Adsorption

Lecture Series: “Modern Methods in Heterogeneous Catalysis”
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Organization

1. Introduction: Terms and definitions, the role of adsorption in surface catalysis
    - Adsorption as a macroscopic (thermodynamic) phenomenon
    - Adsorption as a microscopic (quantum chemical) phenomenon

2. Some essentials in physics and chemistry of adsorption:
    - Associative and dissociative adsorption
    - The adsorption energy: physisorption and chemisorption
    - Initial adsorption energy and a-priori heterogeneity
    - Coverage dependence of the adsorption energy: a-posteriori heterogeneity
    - Ensemble and ligand effects
    - Adsorbate-induced changes of the surface morphology
    - Adsorption kinetics - terms and definitions; sticking and desorption phenomena

3. Summary and conclusions; literature

1. Introduction: Terms and definitions

Terminology: **What is adsorption?**

In a typical adsorption process, a foreign material (mostly in gaseous or liquid form) called the ***adsorbate*** becomes attached to a solid surface, the ***adsorbent***, and forms the ***adsorbate phase***.

Consequence: **No adsorption can occur without a surface** (sometimes this may be a liquid surface, in most cases, however, one considers a surface of a **solid** material).

Since the adsorbate is usually altered upon the adsorption reaction, the chemical and physical properties of the *adsorbate* may differ from those of the *adsorbate phase*. Note that the adsorbate phase includes part of the adsorbent, i.e., its surface atoms (which is particularly evident, if a discrete surface complex is formed).

In heterogeneous catalysis, **adsorption is one of the most essential elementary processes** which activates the decisive chemical bonds of the (adsorbed) reactants.

Some solids are ideal for adsorption. They have a large surface area compared to their volume because they are pockmarked with micropores. Among these solids are charcoal (active carbon), alumina, silica, zeolites or carbon nanotubes.

1. Introduction: Terms and definitions

Terminology: **What is a surface?**

There exist a lot of definitions among which the most rigorous ones are:

- **A surface represents the outer or the topmost boundary of a solid or liquid object, where the bulk properties are no longer in effect.**
- **A surface always determines a thermodynamic phase boundary, where the physical and chemical properties of the adjacent phases change abruptly.**

Consequence:

In the surface region, the interaction forces which govern the bulk properties, *change*, they become asymmetric with the outermost bonds being unsaturated, resulting in a peculiar chemical reactivity of the surface. In the context of catalysis the most important consequence is that the surface becomes capable of adsorbing foreign atoms or molecules. Accordingly, the adsorbate helps to saturate the surface‘s free valencies.

1. Introduction: The role of the surface

The role of the surface

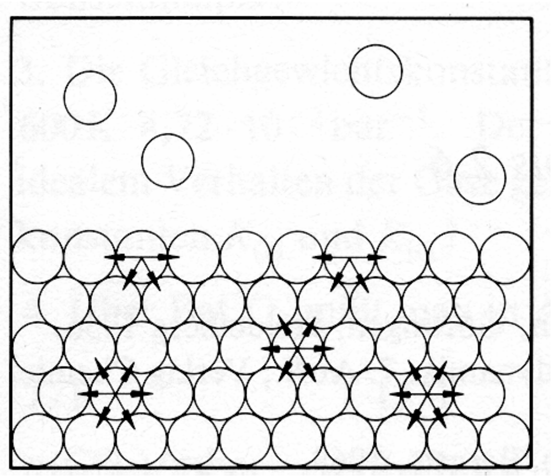
- A surface *concentrates* the gas particles from the very dilute (gas) phase to a much more condensed (adsorbate) phase:

Average particle – particle distances in the gas phase (p = 1 bar) [mean free path $\lambda \sim 1/P$] $\approx 4{,}3 \times 10^{-8}$ m.

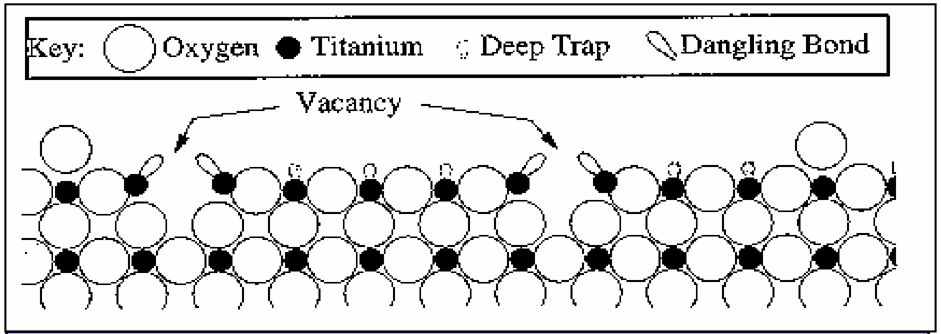
Distance between adjacent particles adsorbed on a typical metal surface $\approx 4 \times 10^{-10}$ m: Much closer distances facilitate chemical reactions between adsorbed molecules.

- A surface helps to activate or even break chemical bonds within the adsorbing molecules. In turn, these altered molecules may then undergo new chemical reactions leading to the desired products. This is one of the secrets of heterogeneous catalysis!

1. Introduction: Asymmetric interaction forces; dangling bonds



Schematical illustration of the asymmetry of the interactions in the surface



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

Interaction forces that can lead to adsorptive bonds of:

a) van-der-Waals,
b) ionic (electrostatic),
c) covalent,
d) metallic

nature.

Strength of these bonds are

- very weak in case a);
- but may be of the order of typical chemical bonds in the cases b) ... d), i.e. may range between 80 und 300 kJoule/Mol.

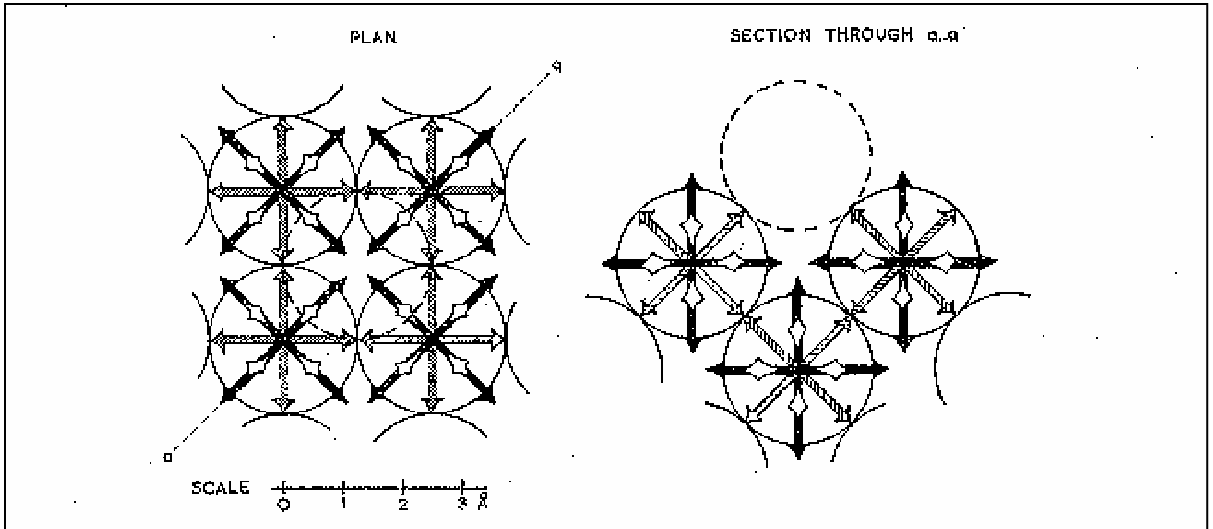
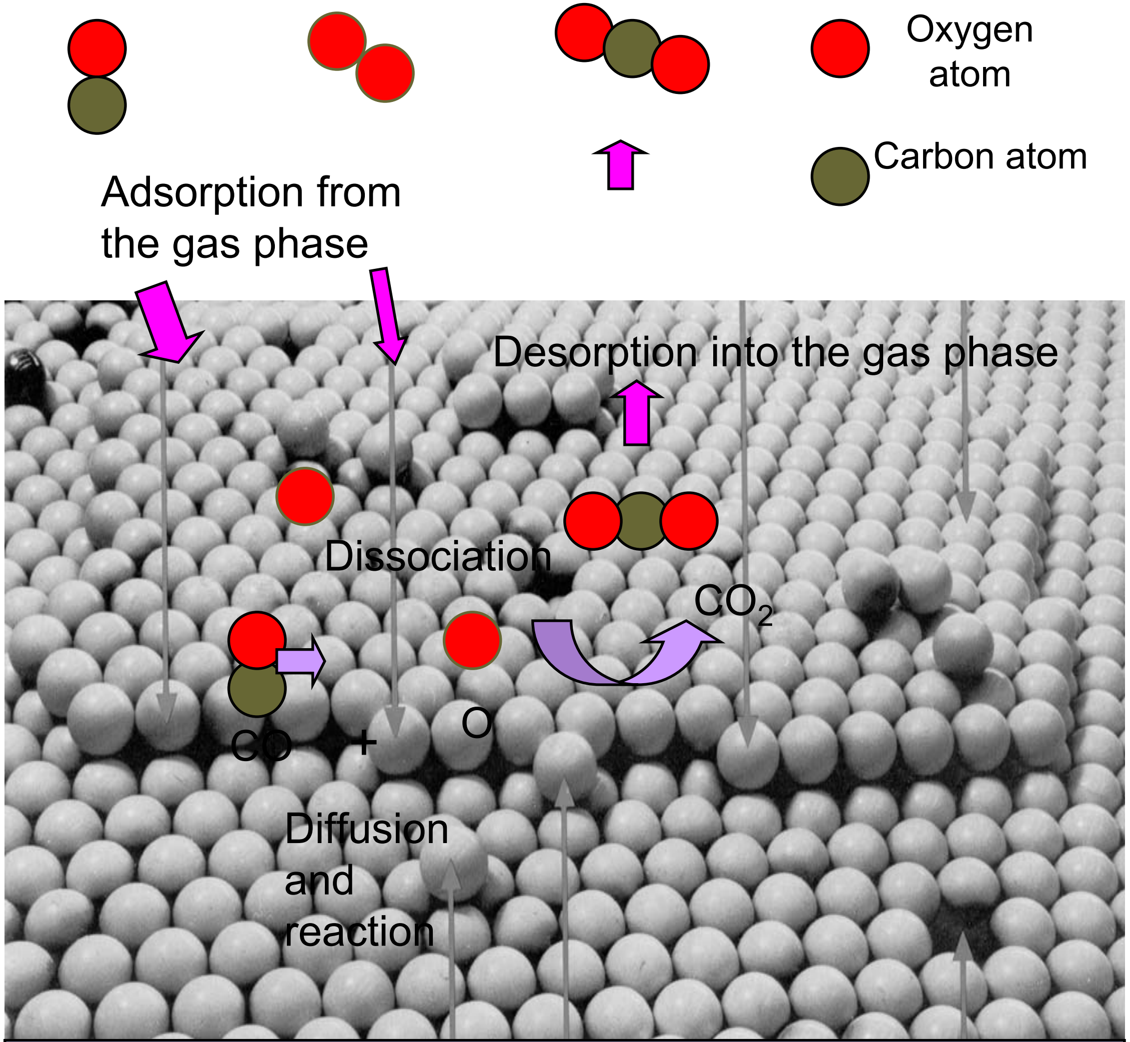


FIG. 5.—Diagrammatic representation of the emergence of orbitals at the (100) face of a face-centred cubic metal. Filled arrows: e_g orbitals in plane of paper; hatched arrows: t_{2g} orbitals in plane of paper; open arrows: t_{2g} orbitals emerging at 45° to plane of paper. The broken circle shows the 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.

1. Introduction: A typical scenario occurring at a solid surface



Ball model of a real solid surface (with numerous defects, edges, corner and kink atoms as well as foreign atoms which all affect the chemical reactivity of this system.

Example of a surface process that involves adsorption:

CO oxidation reaction on a Pd surface. This reaction is essential for decontamination of automobile exhaust gas and takes place in the three-way catalyst of cars.

1. Introduction: Adsorption as a thermodynamic phenomenon

Some general points of interest in an adsorption process:

- How many particles can be adsorbed by a given amount of material?
- How does this amount depend on the state variables (temperature and pressure)?
- How can one determine the adsorbed amount?
- Where are the adsorbed particles located (local symmetry of the site)?
- How much energy is required to remove these particles from the surface, i.e., how strong are the adsorptive bonds to the surface?

Relatively straightforward answers to these questions are provided, among others, by (surface) thermodynamics.

1. Introduction: Thermodynamics of adsorption - Gibbs Fundamental equation

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

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

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

$$dG = V\,dP - S\,dT + \sigma\ dA + \sum_i \mu_i dn_i$$

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

The surface tension [N/m] is entirely equivalent to the surface energy σ [Nm/m^2], which is the **driving force** for all surface phenomena. Thermodynamics describes the behaviour of matter as a function of state variables (P, T, chemical composition etc.). However, since it is just 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.

1. Introduction: Thermodynamics of adsorption - The heat of adsorption

Thermodynamical derivation of the so-called isosteric enthalpy of adsorption, q_{st}, one of the most important system quantities:

Chemical equilibrium between adsorbate and gas phase leads to a *constant surface concentration* Γ [moles/m^2]. Constant Γ is maintained when the fluxes of adsorbing and desorbing particles are equal. We now consider the pressure and temperature dependence of this phase equilibrium. A common procedure is to equate the chemical potentials and their derivatives of the phases involved. Remember that the chemical potential μ is the derivative of the Gibbs energy with respect to the mole number in question, n_i :

$$\mu_i = \left(\frac{dG}{dn_i} \right)_{P,T,\ \text{other mole numbers}}$$

In the (dynamical) phase equilibrium, the chemical potentials μ_{ad} and μ_{gas} are equal and *remain* equal (“persisting” equilibrium) :

$$\mu_{ad} = \mu_{gas} \quad \text{and} \quad d\mu_{ad} = d\mu_{gas}\ ; \quad \Gamma = n_{ad}/A$$

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

1. Introduction: Thermodynamics of adsorption - the heat of adsorption, cont‘d

Rearranging leads to the well-known **Clausius - Clapeyron equation** for the “ongoing” phase equilibrium between gas phase and adsorbate phase(s):

$$\left(\frac{dP}{dT}\right)_\Gamma = \frac{s_g - s_{ad+OF}}{V_g - V_{ad+OF}}$$

Setting $V_{ad+OF} << V_g$ and applying the ideal gas equation, yields $V_g = \frac{RT}{P}$. We then obtain $\frac{1}{P}\left(\frac{dP}{dT}\right)_\Gamma = \frac{s_g - s_{ad+OF}}{RT}$. Recalling that the entropy is the “reduced” heat $s = \frac{h}{T}$ finally leads to the expression:

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

q_{st} is called *differential isosteric heat of adsorption* and represents the energy difference between the state of the system before and after the adsorption of a differential amount of adsorbed particles. q_{st} can be obtained from equilibrium measurements (adsorption isotherms).

1. Introduction: Thermodynamics of adsorption - The adsorption isotherm

The adsorption isotherm provides us with information of how much material will adsorb for a given set of state variables (pressure und temperature). It is one of the most important criteria for an adsorption process.

A simple way of getting to the adsorption isotherm is to equate the rates of adsorption and desorption. (The respective rate equations will be dealt with in the kinetics section and are used here without derivation):

$$r_{ad} = \frac{dN_{ad}}{dt} = s_0 \, f(\Theta) \frac{p}{\sqrt{2\pi \, mkT}}$$

with s_0 = initial sticking probability, f(Θ) = coverage function (= 1 - Θ for one-point-adsorption)

$$r_{des} = -\frac{dN_{ad}}{dt} = \nu_x \, N_{ad}^{x} \exp\left(-\frac{E_{des}}{kT}\right)$$

x = reaction order = 1 for associative and 2 for dissociative adsorption, ν = frequency factor, E_{des} = desorption energy (depth of potential well). Usually, the term ***coverage*** Θ as the fraction of covered surface is introduced: $\Theta = N_{ad}/N_{max}$

Considering associative adsorption and desorption (x = 1) we arrive at the expression:

$$\frac{s_0}{N_{\max}}(1-\Theta)\frac{p}{\sqrt{2\pi \, mkT}} = \nu_1 \, \Theta \, \exp(-\frac{E_{des}}{kT})$$

1. Introduction: Thermodynamics of adsorption - The adsorption isotherm, cont'd

Solving for Θ yields the famous **Langmuir isotherm**:

$$\Theta(p)_T = \frac{b(T)\,P}{1+b(T)\,P}$$

with $b(T)=\frac{s_0}{\nu\,N_{\max}}\left(2\pi\,mkT\right)^{-\frac{1}{2}}\exp\left(\frac{E_{des}}{kT}\right)$ as T-dependent coefficient.

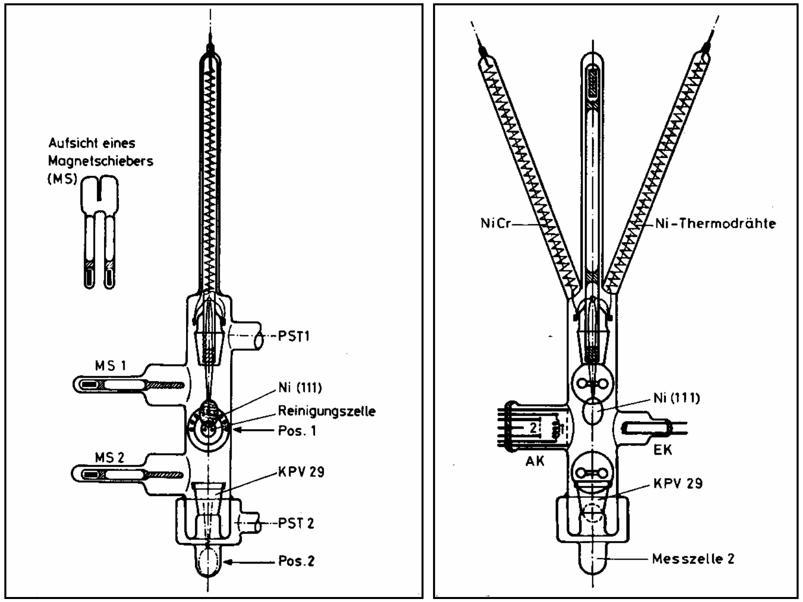
Takíng into account x = 2 , a very similar expression can be derived for dissociative adsorption/ desorption:

$$\Theta(p)_T = \frac{\sqrt{b^{'}(T)P}}{\sqrt{1+b^{'}(T)P}}$$

From the initial slope of a log - log plot of an adsorption isotherm (b(T)P << 1), the order of adsorption can easily be determined (slope 1 = 1st order adsorption; slope 0,5 = 2nd order adsorption).

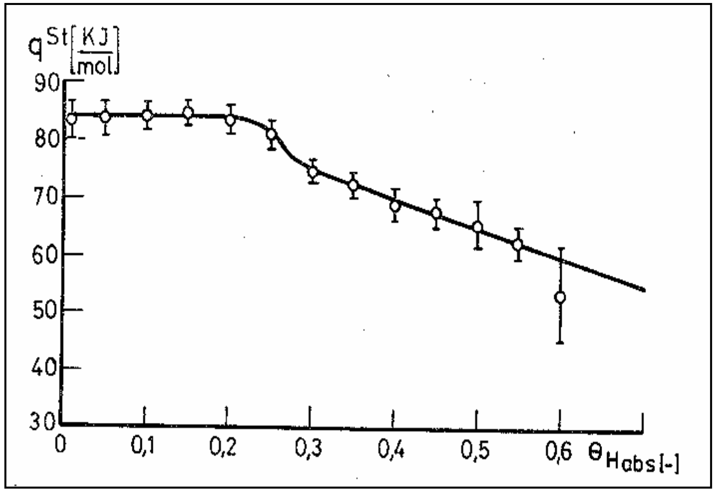
1. Introduction: The measurement of adsorption isotherms and determination of the heat of adsorption (example: H_2/Ni(111))

Principally, there exist various methods to get access to the heat of adsorption and its coverage dependence, E_{ad} (Θ). Particular reliable are thermodynamic measurements using **adsorption isotherms**. Especially accurate is the **direct volumetric determination** of the adsorbed amount; however, only a single report is known where such a measurement has been carried out with a metal single crystal [H. Rinne, Ph.D. thesis, TU Hannover 1972]. Usually, the equilibrium adsorbed amount is determined *indirectly*, i.e., by monitoring the adsorbate-induced work function change or the signal intensity of photoemission peaks, a successful procedure as long as these are 1:1-correlated with the adsorbed amount. Furthermore, **direct calorimetric methods** are suited as well; I recall Wedler's early work on the calorimetric determination of the heat of hydrogen adsorption on polycrystalline Ni films [G. Wedler, Z. Phys. Chem. NF **24** (1970) 73] and the modern area of microcalorimetry developed in the laboratories of D.A. King or C.T. Campbell [Al-Sarraf et al., Nature **360** (1992) 243].

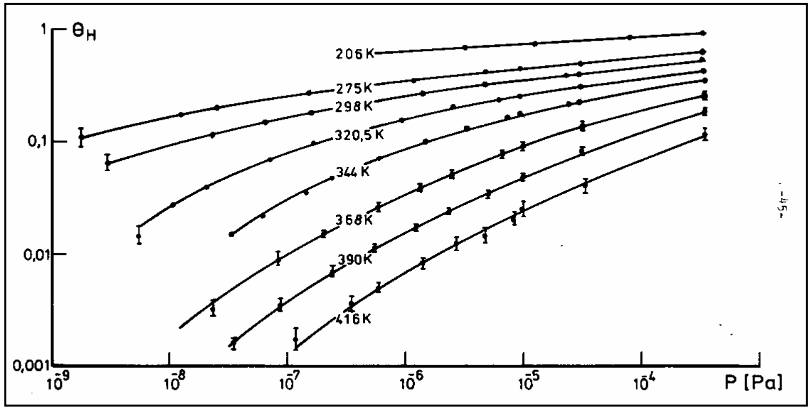


Glas cell for direct volumetric measurement of adsorbed hydrogen on a Ni(111) surface developed by H. Rinne 1972.

H/Ni(111)



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

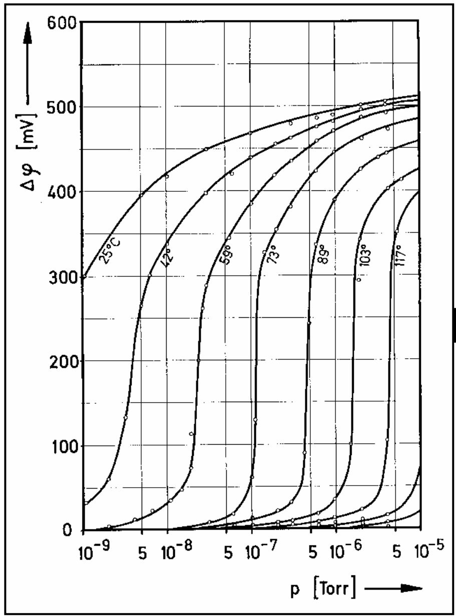


Volumetrically determined adsorption isotherms of hydrogen on a Ni(111) surface

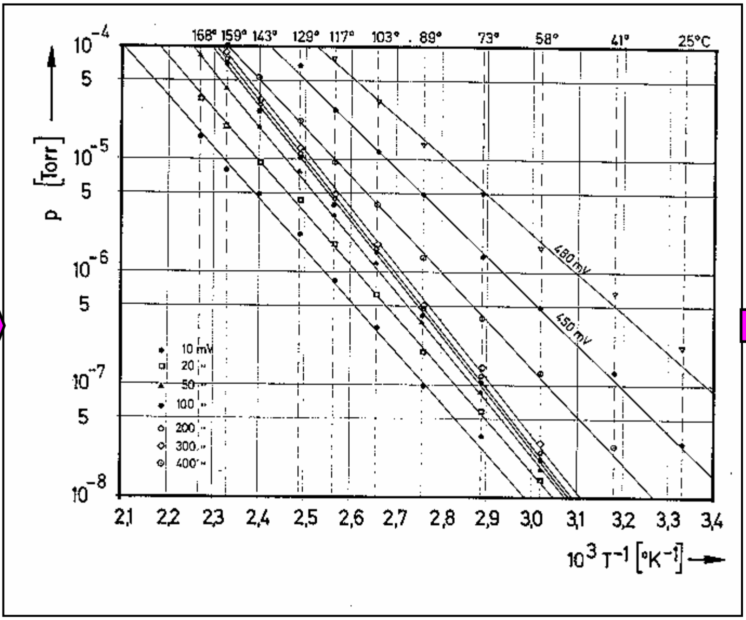
1. Introduction: Measurement of adsorption isotherms using indirect methods

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

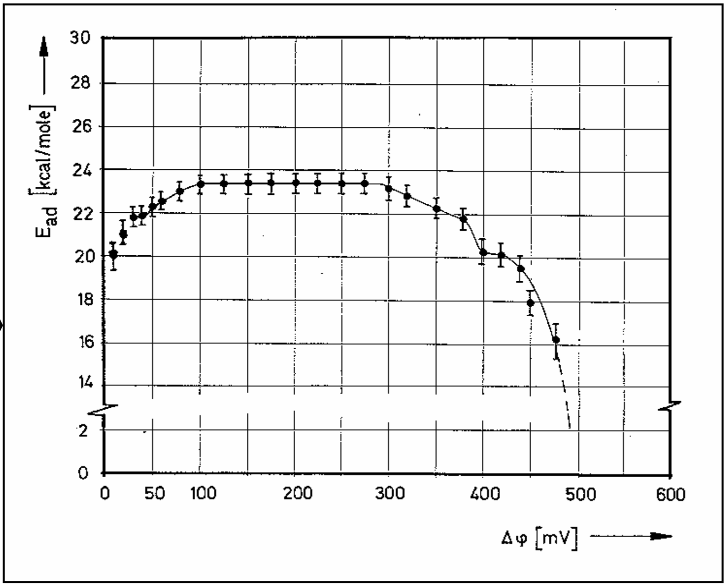
1. Monitor the adsorbed amount $\Gamma = n_{ad}/A$ as a function of gas pressure P for constant temperature T, by measuring e.g. adsorbate-induced work function changes ($\Delta\varphi$) or XPS or AES adsorbate peak areas etc.
2. Construct horizontal cuts in the Γ-P-plane; determine and write down the respective triples of Γ-P-T values.
3. Plot ln P 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 ratio $\mathbf{q_{st}/R}$.



Ni(110)/H_2: Adsorption isotherms



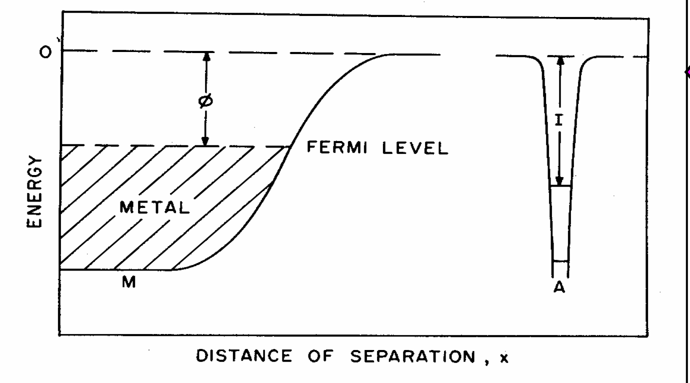
Ni(110)/H_2: Adsorption isosteres



Ni(110)/H_2: Coverage dependence of the isosteric heat of adsorption (K.C. et al, JCP **60** (1974) 4528

1. Introduction - Microscopic view of adsorption

Due to quantum chemical interaction between the approaching molecule and the surface there operate, even at larger distances, attractive forces on the adsorbate resulting in the formation of a chemical bond between the surface and the adsorbate. The equilibrium is reached when the adsorbed particle resides at the bottom of the potential energy well, whose depth in turn 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.).

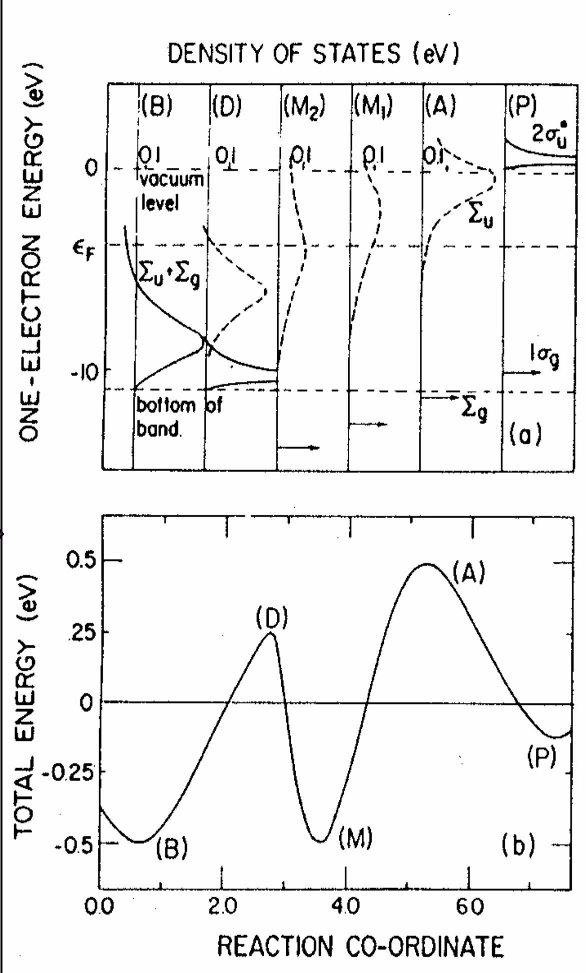
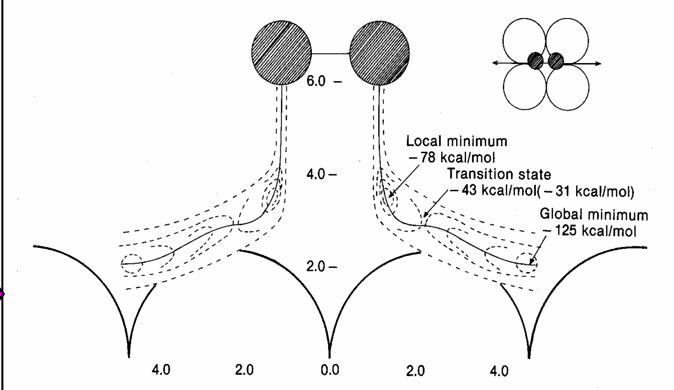
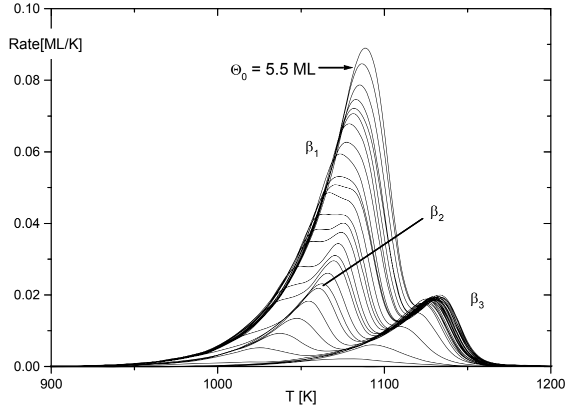


Illustration of the reaction path and the total energies for the oxygen adsorption on a Ni_{25}-cluster with square symmetry (after Panas et al.)

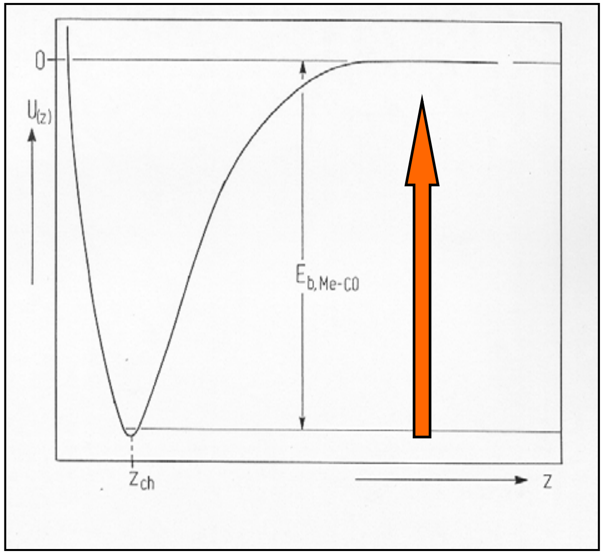


1. Introduction - Microscopic view of adsorption, cont'd

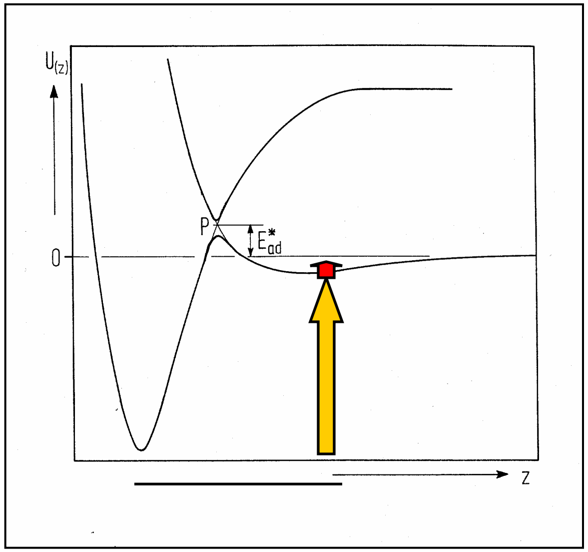
In the adsorbed state and in thermal equilibrium the trapped particle resides at the bottom of the potential well. It is either physically or chemically adsorbed to the solid surface.
In order to remove it from the surface, one has to supply it thermally or electronically with the energy required to break the adsorptive bond. In case there are activation barriers involved, these have to be additionally overcome, and the desorbing particle will possess more energy than if it were 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

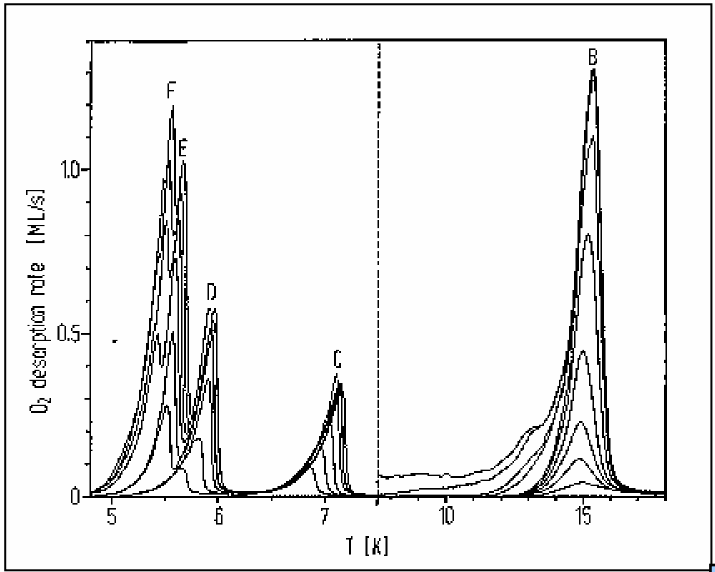
Thermal Desorption spectroscopy

(see also lecture D. Rosenthal 15.2.2008):

The most frequently used method to obtain information on the energetics and kinetics of adsorbed particles is **thermal** desorption. 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.

1. Introduction: Microscopic view of adsorption; strength of adsorbate bond

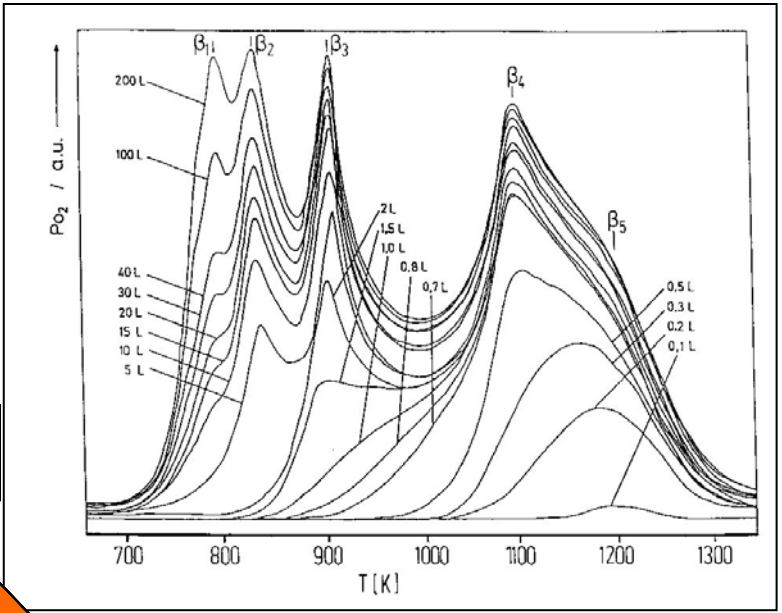
Depending on the strength of the interaction energy one distinguishes between physisorption and chemisorption. This distinction is, however, not rigid. Below, say, 20 kJ/Mol there is genuine physisorption, the interaction is dominated by **van-der-Waals-forces**. Example: Rare gas adsorption on graphite, 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.



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

Notice the extremely low desorption temperatures !

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

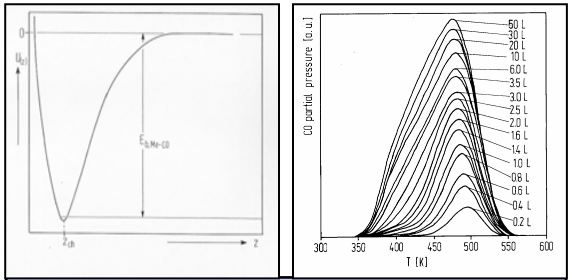


Oxygen desorption from a Rh(110)-surface

Notice the extremely high desorption temperatures!

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

2. Some essentials in adsorption: Associative and dissociative chemisorption



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

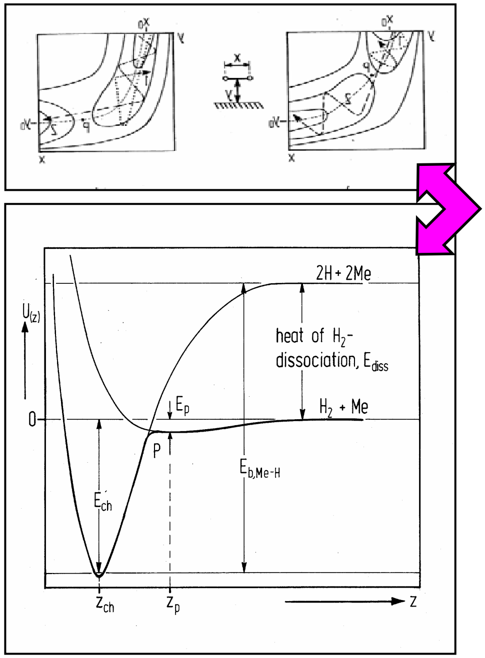
Associative (molecular) adsorption leaves the adsorbing molecule intact. Example: CO adsorption on a palladium surface. The adsorption energy equals the depth of the potential energy well:

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

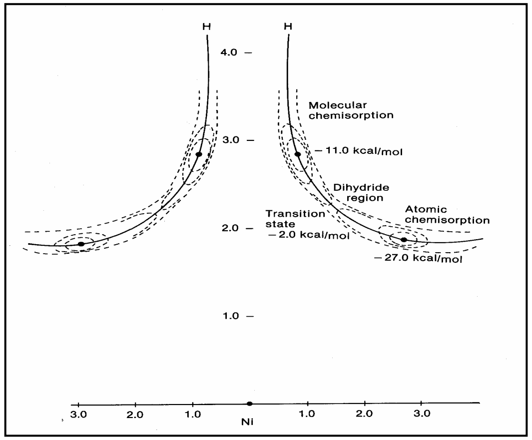
Dissociative chemisorption makes the molecule fall apart upon adsorption, either in a heterolytic or in a homolytic manner. In this process the dynamics of the reaction is of great interest, but also the dependence of the binding energy of the species formed by dissociation as a function of the distance 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:

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

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.

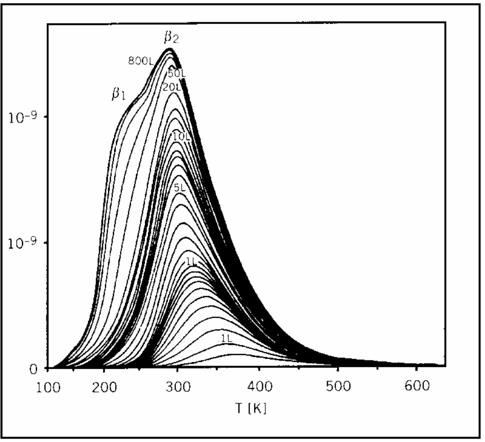


One-dimensional (left) and two-dimensional (top) representation of the potential energy surface for the homolytic dissociative adsorption. Example: H_2 on Nickel.



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

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



2. Some essentials in adsorption: Initial adsorption energy and a-priori heterogeneity

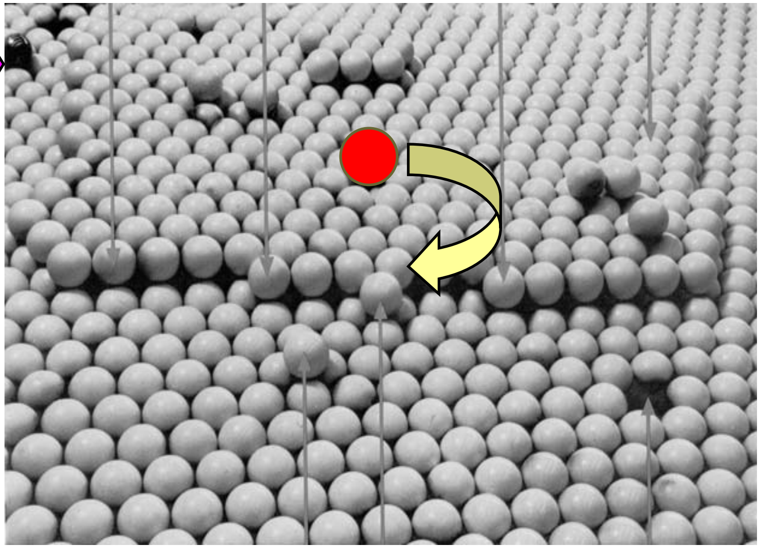
Table: Initial adsorption energies for some typical intetraction systems

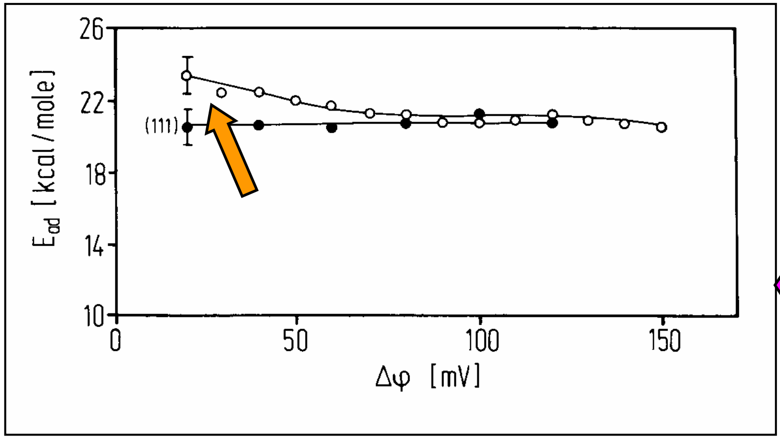
Adsorbat	**Oberfläche**	**E_0 von...bis [kJ/Mol]**
Wasserstoff H_2	Ru(0001)(1x1)-H	2...5
Sauerstoff O_2	Ru	10...20
Kohlendioxid CO_2	Cu	10...30
Xenon Xe	Ni(aus H_2)	15...25
Xenon Xe	Pd	20...40
Wasserstoff H (aus H_2)	Pt	60...80
Wasserstoff H (aus H_2)	Co, Ni, Ru, Rh, Pd	30...100
Wasserstoff H (aus H_2)	Mo, W, Re	125...175
Kohlenmonoxid CO	Ni, Pd	100...150
Sauerstoff O (aus O_2)	Ru, Pd	200...250
Sauerstoff O (aus O_2)	Rh, Re	200...300
Kupfer Cu	Ru, W, Re	250...330

A so-called **initial adsorption energy** is defined that is felt by the very first particle arriving on a clean surface. It is a system-specific quantity that directly reflects the strength of the interaction between adsorbate and substrate (c.f. left Table).

It is well-known that on a given surface sites with quite different adsorption geometry and binding strength may exist. A good example is „stepped“ surfaces which provide sites with a higher coordination right at the steps. A case study is presented for H interaction with a flat and a stepped Pd surface.

Representation of a real surface with defects (steps, kinks, adatoms, holes etc.)



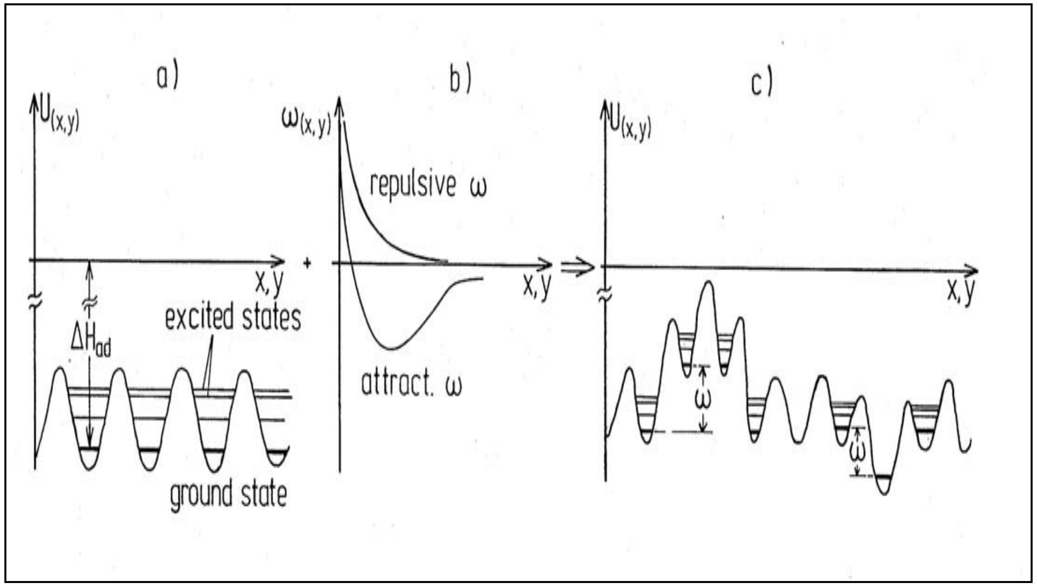


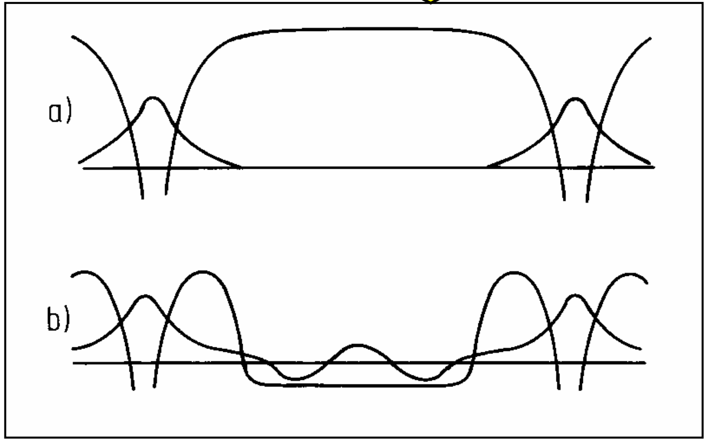
Heat of adsorption for a flat and a stepped Pd(111) surface (after Conrad et al.)

2. Some essentials in adsorption: a-posteriori heterogeneity; induced lateral interactions

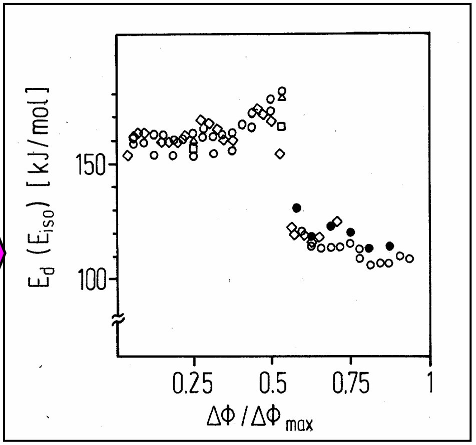
Already the very first adsorbing particle possibly changes the shape and depth of potential energy wells of its neighboring sites due to lateral interaction forces. These forces may be attractive or repulsive, depending on the quantum-chemical details of the interaction. The distance dependence of the resulting potential (c) is in fact a superposition of the periodic adsorption potential of the crystal's surface (a) and the mutual particle – particle interactions (b).

The respective interactions are either due to **direct** orbital – orbital repulsions (direct interactions) or due to substrate-mediated interactions (**indirect** interactions) that are caused by a sharing of substrate bondíng electrons between adjacent adsorbed molecules.





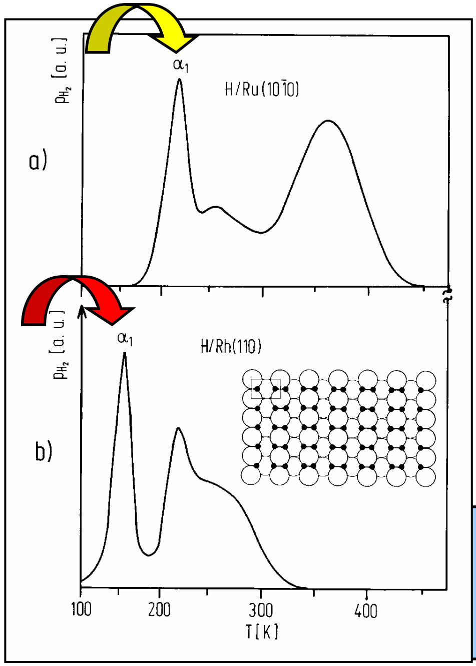
Often the lateral interactions are induced only at a certain critical coverage.
Example: CO adsorption on Ru(0001) [Pfnür et al.]: Up to a ×3x×3-R30°-structure the CO molecules have enough space; at higher coverages suddenly the repulsion becomes dominant resulting in a step-like decrease of the adsorption energy..



2. Some essentials in adsorption: induced heterogeneity; ensemble and ligand effects

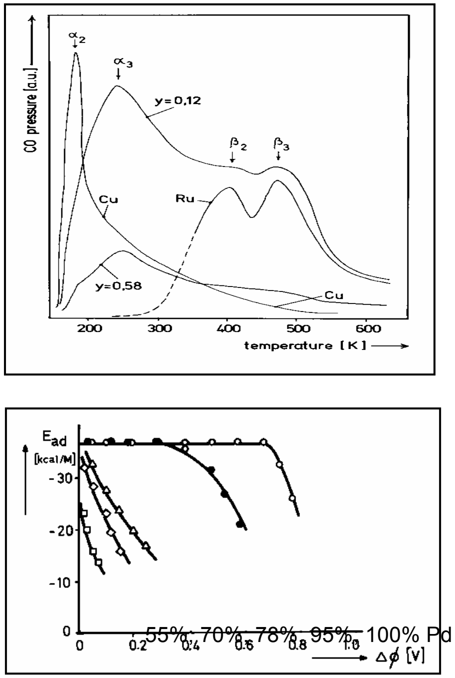
As the coverage increases beyond a critical limit, induced lateral heterogeity causes a dramatic decrease of the adsorption energy which appears in TD spectra often as a low-temperature split-off state. Examples are (1x1) phases of adsorbed hydrogen on Rh(110) and Ru(10-10) surfaces.

The amount of the decrease of the adsorption energy allows conclusions to be made especially on the strength of the particle – particle repulsion.



Schematic representation of TD spectra of hydrogen desorbing from (1x1)H phases formed on Ru(10-10) and Rh(110)

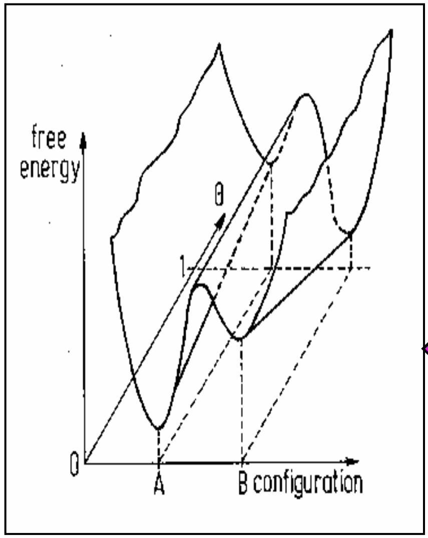
Co-adsorbed foreign atoms can (and usually will) cause energetic heterogeneities. Noble metals (Cu, Ag, Au) often have a reduced chemisorption capacity as compared with group VIII transition metals. A Ru surface that is partially covered with Cu looses its ability to chemisorb hydrogen, because a defined ensemble of adjacent Ru atoms is required to dissociate a H_2 molecule. Admixture of only a few Cu atoms destroys these ensembles effectively **(ensemble effect**). The vicinity of Cu atoms ‚spoils' good adsorption sites (for CO or H) because of a local modification of the metal's local electronic band structure resulting in a marked lowering of the adsorption energy (**ligand effect**). Both effects are of central importance in heterogeneous catalysis.



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

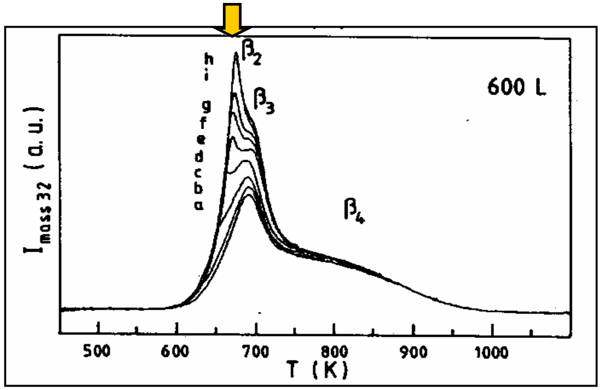
2. Some essentials in adsorption: adsorbate-induced structural changes: relaxation, reconstruction; subsurface phase formation

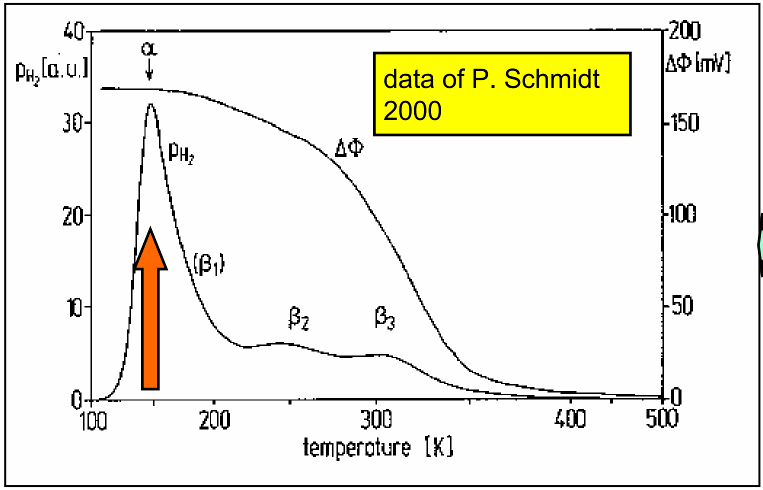
If the adsorbate interacts strongly with the surface, the position of the substrate atoms may change somewhat, whereby their new positions provide a more favorable energetic situation. In a „mild“ case, only the perpendicular distances between the substrate atomic layers become altered (**relaxation**); for more vigorous interactions the lateral periodicity of the surface atoms change, a process that is called **surface reconstruction.** If there are no activation barriers, the total Free Energy of the system (substrate + adsorbate phase) determines the equilibrium surface geometry.



Free energy as a function of the atom configuration and coverage of the adsorbate Θ.

Development of an oxygen subsurface state β_2 (yellow arrow) with the O_2 exposure observed with a Pt(210) surface. The other states (β_3 and β_4) are due to chemisorbed oxygen on Pt(210).

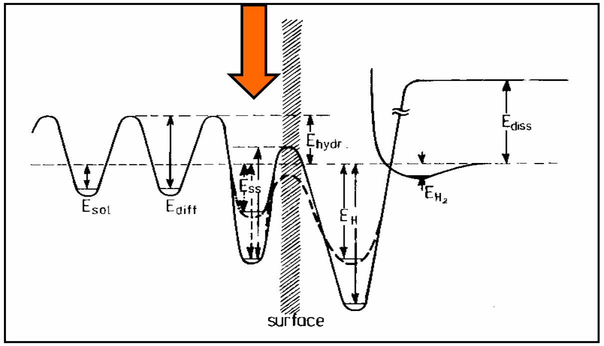




data of P. Schmidt 2000

Formation of surface (β-states) and subsurface (α)-state as H_2 interacts with a Pd(210) surface. Expectedly, the SS state does not contribute anything to the work function change Δφ!

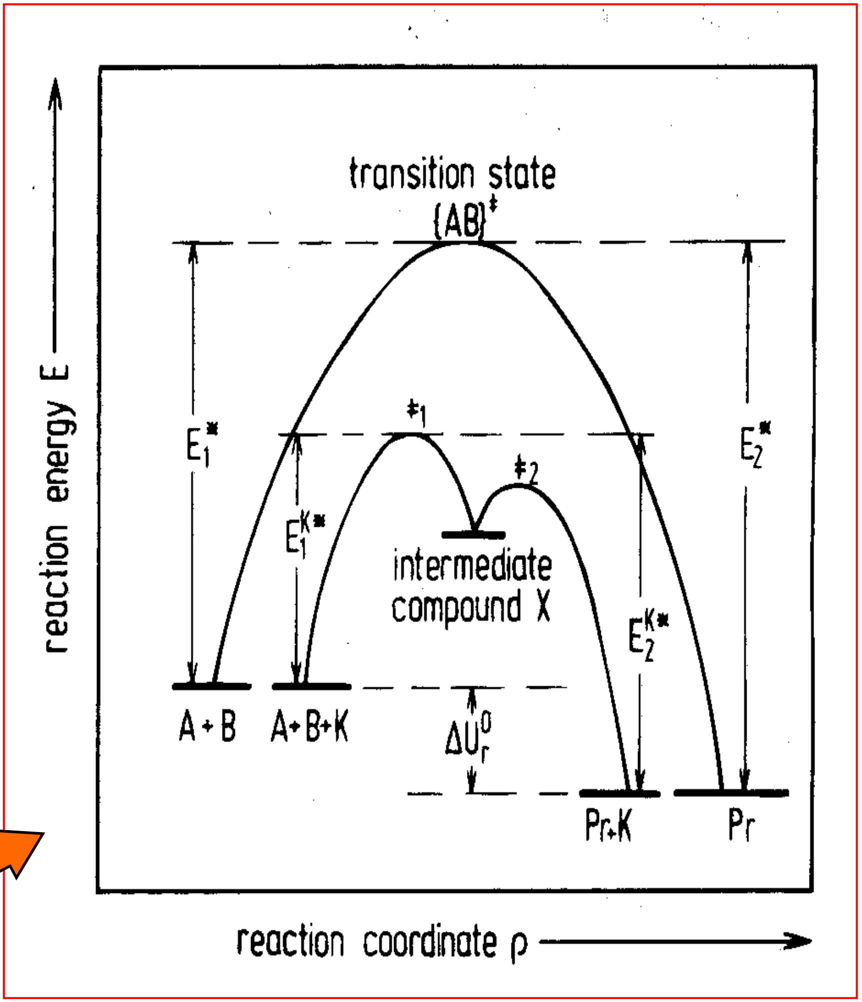
Sometimes, sites between the 1st and 2nd or the 2nd and 3rd or the 3rd and 4th etc. layer become occupied by adsorbing particles. These so-called subsurface sites have been observed with varios interaction systems; among others with H + Pd or O + Pt. The subsurface species usually are more weakly bound than the chemisorbed species resulting in split-off states at lower temperatures. In the course of catalytic surface reactions the presence of subsurface species can decisively influence the reaction rate.



H/Pd potential energy diagram showing surface, subsurface and bulk hydrogen states

2.Some essentials in adsorption: Kinetics of adsorption

- As in any chemical reaction, surface processes involve **breaking and making of bonds**. As we have seen, this often requires or involves substantial amounts of energy.
- However, as one can infer 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 in that it offers 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. Some essentials in adsorption: The rate of adsorption – terms and definitions

Consider the rate of an ordinary chemical reaction of type A → B. The general **definition of the reaction rate** is *change per time*, i.e. number of molecules per time, or concentration change of a certain species per 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** reactions, **two-dimensional** concentrations must be considered instead (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 dΘ/dt $\Theta = \frac{N_{ad}}{N_{ad,\max}}$ $0 < \Theta < 1$.

2. Some essentials in adsorption: The rate of adsorption – terms and definitions cont‘d

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:

“Collision frequency”

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

The decisive process now is the so-called **trapping** or **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 accordingly

- $s(\Theta) = (1- \Theta)(1- \Theta) = (1 - \Theta)^2$ → *2nd order adsorption*.

Sometimes, the adsorption reaction requires a certain activation energy E^*_{ad} . Only particles having at least this energy will be able to stick.

2. Some essentials in adsorption: The rate of adsorption – terms and definitions, cont‘d.

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 (Θ) = 1 - Θ, for a second-order process, f (Θ) = (1 - Θ)^2). This rate expression allows us 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

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

which is a typical saturation function. The larger the initial sticking coefficient, the more rapidly the surface becomes covered. 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.

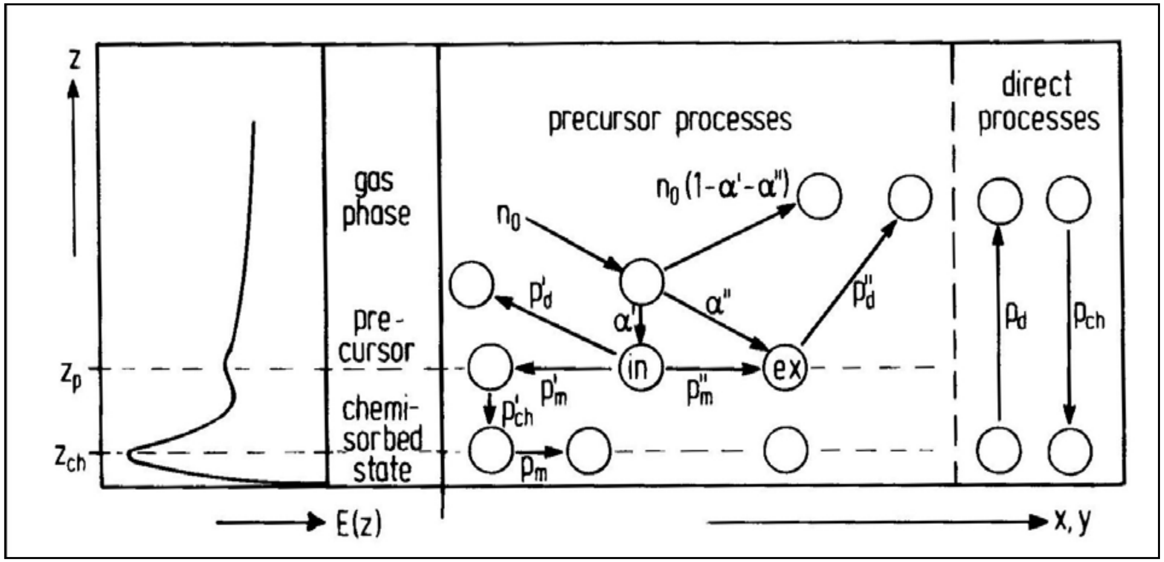
2. Some essentials in adsorption: The rate of adsorption – initial sticking probability

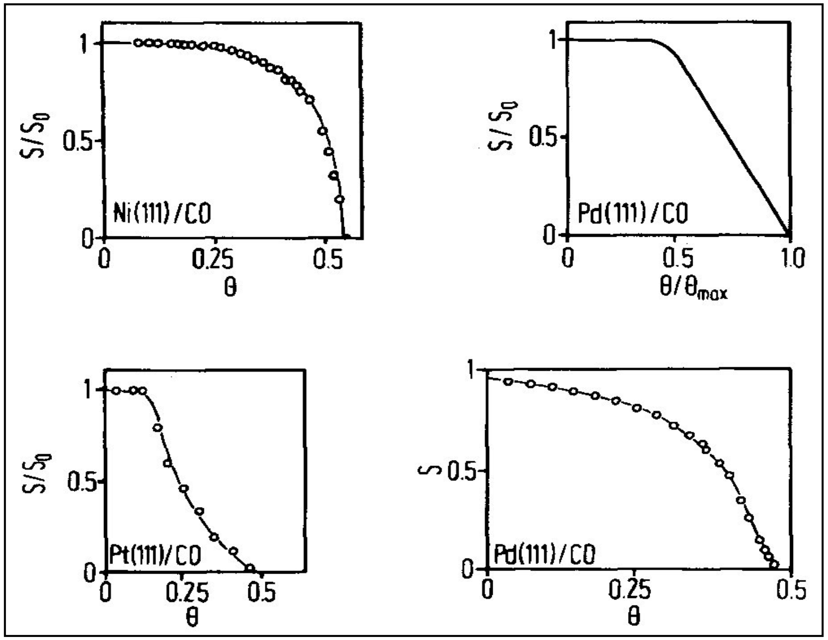
The initial sticking probability s_0 is an interesting quantity; it contains all dynamical and steric effects and is governed by the ability or effectiveness of a given particle to dissipate its kinetic energy to the heat bath of the surface (phonon excitation; electron – hole pair excitation). The sticking of diatomic molecules, hydrogen in particular, is of particular interest, since the sticking at finite temperatures involves the dissociation reaction (activated and non-activated dissociation paths).

An extensive consideration of the quantum-dynamical background of sticking can be found in the book by A. Groß (“*Theoretical Surface Science*”, Springer Berlin 2003)

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 a **precursor.** Major consequence of a precursor state: The sticking – coverage function $f(\Theta)$ is no longer linear, 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 mean diameter of the already covered area (island), the particles can no longer be accommodated and are finally reflected back into the gas phase before they can find an empty site.

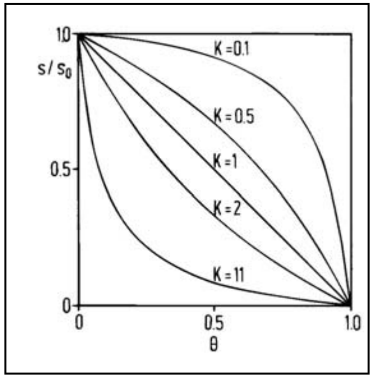
2. Some essentials in adsorption: The rate of adsorption – sticking probability and its coverage dependence





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 underneath)
p'_d = probability that particle desorbs from intrinsic precursor to gas phase
p''_d = probability that particle desorbs from extrinsic precursor (adsorbed Particle underneath)

Adsorption kinetics: 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 with 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 :

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

Inserting this in the first 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:

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

Adsorption kinetics: The rate of desorption

R = rate of desorption: **R = R (Θ, T) =**

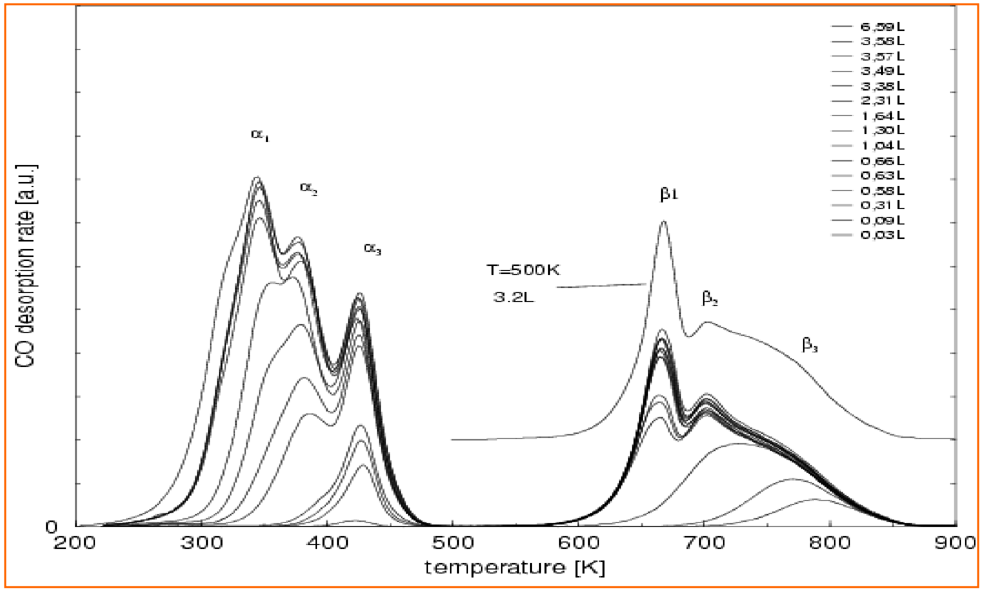
$$-\frac{d\Theta}{dt} = \nu_x \cdot \Theta^x \cdot N_{\max}^{x-1} \cdot e^{-\frac{E_{des}}{kT}}$$

Of interest: To determine the kinetic quantities such as the

- order of the desorption, x, which contains valuable information on the mechanism 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 discussed)

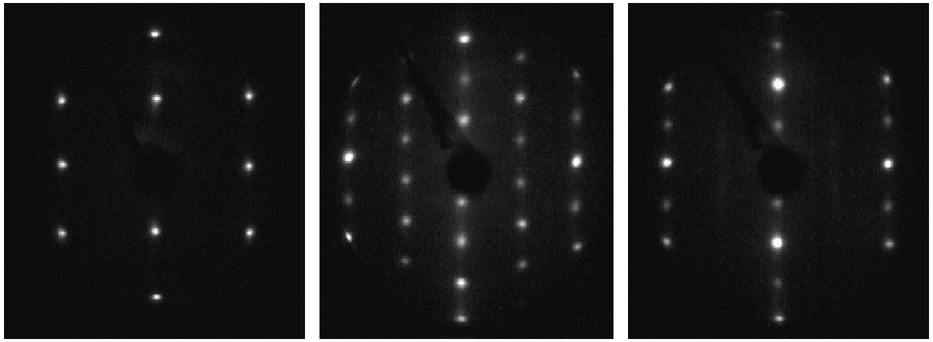
Furthermore: Note that the peak integrals reflect the adsorbed amount prior to application of the temperature program. Using a coverage calibration (LEED pattern etc.), absolute coverages are accessible.
In addition, by plotting the TPD peak integrals versus the exposure, one can determine the **sticking probability as a function of coverage**.

2. Basics: The rate of desorption - examples of TD spectra: CO on Re(10-10)



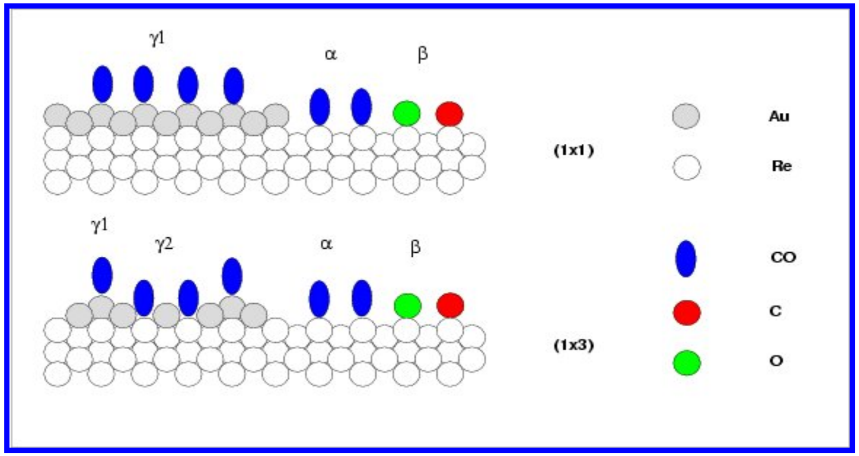
Re(10-10) + CO

T-programmed thermal desorption reveals: At 300K CO adsorbs molecularly (α states) AND dissociatively (β states)



Beyond 500 K CO exists only in the dissociated form (C + O). The sum of the fragments produces a c(2x4) and a (1x2) LEED pattern (θ_{C+O} = 0,5). E_{des} = 200 kJ/Mol

Between 500 < T < 850 K the combined adsorbed C + O phase is in complete equilibrium with gas phase CO.

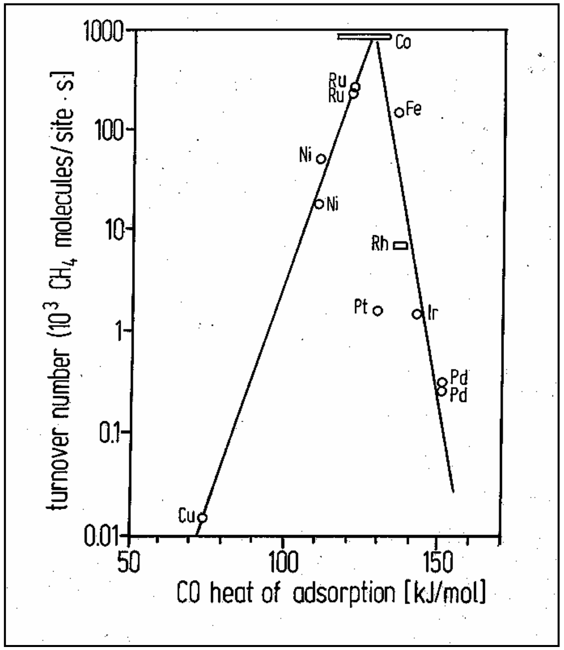


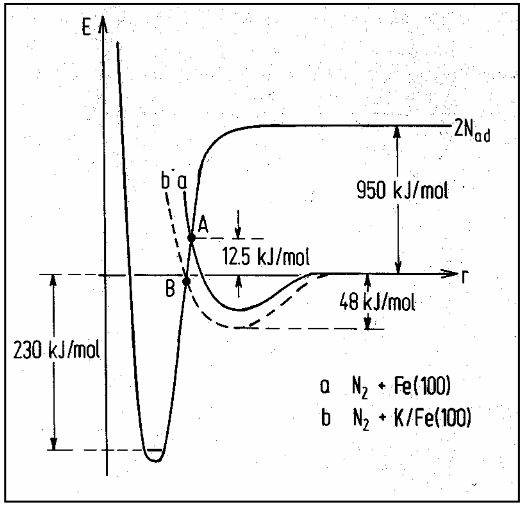
3. Summary and conclusions: Outlook

The importance of the adsorption energy in heterogeneous catalysis

In heterogeneous catalysis, the purpose of using surfaces is to concentrate the dilute reactants of the gas phase at the surface and to make them reactive for (bimolecular) surface reactions by stretching or even cleaving particular bonds. If an adsorbate is too loosely bound, it may - especially at elevated temperatures - leave the surface by thermal desorption and is lost for any surface reaction according to the Langmuir-Hinshelwood mechanism. In other words, their residence time is too short. If, on the other hand, an adsorbate is too strongly bound at the surface, it becomes immobile there and is unable to diffuse to adjacent moelcules which is necessary for any synthesis reaction.

This is the reason, why „medium“ adsorption and binding energy Ies are most favorable to make a given surface a good catalyst. This is illustrated by means of the figure at the right, where the activity for the formation of methane from synthesis gas is plotted versus the heat of CO adsdorption. Apparently, a „vulcano“-curve is obtained, which is typical for a variety of adsorption systems.





There is still another effect considered important: In the course of a surface reaction it is often required that homonuclear molecules with strong innermolecular bonds become dissociated. Since the potential energy minima of the intact molecules are located far outside the surface, there often exist considerable activation barriers for dissociative adsorption. A typical example is N_2 physisorbed on a Fe surface. In this situation the addition of an **electropositive** or an **electronegative** species can influence the local density of states (charge density) and, hence, the quantum-chemical interaction of the molecular species with the surface. In effect, this leads to a reduction or even removal of activation barriers for dissociation; a prominent example being potassium deposited on Fe, which greatly increases the concentration of chemisorbed nitrogen on Fe resulting in a large increase of the rate of ammonia formation under these conditions (G. Ertl and coworkers 1977).

3. Summary and conclusions: Literature for further reading

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.