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3. Adsorption, Desorption, and Catalysis

This chapter deals with fundamental aspects of the interaction of a solid body with its environment, namely the interaction between mobile atoms or molecules from the gas or liquid phase with the surface of the solid body. Following a logical sequence we will first study how a molecule gets into contact with the surface and eventually binds to it (adsorption.) Thereafter, we will look at the reversed process: The energetics and kinetics of desorption. Finally, we will take a look at the chemistry that can happen in between adsorption and desorption (heterogeneous catalysis). Note that the huge technical importance of catalysis is one of the big driving forces for the whole field of surface science.

3.1. Adsorption

Adsorption is the process by which a molecule (an adsorbate) originating from the gas phase (or the liquid phase) forms a bond to the surface of a solid (the substrate).
According to the type of bonding between the adsorbate and the substrate, two broad classes of adsorption processes are distinguished: Physisorption and Chemisorption. Over-simplified, physisorption is weak and chemisorption is strong

Physisorption

Physisorption denotes the case of weak adsorbate-substrate-interaction due to van-der-Waals forces. Van-der-Waals-interaction (attraction of transient electrical dipoles) is always present between two molecules („Materie hat sich lieb"). For a molecule interacting with an extended surface the vdW-potential has the following form: *

minimum of potential well

Pauli repulsion

vdW-attraction

$$V(z) = 4\pi\varepsilon N_{surf}\,\sigma^3\left[\frac{1}{45}\left(\frac{\sigma}{z}\right)^9 - \frac{1}{6}\left(\frac{\sigma}{z}\right)^3\right]$$

height perpendicular to surface

$\frac{\text{surface atoms}}{\text{unit area}}$

$\sigma = 2^{-\frac{1}{6}} r_m$, the equilibrium distance

This function is depicted in $\boxed{\text{Fig. 3.1.}}$
The typical binding energies for this kind of interaction are 10-100 meV, typical bond lengths are 3-10 Å. The classic example of physisorption are noble gases on metals, see $\boxed{\text{Fig 3.2}}$

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Chemisorption

In the case of chemisorption, a much stronger interaction between the adsorbate and the substrate takes place. The interaction can be covalent, ionic, or metallic (we will take a more detailed look at the resulting changes in the electronic structure later. Here, typical binding energies are 1-10 eV and typical bond distances are ≈ 1 Å (Remember: Nature does not care what we call her.)

* Note: You may be more familiar with this form: $V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$. This is the formula for two particles which yield the above via summation over half space.

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Dissociative chemisorption

Now we will get a first glimpse on how the surface can induce chemical reactions, i.e. how catalytic activity can happen: The redistribution of charge in a molecule in order to form new bonds in chemisorption can lead to a weakening or disruption of existing bonds. As a consequence, molecules can dissociate upon adsorption. This is illustrated in Fig 3.3 for the dissociative adsorption of a diatomic molecule. For simplicity, a potential similar to the van-der-Waals case is shown also for the chemisorbed species. Note that there is almost always a physisorbed precursor state before chemisorption. Depending on the height of the potential barrier separating the physisorbed and the chemisorbed state, we distinguish activated dissociation (barrier $\varepsilon_a > \varepsilon_d$, the energy barrier for desorption) and non-activated dissociation ($\varepsilon_a < \varepsilon_d$). A typical example for non-activated dissociation is the adsorption of H_2 on metals.

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Sticking coefficient

In the potential diagrams shown in Fig 3.3. the only coordinate used to describe the adsorbing molecule is the height above the surface z. This is of course a strong oversimplification of the process. For a full description, also other degrees of freedom have to be taken into account, namely the lateral position, the orientation

of the molecule, and rotational and vibrational excitations. As all these properties follow well defined distribution functions, it is possible to introduce an overall <u>sticking coefficient</u> to describe the problem.

Definition: $S = \dfrac{\#\text{ of adsorbing molecules}}{\#\text{ of impinging molecules}}$

The sticking coefficient depends on temperature and coverage. Coverage is defined as:

$$\Theta = \frac{N_{ads}}{N_{surface}}$$

N_{ads} ← # of adsorbed molecules

$N_{surface}$ ← # of adsorption sites

Note: Frequently, $N_{surface}$ is equal to the number of surface atoms. However, this is not necessarily the case (e.g. very big adsorbates)

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Kinetics of adsorption

Given the sticking coefficient, it is possible to define a <u>rate of adsorption</u>:

$$\left.\frac{d\Theta}{dt}\right|_{Ads} = \frac{S \cdot \phi}{A_{ads}} \underbrace{(1-\Theta)}_{\text{probability to hit free spot}} = \frac{S}{A_{ads}} \cdot \frac{P}{\sqrt{2\pi m k T}} (1-\Theta)$$

ϕ: impingement rate

A_{ads}: area of an adsorption site

$\sqrt{2\pi m k T}$: from kinetic gas theory

Integration yields:

$$\Theta = 1 - e^{-\frac{p \cdot t \cdot S}{A_{ads}} \Big/ \sqrt{2\pi m k T}}$$

This equation can be used to determine S experimentally, see Fig. $\boxed{3.4}$

It is sometimes convenient to put all dependencies except the pressure into one term and simply write:

$$\left.\frac{d\Theta}{dt}\right|_{ads} = k_{ads} \cdot p \cdot (1-\Theta)$$

For dissociative adsorption, two free sites have to be provided for one adsorbing molecule, so the above equation becomes:

$$\left.\frac{d\Theta}{dt}\right|_{ads} = k'_{ads} \cdot p \cdot (1-\Theta)^2$$

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