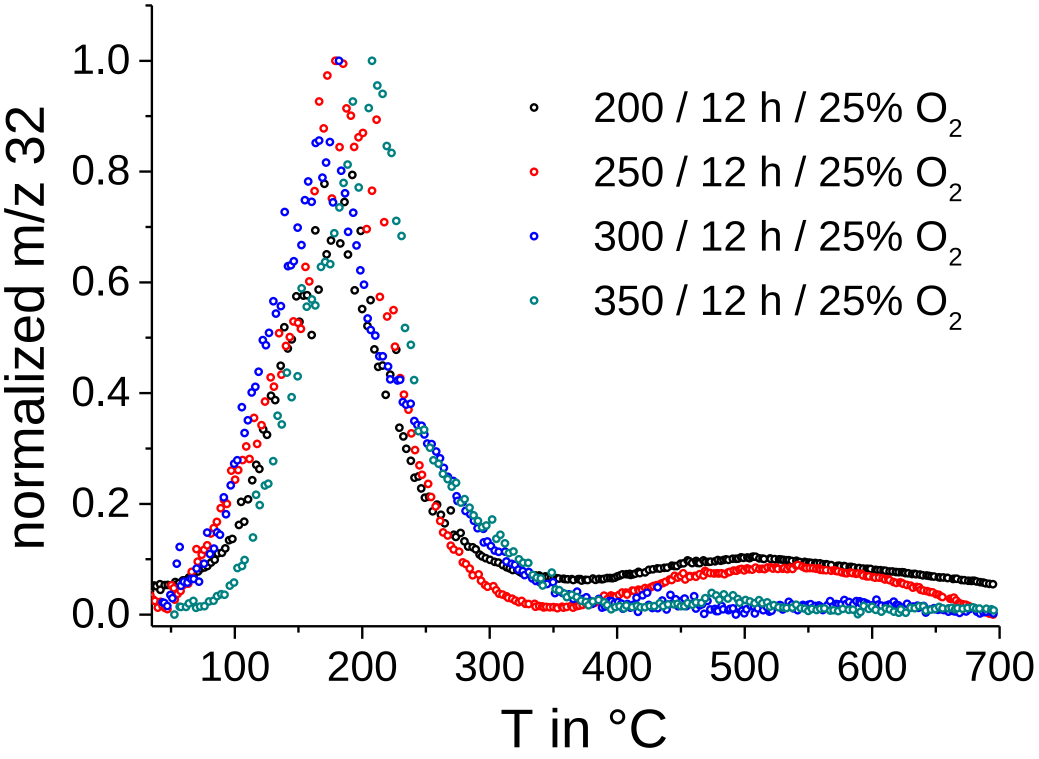
Oxygen TDS on Ag powder

The only desorption event which is recovering belongs likely to oxygen disolved in the Ag bulk invisible for supported samples.

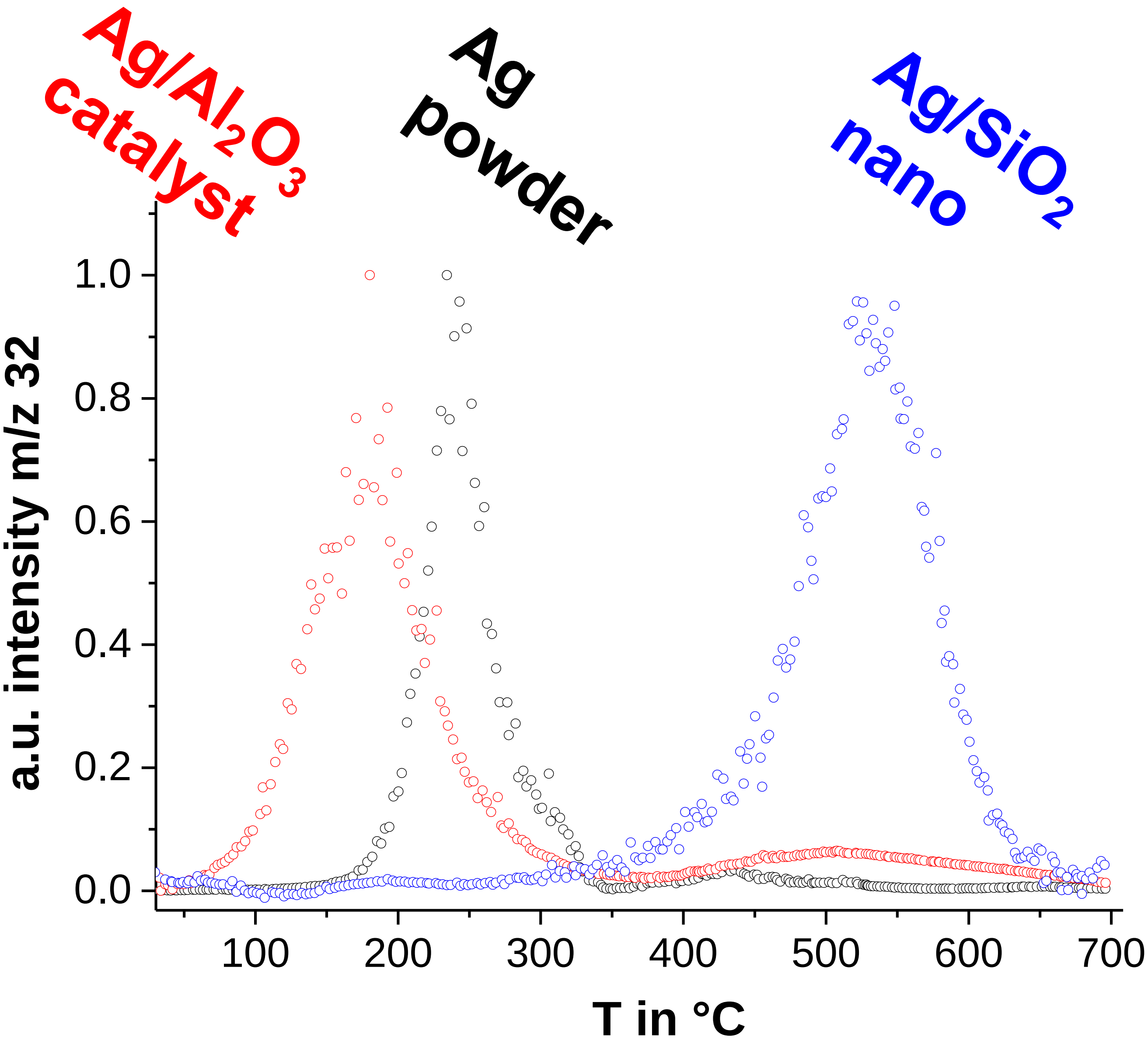


Oxygen TDS on Ag@α-Al_2O3

Only one main de-sorption event is visible independent from the pre-treatment temperature.



High quality powder TDS data



Adapted Polanyi-Wigner Equation

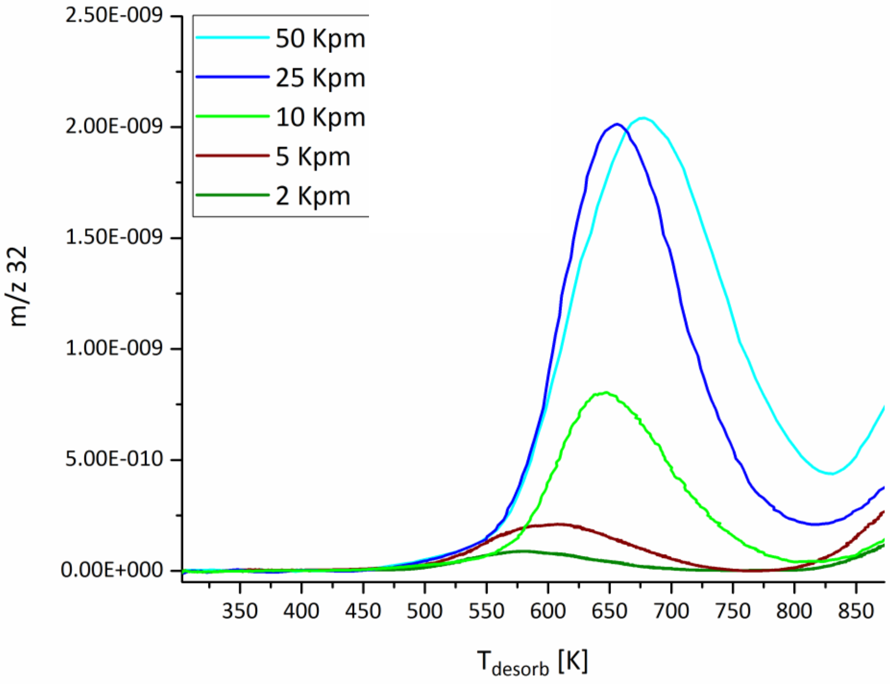
$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{R\,A_{des}\,n_m^{n-1}}{E_{des}}\,n\,\Theta_m^{n-1}\right) - \frac{E_{des}}{RT_m}$$

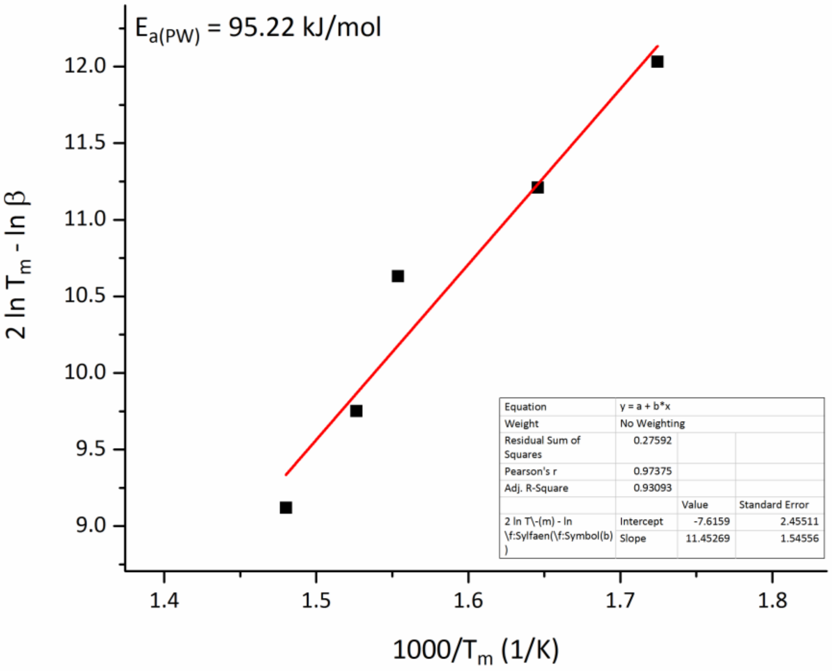
HRV Analysis

(Heating rate variation)

Adapted Polanyi-Wigner Equation

- ⇨ 2nd order desorption
- ⇨ No readsorption or transport limitations



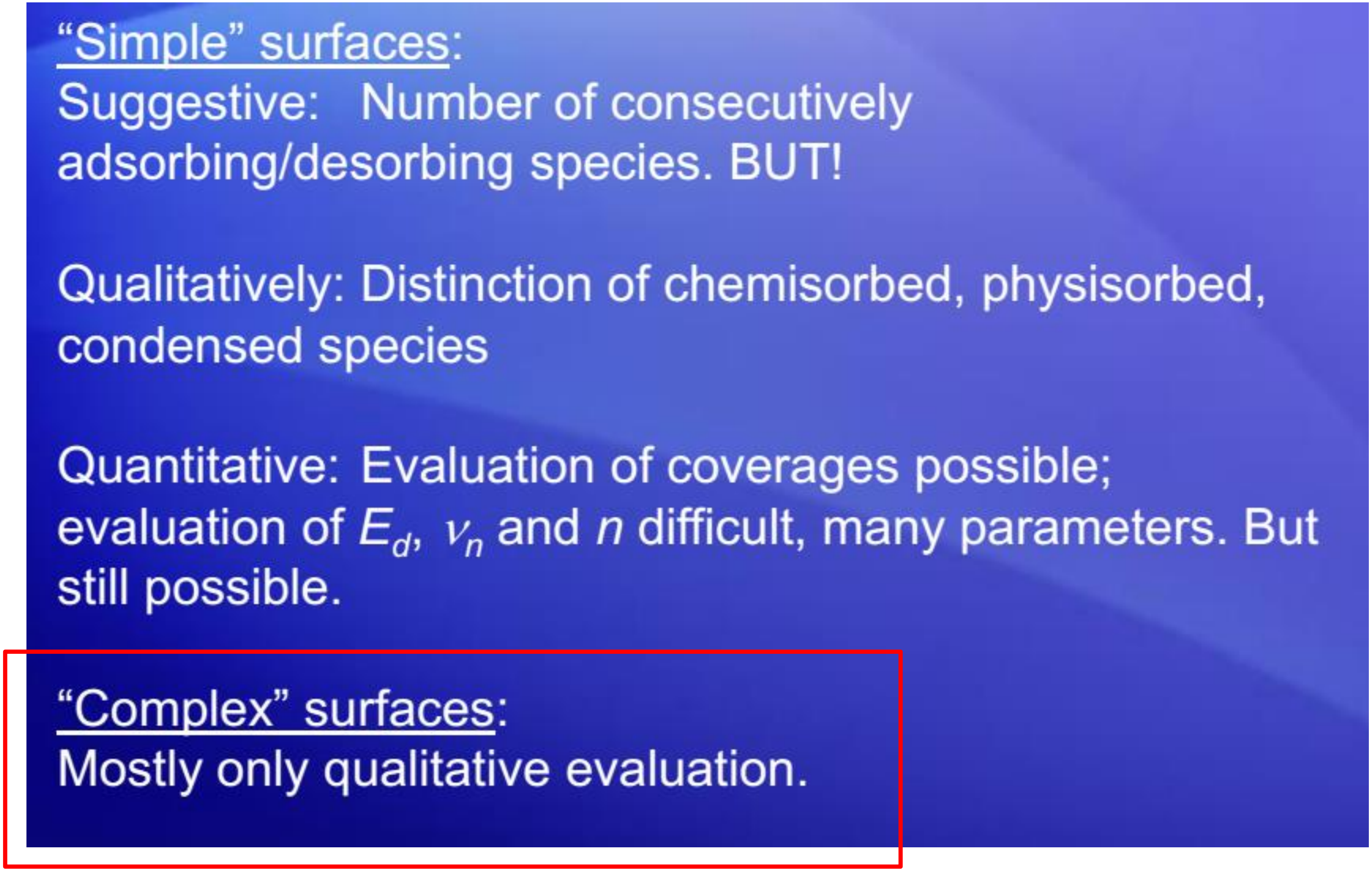


Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.27592		
Pearson's r	0.97375		
Adj. R-Square	0.93093		
		Value	Standard Error
2 ln T\-(m) - ln \f:Sylfaen(\f:Symbol(b))	Intercept	-7.6159	2.45511
	Slope	11.45269	1.54556

Determination of activation energy for oxygen desorption based on Polanyi-Wigner.

Ag(111): E_{des} = 51.9 kJ/mol
C.T. Campbell, Surf. Sci. 157 (1985) 43.

Summary from previous TDS lectures



“Simple” surfaces:

Suggestive: Number of consecutively adsorbing/desorbing species. BUT!

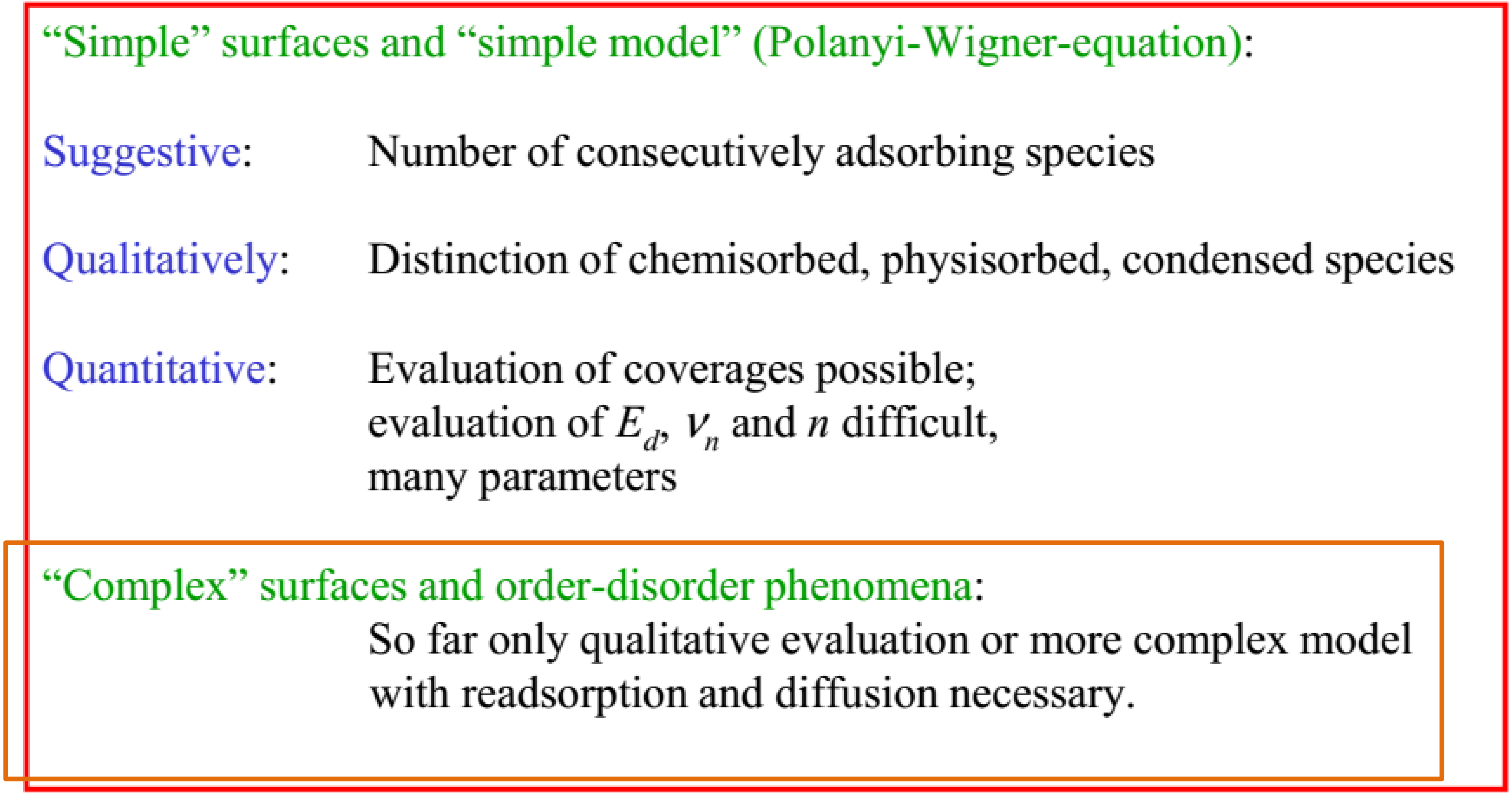
Qualitatively: Distinction of chemisorbed, physisorbed, condensed species

Quantitative: Evaluation of coverages possible; evaluation of E_d, ν_n and n difficult, many parameters. But still possible.

“Complex” surfaces:

Mostly only qualitative evaluation.

Summary from previous TDS lectures



"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.

⇒ **See above, quantitative information are extrated!!**