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Adsorption

“Modern Methods in Heterogeneous Catalysis”

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Organisation

Part I: Thermodynamics and Energetics of Adsorption and Desorption

(Part II: Kinetics of Adsorption and Desorption)

1. Introduction and motivation
2. Basics: The process of adsorption - Thermodynamical background,
   quantum chemical bonding situation

   The process desorption - Desorption energy
3. The adsorption energy:

- Physisorption and chemisorption, associative und dissociative adsorption
- Initial heat of adsorption and a-priori-heterogeneity
- A-posteriori heterogeneity; induced lateral interactions
- Ensemble and ligand - effects; reconstruction and subsurface states

4. The experimental determination of heats of adsorption and desorption:

   Examples taken from selected physisorption and chemisorption systems
   with and without adsorbate-induced changes of the substrate morphology
5. Summary and outlook: The importance of the heat of adsorption in heterogeneous catalysis

Energetics of Adsorption and Desorption

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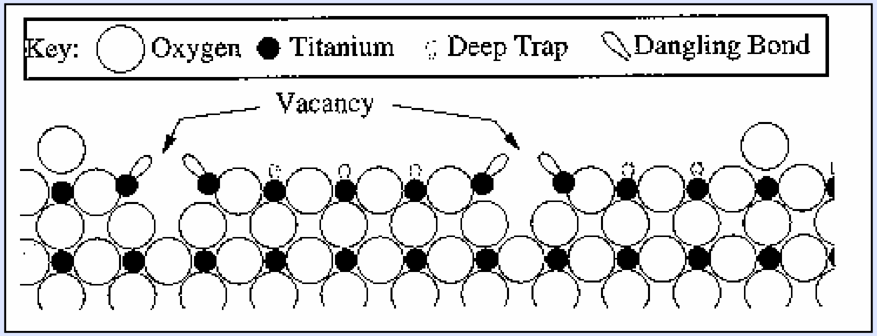
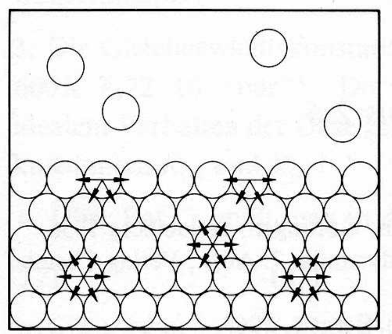
1. Introduction and motivation

- Altered interaction forces in the region of the phase boundary
- “free” valencies, broken (“dangling”) bonds at the surface
- Nature of interaction forces will depend on the system:
  - a) van-der-Waals (always present),
  - b) ionic (electrostatic),
  - c) covalent,
  - d) metallic
- Strength of the interaction forces for b) ... d) comparable to typical chemical bonds, i.e. between **80** and **300** kJoule/Mol



„Dangling bond“-states at a titanium dioxide surface (after Elian & Hoffmann 1975 and van Santen 1991)



Asymmetry of the interaction forces in the surface region of a liquid

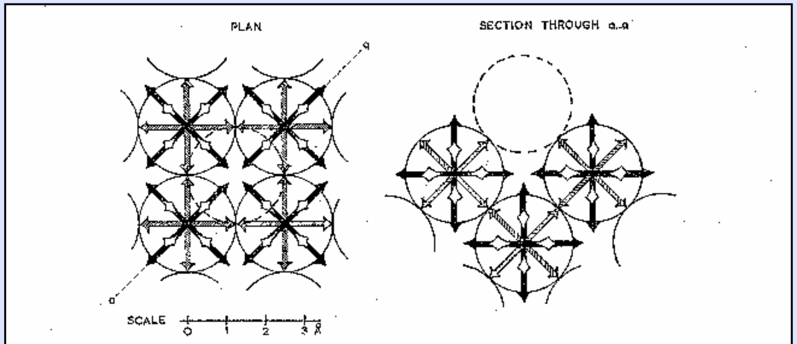


Fig. 5.—Diagrammatic representation of the emergence of orbitals at the (100) face of a face-centred cubic metal. Filled arrows: e_g orbitals in plane of paper; hatched arrows: t_{2g} orbitals in plane of paper; open arrows: t_{2g} orbitals emerging at 45° to plane of paper. The broken circle shows the position of an atom in the next layer above the surface layer. In both the plan and section, an e_g orbital emerges normal to the plane of the paper from each atom. The scale applies to nickel.

Directed orbitals on a fcc(100) surface

2. Basics: The process of adsorption – thermodynamical background

Consider the change of Free Enthalpy G (Gibbs Energy) of a thermodynamical system during any change of state (differential description):

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,A} dP + \left(\frac{\partial G}{\partial T}\right)_{P,A} dT + \left(\frac{\partial G}{\partial A}\right)_{P,T} dA + \left(\frac{\partial G}{\partial n_i}\right)_{T,P,A} dn_i$$

$$\left(\frac{\partial G}{\partial P}\right)_{T,A} = +V;$$

$$\left(\frac{\partial G}{\partial T}\right)_{P,A} = -S$$

$$\left(\frac{\partial G}{\partial A}\right)_{P,T} = \sigma$$

$$dG = VdP - SdT + \sigma dA + \mu_i dn_i$$

with P = pressure, T = temperature, A = surface area, σ = surface tension, V = volume, μ = chemical potential and S = entropy. The third term becomes only important, if the surface area is large in relation to the bulk phase (high degree of dispersion). Example: Raney-Nickel as a catalyst in hydrogenation reactions.

The surface tension is equivalent to the surface energy [Nm/m^2], which governs the macroscopic energetics of both adsorption and desorption phenomena. Since, however, thermodynamics is a *continuum* description of the chemical state of systems, it is unable to describe or predict *microscopic* details or elementary *processes on the atomic scale*.

2. Basics: The process of adsorption - thermodynamical background

Thermodynamical derivation of the so-called isosteric enthalpy of adsorption, q_{st}:
Chemical equilibrium between adsorbate+substrate and gas phase leads to a *constant surface concentration* G. A constant Γ is obtained as soon as there adsorb, within the unit of time, as many particles as there desorb. We now consider the pressure and temperature dependence of this phase equilibrium. In equilibrium, the chemical potentials μ_{ad} and μ_{gas} are identical and remain identical ("ongoing" equilibrium):

$$\mu_{ad} = \mu_{gas} \quad \text{und} \quad d\mu_{ad} = d\mu_{gas}\,; \quad \Gamma = n_{ad}/n_{OF}$$

$$dG_{ad+OF} = - S_{ad+OF}dT + V_{ad+OF}dP + \mu_{ad}\,dn_{ad} + \mu_{OF}dn_{OF} = dG_{gas} = - S_g dT + V_g dP.$$

Using partial molar quantities and recalling that all terms which contain the mole numbers n_{ad} and n_{OF} vanish for constant surface concentration Γ, one obtains the well-known **Clausius-Clapeyron** equation for the phase equilibrium "gaseous" – "adsorbed" state

$$\left(\frac{dP}{dT}\right)_\Gamma = \frac{s_g - s_{ad+OF}}{V_g - V_{ad+OF}} \approx \frac{1}{P}\left(\frac{dP}{dT}\right)_\Gamma = \frac{h_g - h_{ad+OF}}{RT^2} = \left(\frac{d\ln P}{dT}\right)_\Gamma = \frac{q_{st}}{RT^2}$$

q_{st} is called *differential isosteric heat of adsorption* and can be obtained from equilibrium measurements (adsorption isotherms).

2. Basics: The adsorption isotherm

Idea: Under adsorption equilibrium the rate of adsorption equals the rate of desorption.

If:

- All adsorption sites are equivalent
- All sites can be occupied with the same probability
- The adsorption energy drops sharply to zero once the last site has become occupied

One can derive the so-called **LANGMUIR isotherm** for atomic (one-point) adsorption

$$\Theta(P)_T = \frac{bP}{1+bP} \quad ,$$

and for dissociative (two-point) adsorption

.

$$\Theta(P)_T = \frac{\sqrt{bP}}{1+\sqrt{bP}}$$

with b = T-dependent constant.

In the initial part of the graph a log-log plot of coverage θ versus pressure P reveals a slope of 1 for the case of molecular adsorption, but plot of o,5 for dissociative adsorption.

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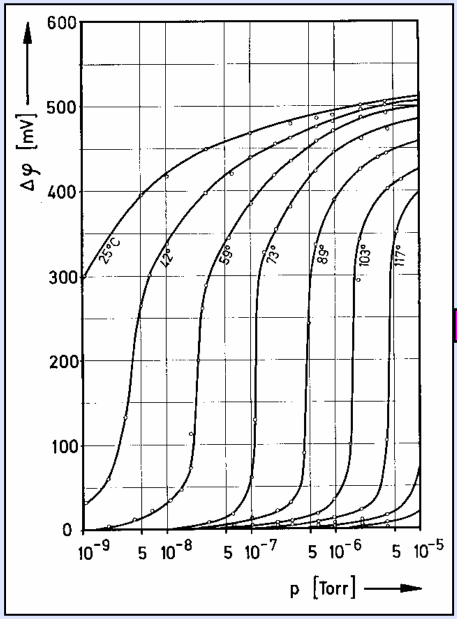
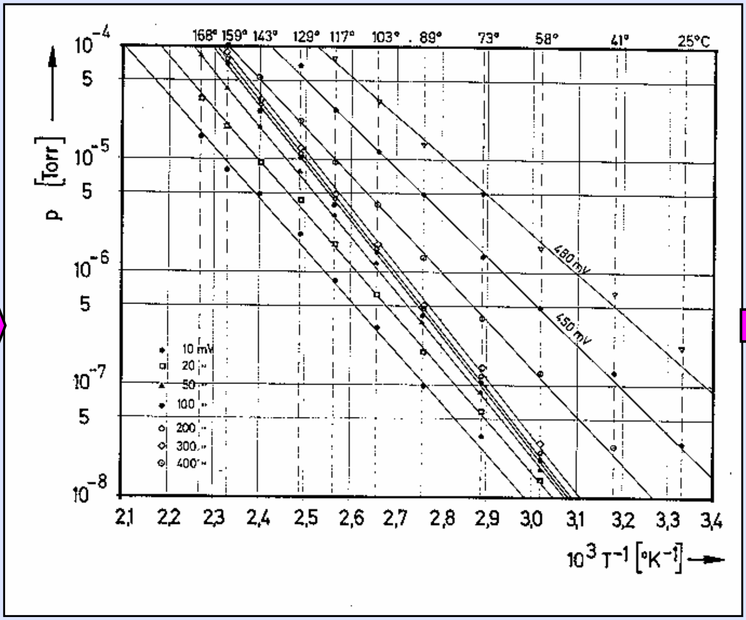
2. Basics: The process of adsorption - thermodynamical background

Determination of the isosteric heat of adsorption, q_{st} , from measurements of adsorption isotherms:

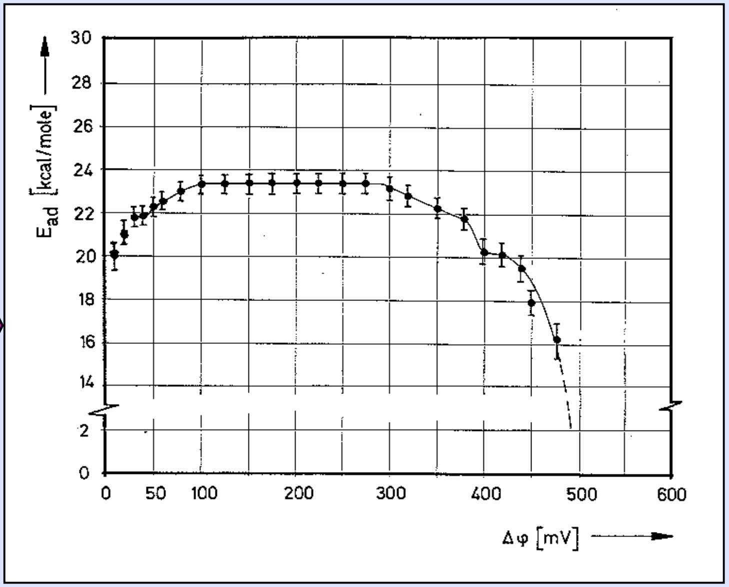
1. Monitor the adsorbed amount $\Gamma = n_{ad}/n_{OF}$ as a function of gas pressure P for constant temperature T, by measurement of adsorbate-induced work function changes ($\Delta\varphi$) or XPS or AES peak areas etc.
2. Construct horizontal cuts in the Γ-P-plane; determine and write down the respective triples of Γ-P-T values.
3. Plot lnP versus 1/T for different Γ and determine the slope of the straight lines, which is, according to the simplified Cl.-Cl. equation, equal to the expression **q_{st}/R** at the respective surface concentration Γ.



Ni(110)/H_2: Adsorption isotherms



Ni(110)/H_2: Adsorption isosteres



Ni(110)/H_2: Coverage dependence of the isosteric heat of adsorption

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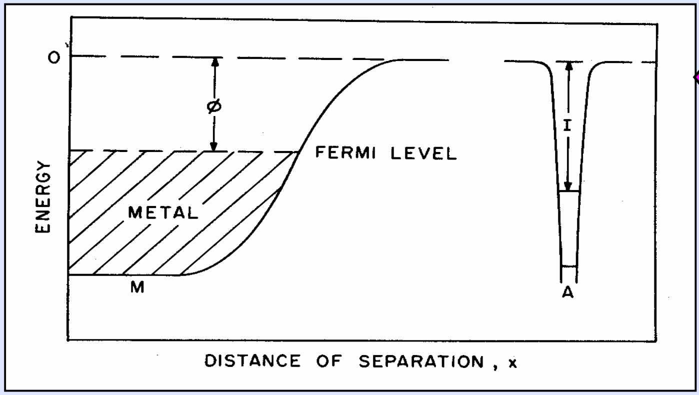
2. Basics: The process of adsorption - the quantum chemical bond formation

Due to quantum chemical interaction between the approaching molecule and the surface there act, even over larger distances, attractive forces on the adsorbate leading finally to the build-up of a chemical bond. The equilibrium is reached when the adsorbed particle resides at the bottom of the potential well, whose depth reflects the energy of the respective bond, if the adsorption is molecular and non-activated. Principally, one has to distinguish between **associative** and **dissociative** as well as between **activated** and **non-activated** adsorption.



Schematic illustration of the orbital energies before the particle approaches the surface (left) and after it has interacted with the substrate (right). (Example: H_2/Mg(0001), Nørskov et al.)

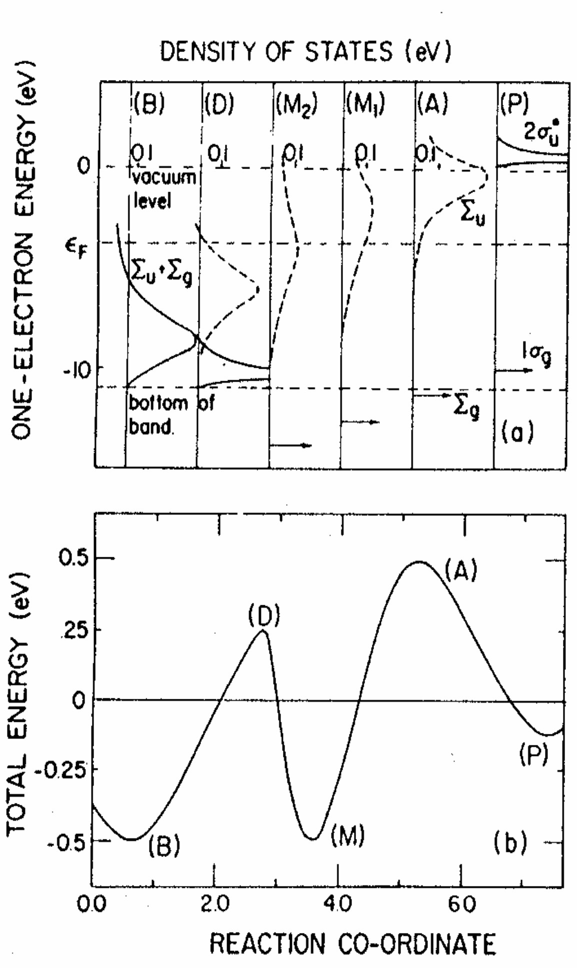
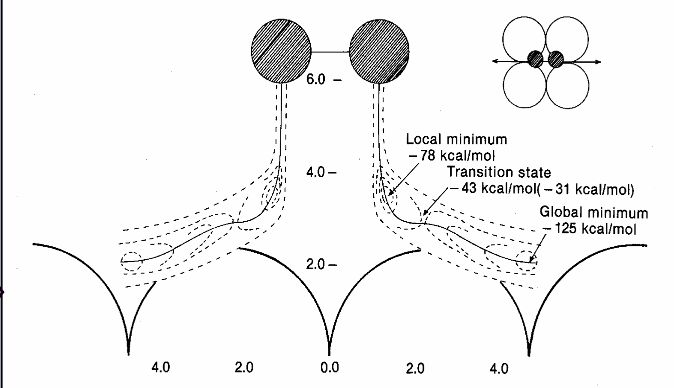


Illustration of the reaction path and the total energies for oxygen adsorption on a Ni_{25}-cluster with square symmetry (after Panas et al.)



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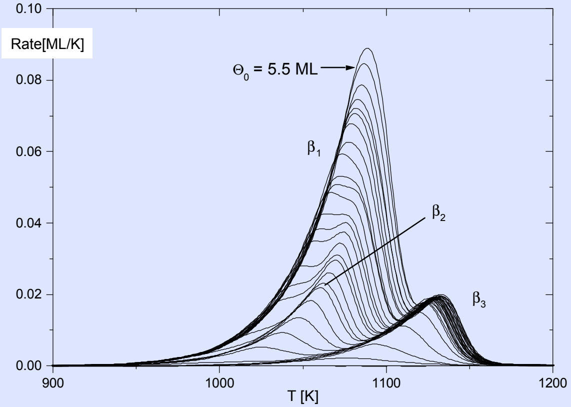
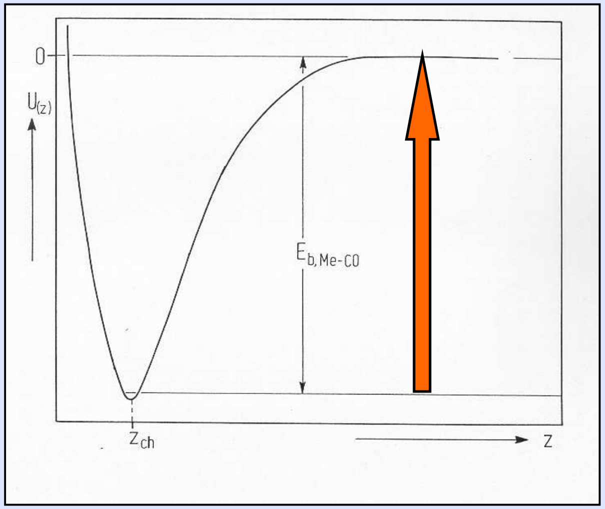
2. Basics: The process of desorption - energetic aspects

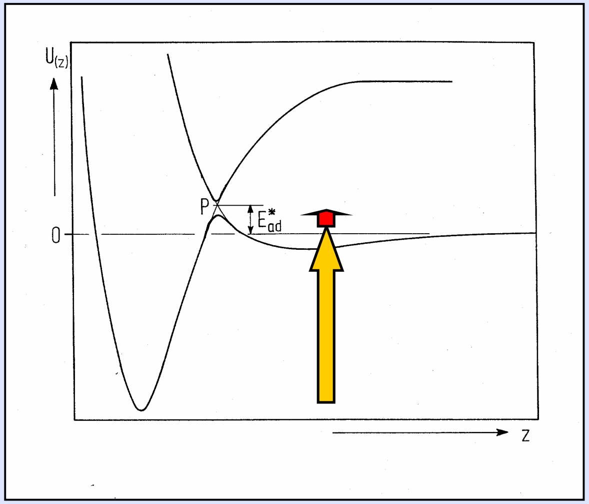
In the adsorbed state and in thermal equilibrium the trapped particle resides at the bottom of the potential well. It is either physically or chemically adsorbed to the solid surface.
In order to remove it from the surface, one has to supply (thermally or electronically) the **energy** required to transfer it to the gas phase. In case that there are activation barriers involved, these have to be additionally overcome, and the desorbing particle possesses more energy than it had when it was in thermal equilibrium with the surface.



TD-Spectra of Cu from a Re0001)-surface



Non activated (spontaneous) adsorption: hydrogen on Ni(110)



activated adsorption: hydrogen on a copper surface

Thermal Desorption spectroscopy:

The most frequently used method to obtain information on the energetics and kinetics of adsorbed particles is **thermal desorption spectroscopy**. The adsorbate-covered surface is heated (mostly in a time-linear fashion), while the desorbing particles are collected and monitored with a mass spectrometer. In a pumped recipient one obtains pressure maxima right at those temperatures, where most of the substrate – adsorbate bonds are thermally cleaved. These desorption peaks contain all relevant information about activation energies for desorption, reaction orders and surface concentrations.

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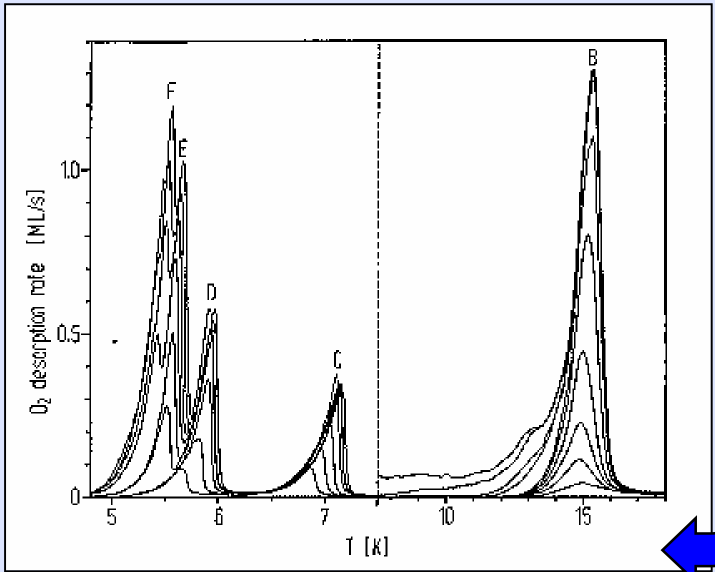
3. The adsorption energy: physisorption and chemisorption

Depending on the strength of the interaction energy one distinguishes between physisorption and chemisorption. This distinction is, however, not rigid. Below, say, 20 kJ/Mol there is genuine physisorption, the interaction is dominated by **van-der-Waals-forces**. Example: Rare gas adsorption on graphite, hydrogen adsorption on Ru(0001)/(1x1)-H. Beyond 50 kJ/Mol there dominates chemisorption with „**chemical**" binding forces. Example: oxygen adsorption on a rhodium(110) face.

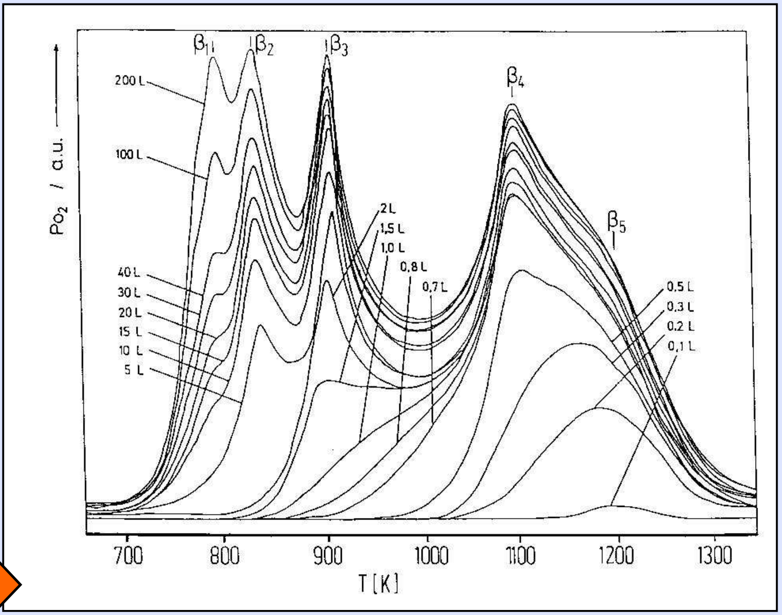


Notice the extremely low desorption temperatures !

TD spectra of H_2 from a Ru(0001) surface (after Frieß et al.)

The heats of adsorption and desorption range only between 1,6 and 2,9 kJoule/Mol !

Notice the extremely high Desorption temperatures!



Oxygen desorption from a Rh(110)-surface

The heats of adsorption and desorption range between 200 and 300 kJoule/Mol !

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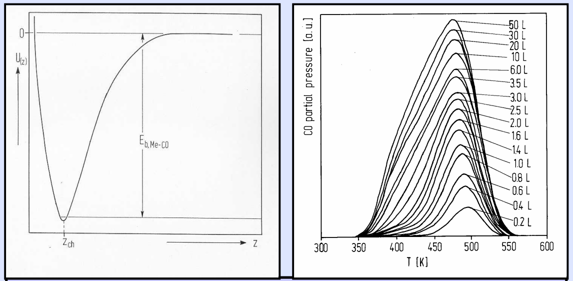
3. The heat of adsorption: associative and dissociative chemisorption



CO-Pd-Interaction potential (left frame) and corresponding TD spectra exhibiting 1st order kinetics (right frame)

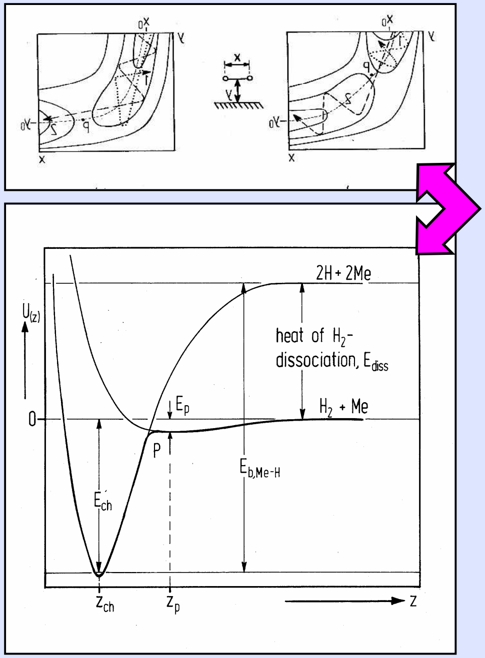
Associative (molecular) adsorption leaves the adsorbing molecule intact. Example: CO adsorption on a palladium surface. The adsorption energy equals the depth of the potential energy well:

$E_{ad} = E_{chem}.$

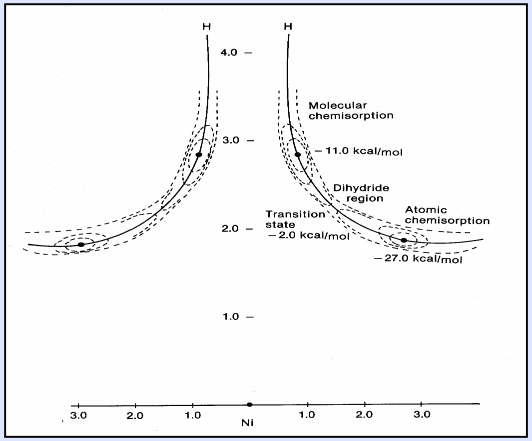
Dissociative chemisorption makes the molecule fall apart upon adsorption, either in a heterolytic or in a homolytic manner. In this process the dynamics of the reaction is of great interest, but also the dependence of the binding energy of the species formed by dissociation as a function of the distance to the substrate: The adsorption energy depends largely on the bond energy (heat of dissociation) which has to be fed to the system, c.f. the figure in the left bottom:

$$E_{ad} = 2 \cdot E_{Me\text{-}H} - E_{diss}.$$

Information on the mechanism of adsorption may be obtained from measurements of adsorption isotherms or from thermal desorption spectra. The latter exhibit constant peak position for associative adsorption, but a low-temperature shift of the maxima with increasing coverage for dissociative (recombinative) adsorption.

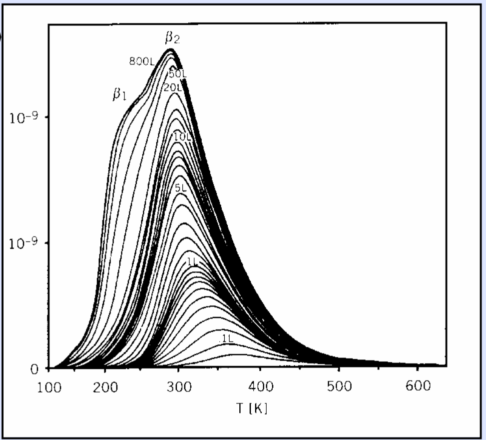


One-dimensional (left) und two-dimensional (top) representation of the potential energy surface for the homolytic dissociative adsorption. Example: H_2 on Nickel.



Energy – distance dependence for a H_2-molecule interacting with a Ni_{13}-cluster

TD spectra of H_2/Pt(111) showing 2nd order



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3. The adsorption energy: Initial heat of adsorption and a-priori heterogeneity

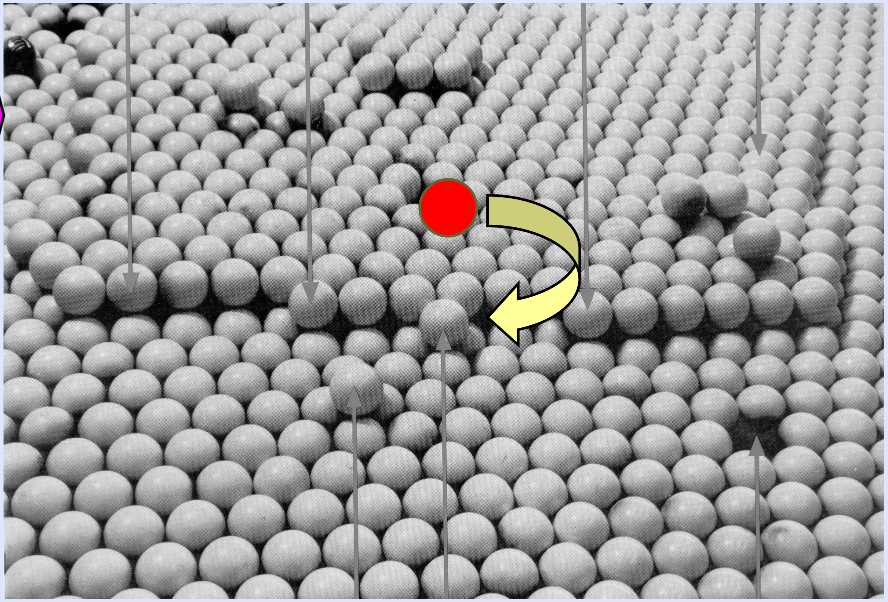
Table: Initial heats of adsorption for some selected adsorption systems

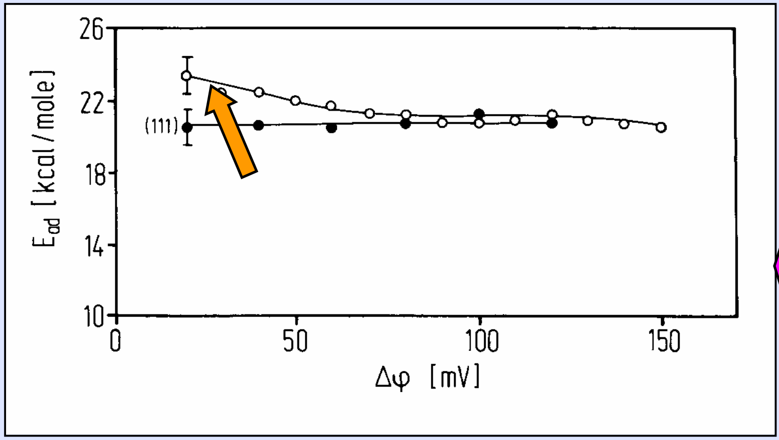
Adsorbate	Surface	E_0 from...to [kJ/Mol]
hydrogen H_2	Ru(0001)(1x1)-H	2...5
oxygen O_2	Ru	10...20
carbon dioxide CO_2	Cu	10...30
xenon Xe	Ni	15...25
xenon Xe	Pd	20...40
hydrogen H (from H_2)	Pt	60...80
hydrogen H (from H_2)	Co, Ni, Ru, Rh, Pd	30...100
hydrogen H (from H_2)	Mo, W, Re	125...175
carbon monoxide CO	Ni, Pd	100...150
oxygen O (from O_2)	Ru, Pd	200...250
oxygen O (from O_2)	Rh, Re	200...300
copper Cu	Ru, W, Re	250...330

We define the so-called **initial adsorption energy**, which is felt by the very first particle arriving at the bare surface. This initial adsorption energy E_0 is a characteristic quantity for a given adsorption system which reflects the strength of the interaction between adsorbate and substrate (cf. Table on the left-hand side).

On a given surface there can inherently exist adsorption sites with different local geometry providing different chemical coordination; good examples being surfaces with regular steps. Usually, the strength of adsorbate – substrate interaction increases with the coordination number. Example: H/Pd.

Real-space model of a real surface with various defects (steps, kinks, holes etc.)





Coverage dependence of E_{ad} for Pd(111)/H: full circles: smooth (111) surface; open circles: periodically stepped Pd(111) surface (after Conrad et al.)

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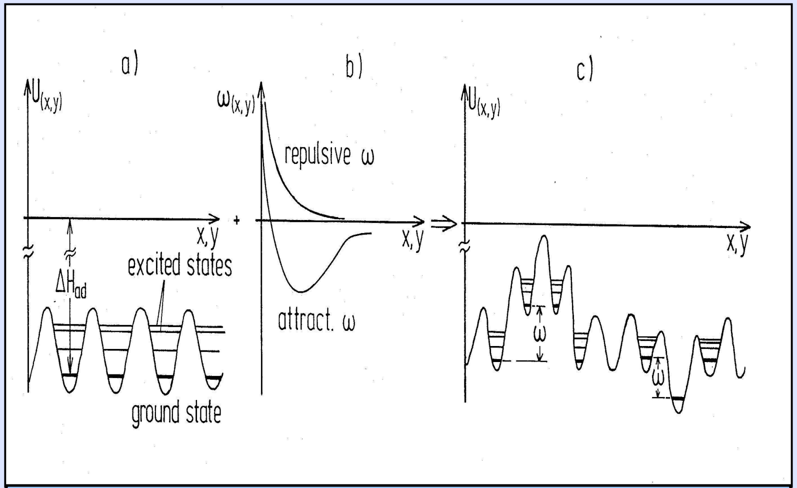
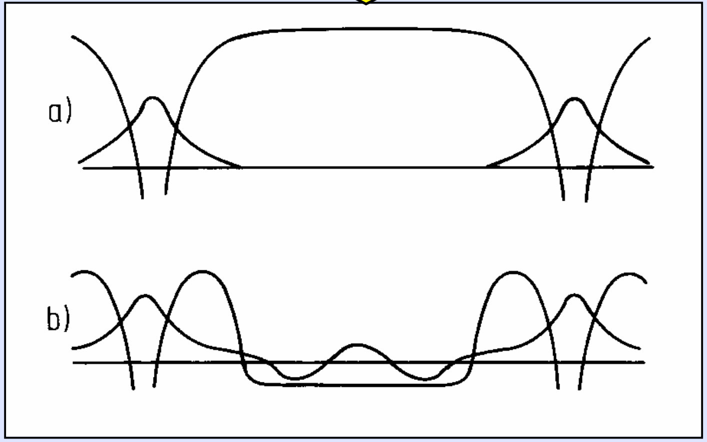
3. The adsorption energy: a-posteriori heterogeneity; induced lateral interactions

Already the very first adsorbing particle alters the shape and depth of the adsorption potentials of the neighboring sites, owing to **lateral interactions**. The corresponding forces can be **attractive** or **repulsive**. The distance dependence of the total potential (c) is practically a superposition of the periodic potential of the uncovered crystal surface (a) and the particle pair potential (b).

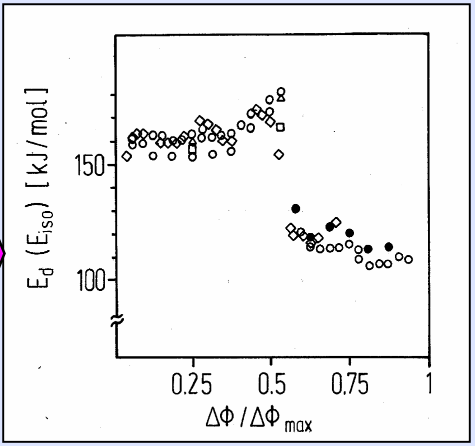
The interaction potentials can be mediated either by direct orbital – orbital repulsions („**direct“ interactions**) or through the substrate („**indirect“ interactions**). The reason being that the charge density around a given adsorption site is shared between to adjacent adsorbed particles, as illustrated in the figure below.



Schematic representation of the potential modulation



Often, lateral interactions become feasible only beyond a certain critical adsorbate surface concentration. Since they are mostly repulsive, one observes a sudden drop in the heat of adsorption. **Example:** CO adsorption on Ru(0001) [Pfnür et al.]: Up to a sqrt 3 x sqrt 3-R30° structure the CO molecules can occupy equivalent sites; thereafter the adsorbed COs feel the repulsive forces to the neighbors. Consequently, the heat of adsorption falls abruptly by ca. 50 kJ/Mol.



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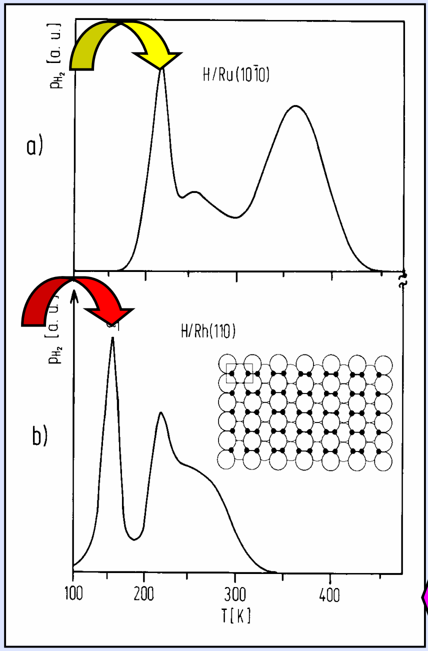
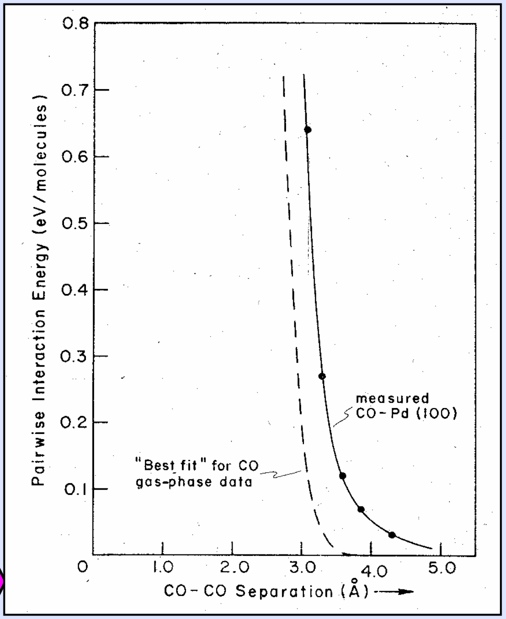
3. The adsorption energy: induced heterogeneity; ensemble and ligand effect

At a certain critical adsorbate coverage, the **induced energetic heterogeneity** (caused by repulsive mutual interactions) causes a more or less pronounced decrease of the adsorption energy. In thermal desorption spectra this can be seen as split-off states (TD peaks). Example: **Hydrogen (1x1) phases on Rh(110) and Ru(10-10) (left frame).** From the decrease of the heat of adsorption conclusions on the particle – particle repulsion and its distance dependence can be drawn. Example: **CO on Pd(100):** [Tracy & Palmberg 1969] **(right frame)**

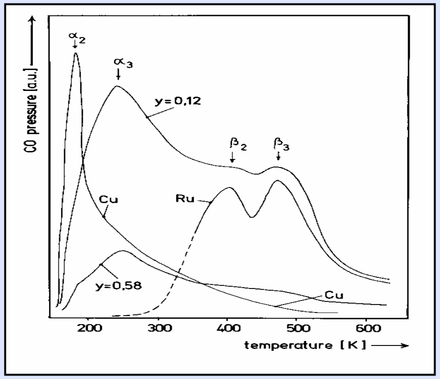


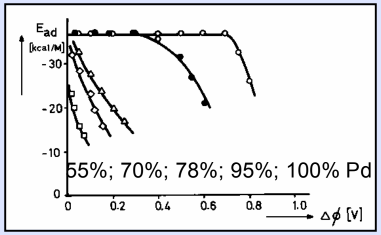
TD spectra of the (1x1)H phases formed on Ru(10-10) und Rh(110)



Distance dependence of the CO-CO-repulsion on a Pd(100) surface (after Palmberg & Tracy)

Heterogeneities of the adsorption energy can also be caused by foreign atoms. Noble metals (Cu, Ag, Au) usually have a much lower ability to chemisorb active molecules compared to typical transition metals (Ni, Pd, Pt). In this respect, a Ru surface sparsely covered with copper atoms loses its ability to chemisorb H almost completely, because the dissociation of H_2 requires fairly large intact ensembles of adjacent Ru atoms. The admixture of few Cu atoms destroys these ensembles effectively **(ensemble effect)**. Vicinity to Cu atoms turns „good“ CO adsorption sites to average or bad sites, owing to a local modification of the band structure **(ligand effect)**. Both effects are significant in heterogeneous catalysis.





Ligand and ensemble effect: CO/Ru+Cu (left); CO/Pd+Ag (top)

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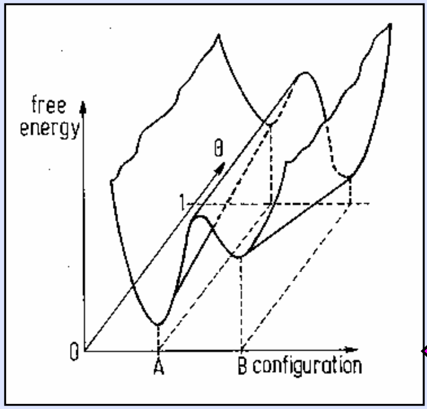
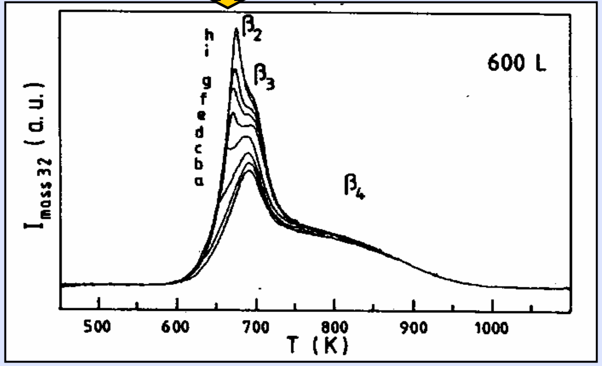
3. The adsorption energy: Surface reconstructions and „subsurface“ states

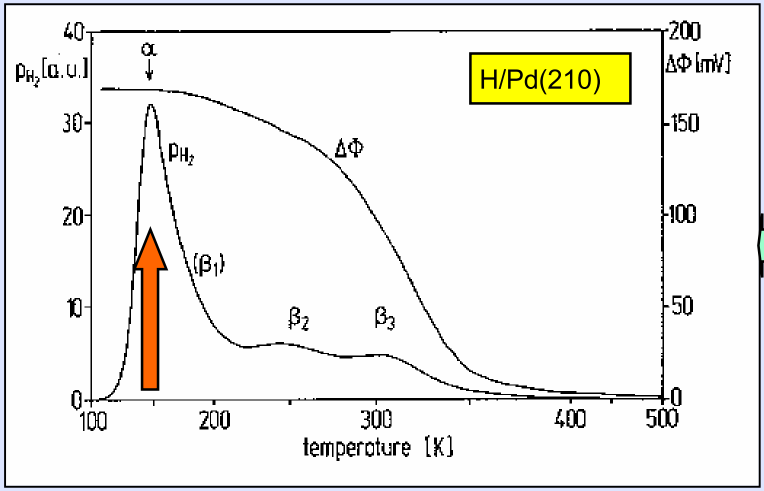
If the adsorbate interacts strongly with the substrate, the surface atoms may be displaced from their original crystallographic positions, a consequence of the minimisation of the surface free energy. If this process leads to new periodicities, we talk about surface **reconstruction.** In the absence of kinetic barriers, solely the **Free surface energy** of the total system determines the equilibrium surface geometry (right frame).



Change of the Free Energy as a function of the configuration and the adsorbate coverageΘ.

Development of a Subsurface-oxygen state β_2 (yellow) with the O_2 exposure of a Pt(210)-surface (β_3 and β_4 states are *surface* oxygen binding states).

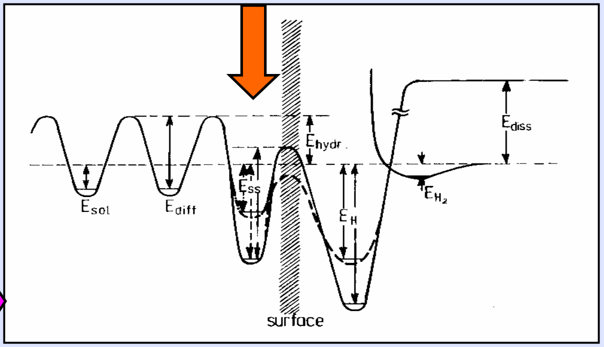




Surface (β-states) and subsurface-(α)-state during hydrogen interaction with a Pd(210) surface. TheSS state does not at all contribute to the H-induced work function change Δφ!

Sometimes sites between the 1st, 2nd, or 3rd substrate layer become occupied by adsorbate atoms. These **subsurface states** are known from the Pd/H system. Subsurface states are usually more weakly bound than surface species. On many Pt metal surfaces also **subsurface oxygen** has been reported. Subsurface states can be essential in chemical (catalytical) surface reactions at higher pressures.

H/Pd-potential energy diagram with surface, subsurface and bulk H states



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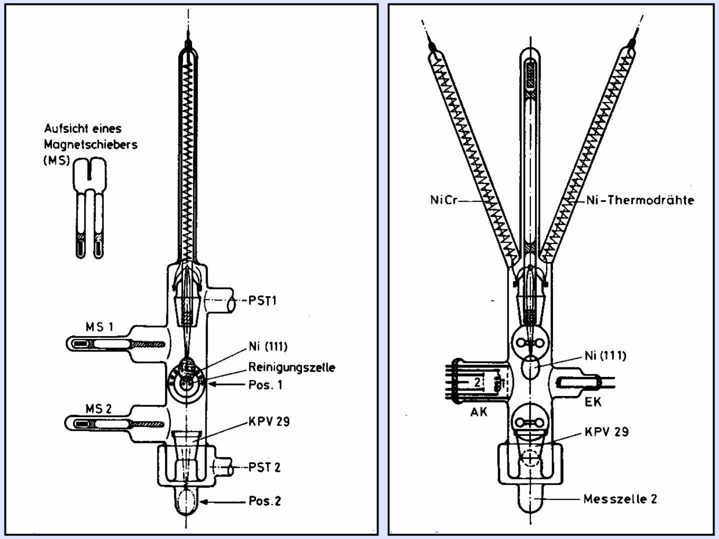
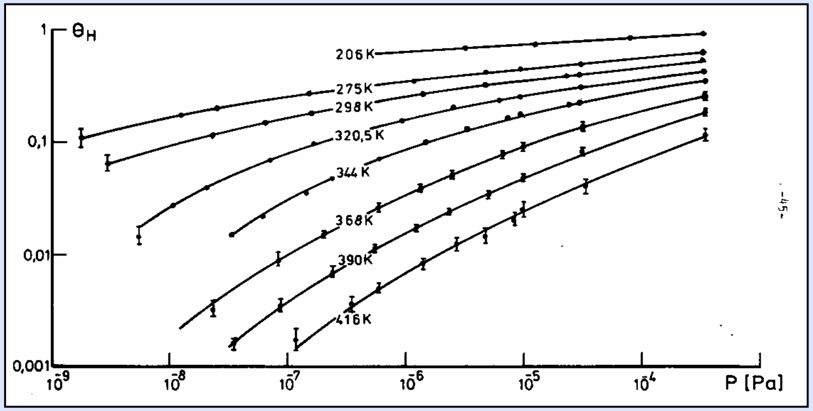
4. The experimental determination of the adsorption energy (example: H_2/Ni(111))

Principally, there exist several methods to determine E_{ad} and its coverage dependence $E_{ad}(\Theta)$. Particularly reliable are thermodynamic techniques based on measurements of adsorption isotherms as discussed before. Most precisely is the direct **volumetric determination of the adsorbed amount**; I know about a single measurement only [H. Rinne, Ph.D. thesis TU Hannover 1972], c.f. right and bottom frames. Mostly, the adsorbed amount is measured indirectly, for example, by monitoring the adsorption-induced change of the work function or the signal intensities of photoemission, Auger spectra, or He scattering spectra., as long as these are uniquely related to the adsorbed amount. Quite accurate are also direct calorimetric techniques (introduced by Suhrmann and Wedler [G. Wedler, Z. Phys. Chem. NF **24** (1970) 73]. Recently a very sophisticated calorimetric method was introduced by D. King [Al-Sarraf et al., Nature **360** (1992) 243].

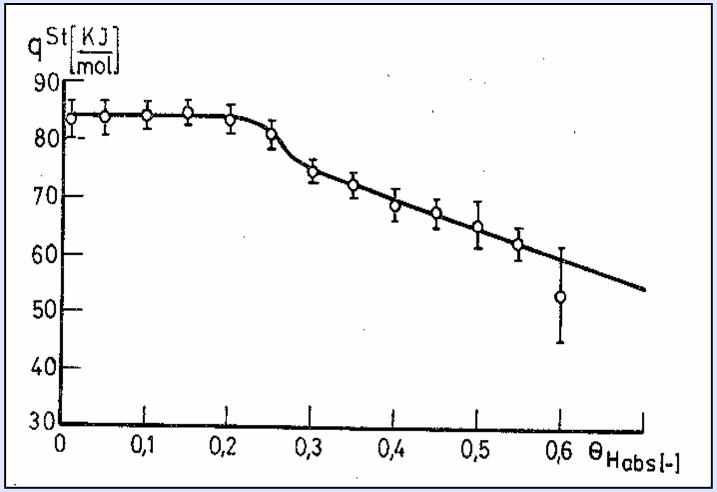


Glass cell with volumetric determination of the adsorbed hydrogen developed by H. Rinne applied for H on a Ni(111) single crystal.

H/Ni(111)



Volumetrically determined adsorption isotherms of hydrogen on Ni(111).



Coverage dependence of the isosteric heat of adsorption of hydrogen on a Ni(111) surface (after **Rinne**).

Energetics of Adsorption and Desorption

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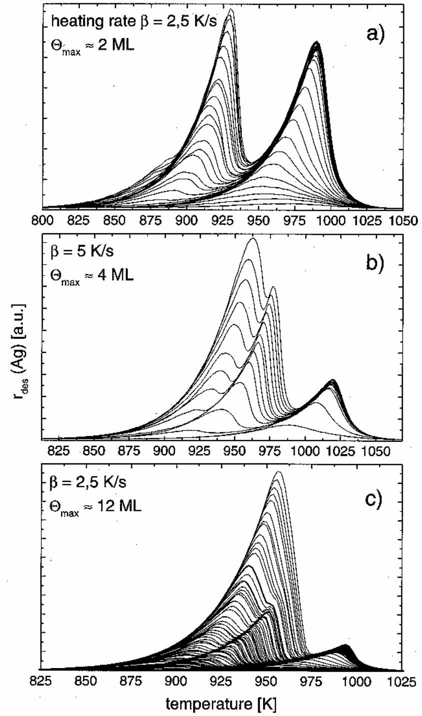
4. The experimental determination of the desorption energy (example: Ag on Re(0001))

The technique of thermal desorption spectroscopy (TDS) and its basics have been mentioned above. Here we would like to show by means of some examples how one can exploit TDS to receive information about the desorption energy. Central point is the **Polanyi-Wigner equation** for the **desorption rate R**:

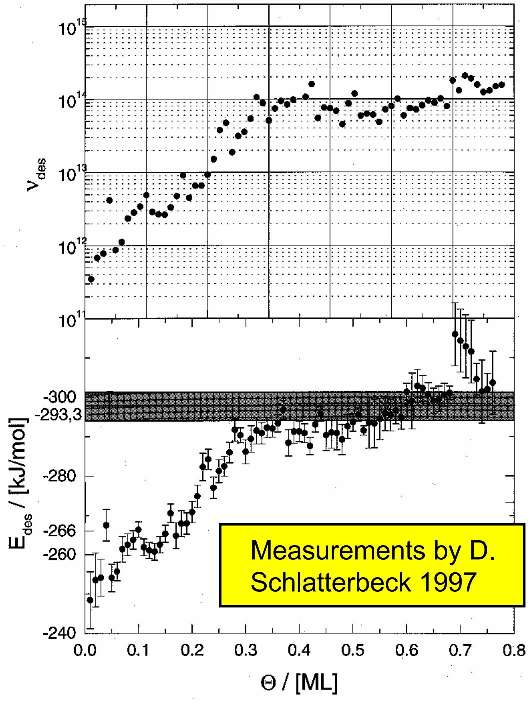
$$R = -\frac{dn_{ad}}{dt} = -k \cdot n_{ad}{}^{x} = -\nu\left(n_{ad}\right) \cdot n_{ad}{}^{x} \cdot \exp\left(-\frac{E_{des}\left(n_{ad}\right)}{kT}\right)$$

n_{ad} = adsorbed amount,
k = desorption constant
x = order of desorption,
ν = frequency factor,
E_{des} = desorption energy

There are different procedures to evaluate TD spectra. Especial simple is the Redhead analysis [P.A. Redhead, Vacuum **12** (1962) 201], which neglects coverage deopendences. More accurate, but more complex are line-shape analyses such as the ones described by Bauer [Surf.Sci. **53** (1975) 87] or by King [Surf.Sci. **47** (1975) 384]. Here briefly commented: *line shape analysis* by King.

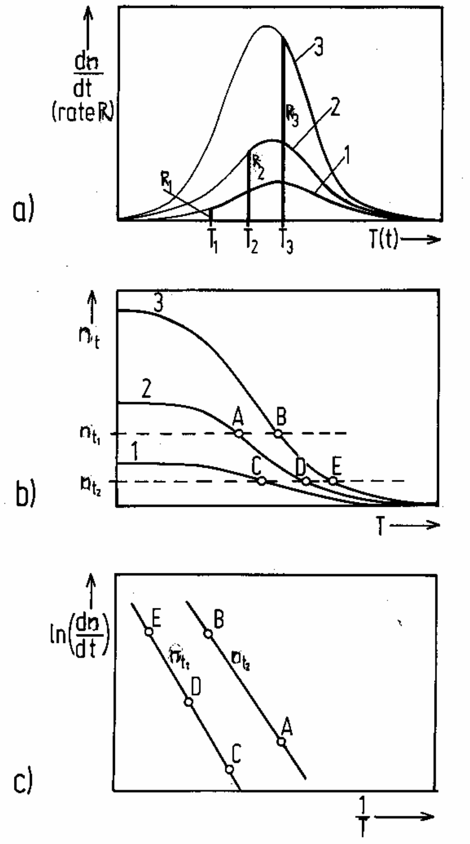


TDspectra of Ag from Re(0001)



Measurements by D. Schlatterbeck 1997

Θ-dependence of ν and E_{des} Ag/Re



Energetics of Adsorption and Desorption

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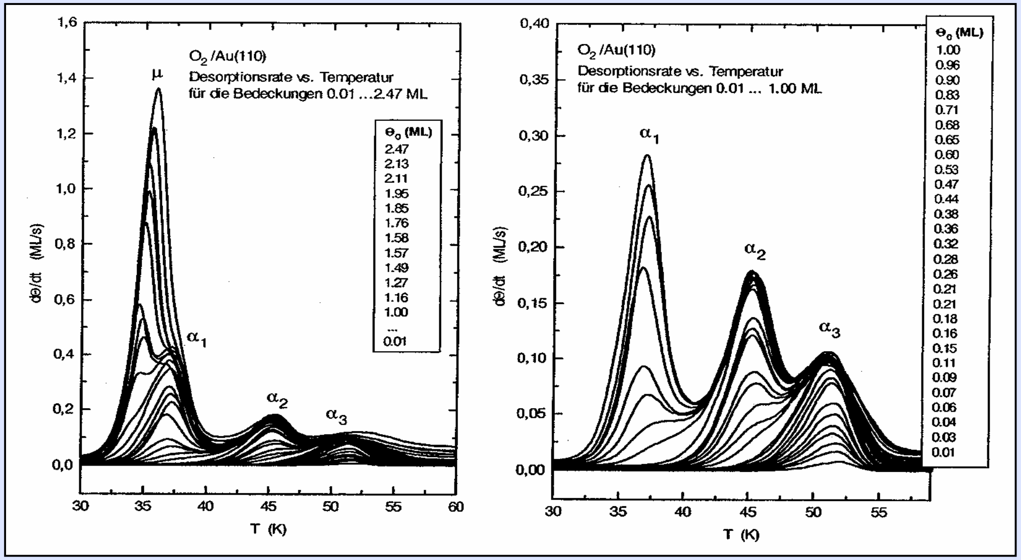
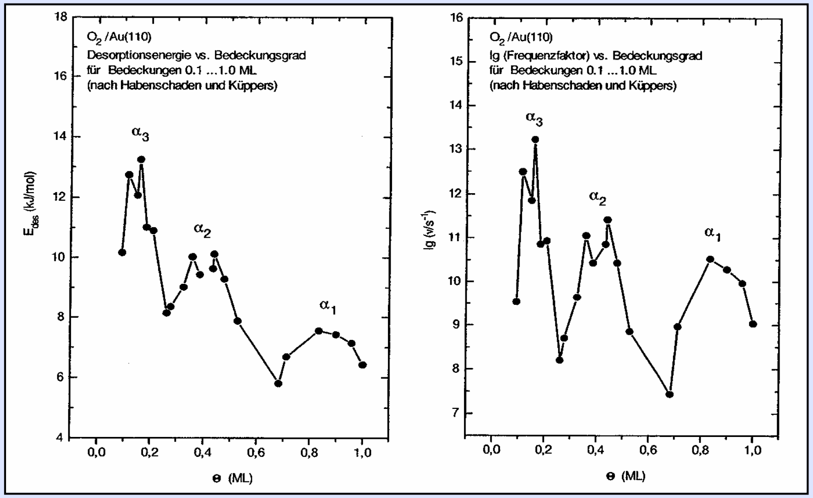
4. Further example (no reconstruction)

O_2 on Au(110)



TD spectra of O_2/Au(110)

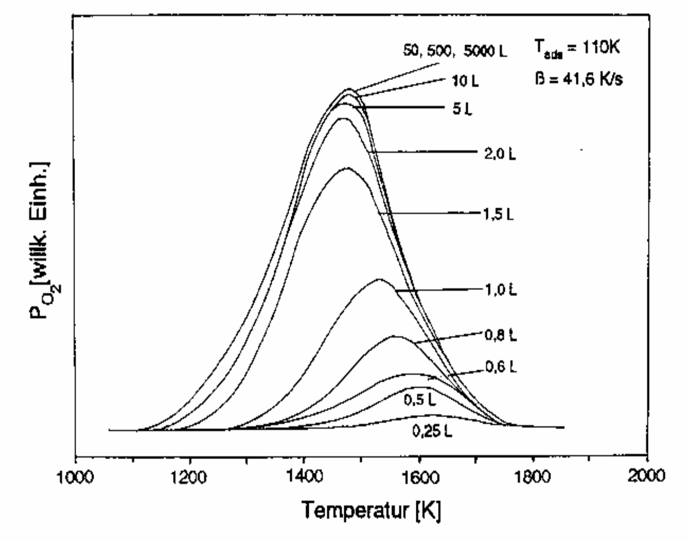


Θ-dependence of ν and E_{des}

Data by M. Gottfried 1999

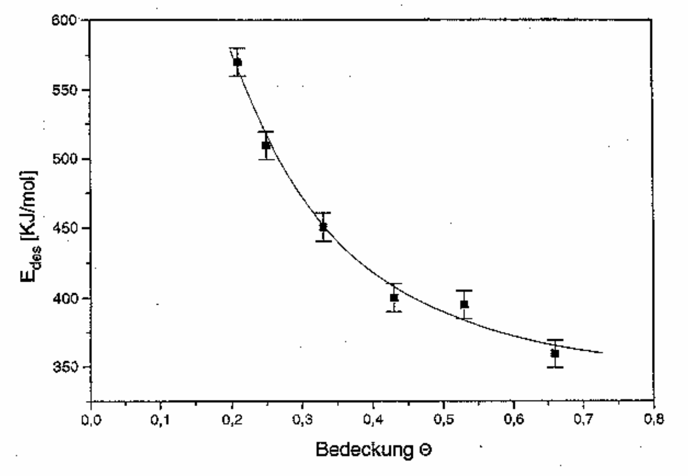
Further example (with reconstr.)

O_2 on Re(10-10)



Thermal desorption spectra of oxygen from a Re(10-10) surface which reconstructs under oxygen O_{ad}.

Data by J. Lenz 1994



Coverage dependence of the oxygen desorption energy from Re(10-10).

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Energetics and Kinetics of Adsorption and Desorption

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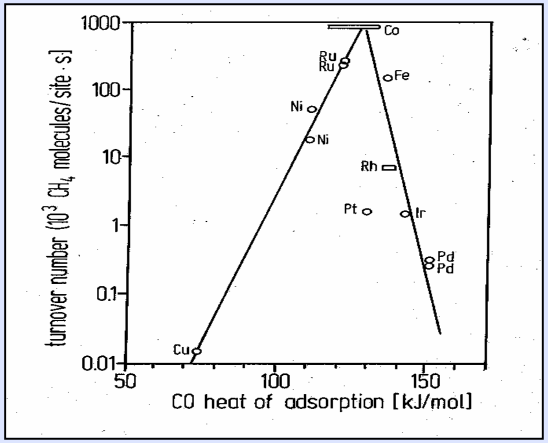
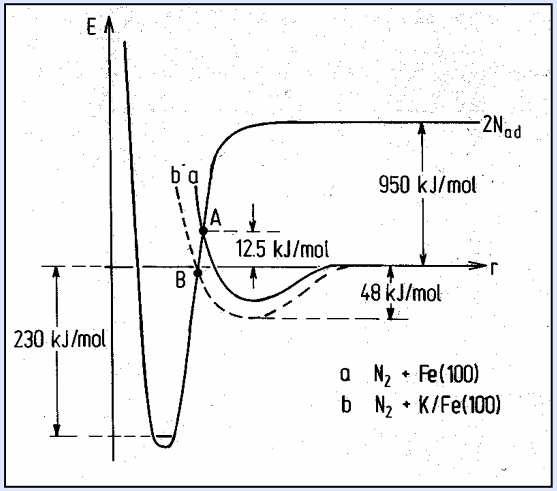
5. Summary and outlook: About the importance of the adsorption in heterogeneous catalysis

In heterogeneous catalysis surfaces help to concentrate the reactants from the gas phase at phase boundaries and, more importantly, to stretch or even break inner-molecular bonds and to facilitate bond-making with coadsorbed species. However, too loosely bound molecules may stay only very shortly on the surface and are immediately lost by dersorption, while too strongly bound species are immobile and cannot take part in Langmuir-Hinshelwood surface reactions. Consequently, it is advantageous, if adsorbates are bound **moderately** strong. This is illustrated in the right-hand frame showing the activity for methane formation from synthesis gas ($CO+H_2$). These typical **vulcano curves** are known for various adsorbates.





A second effect is crucial: In surface reactions, often homonuclear diatomic molecules with strong covalent bonds must be cleaved. However, because the potential energy minima of these molecules lie far outside the surface there exist strong activation barriers for dissociation, an example being nitrogen N_2 interacting with Fe surfaces. Adding electropositive or –negative species changes the local surface charge density and often increases the adsorption energy of the molecules. Consequently, **activation barriers for dissociation are reduced**.
An effect of this kind was found, for example, by Ertl and coworkers for nitrogen molecules interacting with clean and potassium-covered Fe single crystal surfaces. It can also be made responsible for the acceleration of CO hydration reactions by coadsorbed alkali metals.

1) G. Ertl & J. Küppers, *Low-energy Electrons and Surface Chemistry,* 2. Auflage, Verlag Chemie, Weinheim 1985
2) W. Göpel & M. Henzler, *Oberflächenphysik des Festkörpers*, Teubner-Verlag, Stuttgart 1993
3) K. Christmann, *Introduction to Surface Physical Chemistry*, Steinkopff-Verlag, Darmstadt 1991
4) M.W. Roberts & C.S. McKee, *Chemistry of the Metal-Gas Interface*, Clarendon, Oxford 1978
5) A. Clark, *The Theory of Adsorption and Catalysis*, Academic Press, New York 1970
6) A. Clark, *The Chemisorptive Bond - Basic Concepts* , Academic Press, New York 1974
7) E. Shustorovich, Hrsg., *Metal - Surface Reaction Energetics*, VCH-Verlagsges. Weinheim 1991
8) G. Ertl, in: *The Nature of the Surface Chemical Bond* (G. Ertl & T.N. Rhodin, eds.), North Holland Publishing Company, 1979, Ch. V, pp. 315 - 380.
9) D. Menzel in: *Interactions on Metal Surfaces* (R. Gomer, ed.), Series: Topics in Applied Physics, Vol. 4, Springer-Verlag Berlin, Heidelberg, New York, 1975, Ch. 4, pp. 101 - 142
10) R.I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces*, Wiley, New York 1996

As well as various original publications.

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Part II Kinetics of Adsorption and Desorption

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Organisation

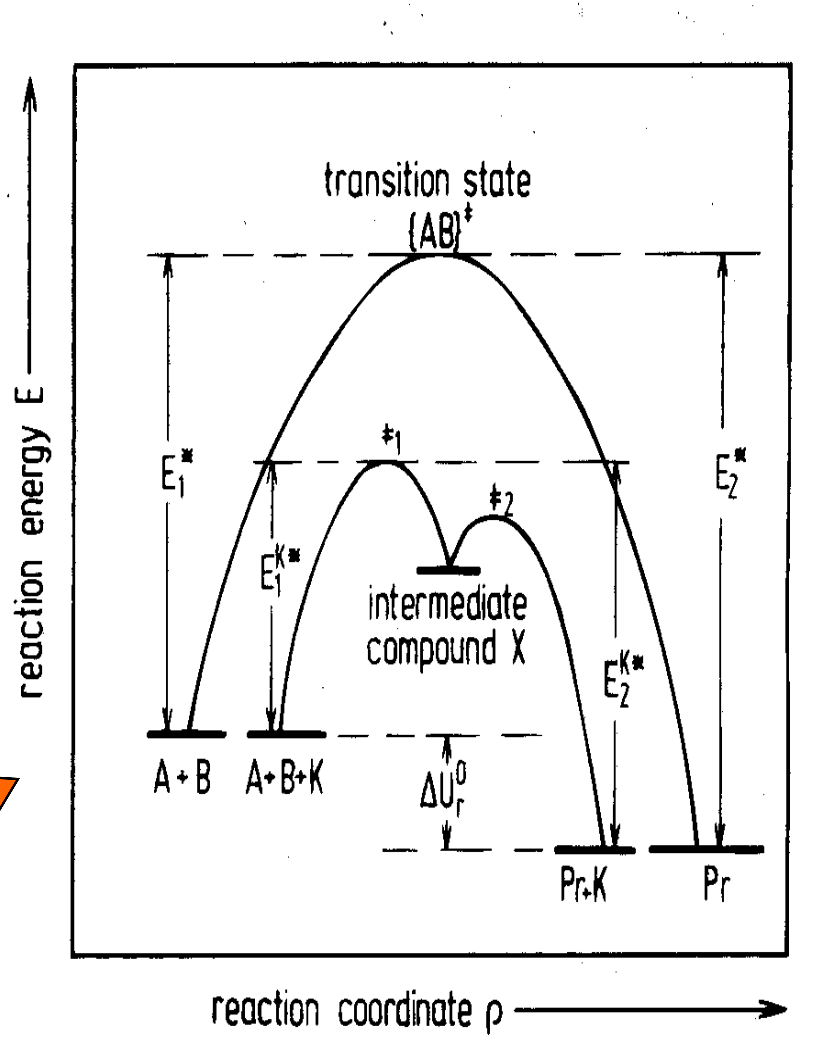
1. Introduction and motivation
2. Basics: how a non-equilibrium system approach equilibrium: kinetics as a *time*-dependent process; terms and definitions: rates; order of a reaction, pre-exponential, activation energy;
3. The rate of adsorption: trapping and sticking; coverage dependences

   1st order processes (molecular adsorption); 2nd order processes (dissociative adsorption);

   sticking probabilities; precursor processes; the rate of desorption: kinetic derivation; order and mechanism of a desorption reaction: 0; 1; 2
4. Experimental means to monitor surface kinetic processes: Thermal desorption spectroscopy; molecular beam techniques
5. Summary and outlook: The interplay between thermodynamics and kinetics in heterogeneous catalysis

1. Introduction and motivation

- As in any chemical reaction, surface processes involve breaking and making of bonds. As we have seen, this often requires substantial amounts of energy.
- However, as one can see from the oxidation of hydrogen gas by gaseous oxygen, there are many **metastable** reaction systems which cannot (at least not without external support) reach equilibrium. Reason: Large activation barriers slow down the reaction rate to almost zero at room temperature. This is what catalysis is all about: A catalyst provides an easier reaction path offering a greatly reduced activation energy barrier. In a sense, an active surface which readily adsorbs and dissociates molecules from the gas phase is nothing but an efficient catalyst.



2. Basics: The rate of adsorption – terms and definitions

Consider the rate of a chemical reaction of type A → B. The general **definition of reaction rate** is *change per time*, i.e. number of molecules per time, or concentration change of a certain species in the unit time interval:

$$Rate\ \ R = -\frac{d[A]}{dt} = +\frac{d[P]}{dt}\ \ in\ \ [\frac{moles}{dm^3 \cdot s}]\ \ or\ \ R = -\frac{dN_A}{dt} = +\frac{dN_P}{dt}\ \ in\ [\frac{particles}{Volume \cdot s}]$$

For surface kinetics, two-dimensional concentrations must be considered (quantities related to unit area)

$$Rate\ \ R = -\frac{d[A]}{dt} = +\frac{d[P]}{dt}\ \ in\ \ [\frac{moles}{dm^2 \cdot s}]\ \ or\ \ R = -\frac{dN_{S,A}}{dt} = +\frac{dN_{S,P}}{dt}\ \ in\ [\frac{particles}{unit\ area \cdot s}] = \frac{d\Theta}{dt}$$

Often, rates are expressed in terms of change of coverage Θ. $\Theta = \frac{N_{ad}}{N_{ad,\max}}$ = dimensionless number $0 < \Theta < 1$.

In an adsorption experiment, an initially bare surface is exposed to a certain gas pressure P, and the rate of collision of the gas particles with the unit surface is given by kinetic theory:

$$\frac{dN}{A \cdot dt} = \frac{P}{\sqrt{2\pi mkT}} \left[\frac{particles}{m^2 \cdot s}\right]$$

The decisive process now is **trapping/sticking**: will the impinging particle stay on the surface or will it be reflected? The respective probability is called (initial) “sticking probability” s_0 and varies between zero and one. As the surface is gradually covered, s decreases – simply because the number of empty adsorption sites gets smaller. If an adsorbed particle statistically occupies a single site, $s(\Theta) = 1 - \Theta$; *1st order adsorption*; if it dissociates, two sites are blocked by one collision event, and $s(\Theta) = (1-\Theta)(1-\Theta)$, *2nd order adsorption*. In case the adsorption requires a certain activation energy E^*_{ad} only particles having this energy will be able to stick.

2. Basics: The rate of adsorption – terms and definitions

The rate of adsorption is then:

$$R_{ad} = \frac{d\Theta}{dt} = \frac{s_0}{N_{\max}} \cdot f(\Theta) \cdot \frac{P}{\sqrt{2\pi mkT}} \cdot e^{-\frac{E_{ad}^*}{kT}}$$

(for a first-order process, f $(\Theta) = 1 - \Theta$, for a second-order process, f $(\Theta) = (1 - \Theta)^{2)}$. This rate expression allows to calculate the actual coverage after a certain time of gas exposure, simply by integrating the rate equation. For a non-activated 1st order process, one obtains

$$\Theta(t) = 1 - e^{-k_{ad} \cdot t}\ ,\ with\ k_{ad} = \frac{s_0}{N_{\max}} \frac{P}{\sqrt{2\pi mkT}}$$

which is a saturation function. Typical metal single crystal surfaces (Ni) contain ca. 10^{19} adsorption sites/m^2. A rough estimate neglecting the coverage dependence of the sticking function (constant unity sticking probability) yields that a surface would be completely covered in one second, if one maintains a pressure of ~10^{-6} mbar.

The initial sticking probability s_0 is an interesting quantity; it contains all the dynamical and sterical effects and is determined by the ability or effectiveness of a given particle to dissipate its kinetic energy to the heat bath of the surface (phonon excitation; electron – hole pair excitation).

Complications can arise when the colliding particle is trapped for some time (typically microseconds) in a weak potential in which it can freely move across the surface and search for an empty adsorption site. This weakly bound state is called **precursor state.** Consequence of a precursor state: The sticking – coverage function f(Θ) is no longer linearly decreasing, but has a convex shape: At not too large coverages the sticking remains high, but as the diffusion length in the precursor state becomes shorter than the radius of the already covered area (island), the particles can no longer be accommodated and are reflected back into the gas phase.

This is schematically illustrated in the following transparency.

Kinetics of Adsorption and Desorption

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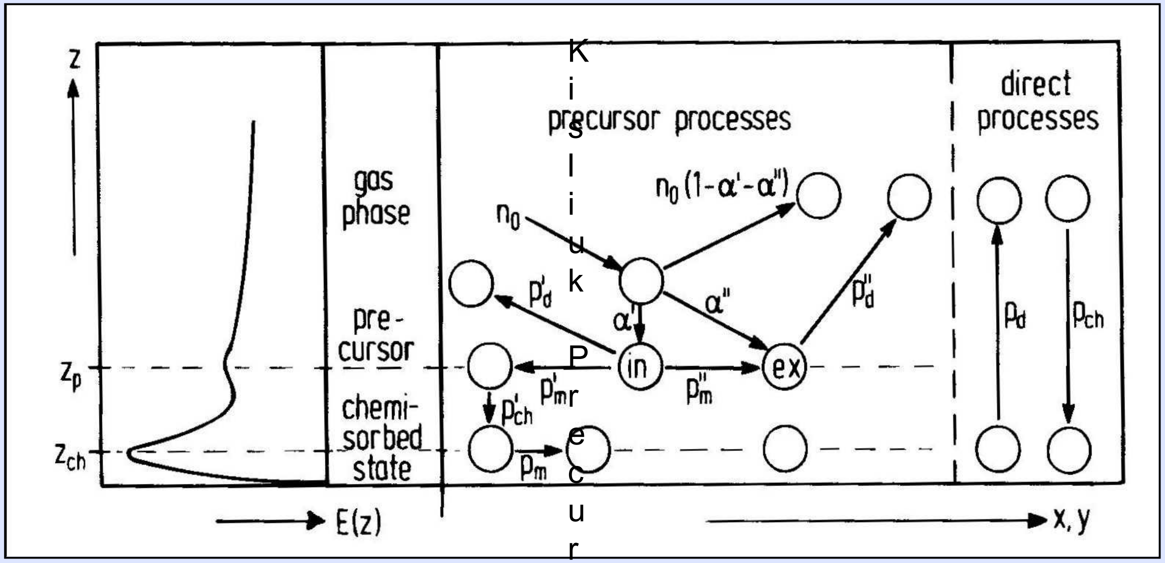
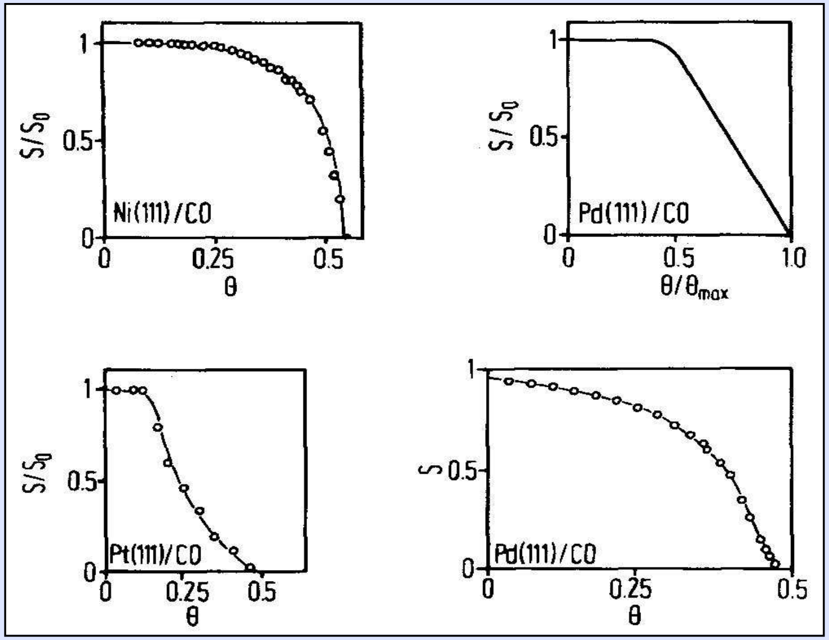
2. Basics: The rate of adsorption – precursor kinetics



Kisliuk Precursor kinetics

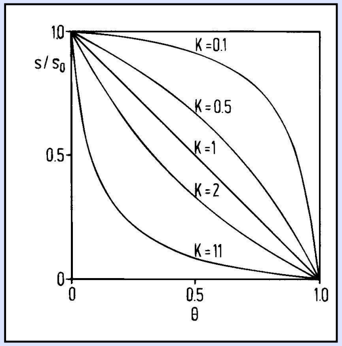


Kisliuk precursor kinetics:
(P.J. Kisliuk 1955)

$$s(\Theta) = s_0 \cdot \frac{1}{1+\frac{\Theta}{1-\Theta}K}$$

$$K = \frac{p''_d}{p'_{ch}+p'_d}$$

p'_{ch} = probability that the particle adsorbs from an intrinsic precursor (no adsorbed atom underneat´h)
p'_d = probability that particle desorbs from intrinsic precursor to gas phase
p''_d = probability that particle desorbs from extrinsic precursor (adsorbed Particle underneath)



2. Basics: The rate of desorption

The removal of particles from the adsorbed state back to the gas phase is called **desorption**. It can be achieved by thermal energy (thermal desorption, temperature-programmed desorption), electron impact (EID, DIET), ion impact, resonant photon irradiation etc. Here, only thermal desorption will be considered. Again, the desorption is understood as a normal chemical reaction and described by the respective kinetic formalism: $A_{ad} \rightarrow A_{gas}$ with rate constant k_{des}.

$$-\frac{dN_{ad}}{dt} = k_{des} \cdot N_{ad}^{x} \left[\frac{particles}{m^2 \cdot s}\right]$$

Upon introducing the coverage $\Theta = N_{ad}/N_{max}$ this equation takes the form:

$$-\frac{d\Theta}{dt} = k_{des} \cdot \Theta^{x} \cdot N_{\max}^{x-1}$$

As in any chemical reaction involving an activation barrier, k_{des} can be expressed as a product of a pre-exponential factor, ν_{des} and an exponential term containing the activation energy :

$$k_{des} = n \cdot \exp\left(-\frac{E_{des}}{kT}\right)$$

Inserting this in the rate equation yields the well-known Polanyi-Wigner equation which is the basis for a determination of both energetic and kinetic quantities from a thermal desorption spectrum:

$$-\frac{d\Theta}{dt} = n_{x} \cdot \Theta^{x} \cdot N_{\max}^{x-1} \cdot e^{-\frac{E_{des}}{kT}}$$ = R = rate of desorption: **R = R (**Q**, T)**

Kisliuk Precursor kinetics

2. Basics: The rate of desorption

R = rate of desorption: **R = R (Q, T) =** $$-\frac{d\Theta}{dt} = n_x \cdot \Theta^x \cdot N_{\max}^{x-1} \cdot e^{-\frac{E_{des}}{kT}}$$

Of interest: to determine the kinetic quantities such as

- order of the desorption, x, which contains valuable information on the machanism of the desorption process
- Pre-exponential factor ν which allows conclusions on the configuration and mobility of the adsorbed phase (mobile or immobile adsorbed layer
- Activation energy (which we have already talked about)

Furthermore: Note that the peak integrals reflect the adsorbed amount prior to application of the temperature programm. By plotting the peak integrals versus the exposure, one can determine the sticking probability as a function of coverage.

Kisliuk Precursor kinetics

Kinetics of Adsorption and Desorption

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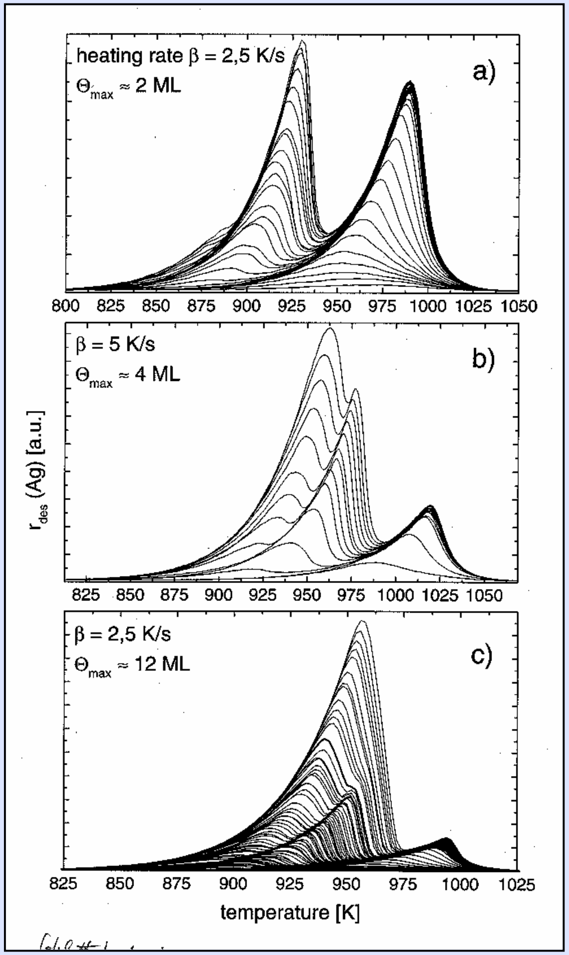
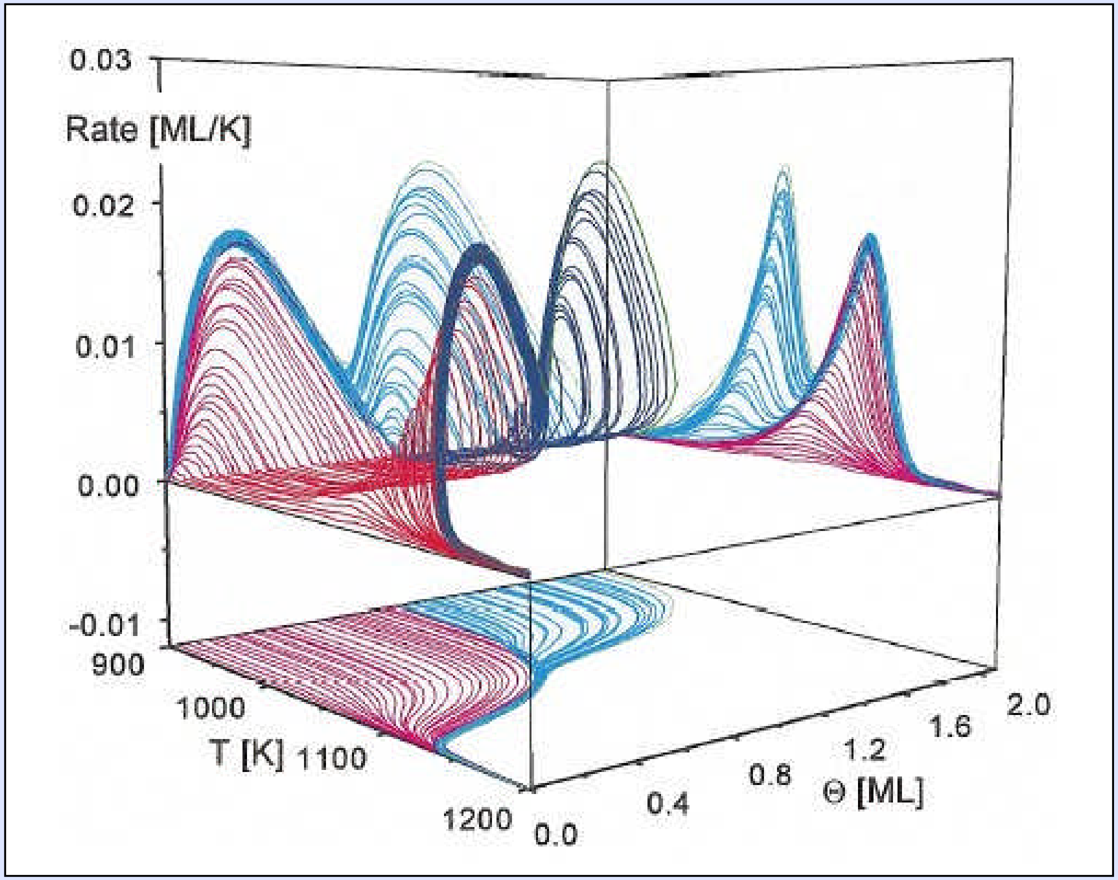
3. The experimental procedure: Taking TPD spectra



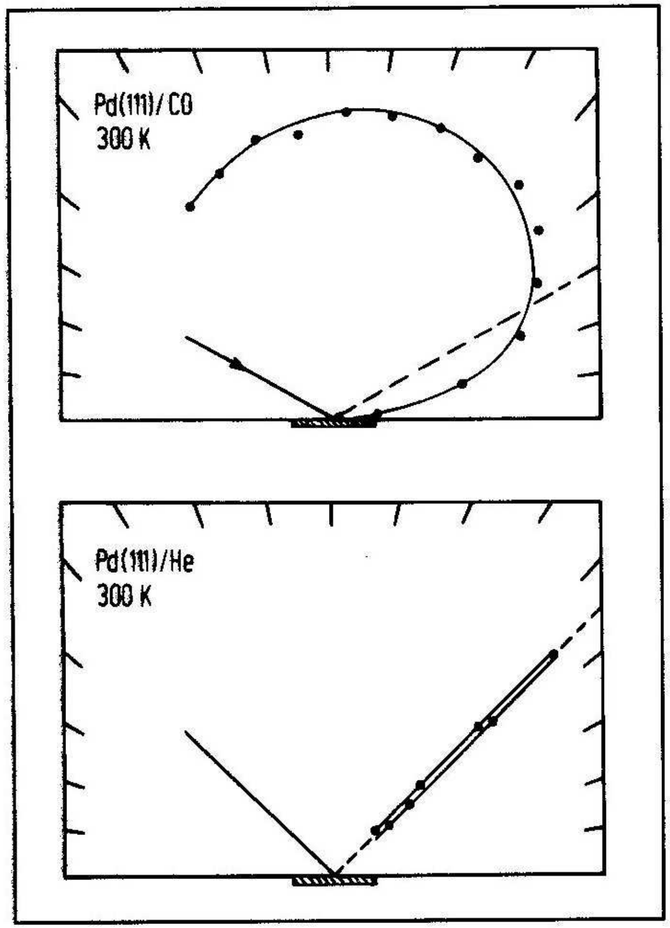
TDspectra of Ag from Re(0001)



Θ-dependence of ν and E_{des} Cu/Re

Ronald Wagner 2001

3. The experimental procedure: Molecular beam techniques



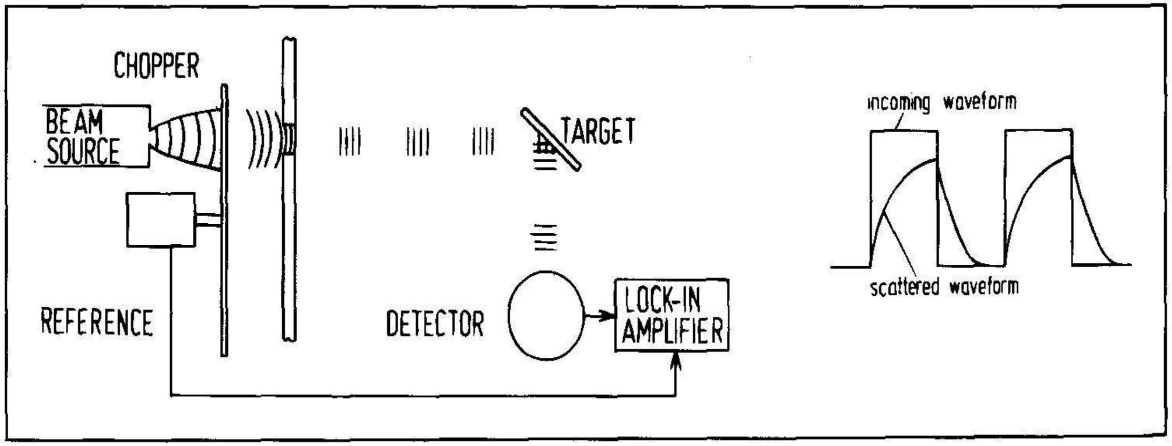


Fig. 5.7. Typical set-up for a chopped molecular beam experiment. The particle beam emitted by the source passes a chopper wheel which divides it into short particle pulses with frequency ω_0. These pulses interact with the surface (in the simplest case they are elastically reflected), and the particles emitted from the target are collected in the detector and analyzed with respect to their time dependence using lock-in technique. Inelastic interaction with the surface causes the initially rectangular shaped pulses to become distorted in a way shown in the right part of the figure. After Engel [32]

Kinetics of adsorption and desorption: literature

1) M.W. Roberts & C.S. McKee, *Chemistry of the Metal-Gas Interface*, Clarendon, Oxford 1978

2) K. Christmann, *Introduction to Surface Physical Chemistry*, Steinkopff-Verlag, Darmstadt 1991

3) D. Menzel in: *Interactions on Metal Surfaces* (R. Gomer, ed.), Series: Topics in Applied Physics, Vol. **4**, Springer-Verlag Berlin, Heidelberg, New York, 1975, Ch. 4, pp. 101 – 142

4) P.A. Redhead, Vacuum **12** (1962) 201

5) L.A. Peterman, Progr. Surf. Sci. **1** (1972)

6) D. A. King, Surf. Sci. **47** (1975) 384

7) E. Bauer et al., Surf. Sci. **53** (1975) 87

As well as various original publications.