Adsorption

Lecture Series 2010/2011: "Modern Methods in Heterogeneous Catalysis Research"
Klaus Christmann
Institut für Chemie und Biochemie, Freie Universität Berlin

Organization

1. Introduction: Terms and definitions, the role of the adsorption in heterogeneous catalysis

   - Adsorption as a macroscopic (thermodynamic) phenomenon:

   - Adsorption isotherms: Langmuir isotherm and BET isotherm

   - Adsorption as a microscopic (quantum chemical) phenomenon

2. Some essentials for adsorption on single crystal surfaces:

   - Associative and dissociative adsorption

   - The adsorption energy: Physisorption and chemisorption

   - Initial adsorption energy and a-priori heterogeneity

   - Coverage dependence of adsorption energy: a-posteriori heterogeneity

   - Adsorption kinetics; sticking probabilities and precursor states

3. Summary and conclusions

Practical relevance of adsorption processes

Technical applications of <u>adsorption</u> concerns:

Separation processes of gaseous and liquid mixtures via molecular sieves

Heterogeneous catalysis

Chemical analyses (various types of chromatography)

Flotation processes

Gas mask filters

Lubrication phenomena

As we will see later, one distinguishes
chemical adsorption (chemisorption)
and
physical adsorption (physisorption),

depending of the strengths of the interaction between adsorbent and adsorptive.

While chemisorption is most essential for heterogeneous surface reactions, physisorption plays a major role during separation and enrichment processes at and near phase boundaries.

Terms and definitions
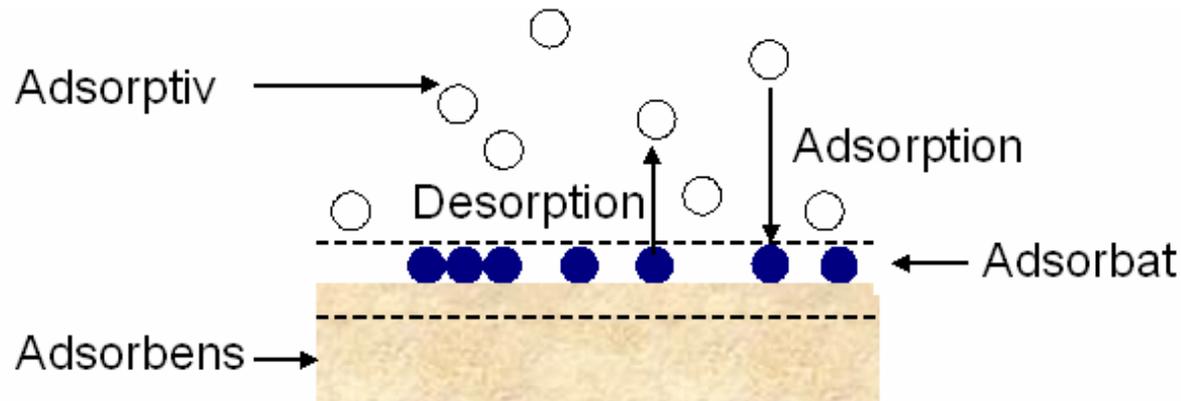
In heterogeneous catalysis, **adsorption** **is one of the most essential elementary processes** because *it activates the decisive chemical bonds* of the (adsorbed) reactants.

Terminology: What is adsorption?

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

Consequence: No adsorption without a surface (or, more generally, a phase boundary including liquid surfaces). In heterogeneous catalysis, however, we mostly deal with **solid** surfaces).

Since the adsorptive and the adsorbent often undergo a chemical reaction, the chemical and physical properties of the *adsorbate* is not always just the sum of the individual properties of the adsorptive and the adsorbent, but often represents a phase with new properties.

Terms and definitions (ctn'd)

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 sufficient to describe the system's properties.**

- **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 responsible for the bulk properties *change*, they become *asymmetric*, since the outermost bonds are unsaturated, resulting in a peculiar chemical reactivity of the surface. In our context the most important consequence is that the surface becomes capable of adsorbing foreign atoms or molecules.
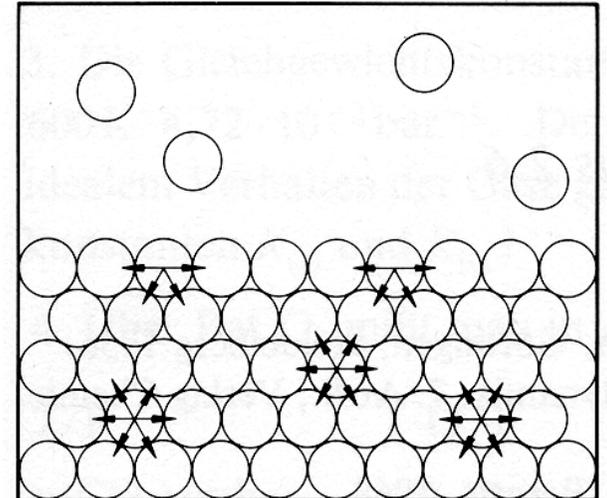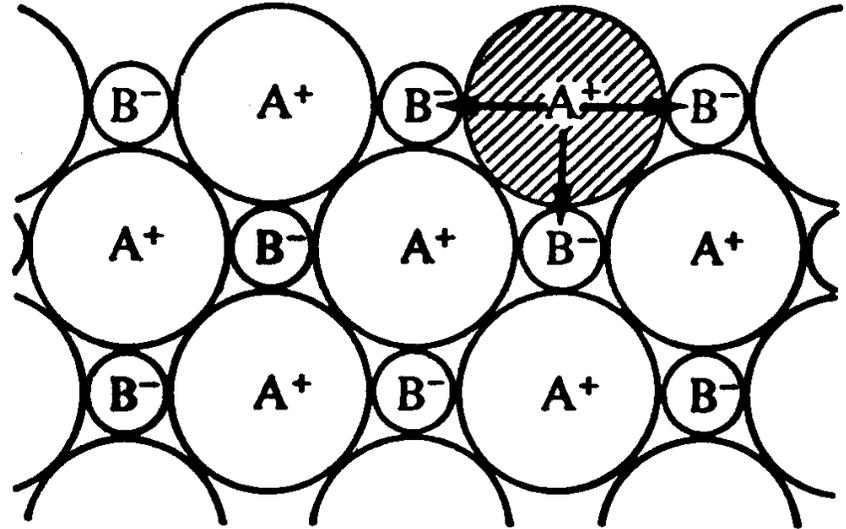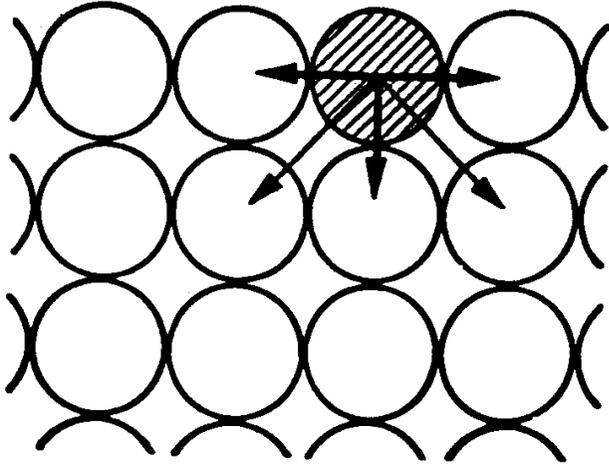
Pictorial representation of the surface energy of a covalent solid.

Pictorial representation of the surface energy of an ionic solid.

Kind of surfaces of interest

We shall subdivide our surfaces in two classes:

- **Single crystal surfaces** are geometrically and electronically well-defined. While they are never really used in heterogeneous catalysis, they yet have the advantage to provide access to the physics and chemistry of the elementary steps of a catalytic reaction ("model systems"). The adsorption on single crystal surfaces can often be described by a simple adsorption isotherm. Furthermore, the well-developed scientific field of classical Surface Science - practiced among others, by Gerhard Ertl (Nobel Laureate 2007) - can be most successfully applied.

- **Polycrystalline, heterogeneous surfaces** are very important in *practical heterogeneous catalysis*, since they have a large surface area due to micro-, meso- or macropores. Among these solids are **charcoal** (active carbon), **alumina**, **silica**, **zeolites** or **carbon nanotubes**. Adsorption on these porous surfaces is often well described by the BET adsorption isotherm. In addition, the existence of mesopores (pore radius r_p) can modify the thermodynamic phase equilibria due to a vapour pressure depression predicted by the Kelvin equation (curvature effect).

$$\frac{p}{p_0} = \exp\left(-\frac{2\sigma V_m}{RT \cdot r_{p,Kelvin}}\right)$$

Kelvin equation

$$p_{konkav} \quad < \quad p_0$$

Furthermore, often small metal particles are additionally deposited on these surfaces and cause further modifications of the chemical properties of the combined catalytic system (SMSI effect).
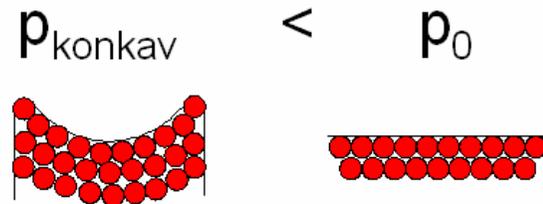
The role of the surface

Why surfaces?

A surface *concentrates* the gas particles from the very dilute (gas) phase to a much more condensed adsorbate phase (which can be two- or three-dimensional). <u>Example:</u> The average particle – particle distances in the gas phase (p = 1 bar) amount to $\approx 4 \cdot 10^{-8}$ m [note that the mean free path $\lambda \sim 1/P$]. By contrast, the distance between adjacent particles adsorbed on a typical metal surface is $\approx 4 \times 10^{-10}$ m. Consequence: Much closer distances facilitate or often enable chemical reactions between adsorbed molecules.

A surface helps to activate or even break chemical bonds within the adsorbing molecules as pointed out before. In turn, these modified molecules may then undergo new chemical reactions leading to desired products. In addition, the surface often provides specific sites with a peculiar coordination due to unsaturated valences (dangling bonds).
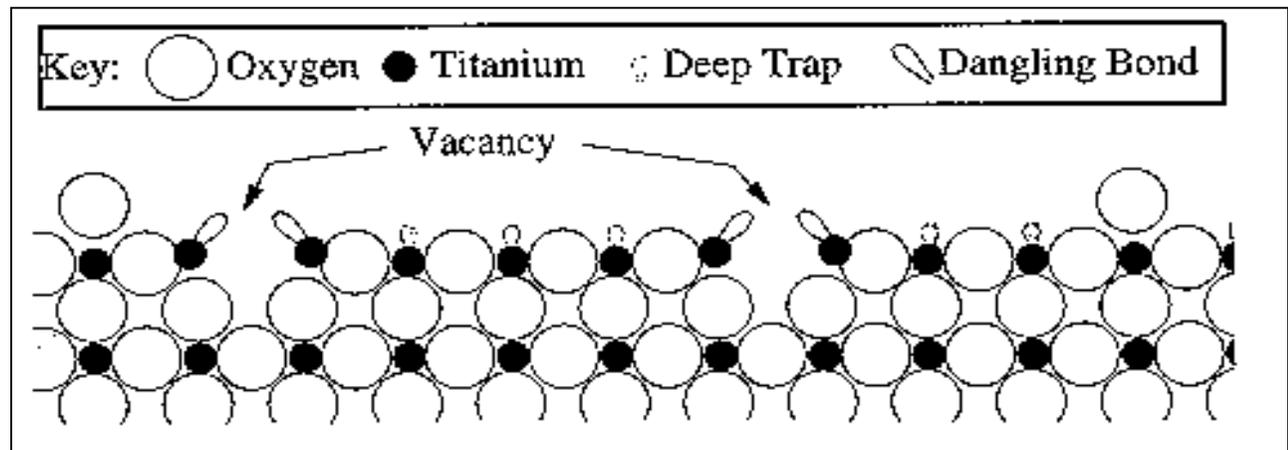
„Dangling bond" states at a titanium dioxide surface (after Elian & Hoffmann 1975 and van Santen 1991)

Terminology: Strength of interaction forces - physisorption and chemisorption

Interaction forces responsible for adsorptive bonds

Kind of interaction	Strength of interaction
van-der-Waals	Very weak (usually less than 50 kJ/mole)
ionic	Strong (Coulombic origin) > 100 kJ/mole
covalent	Strong (quantum-chemical origin) > 50 kJ/mole
metallic	Strong (quantum-chemical origin), E > 50 kJ/mole

Terminology: activated and non-activated (spontaneous) adsorption

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 desorb it from the surface, one has to supply it thermally or electronically with 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.
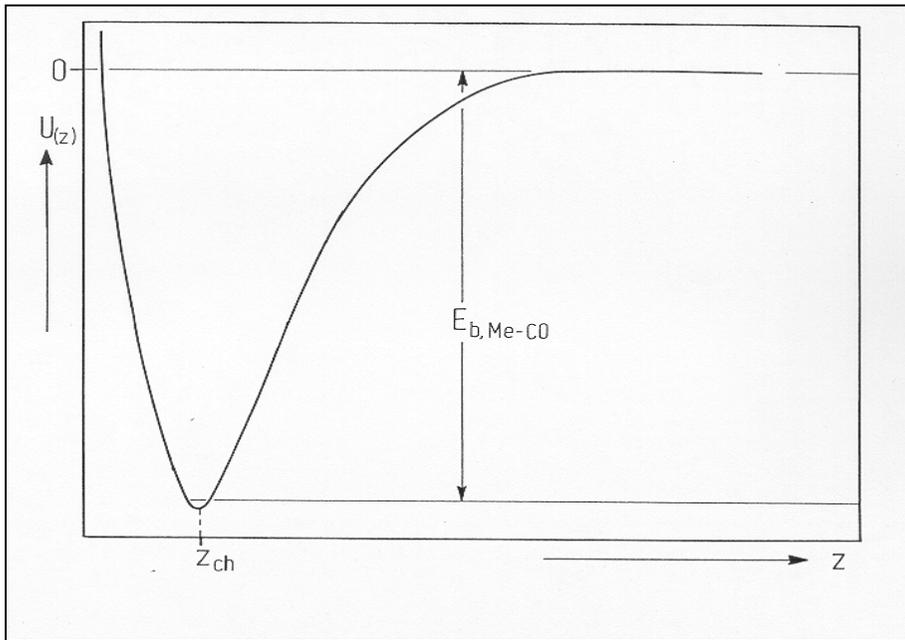
Non activated (spontaneous) adsorption: hydrogen on Ni(110)
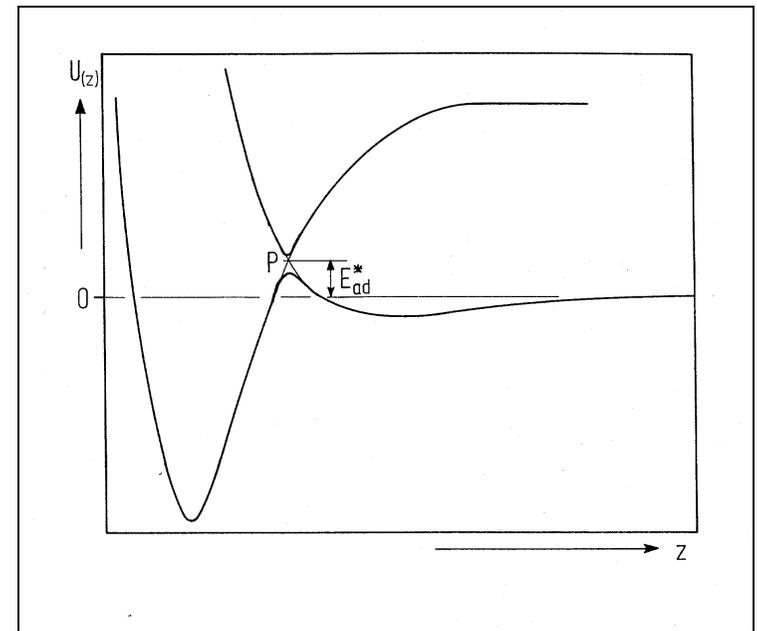
activated adsorption: hydrogen on a copper surface

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), i.e. how can one increase the adsorbate concentration by an appropriate choice of P and T?

- How can one determine the stationary and maximum adsorbed amount?

- Where are the adsorbed particles located at and on the surface?

- 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 by (surface) thermodynamics.

Thermodynamics of adsorption - Fundamental Gibbs equation

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

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

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

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

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

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

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 often used 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, nor is it capable of predicting activation energies and, hence, provides **no information about time dependencies** of chemical reactions.

Thermodynamics of adsorption - The heat of adsorption

Thermodynamical derivation of the so-called isosteric enthalpy of adsorption, q_{st}:

Chemical equilibrium between adsorbate and gas phase leads to a *constant surface concentration Γ* [moles/m²]. 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 :

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

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

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

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

Thermodynamics of adsorption - the heat of adsorption, cont'd

Rearranging yields 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 $V_{ad+OF} \ll V_g$ 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 particles on that surface. **It can be obtained from equilibrium, i.e., adsorption isotherm measurements.** These considerations describe the situation best for *homogeneous single crystal* surfaces, for which we shall provide examples later. Nevertheless, q_{st} is often coverage-dependent due to lateral particle – particle interactions.

Inhomogeneous, porous surfaces that one encounters in practical heterogeneous catalysis require a modified view and thermodynamic treatment, since they can provide a whole variety of energetically and geometrically different adsorption sites.

Thermodynamics of adsorption:
The concept of the adsorption isotherm

The adsorption isotherm displays information of how much material will adsorb for a given set of state variables (pressure P and temperature T when using <u>gases</u> as adsorptives, concentration c and temperature T when dealing with adsorption from <u>solutions</u>). The amount of adsorbed material can be given as surface coverage Θ, i.e., the fraction of occupied/available sites, or by the volume v_m taken up by the sum of particles adsorbed in the first monolayer.

The adsorption isotherm is one of the most important criteria for an adsorption process. In practice, the **uptake** of adsorptive of a given catalyst material is a decisive quantity, since a high uptake usually means a (desired) high catalyst efficiency. The respective uptake is often called ‚sorption capacity' and characterised by the **sorption** (or adsorption) **isotherm**. The form of the sorption isotherm provides a lot of first-glance information about the chemical and physical properties of the catalyst material and about how the adsorption process proceeds over a given surface. In principle, various kinds of isotherms can be distinguished, depending on the nature of the catalyst and the kind of interaction.

Some examples of experimental adsorption isotherms

I   Benzol/Silicagel bei 303,15 K,
II   Wasser/Al₂O₃ bei 303,15 K,
III   Brom/Silicagel bei 352 K,
IV   Wasser/Silicagel bei 313 K,
V   Wasser/Aktivkohle

Langmuir isotherms (type I) are usually observed during adsorption of chemically active gases on metal surfaces, but also with non-polar gases (methane, nitrogen N_2, ethane) on zeolites, whereas the adsorption of water vapour on γ-Al_2O_3 leads to isotherms of type II with condensation. Using an unpolar surface like charcoal and polar molecules as adsorptive (methanol or H_2O) the situation is characterised by initially rather repulsive interactions leading to a reduced uptake, while the increasing presence of adsorbate molecules facilitate the ongoing adsorption leading to isotherms of type III. If porous adsorbents are used, additional capillary condensation effects lead to isotherms of type IV and V.

Distinction: monolayer and multilayer adsorption
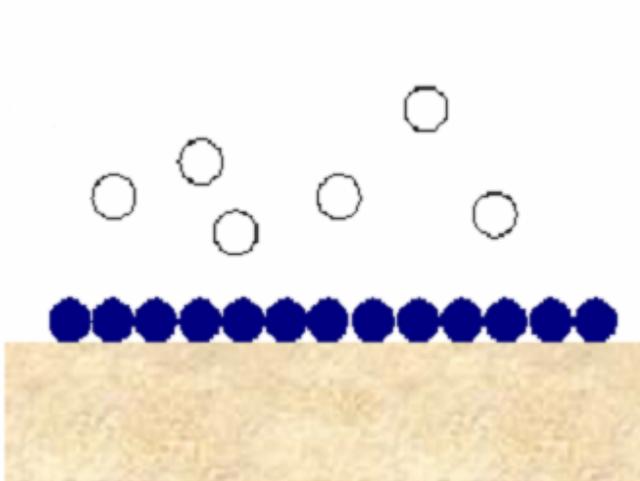
Monolayer adsorption on a homogeneous surface at equilibrium pressure p/p_0. The heat of adsorption of the first monolayer is much stronger than the heat of adsorption of the second (and all following) layers (typical chemisorption case)
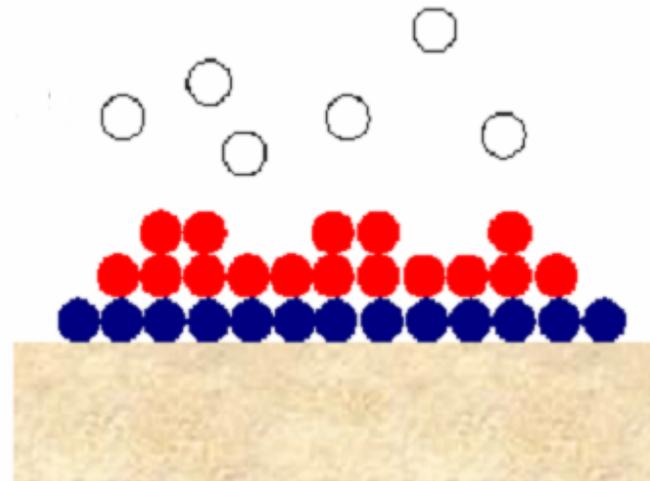
Multilayer adsorption/condensation on a homogeneous surface at equilibrium pressure p/p_0. The heat of adsorption of the first (blue) layer is comparable to the heat of condensation of the subsequent (red) layers. Often observed during physisorption.

Thermodynamics of adsorption -
The Langmuir adsorption isotherm

A way of getting to the adsorption isotherm is to consider the adsorption - desorption equilibrium.
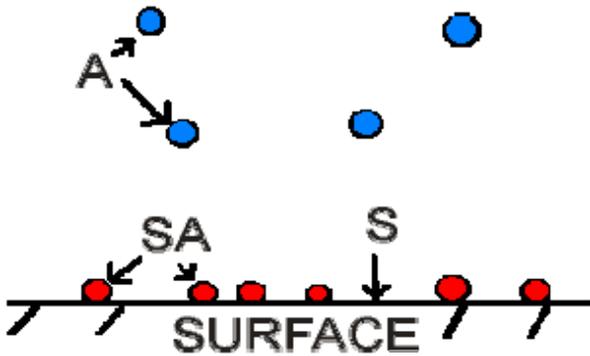
The adsorption process between gas phase molecules, A, vacant surface sites, S, and occupied surface sites, SA, can be described by the equation

$$S + A \leftrightarrow SA$$

assuming that there are a fixed number of surface sites present on the surface. An equilibrium constant, K, can be written:

$$K = \frac{[SA]}{[A] \cdot [S]}$$

If we introduce the symbol θ for the fraction of surface sites occupied ($0 < \theta < 1$) and consider that [SA] is proportional to the surface coverage of adsorbed molecules, i.e., proportional to θ, whilst [S] is proportional to the number of vacant sites, 1 - Θ, and [A] is proportional to the collision number, i.e., the gas pressure P, we arrive at an expression:

$$K = \frac{\Theta}{(1-\Theta)P}$$ or, rearranged for Θ, $$\Theta = \frac{K \cdot P}{1 + K \cdot P}$$

which has been derived as early as 1916 by Irving **Langmuir**. Note that K is only a constant if the enthalpy of adsorption is independent of coverage. As with all equilibrium constants, K and, hence, the position of adsorption - desorption equilibrium, will depend on (i) the relative stabilities of the adsorbed and gas phase species involved, (ii) on the temperature of the system, and (iii) on the pressure of the gas above the surface. Factors (ii) and (iii) exert opposite effects on the concentration of adsorbed species - that is to say that the surface coverage may be increased by raising the gas pressure but will be reduced if the surface temperature is raised.

A somewhat more revealing derivation of the Langmuir adsorption isotherm is based on the fact that in adsorption - desorption equilibrium the rates of adsorption and desorption are equal. While the rate of adsorption is determined by the collision frequency of the gas phase particles with the surface according to:

$$R_{ad} = \frac{P}{\sqrt{2\pi mkT}} S_0 = k_{ad}^{(1)} P S_0 \left[\frac{particles}{m^2 \, s} \right]$$

(S_0 stands for the uncovered fraction of the surface ($\propto (1 - \Theta)$), P for the gas pressure), the desorption rate can easily be formulated as being proportional to the fraction of the surface covered by adsorbed particles (here denoted as S_1), a frequency factor ν, and an exponential term containing the depth of the potential well, i.e., the adsorption energy:

$$R_{des} = S_{(1)} \nu \exp\left(-\frac{E_{des}}{kT}\right) = S_{(1)} k_{des}(T) \left[\frac{particles}{s} \right]$$

Equating R_{ad} and R_{des} and introducing the coverage Θ by noting that $S_1 \propto \Theta$ and $S_0 \propto (1 - \Theta)$ yields immediately the Langmuir expression derived before.

Thermodynamics of adsorption - The Langmuir adsorption isotherm, cont'd

This closer inspection of the adsorption/desorption equilibrium helps to interpret the constant K(T) which comes out as :

$$K(T) = \frac{s_0}{\nu \, N_{max}} \left(2\pi \, mkT\right)^{-\frac{1}{2}} \exp\left(\frac{E_{des}}{kT}\right)$$

with s_0 representing the initial sticking coefficient, ν the frequency factor of the desorption reaction and N_{max} the maximum number of adsorbed particles: For non-activated adsorption, the desorption energy E_{des} is equal to the energy of adsorption, E_{ad}. In the derivation given above we have assumed first-order processes both for the adsorption and the desorption reaction. For second-order processes, e.g. adsorption/desorption reactions involving rate-limiting dissociation steps, a similar expression can be derived

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

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

Thermodynamics of adsorption -
The Langmuir adsorption isotherm (cont'd)
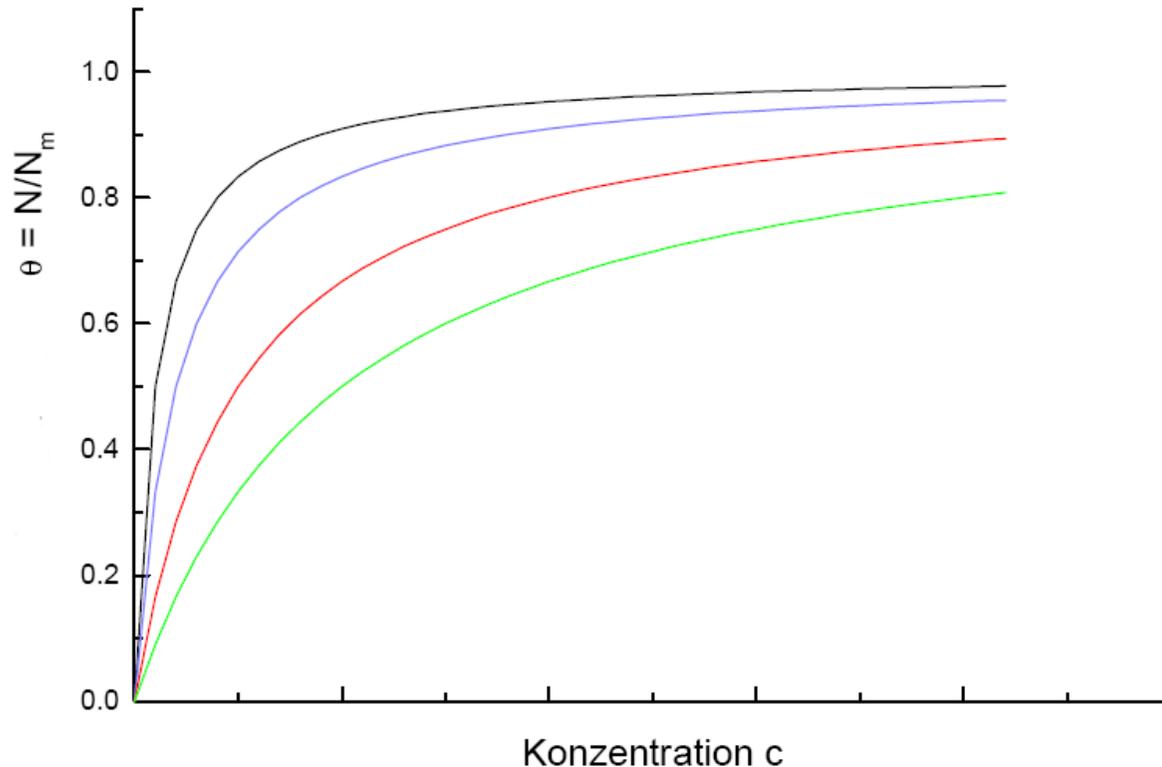
For **single crystal surfaces**, this famous **Langmuir isotherm** describes the adsorption processes often quite well.

However, it fails if **porous polycrystalline surfaces** are involved. Then, better the **BET isotherm** is used.

If we plot the surface coverage against the concentration or the pressure of particles of the adsorbing phase, we arrive at typical saturation curves: Near the monolayer capacity all surface sites are occupied, and higher pressures cannot increase the occupancy anymore.

What are the prerequisites for applying the Langmuir adsorption model?

- All adsorption sites must be equivalent regardless of whether we look at the very first or the final adsorbing particle: All have the same binding energy to the surface, and consequently, there is no coverage dependence of the heat of adsorption.

- The adsorption capacity is strictly limited to one and only one monolayer. Adsorption into multilayers does not occur.

Apparently, the Langmuir model is quite limited and seldom applicable for practical purposes - in fact, the coverage dependence of the heat of adsorption must be taken into account as well as the possibility that more than just a single monolayer will adsorb. Various more sophisticated isotherms have been developed, among others the Temkin isotherm or the BET isotherm.

Thermodynamics of adsorption - The BET adsorption isotherm

The famous BET Isotherm first introduced in the 1930s by Brunauer, Emmett and Teller now considers also the possibility of multilayer adsorption and condensation as shown below.
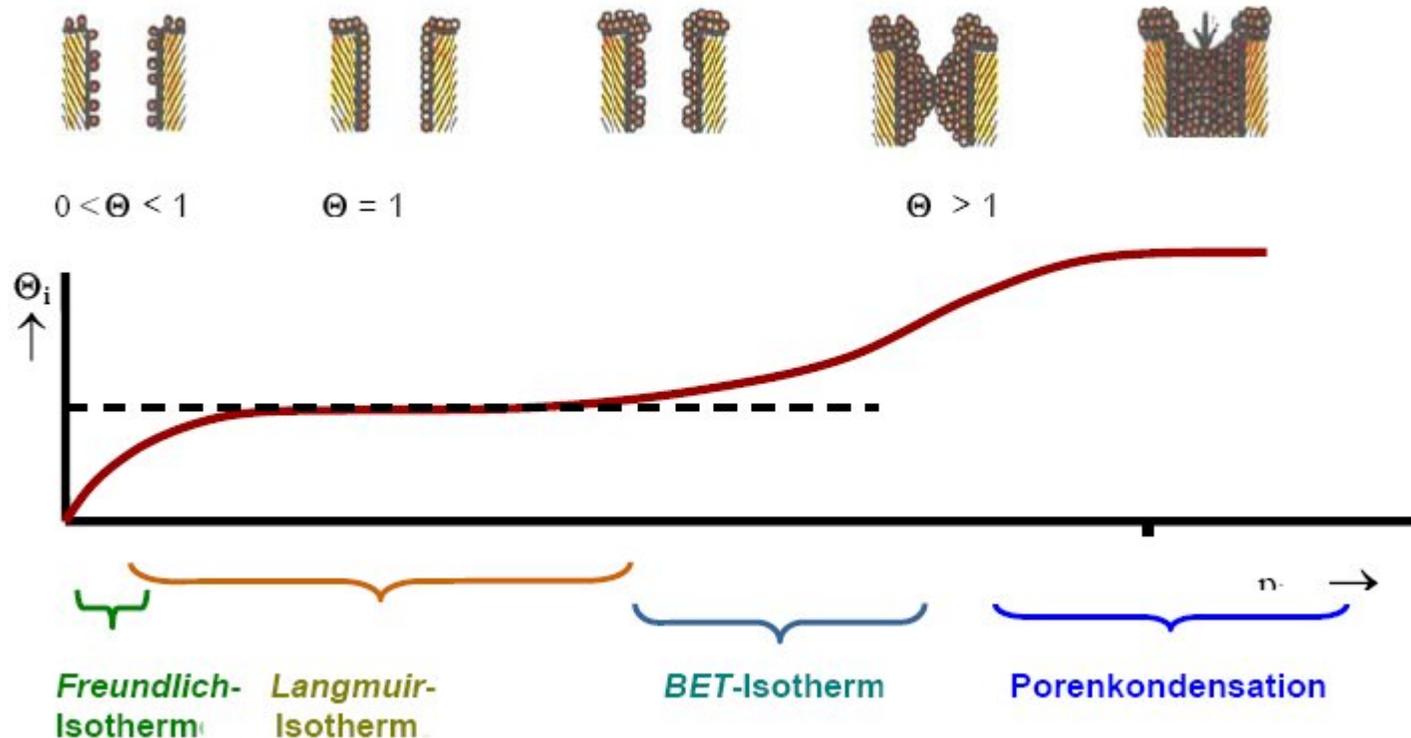
The forces responsible for the build-up of the second, third, and all following layers are van-der-Waals-like and are supported by low temperatures and high gas pressures. In contrast to the Langmuir behaviour, no saturation occurs at high pressures, but a true condensation of a liquid phase. Concerning the adsorption energies involved, one can clearly distinguish the adsorption enthalpy of the very first layer (which may well behave Langmuir-like), i.e., $E_{(1)}$, and the heat of condensation (= heat of evaporation) of all following layers, $E_{cond} = E_L$. For the derivation of the BET isotherm it is essential to use a strict terminology, and we distinguish the following quantities[*]:

- the rate of adsorption into the ith layer (clean surface = index o)
  P = pressure, $S_{(i)}$ = free surface area ($\propto$ to empty surface sites)

$$R_{ad}^{(i)} = k_{ad}^{(i)} \cdot P \cdot S_{(i)}$$

- the rate of desorption from the ith layer

$$R_{des}^{(i)} = k_{des}^{(i)} \, S_{(i)} \cdot e^{-\frac{E_{(i)}}{kT}}$$

[*] The surface models presented in this BET section have been taken from an elaboration of the Physical Chemistry Institute of the University of Stuttgart
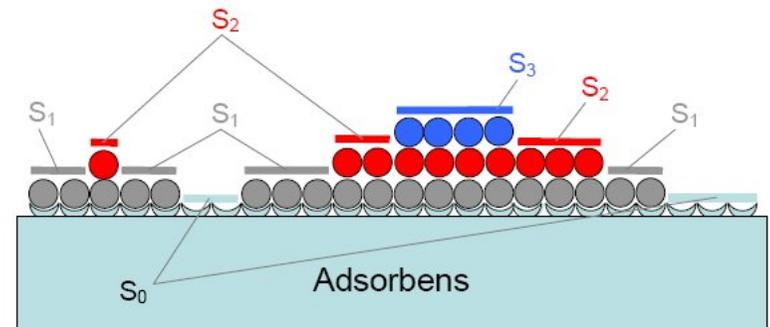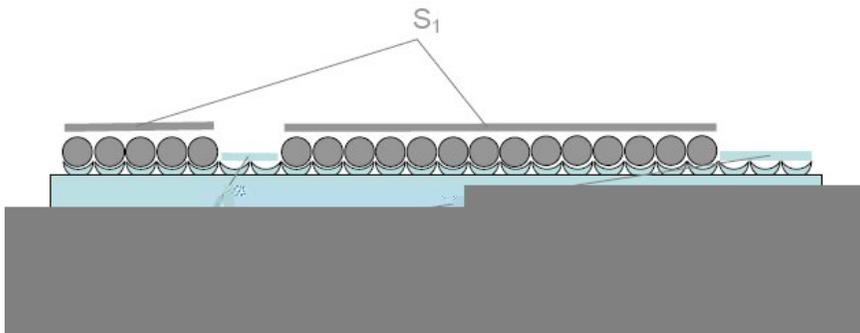
Thermodynamics of adsorption -
The BET adsorption isotherm

We deal with a strict (dynamic) equilibrium between adsorbate and the gas phase containing the adsorptive molecules, which is characterised by the identity of adsorption rate and desorption rate. Hence, for the first layer and the bare surface sites we have:

$$k_{ad}^{(1)} \cdot P \cdot S_{(0)} = k_{des}^{(1)} S_{(1)} \cdot e^{-\frac{E_{(1)}}{kT}} \quad (eq.\,I)$$

Adsorbens

If we now consider the principal situation we first have a look how the surface S_1 can change:

Altogether we have four processes that cause a change, namely:

- adsorption of a particle on the bare surface (1.) $\rightarrow$ $R_{ad}^{(1)} = k_{ad}^{(1)} P S_0$

- desorption of a particle from the sample (2.) $\rightarrow$ $R_{des}^{(1)} = k_{des}^{(1)} S_{(1)} \cdot e^{-\frac{E_{(1)}}{kT}}$

- adsorption of a particle onto the first layer (3.) $\rightarrow$ $R_{ad}^{(2)} = k_{ad}^{(2)} S_{(1)} \cdot P$

- desorption of a particle from the second layer (4.) $\rightarrow$ $R_{des}^{(2)} = k_{des}^{(2)} S_{(2)} \cdot e^{-\frac{E_{(2)}}{kT}}$
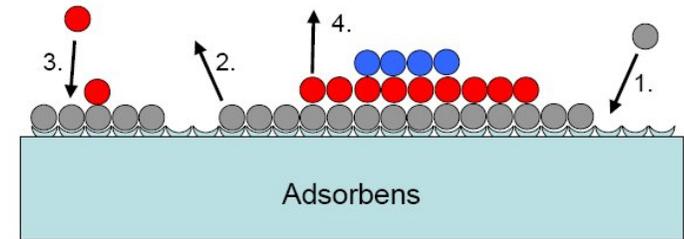
In equilibrium, however, the surface area S_1 does NOT change, and all four processes taken together must not change the overall concentration c. Hence, processes I and IV increase S_1, while II and III decrease it:

$$k_{ad}^{(1)} P S_{(0)} + k_{des}^{(2)} S_{(2)} e^{-\frac{E_{(2)}}{kT}} = k_{des}^{(1)} S_{(1)} e^{-\frac{E_{(1)}}{kT}} + k_{ad}^{(2)} S_{(1)} P \quad (eq.\,(II))$$

Subtracting Eq. (1) from Eq. (2) yields immediately

$$k_{des}^{(2)} \cdot S_{(2)}\, e^{-\frac{E_{(2)}}{kT}} = k_{ad}^{(2)}\, S_{(1)} \cdot P \quad (eq.\,III)$$

Following this scheme, one realizes that we can continue these considerations for all following layers and obtain a general expression of the kind:

$$k_{des}^{(i+1)} \cdot S_{(i+1)}\, e^{-\frac{E_{(i+1)}}{kT}} = k_{ad}^{(i+1)}\, S_{(i)} \cdot P \quad (eq.\,IV)$$

for all surface parts S_i, with i = 1, 2, 3...∞. The total volume adsorbed is obtained when we multiply the surface part S_i of each layer with the number of layers below and additionally multiply this with the specific volume per surface part S, V_0
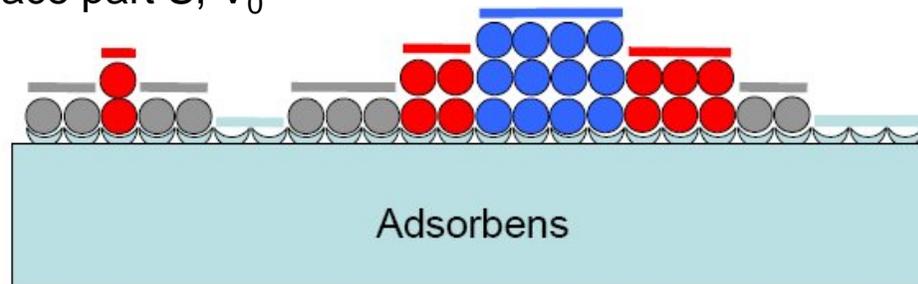
Adsorbens

$$V_{total} = V_0 \sum_{i=1}^{\infty} i \cdot S_i \quad = \; V_0\,(S_0 + 1 \cdot S_1 + 2 \cdot S_2 + 3 \cdot S_3 + ...)$$

Of interest is now the ratio between the total adsorbed volume V_{tot} and the volume of a perfect complete monolayer, V_m (which is nothing but the coverage Θ) :

$$\Theta = \frac{V_{total}}{V_{mono}} = \frac{\sum_{i=1}^{\infty} i \cdot S_i}{\sum_{i=1}^{\infty} S_i}$$

In order to carry out these summations we have to make some (plausible) assumptions: First, all adsorption energies of the second and all higher layers will be set equal $= E_L$, and second, we assume that all the ratios of adsorption/desorption constants are equal to a constant g:

$$\frac{k_{des}^{(2)}}{k_{ad}^{(2)}} = \frac{k_{des}^{(3)}}{k_{ad}^{(3)}} = \ldots = \frac{k_{des}^{(n)}}{k_{ad}^{(n)}} = g$$

as expected for a liquid-like behaviour. Note that the very first adsorbed layer is treated differently, because its rate constants as well as its adsorption energy is very different from those of the higher layers. By defining

$$x = \frac{P}{g} \exp\left(\frac{E_L}{RT}\right) \ \text{ with } L \geq 2 \ \text{ and } \ y = \frac{k_{ad}^{(1)}}{k_{des}^{(1)}} \exp\left(\frac{E_1}{RT}\right)$$

and introducing the constant c = y/x   we can express all surface parts S_i by S_0 according to:

$S_1 = y\, S_0;$

$S_2 = x\, S_1 = x\, y\, S_0;$

$S_3 = x\, S_2 = x^2\, S_1 = x^2\, y\, S_0\,;$

$S_4 = x\, S_3 = x^3\, S_1 = x^3\, y\, S_{0;}$ or generally: $\quad S_i = x\, S_{i-1} = x^{i-1}\, S_1 = c\, x^i\, S_0$

If we define the ratio of the total volume adsorbed / the volume of the monolayer as coverage Θ we obtain:

$$\Theta = \frac{V_{total}}{V_{mono}} = \frac{c \cdot S_0 \cdot \sum_{i=1}^{\infty} i \cdot x^i}{S_0 \left(1 + c \sum_{i=1}^{\infty} x^i\right)} = \frac{c \sum_{i=1}^{\infty} i \cdot x^i}{\left(1 + c \sum_{i=1}^{\infty} x_i\right)}$$

In the denominator we have the sum of an infinite geometric progression: $\quad \sum_{i=1}^{\infty} x_i = \frac{x}{1-x}$

And similarly, we have:

$$\sum_{i=1}^{\infty} i \cdot x_i = x^1 + 2x^2 + 3x^3 + \ldots = x \sum_{i=1}^{\infty} 1 + 2x + 3x^2 + \ldots = x \cdot \frac{d}{dx} \sum_{i=1}^{\infty} x^i = x \frac{d}{dx}\left(\frac{x}{1-x}\right) = \frac{x}{(1-x)^2}$$

$$\Theta = \frac{V_{total}}{V_{mono}} = \frac{c \cdot x}{(1-x)^2} \cdot \frac{1}{\left(1+\frac{cx}{1-x}\right)} = \frac{cx}{(1-x)^2 \cdot \left(\frac{1-x+cx}{1-x}\right)} = \frac{cx}{(1-x) \cdot (1-x+cx)}$$

This expression can be rearranged to yield:

$$\frac{1}{V_{tot}}\left(\frac{x}{1-x}\right) = \frac{1}{V_{mono} \cdot c} + \frac{c-1}{c} \cdot \frac{1}{V_{mono}} x$$

The unknown quantity x can be substituted by the fact that the volume V_{total} must become infinite for p = p_0. Since V_{mono} is always finite, x has to become 1 for this case. Otherwise, $x = p/p_0$. Since p as well as p_0 are measurable quantities, we have thus eliminated the unknown quantity x. We finally obtain the famous BET isotherm in the common form:

$$\frac{1}{V_{total}}\left(\frac{p}{p_0 - p}\right) = \frac{1}{c \cdot V_{mono}} + \frac{c-1}{c} \cdot \frac{1}{V_{mono}} \cdot \frac{p}{p_0}$$

Two limiting cases can be distinguished: a) the constant C >> 1, then the heat of adsorption of the very first monolayer is large compared to the condensation enthalpy, and adsorption into the second layer only occurs once the first layer is completely filled. For C >> 1 and p << p_0 the BET isotherm changes to the Langmuir isotherm. Conversely, if C is small, then E_1 is smaller or comparable to E_{cond}, and a multilayer adsorption already occurs while the first layer is still incomplete.

For a successful determination of a „BET surface" the limiting case a) is required, i.e., $C \gg 1$. In this case, a plot of $\dfrac{1}{V_{total}} \dfrac{p}{p_o - p}$ vs. $\dfrac{p}{p_0}$ yields a straight line with positive slope and intercept $\dfrac{1}{c \cdot V_{mono}}$ from which the constant c and the monolayer sorption capacity can be obtained. Knowing the space requirement of the adsorbed gas then enables one to calculate the specific active surface of the respective catalyst material. In the graph given below the amount of material n_{ad} has been used in the plot instead of the volume: n_{ad} and V are proportional to each other.
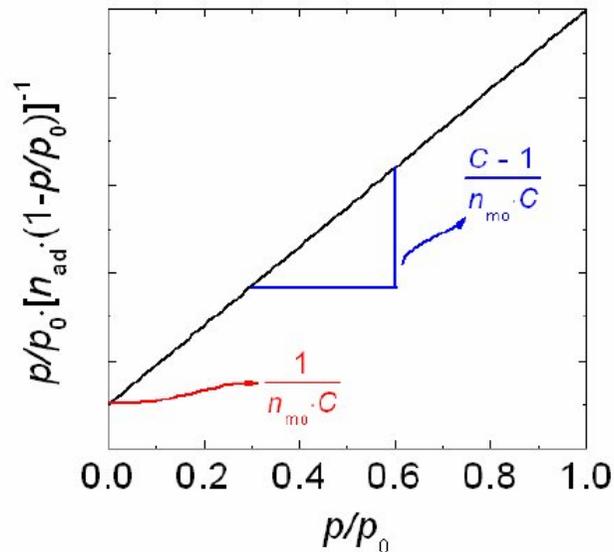
Thermodynamics of adsorption: The heat of adsorption

What quantities is one finally interested in?

In heterogeneous catalysis, an important property is, of course the active surface area of a catalyst, and this is usually accessible by a BET isotherm measurement as pointed out above. Special active sites can additionally be probed by specific adsorption of a certain gas, e.g., ammonia. All in all, the catalyst people have developed a whole zoo of methods and procedures to characterize their materials. In the following, however, I shall enter some problems in adsorption that one encounters when working with metal single crystal surfaces.

A decisive quantity when studying adsorption of simple gases on metal single crystal surfaces is , e.g., the heat of adsorption q_{st} and its coverage dependence, as well as the kind and number of binding states. All this information is contained in the adsorption isotherm, since the strength of the adsorbate bond determines how high the temperature must be to remove an adsorbed particle from the surface and how one has to pressurize the system in order to push this particle back to the surface by increasing the rate of adsorption accordingly. The physical basis has been given before; it is the Clausius - Clapeyron equation:

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

Accordingly, a plot of the log pressure against the inverse temperature should yield straight lines with negative slope with the slope containing the isosteric heat at that coverage. Altogether, one obtains the most important coverage dependence of the heat of adsorption. In the following section, I am going to present you some examples of how one gets access to an adsorption isotherm and how one can deduce the isosteric heat of adsorption.

Thermodynamics of adsorption -
Isotherm measurements with metal single crystals

Determination of the isoteric 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.
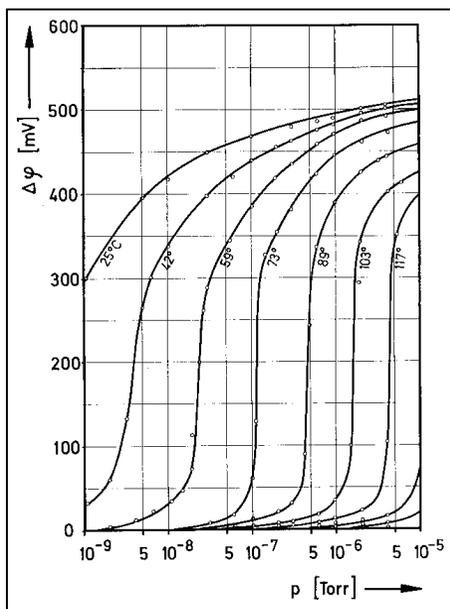
Ni(110)/H_2: Adsorption isotherms
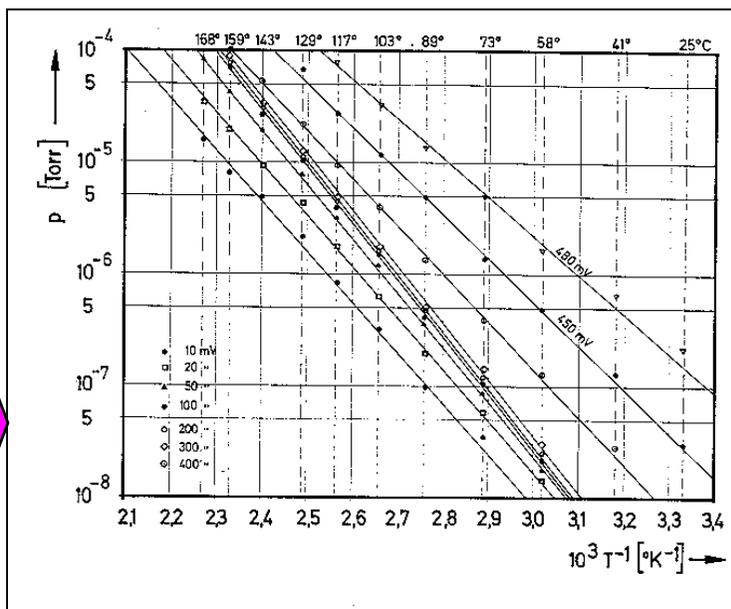
Ni(110)/H_2: Adsorption isosteres
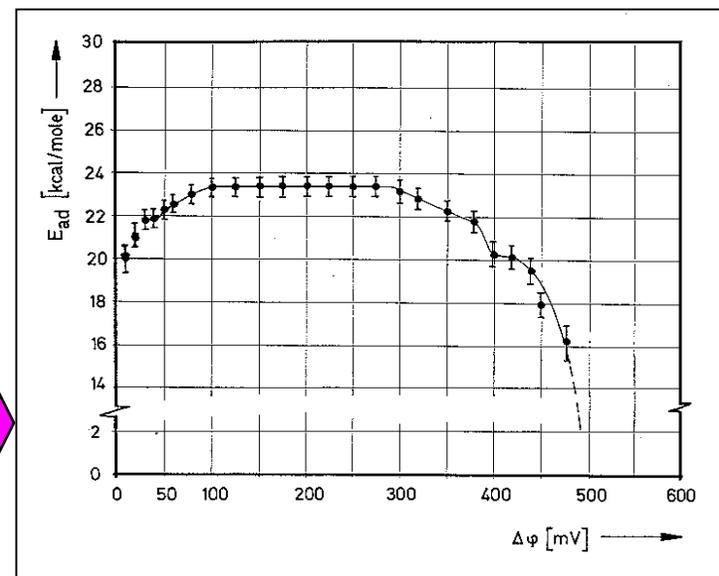
Ni(110)/H_2: Coverage dependence of the isosteric heat of adsorption

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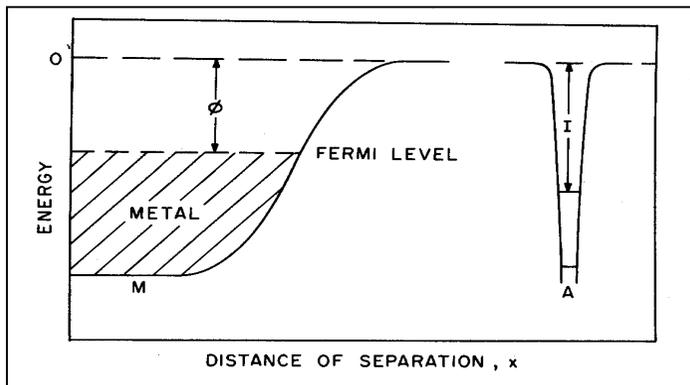
Schematic illustration of the orbital energies before the particle approaches the surface (left) and after it has interacted with the substrate (right). (Example: H_2/Mg(0001), Nørskov et al.)

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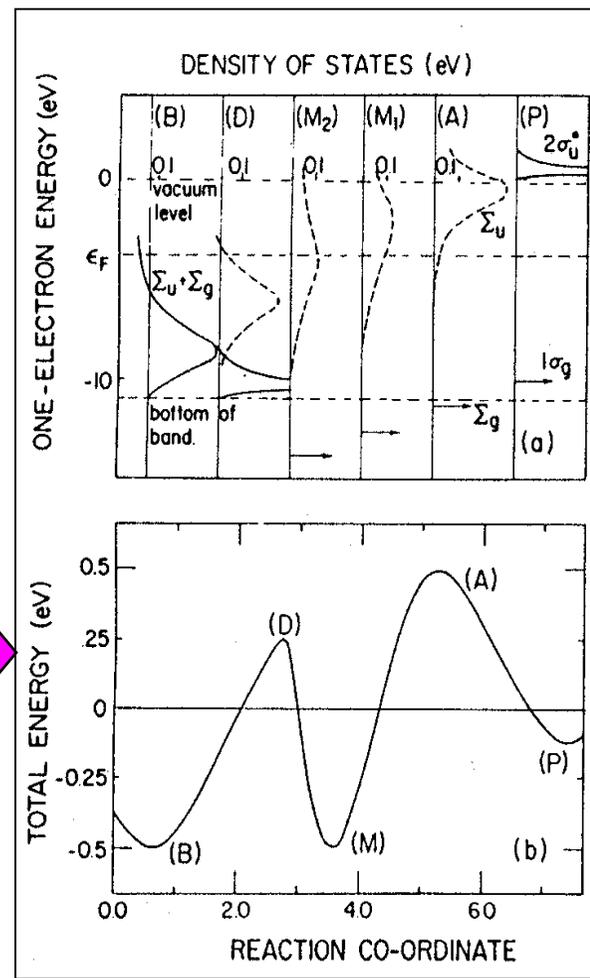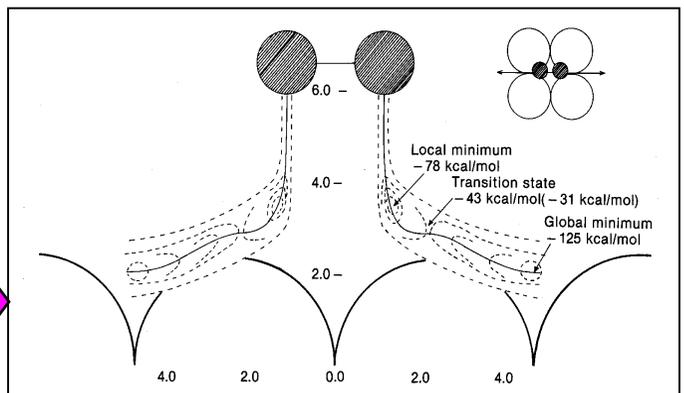
Microscopic description of adsorption -
Quantum chemistry of particle - particle interaction

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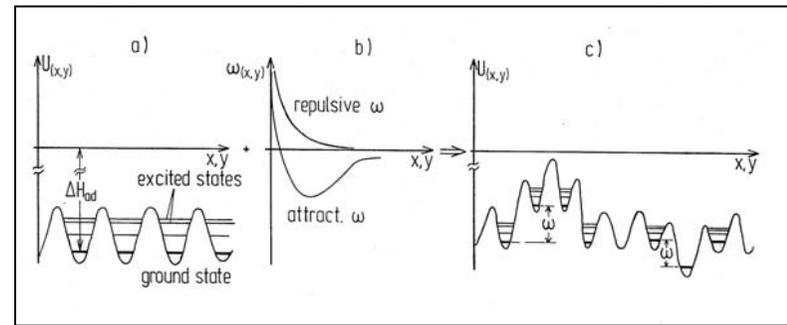
Schematic representation of the potential modulation
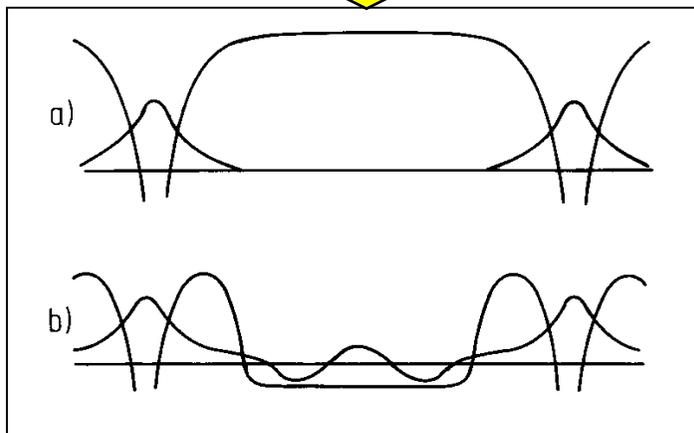
Often, lateral interactions become feasible only beyond a certain critical adsorbate surface concentration. Since they are mostly repulsive, one observes a sudden drop in the heat of adsorption. **Example:** CO adsorption on Ru(0001) [Pfnür et al.]: Up to a sqrt 3 x sqrt 3-R30° structure the CO molecules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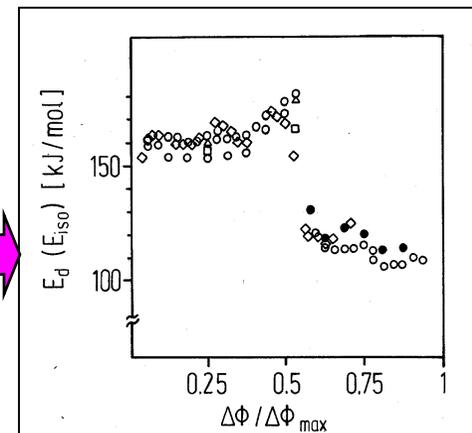
Experimental means to access the energy of adsorption/desorption: Thermal desorption spectroscopy

Thermal Desorption spectroscopy
Is probably the most frequently used method to obtain information on the energetics and kinetics of adsorbed particles.

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. The obtained desorption peaks contain all relevant information about activation energies for desorption, reaction orders and surface concentrations.
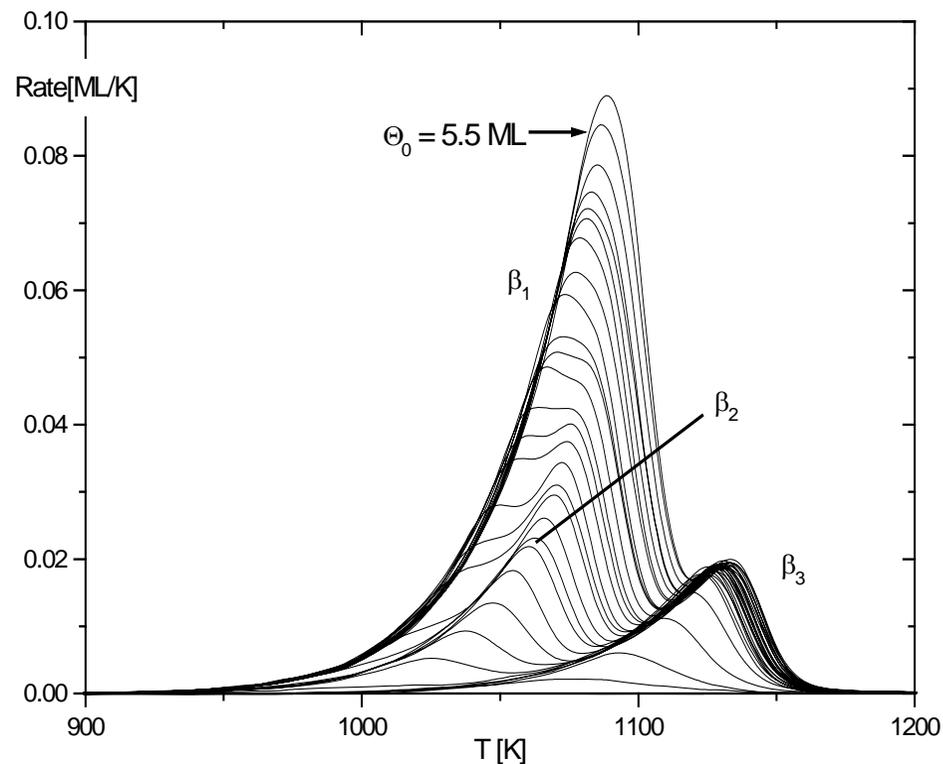
Series of TD spectra of Cu from a Re0001)-surface

Physisorption and chemisorption as monitored by thermal desorption spectroscopy

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**. <u>Example:</u> Rare gas adsorption on graphite, hydrogen adsorption on Ru(0001)/(1x1)-H. Beyond 50 kJ/Mol there dominates chemisorption with „**chemical**" binding forces. <u>Example:</u> oxygen adsorption on a rhodium(110) face.

TD spectra of H_2 from a Ru(0001) surface (after Frieß et al.)
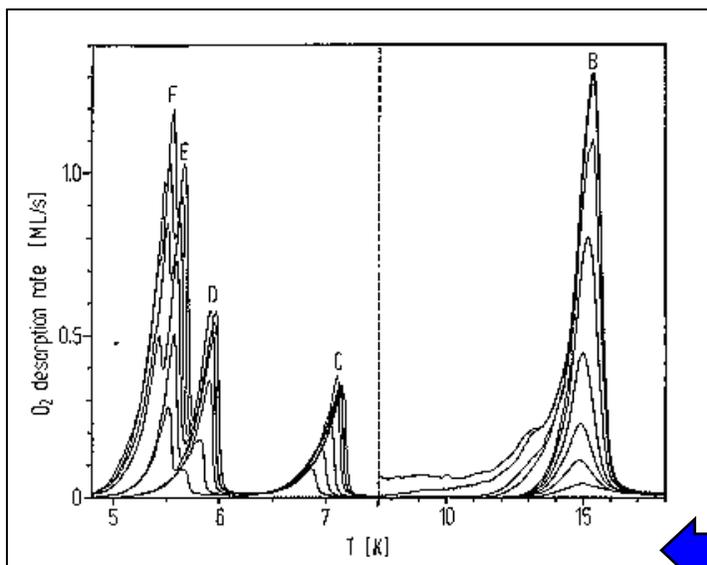
Notice the extremely low desorption temperatures !

The heats of adsorption and desorption range only between 1,6 and 2,9 kJoule/Mol !
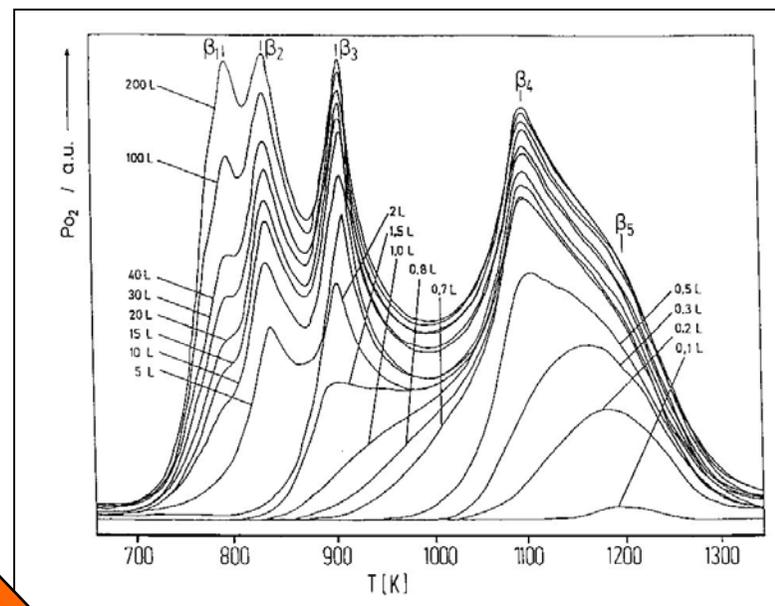
Notice the extremely high Desorption temperatures!

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

Oxygen desorption from a Rh(110)-surface

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:

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

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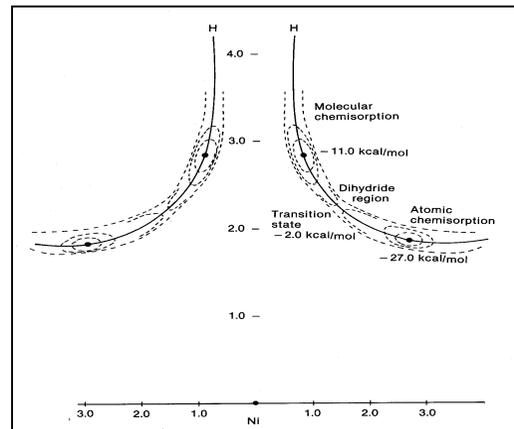
TD spectra of H_2/Pt(111) showing 2nd order

Energy – distance dependence for a H_2-molecule interacting with a Ni_{13}-cluster
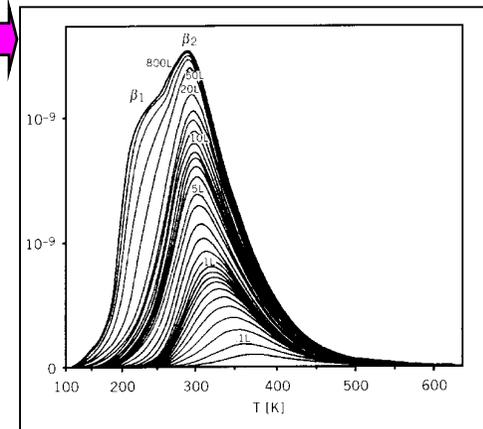
Kisliuk precursor kinetics:
(P.J. Kisliuk 1955)

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

$$K = \frac{p_d^{''}}{p_{ch}^{'} + p_d^{'}}$$

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)
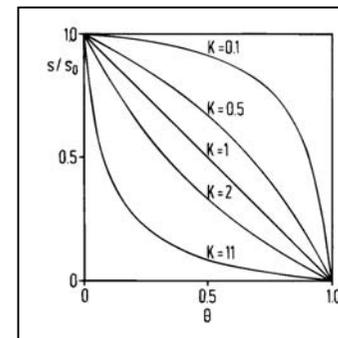
Summary and outlook

One additional remark 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 co-adsorbed species. However, too loosely bound molecules may stay only very shortly on the surface and are immediately lost by desorption, 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.
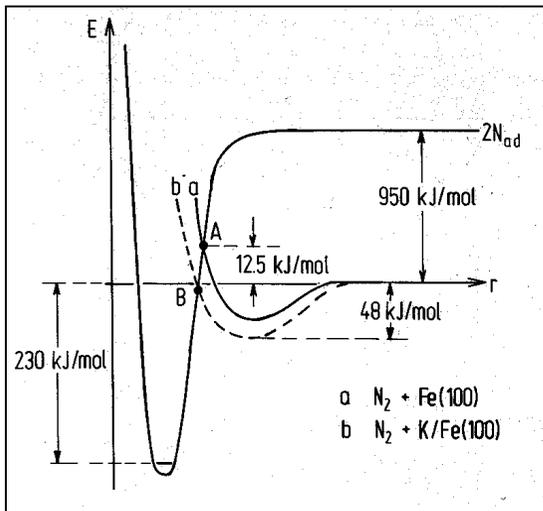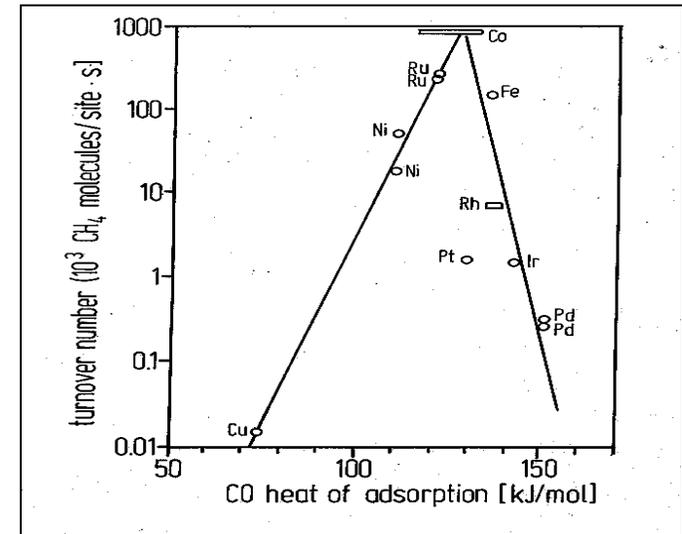
A second effect is crucial: In surface reactions, often homonuclear diatomic molecules with strong covalent bonds must be cleaved. Their potential energy minima lie far away from the surface, and there exist strong activation barriers for dissociation, an example being nitrogen N_2 interacting with Fe 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 co-workers 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 co-adsorbed alkali metals.

Some 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 and textbooks on adsorption/desorption phenomena.