Adsorption and desorption

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Literature:

R.I. Masel, Principles of adsorption and reaction on solid surfaces, Wiley, New York(1996).
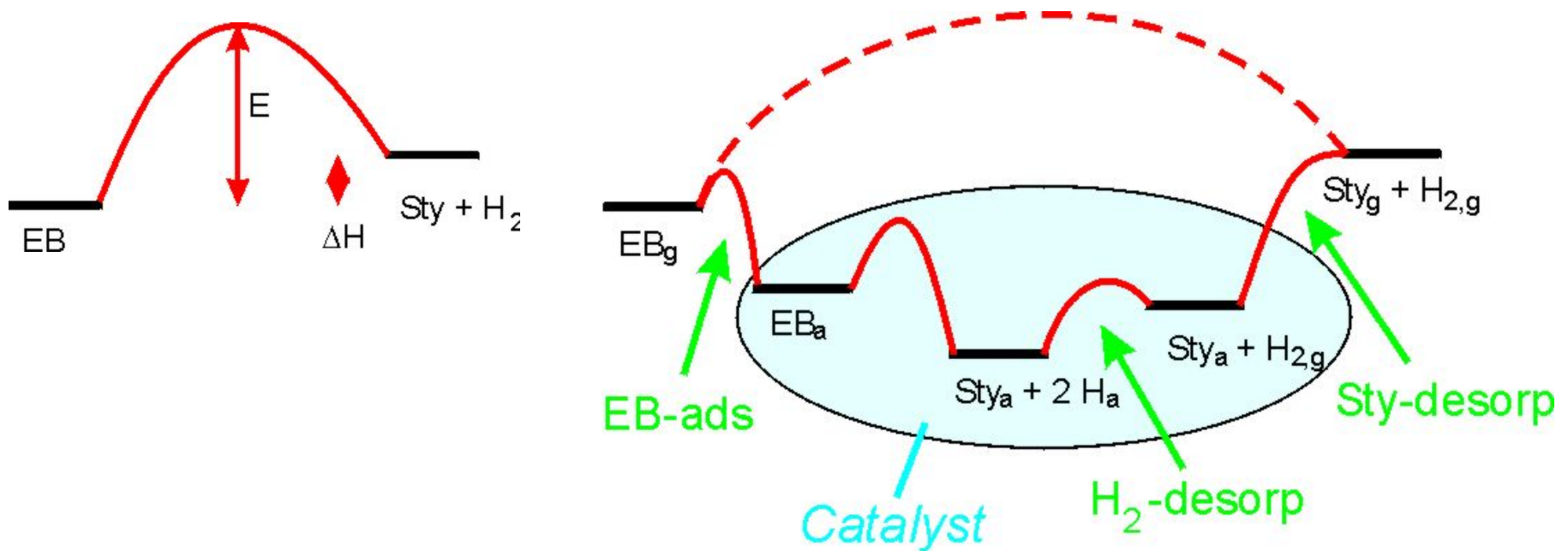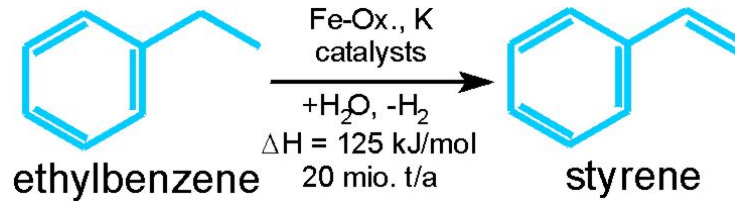
K. Christmann, Surface physical chemistry, Steinkopff, Darmstadt (1991).

G.A. Somorjai, Introduction to surface chemistry and catalysis, Wiley, New York (1994).

M. Henzler, W. Göpel, Oberflächenphysik des Festkörpers, Teubner, Stuttgart (1991).

W. Ranke and Y. Joseph, Determination of adsorption energies and kinetic parameters
by isosteric methods, Phys. Chem. Chem. Phys. 4 (2002) 2483.

FHI-Berlin, 28.11.2008

W. Ranke, Dept. AC, Fritz Haber Institute of the MPG, Faradayweg 4-6, 14195 Berlin, Germany

Adsorption and catalysis

ethylbenzene $\xrightarrow[\Delta H = 125 \text{ kJ/mol}]{\substack{\text{Fe-Ox., K} \\ \text{catalysts} \\ +H_2O, -H_2}}$ styrene

20 mio. t/a

E

ΔH

Sty + H$_2$

EB

EB$_g$

EB$_a$

Sty$_a$ + 2 H$_a$

Sty$_a$ + H$_{2,g}$

Sty$_g$ + H$_{2,g}$

EB-ads

H$_2$-desorp

Sty-desorp

Catalyst

Contents

1. Some definitions and concepts

adsorption →
← desorption

accomo-
hit   date   dissociate   bind, relax

free molecule,   precursor   transition   chemi-
free substrate   (mobile)   state   sorbate

$H_2O/Si(001)$
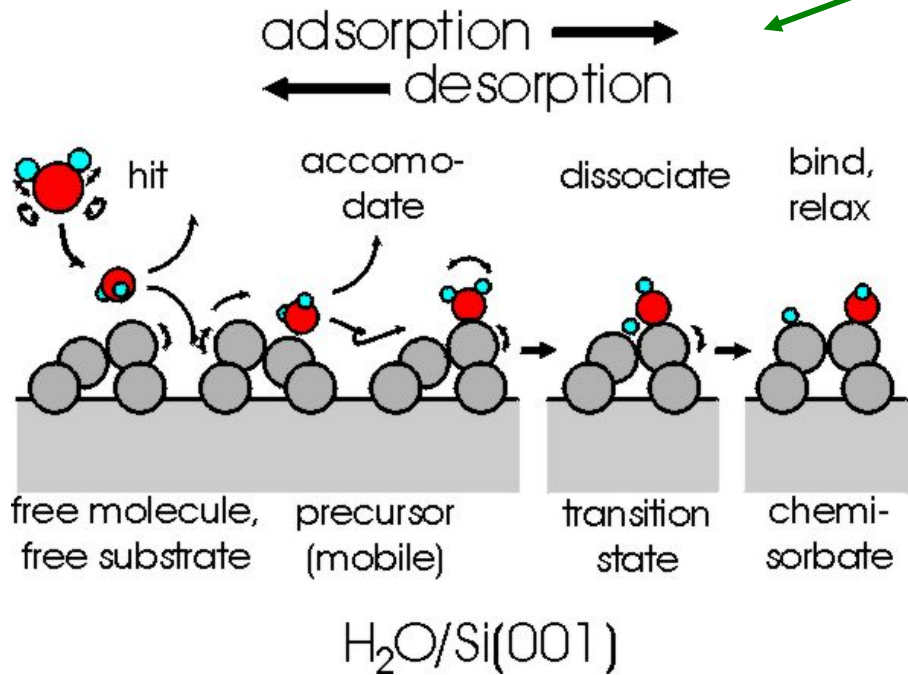
The sticking process. Example: Dissociative adsorption of H_2O on Si(001).
The Si(001) surface relaxes in order to minimize the number of unsaturated ("dangling") bonds by formation of asymmetric dimers. Relaxation is changed upon adsorption.

(Review on water: M.A. Henderson, Surf. Sci. Reports 46 (2002) 1; calculations: A. Vittadini et al. Phys. Rev. B 52 (1995) 5885)

Adsorption:

molecules from gas phase or solution bind in a layer of condensed phase on a solid or liquid surface. The molecules are called **adsorbate,** the substrate is called **adsorbent**. The process of binding is called **adsorption**. Removal of the molecules is called **desorption**.
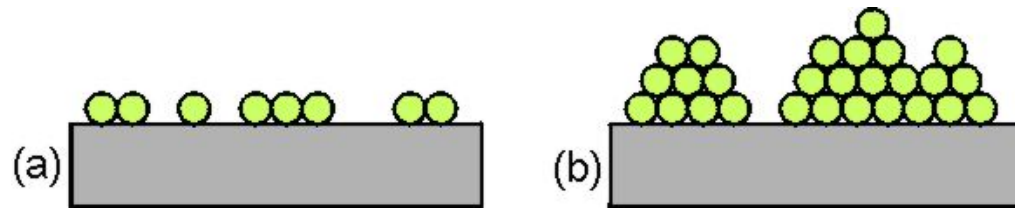
Accomodation and **Sticking**:

The incoming particle has to get rid of its **translational** and **rotational energy** and has to assume a suitable **spatial configuration**. The surface may have to rearrange: **Accomodation**. If this does not happen: **Reflection**.
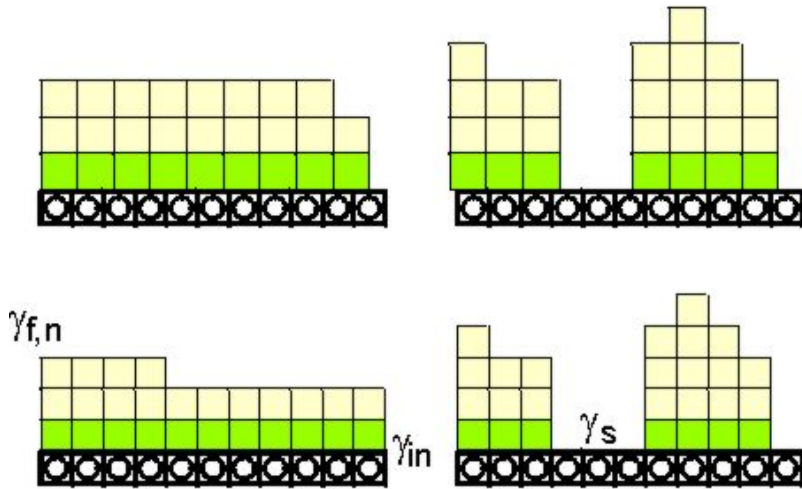
Sticking: The **sticking coefficient** s or **sticking probability** is the ratio of particles being bound compared to those hitting the surface.

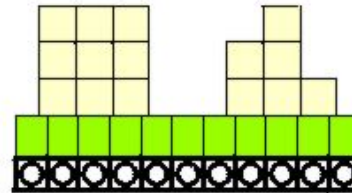The value of s often reaches 1 but may also be almost infinitely small.

Rate of molecules striking 1 cm² of surface:
 	
$j_N = 2.63\times10^{22}\, p/(MT)^{1/2}$ cm⁻² s⁻¹,
    p in mbar, M in g/mol.
 	
For comparison:
Density of atoms on solid surfaces
   Pt(111): 1.5×10^{15} cm⁻²
   Si (001): 6.8×10^{14} cm⁻²
	N₂ at 273 K:
	
	1000 mbar
	1 mbar
	10^{-3} mbar
	10^{-6} mbar
	10^{-10} mbar
		j_N (cm⁻² s⁻¹)
		
		3×10^{23}
		3×10^{20}
		3×10^{17}
		3×10^{14}
		3×10^{10}
			Time needed for 1 ML ($s=1$)
			5×10^{-8} s
			5×10^{-6} s
			5×10^{-3} s
			5 s
			5×10^{3} s

Monolayer and multilayer adsorption

$\Delta\gamma_n = \gamma_{f,n} + \gamma_{in} + \gamma_s$

Multilayer incommensurate

SK-growth: 1st layer commensurate, further layers incommensurate

Multilayer commensurate

Layer by layer
(Frank - Van der Merwe)
$\Delta\gamma_n < 0$

Island
(Volmer - Weber)
$\Delta\gamma_n > 0$

Island on layer
(Stranski - Krastanov)
$\Delta\gamma_n = f(n)$

γ_s free energy of bare substrate;
$\gamma_{f,n}$ free energy of adlayer-film of thickness n;
γ_{in} free energy of interface;
commensurate growth for first layer assumed;
misfit causes strain

Free **surface energies** (= surface tensions) are **always positive**: making a surface costs always energy.

If γ_{in} is negative: dissolution.

Not treated here:

Formation of new bulk components or bulk phases
as result of
    reactions like oxidation
    alloying
    dissolution
    etc.

Adsorption from liquid phase

2. Physisorption and chemisorption
2.1 Physisorption

Nonpolar gases on nonpolar surface, no chemical interaction:
Van-der-Waals (induced-dipole – induced-dipole) interaction.
Starting from the Lennard-Jones 6-12 potential (interaction between single atoms or molecules),

$$V(R) = 4\varepsilon\,[(\sigma/R)^{12} - (\sigma/R)^6],$$

ε depth of potential minimum; $\sigma=0.891\,R_e$ (equilibrium distance).

the London-equation,

$$E_{Ms}(z_M) = \rho_s \pi\; C_{Lond}\left(\frac{0.2(r_e^s)^6}{z_M^9} - \frac{1}{z_M^3}\right)$$

ρ_s: density of surface atoms;
C_{Lond}: London constant, depends on polarizabilities and ionization potentials;
r_e^s: equ. distance when the adatom interacts with one atom only;
z_M: distance of adatom from surface.

was derived for non-polar gases on non-polar non-conducting surfaces.
on conducting surface: Same functional dependence.

<div>

Characteristic:
$z_M > 2\text{Å}$;
ΔH_{ad}: 1.4 kJ/mol (He/graphite) – 42 kJ/mol (C_5H_{12}/graphite).

</div>

Compare:
Thermal E
(300 K)
RT~2.5 kJ/mol

Even if ΔH_{ad} is small, Θ may be high at high pressure, see isotherms/isobars

Van-der-Waals interaction is responsible for condensation of nonpolar gases like
inert gases, alkanes, aromatics...

2.2   Chemisorption

Electronic structure, bond lengths and bond angles strongly affected.
Substrate and adsorbate **not** separable. Simple models do not exist.
Theoretically, the whole system (substrate + adsorbate) has to be treated quantum
        mechanically which has become feasible during the last years.

> Characteristic:
> $z_M = 1 - 1.5$ Å;
> ΔH_{ad} up to several hundred kJ/mol.

Covalent -   (Example: $H_2O/Si(001)$., see above.
Ionic -   (Example: Alkali adsorption)
Acid-base -   (Example: $H_2O/Fe_3O_4(111)$)
H-bond -   (Example: H_2O-dimers and islands, lateral interaction)
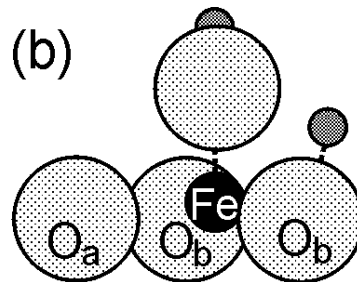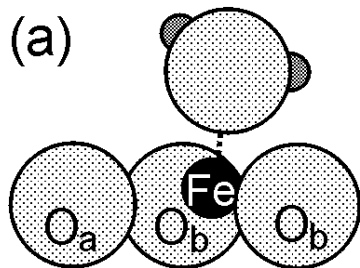
Model for the interaction and dissociation of water on an acidic Fe-site on the surface of $Fe_3O_4(111)$; the Fe is formally Fe^{3+} (Y. Joseph et al. Chem. Phys. Lett. 314 (1999) 195).

Hardness (Pearson) η:

Measure of the capability to share electrons.

Hard (η large): Species that form strong ionic bonds;

Medium: Species that form mixed covalent and ionic bonds;

Soft (η small): Species that form strong covalent bonds;

Charge acceptor: acid; charge donor: base.

Strong interaction between a **hard** acid and a **hard** base or

a **soft** acid and a **soft** base.

Weak interaction between a **hard** acid and a **soft** base.

Hard acids	H^+, Li^+, Mg^{2+}, Cr^{3+}, Co^{3+}, Fe^{3+}, Al^{3+}, $Al(CH_3)_3$, bulk Si
Borderline acids	Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ru^{2+}, Os^{2+}, Ir^{3+}, Rh^{3+}
Soft acids	Cu^+, Ag^+, Pd^{2+}, Pt^{2+}, $Ga(CH_3)_3$, O, Cl, N, RO, ROO, metallic atoms, metal clusters
Soft bases	I^-, CO, C_2H_4, $P(C_6H_5)_3$, C_6H_6, H^-, H_2S, metal surfaces
Borderline bases	C_5H_5N, NO_2^-, SO_3^{2-}, $C_6H_5NH_2$
Hard bases	F^-, Cl^-, H_2O, NH_3, OH^-, CH_3COO^-, RO^-, ROH, O^-

(Masel Table 3.8, p. 145)

3.   Energetics: Potential curves
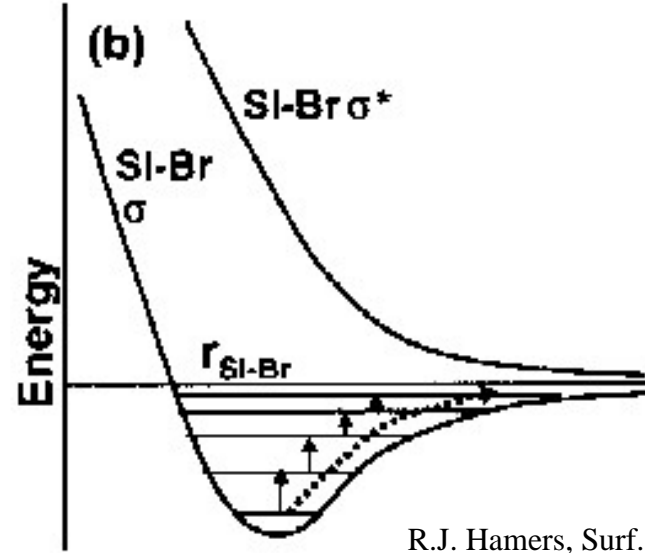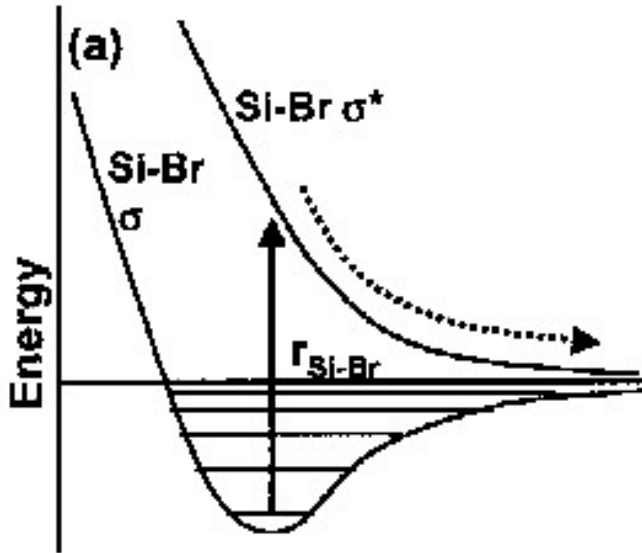
R.J. Hamers, Surf. Sci. 583 (2005) 1.

„Ten or twenty phonons"transfer their energy collectively to an electron which is excited into an antibinding state from which dissociation occurs.

A number of phonons is sequentially absorbed. The adsorbate-substrate vibration gains amplitude until dissociation occurs.
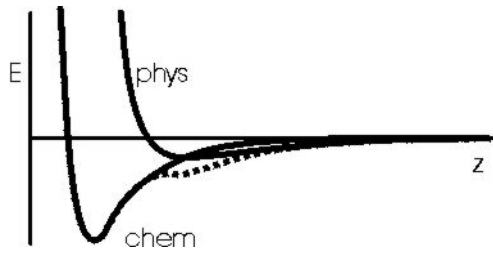
Classical analog:

Interference-generated freak wave (Monsterwelle, Kaventsmann)

Resonance-like amplitude build-up (Resonanzkatastrophe)
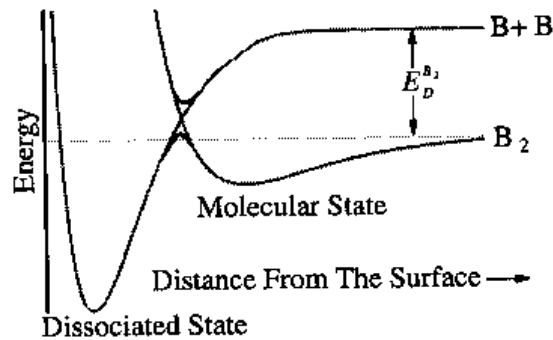
Adsorption, accomodation: invert all arrows

Potential curves for approach of a non-dissociated particle to a surface:
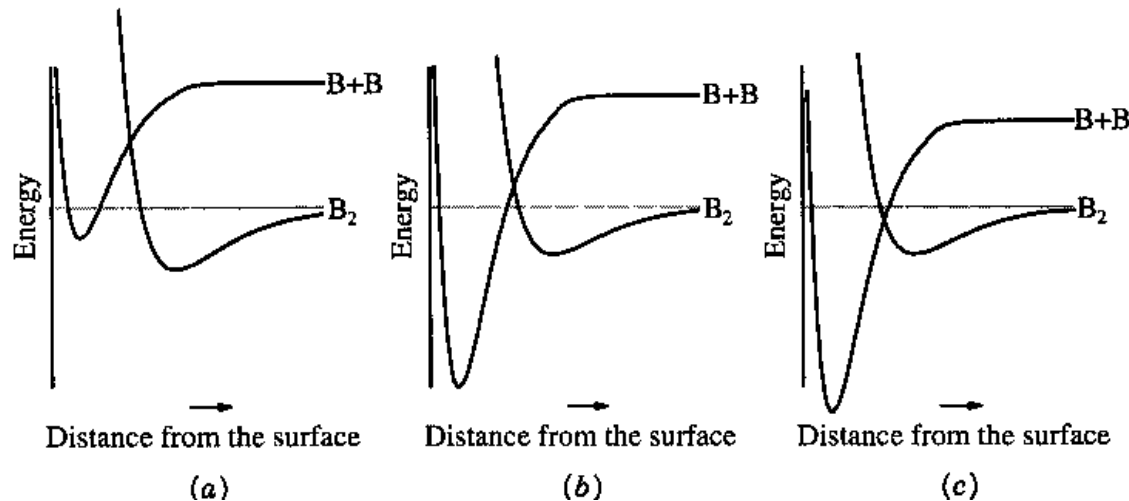*physisorption, chemisorption and sum curve (dotted).*

$\Delta H_{phys} << \Delta H_{chem}$
typically $\Delta H_{phys} = 20 - 80$ kJ/mol, $\Delta H_{chem} > 100$ kJ/mol.

But: Magnitude of ΔH_{ad} alone is
not a sufficient criterion for the distinction:
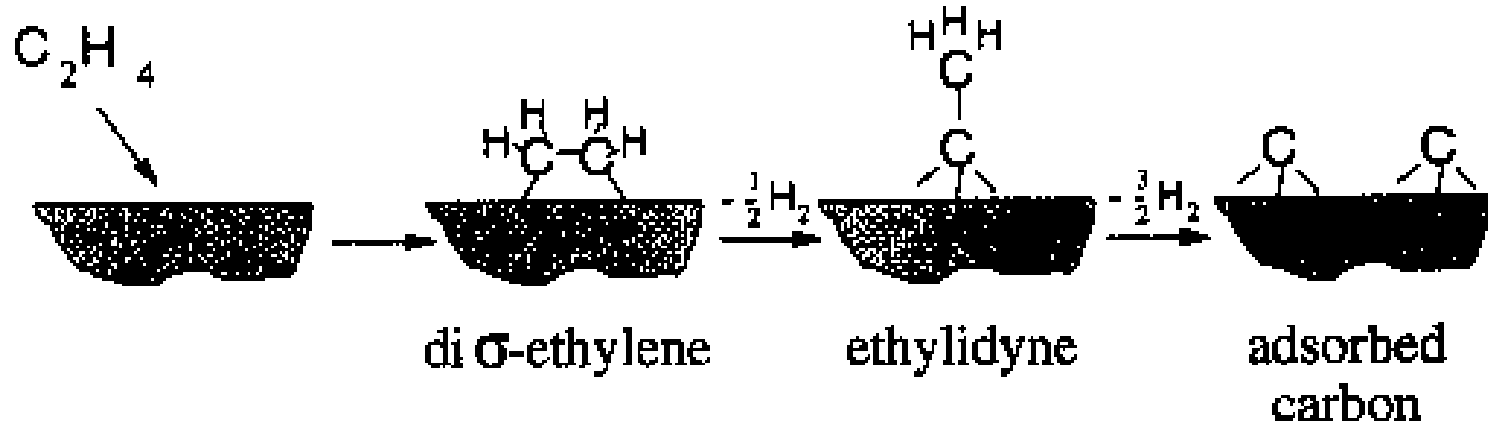Change of geom. and electron. structure possible.

Potential curve for the dissociative adsorption of a
B_2 molecule on a surface (Masel fig. 3.8, p.119.)

Potential curves for
(a) pure molecular adsorption,
(b) activated dissociative
*   adsorption*
(c) nonactivated dissociative
*   adsorption*
(Masel fig. 3.9, p.119)

3.2　　　Dissociative adsorption, several sequential steps

The mechanism of ethylene decomposition on Pt(111).
(Proposed by Kesmodel et al. [1979] and confirmed by Ibach and Lehwald [1979], Masel fig. 3.10, p.121).

Example for **"irreversible"** adsorption.

Irreversible is not strictly the correct term:

It is irreversible under usual experimental conditions where a part of the formed species (here hydrogen in the form of gaseous H_2) is irreversibly removed from the system.
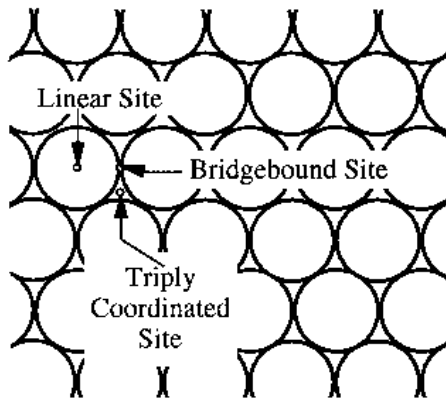
3.3 Adsorption site

Surfaces are inhomogeneous

interaction with certain sites is stronger than with others.

Intrinsic inhomogeneity from periodic atomic structure

ordered adsorbate structures
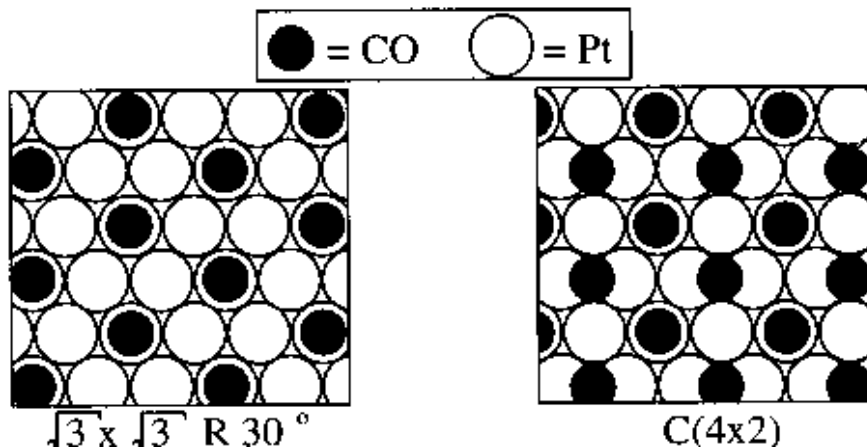

Different adsorption sites on a close-packed surface:
Linear or on-top site,
bridgebound site and
triply coordinated or threefold hollow site

(Masel fig. 3.13, p.123).
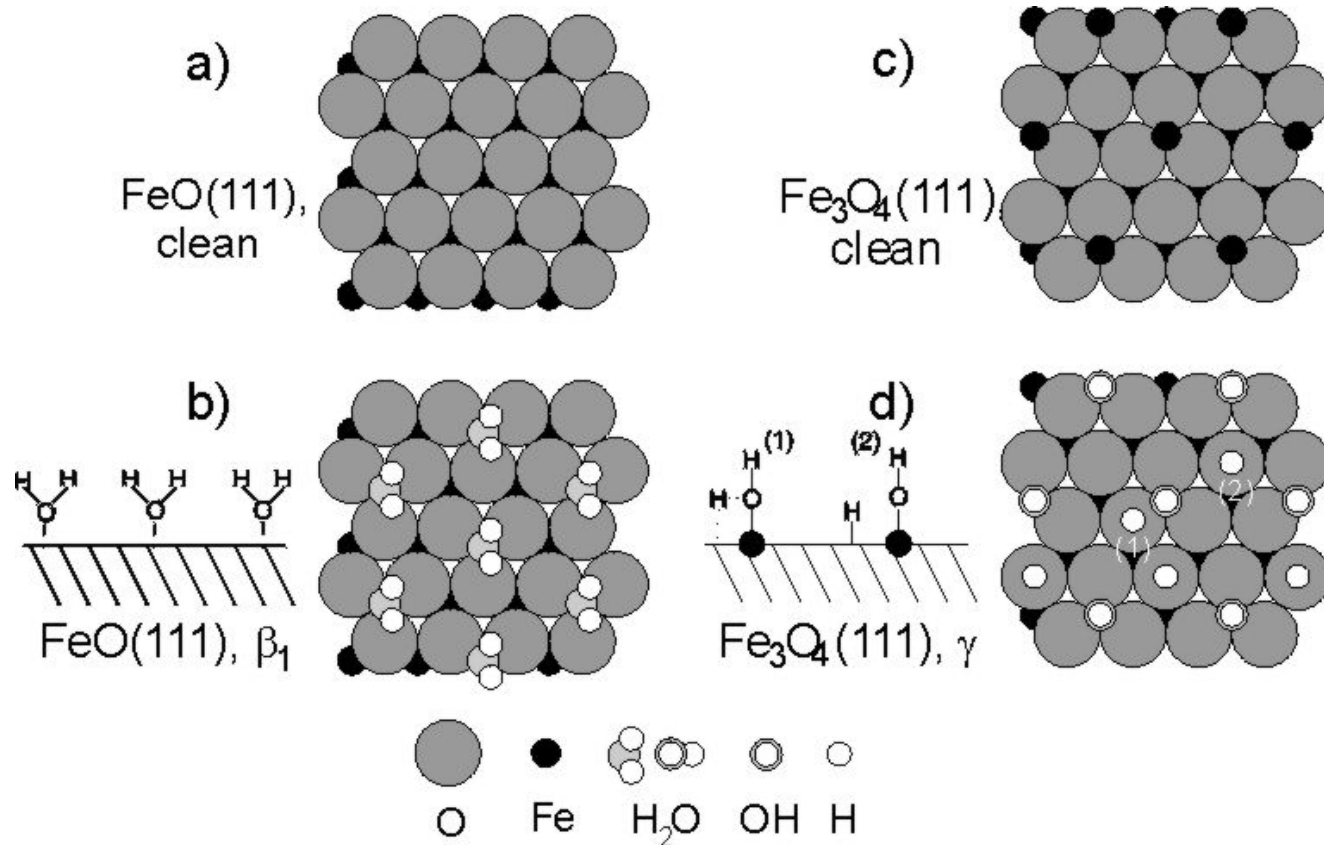
Example: CO/Pt(111)

Binding sites for CO on Pt(111):
Two ordered adsorption arrangements
assumed sequentially with
increasing coverage:
$\Theta_r = 0.33$ and 0.5

(Masel fig. 3.14, p.123).

Example: $H_2O/Fe_3O_4(111)$,

a) FeO(111), clean

b) FeO(111), β_1

c) $Fe_3O_4(111)$ clean

d) $Fe_3O_4(111)$, γ

O Fe H_2O OH H

Clean and water covered surfaces of FeO(111) and $Fe_3O_4(111)$.
Coverages and kind of adsorbed species deduced from UPS measurements.
FeO(111) is O-terminated. The interaction is weak but still determined by
the position of Fe in the second layer. Fe_3O_4 is terminated by ¼ ML of Fe.
Water dissociates. The coverage is compatible with OH being adsorbed on the
Fe sites and H binding to O-sites. Site (1) in (d) is the proposed transition state.
(Y. Joseph et al. J. Phys. Chem. B 104 (2002) 3224;).
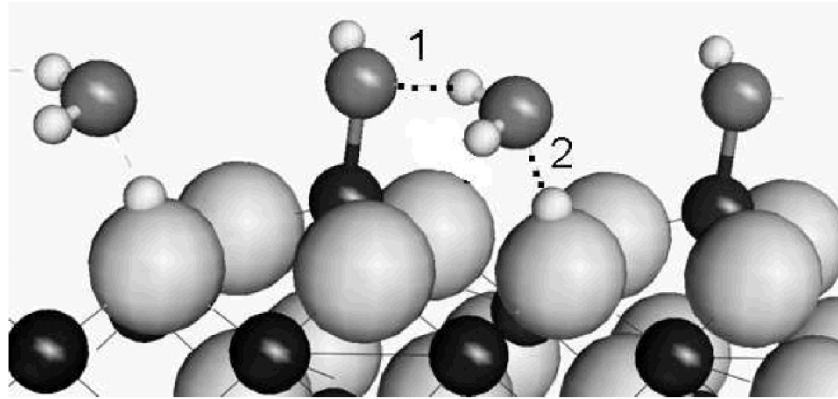
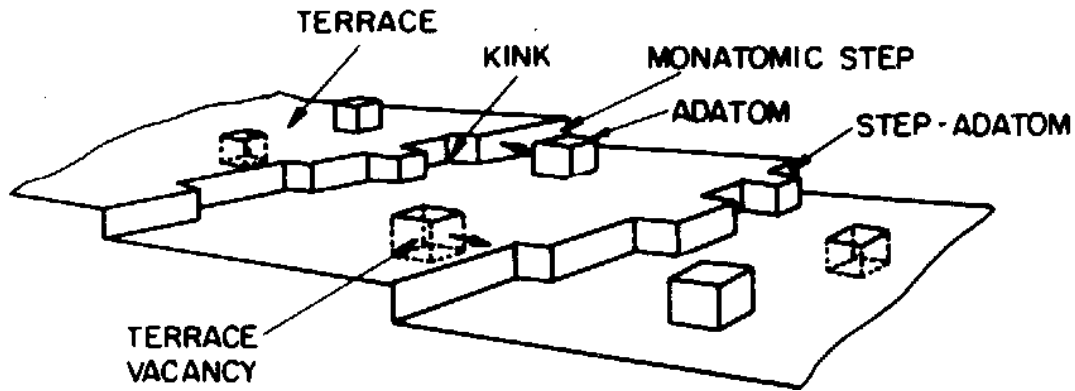*Further water bridges OH and H via H-bonds.*
A H$_3$O-OH like "dimer" is formed.
(M.E. Grillo et al., Phys. Rev. B 77 (2008) 075407)

Extrinsic inhomogeneity from defects
(steps, domain boundaries, kinks, adatoms, vacancies, contaminants…)

Model of a heterogeneous surface with different surface sites.
They are distinguished by their number of nearest neighbours.
(Somorjai, fig. 2.6, p. 41.)

$$\Delta H_{ad} = \text{f(substrate, }\Theta).$$

- material dependence
- site dependence
- ads.-ads.-interaction: repulsive or attractive
- ads.-subs.-interaction may induce structural changes in substrate (reconstruction, relaxation)

Remember these terms:

adsorption, desorption, adsorbent, adsorbate, substrate,

accomodation, sticking, sticking coefficient, monolayer, multilayer;

physisorption, chemisorption, hardness, hard/soft acid/base;

potential curve;

adsorption: molecular, dissociative, non-activated, activated
reversible and irreversible;

adsorption sites: linear, on-top, bridge,
triply coordinated, threefold hollow site;

4.   Adsorption-Desorption-Equilibrium: Isotherms and isobars

Adsorption rate:

$$r_a = r_a(p,\, s_0,\, n,\, T,\, E_a,\, \Theta).$$

(s_0: initial sticking coefficient, n : reaction order for adsorption ; E_a: activation energy for adsorption, Θ : coverage)

Desorption rate:

$$r_d = r_d(\nu,\, n,\, T,\, E_d,\, \Theta),$$

increases with Θ.

(ν: frequency- or prefactor for desorption; n: reaction order for desorption; E_d: activation energy for desorption)

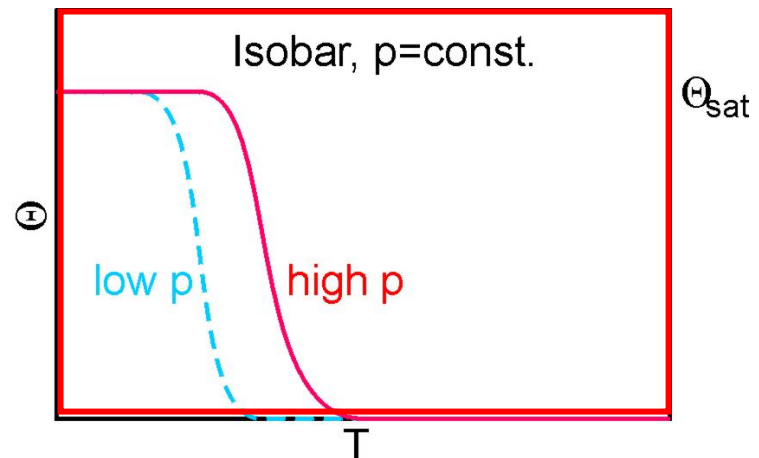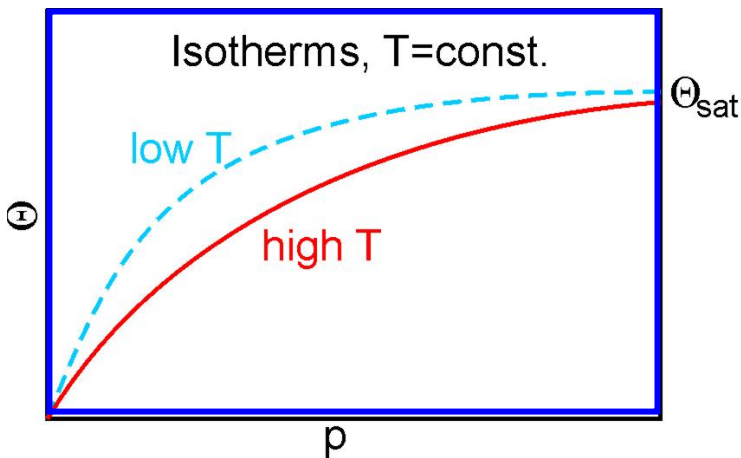After a while, when

$$r_a = -\,r_d\,,$$

⬅ adsorption-desorption equilibrium condition

an equilibrium coverage Θ_{eq} will establish.

$\Theta_{eq}(T)_p$ T variable, p constant: **Isobar**
$\Theta_{eq}(p)_T$ p variable, T constant: **Isotherm**

Isotherms, T=const. Θ_{sat}
low T
high T
Θ
p

Isobar, p=const. Θ_{sat}
low p   high p
Θ
T

How to determine Θ ?

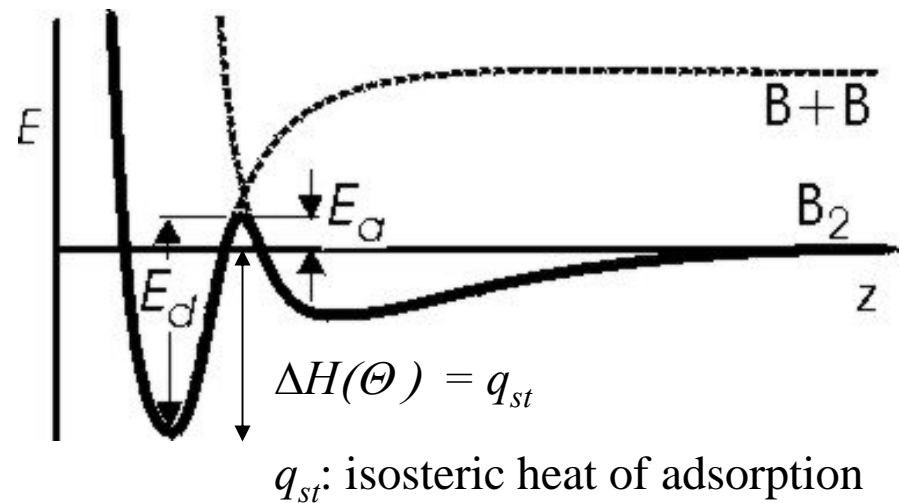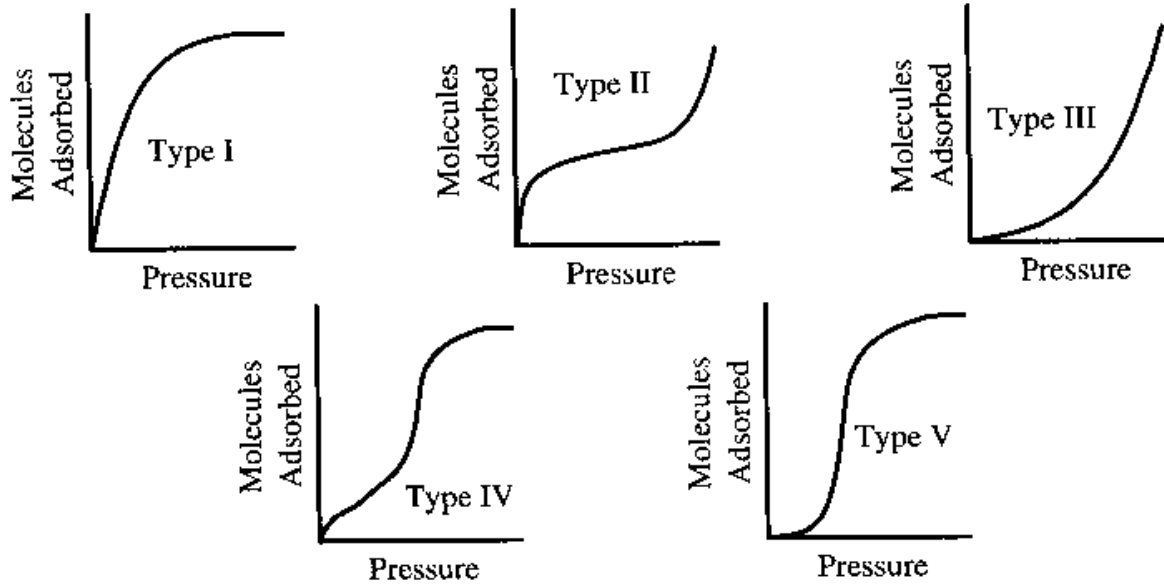High surface area (powders, pellets…): pressure decrease by adsorption (e.g. BET), TDS.

Low surface area (single crystals): $\Delta\phi$, LEED, IRAS, UPS, TDS.

The difference and $E_d - E_a$
determines the adsorption energetics

p, s_0, n and ν determine the kinetics.

Aim: measure $\Theta(p,T)$, deduce energetic
and kinetic parameters from it.

$\Delta H(\Theta) = q_{st}$

q_{st}: isosteric heat of adsorption

The fife types of adsorption isotherms described by Brunauer[1945]

(Masel fig. 4.4, p.238).

Type	Where to be found
I	monolayer adsorption
II	multilayer adsorption, BET isotherm
III	island or droplet nucleation necessary for adsorption
IV	pore filling, followed by outer-surface adsorption
V	pore filling with nucleation (like III), followed by outer surface adsorption

5.   A-D energetics: Isosteric heat of adsorption

Measure a set of isotherms or isobars,
deduce p-T-pairs for Θ_{eq}=const,
plot $\ln(p)$ vs$(1/T)$,
use Clausius-Clapeyron equation

Strictly, CC is only applicable if
adsorbate is separable from substrate
(no strong interaction, physisorption).
Kinetic considerations:
Applicable if $r = C \exp(-E_{act}/RT)$
(Arrhenius law).
(W. Weiss, W. Ranke, Prog. Surf. Sci. 70 (2002) 1).

$$\mathrm{d}(\ln p)/\mathrm{d}(1/T) = -\Delta H/R \text{ or}$$
$$\ln p = -\Delta H/RT + \text{const.}$$

or, since ΔH may be Θ-dependent,
$\Delta H(\Theta) = q_{st} = $ isosteric heat of adsorption;
isosteric means: for constant coverage.

Isosteric methods

Advantage:
        CC is deduced from equilibrium thermodynamics and independent of kinetics.
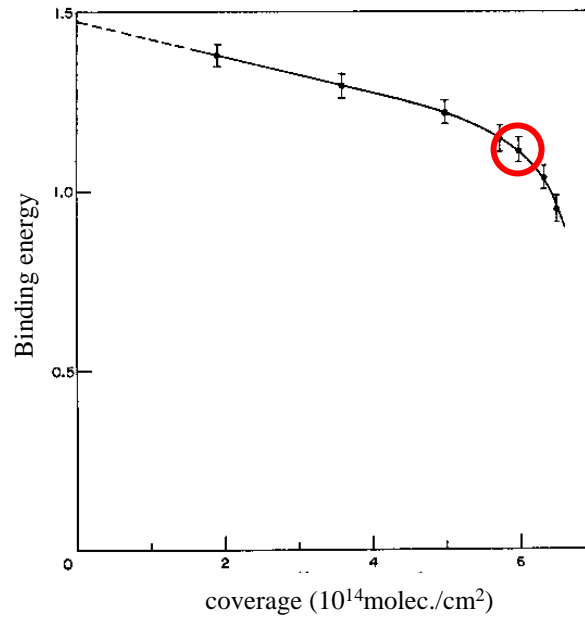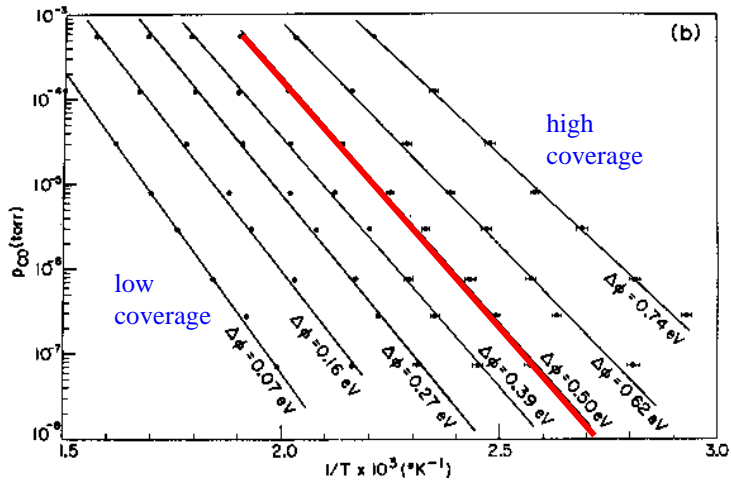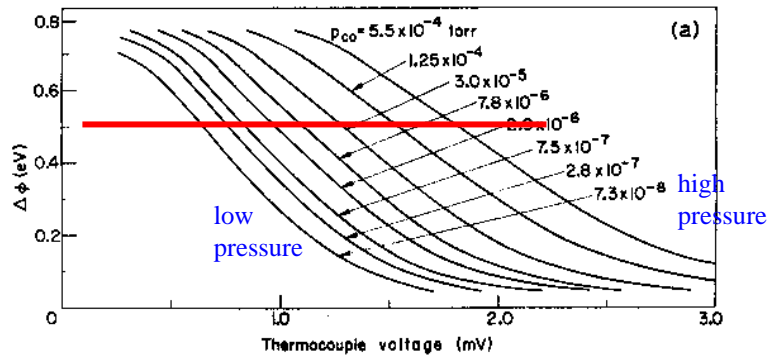Disadvantage:
        adsorption must be reversible. (If not: => calorimetric methods).
        adsorption and desorption must be sufficiently fast
        (equilibrium established within reasonable time) .

Examples: 1. Adsorption on a metal: CO/Pd(100)

Coverage dependence of q_{st} deduced from the slopes of the curves in (b).

(J.C. Tracy, P.W. Palmberg, Surf. Sci. 14 (1969) 274).

a) Isobars for CO adsorption on Pd(111). As a measure for the coverage, the work function change $\Delta\phi$ was used. In special cases, $\Delta\phi$ is proportional to Θ.
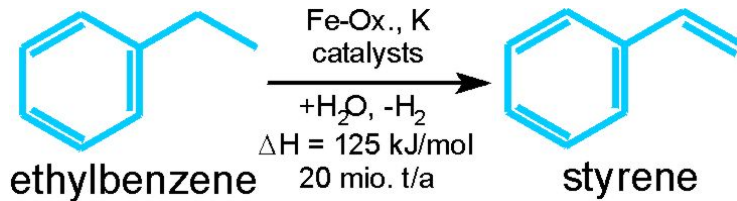*b) Arrhenius-plots ln p vs. 1/T for different coverages (in terms of $\Delta\phi$).*

2. Adsorption on a semiconductor: NH_3/Ge

(W. Ranke, Surf. Sci. 342 (1995) 281; W. Ranke, J. Platen, Phys. Rev. B 54 (1996) 2873)

3. Adsorption on an ionic material: Ethylbenzene/FeO(111), $Fe_3O_4(111)$

(W. Weiss, W. Ranke, Progr. Surf. Sci. 70(2002) 1, Figs. 54, 56, 57, 58b)

ethylbenzene → Fe-Ox., K catalysts, $+H_2O$, $-H_2$, $\Delta H = 125$ kJ/mol, 20 mio. t/a → styrene

Adsorption of ethylbenzene (EB) is studied in connection with the investigation of its catalytic dehydrogenation to styrene.
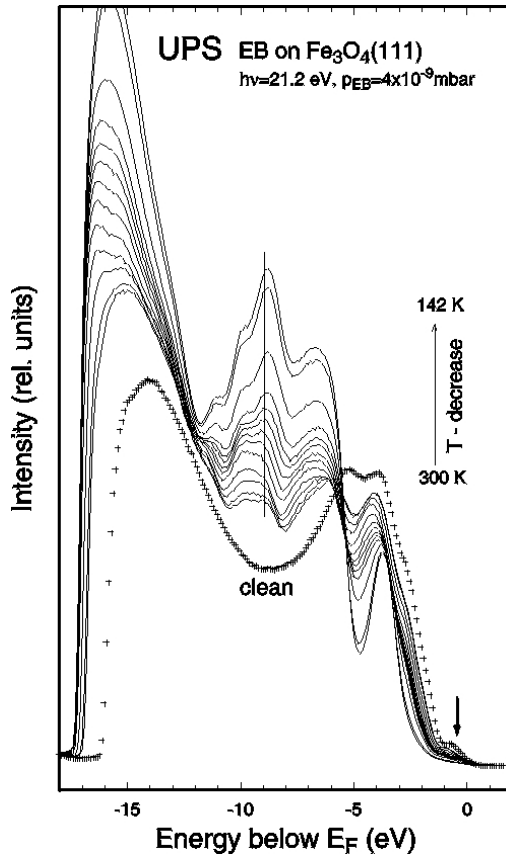
Photoelectron spectra of clean $Fe_3O_4(111)$ and after equilibrium coverage by EB at $p_{EB}=4x10^{-9}$ mbar and different T.
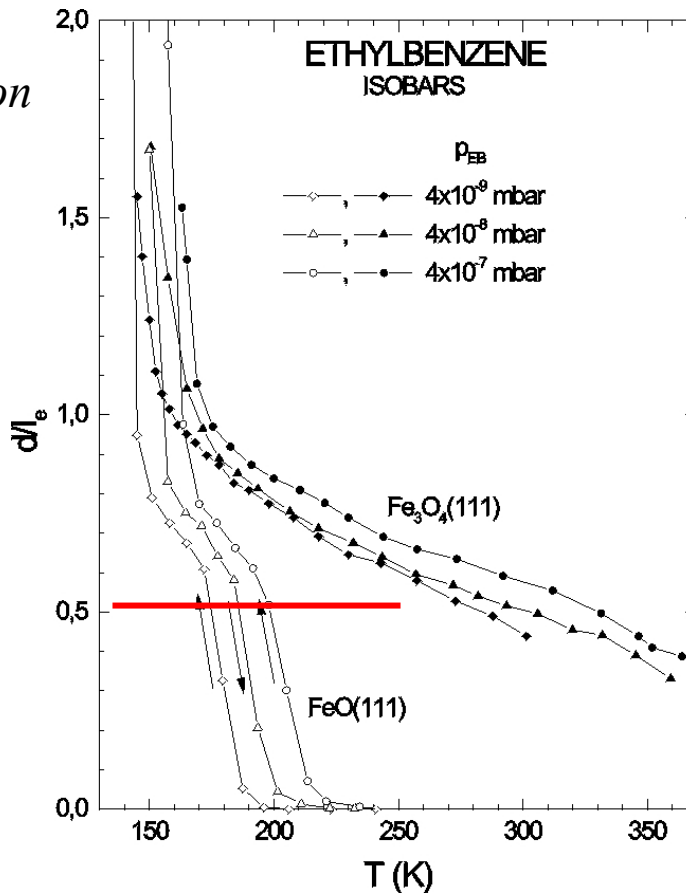
Adsorption isobars deduced from UPS measurements of EB on FeO(111) and $Fe_3O_4(111)$ for three values of p_{EB}. d/l_e is proportional to the coverage.
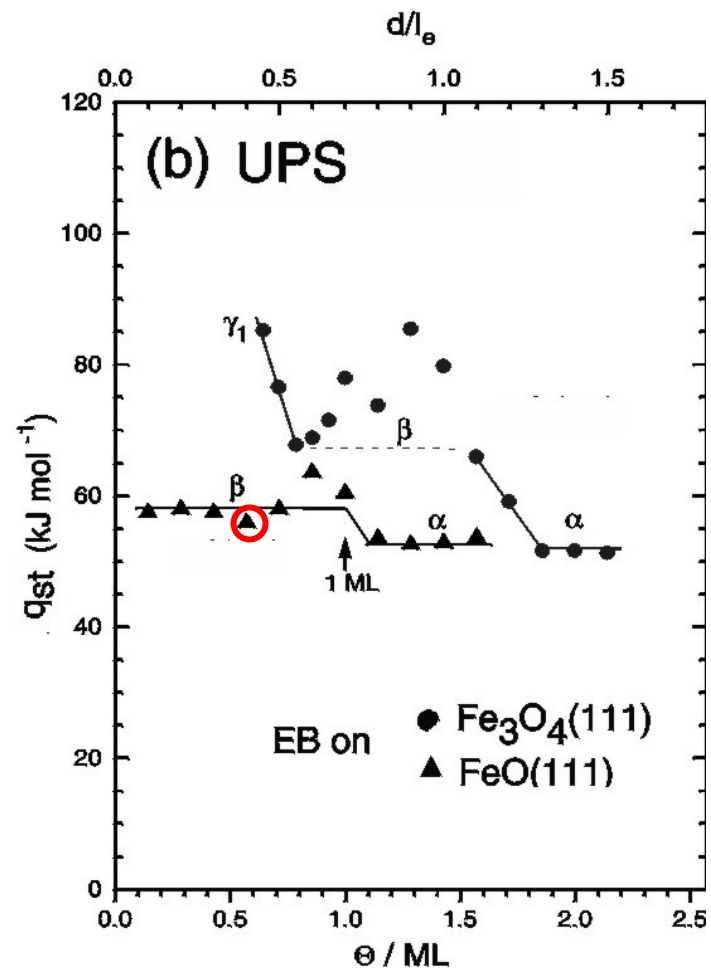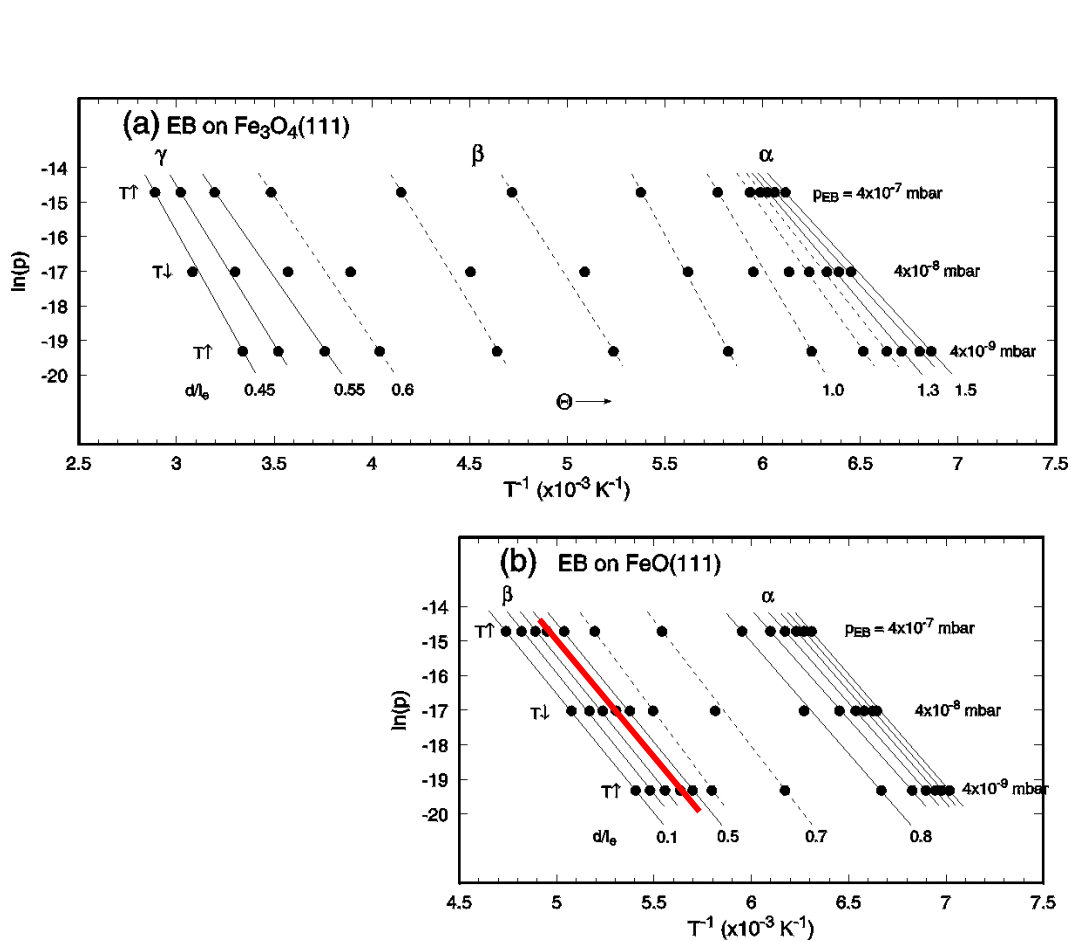
*For different coverages (in terms of d/l_e),
p-T- values are taken from the isobars.
ln(p) vs. 1/T yields mostly straight lines.
Their slope yields q_{st}.*

*Coverage dependence of q_{st}
deduced from the CC-analysis
of isobars.*

==> TDS (TPD), a transient method, evaluation depends on kinetics.

6.   A-D kinetics: The shape of isotherms/isobars

Kinetics: rate of adsorption and desorption

$$r_a = \frac{\sigma_A \, d\Theta_r}{dt} = \frac{p}{\sqrt{2\pi \, mkT}} \, s_0 \, \exp(-E_a/kT) \, f(\Theta_r) \quad = \quad A \, f(\Theta_r)$$

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

E_a, E_d: activation energies for adsorption and desorption;
s_0: initial sticking probability:
σ_A: density of adsorption sites;
$\Theta_r = \Theta/\Theta_{sat}$: relative coverage ($0 < \Theta_r < 1$);
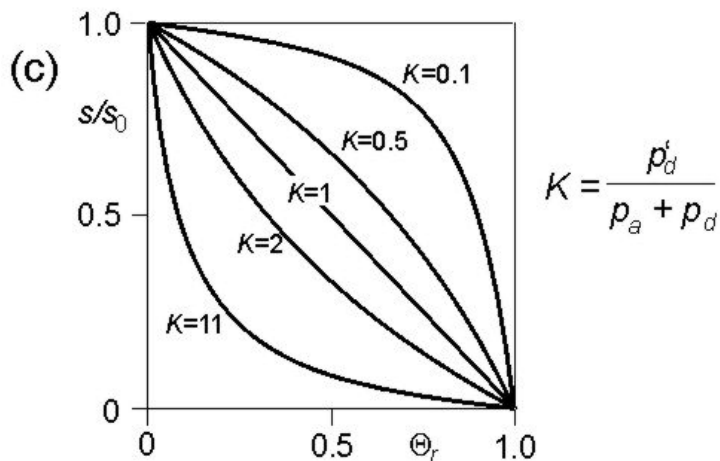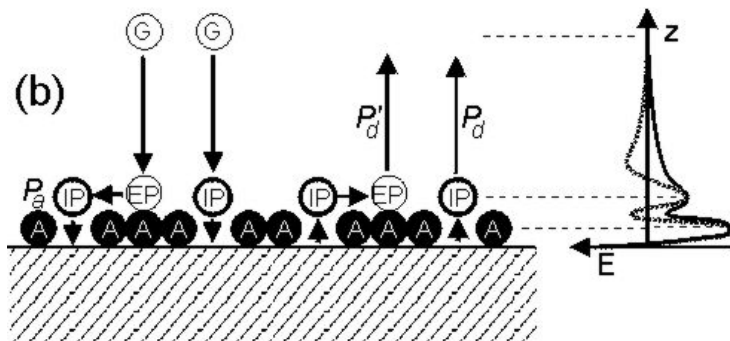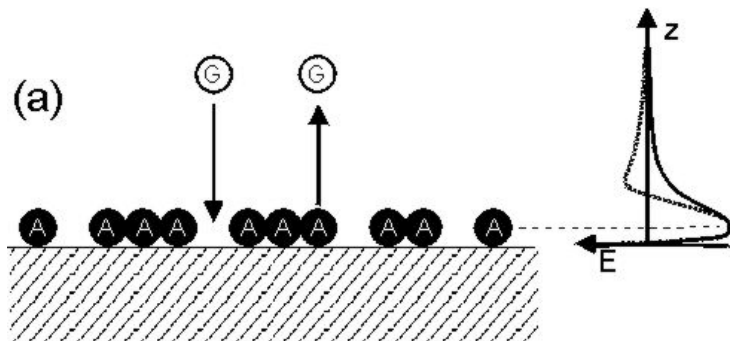v_n: the frequency factor for reaction order
n; n: reaction order.
I follow the convention that r_d is negative since $d\Theta/dt$ is negative for desorption.

$f(\Theta_r)$ describes the dependence of the sticking probability s on the coverage,
$$s = s_0 f(\Theta_r).$$

Langmuir:

Sticking only if unoccupied site is hit.

1st order (molecular): $f(\Theta_r) = 1 - \Theta_r$.

2nd order (dissociative): $f(\Theta_r) = (1 - \Theta_r)^2$.

Mobile precursor kinetics:

(G) may hit an empty site: *intrinsic precursor* state (IP) which may be mobile. It may transform into the adsorbate state (A) (probability P_a) or desorb (probability p_d).

(G) may hit an occupied site: *extrinsic precursor* (EP) which may migrate to an empty site and transform into an (IP) and adsorb (see above) or desorb directly (probability p_d').

Kisliuk: sticking behavior is determined K which depends on these probabilities only (P. Kisliuk, J. Phys, Chem. Solids, 3 (1957) 95).

If p_d' is small (stable (EP)), the sticking coefficient may be quite high almost until saturation ($\Theta_r = 1$).

1st order: $f(\Theta_r) = \dfrac{1 - \Theta_r}{1 + \Theta_r(K - 1)}$ with K>0.

K=1 corresponds to Langmuir case.

(W. Ranke, Y. Joseph, Phys. Chem. Chem. Phys. 4 (2002) 2483)

$$K = \frac{p_d'}{p_a + p_d}$$

Check of kinetics: determine $s(\Theta)$. Example: $H_2O/Si(001)$:
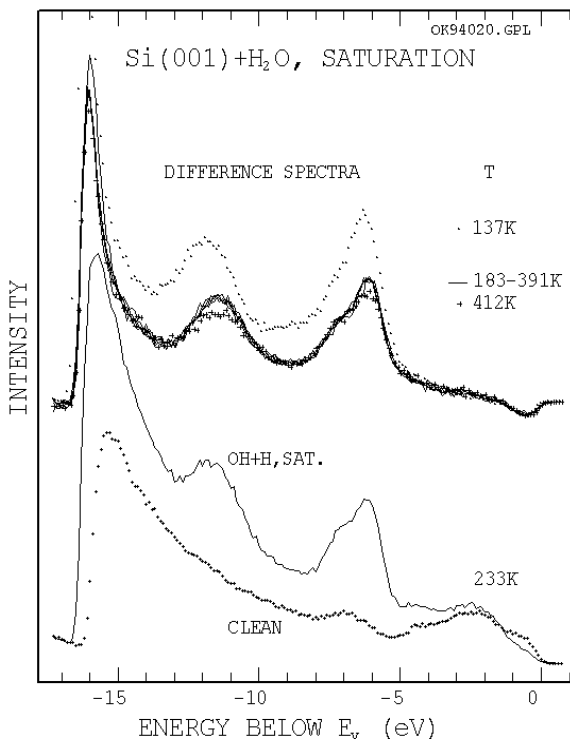
UP-spectrum ($h\nu=21.2$ eV) of Si(001), clean and after saturation with H_2O which adsorbs as OH+H. Equal species and saturation for $183 \leq T \leq 391$ K. At 137 K, condensation of H_2O occurs, at 412 K, saturation is not yet reached.
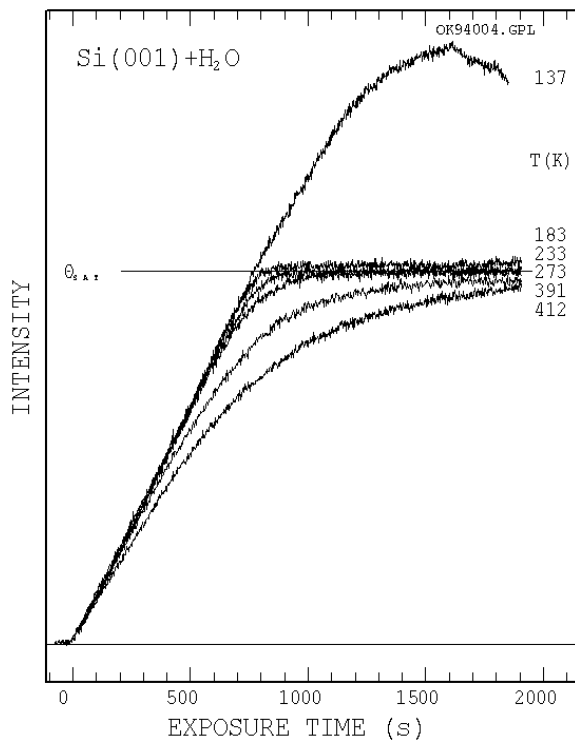
Adsorption curves. Intensity increase of the -6.2 eV peak of OH with exposure time for $p_{H2O}=2\times10^{-9}$mbar for the same values of T.
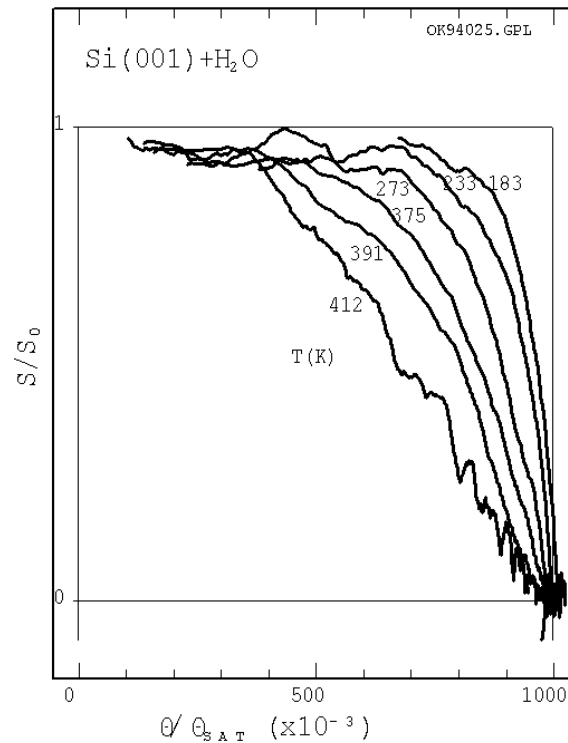
The first derivative of the adsorption curves represents the sticking coefficient $s(\Theta)$. The wiggles originate from pressure adjustments in the adsorption curves.

(W. Ranke, Surf. Sci. 369 (1996) 137)

In **adsorption-desorption equilibrium** we have $r_a + r_d = 0$.

We had $\qquad\qquad r_a = A(p,T) f(\Theta_r)$, $\quad r_d = -B(p,T)\, \Theta_r^n$.

Inserting and resolving for Θ_r yields the equations for isotherms/isobars:

Langmuir 1st order: $\qquad \boxed{\Theta_r(T,p) = \dfrac{b_1(T)\, p}{1 + b_1(T)\, p}} \qquad\qquad$ with $n = 1$, $\; f(\Theta_r) = 1 - \Theta_r$,

Langmuir 2nd order: $\quad \boxed{\Theta_r(T,p) = \dfrac{\sqrt{b_2(T)\, p}}{1 + \sqrt{b_2(T)\, p}}} \qquad\quad$ with $n = 2$, $\; f(\Theta_r) = (1 - \Theta_r)^2$.

Holds if the adsorption sites for the dissociation products are equivalent and for inequivalent sites as long as their site concentrations are equal.

Langmuir 2nd order adsorption, quasi-1st order desorption (dissociated species immobile):

$$\boxed{\Theta_r(T,p) = \frac{1 + 2\, b_1(T)\, p - \sqrt{1 + 4\, b_1(T)\, p}}{2\, b_1(T)\, p}} \qquad \text{with } n = 1,\ f(\Theta_r) = (1 - \Theta_r)^2 .$$

Kisliuk 1st order:
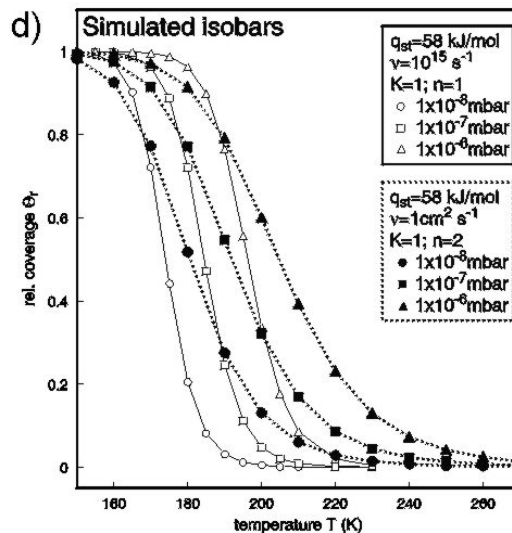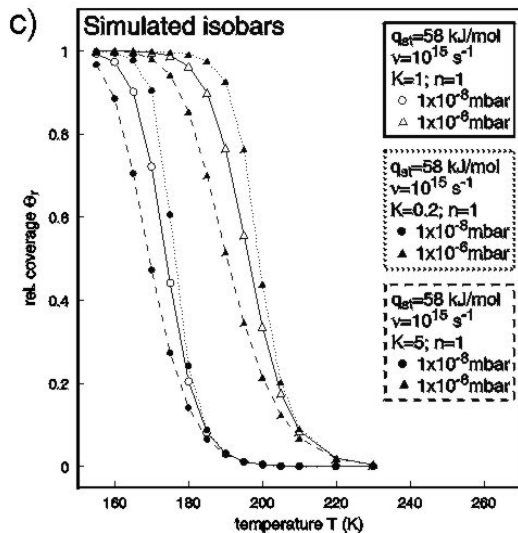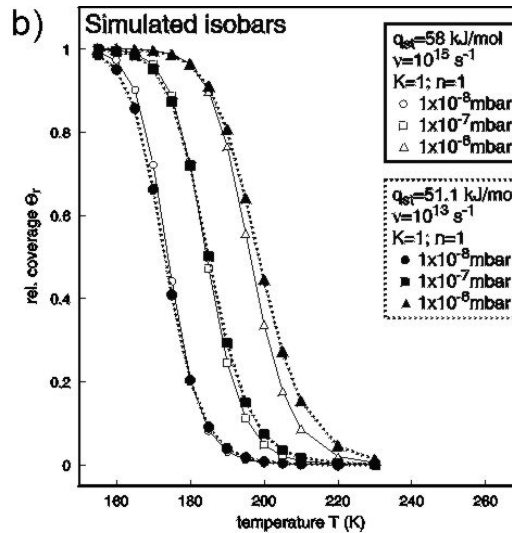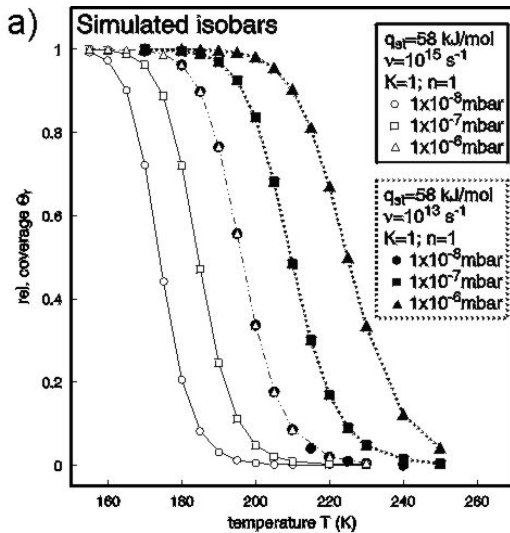
$$\boxed{\Theta_r(T,p) = \frac{1 + b_1(T)\, p - \sqrt{[1 - b_1(T)\, p]^2 + 4\, K\, b_1(T)\, p}}{2\, (1 - K)}}$$

with $n = 1$,

$$f(\Theta_r) = \frac{1 - \Theta_r}{1 + \Theta_r(K - 1)}$$

$$\boxed{b_1(T) = \frac{s_0 \exp(q_{st}/kT)}{v_1\, \sigma_A \sqrt{2\pi\, mkT}}} \qquad \boxed{b_2(T) = \frac{s_0 \exp(q_{st}/kT)}{v_2\, \sigma_A^2 \sqrt{2\pi\, mkT}}} \qquad \boxed{q_{st} = E_d - E_a}$$

What should these isobars look like?

Simulated isobars

a) q_{st}=58 kJ/mol; ν=10^{15} s^{-1}; K=1; n=1
○ 1x10^{-8} mbar
□ 1x10^{-7} mbar
△ 1x10^{-6} mbar

q_{st}=58 kJ/mol; ν=10^{13} s^{-1}; K=1; n=1
● 1x10^{-8} mbar
■ 1x10^{-7} mbar
▲ 1x10^{-6} mbar

b) q_{st}=58 kJ/mol; ν=10^{15} s^{-1}; K=1; n=1
○ 1x10^{-8} mbar
□ 1x10^{-7} mbar
△ 1x10^{-6} mbar

q_{st}=51.1 kJ/mol; ν=10^{13} s^{-1}; K=1; n=1
● 1x10^{-8} mbar
■ 1x10^{-7} mbar
▲ 1x10^{-6} mbar

c) q_{st}=58 kJ/mol; ν=10^{15} s^{-1}; K=1; n=1
○ 1x10^{-8} mbar
△ 1x10^{-6} mbar

q_{st}=58 kJ/mol; ν=10^{15} s^{-1}; K=0.2; n=1
● 1x10^{-8} mbar
▲ 1x10^{-6} mbar

q_{st}=58 kJ/mol; ν=10^{15} s^{-1}; K=5; n=1
● 1x10^{-8} mbar
▲ 1x10^{-6} mbar

d) q_{st}=58 kJ/mol; ν=10^{15} s^{-1}; K=1; n=1
○ 1x10^{-8} mbar
□ 1x10^{-7} mbar
△ 1x10^{-6} mbar

q_{st}=58 kJ/mol; ν=1cm^2 s^{-1}; K=1; n=2
● 1x10^{-8} mbar
■ 1x10^{-7} mbar
▲ 1x10^{-6} mbar

axes: rel. coverage Θ_r vs temperature T (K)

Assumption:
Langmuir 1st order (n = 1),
$\nu_1 = 10^{15}$ s^{-1},
$q_{st} = 58$ kJ/mol
(both independent of Θ,
data for ethylbenzene physisorbed
on FeO(111)). Pressures as indicated
a) comparison: ν_1 varied ($\rightarrow 10^{13}$ s^{-1});
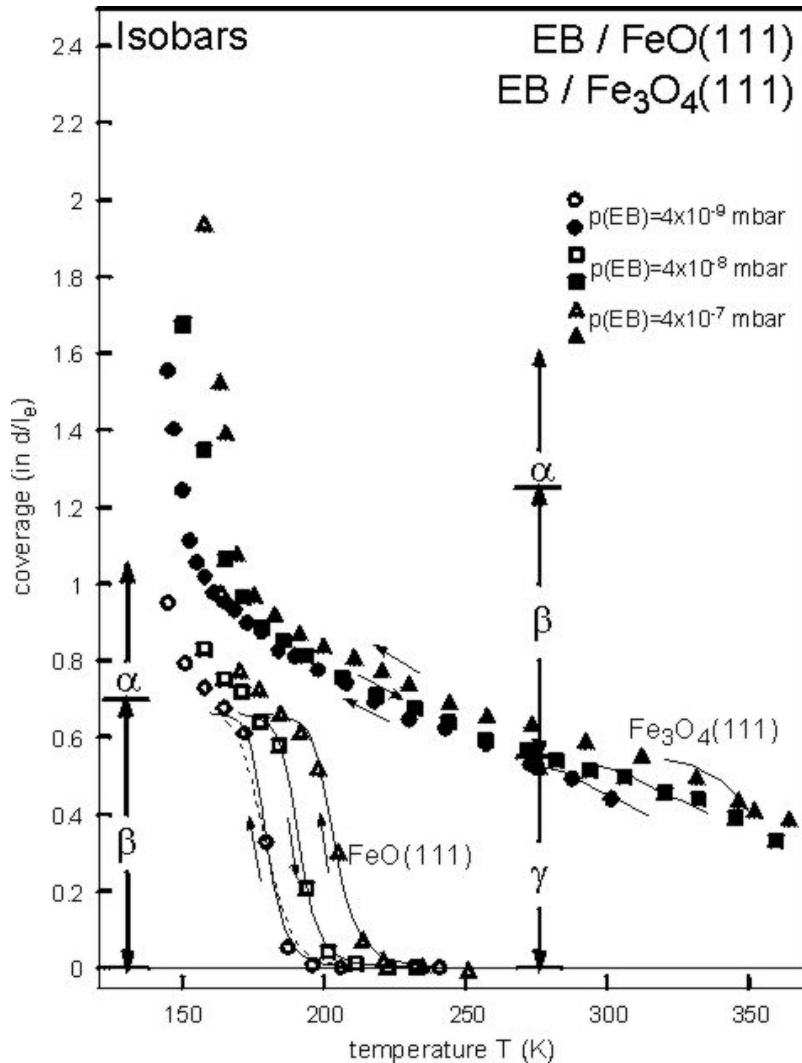*b) comparison: $\nu_1 \rightarrow 10^{13}$ s^{-1},*
* q_{st} adjusted to yield best-possible*
*   agreement;*
c) comparison: Kisliuk kinetics
*   (mobile precursor), K varied;*
d) comparison: Langmuir 2nd order.

(W. Ranke, Y. Joseph, Phys. Chem. Chem. Phys.
4 (2002) 2483).

Example: Ethylbenzene / FeO(111), Fe_3O_4(111)

Same measurement as shown above, lines: fitted isobars.

FeO(111),
β-range: q_{st} = 58 kJ/mol,
v_1 = 4.75x10^{14} s^{-1}.
Dotted: Langmuir 1st order gives too smooth curves.
Lines: Kisliuk 1st order, K = 0.2.

Fe_3O_4(111),
γ-range: q_{st} = 94...74 kJ/mol,
v_1 = 5x10^{12}...2x10^{10} s^{-1} (Θ-dependent);
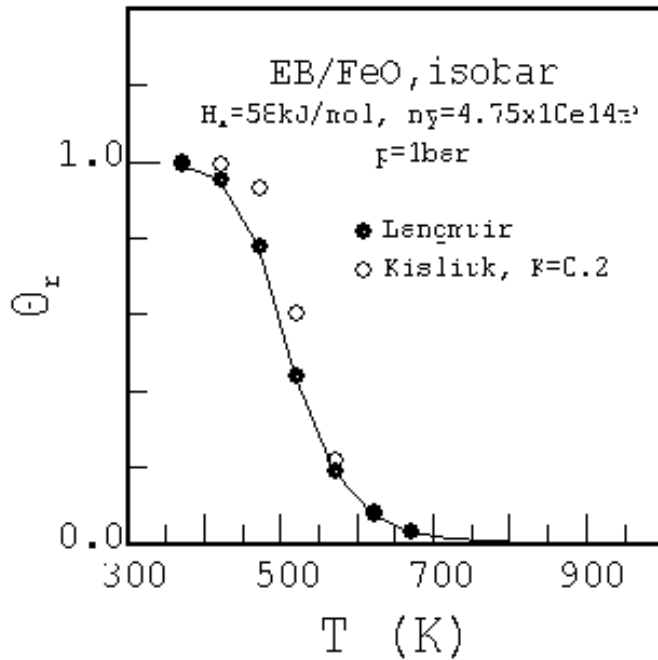*Langmuir or Kisliuk possible.*
β-range: Fit impossible
reason: phase transitions in adlayer.

(W. Ranke, Y. Joseph, Phys. Chem. Chem. Phys. 4 (2002) 2483).

What should these isobars look like?

Isobars for EB/FeO(111) for high pressure conditions,
extrapolated from data measured at low p, T:
Although $\Delta H_a = q_{st}$ is small,
Θ gets quite high if only p is high enough.

7.   The magnitude of ν: Entropy of the activated state
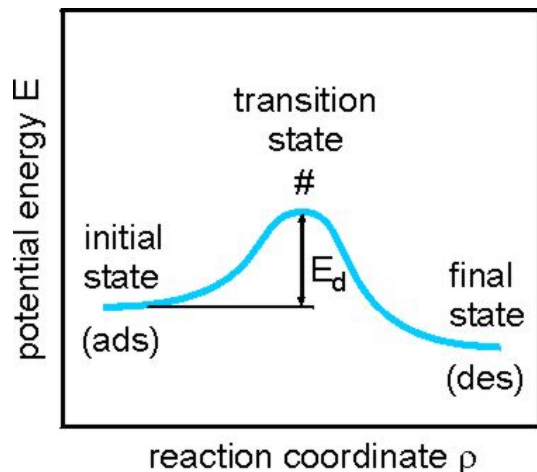
The transition state theory starts from the assumption that the molecule is in thermodynamic equilibrium with its environment, even during the desorption reaction.
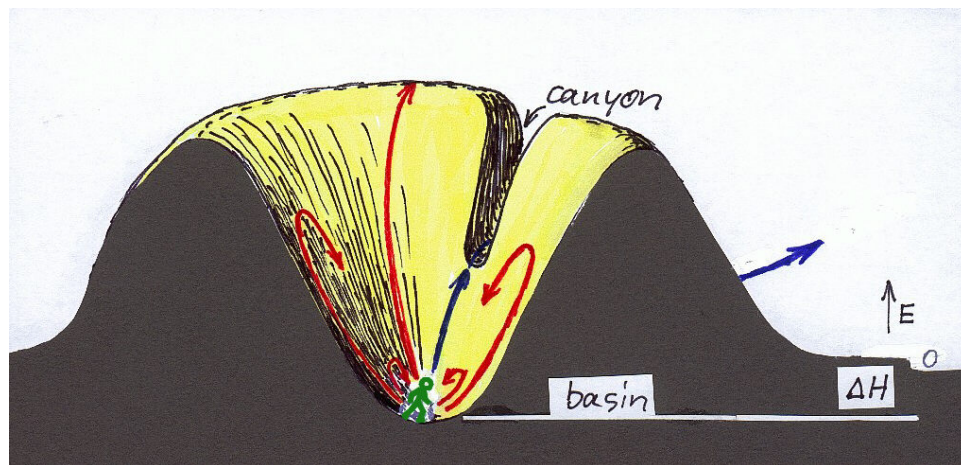
$\nu_{des} \sim$ probability to realize the transition state
dominating: Boltzmann factor $\exp(-E_d/kT)$;
determining: configuration (here restricted direction, rotation).

probability to realize a state:
partition function

It can be shown that
(for 1st order desorption)

$$\nu_{des} \approx \frac{kT}{h} \frac{q^{\#}}{q_{ad}} \approx \frac{kT}{h} \exp\left(\frac{\Delta S^{\#}}{R}\right)$$

partition functions
$q^{\#}$ in the transition state
q_{ad} in the adsorbed state

(see e.g. K. Christmann, Surface physical chemistry, Steinkopff, Darmstadt (1991), p.27ff).

If $\qquad q^{\#} = q_{ad}$, $\qquad\qquad \nu_{des} \approx 10^{13}$ s^{-1} $\qquad\qquad$ (T=300K).

If the adsorbed state is immobile and the transition state is mobile and may even rotate, $q^{\#}$ and consequently ν_{des} may get much larger.

If the transition state requires a complicated or "demanding" configuration which has a low probability of realization $q^{\#}$ and ν_{des} may get much smaller.

The agreement between measured and calculated values of ν_{des} is poor. Nevertheless, transition state theory gives an idea why ν_{des} values vary so strongly.

Experimentally, ν_{des} values between about 10^{10} s^{-1} and 10^{19} s^{-1} have been observed while values around 10^{13} s^{-1} do not appear to be especially probable.

Excursion: Partition function, probability and entropy

Partition function of a system: $\qquad\qquad q = \Sigma_i \exp(-\varepsilon_i / kT)$
$\qquad\qquad$ = sum over all possible states, weighted by $\exp(-\varepsilon_i / kT)$, the prob. of occupation (Boltzmann)
or $\qquad\qquad$ number of thermally accessible states at given T;
or $\qquad\qquad$ probability to „materialize" in the suggested arrangement or configuration
$\qquad\qquad$ ($\rightarrow$ entropy, $S=k \ln W$).

Quantum mechanically: Discrete states, different contribution to q at 300 K:
$\qquad\qquad$ Translation: densely spaced, $\Delta\varepsilon \approx 10^{-16}$ kT dominating in gas phase, zero in immob. ads.
$\qquad\qquad$ Rotation: less densely spaced, $\Delta\varepsilon \approx 0.1$ kT small in gas, usually zero in ads.
$\qquad\qquad$ Vibration: not densely spaced, $\Delta\varepsilon \approx 10$ kT very small in gas, dominating in ads.
$\qquad\qquad$ Electronic: separated $\qquad \Delta\varepsilon \approx 40$ kT virtually zero

Adsorbed state:
q much smaller than in gas
$\rightarrow$ compensation by
$\quad E_{ad}$ necessary

8. Further isotherms for monolayer and multilayer adsorption

8.1 Other isotherms / isobars for monolayer adsorption:

Isotherm	Advantages	Disadvantages
Langmuir	Best one-parameter isotherm	Ignores adsorbate-adsorbate interactions
Freundlich, Toth	Two parameters	No physical basis for equation
Multisite	Many parameters	Good for inhomogeneous surfaces. Wrong physics for single crystals
Tempkin Fowler Slygin-Frumkin	Account for adsorbate-adsorbate interactions in an average sense	Does not consider how the adsorbate layer is arranged
Lattice gas	Complete description of adsorbate-adsorbate interactions for commensurate layers. Predicts arrangement of adsorbed layer	Requires a computer to calculate isotherm. Assumes commensurate adsorption. Parameters used in the model are difficult to determine

(R.I. Masel, Principles of adsorption and reaction on solid surfaces, Wiley, New York (1996), table 4.1, p.246).

8.2   Multilayer adsorption: The BET isotherm (Brunauer-Emmett-Teller)

Multilayer adsorption with different ΔG_1, ΔG_m and
ΔG_1, ΔG_2, ΔG_m, respectively.
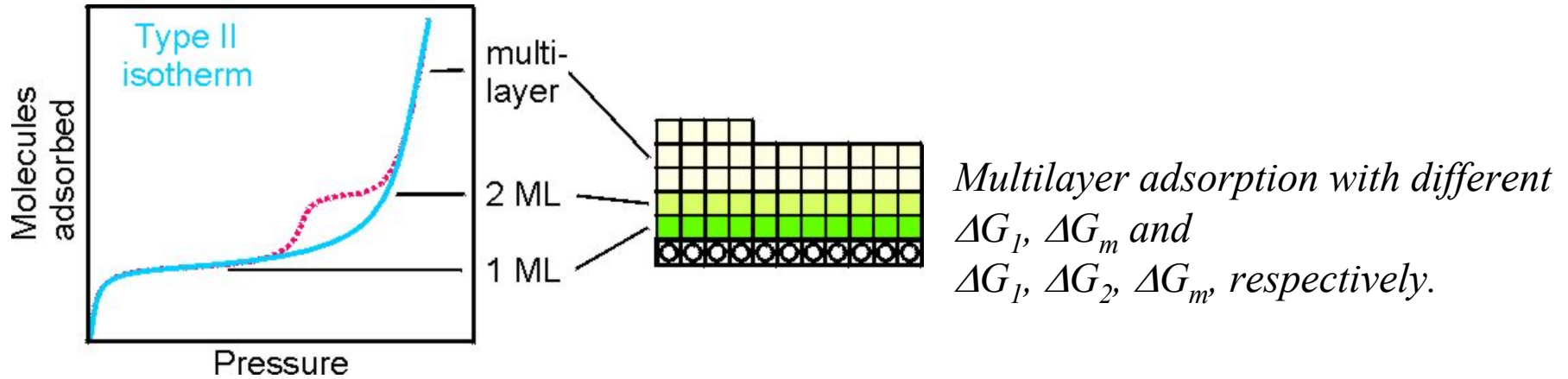
Either:

Consider each step in the isotherm separately with its own n, v, s_0, q_{st}, add isotherms
(e.g. Langmuir) for 1st, 2nd … layer. Problem: Multilayer condensation.

Or:

Develop an isotherm for multilayer adsorption: Brunauer-Emmett-Teller, BET-isotherm.

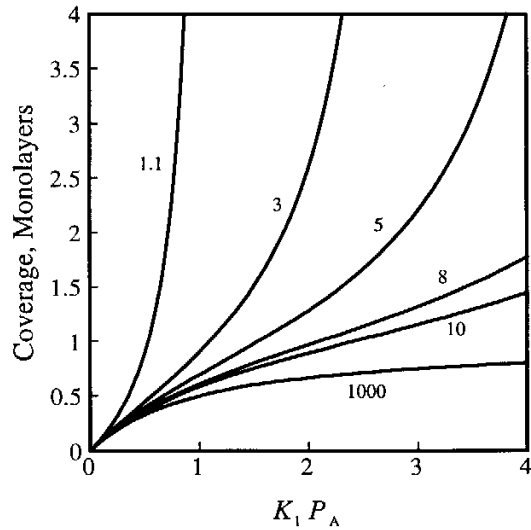$$\frac{V}{V_M} = \frac{c_B \, x_B}{(1 - x_B)\,[1 + (c_B - 1)\, x_B]}$$

(V : total volume of adsorbed gas; V_M : volume gas in 1st layer (monolayer saturation));

$$x_B = p/p_{sat}$$

(p the gas pressure and p_{sat} the saturation vapor pressure of the gas at the temperature of the measurement).

$c_B = K_1/K_m$ ratio of equilibrium constants for 1st layer and multilayer adsorption:

$$c_B = \frac{K_1}{K_m} = \frac{\exp(-\Delta G_1 / RT)}{\exp(-\Delta G_m / RT)} = \exp[-(\Delta G_1 - \Delta G_m)/RT]$$

A plot of adsorption isotherms predicted by the BET equation for various values of c_B.

(Masel fig. 4.30, p.302)

In fact, the BET isotherm does in general not very well fit measured isotherms.
However, in the environment of ML saturation it usually does.
If, however, ML.saturation can be unambiguously be identified in the isotherm
by step structure, the ML capacity can directly be taken from the isotherm.

Remember these terms:

adsorption-desorption equilibrium,

isotherm, isobar, isosteric heat of adsorption;

rates of adsorption and desorption,

order of adsorption and desorption.,

frequency- or pre-factor;

Langmuir adsorption, mobile precursor;

transition state;

BET isotherm.