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5.1 Chemisorption

5.1.1 Principles of Chemisorption

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5.1.1.1 Introduction

The term chemisorption was coined in order to classify the interaction between a particle in the gas phase and a solid surface, i.e. the result of the adsorption process [1]. If the interaction leads to the formation of a chemical bond the adsorbate formed is called a chemisorbate. Where chemical bond formation is not important the process is classified as physisorption. There are several conceptual problems with such a differentiation which we briefly address in the following, and which indicate that a more detailed look at the entire process of adsorbate formation is needed before a reliable classification may be carried out. In fact, as it turns out, for a conclusive classification one would need the full theoretical and experimental understanding of the system under investigation. Such an approach must include the static aspects, i.e. the energies involved, as well as the dynamic aspects, i.e. the processes involved in the formation of the adsorptive interactions.

Irving Langmuir in 1916 introduced and investigated the idea that there can exist strong, short-range forces between adsorbates and a substrate [2, 3]. Previously, it

was generally believed that more or less unspecified long-range forces - we would today call this physisorption - draw gases towards a solid. Langmuir, shortly after the introduction of the concept of an ordered lattice for the arrangement of the atomic constituents of a bulk solid by von Laue [4], considered an arrangement of atoms at the surface, a surface lattice, that defines a specific density of adsorption sites. Atoms from a gas phase, for example, striking the surface may either bounce back into the gas phase or establish a bond to one of these sites. This process is equivalent to the formation of a surface chemical bond and was termed chemisorption [5-7]. Chemisorption lowers the free energy of the closed system containing the uncovered, "clean" surface and atoms or molecules from the gas phase. This lowering in energy can be measured via calorimetry or - less well defined - by a Clausius-Clapeyron analysis of isostere data. It was therefore tempting to differentiate chemisorption with respect to physisorption via the energy that is deliberated in bond formation [1]. Such a definition involves a limiting energy which separates chemisorption and physisorption regimes. It was put in the neighborhood of 40 kJ mol^{-1} [1]. Obviously, such a definition is rather artificial, and today one generally disregards this kind of differentiation solely on the basis of the enthalpy of formation. The accepted definition of chemisorption today is independent of thermochemical data and rests on the concept of a short-range chemical bond, which only forms when there is direct intermingling of the substrate and the adsorbate charge densities. In order then to differentiate between chemisorption and physisorption one has to understand the electronic structure of the system [6, 8]. Experimentally, this means that we cannot rest the definition on a single measurement of the heat of adsorption but rather on an as complete as possible spectroscopical characterization of the surface interacting with the adsorbate in comparison with the same measurements of the separated systems.

The interaction between say a gas phase, containing molecules AB, and a surface is discussed by considering various aspects of the process of AB-surface bond formation. We cover the dynamic aspects connected with the sticking of AB such as its dependence on the

population of internal and external degrees of freedom of AB in the collision, mobility on the surface, i.e. surface diffusion etc., and the energetics, which will be the starting point, all as a function of the surface coverage. We shall discuss associative versus dissociative chemisorption and its dependences on surface structure. Consideration of coadsorption and cooperativity in the adsorption process is as important as invoking the structure of the adsorbate, as well as the restructuring of the surface as it interacts with an adsorbate.

5.1.1.2 Thermodynamics and Energetics

As this point it is important to differentiate between macroscopic and microscopic surface phenomena. Surface phenomena can be treated macroscopically by chemical thermodynamics, in which atomic concepts are not neccessary. Accordingly, the thermodynamic relationships can be derived on the basis of pressure, volume, surface area, composition, and temperature, which can be measured in a straightforward manner. Historically, therefore, the thermodynamic approach was pursued first. Before discussing the atomic aspects of the energy content of an adsorbate phase we shall briefly summarize the important thermodynamic aspects noting, however, that this cannot be a comprehensive treatment. For the latter we refer to the literature [1, 7, 9-12].

Consider an adsorbate phase consisting of n_a moles of a nonvolatile adsorbent (surface) and n_s moles of an adsorbate (gas phase). They are assigned internal energy U, entropy S and volume V. The surface A of the adsorbent is assumed to be proportional to the adsorbent volume. The Gibbs fundamental equation for the full system is then

$$dG = -S dT + V dP + \mu_a dn_a + \mu_s dn_s \qquad (1)$$

For the pure adsorbent,

$$\mathrm{d}G^{\mathrm{o}} = -S_{\mathrm{a}}\,\mathrm{d}T + V_{\mathrm{a}}\,\mathrm{d}P + \mu_{\mathrm{a}}^{\mathrm{o}}\,\mathrm{d}n_{\mathrm{a}} \tag{2}$$

Consequently, for the interacting adsorbate-adsorbent system, the difference $dG^s = dG - dG^o$ gives

$$\mathrm{d}G^{\mathrm{s}} = -S_{\mathrm{s}}\,\mathrm{d}T + V_{\mathrm{s}}\,\mathrm{d}P + \Phi\,\mathrm{d}n_{\mathrm{a}} + \mu_{\mathrm{s}}\,\mathrm{d}n_{\mathrm{s}} \qquad (3)$$

where $S_s = S - S_a$, $V_s = V - V_a$, and $\Phi = \mu_a - \mu_a^o$. Using the above mentioned proportionality between adsorbent volume and adsorbent surface,

$$\Phi \,\mathrm{d}n_{\mathrm{a}} = f \Phi \,\mathrm{d}A \tag{4}$$

where f is a proportionality factor, the surface tension φ is given by

$$f\Phi = \varphi = \left(\frac{\partial G^{s}}{\partial A}\right)_{T,P,n}$$
(5)

which has the dimension of a two-dimensional pressure. This leads to the final equation

$$\mathrm{d}G^{\mathrm{s}} = -S_{\mathrm{s}}\,\mathrm{d}T + V_{\mathrm{s}}\,\mathrm{d}P + \varphi\,\mathrm{d}A + \mu_{\mathrm{s}}\,\mathrm{d}n_{\mathrm{s}},\tag{6}$$

This equation refers to a system where the adsorbate resides on a truly inert substrate. In other words, eq 6 can only rigorously be applied to weakly interacting physisorbate systems. For chemisorbates this equation is not strictly applicable because the thermodynamic parameters of adsorbate and adsorbent cannot be separated.

Bearing this restriction in mind, and assuming that the adsorbate phase is in equilibrium with the gas phase, a Clausius-Clapeyron analysis yields

$$\left(\frac{\partial \ln P}{\partial T}\right)_{\varphi} = \frac{(s_{g} - s_{s})}{RT} = \frac{(h_{g} - h_{s})}{RT^{2}} = -\frac{\Delta h_{ads}}{RT^{2}}$$
(7)

where we have changed to molar quantities s, v, and the enthalpy h. The slope of a semilogarithmic plot of the equilibrium pressure versus the inverse temperature at constant φ yields the adsorption enthalpy, Δh_{ads} , released upon adsorption of one mole of gas. The problem, of course, arises because the surface tension is hard to determine in general. However, the problem may be circumvented by considering the so-called surface coverage Θ instead:

$$\Theta = \frac{n_{\rm s}}{n_{\rm a}} \tag{8}$$

and resorting to partial molar quantities, e.g.

$$\tilde{v}_{s} = \left(\frac{\partial v}{\partial n_{s}}\right)_{T,P,n_{s}}$$
(9)

Then, a similar Clausius-Clapeyron analysis leads to

$$\begin{pmatrix} \partial \ln P \\ \partial T \end{pmatrix}_{\Theta} = \frac{(s_{g} - \tilde{s}_{s})}{RT} = \frac{(h_{g} - \tilde{h}_{s})}{RT^{2}} = \frac{-q_{st}}{RT^{2}}$$
(10)

where q_{st} is the isosteric heat of adsorption. This quantity can be measured quite easily because constant coverage is not too difficult to establish experimentally. However, q_{st} represents the difference between molar enthaply in the gas phase and partial molar enthalpy in the adsorbed phase, a quantity not easily connected to microscopic considerations.

In order to directly see how the isosteric heat of adsorption is measured, eq 10 is written in the form

$$\frac{\mathrm{d}P}{P} = \begin{pmatrix} -q_{\mathrm{st}} \\ RT^2 \end{pmatrix} \mathrm{d}T \tag{11}$$

and integrated for a reasonably small pressure and temperature interval so that we can assume the isosteric heat to be constant. This yields

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{q_{\rm st}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{12}$$



Figure 1. Determination of the isosteric heat of adsorpton from the measurement of adsorption isotherms for the system Xe/ Ni(100) [13].

for two pairs of temperatures and pressures that produce the same surface coverage. For true equilibrium conditions, a straight line with negative slope should be obtained for the semilogarithmic plot, which in turn yields the isosteric heat of adsorption. Repeating this procedure for various coverages allows the coverage dependence of the heat of adsorption to be determined. It is obvious that the isosteric heat is a differential quantity, in contrast to the equilibrium heat of adsorption. Both are, of course, isothermal quantities. From the differential heats of adsorption the integral heat of adsorption can be obtained as

$$Q_{\rm integr} = \int_{0}^{n_{\rm s}} q_{\rm st} \, \mathrm{d}n_{\rm s} \tag{13}$$

In the following we present an example of isosteric heat determination [13]. Figure 1 shows, in the upper panel, a set of four isotherms for the physisorption system Xe/Ni(100). The second panel contains the data set in the upper panel as a plot of $\ln p_{Xe}$ versus reciprocal temperature for various values of Θ_{Xe} . From the shape of the individual straight lines the isosteric heat has been determined and plotted in the third panel as a function of Θ_{Xe} . From the plot we see that the isosteric heat slowly varies with temperature, the decrease indicating repulsive interactions.

As mentioned above, the application of an isosteric heat analysis to a chemisorption system is rather problematic, because inherently the analysis starts from the



Figure 2. Schematic drawing of the spherical calorimeter [19].

assumption of truly separable subsystems. Therefore, for such systems it is more appropriate to resort to a direct calorimetric measurement of the adsorption en-thalpy. Until very recently, it has not been possible to undertake such measurements for thin-film systems [1, 14-19]. The reason was that the increase in temperature of the calorimeter depends on the heat capacity of the system and the absolute number of adsorbed particles. The most complete set of data for such thinfilm systems has been reported by Wedler and coworkers [1, 20]. They used the so-called "spherical calorimeter" shown in Fig. 2 [17]. Briefly, the calorimeter sphere is located inside an ultrahigh-vacuum glass recipient and temperatures change of less than 10⁻⁵ K are registered with a thermometer connected to the calorimeter sphere. The metal film is evaporated onto the sphere and gas is admitted. The change in temperature measured by the thermometer surrounding the calorimeter sphere upon gas exposure is plotted versus time in Fig. 3. The heat of adsorption is determined from the integral of the T versus t curve. The example here is the adsorption of H₂ onto a Pd film [21]. Converting the temperature-time curve into a heat of adsorption yields 88 kJ mol^{-1} [21].

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Figure 3. Temperature-time curve of a calorimetric measurement for the system H_2/Pd [21].

In Table 1 are assembled the heats of adsorption for various absorbate systems on different substrates determined via isosteric heat measurement as well as calorimetric measurements. In some cases the heat of adsorption for one system has been measured using different techniques. This allows an estimation of the error involved in using those values based on different measurements. It is clear that the value for CO adsorption on Fe, for example, is considerably higher than values for other CO-adsorbate systems. In order to judge this, it must be understood that at room temperature CO partly dissociates on polycrystalline Fe which contributes to the observed calorimetric value. This is a useful reminder that consecutive processes have to be considered in calorimetric measurements.

King and co-workers have recently extended calorimetric measurements to single-crystal surfaces by applying molecular beam techniques in combination with IR radiation emission measurements (Fig. 4) [23, 38, 46-48]. There are three important parts of the experiment. First, there is a molecular beam source to provide accurate determination of coverage. Secondly, the sample consists of a unsupported single-crystal thin film to reduce the thermal mass to a minimum. Finally, an infrared detector is used to sense the heat radiated as the gas adsorbs. In order to reduce white noise experiments are performed using a pulsed molecular beam, which must be capable of producing a significant enthalpy change per pulse upon adsorption. A set of results is included in Table 1 where it is compared with results from other thermodynamic measurements. It is interesting to note that the results for the single crystal surfaces are situated in the region of those determined for the polycrystalline films, indicating that the latter consist of many crystallites exposing low-index planes.

The free enthalpy of adsorption is determined by the enthalpy as well as the entropy of adsorption. The entropy of adsorption, which is the quotient of the reversibly exchanged heat and the temperature, may be calculated from the equilibrium heat of adsorption, if the surface tension is known, or from the isosteric heat of adsorption. Prerequisite is the knowledge of the corresponding equilibrium gas pressure. Table 2 collects typical values for the entropy of adsorption of several adsorbate systems.

The number of values available is much smaller than for the enthalpies of adsorption. The interpretation of entropies is considerably more involved than the interpretation of enthalpies. Often the observed values and, in particular, the coverage dependences, cannot be reconciled on the basis of theoretical predictions. It appears that the predictions as to how the various degrees of freedom of the adsorbate contribute are not accurate enough to date. However, in most cases large entropy values are found when the mobility of the adsorbate was expected or known (from other methods) to be large.

However, the most popular method by which to deduce the heat of adsorption of an adsorbate system is thermal desorption spectrometry (TDS) [53-57]. A schematic setup for a TDS measurement is shown in Fig. 5 [58]. The sample is heated resistively and the temperature is monitored by a thermocouple. If the sample is a single crystal it responds rather rapidly to heating so that relatively high heating rates may be used. The concentration of desorbing species is measured with a quadrupole mass spectrometer (QMS). Pumping capacity is important in thermal desorption, because only if it is high enough, readsorption of the desorbing species back onto the surface is excluded. If the pumping speed is infinitely high we can ignore readsorption and the change in adsorbate coverage per unit time; a measure for the desorption rate (r_{des}) , is given by the Wigner-Polanyi equation [7, 59]:

$$r_{\rm des} = -\frac{d\Theta}{dt} = k_{\rm des}\Theta^n$$
$$= \nu(\Theta)\Theta^n \exp\left\{-\frac{E_{\rm des}(\Theta)}{RT}\right\}$$
(14)

where $T = T_o + \beta t$. This is the basis for the analysis of thermal desorption spectra.

Figure 6 schematically shows a set of TD spectra for various initial coverages Θ_0 and a given heating rate β [7, 58]. The first step is the integration of the spectra starting from highest temperature, i.e. coverage $\Theta = 0$, to a given coverage Θ' , say 0.15. This yields a pair of (r, T) values for each initial coverage larger than $\Theta' = 0.15$. A plot of $\ln r$ versus 1/T yields $E_{des}(\Theta')$ from the slope and $v(\Theta')$ from the intercept, which is given by $n \ln \Theta' + \ln v(\Theta')$, if the order *n* of the desorption reaction is known. However, for coverages above 0.1, the second term is much larger than the first,

Adsorbate	Substrate	q (kJ mol ⁻¹)	Remarks	References	
<u> </u>	Ni(111)	111 (±5)	WF ¹⁾	22	
0	()	130	Microcalorimetry	23	
	Ni(100)	125 (0+5)	WF	24	
	11(100)	115	TDS^{2}	25	
		119	TDS	26	
		138	TDS	27	
		109	isosteric Ead	28	
		123	isosteric E _{ad}	24	
		130	isosteric E_{ad}	29	
		134	isosteric E_{ad}	30	
		123	Microcalorimetry	23	
	Ni(110)	133	Microcalorimetry	23	
	Pd(100)	150 (+5)	WF	31	
	10(100)	$161 (\pm 8)$	WF. TDS. LEED	32	
	Pd(111)	$142 (\pm 3)$	WF	33	
	$P_{11}(0001)$	$160 (\pm 10)$	WF	34	
	$\mathbf{P}_{11}(1010)$	$150 (\pm 10)$ 157 (±10)	Contact-not., TDS	35	
	$C_{\rm w}(100)$	$58 (\pm 10)$	WF	36	
	$E_{0}(111)$	325	273 K (dissociative)	37	
	Fc(111)	200	195 K (partially diss.)	37	
	Fe(111)	100	(not dissociative)	20	
60 M	re(111)	100	Microcalorimetry	38	
CO/K	NI(100)	300	195 K (dissociative)	37	
CO_2	FC	$963(\pm 5)$	WF	39	
H_2	NI(100)	$90.3(\pm 3)$	WF	39	
	Ni(110)	$90.0(\pm 5)$	WE	39	
	NI(111)	$90.3(\pm 3)$	WI	40	
	NT:	85 (±3) 75 176			
		20.170 89 (±5)	WF	41	
	Pd(111)	$103 (\pm 5)$	WE	42	
	Pa(110)	$103 (\pm 3)$ $102 (\pm 5)$	WE	41	
	Pd(100)	$102 (\pm 3)$	WE TOS	43	
	Rh(110)	$92 (\pm 3)$	W1, 1D5	44	
	Ru(1010)	80 (±5)		45	
	$C_{0}(1010)$	$80 (\pm 3)$		10	
	Ta	100.1			
	W	100.1			
	Cr	100.1		1	
	Fe	155.0	dissociative (273 K)	20	
	Fe	100		37	
	Fe	97 (±3)		21	
	Pd	80/90		1	
Na	W	133.8		î	
Cs		207.3	IP(300K)	•	
0	Ni(100)	532 (±5)	$\frac{1}{100} \frac{1}{100} \frac{1}$		
		≈432	IK (100 K)	23	
		532 (±5)		23	
	Ni(111)	470 (±15)		25	
	Ni(110)	498 (±5)	272 V	20	
O ₂ /CO	Fe(111)	490	2/3 K	20	

Table 1. Enthalpies of adsorption.

1) WF, work function; 2) TDS, thermal desorption spectroscopy

so the latter may be neglected without large errors. It should be noted that there are methods to determine the order rigorously. This analysis, called the "complete analysis" was first proposed by King in 1975 [55]. The preexponential factor $v(\Theta)$ can be regarded as representing the frequency of attempts of the adsorbed particle to escape the chemisorptive potential. The values determined vary by at least four orders of magnitude, from 10^{12} to 10^{16} s^{-1} [7]. If we adopt the simplest picture and set $\nu(\Theta)$ equal to the frequency of vibration of the adsorbed particle, values near 10^{13} s^{-1} are expected. The problems become even more involved if we consider the number of successful attempts, i.e. after multiplication of $\nu(\Theta)$ by the exponential in eq 14. Here, the activation energy for desorption $E_{\text{des}}(\Theta)$ comes into play; both $\nu(\Theta)$ and



Figure 4. Schematic drawing of the setup for microcalorimetric measurements on single crystals [46].



Table 2. Entropies of adsorption.



Figure 5. Schematic drawing of the experimental setup for a thermal desorption expriment.

 $E_{des}(\Theta)$ depend on coverage. These coverage dependences partly compensate each other for certain systems in the sense that high values of $v(\Theta)$ are associated with large values of E_{des} [7]. This has to be considered when dealing with predictions and interpretations of desorption rates. It is therefore important to resort to a complete or close to complete analysis of desorption data. Simplified analyses were published much earlier. The most popular one is the so-called Redhead analysis, based on the peak maximum temperature observed in a thermal desorption spectrum [54]:

$$E_{\rm des} = RT_{\rm max}[\ln(\nu T_{\rm max}/\beta) - 3.46]$$
 (15)

It results in reliable values only for first-order desorption and provided that a reliable value for v is available. The Redhead equation can be directly derived from the Wigner-Polanyi equation by determining the temperature derivative of the rate, and realizing that it must vanish at the peak maximum temperature [7]. Additional procedures are given in the literature [58, 60-63]. In connection with the initial question concerning the heat of adsorption, it must be realized that the desorption energy may be directly related to the heat of adsorption if adsorption is a nonactivated process. In other words the adsorption process is, energetically, continuously "downhill". A detailed understanding, however, necessitates an understanding of the dynamics of adsorption.

A connection exists between the phenomenological view of the energetics from the standpoint of thermodynamics, and the microscopic view of adsorbate energetics. In this context the question as to whether a process is activated or nonactivated may already have been answered.

This approach goes back to Lennard-Jones who discussed adsorption energetics in a landmark paper in 1932 applying a quasi-one-dimensional approach [64]. Neglect for the moment all problems connected with the question as to how a gas-phase particle is actually trapped in a bound state at the surface of a solid, and simply consider the interaction potential between the gas-phase particle and a surface. Figure 7(a) shows the well known Lennard-Jones potential energy diagram. It represents the superposition of attractive (longer range) and repulsive (short range) forces according to

$$E(z) = -Az^{-6} + Bz^{-12}$$
(16)

where A and B are empirical constants and z is the distance between the adsorbed particle and the surface. To describe this interaction on the basis of ab initio



Figure 6. Determination of the desorption energy E_{des} from a model-independent analysis of thermal desorption data. The analysis is carried out for an artificially chosen coverage of $\Theta = 0.15$: (a) TDS data; (b) integration of the TDS data to give Θ versus T plots; (c) plot of $\ln d\Theta/dt$ versus 1/T to determine E_{des} according to eq 14. The basis for the diagram are data for Ag/Ru(0001) [58].



Figure 7. Schematic potential energy diagrams for a molecule AB approaching a surface: (a) associative chemisorption (E_{ads}) ; (b) associative chemisorption $(^2E_{ads})$ with precursor $(^1E_{ads})$; (c) dissociative chemisorption $(^dE_{ads})$ with molecular precursor $(^mE_{ads})$.

quantum mechanical calculations it would be necessary to consider a semiinfinite solid interacting with an atom or a molecule. This can be done in favorable, simple cases using various approaches [65-68]. The most prominent one, at least for metal surfaces, is the density functional approach with which one can come close to the exact solution [65, 67]. Another approach is the so-called embedded cluster ab initio approach where the solid surface is represented by a cluster of atoms, augmented by an embedding scheme to represent more accurately the infinite extension of the twodimensional system [68]. Assume for the moment that this problem has been solved. Then, the potential energy curve in Fig. 7(a) represents the case where the particle incident from the gas phase "sees" a continuously "downhill" energy change until it reaches the equilibrium position at z_0 . (Note that, for the present, the dynamics of the trapping process is being reglected.) In such a case the desorption energy, as determined from thermal desorption data, is equivalent to the heat of adsorption. It is this situation that is often considered for associative molecular adsorption. However, the situation becomes more difficult if either a molecule which is associatively adsorbed may assume different adsorption geometries on the surface, or the molecule may dissociate upon adsorption and - to increase complexity - may do so via a molecularly adsorbed precursor state. Figures 7(b) and 7(c) schematically show the corresponding quasi-one-dimensional



Figure 8. Two-dimensional potential energy surfaces (schematic) for (a) early and (b) late barrier (B) of dissociation of H_2 on a transition metal surface.

potential energy diagrams. In Fig. 7(b) there is a second minimum in the potential energy diagram representing the two possible adsorption geometries. It is already obvious that, in this case, the use of such a quasi-one-dimensional diagram becomes very problematic because only a single spatial coordinate is used to represent the molecule-surface interaction. Therefore, such a situation calls for a multidimensional potential energy diagram, and we shall come back to this more general requirement later on. For the moment, however, Fig. 7(b) already allows us to visualize the transformation between the two inequivalent molecular adsorption geometries as an activated process. It is immediately clear that a desorption experiment will probe this more complicated potential energy curve, and thus a simple interpretation of the measured desorption energy as the heat of adsorption will not be possible in general.

The situation becomes even more complicated if, upon interaction with the surface, the molecule dissociates. This is depicted in Fig. 7(c). In this case it is necessary to consider two intersecting potential energy curves which refer to two different zero-energy levels, namely the diatomic molecule being infinitely separated from the surface for the associative interaction, as well as the two constituent atoms being infinitely separated from the surface. The difference between the reference levels, of course, represents the heat of formation of the diatomic molecule in the gas phase. In this case, the above-mentioned difficulty with the quasione-dimensional representation becomes particularly clear, in the sense that here the coordinate representing the separation between the two constituent atoms has not been considered at all. Nevertheless, it can be seen that there may be a rather large activation energy between the molecularly adsorbed precursor and the dissociatively adsorbed atoms, which is very crudely represented by the energy near the crossing point with respect to the potential energy minimum of the molecular precursor. Clearly, the point of intersection may

be situated well above the reference level corresponding to the infinitely separated molecule and surface, which in turn has strong consequences for the ability to populate the dissociative adsorbate. As will become clearer considering multidimensional potential energy surfaces in such a situation, the molecule has to have a certain impact energy to be able to surmount the activation barrier. Whether this impact energy should be represented by translational degrees of freedom or internal (rotational or vibrational) degrees of freedom cannot be concluded on the basis of the quasi-one-dimensional potential energy surface. However, it is already fully transparent that the shape of the potential energy surfaces will determine the kinetics as well as the dynamics of the system, and thus the probability to chemisorb. Experimentally, we measure (for example) the sticking probability of a particle from the gas phase into a particular adsorbate channel by probing the number of adsorbed species as a function of gas pressure and surface temperature. In other words, a relatively complex scenario is condensed into basically a single number. As the next section shows, it is far from easy to resolve the details.

Before tackling the problem of sticking consider, as alluded to above, potential energy diagrams that allow the incorporation of some essential additional features such as simultaneous motion along several coordinates (often normal coordinates). Clearly, the situation becomes very complicated as soon as many such coordinates come into play. Consider therefore, for simplicity the most simple case of a hydrogen molecule interacting with a transition metal surface. In recent years, this problem has been treated experimentally as well as theoretically in great detail so that a clear picture of the factors influencing the activation process has emerged. A good review for the case of H_2/Cu can be found in Ref. 69.

Figures 8(a) and 8(b) show potential energy diagrams for such a system [70]. The potential energy is plotted as equipotential lines in a coordinate system

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where the ordinate represents the surface-molecule (center of mass) distance, and the abscissa the interatomic distance of the diatomic molecule, i.e. the hvdrogen molecule in this case. Denoting the intermolecular distance in the molecule by x and the distance of the center of gravity of the bond to the surface by y, small x values are found for large y values, indicating the intact bond between the hydrogen atoms. As the molecule gets closer to the surface, i.e. y decreases, x finally increases to large values that are characteristic of the bond-breaking process. It is the exact position of the barrier, indicated by the letter B at the top of the saddle point in the potential energy diagram, that now governs the dynamics of the process. Two different situations are depicted. In Fig. 8(a) the activation barrier is located in the entrance channel. A molecule entering the entrance channel with sufficiently high translational energy can surmount the barrier, as indicated by the trajectory. However, it may well move up the wall before it can follow the bend (as if on a "bobsleigh" course) and the system will consequently come out the exit channel vibrationally excited (i.e. the hydrogen surface modes are excited) as indicated by the curved trajectory. In Fig. 8(b) the activation barrier is located more towards the exit channel. Here a vibrationally excited molecule has a better chance to surmount the activation barrier as indicated by the full trajectory. An unsuccessful attempt with a translationally excited molecule is shown for comparison. Once the vibrationally excited molecule has crossed the barrier, the hydrogen atoms formed will move across the surface with relatively high translational energy. The whole problem outlined so far can be mapped almost perfectly onto the so-called Polanyi rules [71], whereafter an exergonic reaction of type $A + BC \rightarrow AB + C$ with an early barrier request translational energy, whereas, if the reaction has a late barrier, it requires vibrational excitation of the reactants.

Molecular beam studies [72] have been undertaken in recent years to prepare selectively translationally or vibrationally excited molecules before they were scattered off the surface, and a great deal has been learned about how the molecules stick to a metal surface, specifically for hydrogen-transition metal systems [65-73]. In the case of hydrogen absorption on Cu, the barrier [74-77] is in an intermediate position, so that both translational as well as vibrational excitation helps to surmount the barrier. There are still a lot of open questions as to which role rotational excitation plays [69]. However, even with a full understanding of the processes occurring on the potential energy surfaces shown in Figs. 8(a) and 8(b), there are still some important ingredients missing. This has particularly to do with the fact that in the discussion so far the geometric and electronic structure of the surface has not been considered. It is known that chemisorption is structure

sensitive, and therefore these aspects have to be considered. It should be pointed out that hydrogen adsorption on Cu surfaces may not be typical for interaction with transition metals in general [78]; in particular, remember that H₂ dissociates with almost no barrier on metals such as Ni, Pd, etc. [73]. It is clear that in order to understand the barrier heights electronic structure calculations must be resorted to [79. 80]. However, the difference between Cu and Ni may be argued on a qualitative basis [79, 80]. Cu has the electronic configuration 3d¹⁰4s¹, with the rather diffuse 4s orbitals occupied. If a closed-shell H₂ molecule approaches the Cu surface it will be repelled by the diffuse 4s electrons so that it is hard for the H₂ to come in close to dissociate. Ni has the electronic configuration 3d⁹4s¹ in which the 4s orbital is occupied, which again leads to Pauli repulsion with the H₂ molecule. However, in Ni the 4s electron may be promoted into the hole within the d shell, forming a 3d¹⁰4s⁰ configuration - this reduces the repulsion dramatically and allows the H₂ molecule to come in close and dissociate. Therefore, the barrier for Ni is much lower than for Cu where it is in the range of 1 eV [69].

Another aspect that is important in connection with the discussion of adsorbate thermodynamics and energentics, so far neglected, is the aspect of interaction between adsorbed species. In Langmuir's picture of adsorption [2, 3], mentioned in the introduction, the adsorbed particles occupy the lattice points of a twodimensional substrate with equal probability and with hard wall potentials between them, preventing double or multiple occupancy of any particular site, and with well defined adsorption energies typical of the site. (Note that at this point structure sensitivity comes into the picture; however, this aspect is deferred until later.) As a result of this view of adsorption, saturation would be characterized by complete coverage and the formation of a true 1×1 adsorbate layer. Obviously, the formation of ordered layers with coverages far below complete coverage are more the rule than the exception, and are a direct consequence of the existence of interaction potentials. Such an interaction potential is shown in Fig. 9 for the system CO/Pd(100) reported by Tracy and Palmberg in 1969, compared with a CO-CO interaction potential in the gas phase [31]. Interaction potentials may be either attractive or repulsive and may be classified into direct and indirect interactions [81-83]. Direct interactions involve dipoledipole (multipole-multipole) and orbital-overlap interactions, and are often repulsive. On the other hand, indirect interactions mediated through the metal surface may be either attractive or repulsive depending on distance and surface sites, i.e. the kind of charge modification of the electronic structure of the substrate by

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Figure 9. Intermolecular potential for CO in the gas phase and CO adsorbed on a transition metal surface.

the adsorbate. The interplay of the interaction potential and the adsorption energy of the isolated particle with the clean surface finally determines the observed properties of the adsorbed layer. In other words, the structure of the adsorbed layer depends on the heat of adsorption as well as on the coverage [5].

The situation again may be depicted in the form of a potential energy diagram; however we have to include the existence of different surface sites [84]. Figure 10(a) [7] shows a one-dimensional potential energy diagram where the spatial coordinate extends parallel to the surface. It has been assumed that every surface site provides identical binding conditions. All identical

adsorption sites are separated by a small activation energy if compared with the activation energy for desorption, which gives rize to a sinusoidal energy dependence across the surface. At low enough temperature the adsorbed particles will reside within the potential wells because their thermal energy is too small to overcome the activation barrier for diffusion. Correspondingly, for higher thermal energies, particles will site exchange resulting in a mobile adsorbed layer with short residence times in the individual wells. We shall discuss this situation in more detail further below. The potential energy diagram parallel to the surface changes significantly if the interaction between adsorbed particles is taken into account. This is schematically depicted in Fig. 10(b) where we have added an attractive as well as a repulsive potential to the onedimensional diagram of Fig. 10(a). The consequences are energetic heterogeneities, weakening the adsorbate surface bond in the case of the repulsive interaction, and strengthening the adsorbate surface interaction in the case of attractive interaction potentials. As mentioned above, phenomenologically this leads to the formation of ordered phases on surfaces. In fact, there may be several different ordered structures depending on both temperature and coverage, because surface diffusion may act against the formation of ordered structures, i.e. favoring disordered layers while, for example, coverage increase locks in certain structures. A way to represent the various structures is to plot a so-called phase diagram [85]. An example is shown in Fig. 11. For the system CO/Cu(100), two ordered phases are found in the given temperature range [86]. These are denoted by I and II₊, and they occur at coverages 1/2 and 4/7. Phase I is a $c(2 \times 2)$ structure, while phase II₊ consists of stripes of the $c(2 \times 2)$ structure of width n = 3 separated by domain walls. The main part of the phase diagram is filled by a disordered phase. A very interesting and frequently studied aspect of such phase diagrams are the two-dimensional phase transitions. In two dimensions, similar to



Figure 10. One-dimensional potential energy parallel to the surface: (a) empty surface with a single particle bound with adsorption energy E_{ads} ; (b) superposition of the potential energy in (a) with a pairwise interaction potential of particles on the surface (E_{pair}), which may be either attractive or repulsive.



Figure 11. Phase diagram for the system CO/Cu(100), also showing the ordered structures [86].

three dimensions, phase transitions may be classified as discontinuous first-order, and continuous higher order. In general, phase transitions may be evaluated according to the temperature dependence of the thermodynamic functions. This subject is considered in greater detail elsewhere [87-90].

More important with regard to the heat of adsorption are the particle-particle interactions. As stated above, according to the Langmuir picture of adsorption [2, 3] we would expect constant adsorption energy until saturation of the surface is reached. In reality, this is never the case [85]. Rather, the adsorption energy generally decreases at medium and high coverages due to interactions between the adsorbed particles. It is possible to estimate the interactions from the coverage dependence of the isosteric heat of adsorption. In Fig. 12 [7] are several examples [22, 32, 39] where the work function has been used as a measure for the coverage (which may be sometimes dangerous). It is obvious from Fig. 12 that in all cases the adsorption energy sharply decreases as saturation is approached. At low coverge, however, the isosteric heat turns out to be either constant, decreasing, or increasing with coveage. The observed changes are a consequence of the particle-particle interactions on the surface, in the sense that increase means attractive interactions, as for example in the case of hydrogen for low coverage [39], decrease repulsive interaction, as in the case of CO on Ni(111) [22]. The step-like decrease of the heat of ad-



Figure 12. Adsorption energy (E_{ads} as a function of surface coverage Θ [7]: (\blacktriangle) CO/Pd(100) [32]; (\checkmark) CO/Ni(111) [22]; (\bullet) H/Ni(110) [39].

sorption close to saturation for CO/Pd(100) [32] is due to the population of additional weakly bound species on the surface [91, 92]. These weakly bound species may be rather reactive. Owing to their small heat of adsorption they may react rather easily with coadsorbed, neighboring functional groups. At high reactant pressures and not too elevated substrate temperatures this kind of scenario may play a significant role.

5.1.1.3 Sticking

This section considers the traditional description of the process where a molecule approaches a solid surface and eventually is trapped by the potential. A convenient way to gain access to this problem is through the consideration of the rate of adsorption. In the most simple case, the rate of adsorption is proportional to the number of molecules impinging per unit time on the surface, the so-called particle flux, and to the (dimensionless) efficiency with which an impinging particle actually sticks to the surface, i.e. the so called sticking probability. The initial sticking coefficient s_0 is the ratio of the number of adsorbed particles σ_s and the number of impinging particles for the uncovered surface. Therefore,

$$0 < s_0 < \tag{17}$$

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In principle, determination of this quantity is straightforward. In an adsorption experiment a clean surface held at temperature T is exposed to a well defined pressure P for a given time t (exposure is measured in Langmuir: $1 L = 10^{-6}$ torr for 1 s), and the amount of gas taken up by the surface (by a suitable surface science technique) is compared with the total amount of gas that has struck the surface. A method frequently used is the one proposed by King and Wells [93, 94]. In this case a molecular beam strikes the surface and the change in the background pressure of a given gas is measured by a mass spectrometer. The procedure is calibrated with respect to a gold sample that is known not to adsorb any molecules in the considered temperature range.

Knowing how s is measured experimentally, we can turn to further conceptual considerations. The rate of adsorption, i.e. the change of the number of adsorbed particles with time is given by [7]

$$r_{\rm ad} = \frac{\mathrm{d}\sigma_{\rm s}}{\mathrm{d}t} = \frac{P}{\sqrt{2\pi mkT}} s_{\rm o} f(\sigma_{\rm s}) \tag{18}$$

where the flux of impinging particles has been treated according to the kinetic theory of ideal gases, and a function $f(\sigma_s)$ accounts for the loss of empty sites as the adsorption process proceeds. The term s_0 may be written in terms of a preexponential $^{\circ}s$ and an activation energy $^{ads}E_{act}$ as

$$s_{\rm o} = {}^{\rm o}s \exp\left(-\frac{{}^{\rm ads}E_{\rm act}}{{}^{\rm /}_{\rm cc}}\right)$$

There is a different adsorption probability depending on whether the adsorption site is occupied or not. From what has been said before, the sticking coefficient must also depend on the population of internal and external degrees of freedom of the impinging molecule. This can be done in a closed form by assuming the sticking probability s to be composed of terms for the vibrational states involved, each weighted by a Boltzmann factor (F_B) representing the population of the corresponding vibrational state [69]:

$$s(v, E_{\rm e}, T) = \sum_{v} F_{\rm B}(v, T) s_{\rm a}(v, E_{\rm e}) \tag{19}$$

where v represents the vibrational quantum state under consideration, which is populated according to the Boltzmann factor depending on the temperature T of the gas (effectively the nozzle temperature in a molecular beam experiment). The effective translation energy E_e is given by [74]

$$E_{\rm e} = E_{\rm i} \cos^n(\vartheta_{\rm i}) \tag{20}$$

in which E_i is the translation energy of the incident particle, and ϑ_i is the angle of incidence with respect to the surface normal. If n = 2 then the effective translation energy shows a typical "normal energy scaling". in other words an exclusive dependence of the sticking probability on the normal component of the energy of the incident particle, which has been found rather frequently [95–100], and in particular for hydrogen adsorption on transition metals.

With this in mind we can go back to equation (18) and analyse the rate of adsorption further. First, write the rate in terms of coverage and not in terms of the absolute number of particles:

$$r_{\rm ad}(\Theta) = \frac{\mathrm{d}\Theta}{\mathrm{d}t} = \frac{P}{\sqrt{2\pi m k T}} s_{\rm o} f(\Theta) \qquad (21)$$

In the case of the most simple treatment according to Langmuir [2, 3], where it is assumed that each adsorbed particle occupies only one surface site, the adsorbed species does not interact with other adsorbed particles present on the surface. It is further assumed that the adsorption energy is completely exhausted as soon as one monolayer has been formed; the function $f(\Theta)$ reduces to $(1 - \Theta)$. If the particle dissociates upon adsorption – it occupies two sites – the function $f(\Theta)$ becomes $(1 - \Theta)^2$. Remembering that under equilibrium conditions the rate of adsorption must equal the rate of desorption

$$_{\rm ad} = r_{\rm des}$$
 (22)

we arrive at the following condition for the coverage:

$$(\Theta) = \frac{b(T)P}{1+b(T)P}$$
(23)

which is the famous Langmuir adsorption isotherm [2]. In its derivation we have employed eq 14 for the desorption rate assuming a first-order process, and consecutively just solved for Θ . In addition, we have used an abbreviation for a constant b(T) which only depends explicitly on temperature once the adsorbate parameters are known. b(T) is given by

$$b(T) = \frac{{}^{\circ}s}{v\sqrt{2\pi mkT}} \exp\left(-\frac{{}^{\mathrm{ads}}E_{\mathrm{act}} - {}^{\mathrm{des}}E_{\mathrm{act}}}{kT}\right) \qquad (24)$$

In this case the preexponential factor $^{\circ}s$ should not depend on coverage because it has been assumed for the derivation that there is no intermolecular interaction.

Many different adsorption isotherms may be derived where all or some of the basic assumptions going into the derivation have been released or relaxed [101-105]. It should be stated, however, that the general form of the Langmuir isotherm, which is shown for two temperatures in Fig. 13, may be used for a phenomenological description of many processes. It is clear, from the adsorption isotherm, the sticking probability s_0 may also be determined given that all other parameters are known [1, 7].



Figure 13. Plot of the Langmuir isotherm for two temperatures $(T_1 \text{ and } T_2)$.

Table 3 collects a set of sticking probabilities determined for various absorbate systems. The values vary between unity and 10^{-8} , although the range is usually between 0.15 and 1. Obviously, there is a clear trend that sticking is higher for atomically rough surfaces as compared with atomically smooth surfaces depending on the nature of the gas. It seems that energy accommodation is particularly easy on the rough surfaces as compared to the smooth ones. Carbon monoxide and nitric oxide stick quite effectively on many transition

Table 3. Initial sticking coeffici	ients.
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metal surfaces regardless of their crystallographic orientation. On open surfaces they even tend to dissociate. The tendency to dissociate increases when going from the right to the left in the periodic table. Co is approximately on the border line.

We note at this point that in addition to the surface crystallography, surface defects (point defects as well as steps) are important to accommodate chemically active species [112, 127, 128]. Initial sticking probabilities are interesting, but for real systems it is important to consider the coverage dependence of the sticking coefficient. Of course, a model-free discussion of this aspect is very difficult. It is therefore common practice to assume a set of possible kinetic processes which are important in connection with sticking to a surface. A possible scenario is shown in Fig. 14 separately for adsorption and desorption [7]. We introduce precursor states which may be classified as either intrinsic or extrinsic precursor states [129, 132]. The former exist at empty surface sites and the latter at sites already occupied. While trapped into such a precursor state the particle is only weakly held to the surface. Thus it can diffuse across the surface and be eventually trapped into an empty surface site. Given a precursor lifetime of 10^{-6} s, the molecule probes the surface for a sufficiently long time to find an empty site, if the pre-

Adsorbate	Substrate	Sticking coefficient	Remarks	References
	Ni(100)	0.06		106, 107
	Ni(111)	≥0.01		108
	Ni(110)	 ≈1		109
		0.96		110
	Pt(111)	0.1		111
	()	≤0.0001		112, 113
	Rh(110)	1		43
	Ru(1010)	≈1		44
	$C_0(10\overline{10})$	0.75 (±20%)		45
	W(100)			114
	Cu(100)	0.03	300 K	115
	Ni(100)			116
	Pt(111)	0.2		117
CO	Ni(111)			22, 118
00	Ni(110)	0.89		119
	Pd(100)	0.6		32
	Pd(111)	0.96		120
	Ru(1010)	1		35
	Pt(111)			121
N	W(100)	0.2-0.6	see Figure	94
	W(110)	$1-5 \times 10^{-3}$	$\beta - N_2$	122, 123
		0.22	γ-N2	124
	W(111)	0.08		93
N_2	Fe(100)	$10^{-6} - 10^{-7}$		125
~	Fe(111)	$10^{-6} - 10^{-7}$		126
	Fe(111) > (100) > (110)	10 ⁻⁶ -10 ⁻⁸		126



Figure 14. Schematic representation of direct and precursormediated processes on a surface [129, 130]. Processes occurring along the surface normal are plotted along the abszissa. The processes are correlated with the potential energy diagram of Fig. 7(b) (ex = extrinsic precursor, in = intrinsic precursor, n_0 = number of impinging particles from the gas phase, α' and α'' are fractions of trapped molecules, p = probabilities, p''_m = migration probability along the surface).

coverage is not too large. In order to set up a scheme we have to define probabilities (p_i) with which the various states at the surface are populated. On the basis of this (Fig. 14), it is possible to arrive at equations for the rate of adsorption and desorption. However, in the present case, different from the situation discussed above for direct sticking, the sticking probability $s(\Theta)$ will be dependent on the surface coverage. Kisliuk, as one of the first, has proposed a coverage dependent sticking coefficient based upon such considerations [131, 132]:

$$s(\Theta) = \frac{s_0}{1 + \frac{\Theta}{(1 - \Theta)}K}$$
(25)

The constant K is connected with the probabilities to populate a chemisorptive state via the various precursor states or desorb from them, respectively (Fig. 14):



Figure 15. Relative sticking probabilities as a function of surface coverage according to the Kisliuk model [131, 132]. For an explanation of K see text.

$$K = \frac{p_d'}{p_{ch}' + p_d'} \tag{26}$$

The Kisliuk model for a coverage-dependent sticking coefficient contains the linear Langmuir behavior as well as the coverage-independent sticking probability as limiting cases. Clearly, as K = 0, $s(\Theta) = s_0$. Also, as K = 1, $s(\Theta) = s_0(1 - \Theta)$, i.e. the linear Langmuir behavior is retained. As K is always larger than zero, we have to consider two cases, namely for K > 1, and for 0 < K < 1. The result is a convex curve for the former, and a concave curve for the latter case (Fig. 15) [131, 132]. Which behavior is actually encountered is largely determined by the probability p''_d , i.e. the probability for desorption out of the extrinsic precursor. It has to become smaller than the sum of probabilities to desorb out of the intrinsic precursor and the probability to chemisorb out of the intrinsic precursor, in order to achieve K < 1. Under ultrahigh-vacuum conditions, the population of extrinsic precursors is only easy to realize at low substrate temperatures. Therefore, concave sticking probabilities are generally found, as demonstrated for some examples in Fig. 16 [39, 120, 133, 134]. However, at higher pressures, the population of weakly bound precursor states may be of importance, so that the population of the chemisorbed state through the precursor becomes rate limiting. In such cases we may find a convex curve of the sticking probabilities. Of course, additional complications may arise if the structure of the surface changes upon changes of coverage [135]. Then the dependences may become very different altogether. Oscillatory surface chemical reactions are connected with such behavior in some cases [136].

To end the section on sticking we would like to describe a very interesting development that has recently become more visible, namely the experimental in-



Figure 16. Relative and absolute sticking probabilities for carbon monoxide as a function of surface coverage [39, 120, 133, 134].

vestigation of the dependence of sticking on the orientation of the particle, in particular a molecule, upon surface impact. Kleyn and co-workers [137, 138], as well as Heinzmann and co-workers [139–141] have shown that a molecule such as NO can be state selected and focused by taking advantage of a hexapolar electric field, and subsequently oriented in a homogeneous electric field, as schematically indicated in Fig. 17 [140],

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before colliding with the substrate. Depending on the polarity of the electric field in front of the surface, two different orientations can be achieved: preferential Nend and preferential O-end collisions. The rotational temperature of the colliding molecules determines the degree of orientation of the molecules. Therefore seeded pulsed nozzle beams are used to cool the particles before collision. The integral number of molecules leaving the surface after scattering is detected from the NO partial pressure with a quadrupole mass spectrometer located behind the target and thus shielded from the direct beam [93]. Figure 18 shows a typical result in terms of partial pressures (right panel) for the scattering of NO from Pt(100) as a function of field strength and orientation of the NO molecule [142]. The observed asymmetry, which is plotted in the left panel, is very high. Note that the degree of orientation, given as the averaged cosine $(\cos \vartheta)$ of the angle between molecular axis and external electric field 9, is 30%. The result documents the strong preference for trapping in the chemisorptive potential if the molecules approach the surface with the N-end. At higher surface temperatures the asymmetry decreases as expected, because the number of molecules that do not stick increases for both orientations. It seems that for a detailed understanding of the temperature dependence a kinetic model involving precursor states has to be



Figure 17. Experimental setup to study sticking probabilities of oriented NO molecules [139].



Figure 18. (Right) NO partial pressure after scattering from a Pt(100) surface as a function of field strength and NO orientation [141]. (Left) Corresponding orientation asymmetry of the partial pressure of NO [142].

invoked. A fit to a Kisliuk model [131, 132] (see above) indicates that not only chemisorption is favored for N-end oriented molecules but also trapping into a presursor state. If we change the adsorbate system from a chemisorptive system such as NO on Pt(100) to a more weakly interacting system such as NO/Ag(111) [137] we realize that the observed symmetries are actually much smaller even at low temperature, and indeed, slightly favor trapping of NO molecules with the O-end approaching the surface even at lower coverage.

5.1.1.4 Surface Diffusion

The motion of adsorbed particles obviously plays an important role for adsorbates and for surfaces in general, because this process enables the system to achieve its equilibrium structure. Particularly, at elevated temperatures the atoms of the substrate material can move, lowering the free energy content of the surface. The process of diffusion of substrate atoms has been investigated frequently in the past. Applying various methods such as scattering methods, field emission and contact potential measurements Bonzel and co-workers [143-145], Butz and Wagner [146, 147], Ehrlich [148], and Hölzl and co-workers [149, 150] have contributed to this area. Due to the rather high activation energies required for the substrate atom displacements, temperatures up to 1000 K have to be employed in order to obtain reasonable rates of diffusion of substrates atoms. In connection with the discussion of chemisorption, however, we are more concerned with a different type of surface diffusion, namely when diffusion occurs within the adsorbate phase. Such processes may be separated from the motion of substrate atoms because much lower temperatures are needed to induce diffusion. Typical diffusion coefficients are given in Table 4.

Diffusion within the adsorbed layer is instrumental to establish long-range order and to obtain optimal experimental conditions to perform diffraction experi-

Table 4. Diffusivities of adsorbates.

Adsorbate	Substrate	$D_0 (cm^2 s^{-1})$	References
 Cs	W(110)	0.23	151
ĸ	W(tip)	$10^{-4} - 10^{-6}$	152
Ň	WILIO	0.014	153
Ô	W(110)	0.04-0.25	154
Ĥ	Ni(100)	2.5×10^{-3}	155
D	Ni(100)	8.5×10^{-3}	155
H	W(tin)	1.8×10^{-5}	156
D	Pt(111)	8×10^{-2}	157
Ēο	Pt(111)	10 ⁻² -10 ⁻³	157
co	Pt(110) [110]	2.7×10^{-9}	158
co	Pt(110) [001]	0.8×10^{-9}	158

ments, for example, via low energy electron diffraction (LEED). Furthermore, surface diffusion helps to overcome lateral concentration gradients due to nonequilibrium clustering phenomena often found at low temperatures. There is a large amount of information available on surface diffusion [129, 148, 149], both on the experimental methods to measure diffusion coefficients as well as on the theoretical aspects of the problem. We shall only give a brief, nonexhaustive overview of the situation [7].

Conceptually, the process is thought to occur as a random walk where adparticles hop between adjacent sites, i.e. from an occupied to an adjacent empty site. The hopping frequency depends then exponentially on the temperature of the system which leads to the following form of the diffusion coefficient:

$$D = D_0 \exp\left(-\frac{\Delta E_{\text{diff}}}{RT}\right) \tag{27}$$

with the preexponential factor D_0 and the activation energy for diffusion ΔE_{diff} . It is correlated with the height of the energy barrier in Fig. 10 parallel to the surface. An expression for D_0 may be derived from transition state theory and depends on the activation entropy of the process. The important quantity for surface diffusion is the activation energy. Its magnitude is about a tenth of the adsorption energy for a typical chemisorbate such as CO/Pd, i.e. it amounts to approximately 15–20 kJ mol⁻¹. For physisorbates it is probably considerably lower.

The diffusion coefficient may be measured via several experimental techniques. The most prominent ones at present are the direct observation of a diffusion boundary in either a field electron microscope [159, 160] or a photoelectron emission microscope [158] or via laser desorption experiments [161, 162]. In the latter case a short laser pulse is used to heat the surface to momentarily desorb the adsorbate from a well defined region of the crystal. Subsequent laser pulses with well defined time delays with respect to the first one, and measurement of the number of particles leaving the surface, allow one to determine the rate of diffusion into the depleted zone. Other methods to determine surface diffusion are spectroscopic measurements which cover the proper time window, for example magnetic resonance-based methods [163, 164]. In favorable cases these methods may even be applied to single crystal surfaces [165].

As mentioned above, the diffusion process is thought to be a random walk across the surface. Then the mean-square displacement of the adparticles is related to the diffusion coefficient via the relation

$$\langle x^2 \rangle = 4 Dt \tag{28}$$

where is it understood that the surface itself only contains a very low concentration of adparticles which do not interfer with each other. In other words, the model so far is coverage independent. However, we know from previous considerations that coverage dependence has to be considered. For example, if a particle wants to move to an empty site the probability to hop clearly depends on the number of empty sites in the neigborhood, or even on the concerted motion of adparticles. Coverage dependences may be introduced by using the general transport equations, or specifically Fick's law [166]. The solution of Fick's law again yields an exponential dependence of the diffusion coefficient as in equation (27):

$$D(\Theta) = D_0 \exp\left(-\frac{\Delta E_{\text{diff}}(\Theta)}{RT}\right)$$
(29)

where the coverage dependence of the process enters through a coverage dependence of the activation energy:

$$E_{\text{diff}}(\Theta) = E_{\text{diff}}(\Theta = 0) + \frac{ZE_{\text{pair}}}{2} \left[\frac{1 - 2\Theta}{\sqrt{1 - 4\Theta(1 - \Theta)B}} \right]$$
(30)

where *B* is the short-range order parameter, $B = 1 - \exp(E_{\text{pair}}/RT)$, *Z* is the number of nearest neighbor sites, and E_{pair} is the nearest neighbor interaction energy. Using this approach Fick's equation may be solved numerically.

Table 4 contains a collection of diffusion coefficients determined experimentally for a variety of adsorbate systems. It shows that the values may vary considerably, which is of course due to the specific bonding of the adsorbate to the surface under consideration. Surface diffusion plays a vital role in surface chemical reactions because it is one factor that determines the rates of the reactions. Those reactions with diffusion as the rate-determining step are called diffusion-limited reactions. The above-mentioned photoelectron emission microscope is an interesting tool to effectively study diffusion processes under reaction conditions [158]. In the world of real catalysts, diffusion may be vital because the porous structure of the catalyst particle may impose stringent conditions on molecular diffusivities, which in turn leads to massive consequences for reaction yields.

5.1.1.5 Structure Sensitivity

So far we have neglected the fact that the substrate has a particular geometric structure which influences, as we shall see further below, the adsorption behavior in a very pronounced way. Furthermore, in practical cases the macroscopic geometric structure is rather complex. Consider, for example, a real catalyst used in heterogeneous reactions. It may consist of bimetallic precipitates, or of thin films supported on alumina, silica, or

titania, or highly dispersed metals such as platinum black. However, even these materials possess a regular geometric structure on the microscopic scale. Often, microscopically analyzed, these materials expose regular crystallographic planes, which may be characterized via scattering methods or real-space imaging. In catalysis, the correlation between surface geometric and electronic structure, the geometric shape and electronic structure of a molecule, and the observed macroscopic reactivity represents a very important and long discussed, but not yet solved problem. One distinguishes between structure-sensitive and structure-insensitive reactions. Special site requirements have been discussed in terms of the so-called ensemble effect [167-169] whereafter a molecule can only adsorb if a certain group of adjacent surface atoms is available. Studies on bimetallic alloy surfaces have often been used as examples for such ensemble effects [167, 168].

The present section enters into the discussion of the electronic and geometric structure by considering first an example where we can vary the strength of interaction between a given adsorbate and various metal and metal-oxide surfaces. We have chosen carbon monoxide as the adsorbate because it offers the largest available data set, including structure determination. Photoelectron spectroscopy (PES) is a very sensitive tool with which to monitor the change in the electronic structure, which is why it is the method of choice to shed light on this question [170]. Figure 19 shows a set of photoelectron spectra of CO adsorbates on four different hexagonally close packed metal surfaces [171] as well as on two transition metal-oxide surfaces [172-173]. For comparison we show the spectrum of gaseous [174] and condensed CO [175]. The binding energy $(E_b = E_{kin} - hv)$ refers to the vacuum level, which allows us to put adsorbates on metals, on insulators, and molecular solids on the same energy scale. (Often the binding energy is referenced to the Fermi level $(E_{\rm F})$ of the system. The binding energy with respect to the vacuum level and the binding energy with respect to the Fermi level are connected via the work function Φ of the system.) The region where we expect photoelectron emission from the three outer valence levels of CO, i.e. 5σ , 1π , and 4σ levels, is shown, and most of the following discussion will concentrate on these levels. From the bottom to the top the heat of adsorption increases from 19 kJ mol⁻¹ to 142 kJ mol⁻¹ for the metal surfaces. This is accompanied by clearly recognizable changes in the photoelectron spectra. There are several interesting differences in binding energies, line intensities and line shapes between gas phase [174], condensed phase [175] and adsorbate phases [172, 173, 176-179], which we shall comment on in the following. We shall start with the adsorbates on the metal surfaces



Figure 19. Photoelectron spectra of CO adsorbed on metal and metal oxide surfaces in comparison with gaseous and condensed CO. The spectra are taken in normal electron emission.

[176-179], and later turn to the oxide surfaces [172, 173] because bonding considerations are rather different for these systems.

In order to systematically approach an understanding of molecule-metal bonding and to relate the conceptual considerations to experiment we briefly refer to Fig. 20 [171]. In this figure the molecule-metal as well as the molecule-molecule interaction effects are illustrated on the basis of a one-electron level diagram for the valence electrons It shows on the right-hand side a diagram for an isolated CO molecule correlated with a one-electron level diagram for a CO molecule interacting with a single metal atom. On the left-handside the band structure of an isolated CO overlayer is



Figure 20. Schematic diagram for the bonding of an isolated CO molecule to a metal atom (right hand side) and a free twodimensional array of CO molecules (left panel) to a metal surface (middle).

displayed, and compared in the middle with the full band structure of the CO adsorbate interacting with the compact metal substrate with (111) orientation. Both aspects, the molecule substrate as well as the intermolecular interactions, have consequences for the observed spectra, but the main effect we shall dwell on first is the molecule-metal interaction. What happens electronically can easily be explained in the so-called Blyholder model [180]. The carbon lone pair of CO is donated into empty d or s levels of the metal atom, establishing a σ -metal-molecule interaction; synergetically, metal d electrons are donated into empty molecular orbitals (2π) of CO forming a π -metal-molecule interaction. From the view point of the molecule we can look at this charge exchange process as a π -donation- π -backdonation process. This means that the distribution of electrons among the subsystems, i.e. CO molecule and metal atom, in the CO-metal cluster is considerably different to the noninteracting subsystems. For example, the electron configuration of the metal atom in the cluster may be different from the isolated metal atom, or the electron distribution within the CO molecule bonded towards the metal atom may look like the electron distribution of an "excited" CO molecule rather than the ground state CO molecule [181]. This scheme has been used to explain the well known changes in the vibrational properties of adsorbed CO as compared with the gas phase. In addition to the loss of the rotational fine structure upon ad-

sorption, the CO stretching frequency often shifts by more than 100 cm^{-1} to lower values [182–185]. It is the filling of the CO antibonding 2π orbital via the backdonation contribution which weakens the CO bond in the adsorbate and concommitantly shifts the stretching frequency to lower values [186]. Also, as a consequence of this interaction certain electronic levels of the subsystems are strongly influenced. Naturally, the distortions of the molecular as well as the metal levels are reflected by changes in the ionization energies, their ionization probabilities, and the line shapes of the ionization bands. In CO/Ag(111) [176] at T = 20 K CO is physisorbed as documented by the small adsorption energy of 19 kJ mol⁻¹. This explains why a spectrum so similar to condensed CO is observed for this adsorbate. The splittings in the 4σ and 5σ ionizations are connected with the formation of a two-dimensional layer and will not be discussed at this point [187]. If compared with the gas phase, however, rather dramatic changes are found. The bands are shifted by about 1 eV to lower binding energy and the line widths increase, which destroys to a large extent the vibrational fine structure observed in the gas phase, too. Theories have been developed that allow one to understand these processes on the basis of hole hopping and relaxation, i.e. effects in the ionized state, within the quasi-twodimensional solid but for the present review we refer to the literature for details [188-193]. If the heat of adsorption increases to about 47 kJ mol⁻¹ [194], as for example in the case of CO on Cu(111) [177], the features in the spectrum shift and the intensities are altered. Three lines are still found but their assignment is very different as compared with the physisorbate [177].

We only briefly state here that many-particle effects in the ionized state of the adsorbate due to the presence of the highly polarizable metal electrons dominate the spectrum, and this alters the assignment considerably [177]. If we later turn to the oxide surfaces where such effects do not occur as strongly but the bond strength is comparable, we shall see that the interaction may be directly deduced from the spectrum. We note in passing that the assignment of the bands to states of different symmetry has been made on the basis of experimental investigations using angle resolved photoelectron spectroscopy (ARUPS) [170]. Reviews on this subject exist in the literature [170, 195, 196]. The next step is the study of the strongly chemisorbed systems with adsorption energies larger than 100 kJ mol⁻¹. Out of a wealth of experimental data [197-214] we have shown here only two systems, i.e. CO/Ni(111) and CO/ Pd(111). In these cases the spectra show two bands, whose binding energies are almost independent of the particular system under consideration as long as intermolecular interaction does not play an important role. The bands are shifted by more than 2 eV with respect

to the gas phase. Via angle resolved photoelectron spectroscopy [170] it has been shown that the two bands really contain three components as indicated in the figure as well as expected from the simple bonding considerations made above [197]. The carbon lone pair is shifted close to the 1π ionization due to the strong charge exchange and is actually located at higher binding energy. The overall shift of the bands to lower binding energy is a consequence again of the relaxation in the ionized state of the adsorbate due to the presence of the highly mobile metal electrons. Therefore, the experimental observation are in line with our simple charge-exchange model for CO-metal bonding but one has to be careful in the interpretation not to forget the effects of the probe, in the case of PES the creation of a hole in the system [170].

We now come to the comparison of the electronic structure of the adsorbates on the metal surfaces with those on the oxide surfaces [215, 216]. Very detailed electronic structure calculations [217-224] have recently shown that the interaction of molecules with oxide surfaces differs considerably from the interaction with metal surfaces in the sense that in the latter case interaction, at least on the regular surfaces, is much weaker. However, it is not necessarily a physisorptive interaction. Briefly, on the (100) surface of the strongly ionic NiO the interaction of a CO molecule is not governed by short-range charge-exchanges processes as in the case of the metal surface but rather by electrostatic interaction between the multipolar moment of the molecular electron density and the multipolar moment of the ionic surface. The reason for this behavior is that due to the presence of the closed shell oxygen ions in the (100) surface the molecule cannot approach the Ni site close enough to exchange charge. Pauli repulsion sets in at rather large distances from the surface and repels the molecule. The balance between the electrostatic attractive forces and the Pauli repulsion results in a rather weak chemisorptive bond of CO on a typical oxide surface. In addition, due to the rather weak interaction there is no longer a strong preference for one given orientation of the molecule with respect to the surface. For example, the molecular axis may be either perpendicular or tilted, or there may be interaction either with the carbon end or the oxygen end of the molecule with the surface. In other words, from an experimental point of view, we have to check in each case individually which situation is adopted by the system [172].

To a certain extent, the vibrational spectra [225, 226] again provide a clue towards a verification of the general statement made above. On oxide surfaces, in general, the observed shifts of the stretching frequencies



Figure 21. Schematic proposed arrangement of CO on a Cr_2O_3 surface [173].

are considerably smaller as compared to adsorbates on metals [183-185]. The vibrations may be either red or blue shifted depending on the interaction. The small red shift observed in some cases may be interpreted by a limited charge transfer from the oxide to the adsorbed molecule in the same sense as for adsorbates on metal surfaces. The often observed blue shift, however, has a different origin. It can be explained by the so called "wall effect" [219, 220] in which the weakly held CO molecule vibrates against the hard wall of the substrate which shifts the stretching frequency to higher values, thus leading to a blue shift. The statement made above concerning the interaction of CO with the oxide surface can now also be verified via the photoelectron spectra in Fig. 19 [172]. We find the binding energy of the oxygen lone pair located very close to the energy in the condensed CO film indicating that there is no strong intermingling between the oxgen long-pair density and the surface electrons. The same is true for the CO π bond electrons. However, we see a pronounced shift of the carbon lone pair electrons originating from the strong Pauli repulsion with the surface electronic charge. The relaxation shift found for the metal oxide systems is rather small also because the response of the oxide surface towards the creation of holes on the molecule in the ionization process is less pronounced than with the metal surface. Comparing the spectrum for the CO/NiO(100) system with the last example, i.e. CO/Cr₂O₃(111) [173] indicates a similar situation as far as the overall position of the adsorbate induced features are concerned. However, a detailed analysis of this $\sqrt{3} \times \sqrt{3}$)-ordered adsorbate system shows that the individual ionizations are considerably shifted with respect to the CO/NiO(100) system. The reason is simple, and it can be proved by angle resolved photoelectron measurements or X-ray absorption measurements, that the orientation of the molecule with respect to the surface has changed. CO is no longer vertically oriented on the surface but rather strongly inclined. A schematic model of the local bonding situation is shown in Fig. 21. The analysis of the chromium oxide system underlines the necessity of determining individually the orientation of the molecular axis before we discuss the



Figure 22. Stretching frequency of CO adsorbed on Ni(111) as a function of CO coverage. The surface was dosed at 90 K and subsequently annealed to 240 K [184].

details of the electronic structure of a system, in particular on an oxide surface.

The next step in the discussion of structure sensitivity of chemisorption is to consider the site of adsorption on a given surface and to answer the question as to whether and how the site changes as the coverage of the adsorbate is increased. Figure 22 shows the famous dependence of the CO stretching frequency on coverage for the system CO/Ni(111) [184]. This dependence has been interpreted as being due to two effects, namely a change of adsorbate site upon increase of coverage and additionally a shift caused by the coupling of the dynamic dipoles which depends on intermolecular distance [183-185]. Figure 22 indicates the adsorbate geometry deduced for the various coverage ranges based on the stretching frequency data. In recent years it has become more and more clear, however, that a structural assignment based on vibrational data has to be taken with caution. At low coverage a CO stretching vibration at 1816 cm⁻¹ shows up. This is replaced by a band at 1831 cm⁻¹ if the coverage increases and eventually shifts to $1905 \,\mathrm{cm}^{-1}$ at $\Theta = 0.5$ corresponding to a $c(4 \times 2)$ structure. On the basis of the suggestions by Eischens and Pliskin [182] the band at 1816 cm⁻¹ has been interpreted to be due to adsorption in a threefold hollow site at low coverage and the band shifting in the



Figure 23. Schematic drawing of the geometric arrangement CO on Ni(111) in the $c(4 \times 2)$ superstructure. Values are distances as determined by XPD [228].

range $1831-1905 \text{ cm}^{-1}$ to a CO bridge site. In a very convincing study based on the analysis of X-ray photoelectron diffraction data Bradshaw and coworkers [227-229] have shown that the adsorbate site over the whole coverage regime remains the same and is a threefold hollow site as indicated in Fig. 23. The observed shift in the stretching frequency is then purely due to intermolecular dynamic dipole coupling. Note that both the inequivalent threefold hollow sites (fcc and hcp) are occupied in this structure [228]. Another important factor in chemisorption becomes obvious by looking at the structures in Fig. 23, namely the cooperativity of the process. There is a 3% expansion (+0.07 Å) of the outermost Ni-Ni lattice spacing. This is meant here to stress the finding that although the surface provides a particular site for adsorption, the final geometry is determined via the interaction with the adsorbate and therefore depends on its chemical identity. This phenomenon is important in connection with the well known adsorbate induced reconstructions of surfaces [135]. If the reactivity of the surface towards another adsorbate changes through the reconstruction then cooperative phenomena are essential for the overall chemical reactivity in the system.

Whereas in the above example the local structure remains the same for increasing coverage, there are other cases where intermolecular interaction changes the geometry of the adsorbate. In the case of CO on Ni(110) at low coverage CO molecules adsorb in two different adsorption sites, namely on atop and on bridge sites with vertically oriented axis, as shown in Fig. 24 [230-233]. The molecule-substrate bond in this case is so strong that the system can tolerate even large lateral intermolecular stress. At a coverage of $\Theta = 1$



Figure 24. Geometric arrangement of CO molecules on a Ni(110) surface at low coverage (right) and high coverage (left).

the intermolecular distance would be 2.5 Å if the molecular axis remained perpendicular. Therefore the molecular axis tilts from the normal orientation in order to enlarge the average distance between molecules [234–236]. The equilibrium structure assumed is shown in Fig. 24, on the left. This system has been studied in some detail in order to understand the electronic structure of the system [237-240]. In line with Fig. 20 where the schematic band structure of an adsorbate system is shown, the present system has been studied with angle resolved photoelectron spectroscopy and the band structure has been experimentally determined [187]. Figure 25 shows the complete experimental band structure in the occupied region, i.e. of the 5σ , 1π , and 4σ levels [237, 239, 240]. Included is the band structure in the unoccupied region as determined by inverse photoemission. The 5 σ , 1 π , and 4 σ levels lead to twice the number of bands due to the nonsymmorphic space group symmetry of the system with two molecules per unit cell [234]. Following the bands through the Brillouin zone shows that the energetically close 5σ and 1π bands hybridize. Also, one can clearly identify the CO(2π)-Ni(3d) backbonding states below the Fermi edge. The unoccupied 2π derived levels are located above the Fermi edge. It is interesting to note the different magnitudes of the band dispersions for the different levels. This is clearly due to the variations in interaction strength for the different molecular orbitals depending on directionality and spatial extent. The largest dispersions are exhibited by the π orbitals. In fact, the 2π orbital shows the largest effects because they are most diffuse and show large electron density off the molecular axis. To summarize, the strong intermolecular interaction is reflected in the adsorbate band structure and mainly due to $\pi - \pi$ interaction.

We now turn to the question of how the adsorption properties of a given molecule changes when we change the geometric structure of the surface keeping its



Figure 25. Measured band structure in the range of occupied and unoccupied levels for $CO(2 \times 1)p2mg/Ni(110)$. The wave vector K is determined along the two orthogonal directions in the surface Brillouin zone as shown at the top and its energy dependence according to $K_{\parallel} = (2m_e\hbar^{-2}E_{kin})^{1/2}\sin\vartheta$,

chemical constitution constant. There are many examples in the literature. Again CO adsorption could be chosen [241]. Also, hydrogen chemisorption [73] or oxygen chemisorption [242, 243], which has been studied and reviewed in detail by Christmann [73], Wandelt [242], Brundle [243] and others are prominent examples for the structure sensitivity of chemisorption on metal



Figure 26. Structure of the close packed surfaces of iron (bcc).

surfaces. The adsorption of nitrogen on iron is chosen because of its importance in connection with ammonia synthesis [244]. In particular, Ertl and co-workers [125, 126] have investigated the structure sensitivity of dissociative nitrogen adsorption on the low-index surfaces of iron, i.e. the (100), (110) and (111) surface orientations. Figure 26 shows the arrangement of these surface structures on top of the body-centered cubic iron crystal. The (110) surface has a very low sticking coefficient for dissociative adsorption while the most open (111) surface has a much higher sticking coefficient [125, 126]. With a combination of photoelectron spectroscopy [245] and vibrational spectroscopy [246-248] the important factors influencing this face specificity have been uncovered. Briefly, on Fe(111) high resolution electron energy loss spectra (HREELS) [248] are observed as a function of temperature (Fig. 27). At about liquid nitrogen temperature a dominant feature with a stretching frequency at $2100 \,\mathrm{cm}^{-1}$ is found. With angle resolved photoelectron spectroscopy [245] it has been shown that this species is oriented perpendicular to the surface. It is most likely to be bound to an atop site. The same species is found on all low-index iron surfaces [244]. It is weakly held by the surface. Upon heating the system slightly above 100 K a second molecular nitrogen species shows up in the vibrational spectra of N₂/Fe(111) at a lower stretching frequency (1415 cm⁻¹). Again, photoelectron spectroscopy has been used to show that this species is bound in a strongly tilted geometry, in line with the low stretching frequency typical for side-on bonded dini-



Figure 27. Electron energy loss spectra of ${}^{15}N_2$ on Fe(111) as a function of surface temperature [248].



Figure 28. Proposed arrangement of N₂ on Fe(111) [245].

trogen complexes. This species only exists on the surface within limited temperature range. Above 160 K the stretching frequency typical for molecular nitrogen species disappears and only atomic nitrogen (460 cm⁻¹) is present on the surface. This scenario is typical for the (111) surface, while the existence of the intermediate species cannot be detected on the other low-index planes, i.e. (110) and (100) [244]. It is now generally accepted that the intermediate with the low stretching frequency is a precursor to nitrogen dissociation, and it is thought that the "(111) surface provides the sites, necessary to assume the strongly tilted geometry [244]. Figure 28 shows the bonding geometry for the intermediate species [245]. The nitrogen molecule can donate both its lone pair as well as the 1π electrons into empty metal orbitals, and at the same time establish a



Figure 29. Two-dimensional potential energy diagram for the convesion of γ -N₂ (vertically adsorbed) to α -N₂ (side-on bonded) [246–248] on the Fe(111) surface [249].

back-donative bond via the unoccupied π orbital. The back donation will weaken the nitrogen-nitrogen bond which finally leads to dissociation. Since both nitrogen atoms are already in close contact with the metal surface, this picture appears to provide a natural pathway to dissociation. It is believed to explain the observed strong face specificity of dissociative nitrogen chemisorption on Fe surfaces. Figure 29 shows a semiempirical potential energy diagram for N₂/Fe(111) where the pathway from the molecular precursor to the dissociative adsorption is shown [249]. The value for the activation barrier is based on experimental date [250].

Finally, we would like to have a look at the structure sensitivity of transition metal oxide surfaces [215]. For such systems [251, 252] it is necessary to resort to some basic considerations about the electrostatics of ionic or partly ionic systems with respect to surface stabilities. Figure 30 schematically shows the arrangements of planes in a crystal of rock salt (AB) structure for the termination of (100) type on the left and of (111) type on the right [254]. The (100) surface of an AB-type solid is the typical case for a nonpolar surface with vanishing dipole moments between the planes and full charge compensation within the planes. This arrangement leads to a converged, finite electrostatic surface energy. Upon going to the (111) surface of an AB-type lattice we create a polar surface. In this case there is no charge compensation within each layer and there is also a dipole moment within the repeat unit perpen-

stable/non-polar AB-type	stable/p AB2-t	stable/polar AB2-type		unstable/polar AB-type	
vacuum	vacuum	repeat units	vacuum	repeat units	
.+		++			
crystal +-	- crystal	Ξ÷-	crystal		
+				<u>b</u> +	
into bulk		into bulk		t nto bulk	

Figure 30. Stable and unstable surfaces of AB-type and AB₂-type ionic crystals [253].

dicular to the surface. Consequently, the surface energy does not converge but increases unbound as the number of repeat units increases. In general, polar surfaces are not unstable, as illustrated for the AB₂-type solids. Even though there is no charge compensation in the plane, the dipole moment in the repeat unit perpendicular to the surface vanishes, thus leading to a stable situation. Returning to polar surfaces of the AB-type to consider the surface potential V in more detail [253],

$$V = \frac{2\pi}{S} [Nb(2\sigma - 1) + (1 - \sigma)b]$$
(31)

where S is the area of the unit cell. Equation 31 gives the surface potential as a function of the number of layers N, their separation b, and the parameter σ which describes the difference in charge of the surface layer with respect to the bulk layer. It is quite obvious that the reduction of the surface charge such that $\sigma = 1/2$ leads to the disappearence of the first term in eq 31, and thus to a converging surface potential independent of the number of layers. While this is only a qualitative argument, it shows possible routes for the system to respond in order to stabilize polar AB-type surfaces. Surface-charge reduction may be accomplished by reconstructing [254], i.e. removing half of the ions, or by the creation of steps. The latter leads to the coexistence of A-terminated and B-terminated patches on the same surface and thus to a microscopic charge compensation. Also, relaxations in the layer distance are expected to occur in the near surface region which could help to reduce the surface potential. In certain cases other causes of stabilization may be considered. Upon adsorption of H⁺, provided by exposure to water, for example, OH⁻ may form on an oxygen terminated surface thus effectively reducing the surface charge [252]. Thus one would predict a strong structure sensitivity of water adsorption on oxide surfaces which, indeed, has been observed [254, 255] and is exemplified in Fig. 31. The O(1s) XP spectra are shown for three different samples [255]. The lower trace shows the spectrum of a cleaved NiO(100) surface with very low defect concentration (sharp LEED pattern). The feature is symmetric after cleavage and it remains symmetric even after exposure to water at room temper-



Figure 31. O(1s) XP spectra of a cleaved NiO(100) crystal: (a) a grown NiO(100) film; (b) a grown NiO(111) film. The corresponding LEED patterns are shown [254, 255].

ature [256]. At low temperature an ice layer forms which can be removed without residue by heating to room temperature. This indicates that a NiO(100) surface does not dissociatively chemisorb water. The situation is different for a NiO(100) surface containing defects, as indicated by the much broader LEED spots as compared with the cleaved surface [252, 255]. Here a small feature is found at 2.2 eV higher binding energy. It becomes particularly pronounced in the spectra if they are recorded at grazing electron excidence in order to amplify the surface sensitivity of the method. EELS investigations have shown that the feature is due to hydroxyl groups on the surface. These hydroxyl groups may be removed from a NiO(100) surface by thermal treatment. Exposure of the cleaned surface to water leads to the reappearence of hydroxyl, indicating that water dissociatively chemisorbs on defect sites of a NiO(100) surface. Dissociative chemisorption becomes even more pronounced on the NiO(111) surface. The



Figure 32. Schematic drawing of OH-terminated (left), bulk-terminated (middle) and octopolar reconstructed (right) NiO(111) surfaces.

upper trace in Fig. 31 indicates a rather high concentration of hydroxyl groups at the surface. When (111) polar surfaces are prepared they often become OH stabilized, due to the electrostatic instability discussed above. In favorable cases such as NiO(111), the hydroxyl groups can be removed from the NiO(111) surface as water by thermal treatment. As a consequence, the OH-free unstable surface reconstructs. The most stable reconstruction of a polar surface of an ionic crystal is, according to Lacman [257] and to Wolf [258], the so-called octopolar arrangement, shown in Fig. 32 in comparison to the ideal (1×1) surface. The octopolar reconstruction leads to $p(2 \times 2)$ unit cell on the surface and is characterized by the removal of three out of four oxygen ions in the first layer (in the case of an oxygen terminated surface) and one out of four nickel ions within the second layer [254, 259]. The third layer contains then again a complete hexagonally close packed oxygen layer. A $p(2 \times 2)$ reconstruction has been observed for iron oxide and nickel oxide but only in the latter case are there clear indications that an octopolar reconstruction has actually taken place [255].

Readsorption of water leads to a lifting of the reconstruction and the reoccurrence of the (1×1) structure [254]. Note for completeness that the reconstructed surface exhibits a considerably higher chemical activity, for example in the DeNO_x reaction, than the hydroxyl-covered surface which is basically inactive towards further chemisorption [256]. In other words, water desorption and readsorption leads to a strong change in the chemical activity of certain crystallographic planes of oxide surfaces which may be relevant with respect to the catalytic activity of powders of real samples.

Previous sections have discussed the interaction between adsorbed species in connection with the coverage

dependence of adsorbate properties and especially energetics. Coadsorption of different chemical species is the general case in connection with the discussion of intermolecular interaction. Intermolecular interaction. however, is the basis for the understanding of chemical reactions between adsorbed species. There is such a vast literature on the subject [260] that a comprehensive and exhaustive review of the field cannot be provided here. Nevertheless, we would like to briefly address two coadsorbate systems where a broad knowledge has been accumulated over the years. To represent the limiting cases we resort again to carbon monoxide as one component and study its coadsorption with an electropositive additive, and also with electronegative additives. Needless to say, all aspects discussed above for chemisorbate systems in general are important, even at a more complex level, for coadsorbate systems. In the latter case it is necessary to consider the different chemical identities of the adsorbed species, and more importantly their influence on the electronic structure of the substrate, and on each other. In other words, the aspect of cooperativity that adsorbates and substrate interfere and determine each others properties becomes particularly noteworthy.

The most prominent and most frequently studied electropositive additives are alkali metals. Several comprehensive reviews have been published on the subject which provide more detailed information [260– 262]. Characteristically, adsorption of alkali leads to dramatic changes of the work function of the system [260–262]. An example, K on Pt(111), is shown in Fig. 33 [263]. In general, small alkali coverages already lower the workfunction considerably before monolayer coverage is reached (in the present case more than

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Figure 33. Work function of Pt(111) as a function of potassium coverage at 300 K [263].

4 eV). Before completion of the first monolayer coverage the work function reaches a minimum, turns around and then approaches, for increasing coverages, the value of the work function of the bulk alkali [260-262]. We are concerned only with the regime of alkali coverages below or close to monolayer coverage. It is generally accepted that in the low coverage regime the alkali atoms transfer charge towards the substrate, setting up a strong adsorbate-surface dipole which lowers the work function, hinders the alkali atoms to cluster on the surface, and allows them to adsorb as isolated atoms well separated from each other [264]. The energy needed to remove the alkali from the surface has been determined from TDS and calorimetric investigations to vary between 130 and 250 kJ mol⁻¹. Coadsorption of CO onto such an alkali-precovered surface leads to considerable effects on the energetics of the CO-substrate interaction as compared with the pure CO adsorbate. TD spectra of the pure and the coadsorbate system are shown in Fig. 34 [265]. The molecule still adsorbs associatively on the surface but note that the dissociative sticking coefficient increases considerably in the coadsorbate as has been observed for several CO-alkali coadsorbates [260]. The adsorption enthalpy increases for a typical CO-metal system from 130 kJ mol⁻¹ to 197 kJ mol⁻¹ for the alkali-adsorbed system [266]. There are coverage dependences as well, but we shall concentrate here on a single coverage. To learn more about how the observed energetic changes come about, consider the vibrational spectra of the system shown in Fig. 35 [267]. As compared with the pure CO adsorbate the CO stretching frequency in the coadsorbate is lowered by several hundred wavenumbers, indicating a weaker C-O bond in the co-



Figure 34. Thermal desorption spectra of (a) clean and (b) potassium covered ($\Theta = 0.015$) Pt(111). Various CO coverages are plotted indicating the population of sites close to the alkali at low CO coverage. On the unmodified Pt(111) surface at higher coverages similar sites are observed [265].



Figure 35. Electron energy loss spectra of CO on clean (lower trace) and K-modified (upper trace, $\Theta_{\rm K} = 0.02$) Pt(111) [267].

adsorbate. The explanation is straightforward: electrons from the electropositive additive are transferred either directly or via the substrate surface into the unoccupied CO antibonding orbitals thus weakening the CO bond [261]. Simultaneously, this stabilizes the COalkali interaction on the substrate surface and enhances the CO substrate interaction. It turns out, however, to be rather difficult to exactly partition the interaction strength between CO-alkali and CO-substrate. It was

Adsorbate	Surface	Modifier	E_d^0 (kJ mol ⁻¹)	References	
	Ni(100)	_	140	270	
00		$P(2 \times 2)S$	90		
		· · ·	110		
		$C(2 \times 2)S$	≈30		
		$P(2 \times 2)O$	120		
		$P(2 \times 2)N$	≈90	271	
		$(2 \times 2)p4gC$	93	272	
	Ni(111)	_	140	273	
		$P(2 \times 2)S$	91	273	
		$P(2 \times 2)O$	105	274	
	Pd(100)	-	160	275	
		$P(2 \times 2)S$	86		
			60		
	Pt(111)		154	276	
		$P(2 \times 2)S$	106	276	
		$P(2 \times 2)Se$	110	277	
	Ru(0001)	-	170	278	
		$P(2 \times 2)S$	105	278	
Н	Ni(100)	-	102 ± 5	279	
		$P(2 \times 2)S$	84 <u>+</u> 10		
		$C(2 \times 2)S$	48 <u>+</u> 16		
	Fe(100)		87 <u>+</u> 50	280	
		P(1 × 1)O	60 ± 10	280	
	Pd(100)		85	281	
		0.15S	49	281	

Table 5. Desorption energies for some transition metal surfaces modified by electronegative additives.

believed for some time that in the coadsorbate the COsubstrate interaction changes dramatically, leading to a change in the CO bonding geometry on the surface, i.e. from a vertically bound CO in the pure adsorbate to a side-on-bonded CO in the coadsorbate [268]. Near edge X-ray absorption fine structure (NEXAFS) has again been instrumental in showing that this is not the case [269]. In fact, CO remains vertically bonded on the surface and possibly interacts side-on with the coadsorbed alkali atom. The side-on geometry was particularly attractive because, similar to the case of nitrogen adsorption, this geometry could easily explain the increased dissociative sticking coefficient [260]. However, as it stands today, either the molecules transiently pass through such a side-on geometry before dissociation, and the concentration is so low that it cannot be identified, or dissociation can also start from vertically oriented, but electronically strongly modified CO. The described interaction between alkali and CO in a coadsorbate may be considered as special case of alkali promotor action, which is well established in catalysis [260].

A completely different situation is encountered when we coadsorb carbon monoxide with an electronegative species. Table 5 [260] collects desorption energies for carbon monoxide absorbed on transition metals modified by electronegative additives. In general, and opposite to the effect observed for the electropositive modifier, coadsorption with electronegative modifiers

leads to a decrease in the desorption energy. This may have different reasons. It could be due to repulsive modifier-CO interaction, or it could be due to the fact that the modifier blocks those sites of the surface leading to the strong CO-substrate interaction for the clean surface [260]. As judged from the vibrational data the influence of an electronegative additive onto the CO stretching frequency is much less pronounced if compared to the electropositive additives [282]. Often, instead of a strong red shift as observed for electropositive coadsorbates, a weak blue shift is observed which in certain cases may even lead to stretching frequencies higher than in the gas phase [282]. In this case it is even more difficult to disentangle the various contributions, i.e. direct and substrate-mediated interactions. The wealth of data presently available suggest than an electronegative additive mainly influences the substrate locally, i.e. in its direct vicinity, in the sense that (a) the adsorption sites which involve substrate atoms directly coordinated to the modifier are blocked, and (b) the adsorption sites sharing some substrate atoms with the modifier are substantially perturbed. This means, as schematically shown in Fig. 36 [260], that for a fcc(100) plane and a modifier residing in a fourfold site four atop sites and four bridge sites are blocked, and eight bridge sites, four close and four remote fourfold sites are perturbed. With increasing



Figure 36. Schematic representation of the influence of an adsorbed electronegative modifier in a fourold hollow site (black circle) on the neighboring sites. Neighboring fourfold hollow sites which are strongly (+) or less strongly (-) influenced are indicated [260].

modifier coverage, the number of affected sites per modifier atom decreases, because of overlap of effects. Following this simple model, obviously the most tightly bound states of the coadsorbate associated with the unaffected surface should be rapidly removed with increasing modifier coverage. In the case of Ni(100) where CO favors the atop site on the clean surface, one S atom, for example, is found to remove four atop CO molecules [270]. In addition, as evidenced by EELS data and TD spectra [270], CO is pushed to occupy the close bridge sites and the close fourfold hollow sites, in which the coupling with the substrate is reduced. Generalizing this observation if can be stated that coadsorption of electronegative additives often leads to a situation where a coadsorbate accesses the less strongly bound surface sites, which in turn leads to a strong modification of the reactivity in the presence of the modifier [260]. In catalysis such coadsorbate-induced effects are summarized as poisoning, particularly in connection with sulfur. However, as we have tried to indicate, due to the complexity arising from the specificity of the modified systems and the variety of possible interactions in the coadsorbed layer, there is still no uniform model for the mechanism of the poisoning action, even for the idealized model systems considered in this section [260]. The situation becomes even more complex if the additive induces surface reconstruction or even surface compound formation. Also, if there is a lack of a tendency to ordering and occupation of a definite adsorption site, coadsorption phenomena become increasingly complicated. In the case of modifying the surface with C, N, or O as opposed to S, P etc., transition metal surfaces may reconstruct or carbides,

nitrides, and oxides are formed [260]. Then, of course, the activity of the surface is determined by the properties of the new types of compounds formed. Often island formation is encountered in these systems which leads to a considerable reduction in the relative number of modified surface sites because the effect is restricted to the neighbors of the modifier island boundary. Summarizing, in such systems the problem of cooperativity, i.e. the phenomenon that the adsorbate and coadsorbate create their own active sites which are not present on the clean surface becomes particularly important. The future study of these effects in chemisorption is essential, even under ambient conditions, in order to identify which are the key effects that operate during catalysis at a microscopic level.

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5.1.2 Chemisorption Theory

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5.1.2.1 Introduction

Computational quantum chemistry and solid state physics have reached the stage where quantitatively reliable predictions on the interaction of small and moderate sized molecules with transition metal clusters or surfaces are now possible. Computation therefore be-

gins to enrich experimental information by providing results of model systems that are not easily accessible to experiment. In addition they allow us to probe the nature of transient surface species such as short-lived intermediates and activated complexes. Nonetheless, the qualitative theoretical framework that has been established over the past 50 years remains highly relevant. It provides a sound framework for conceptual analysis and interpretation. Computation and experiment then can be used to test ideas on the electronic and structural parameters which control the geometry, energetics, and dynamics of the chemisorbed molecule.

Two different schools of thought in chemisorption theory can be distinguished. The first is born out of the solid-state physics community, while the second originates from the theoretical chemistry community. Formal chemisorption theory dates back to the 1950s and 1960s where the relevant electronic factor for chemisorption was considered to be the local electron density of states at the Fermi level. This is especially true in catalysis. Magnetic and conductivity measurements were usually interpreted in these terms. With progress in solid state physics, theory became more refined and surface physicists developed a more physically realistic view of the surface chemical bond. Koutecky [1], Newns [2], Grimley [3], and Schieffer [4] are considered to be the founders of formal chemisorption theory. Many of their concepts remain today and are the basis of our current views on chemisorption. Formal chemisorption theory is therefore the subject of the first section. One of the most important results derived from formal chemisorption theory was the rationalization of strength of adsorbate-surface interaction in terms of the ratio of adsorbate-surface-atom strength versus the interaction energy between the surface atoms. It raised the issue of the existence of the concept of a surface adsorption complex, hence identifying chemisorption physics with surface complex chemistry.

The theoretical chemical application of surface chemical bonding theory, highlighted next, is related to formal chemisorption theory as developed in surface physics, but concentrates on quantum chemical concepts as the electron distribution over bonding and antibonding orbital fragments [5, 6]. It will be seen that both approaches complement each other. The notion of a surface molecule relates to the surface physicists' concept of surface state.

The final section provides an overview of the current understanding of the factors that govern the physical chemistry of chemisorption. Our understanding of the factors that determine the site preference of surface dependence of chemisorption is summarized. We demonstrate many of those concepts through a series of first-principle quantum chemical results on different example systems. The results allow us to specifically quantify different aspects of the interaction, such as